Excess Enthalpies
of
Binary and Ternary Mixtures

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Abstract

The research work involved in this study can be described in two aspects: the experimental determination of excess enthalpies, H^E, for some binary and ternary liquid mixtures; and a theoretical study of various approaches for the representation of experimental H^E data.

To determine the excess enthalpies of desired systems, a series of calorimetric experiments has been carried out for 15 binary and six ternary mixtures with an LKB flow microcalorimeter.

A new model, based on statistical thermodynamic principles, has been developed for representing and predicting the excess enthalpy of a ternary mixture from correlation of the H^E values of its constituent binaries.

The analyses of experimental results were carried out with several solution models, such as the Flory theory model, an association model, the DISQUAC model, the NRTL model, the UNIQUAC model, and the model developed in this study.

The applicability of the proposed model for predicting ternary H^E values was further investigated. In addition to the six ternary systems experimentally studied in this work, six more ternary systems were selected from the literature. For comparison, the same calculations were also carried out with the 3-parameter NRTL and 2-parameter UNIQUAC models.

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Nomenclature

a	cohesion parameter in cubic equation of state
a_0, a_1	equation constants for calibration lines
A	Helmholtz free energy, J
A_k	parameters in Equation 2.2
A_{ii}, A_{ij}	numbers of contact pairs used in the Flory theory
B_l	parameters in Equation 2.2
c	parameter representing the external degree of freedom in the Flory theory
c_i	parameters in $H^E_{m,T}$ expression
d	density, $g \cdot cm^{-3}$
E	electrical potential, V
E_0	mean intermolecular energy used in the Flory theory
f	volumetric flow rate, $cm^{-3} \cdot s^{-1}$
G or g	Gibbs free energy, J, or $J \cdot mol^{-1}$
g(v)	a function of molar volume
$g_{ji}(r)$	radial distribution function
H,or h	enthalpy, J, or $J \cdot mol^{-1}$
h_j	coefficients in Equations 4.10 and 4.11
I	current, A
k	Boltzmann constant, $J \cdot K^{-1}$
M	property of a real solution
M	molar mass, $g \cdot mol^{-1}$
N	number of molecules used in the Flory theory, or number of data points,
N_j	number of j molecules in volume V
N_A	Avogadro's number, 6.023×10^{23} mol^{-1}
N_{ji}	number of j molecules interacting with a central i molecule
p	number of adjustable parameters used in RMSD expression
P	pressure, $N \cdot m^{-2}$

p^*	characteristic pressure used in the Flory theory
q_i	total relative molecular area of i type molecule used in the DISQUAC model; or UNIQUAC surface area parameter, cm^2
Q_{comb}	combinatorial factor used in the Flory theory
Q_p	partition function used in the Flory theory
r	number of segments in a molecule used in the Flory theory; or the separation of the molecules
r_i	UNIQUAC volume parameters
R	calibration resistance in chapter 3, Ω; or gas constant, $J \cdot K^{-1} \cdot mol^{-1}$
R_c	standard resistance, Ω
R_w	reduced well width, cm
s_i	the number of contact sites per segment of a molecule of species i used in the Flory theory
T	temperature, K
T^*	characteristic temperature used in the Flory theory
u	potential energy function, J
U	internal energy, J
v	molar volume, $cm^3 \cdot mol^{-1}$; or volume per segment used in the Flory theory
$\tilde{v}$	reduced volume used in the Flory theory
v^*	hard core volume per segment used in the Flory theory, cm^3
V	volume, cm^3
V^*	characteristic volume used in the Flory theory
V(f)	voltage deflection from the baseline voltage, mV
V°(f)	baseline voltage, mV
W	mass, g
x	mole fraction
x_{ij}	local composition
X(i)	interim parameters used in UNIQUAC model
W_p	electrical power, $J \cdot s^{-1}$
z	lattice coordination number used in the DISQUAC model (=4)

Z	coordination number used in the proposed model (=10), or compressibility factor

Greek letters

α	parameter used in the NRTL model, or volume fraction used in the association model
α_i	correction factor used in the proposed model, or surface ratio in the DISQUAC model
α_p	isobaric expansivity, kK^{-1}
α_{si}	molecular surface fraction of surface type "s" on an "i" type molecule used in the DISQUAC model
γ	geometric factor used in the Flory theory
Δ,δ	change, or difference
ϵ	calibration constant of the calorimeter, $J{\cdot}s^{-1}{\cdot}V^{-1}$
ϵ_{ii}, ϵ_{ij}	energies associated with respective contact pairs used in the Flory theory
ϵ_{ji}	molar value of the potential function $u_{ji}(r)$ at the lowest potential level used in the proposed model
θ_i	site fraction, or contact surface area fraction used in the Flory theory, or local area fraction of molecule i used in the UNIQUAC model
κ_T	isothermal compressibility, TPa^{-1}
λ	number of contact surfaces used in the DISQUAC model
ξ_i	surface fraction of component i in mixture used in the DISQUAC model
σ_{ji}	collision diameter, cm
τ_{ij}	parameters used in the NRTL and UNIQUAC models
ϕ	volume fraction
X_{12}	Flory interchange energy parameter, $J{\cdot}cm^{-3}$
X_s,X_t	quantities used in the DISQUAC model
X_{si},X_{ti}	solutions of Equation 3.46 for $x_i=1$
Ψ	parameter used in the Flory model

Superscripts

°	standard
b	binary
dis	dispersive contribution
E	excess property
id	ideal solution
quac	quasichemical contribution

Subscripts

1,2,3,A,B,C,i,j,k	component indices
123	ternary mixture of components 1, 2, and 3
1+23	pseudo-binary mixture of component 1 and a specific binary mixture of components 2 and 3 having a fixed composition
A	attractive
b	binary mixture
c	critical condition
config,m	configurational molar property
F	Flory term used in the association model
H	Hydrogen-bond formation
m	molar quantity, or mixture, or mixing process
MK	Mecke-Kempter term used in the association model
st	contact sites of s and t used in the DISQUAC model
T	Ternary

Abbreviations

2,2,4-TMP	2,2,4-Trimethylpentane
2,3-DMB	2,3-Dimethylbutane
A-2	Association model
AAD	Average Absolute Deviation
AAPD	Average Absolute Percentage Deviation
AGSM	Analytical Group Solution Method
A-S	Adachi-Sugie
ASOG	Analytical Solution of Groups
DISQUAC	Dispersive-Quasi-Chemical
EOS	Equation of State
PR	Peng-Robinson equation (1976)
PRSV	modified PR equation by Stryjek and Vera (1986)
PT	Patel and Teja equation (1982)
SRK	modified RK equation by Soave (1972)
SW	Schmidt and Wenzel equation (1980)
IUPAC	International Union of Pure and Applied Chemistry
LB-2	Lorentz-Berthelot mixture
LKB	Name of the calorimeter manufacturer
LLE	Liquid-Liquid Equilibrium
LS	Least-Squares
MC	Monte Carlo
MD	Molecular Dynamics
MTBE	Methyl Tert-Butyl Ether
NRCC	National Research Council of Canada
NRTL	Non-Random Two-Liquid
P-V-T	Pressure-Volume-Temperature
R-K	Redlich-Kister
RMSD	Root-Mean-Square-Deviation

S-2	Solvation model
SIGMA	Simplified Group Method Analysis
UNIFAC	Universal Functional Activity Coefficient
UNIQUAC	Universal Quasi-Chemical
VLE	Vapor-Liquid Equilibrium

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Chapter 1

Introduction

Mixing is a process people deal with frequently in their daily lives. They are so used to it that they usually assume that adding "one" to "one" must lead to a "two." For example, when one liter of alcohol is mixed with one liter of water, would the resulting solution be a two liter diluted alcohol? Many people would not have any doubt about it, although it is not true. Mixing behaviours are not as simple as $1+1=2$, mathematically, because excess properties caused by the mixing process have to be considered. In general, excess properties have relatively small values. However, in certain circumstances, they would show their effects in a big way.

1.1 Objectives

To discuss an excess property, it is necessary to begin with the concept of an ideal solution, because the simple ideal behaviour provides a convenient basis on which correction factors are introduced to express quantitatively the real behaviour. The components of an ideal solution are considered to have no differences in their molecular shape, size, mass, and chemical type (electronic configuration). In other words, all the molecules in an ideal solution interact in the same way (Chao and Greenkorn, 1975).

In thermodynamics, the excess property of a solution is a measure of the difference between the property value of a real solution and the value it would have as an ideal solution at the same temperature, pressure, and composition. By definition,

$$M^E = M - M^{id}$$

where M^E represents the excess property, M is the property of the real solution and M^{id} is the property of an ideal solution under the same conditions. In other words, the excess property indicates quantitatively how far the real solution deviates from an ideal solution whose behaviour is well known. Thus, studies of excess properties occupy an important place in thermodynamics.

This study was focused on the excess enthalpy, H^E, or the so-called heat of mixing. The goals of the research were to carry out experimental measurements of excess enthalpy values for some selected systems, to represent the experimental findings by

using appropriate models, and to further predict H^E values for multicomponent systems. The objectives of the study can be described in two aspects:

- the experimental determination of excess enthalpies for some binary and ternary organic liquid mixtures, and
- a theoretical study of various approaches for correlating and predicting H^E values.

1.2 Importance of the subjects

1.2.1 Experimental excess enthalpy data

Among excess properties, excess enthalpy H^E, being of considerable importance for mixing or separation processes in chemical and petroleum industries, has drawn great attention. Experimental excess enthalpy data are required for a proper design of distillation columns. They provide basic information for testing the feasibility of existing solution theories and serve as a guide for formulating a new solution theory, because they are a reflection of the intermolecular force change caused by a mixing process. They can also be used for testing thermodynamic consistency of isobaric vapour-liquid equilibrium results.

1.2.2 Representation of experimental excess enthalpy data

The representation of experimental excess enthalpy data by means of certain

expressions, empirically or theoretically, is a necessary step in experimental thermodynamics. It functions as a tool for verifying and smoothing the experimental data. It also provides a measure for data interpolation and possible extrapolation, which would extend the application of the experimental findings over a broader range. For the theoretical or semi-empirical models, a better representation of the experimental results contributes to a better understanding of the fluid behaviour.

1.2.3 Predicting excess enthalpy values for multicomponent systems

For a long time, excess enthalpies of binary systems have been investigated extensively. Due to the difficulties involved in the experimental measurements and the increasing time consumption with each additional component of a multicomponent mixture, experimental investigations of the excess enthalpies of multicomponent systems have been very limited. It is, therefore, highly desirable to develop suitable methods capable of predicting excess enthalpies of multicomponent systems from binary data.

1.2.4 Systems studies

In arranging the project, special attention was paid to the possible practical usage of the systems selected. It is well known that as a result of changes in economic and environmental requirements, alternative transportation fuels have begun to attract

increasing attention. A portion of regular gasoline currently available in the market can be replaced by alternatives, such as alcohols or ethers. Among them are ethanol, propanol and methyl tert-butyl ether (MTBE), *etc.*, which may be obtained from processes other than petroleum refining and used to increase the gasoline's octane number. The alternative fuels help to reduce our dependence on crude oil supply and to meet clean air standards. In some large cities in the United States, it has become mandatory to use alcohol-blended gasoline as transportation fuel (Hunt, 1982).

Also, as mentioned by the International Union of Pure and Applied Chemistry, "ethers alone, and with hydrocarbons, are very important in electro-refining, electro-machining, electro-polishing and electro-deposition, because they can be mixed with salts to produce a wide electrochemical window. These require a careful study of the thermophysical and thermochemical properties of these pure components and mixtures" (IUPAC, 1994).

With the consideration of their practical importance, the following binary and ternary systems formed by mixing ethanol, propanol or methyl tert-butyl ether (MTBE) with some normal and branched alkanes were chosen for experimental studies in this work: ethanol + n-hexane + n-decane, ethanol + n-hexane + n-dodecane, 1-propanol + n-hexane + n-decane, 1-propanol + n-hexane + n-dodecane, MTBE + n-hexane + n-decane, MTBE + n-hexane + n-dodecane, together with six additional binary systems: ethanol + 2,3-dimethylbutane, ethanol + 2,2,4-trimethylpentane, 1-propanol + 2,3-

dimethylbutane, 1-propanol + 2,2,4-trimethylpentane, MTBE + 2,3-dimethylbutane, MTBE + 2,2,4-trimethylpentane.

1.3 An overview of the contents

A literature review is given in Chapter 2 which presents a survey of different calorimetric methods and approaches for representing excess enthalpy values. A study of the previous investigations of the selected system reported in the literature is also introduced in this chapter.

A presentation of theories and methodologies involved in this study is included in Chapter 3.

Chapter 4 covers a description of the equipment and the experimental procedures employed. The experimental results are also illustrated and discussed in this chapter.

The representations of experimental excess enthalpy values by means of various models are presented and discussed in Chapter 5. A description of the new model developed in this study is also included in this chapter.

Some conclusions are summarized in Chapter 6.

In the appendices, detailed experimental results, as well as the computational approaches, programs, and calculation results are presented. Some specific experimental treatments are also explained.

Chapter 2

Literature survey

This chapter covers a review of different calorimetric methods, a literature search for excess enthalpy values of relevant systems, and an evaluation of a number of existing approaches for correlating and predicting excess enthalpy values, such as empirical representations, solution theories, and group contribution models, whose advantages and shortcomings are suggested.

2.1 Calorimetric methods

To obtain precise values of excess enthalpy, the most reliable way is to measure it directly using a calorimeter, although H^E can be derived from other excess properties, such as from the temperature dependence of the excess Gibbs free energy, as shown in Equation (2.1):

$$H^E = -T^2 \left(\frac{\partial G^E / T}{\partial T} \right)_P \qquad (2.1)$$

The word *calorimeter* comes from the Latin word for *heat* and the Greek word for *measure*. A calorimeter can measure the heat involved by comparison either directly with a known electrical energy or indirectly with materials whose thermal properties are known. Direct measurement usually involves the addition of a known amount of electrical energy in the form of heat, because with modern techniques, electrical energy can be measured more accurately and conveniently than other forms of energy. In an indirect measurement, one can avoid the use of electrical energy measurements by utilizing some thermal properties that have already been determined electrically.

There are various calorimetric methods leading to different types of commercialized calorimeters available, such as adiabatic calorimeters, isothermal calorimeters, isothermal jacket calorimeters and flow calorimeters. These calorimeters are designed to be capable of producing reliable results for different purposes. Usually, they are classified according to which physical variables are kept constant (McCullough and Scott, 1968).

2.1.1 Adiabatic calorimeter

The type of adiabatic batch calorimeter designed originally by McGlashan is among the most successful ones for measuring the heat effect of solid and/or liquid systems over a wide range of temperatures, which includes heat of formation, heat of chemical reaction, latent heat of phase changes, heat capacity, heat of mixing, etc. (Larkin and McGlashan, 1961; Armitage and Morcom, 1969; Hill and Swinton, 1980a,b; Miltenburg

et al. 1987). An adiabatic calorimeter contains a calorimetric vessel that is thermally isolated from its surroundings. Strictly speaking, no practical calorimeter is truly adiabatic. A calorimeter can be made nearly adiabatic by reducing the heat exchange between the calorimetric vessel and its surroundings. This can be achieved by minimizing three important factors involved in calorimetric measurement.

One is to minimize the temperature difference between the calorimetric vessel and its surroundings. If the heat has a positive value (endothermic), there would be a lowering of the temperature. In practice, electrical energy is usually supplied to the calorimeter to compensate for the temperature drop. On the other hand, a negative value heat effect (exothermic) would cause a temperature increase in the calorimetric unit. A second apparatus is necessary to determine the amount of energy required to produce the same temperature rise. Alternatively, two identical calorimeters can be used (Armitage and Morcom, 1969). A known amount of electrical energy is added to the second calorimeter in such a way that the temperature difference between the two calorimeters is minimized.

The other two ways to reduce the heat exchange between the calorimetric unit and its surroundings are to minimize the heat transfer coefficient, and to minimize the time for the heat exchange.

It should be noticed that the basic definition of adiabatic refers to heat, not any other forms of energy. The accepted meaning of an adiabatic calorimeter permits measured

electrical energy to enter the calorimeter and be transformed into heat, as via a calorimeter heater.

The utilization of an adiabatic calorimeter is restricted by the accuracy of the temperature control system. Although the adiabatic calorimeter has increased in use along with the availability of modern electronic instruments for temperature control and recording, the design of the calorimeter and its auxiliary parts is at least as important as the external instruments in obtaining good temperature control. Also, the calorimeter becomes more difficult to operate at higher temperatures, because of increased heat leakage due to the non-ideality of the calorimeter and its application.

2.1.2 Isothermal calorimeter

The isothermal calorimeter originally developed for mixtures by Van Ness (Mrazek and Van Ness, 1961; Savini *et al.*, 1966) has been further improved by Marsh and his coworkers (Stokes, *et al.*, 1969; Ewing *et al.*, 1970). This type of calorimeter is capable of producing highly precise and accurate results for different types of heat effect and is widely used for heat of mixing measurement (Alonso *et al.*, 1987; Lim *et al.*, 1994).

An isothermal calorimeter, as the name implies, is one in which no temperature change occurs during the experiment. There are two ways to achieve this purpose. One is based on solid-liquid or liquid-vapour phase change. For example, solid-liquid phase change is used in the ice calorimeter (Ginnings, *et al.*, 1950). The volume change

involved is used as a measure of the heat added or removed. The major disadvantage of this method is that measurements can only be carried out at the phase change temperature of the calorimeter fluid. Another way to keep the temperature of the calorimeter constant during an experiment is to use electrical heating to balance the removal of heat, or to use electrical cooling (Peltier effect) to balance the addition of heat (Mann, 1954; Rossini, 1956).

The major advantages of this type of calorimeter include easier control of heat leakage and the independence of the results from the heat capacity of the calorimeter since its temperature does not change.

2.1.3 Isothermal jacket calorimeter

An isothermal jacket calorimeter or isothermal shield calorimeter is one whose surrounding shield is kept at a constant temperature, rather than at the calorimeter temperature. One obvious advantage of this method is the simplicity of the operation of the shield. During an experiment, the calorimeter may change temperature while the shield is kept at a constant temperature.

2.1.4 Flow calorimeter

A flow calorimeter is one of the best choices in determining the heat of mixing for

most liquid systems. In a flow calorimeter, two fluid samples flow through a mixing cell at steady and known rates. The flow rates can be varied in a continuous, known manner so that a complete H^E-composition curve can be produced quickly with a precision of around 1 per cent (Rowlinson and Swinton, 1982). With flow techniques, it is possible to avoid several of the difficulties which may arise in batch calorimeters of more conventional design. In particular, it is unnecessary to use mercury to separate the component liquids before mixing, and the mixing can readily take place in the absence of any vapour space. In addition, any desired composition is obtained directly by setting the relative flow-rates of the components, and transient effects during the initial formation of the mixture are unimportant (Tanaka *et al.*, 1975). Typically, one mole of each of the pure components is required to produce a complete set of results. This type of calorimeter is not suitable for viscous fluids, or for liquids with large differences in density.

In practice, the choice of calorimeter depends on the research requirements. As for the nature of the calorimetric experiment, a batch type calorimeter is usually suitable for processes such as chemical reaction, phase change, and bio-processes, while a flow calorimeter is much more efficient for measuring heat of the mixing of liquid systems. Especially when the experiments involve multicomponent systems, this advantage appears to be more important.

2.2 Systems studied

As for heat of mixing of related systems, there have been several previous investigations reported in the literature, for the ethanol + n-hexane system (Brown *et al.* 1964; Jones and Lu, 1966; Stokes and Burfitt, 1973) and for the 1-propanol + n-hexane system (Brown *et al.*, 1964; Veselý *et al.*, 1982). Unfortunately, there is a lack of resutls at the two ends of the alcohol concentration range for the work by Brown *et al.*, while there are no results reported by Stoke *et al.* in the large range of ethanol concentration from 0.06 to 0.69. Jones' results covered the whole ethanol concentration range quite well, but failed to produce a relatively smooth regression curve, which might be related to the point-by-point method employed. The comparison of these results and those obtained in this work will be discussed further in Chapter 4.

The systems of n-decane + ethanol or 1-propanol have also been studied previously (Christensen *et al.*, 1979), but at a somewhat elevated pressure, 170 kPa.

H^E measurements for the n-hexane + n-decane and n-hexane + n-dodecane systems were reported by Marsh, Ott and their colleagues in the early 1980's (Marsh *et al.*, 1980; Ott *et al.*, 1981). Since the components in each of these binary systems are quite similar, the values of the heats of mixing for both systems are relatively small. For the n-hexane + n-dodecane system, the values of H^E are less than 40 $J \cdot mol^{-1}$, while the maximum value of H^E is only 14.51 $J \cdot mol^{-1}$ for the n-hexane + n-decane system.

Directly comparable results for the mixtures of MTBE with n-hexane, n-decane, and n-dodecane are not available in the literature. However, the system of MTBE + n-heptane has been recently investigated by Tusel-Langer *et al.* (1991), and will be used later for comparison with the experimental results obtained in this study. For the other 14 binary and 6 ternary systems involved in this work, there are no experimental results reported in the literature.

2.3 Correlation and prediction approaches

The main purpose of experimental data correlation is to provide convenience and maximized extent of usage of the experimental data. Also, due to the difficulties involved in the experimental measurements and the increasing time consumption with each additional component of a multicomponent mixture, it is highly desirable to develop practical approaches capable of predicting excess enthalpies of multicomponent systems from binary data. In the last two decades, great efforts have been made in this field, which encompass various approaches for H^E correlation and prediction for multicomponent systems. In the following section, discussion will be focused on three different approaches for H^E correlation and prediction, which include empirical expression methods, solution theory-related methods, and group-contribution methods.

2.3.1 Empirical expressions

Although empirical expressions are very useful and convenient for data correlation and/or for prediction, there are limitations. The parameters in these formulas are fitted to the experimental data and the number of parameters can be determined according to the correlation accuracy required. Pando *et al.* (1987) reviewed many useful empirical expressions for estimating ternary excess enthalpies from the heat of mixing data of their three constituent binary mixtures. However, due to the uncertainty of the expressions, predictions with this method involve some arbitrariness. For example, the equation proposed by Toop (1965)

$$H^E = x_1x_2\frac{\sum^{n} A_k(2x_1-1)^k}{\sum^{m} B_l(2x_1-1)^l} + x_1x_3\frac{\sum^{n'} A'_k(2x_1-1)^k}{\sum^{m'} B'_l(2x_1-1)^l}$$

$$+x_2x_3\left[\sum^{n''} A''_k\left(\frac{x_2-x_3}{x_2+x_3}\right)^k\right] / \left[\sum^{m''} B''_l\left(\frac{x_2-x_3}{x_2+x_3}\right)^l\right] \quad B_0, B'_0, B''_0=1 \qquad (2.2)$$

is considered a good equation for ternary excess enthalpy prediction, where A_k and B_l are the equation parameters. But the accuracy of predictions with this equation strongly depends on which component of the mixture is chosen as component 1. In other words, there is only a 33 per cent chance to have a good prediction of ternary excess enthalpies by using this equation. Therefore, empirical methods are not recommended in general, unless their reliability can be proved in special circumstances.

2.3.2 Solution theory-related methods

Another approach for H^E correlation and prediction is based on solution theories, such as the regular solution theory, the quasi-lattice theory, the two-liquid theory, the associated solution theory, and the Flory theory. Solution theories aim at representing the behaviour of a solution in terms of its intermolecular forces and structure. With certain theoretical background, this approach is more sensible and helpful for understanding the solution behaviour better. However, this approach is presently still at a semi-empirical stage. It usually involves one or more characteristic parameters which are fitted to the experimental data.

The Wohl type of equation (Wohl, 1946; 1953; Hala *et al.*, 1965) is based on the regular solution theory, which is defined as one in which the components mix with no excess entropy, S^E, provided that there is no volume change upon mixing (Prausnitz *et al.* 1986), i.e. $S^E = 0$ and $V^E = 0$. One of the main advantages of this equation is that some rough physical significance can be assigned to the equation parameters. Since a regular solution behaves as an ideal solution, except for non-zero interaction energies among the molecules, this type of equation provides a good representation of interactions of the molecules, especially when the contributions of groups with three, four or more molecules are considered. However, this equation is better viewed as an empirical or semi-empirical treatment, because all of its parameters, corresponding to the contributions of different groups of molecules, must be fitted to the experimental data.

Generally, the greater the number of molecules that are in a group, the greater the number of parameters that are required, and therefore more empirical factors are involved. This equation also has the merit of mathematical simplicity, easy evaluation of its parameters, and often adequate representation of even fairly nonideal binary mixtures, including partially miscible liquid systems. It is not applicable to multicomponent systems without ternary or higher interaction parameters.

Wilson (1964) proposed his famous equation based on the local composition concept. By replacing the mole fractions in the Flory-Huggins equation (Flory, 1941; 1942; Huggins, 1941) with the local compositions, the Wilson equation provides better representations of the non-ideal behaviour of real systems, especially alcohol-hydrocarbon mixtures, than the Wohl type of equation with the same number of parameters. It is also capable of representing multicomponent behaviour with only binary parameters. A drawback of the Wilson equation is that it cannot handle liquid-liquid immiscibility. It also fails to provide reasonable results for systems with relatively high H^E values.

Based on the two-liquid theory, Renon and Prausnitz (1968a; 1968b; 1969) developed the Non-Random Two-Liquid (NRTL) model. This model assumes that in a binary mixture the liquid has a structure made up of cells of molecules of types 1 and 2, each surrounded by assortments of the same molecules, with each of the surrounding molecules in turn surrounded in a similar manner, and so on. It has been proven that the NRTL equation provides accuracies of correlation and prediction similar to the

Wilson equation, but importantly that it can be used for liquid-liquid immiscible systems. The requirement of three parameters for each pair of constituents is the NRTL's main handicap in comparison with the Wilson model. The NRTL model has been modified since its original formulation. It was extended to electrolytes by Cruz and Renon (1978) and Chen *et al.* (1982). It was combined with associated solution models and provided very good results in the representation of the excess enthalpies of alcohol solutions (Nagata and Tamura, 1984; 1985; 1987). It was modified by Gierycz and Nagata (Gierycz, 1990; Gierycz and Nagata, 1990) as the NRTLM equation and then adopted by Moorthi *et al.* (1991) for the correlation and prediction of the excess enthalpy and excess Gibbs energy of polar-nonpolar systems.

The two-liquid model and the concept of local compositions were adopted by Abrams and Prausnitz (1975) in the semitheoretical development of the Universal Quasi-Chemical (UNIQUAC) equation. They assumed that the expression for the activity coefficients contains two parts: the combinatorial part, essentially due to differences in size and shape of the molecules, and the residual contribution, essentially due to energetic interactions. They showed that the Wohl type of equation, the Wilson and NRTL equations are special cases of the UNIQUAC equation when suitable values of the parameters are assigned. Major characteristics of the UNIQUAC equation are: (a) applicability to multicomponent mixtures in terms of binary parameters only, the same requirement as for the Wilson and NRTL models; (b) applicability to liquid-liquid

equilibria; (c) a built-in temperature dependence valid over at least a moderate range; (d) possibly superior representation of mixtures of widely different molecular sizes. Perhaps the main disadvantages of the UNIQUAC equation are its somewhat greater algebraic complexity and the fact that the representation of data is often poorer than by some simpler equations (Walas, 1985). The UNIQUAC model has been modified as the UNIQUAC associated-solution model (Nagata and Kawamura, 1979) for better representations of polar-nonpolar systems (Brandani and Evangelista, 1984; 1987; Nagata and Miyazaki, 1987; Nagata and Miyamoto, 1990).

All the above mentioned equations are also called activity coefficient models. They were originally developed for the purpose of phase equilibrium calculations. Since equilibrium relations and enthalpy balances are commonly involved together in many practical calculations, it would be convenient to have them expressed in terms of the same parameters. Unfortunately, at least with the local composition models (Wilson, NRTL, UNIQUAC), simultaneous correlation of VLE and H^E values usually leads to a worsening of the fit to one or both of the data types. Making the parameters temperature-dependent often helps, but this procedure at least doubles the number of parameters, which becomes a serious matter with multicomponent systems. Further studies are needed for better representation of both VLE and H^E values by means of activity coefficient models.

The Flory theory (Flory, 1965; Abe and Flory, 1965) is considered a semi-empirical

theory, since the core of the theory is a semi-empirical partition function suggested by Flory. Based on the partition function, a liquid equation of state was derived which is related to the excess functions of mixtures. An evident advantage of the Flory model is that all its parameters can be derived from properties of pure substances, such as the isobaric expansivity α_p, the isothermal compressibility κ_T, or the thermal pressure coefficient γ ($=\alpha_p/\kappa_T$), the derivative $(\partial P/\partial T)_v$, except its interchange energy parameter X_{ij}, which is usually determined from regression of experimental data. This distinguishing feature has made this theory very attractive, since the main purpose of a solution theory is to be able to describe the behaviour of a mixture by means of the properties of its constituent pure substances. It has been found that the Flory theory can well represent excess properties, especially for ether-containing systems (Benson *et al.*, 1988; Luo *et al.*, 1988; Wang *et al.*, 1989a,b, 1990b). It can also be used to predict the values of an excess property from another excess property. For example, some successes have been reported for V^E prediction from H^E data (Hu *et al.*, 1984; Wang *et al.*, 1989b). It was also suggested, however, that inadequate representation would be reached if V^E data were used to predict H^E values (Wang *et al.*, 1990b).

The development of solution theories relies on our basic understanding of the solution at the molecular level. Although this method is still far from ideal, it has demonstrated its great potential and promising future.

2.3.3 Group contribution method

This approach is based on the assumption that a real solution is composed of the constituent groups of its components. Calculation of thermodynamic properties from group contributions was first suggested by Langmuir (1925).

A systematic development known as the Analytical Solution of Groups (ASOG) was established by Deal, Derr, and Wilson (Wilson and Deal, 1962; Derr and Deal, 1969; Kojima and Tochigi, 1979), and modified by Vera and Vidal (1984) with the Analytical Group Solution Method (AGSM) (Lai *et al.*, 1978), leading to a Simplified Group Method Analysis (SIGMA) (Ashraf and Vera, 1980). However, a fully developed method was not provided (Vera and Vidal, 1984).

Similar to the ASOG method, another more convenient treatment, called the Universal Functional Activity Coefficient (UNIFAC) method, has been extensively used. Developed by Fredenslund *et al.* (1975; 1977a), this model is based on the UNIQUAC method with a combinatorial part for differences in both molecular size and molecular shape, and a residual part for group interactions. The constants representing the group sizes and surface areas are obtained from atomic and molecular structure data. Thus, the UNIFAC method avoids the arbitrariness in determining the combinatorial term which exists in ASOG calculations (Fredenslund *et al.*, 1977b). By reducing the interactions between molecules to the interactions between their functional groups, UNIFAC allows one to represent a large variety of experimental data with a reduced set of parameters and

to predict with reasonable confidence the behaviour of systems for which experimental data are unavailable.

As a simple extension of the quasi-chemical theory, the Dispersive-Quasi-Chemical (DISQUAC) model has been recognized as one of the good group contribution models. It improves the quality of the predictions by using structure-dependent interaction parameters (Artal, 1991). In this model, each contact, either polar or non-polar, is characterized by a single parameter, the dispersive interchange energy, and the polar contacts by two additional parameters, the quasi-chemical interchange energy and the coordination number (Kehiaian, 1983). It has been successfully applied to many classes of substances (Kehiaian and Velasco, 1987; Kehiaian and Marongiu, 1988a; 1988b; Muñoz Embid *et al.*, 1987; García Vicente *et al.*, 1989; García-Lisbona *et al.*, 1989; Soriano *et al.*, 1989).

The applicability of group-contribution methods has been extended by combining them with different equations of state (Gupte and Daubert, 1986; Gupte *et al.*, 1986; Gani *et al.*, 1989; Schwartzentruber and Renon, 1989; Tochigi *et al.*, 1985: 1990; Dahl *et al.*, 1990; Abdoul *et al.*, 1991; Lermite and Vidal, 1992) to calculate the VLE and excess properties for partly/completely miscible systems, and to treat polar and non-polar compounds, as well as multicomponent systems at different temperatures and pressures. Generally speaking, application of any group-contribution model only requires very basic information about the constituent groups of each component, but demands much more

time and effort for calculations (Gonzalez *et al.*, 1990; 1991). Also we are aware of the fact that for some systems, such as ether + hydrocarbon systems, the prediction of H^E values with group contribution methods is not yet acceptable (Larsen *et al.*, 1987).

In conclusion of the literature survey, a flow calorimeter is more suitable for heat of mixing measurements for liquid systems than other types, especially when multicomponents are involved.

The experimental H^E data for the systems of alcohol or ether with hydrocarbons are in great demand for industrial and environmental usage.

For the representation of experimental H^E data for binary and multicomponent liquid systems, solution theory-related models are generally superior to the other methods reviewed. It is a fact that a solution theory is usually able to describe the behaviour of certain systems, but fails to do the same for other systems. Evidently some modifications are needed. Also, it would be appropriate to predict ternary H^E values based on solution theory-related models.

In the following chapters, the works involved in this study will be presented in details including four major parts: the experimental measurements of H^E data for 15 binary and six ternary systems; the representation of the experimental data with various models; the development of a new model for representing H^E values, based on solution theories; and the prediction of ternary H^E values from binary data.

Chapter 3

Theory and methodology

Theoretical study of real mixture behaviour should start with and always be based on experimental investigations. In this study, a series of calorimetric measurements was carried out. The experimental methodologies employed and the calorimetric theory behind it are described in this chapter.

Practically, however, experiments are usually restricted by many factors, such as available equipment, experimental materials, operation conditions and financial situation. It has been suggested that there is a strong need for choosing suitable models which are able to represent mixture behaviour well, on the basis of limited experimental data. A brief discussion of some solution theories and models used for representing excess enthalpy values, such as the Flory theory and its association model, the DISQUAC, NRTL, and UNIQUAC models, is presented in this chapter.

3.1 Calorimetry

All chemical and physical processes involve energy changes. Calorimetry is concerned with the measurement of these changes. According to the First Law of Thermodynamics, the energy of a system is a single-valued function of its state. Therefore, the energy change associated with the change of the system from one state to another is dependent only on the initial and final states, and not on the path the system followed. For a closed system involving only liquids, the amount of heat produced in a process at constant temperature and pressure equals to the energy change ΔH of the system, since comparing the energy change, the amount of work due to volume change could be negligible. The amount of energy changes in the form of heat can be determined by means of calorimetric measurements.

In mixing processes, there are different types of heat effects. To distinguish heats of solution, dilution, and mixing, according to common usage, the heat effect accompanying the solution of a solid or a gas in a liquid is called heat of solution, while that accompanying the mixing of a solution with the corresponding pure solvent, or of two solutions containing the same components in different concentrations is described as heat of dilution. The heat of mixing refers to the mixing of one pure liquid with another. For a mixing process, therefore, the enthalpy value of the system in its initial state is represented by a summation of the enthalpy values of each pure component i as $\Sigma x_i H_i$ and the enthalpy in the final state, H, is that of the mixture. The enthalpy change

of the mixing process can be then expressed as

$$\Delta H = H - \sum x_i H_i \tag{3.1}$$

The enthalpy change of the mixing process at constant temperature and pressure, ΔH, is also called the heat of mixing.

In thermodynamic research, heat of mixing is usually referred to as excess enthalpy. The relationship between them can be shown as

$$\begin{aligned} \Delta H^E &= \Delta H - \Delta H^{id} \\ &= (H - \sum x_i H_i) - (H^{id} - \sum x_i H_i) \end{aligned} \tag{3.2}$$

where ΔH^E is the excess enthalpy change of a mixing process, ΔH is the enthalpy change of the process, or heat of mixing, and ΔH^{id} is the enthalpy change at the same condition of temperature, pressure, and composition to form an ideal solution. Also in equation (3.2), H and H^{id} denote the enthalpies of a real solution and an ideal solution, respectively. For an ideal solution, its enthalpy, H^{id}, can be written as

$$H^{id} = \sum x_i H_i \tag{3.3}$$

Since the formation of an ideal solution results in no change in molecular energies or volume, i.e. $\Delta H^{id} = 0$, equation (3.2) is then reduced to

$$\Delta H^E = H - \sum x_i H_i = \Delta H \tag{3.4}$$

ΔH^E in equation (3.4) can be further reduced to H^E, according to the definition of an excess property, i.e.

$$H^E = H - H^{id} = \Delta H^E \tag{3.5}$$

A comparison of equations (3.4) and (3.5) indicates that the enthalpy change of a mixing process, or heat of mixing is equal to the excess enthalpy of the mixing process.

In calorimetric studies, such a heat effect is measured by using calorimeters. Depending on the design of the calorimeter used, a comparison of the amount of heat detected by the calorimeter with a known electrical energy or with materials which have known thermal properties will determine the actual value of the heat effect. With an LKB flow calorimeter, as adopted in this study, the heat effect of the mixing process is compared with the electrical power, W_p, needed to produce the same thermal effect in the calorimetric unit. Suppose two pure liquids are flowing into a mixing cell at the volumetric flow rates of f_1 and f_2, the excess molar enthalpy, H_m^E, and the mole fraction of component 1, x_1, are given by

$$H_m^E = \frac{W_p}{f_1/v_1 + f_2/v_2} \tag{3.6}$$

and

$$x_1 = \frac{f_1/v_1}{f_1/v_1 + f_2/v_2} \tag{3.7}$$

where the electrical power, W_p, has units of Joule·s^{-1}, and v_1 and v_2 are the molar volumes of the components 1 and 2, respectively.

3.1.1 Verification of a calorimeter

The purpose of verifying a calorimeter before using it is to determine its reliability. There are two main possible sources of uncertainties in experimentally determined H^E values. One is from the errors produced by the calorimeter itself (energy, temperature, mass, etc.). The other is from the uncertainties caused by the impurity and state of the materials to be measured. In order to minimize the errors caused by the calorimeter itself, it is necessary to check its reliability before starting any measurement. The commonly used method for verification of a calorimeter is to measure a "reference" material, or a standard system, whose state is reproducible and well known. If the thermal properties of this standard system are well known, this check yields evidence about the reliability of the calorimeter (McCullough and Scott, 1968).

The system widely used as a standard system for an endothermic mixing process is the benzene+ cyclohexane system. One of the advantages of this system is that the two constituent components are commercially available in a high grade of purity and at a

reasonable price. Also, the excess enthalpy results of this system have been reported extensively in the literature.

Another standard system recommended by the IUPAC commission on Thermodynamics and Thermochemistry (Bulletin, 1970) is the cyclohexane + n-hexane system. This system is suitable for testing calorimeters to be used for measuring positive excess enthalpies, providing that the density difference between the components is not large.

It is logical to use materials with the same degree of purity as for the standard systems recommended, in order to eliminate the errors caused by impurities of the samples.

3.1.2 Calibration methods

The calorimetric procedure used to measure heat effects involves two major steps. One is calibration of the calorimeter and the other the real measurement. For every system, it is required to carry out a calibration before the actual measurement, during which the heat effect, detected by thermocouples attached to the experiment chamber, is recorded in the form of electrical signals. The purpose of the calibration is to find the equivalence between the heat effect and the recorded electrical signals.

A calibration can be carried out either by adding a known electrical energy, in the form of heat, to the calorimeter and measuring the calorimeter's response to it, or by examining the response of the calorimeter to some standard system whose thermal

properties have been well determined before. The former is referred to as a direct or electrical calibration, and the latter one as an indirect calibration. Since electrical energy can be measured more accurately and conveniently than other forms of energy, and no special substances are required as standard, the electrical calibration is considered superior to the indirect calibration.

Figure 3.1 shows schematically how the heat effect is recorded for a flow calorimeter. It is clear from the schema that the heat effect due to a mixing process is reflected as a shift of the voltage curve from the baseline with a blank flow. This fact suggests that the calibration of a flow calorimeter should be carried out while fluid flows through it as in an actual measurement.

In an electrical calibration, a known electrical potential E is applied to the calibration circuit through a standard resistance R_c. In other words, a known current $I(=E/R_c)$ is introduced, which causes a deflection of the voltage curve V(f) from the baseline voltage $V^\circ(f)$ associated with the blank flow alone. Since voltage readings would be different for the same amount of electrical power employed at different flow rates, calibration of a flow calorimeter should be carried out at various flow rates. It has been suggested that for a steady state, in which a power W_p is released within the calorimetric chamber by electrical heating or as the result of a mixing process, W_p is proportional to the corresponding voltage change, i.e.

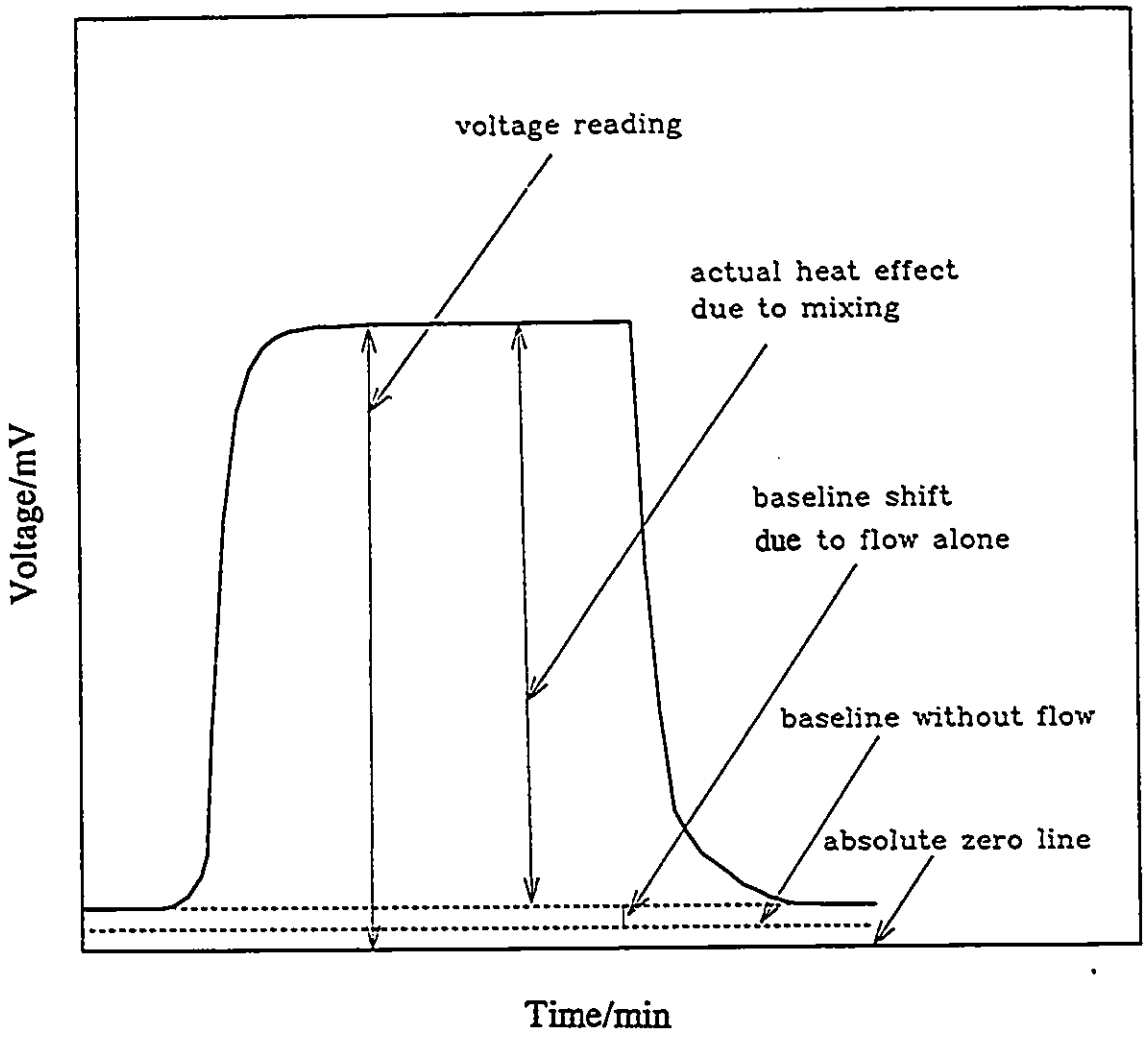


Figure 3.1 Relationship between voltage reading and baselines

$$W_p = \epsilon[V(f) - V^*(f)] \tag{3.8}$$

where ϵ is the calibration constant, which is a characteristic of the calorimeter.

If the electrical heater or calibration resistance R has a known value, the electrical power applied in the form of heat can be expressed as

$$W_p = I^2R \tag{3.9}$$

A combination of equations (3.8) and (3.9) gives the expression for estimating the value of ϵ as

$$\epsilon = \frac{I^2R}{V(f) - V^*(f)} \tag{3.10}$$

As the voltage reading V is a function of the flow rate, a fixed value of W_p will yield different V values at different flow rates. A series of measurements could therefore identify the relationship between the calibration constant ϵ and the flow rate, which will then be used to determine any unknown heat effect H_m^E produced in an actual calorimetric measurement by using the following equation

$$H_m^E = \frac{\epsilon[V(f) - V^*(f)]}{f_1/v_1 + f_2/v_2} \tag{3.11}$$

The calibration of a calorimeter can be considered as the process of determining the calibration constant ϵ, a characteristic of the calorimeter.

3.2 Excess enthalpy of ternary systems

In a mixing process involving three components, excess enthalpy is a function of temperature, pressure, and the mixture composition. Holding the temperature and pressure constant leaves two degrees of freedom (the mole fractions of two of the components). One of the best ways of showing how excess enthalpy varies with the composition of the system is to use a triangular diagram. The following section explains how these are constructed and interpreted.

3.2.1 Triangular diagram

The mole fractions of the three components, A, B, and C, of a ternary system satisfy

$$x_A+x_B+x_C=1 \tag{3.12}$$

A phase diagram drawn as an equilateral triangle, as shown in Figure 3.2, ensures that this property is satisfied automatically because the sum of the distances to a point inside an equilateral triangle measured parallel to the edges is equal to the length of the side of the triangle, which may be taken to have unit length.

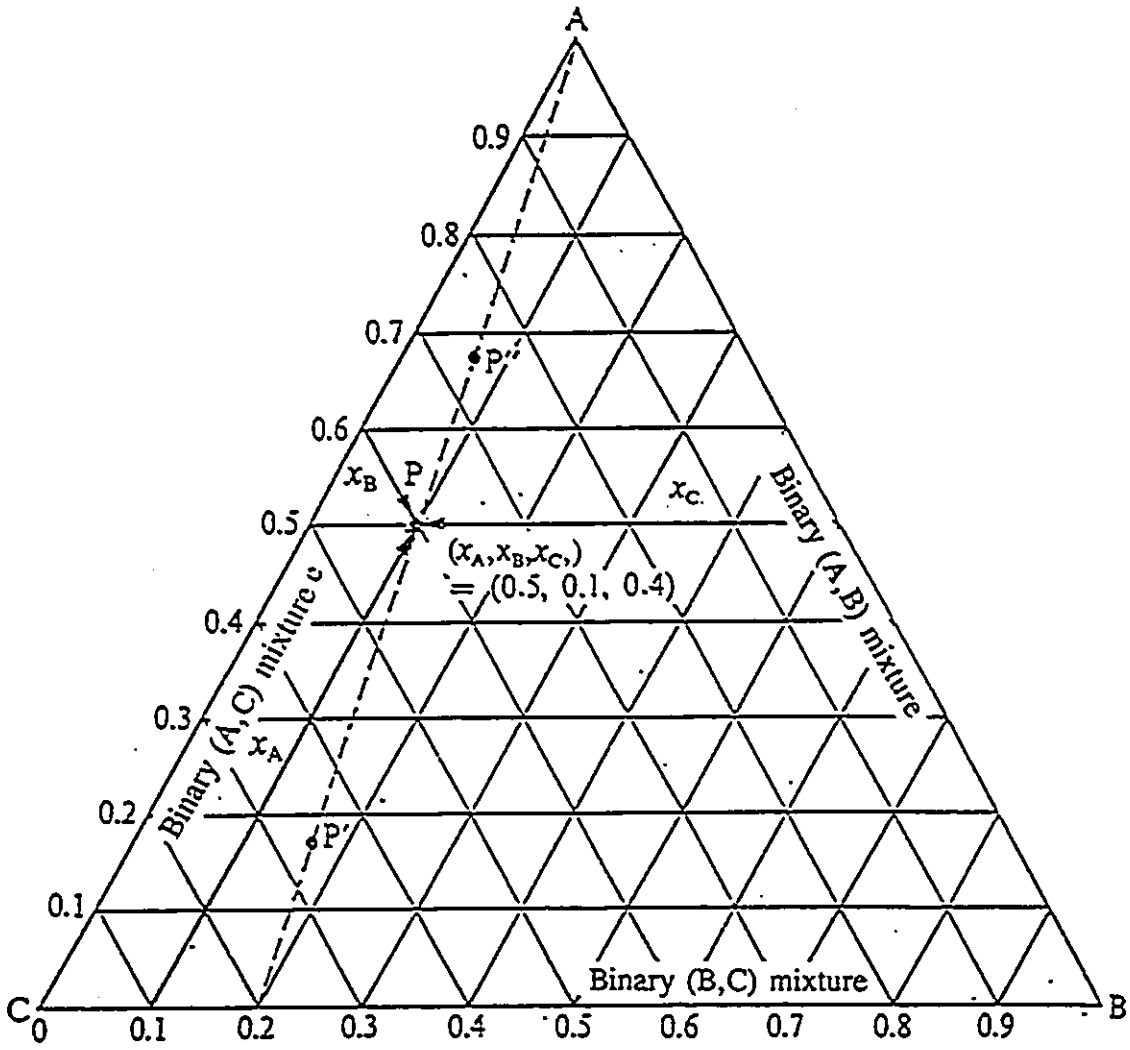


Figure 3.2 Triangular diagram (Atkins, 1994)

Figure 3.2 shows how this works in practice. The edge AB corresponds to $x_C=0$, and likewise for the other two edges. Hence, each of the three edges corresponds to one of the three binary systems (A,B), (B,C) and (C,A). An interior point corresponds to a system in which all three substances are present. The point P, for instance, represents $x_A=0.5$, $x_B=0.10$, and $x_C=0.40$.

Any point of a straight line joining an apex to a point on the opposite edge (shown as the broken line in Figure 3.2) represents a composition that is progressively richer in A the closer the point is to the A apex, but which has the same proportions of B and C. Therefore, if we wish to represent the changing composition of a system as A is added, we draw a line from the A apex to the point on BC representing the initial binary system. Any ternary system formed by adding A then lies at some point on this line.

As an illustration of excess enthalpy values in a triangular diagram, contours for constant values of the excess enthalpy of a ternary mixture are shown as a function of mixture composition. Figure 3.3 shows an example of excess enthalpy values of a ternary mixture. The curves within the triangular diagram are the contours for constant values of the ternary excess enthalpy.

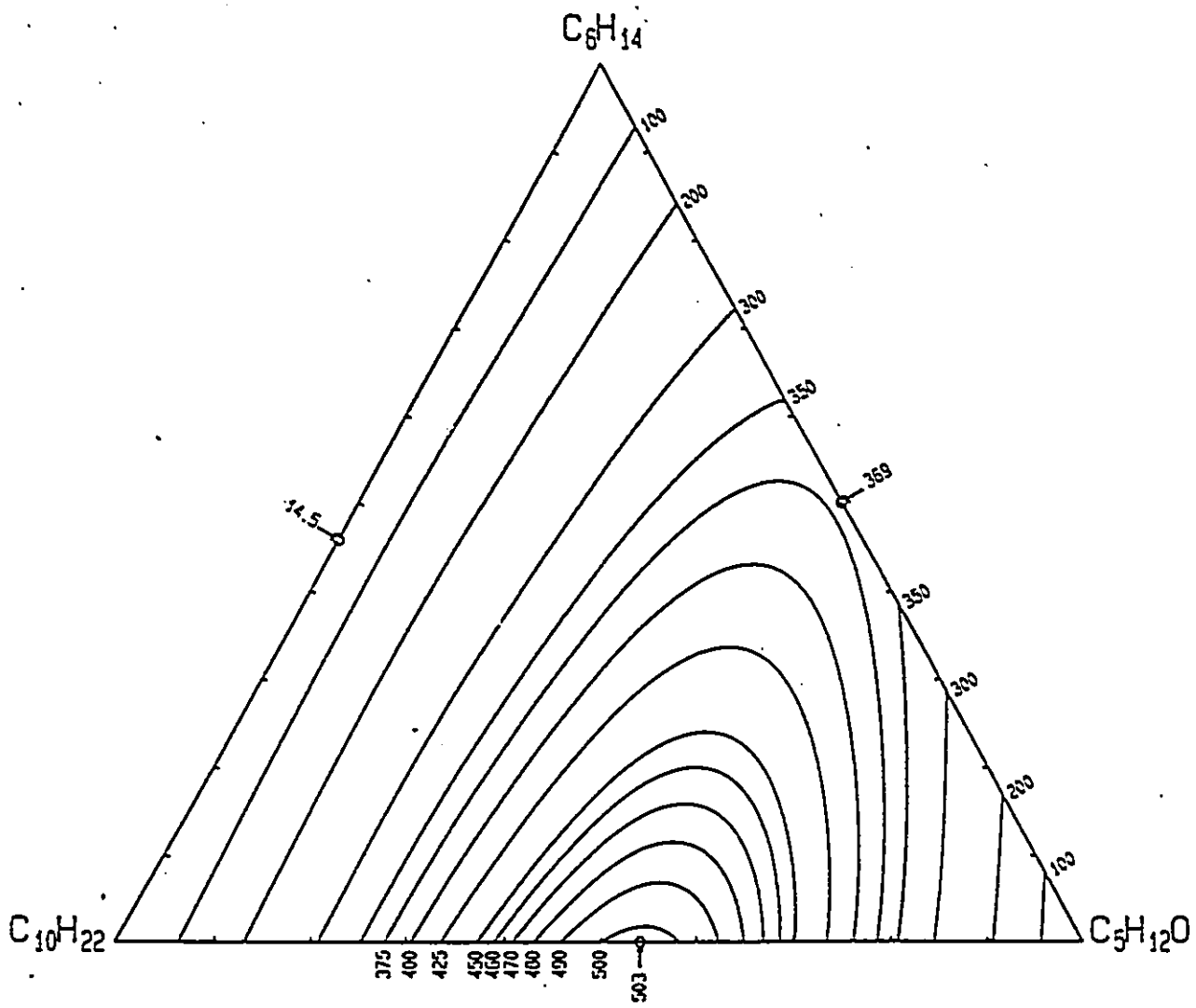


Figure 3.3 Triangular diagram for ternary H^E contours

3.2.2 Pseudo-binary mixtures

The ways to measure ternary excess enthalpy values primarily depend on the calorimetric methods employed. A flow calorimeter is usually designed with two flow channels which allow two pure liquids to flow into the mixing chamber. For a ternary system, however, three flow channels are required for the pure components. In order to solve this problem, a pseudo-binary mixture method can be introduced.

There are five steps involved in this method. First of all, measure the excess molar enthalpy values for the binary mixture of components 2 and 3 over its whole composition range. This is denoted as $H^E_{m,23}$. Secondly, fit the experimental $H^E_{m,23}$ results with a suitable mathematical expression in order to provide binary excess enthalpy values at any composition over the whole composition range. Thirdly, prepare several binary mixtures of components 2 and 3. Then, use each of the prepared binary mixtures as a pure component and measure the excess molar enthalpy values, $H^E_{m,1+23}$, for the "binary" systems which are composed of component 1 and a binary mixture of components 2 and 3 with a fixed composition. Since the mixtures of components 1+23 used in this step are not true binary mixtures, they are referred to as pseudo-binary mixtures. In this step, excess molar enthalpy values $H^E_{m,1+23}$ for each pseudo-binary mixture are determined experimentally. Finally, the excess molar enthalpy $H^E_{m,123}$ of the ternary system is determined from the relation

$$H^{E}_{m,123} = H^{E}_{m,1-23} + (1-x_1)H^{E}_{m,23} \qquad (3.13)$$

where x_1 is the mole fraction of component 1.

Since the pseudo-binary mixture method is an easy way of obtaining ternary excess enthalpy values, this method has been widely used in $H^{E}_{m,123}$ determinations. An important step in this whole procedure is the preparation of the specific binary mixtures of components 2 and 3. Any error involved at this stage will contribute directly to the accuracy of the ternary excess enthalpy $H^{E}_{m,123}$ determined later. Therefore, the preparation process deserves special attention.

3.3 Representation of excess enthalpy

As reviewed in the previous chapter, there are many ways to represent excess enthalpy values. This section describes only the solution theory-related models which were adopted in this study. They are the Flory theory and its association model, the DISQUAC, NRTL, and UNIQUAC models.

The purpose of studying solution theories is to represent the behaviour of a real solution in terms of its intermolecular forces and physical makeup. Hopefully, a solution theory is capable of predicting solution properties from the parameters of its molecules, or predicting mixture behaviour from only the properties of its pure components. It

should be noted, however, that due to a limited understanding of micro-mechanisms at the molecular level, there are always some limitations when these models are used.

3.3.1 The Flory theory

The Flory theory (Flory, 1964; Abe and Flory, 1965) was proposed originally for liquid mixtures of chain molecules. According to the Flory theory, a chain molecule can be divided into several elements, or segments, and each of the segments is considered as an arbitrarily chosen isometric portion of the molecule. The total number of external degrees of freedom per segment is 3c. For a pure component system with N molecules, and r segments in a molecule, according to the Flory theory, the partition function Q_p is expressed as

$$Q_p = Q_{comb}\{\gamma(v^{1/3}-v^{*1/3})^3\}^{rNc}\exp(-E_0/kT) \tag{3.14}$$

where Q_{comb} is a combinatorial factor which takes account of the number of ways of interspersing the rN segments among one another, without regard to the precise location of each relative to its chosen neighbours; γ is a geometric factor, v is the volume per segment and v* is the hard core volume of a segment; k is Boltzmann constant; and E_0 represents the mean intermolecular energy.

For a binary mixture, whose components are indexed by subscripts 1 and 2, the ratio

of segment numbers r_1 and r_2 is defined as the ratio of the respective molar core volumes v_1^* and v_2^*, i.e.

$$\frac{r_1}{r_2} = \frac{v_1^*}{v_2^*} \tag{3.15}$$

Random mixing of the two species is assumed in the theory. The mean intermolecular energy of the mixture then can be written as

$$E_0 = -\frac{1}{v}(A_{11}\epsilon_{11} + A_{22}\epsilon_{22} + A_{12}\epsilon_{12}) \tag{3.16}$$

where A_{11}, A_{22}, and A_{12} represent the numbers of contact pairs between the respective species, ϵ_{11}/v, ϵ_{22}/v, and ϵ_{12}/v are the energies associated with each contact pair. Let s_1 and s_2 be the molecular surface areas of contact sites per segment for the respective components. The site fraction, or contacted surface area fraction θ_i is then defined by

$$\theta_i = \frac{N_i r_i s_i}{\sum_{j=1}^{2} N_j r_j s_j} \tag{3.17}$$

and the volume fraction ϕ_i is defined as

$$\phi_i = \frac{N_i r_i}{\sum_{j=1}^{2} N_j r_j} \tag{3.18}$$

Therefore, A_{11}, A_{22}, and A_{12} can be expressed as

$$A_{11} = \frac{1}{2}N_1 r_1 s_1 \theta_1 \tag{3.19}$$

$$A_{22} = \frac{1}{2}N_2 r_2 s_2 \theta_2 \tag{3.20}$$

$$A_{12} = N_1 r_1 s_1 \theta_2 = N_2 r_2 s_2 \theta_1 \tag{3.21}$$

Substituting Equations (3.19)-(3.21) into Equation 3.16 yields

$$E_0 = -\frac{1}{2v}(N_1 r_1 s_1 \theta_1 \epsilon_{11} + N_2 r_2 s_2 \theta_2 \epsilon_{22} + 2N_1 r_1 s_1 \theta_2 \epsilon_{12}) \tag{3.22}$$

or

$$E_0 = -\frac{1}{2v}(N_1 r_1 s_1 + N_2 r_2 s_2)(\theta_1^2 \epsilon_{11} + \theta_2^2 \epsilon_{22} + 2\theta_1 \theta_2 \epsilon_{12}) \tag{3.23}$$

Defining the interchange energy parameter X_{12} as

$$X_{12} = \frac{s_1(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})}{2v^{*2}} \tag{3.24}$$

and dividing Equation (3.23) by $(N_1 r_1 + N_2 r_2)$ with X_{12} from Equation (3.24) yield

$$\begin{aligned} \frac{E_0}{N_1 r_1 + N_2 r_2} &= -\frac{1}{2v}(\phi_1 s_1 \epsilon_{11} + \phi_2 s_2 \epsilon_{22} - 2\phi_1 \theta_2 X_{12} v^{*2}) \\ &= -\frac{v^*}{v}(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}) \end{aligned} \tag{3.25}$$

where p_1^* and p_2^* are the characteristic pressures for the pure components which are expressed as

$$p_1^* = s_1\epsilon_{11}/2v^{*2} \tag{3.26}$$

$$p_2^* = s_2\epsilon_{22}/2v^{*2} \tag{3.27}$$

By definition,

$$p^*v^*/T^* = ck \tag{3.28}$$

where T^* is the characteristic temperature and c is a parameter representing the external degree of freedom proposed by Prigogine (1957). Two of the three parameters, c, p^* and T^* are independent, and p^* and c are defined as

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1\theta_2 X_{12} \tag{3.29}$$

and

$$c = \phi_1 c_1 + \phi_2 c_2 \tag{3.30}$$

Rearranging Equation (3.28) yields

$$\frac{1}{T^*} = \frac{ck}{p^*v^*} = \frac{1}{p^*}\left(\phi_1\frac{c_1k}{v^*}+\phi_2\frac{c_2k}{v^*}\right) = \frac{\phi_1 p_1^*/T_1^*+\phi_2 p_2^*/T_2^*}{\phi_1 p_1^*+\phi_2 p_2^*-\phi_1\theta_2 X_{12}} \tag{3.31}$$

Ignoring the difference between the energy and enthalpy of a condensed binary system at low pressure, the excess enthalpy H^E can be then expressed as

$$H^E = \Delta H^E = E_0(\text{mixture}) - E_0(1) - E_0(2) \tag{3.32}$$

Expressing Equation (3.25) for a binary mixture by

$$E_0 = -\frac{v^*}{\tilde{v}}(N_1 r_1 p_1^* + N_2 r_2 p_2^* - N_1 r_1 \theta_2 X_{12}) \tag{3.33}$$

and for the two pure components by

$$E_0(1) = -\frac{v^*}{\tilde{v}_1} N_1 r_1 p_1^* = -\frac{v_1^*}{\tilde{v}_1} N_1 p_1^* \tag{3.34}$$

and

$$E_0(2) = -\frac{v^*}{\tilde{v}_2} N_2 r_2 p_2^* = -\frac{v_2^*}{\tilde{v}_2} N_2 p_2^* \tag{3.35}$$

leads to the following expression for the excess enthalpy of a binary mixture:

$$H^E = N_1 p_1^* v_1^*\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + N_2 p_2^* v_2^*\left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right) + \frac{N_1 v_1^* \theta_2}{\tilde{v}} X_{12} \tag{3.36}$$

All the Flory model parameters in Equation 3.36 can be derived from properties of pure substances, which are often available in the literature, except the interchange energy parameter X_{ij}, which is usually determined from regression of experimental data.

It was found previously (Benson, *et al.*,1988; Luo, *et al.*,1988; Wang, *et al.*,1988, 1989a,b, 1990) that the Flory model is able to represent excess enthalpy values well for mixtures of an ether with an alkane. In this study, therefore, the Flory model was applied to the systems containing methyl tert-butyl ether. The details of the application of the model are described in Chapter 5.

3.3.2 An association model with a Flory contribution term

Although being able to represent the excess enthalpies for mixtures of an ether with an alkane fairly well, the Flory model has its limitations for systems containing alcohols. It is evident that specific recognition of the self-association must be included in formulating a model for these mixtures.

Previously, it was found that the excess volume of mixtures formed by an alkan-1-ol with either a normal or a branched alkane could be correlated quite well with an association model of the Mecke-Kempter type (Kempter and Mecke, 1940) with an added Flory contribution term (Treszczanowicz and Benson, 1985, 1988) . In the present work, an extension of this treatment to excess enthalpy was carried out especially for

alcohol-containing systems. The following section explains the outline of the model.

The model assumes that the excess molar enthalpy, H_m^E, is composed of a chemical (Mecke-Kempter) term (a chemical contribution described by an athermal associated model) and a physical or residual contribution term described by the Flory theory:

$$H_m^E = H_{m,MK}^E + H_{m,F}^E \tag{3.37}$$

The chemical term is

$$H_{m,MK}^E = \Delta H_H^* x_1 \{\phi_1 \ln(1+K^{(\phi)}) - \ln(1+K^{(\phi)}\phi_1)\}/K^{(\phi)}\phi_1 \tag{3.38}$$

where

$$\ln K^{(\phi)} = 1 - \frac{(\Delta H_H^* - T\Delta S_H^*)}{RT} - \ln\frac{v_1^*}{17.12} \tag{3.39}$$

In these equations, R is the gas constant, T is the temperature, ϕ_1 and v_1^* are the segment volume fraction and hard-core volume of the associating component, respectively; 17.12 $cm^3 \cdot mol^{-1}$ is the van der Waals molar volume for methane (Bondi, 1968), and ΔH_H^* and ΔS_H^* stand for the standard enthalpy and entropy change of hydrogen-bond formation, respectively. The evaluation of ϕ_1 from the hard-core volumes of the components is the same as in the Flory theory.

The physical contribution term described by the Flory theory has a form of

$$H^{E}_{m,F} = x_1\theta_2(v_1^*/\tilde{v})X_{12} + \sum_{i=1}^{2} x_i p_i^* v_i^* \{(1/\tilde{v}_i) - (1/\tilde{v})\} \qquad (3.40)$$

It takes into account several effects (Delmas *et al.*, 1975; Treszczanowicz *et al.*, 1981): (1) difference in free volumes giving a negative term; (2) specific interactions between the real species (alkane molecules and alkanol monomers and multimers) giving a positive term; (3) differences in internal pressures, which may lead to a term of either sign; and (4) structural effects, due to changes in order and packing (Treszczanowicz and Benson, 1985). The notation and symbols used by Flory are adopted here.

To simplify the procedure, the model suggests that the association parameters and the interchange energy parameter X_{12} are calculated from properties of the mixture, and the characteristic parameters of the components are estimated from properties of the pure liquids. The details on how to determine the model parameters and the application of the model will be discussed in Chapter 5.

3.3.3 The DISQUAC model

The Dispersive-Quasi-Chemical (DISQUAC) model is one of the successful group contribution models. In this approach, the excess enthalpy is the sum of dispersive group contributions $H^{E,dis}$, and quasichemical group contributions $H^{E,quac}$, thus

$$H^{E} = H^{E,dis} + H^{E,quac} \qquad (3.41)$$

The dispersive term is given by

$$H^{E,dis} = (q_1x_1+q_2x_2)\xi_1\xi_2 h_{12}^{dis} \tag{3.42}$$

where

$$h_{12}^{dis} = -\frac{1}{2}\sum_s\sum_t(\alpha_{s1}-\alpha_{s2})(\alpha_{t1}-\alpha_{t2})h_{st}^{dis} \tag{3.43}$$

In Equations (3.42) and (3.43), h_{st}^{dis} is the dispersive interchange parameter, the enthalpy of the (s,t)-contact, α_{si} is the molecular surface fraction of surface type "s" on a molecule of type "i", q_i is the total relative molecular area of a molecule of type i, and ξ_i is the surface fraction of component i in the mixture.

For a binary system, the quasichemical term is expressed by

$$H^{E,quac} = \frac{1}{2}(q_1x_1+q_2x_2)\sum_s\sum_t\{X_sX_t-(\xi_1X_{s1}-X_{t1}+\xi_2X_{s2}X_{t2})\}\eta_{st}h_{st}^{quac} \tag{3.44}$$

where

$$\eta_{st} = \exp(-g_{st}^{quac}/zRT) \tag{3.45}$$

g_{st}^{quac} and h_{st}^{quac} are the quasichemical interchange parameters, referring to the Gibbs energy and enthalpy respectively, of the (s,t)-contact and z is the lattice coordination number with a suggested value of 4 (Tiné and Kehiaian, 1987). The quantities X_s and X_t are obtained by solving the system of λ equations (λ is the number of contact

surfaces)

$$X_s\left(X_s + \sum_t X_t \eta_{st}\right) = \alpha_s \qquad (3.46)$$

where α_s is the surface ratio of surface type s in the system. X_{si} and X_{ti} (i=1,2) are the solutions of the above equation for $x_i=1$ (pure component i).

The DISQUAC model has its limitations, as Kehiaian and Marongiu admitted (1988a). The present version of DISQUAC cannot be expected to give satisfactory results in the case of strongly interacting groups because of the approximations involved in the quasichemical treatment and the assumed additivity of the dispersive and quasichemical contributions.

3.3.4 The NRTL model

The Non-Random Two-Liquid (NRTL) model (Renon and Prausnitz, 1968a) is based on the concept of local composition. As implied in its name, the model assumes that the mixing is not random. In the case of completely random mixing, the local composition must be the same as the bulk composition. It is the difference of intermolecular forces that determines the nature of a non-random mixing and results in the disparity between the local composition and the composition in the bulk.

The following Boltzmann equations are adopted to describe the relationship between the local and bulk compositions for a binary mixture

$$\frac{x_{12}}{x_{11}} = \frac{x_2 \exp(-\alpha g_{21}/RT)}{x_1 \exp(-\alpha g_{11}/RT)}$$
$$\frac{x_{12}}{x_{22}} = \frac{x_1 \exp(-\alpha g_{12}/RT)}{x_2 \exp(-\alpha g_{22}/RT)} \qquad (3.47)$$

where x_{ij} and x_i denote the local composition and the bulk composition, respectively. g_{ij} is an energy parameter characteristic of the interaction between i-j molecules. The parameter α is related to the non-randomness in the mixture.

The NRTL model for the excess enthalpy is

$$H^E = RTx_1x_2\left\{\frac{G_{21}\tau_{21}}{x_1+G_{21}x_2}+\frac{G_{12}\tau_{12}}{x_2+G_{12}x_1} - \alpha\left[\frac{G_{21}x_1\tau_{21}^2}{(x_1+G_{21}x_2)^2}+\frac{G_{12}x_2\tau_{12}^2}{(x_2+G_{12}x_1)^2}\right]\right\} \qquad (3.48)$$

where

$$\tau_{21} = (g_{21}-g_{11})/RT, \quad \tau_{12} = (g_{12}-g_{22})/RT \qquad (3.49)$$

and

$$G_{21} = \exp(-\alpha\tau_{21}), \quad G_{12} = \exp(-\alpha\tau_{12}) \qquad (3.50)$$

For moderately non-ideal systems, the NRTL model offers no advantages over the simpler van Laar and Margules equations. However, for strongly non-ideal mixtures, and especially for partially immiscible systems, the NRTL model often provides a good

representation of experimental data, provided that care is exercised in data reduction to obtain the adjustable parameters (Prausnitz, *et al.* 1986).

In the NRTL model, the parameter α is a correction factor to the quasi-lattice theory. It can be expressed by means of the coordination number Z

$$\alpha = 2/Z \tag{3.51}$$

If Z or α is fixed as a constant, as suggested in the literature (Prausnitz, *et al.* 1986), the NRTL model is then reduced to a two-parameter equation.

The model can be easily extended to multicomponent systems. The equation used in this study to calculate the excess enthalpies for ternary mixture is as follows:

$$\begin{aligned}\frac{H^E}{RT} = {} & x_1\left\{\frac{x_2G_{21}\tau_{21}+x_3G_{31}\tau_{31}}{x_1+G_{21}x_2+G_{31}x_3} - \frac{x_1\alpha(x_2G_{21}\tau_{21}^2+x_3G_{31}\tau_{31}^2)}{(x_1+G_{21}x_2+G_{31}x_3)^2} - \frac{x_2x_3G_{21}G_{31}\alpha(\tau_{31}-\tau_{21})(\tau_{31}-\tau_{21})}{(x_1+G_{21}x_2+G_{31}x_3)^2}\right\} \\ & +x_2\left\{\frac{x_1G_{12}\tau_{12}+x_3G_{32}\tau_{32}}{x_1G_{12}+x_2+G_{32}x_3} - \frac{x_2\alpha(x_1G_{12}\tau_{12}^2+x_3G_{32}\tau_{32}^2)}{(x_1G_{12}+x_2+G_{32}x_3)^2} - \frac{x_1x_3G_{12}G_{32}\alpha(\tau_{32}-\tau_{12})(\tau_{32}-\tau_{12})}{(x_1G_{12}+x_2+G_{32}x_3)^2}\right\} \\ & +x_3\left\{\frac{x_1G_{13}\tau_{13}+x_2G_{23}\tau_{23}}{x_1G_{13}+x_2G_{23}+x_3} - \frac{x_3\alpha(x_1G_{13}\tau_{13}^2+x_2G_{23}\tau_{23}^2)}{(x_1G_{13}+x_2G_{23}+x_3)^2} - \frac{x_1x_2G_{13}G_{23}\alpha(\tau_{23}-\tau_{13})(\tau_{23}-\tau_{13})}{(x_1G_{13}+x_2G_{23}+x_3)^2}\right\}\end{aligned} \tag{3.52}$$

The calculated results from the NRTL model were used mainly for the purpose of comparing with the new model proposed in this study.

3.3.5 The UNIQUAC model

The Universal Quasi-Chemical (UNIQUAC) model (Abrams and Prausnitz, 1975) is also based on the concept of local composition. The reason that the UNIQUAC model was involved in this study is that the model has its advantages, first from its relative simplicity, using only two adjustable parameters, and secondly from its wide range of applicability. As in the case of the NRTL model, the results calculated from the UNIQUAC model were used for the purpose of comparing with the proposed model in this study.

Defining a local area fraction θ_i of molecule i as

$$\theta_i = \frac{x_i q_i}{\sum_k x_k q_k} \tag{3.53}$$

and introducing some interim parameters, X(1) to X(6), to simplify the formula

$$\begin{aligned} X(1) &= \frac{Z}{2}N_A(\varepsilon_{21}-\varepsilon_{11}), \quad X(2) = \frac{Z}{2}N_A(\varepsilon_{12}-\varepsilon_{22}) \\ X(3) &= \frac{Z}{2}N_A(\varepsilon_{31}-\varepsilon_{11}), \quad X(4) = \frac{Z}{2}N_A(\varepsilon_{13}-\varepsilon_{33}) \\ X(5) &= \frac{Z}{2}N_A(\varepsilon_{32}-\varepsilon_{22}), \quad X(6) = \frac{Z}{2}N_A(\varepsilon_{23}-\varepsilon_{33}) \end{aligned} \tag{3.54}$$

the UNIQUAC model for the excess enthalpy of a ternary mixture can be expressed by

$$H^E = \frac{q_1x_1[\theta_2\tau_{21}X(1)+\theta_3\tau_{31}X(3)]}{\theta_1+\theta_2\tau_{21}+\theta_3\tau_{31}} + \frac{q_2x_2[\theta_1\tau_{12}X(2)+\theta_3\tau_{32}X(5)]}{\theta_1\tau_{12}+\theta_2+\theta_3\tau_{32}} + \frac{q_3x_3[\theta_1\tau_{13}X(4)+\theta_2\tau_{23}X(6)]}{\theta_1\tau_{13}+\theta_2\tau_{23}+\theta_3} \quad (3.55)$$

where ε_{ij} is the local characteristic energy parameter, Z denotes the coordination number, N_A is Avogadro's number, and the parameters τ_{ij} are defined by

$$\begin{aligned} \tau_{21} &= \exp\{\frac{-X(1)}{RT}\}, \quad \tau_{12} = \exp\{\frac{-X(2)}{RT}\} \\ \tau_{31} &= \exp\{\frac{-X(3)}{RT}\}, \quad \tau_{13} = \exp\{\frac{-X(4)}{RT}\} \\ \tau_{32} &= \exp\{\frac{-X(5)}{RT}\}, \quad \tau_{23} = \exp\{\frac{-X(6)}{RT}\} \end{aligned} \quad (3.56)$$

It has been suggested that the UNIQUAC model is applicable to a wide variety of nonelectrolyte liquid mixtures containing nonpolar or polar fluids such as hydrocarbons, alcohols, nitriles, ketones, aldehydes, organic acids, etc. and water, including partially miscible mixtures. With only two adjustable binary parameters, it cannot always represent high-quality data with high accuracy, but for many typical mixtures encountered in chemical practice, UNIQUAC provides a satisfactory description (Prausnitz, *et al.* 1986).

3.4 Error estimations

There was a considerable amount of experimental data involved in the present study.

Usually these data could be represented by different mathematical equations. Some of these mathematical expressions have certain physical meanings, such as the ones derived from solution theories, while the others also played valuable roles in data correlation, although they might be physically meaningless. The formulas of these equations vary from simple linear, to polynomial, and to much more complicated forms.

The *deviation* at a data point is the difference between the experimental H_m^E-value and the H_m^E-value computed from a functional relationship. Deviations with different definitions indicate the quality of data representations with different emphases. In this study, three types of deviations were used. They are:

(1) The average absolute deviation (AAD)

$$AAD = \frac{1}{N}\sum_{j=1}^{N}\left|H_m^E(expt)_j - H_m^E(calc)_j\right| \tag{3.57}$$

(2) The average absolute percent deviation (AAPD)

$$AAPD = \frac{100}{N}\sum_{j=1}^{N}\left|1 - \frac{H_m^E(calc)_j}{H_m^E(expt)_j}\right| \tag{3.58}$$

(3) The standard deviation, or the root mean square deviation (RMSD)

$$\text{RMSD} = \left\{ \frac{1}{N-p} \sum_{j=1}^{N} \left[H_m^E(\text{expt})_j - H_m^E(\text{calc})_j \right]^2 \right\}^{1/2} \qquad (3.59)$$

In these expressions, N denotes the number of data points, and p is the number of parameters that were adjusted.

Chapter 4

Experimental

Excess enthalpies of 17 binary and six ternary systems were measured at the temperature of 298.15 K with an LKB isothermal jacket flow calorimeter. Over most of the mole-fraction range, the errors of the excess molar enthalpy and the mole fraction for all the binary and pseudo-binary mixtures are estimated to be less than 0.5 per cent and 5×10^{-4}, respectively.

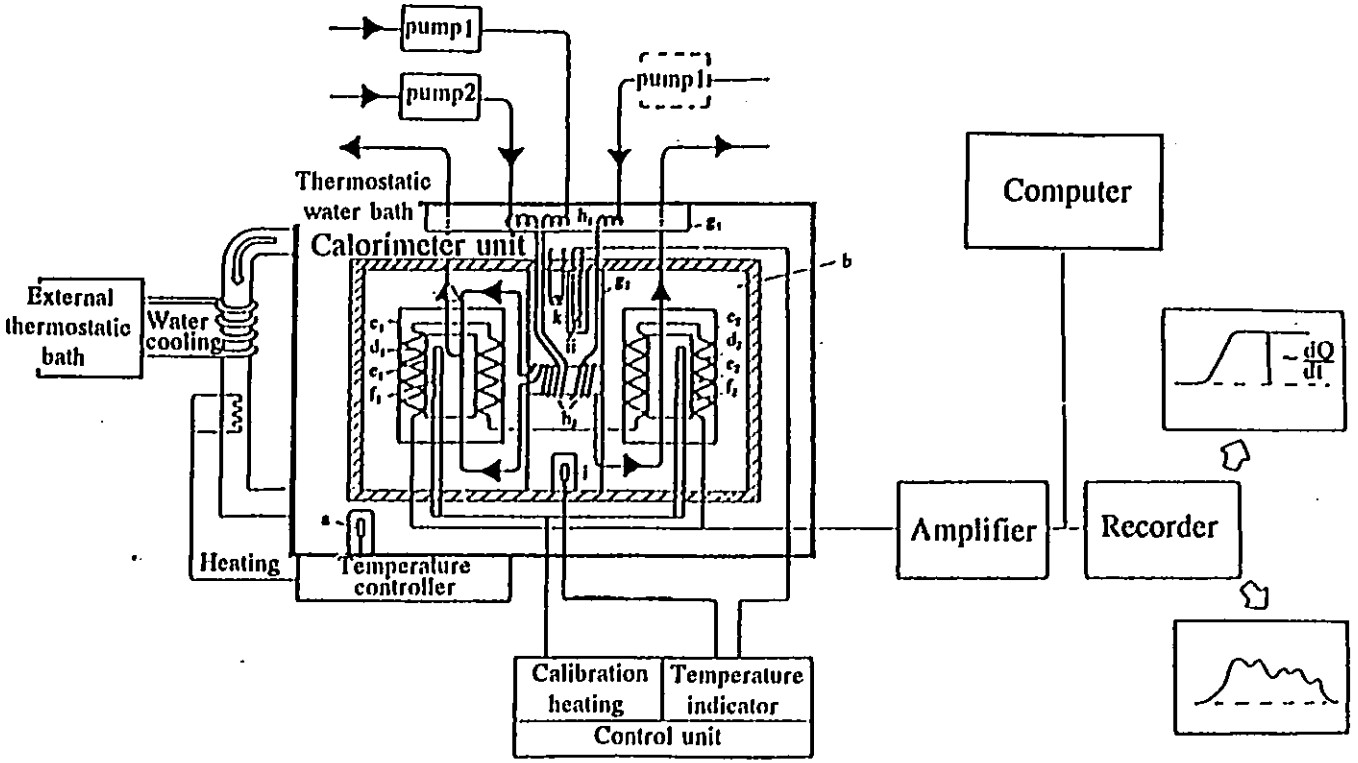
This chapter describes considerations and results related to the experimental measurements of excess enthalpies, which include a description of the equipment used in this study, an examination of the materials involved, explanations of some preliminary treatments (why they are necessary and how they were carried out), and a presentation of how the excess enthalpies were determined. Some experimental results are shown in this chapter as examples. A complete set of the experimental data is listed in Appendix A.

4.1 Equipment

The calorimeter used to determine excess enthalpies in this study is an LKB flow microcalorimeter (Model 10700-1). The prototype of the calorimeter, as supplied by the manufacturer, has been described by Harsted and Thomsen (1974). Figure 4.1 shows schematically the modified calorimeter used in this work (Tanaka *et al.*, 1975; Kimura, 1983).

As shown in Figure 4.1, the calorimeter unit was immersed in a water bath, instead of the thermostatic air-bath originally supplied by the manufacturer. This helped to improve the stability of the thermopile base line. The temperature of the water bath was controlled by a temperature controller, produced by the technicians of the National Research Council of Canada (NRCC), for heating, and a proportional temperature controller (NESLAB, model RTE-110) was used for cooling. In this study, the temperature of the system was maintained at (298.15 $\pm$ 0.002)K, and shown on a quartz thermometer (Hewlett-Packard, model 2804 A).

The calorimetric unit consists of a heat sink (b), in which two calorimetric cells (e1) and (e2), thermopiles (d1) and (d2) consisting of many thermocouples, and other equipment required for the temperature control are housed. The two calorimetric cells are of different designs which make it possible to carry out two types of flow calorimetric experiments in the same calorimeter. Cell (e2) is designed as a reaction



a - sensor, b - heat sink, c1,c2 - detectors, d1,d2 - thermopiles, e1, - mixing cell, e2 - reaction cell, f1,f2 - heaters, g1,g2 - heat exchangers, h1,h2 - heat exchanger coils, ii - sensor, k - cooler

Figure 4.1 LKB flow microcalorimeter

cell. Since there was no reaction involved in this study, only cell (e1), the mixing cell was used. The two component liquids were pumped through different tubes into the mixing cell and mixed there. The thermal signals from the cell are transformed into electrical signals by thermopiles. They were measured by a Keithley 180 nanovoltmeter with both digital and analog outputs. The latter was connected to a recorder (Hewlett-Packard, Model 7133A) to provide a continuous record of the mixing process. The digital output was connected to a computer through an instrument coupler (ICS Electronics Corporation, Model 4880).

There were two groups of heat exchanger coils (h1) and (h2), located in heat exchangers I (g1) and II (g2), respectively. They brought the component liquid(s) to the working temperature before reaching the calorimetric cell.

Component liquids were transported into the mixing cell by two pumps. Pulseless liquid flows were achieved with a pair of piston displacement pumps or syringe pumps, as shown in Figure 4.2, designed and constructed in the shops of the NRCC. The flow from each of these pumps was produced by the linear displacement of an accurately ground stainless steel piston (1.59 cm OD), which was pushed through a tight Teflon seal into a water-jacketed glass cylinder (1.90 cm ID) through which water from the water bath was circulated. The piston was moved by a precision screw which was rotated by a variable speed DC motor (Bodine Electric, Type NSH-12) coupled to it through a gear box with four manually selectable ratios. A transparent disk with 120 equally spaced

radial photomasked sectors was mounted on the shaft of the motor and a light beam passing through the disk fell on a slit with a phototransistor mounted behind it. The sine wave output from the phototransistor was fed to a Schmitt trigger and the resulting pulse counting and averaging circuits provide digital readouts of the total number of counts and of the number of counts per second. A signal from the averager was also fed back through an operational amplifier and power transistors to control the speed of the motor.

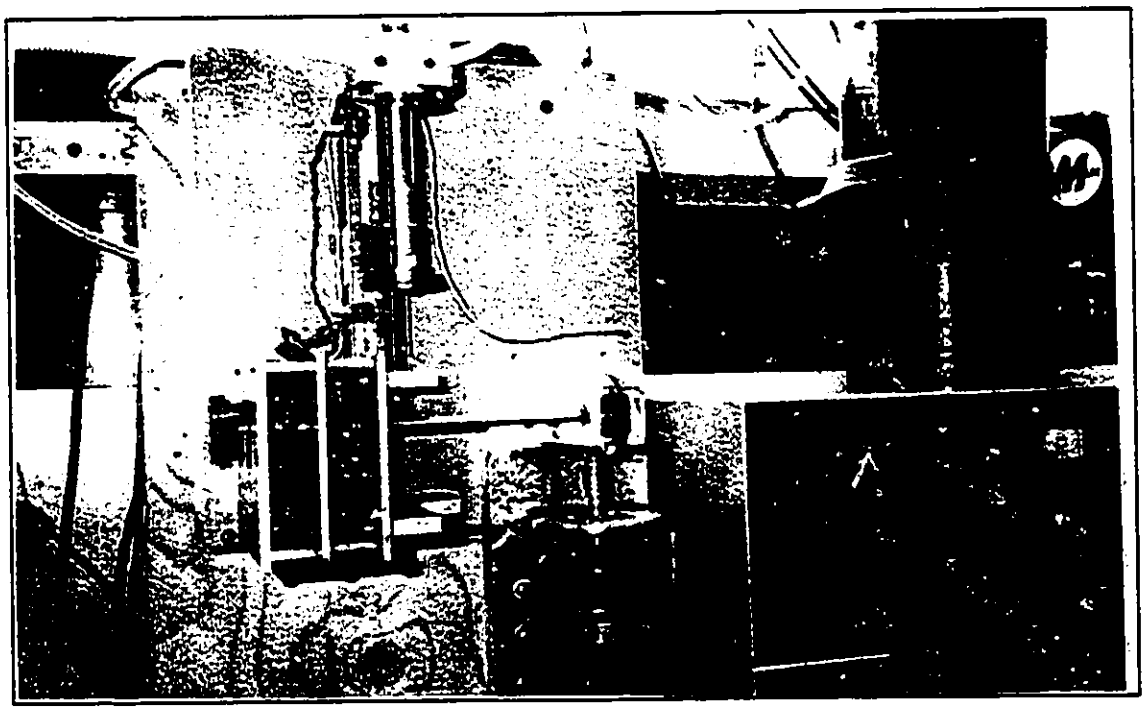


Figure 4.2 Piston displacement pump

4.2 Properties of materials

The 17 binary and six ternary systems involved in this study consist of 8 different materials. They are ethanol, 1-propanol, methyl tert-butyl ether (MTBE), n-hexane, n-decane, n-dodecane, 2,3-dimethylbutane (2,3-DMB), and 2,2,4-trimethylpentane (2,2,4-TMP). All of these materials had purities exceeding 99 mole per cent stated by their suppliers, and were used in this study without further purification. The densities of these materials were determined with an Anton-Paar digital densimeter (DMA 02C, or DMA 45).

The sources and densities (measured at the temperature T=298.15K) of these materials are listed in Table 4.1, along with the density values from the literature for comparison.

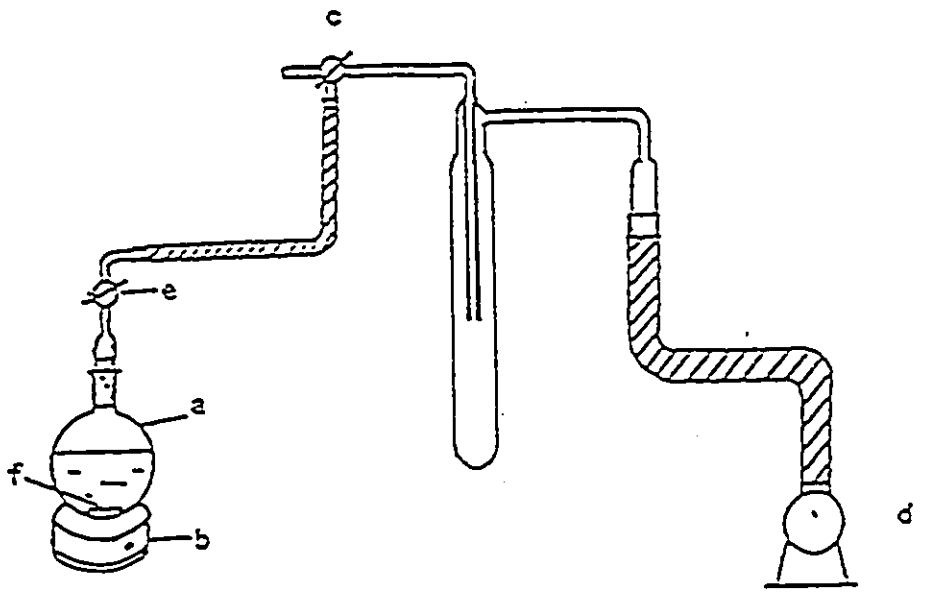
It was found previously that degassing the experimental fluid helps to overcome difficulties due to bubbles collecting in the flow system (Tanaka, *et al.*, 1975). In this study, the same treatment was followed. Before being used, all primary component liquids were degassed in the way shown in Figure 4.3. The flask (a) with a pure component liquid was placed on a magnetic stirrer (b), which drove the stirrer (f) in the flask to agitate the liquid. The outlet of the flask was connected to a vacuum system through a three-way valve (c). When the vacuum pump (d) was turned on, a negative pressure was produced in the system, which evacuated the air in the liquid. The

agitation promoted the separation of air from the liquid. The degassing process took several minutes for each sample.

Table 4.1 Sources and densities of the pure component liquids (T=298.15K)

Material	Supplier	Purity/%	Density/(kg·m^{-3}) Measured value	Density/(kg·m^{-3}) Literature[a] value
Ethanol	British Drug House Ltd.	99.7	785.60	785.09
1-Propanol	Aldrich Chemical Co.	99.5	799.74	799.75
MTBE	Aldrich Chemical Co.	99.8	735.67	735.30
n-Hexane	Phillips Petroleum Co.	99.9	655.12	654.84
n-Decane	Phillips Petroleum Co.	99.0	726.29	726.35
n-Dodecane	Phillips Petroleum Co.	99.5	745.35	745.18
2,3-DMB	Phillips Petroleum Co.	99.9	657.18	657.02
2,2,4-TMP	Aldrich Chemical Co.	99.0	687.91	687.81

[a] Selected values of properties of hydrocarbon and related compounds, TRC thermodynamic tables, Thermodynamic Research Centre, The Texas A & M University College Station, Texas, 1988.



a - flask, b - magnetic stirrer, c - three-way valve

d-vacuum pump, e - two-way valve, f - stirrer

Figure 4.3 Degassing of pure component liquids

4.3 Preliminary Study

Before any actual measurement occurs, the calorimeter must be verified and calibrated. This section describes why these procedures are necessary and how they were carried out in this study.

4.3.1 Verification of calorimeter

As mentioned earlier in chapter 3, verification of a calorimeter is used to check the reliability of the equipment. Measuring the heat effect of a "reference" system or standard system and comparing the results with the values available in the literature provides evidence regarding the reliability of the calorimetric results.

During the "life-time" of a calorimeter, this kind of checking procedure should be carried out periodically. The first one serves mainly to verify the reliability of the calorimeter. Unless modifications are made to the calorimeter later, the rest check whether the calorimeter is working properly and whether the operator is doing the measurement correctly.

The benzene (1) + cyclohexane (2) system is widely used as a standard for testing calorimeters for heats of mixing. The excess enthalpies of this system at 298.15K were measured in this study, and compared with the values from several literature sources. The component liquids stated as research grade, obtained from Phillips Petroleum Co.,

were used without further purification. The densities of these component liquids at 298.15K were measured with an Anton-Paar digital densimeter. Table 4.2 shows the density values measured in this study along with the resutls reported in the literature for comparison.

Table 4.2 Densities of the pure component liquids of the standard system (T=298.15K)

Material	Supplier	Purity/%	Density/(kg·m^{-3})	
			Measured value	Literature[a] value
Benzene	Phillips Petroleum Co.	99.9	873.58	873.70
Cyclohexane	Phillips Petroleum Co.	99.9	772.95	773.89

[a] Selected values of properties of hydrocarbon and related compounds, TRC thermodynamic tables, Thermodynamic Research Centre, The Texas A & M University College Station, Texas, 1988.

The excess enthalpies of the standard system determined in this study are listed in Table 4.3 along with the literature values (Stokes, *et al.*, 1969; Murakami and Benson, 1969). The experimental data were correlated by means of a linear least squares method, and are represented by the expression shown below:

$$H_m^E = x_1(1-x_1)\{3186.645 - 90.03338(1-2x_1)\} \qquad (4.1)$$

The comparison is also shown in Figure 4.4. It can be seen from Table 4.3 and Figure 4.4, that the results obtained in this work agree fairly well with those determined by successive dilution calorimeters (Stokes, *et al.*, 1969; Murakami and Benson, 1969) within most of the mole fraction range, except at both ends of the concentration range. This proves that the equipment is running properly and is capable of producing reliable results. Deviations of those literature results from the representation of the data obtained in this work are plotted in Figure 4.5.

The syringe pumps were calibrated previously (Tanaka *et al.*, 1975) in order to determine the relationship of the three pump factors, the flow-rate Q, the gear ratio G, and the reading S, of the averager circuit (i.e., the motor speed in counts per second)

$$Q = K_p GS \qquad (4.2)$$

where K_p is a constant characteristic of the pump. Since the same pumps were used in this study, the previously determined K_p value (4×10^{-5} $cm^3 \cdot count^{-1}$) was adopted.

Table 4.3 Excess enthalpies of benzene (1) + cyclohexane (2) system at 298.15K

This work		Stokes *et al.*		Murakami & Benson	
x_1	H_m^E/(J·mol^{-1})	x_1	H_m^E/(J·mol^{-1})	x_1	H_m^E/(J·mol^{-1})
0.0991	273.13	0.1000	280.98	0.1178	325.31
0.1995	504.61	0.2000	500.98	0.2063	513.62
0.3004	659.63	0.3000	660.46	0.2960	656.60
0.3999	759.07	0.4000	759.70	0.3885	754.87
0.4996	796.75	0.5000	798.44	0.5040	799.18
0.5995	771.16	0.6000	775.59	0.5941	781.32
0.6998	680.28	0.7000	688.93	0.6897	701.13
0.8000	519.92	0.8000	534.77	0.7984	539.03
0.8999	285.07	0.9000	307.64	0.9208	251.10

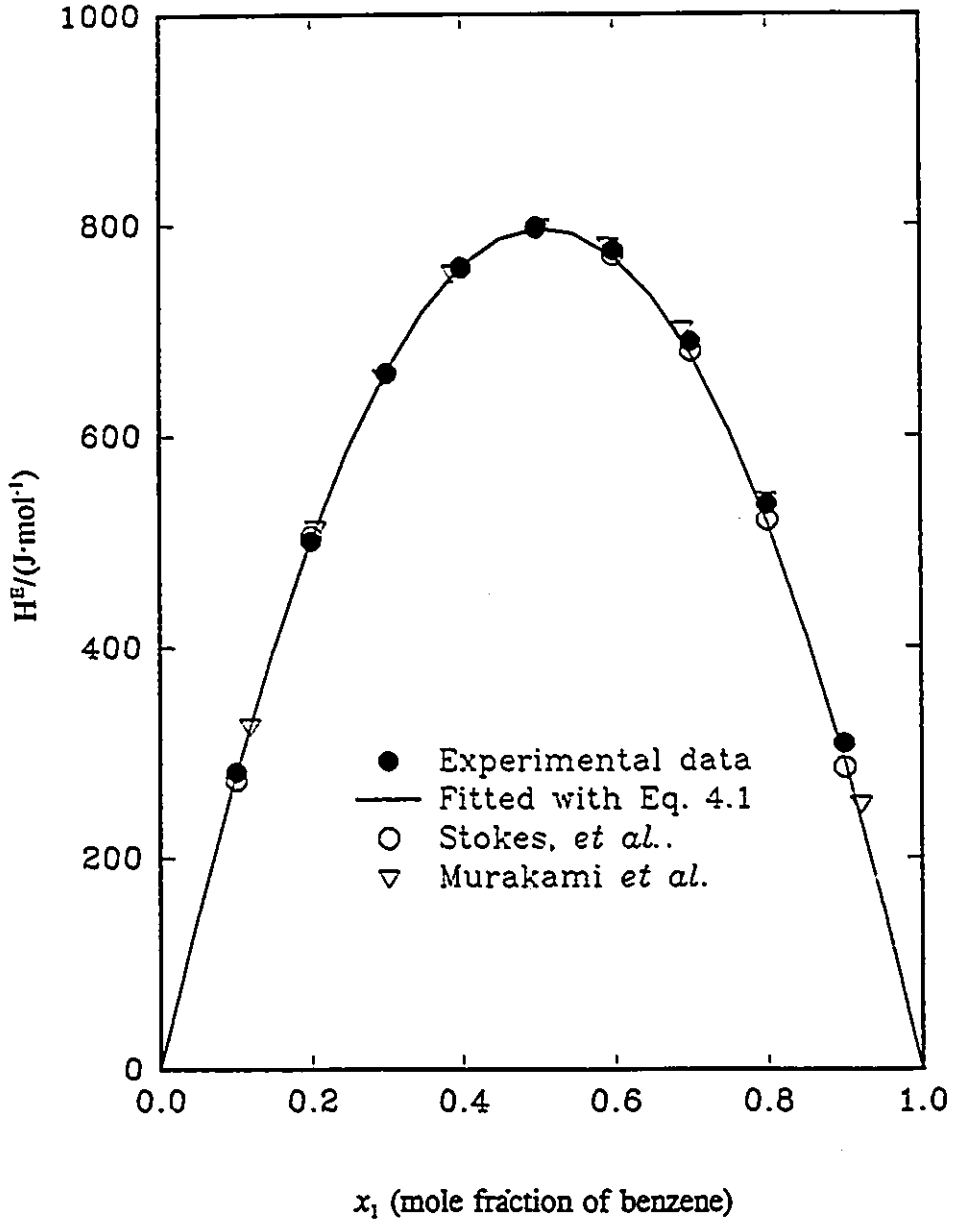


Figure 4.4 Excess enthalpies of benzene + cyclohexane at 298.15K

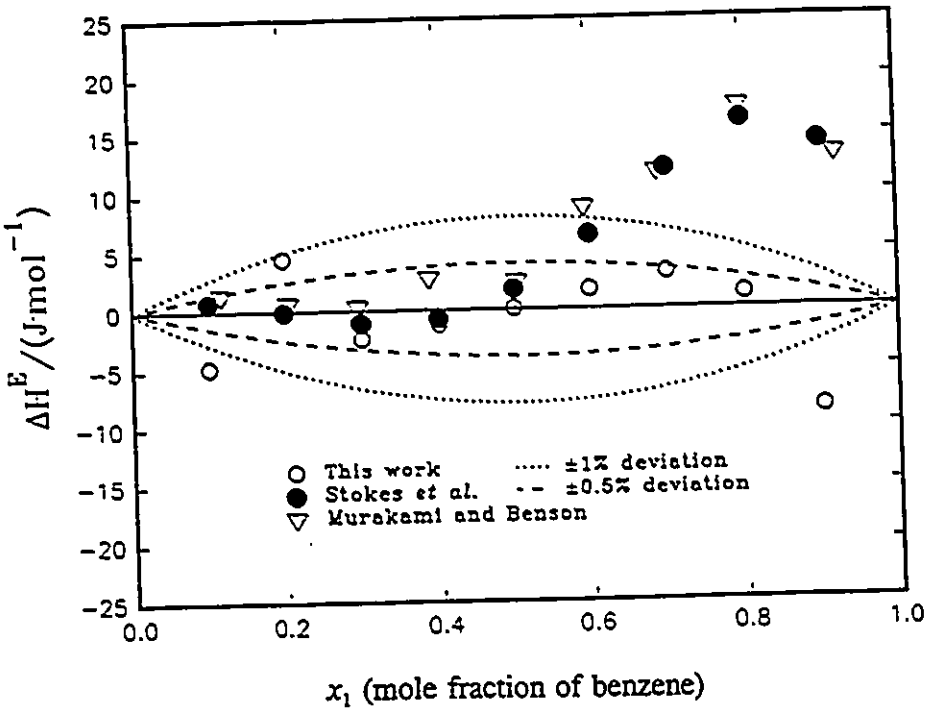


Figure 4.5 Data analysis for the standard system

4.3.2 Calibration of calorimeter

As mentioned previously, a calorimeter needs to be calibrated before being used for calorimetric measurements. Since the thermopile baseline varies with the flow-rate and viscosity of the calorimetric liquid, the calibration procedure should be repeated for each material involved at different flow rates. Also, to minimize errors, calibration should be carried out with the same pump being used in the excess enthalpy measurements.

The operation procedure is briefly described as follows.

The gear ratio of the pump was set at 0.1 and the flow rate at specified values (such as 300, 500, 700, 900, and 1100 counts·s^{-1}). The liquid under consideration was allowed to flow at the set rate until the calorimeter reached steady state, showing a straight baseline of voltage reading $V^{\circ}(f)$. Between 100 to 200 voltage readings were collected, and an average voltage reading for the baseline $V^{\circ}(f)$ was taken.

A constant voltage from a power supply (Trygon Systron-Donner Corp., Model PL5501), was applied to the calorimeter heater and a standard resistance R_c in series, while the liquid flowed through the calorimeter at the selected flow rate. The electrical potential E across R_c was measured with a Keithley digital multimeter (Model 171). The current $I(=E/R_c)$ passing through the calorimeter heater having a resistance R resulted in the release of power $W_p(=I^2R)$ within the calorimetric cell. In response to the electrical power introduced, the voltage reading V(f) shifted away from its baseline position $V^{\circ}(f)$.

After about 10 minutes, the voltage reading became steady, showing a straight line on the recorder. It should be noted that the so-called steady voltage reading was actually still changing within a small range. Therefore, a set of 200 readings was recorded for each calibration point and an average was taken as the actual V(f) value at that specific point.

According to Equation (3.10), the calibration constant ϵ can be determined by

$$\epsilon = \frac{I^2R}{V(f)-V^\circ(f)} = \frac{(E/R_c)^2R}{V(f)-V^\circ(f)} \tag{4.3}$$

With the standard resistance=10.000Ω, and the calibration resistance=49.520Ω, equation (4.3) becomes

$$\epsilon = \frac{(E/10.000)^2 49.520}{V(f)-V^\circ(f)} = \frac{0.4952E^2}{V(f)-V^\circ(f)} \tag{4.4}$$

The same procedure was repeated at different flow rates by adjusting the syringe pump (counts·s^{-1}). A calibration curve (ϵ *vs.* flow rate) was then obtained for each calorimetric liquid.

As an example, Table 4.4 shows the calibration results of pump B with n-hexane. The same results are also presented in Figure 4.6.

Table 4.4 Calibration results of n-hexane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
302.95	0.1	-0.0018381	-0.4110472	-0.4092041	0.1134	15.5618
499.50	0.1	-0.0018769	-0.4104010	-0.4085241	0.1134	15.5879
500.40	0.1	-0.0014829	-0.4248292	-0.4233463	0.1155	15.6044
696.00	0.1	-0.0017302	-0.4213632	-0.4196330	0.1151	15.6336
900.40	0.1	-0.0016392	-0.4159086	-0.4142694	0.1145	15.6714
1005.75	0.1	-0.0017222	-0.4117936	-0.4100714	0.1140	15.6938
1100.80	0.1	-0.0016920	-0.4185928	-0.4169008	0.1150	15.7088

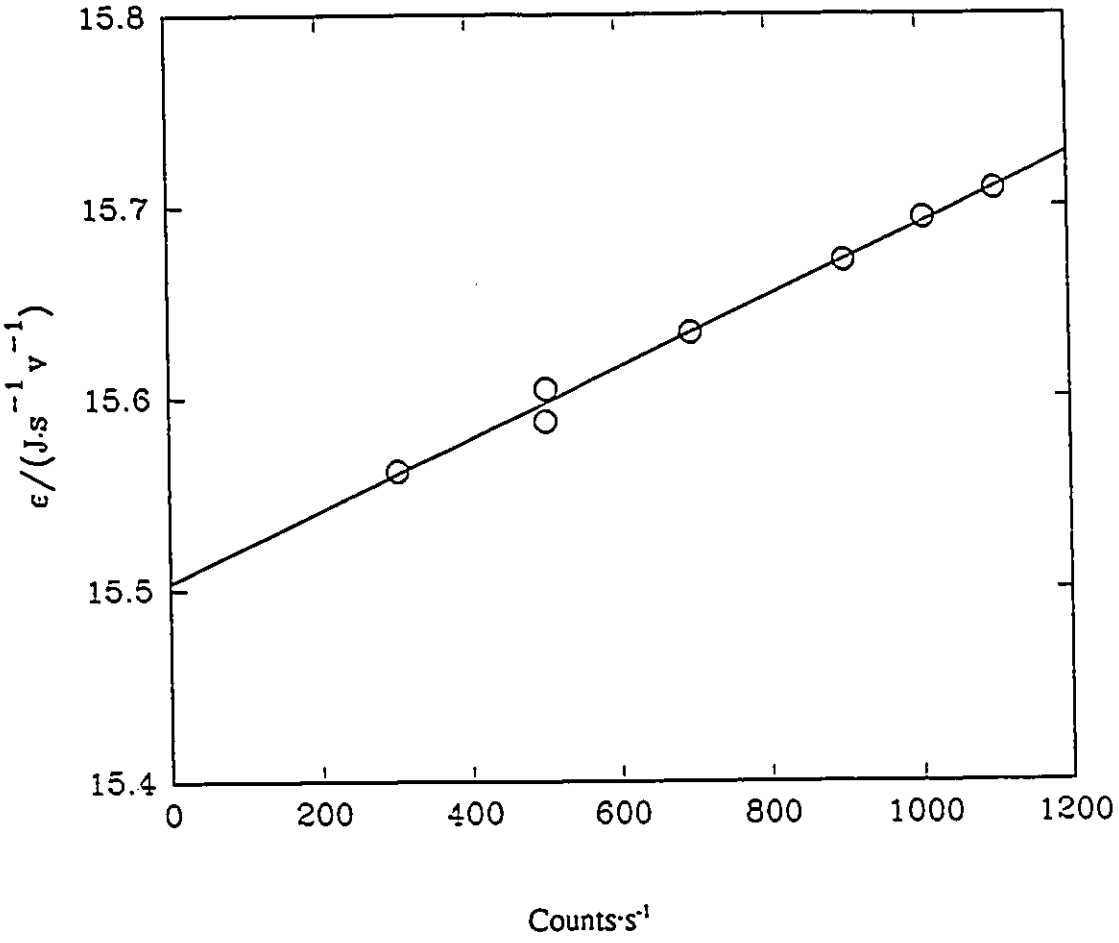


Figure 4.6 A typical calibration curve for ϵ with the flow rate

(results of n-hexane with pump B)

It has been found that the calibration constant ϵ is a linear function of the flow rate F

$$\epsilon = a_0 + a_1 F \tag{4.5}$$

where a_0 and a_1 are constants for a given liquid, and the flow rate F has units of counts·s^{-1}. The calibration results for n-hexane were correlated with Equation (4.5) by means of least-squares. With $a_0 = 15.5036$ and $a_1 = 1.87 \times 10^{-4}$, the root mean square deviation of the calculated ϵ from the experimental values is 0.00534 J·s^{-1}·V^{-1}. Table 4.5 shows the comparison of the calculated ϵ values and the experimental data for each calibration point. The straight line in Figure 4.6 was plotted with values of ϵ calculated from Equation (4.5).

The detailed calibration results for each of the experimental fluids involved in this study are presented in Appendix A-1.

Table 4.5 Comparison of the calibration results with its mathematical representations

Flow rate (count·s^{-1})	$\epsilon_{experimental}$ (J·s^{-1}·V^{-1})	$\epsilon_{correlated}$ (J·s^{-1}·V^{-1})
302.95	15.5618	15.5603
499.50	15.5879	15.5970
500.40	15.6044	15.5972
696.00	15.6336	15.6337
900.40	15.6714	15.6720
1005.75	15.6938	15.6917
1100.80	15.7088	15.7094

4.4 Measurement of excess enthalpy for binary systems

Fifteen binary systems were investigated in this study. A few of them were investigated previously by other researchers. The following section will discuss our experimental studies on the binary systems, along with a comparison with those reported in the literature.

4.4.1 Operational procedure

The calorimeter and all its auxiliary equipment were running for several hours after the temperature of the system reached a steady state at (298.150±0.002)K, since many of them need a warming-up period. The normal length of this period for the amplifier and voltmeter was about an hour.

The component liquids, partially degassed by agitation under reduced pressure, were loaded into the syringe pumps, and then forced through the tubing at selected flow rates and mixed in the mixing cell. All measurements were made with the sum of the flow rates of the components close to 5.000×10^{-3} $cm^3 \cdot s^{-1}$. By doing so, as suggested by Tanaka *et al.* (1975), it was possible to set the motor speed and gear ratio to produce any mole fraction within an estimated error of 0.0005.

The experiments were carried out in a manner to double check the equal concentration point. Each run was started near $x_1=0.5$ and ended with pure component

1 at $x_1=1.0$, with a concentration change of 0.05 between every two adjacent experimental points. This finished one half of a run. The measurement was then restarted again near $x_1=0.5$ in order to check the reproducibility of the experiment. The same procedure was followed to carry out the other half of the run, which ended with pure component 2 at $x_1=0.0$.

The voltage readings at $x_1=0.0$ and $x_1=1.0$, $V_1^\circ(f_1)$ and $V_2^\circ(f_2)$, were taken as the baselines for the pure component liquids. Since previously (Tanaka *et al.*, 1975), it was found that the baseline shifts caused by the flows of the liquids from each pump were additive on a volume fraction basis, the baseline voltage $V_m^\circ(f)$ associated with the mixing process was expressed as

$$V_m^\circ(f) = [f_1 V_1^\circ(f_1) + f_2 V_2^\circ(f_2)]/(f_1+f_2) \tag{4.6}$$

For every experimental point, the deflection of the voltage curve due to the mixing process registered on the recorder and the computer through an instrument coupler (ICS model 4880). When the recorder began to indicate that the voltage curve had reached a steady state, the computer was started to take the voltage readings, one every second. Usually, 500 voltage readings were collected. For the relatively low excess enthalpy values, such as in the low concentration ranges, up to 1000 voltage readings were taken. The deflection of the voltage curve from the baseline voltage, $V_m(f)$, due to the mixing process, was obtained by taking an average of the voltage readings.

The values of the excess molar enthalpy for a binary mixture were calculated from the relation

$$H_m^E = \frac{\epsilon_m[V_m(f) - V_m^\circ(f)]}{f_1/v_1 + f_2/v_2} \tag{4.7}$$

where f_1 and f_2 are the volumetric flow rates of components 1 and 2, respectively, and v_1 and v_2 are the corresponding molar volumes. The ϵ_m is the calibration constant for the mixture which was obtained from ϵ and flow rates of the constituent pure substances as

$$\epsilon_m = \Phi_1\epsilon_1 + \Phi_2\epsilon_2 \tag{4.8}$$

where Φ_1 and Φ_2 are the volume fractions of the components 1 and 2, respectively, defined by

$$\Phi_1 = \frac{f_1}{f_1 + f_2} \quad \text{and} \quad \Phi_2 = \frac{f_2}{f_1 + f_2} \tag{4.9}$$

4.4.2 Experimental results

The pure components constituting the 17 binary systems investigated in this study are listed in Table 4.6 .

Excess enthalpies $H_{m,ij}^E$ for all binaries involved were measured in our laboratory,

Table 4.6 A key to the binary mixtures studied

System	Component 1	Component 2
1	ethanol	n-hexane
2	ethanol	n-decane
3	n-hexane	n-decane
4	ethanol	n-dodecane
5	n-hexane	n-dodecane
6	1-propanol	n-hexane
7	1-propanol	n-decane
8	1-propanol	n-dodecane
9	MTBE	n-hexane
10	MTBE	n-decane
11	MTBE	n-dodecane
12	ethanol	2,2,4-trimethylpentane
13	ethanol	2,3-dimethylbutane
14	1-propanol	2,2,4-trimethylpentane
15	1-propanol	2,3-dimethylbutane
16	MTBE	2,2,4-trimethylpentane
17	MTBE	2,3-dimethylbutane

except for the n-hexane + n-decane and n-hexane + n-dodecane systems, which were taken from the literature (Marsh *et al.*, 1980; Ott *et al.*, 1981).

The experimental results of H_m^E for 15 binary mixtures determined at 298.15K are listed in Appendix A-2 (Table A-9 to A-23).

The smoothing equation

$$H_m^E/(J\cdot mol^{-1}) = x_1(1-x_1)\sum_{j=1}^{m} h_j(1-2x_1)^{j-1} \qquad (4.10)$$

was fitted to each set of the H_m^E data for the mixtures with MTBE. Values of the coefficients h_j, determined by the method of least-squares with all points weighted equally, are given in Table 4.7 along with the standard deviations, or the root mean square deviation (RMSD) of the representations.

The rest of the data were fitted, in the same manner, with a similar smoothing equation having a denominator term:

$$H_m^E/(J\cdot mol^{-1}) = \frac{x_1(1-x_1)}{1+h_0(1-2x_1)}\sum_{j=1}^{m} h_j(1-2x_1)^{j-1} \qquad (4.11)$$

The equation coefficients h_0 and h_j are listed in Table 4.8 along with the root mean square deviation (RMSD) of the representations.

Plots of the experimental results and their representations by Equations 4.10 and 4.11

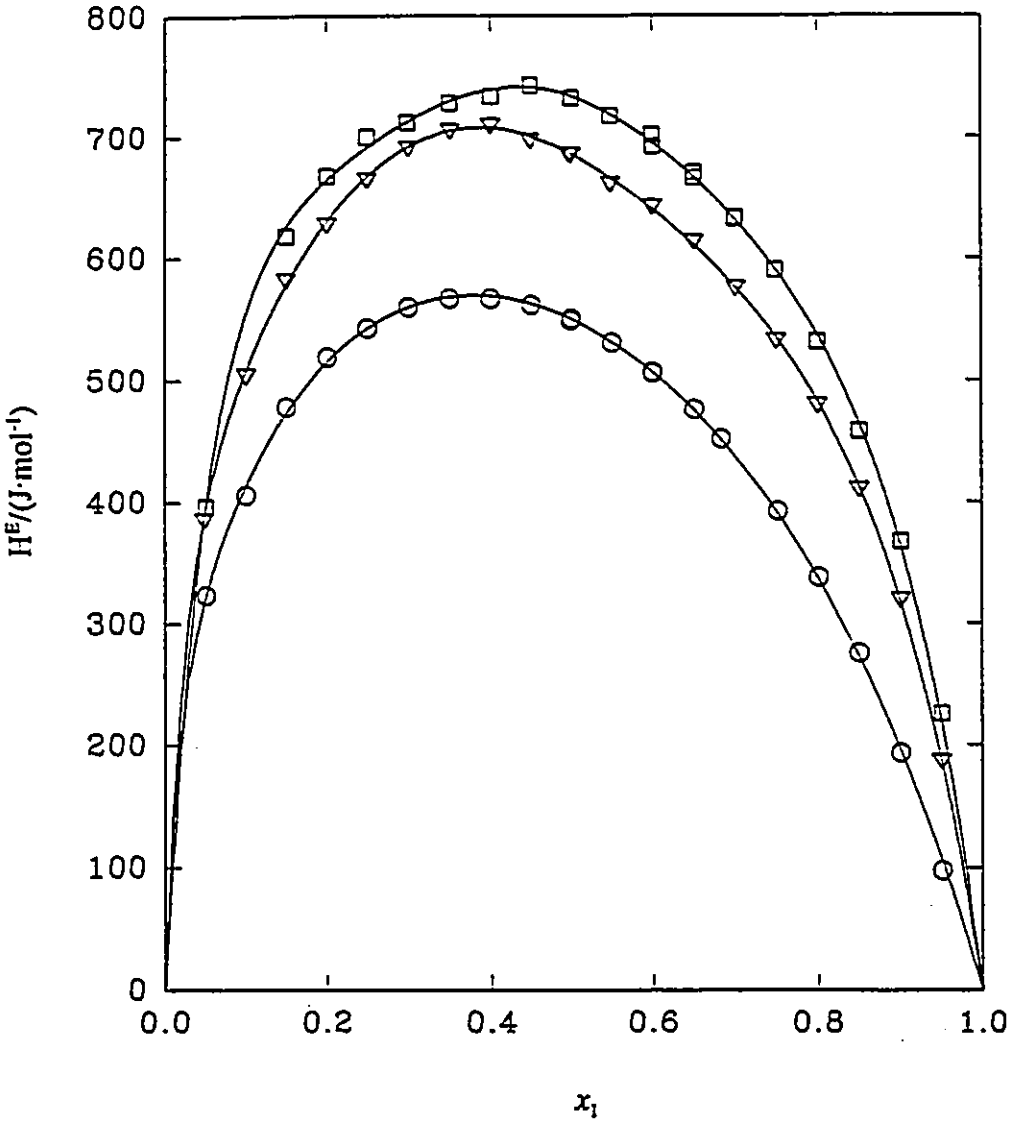
are shown in Figures 4.7 to 4.11. The H_m^E values obtained for these systems, as shown in the figures, are positive at all mole fractions. Over most of the mole-fraction range, the errors of the excess molar enthalpy and the mole fraction for all the binary mixtures are estimated to be less than 0.5 per cent and 5×10^{-4}, respectively.

Table 4.7 Parameters h_j and root mean square deviations (RMSD) for the representations of H_m^E by Equation 4.10

System	h_1	h_2	h_3	h_4	h_5	RMSD
MTBE+n-hexane	1477.80	0.68	64.01	95.22	-213.66	1.5
MTBE+n-decane	2000.50	-313.32	110.94	-100.36	-87.36	1.2
MTBE+n-dodecane	2279.30	-411.74	255.00	-208.78	-215.53	1.5
MTBE+2,2,4-TMP	1242.0	-91.1	-	-	-	1.8
MTBE+2,3-DMB	1231.5	47.8	-	-	-	1.7

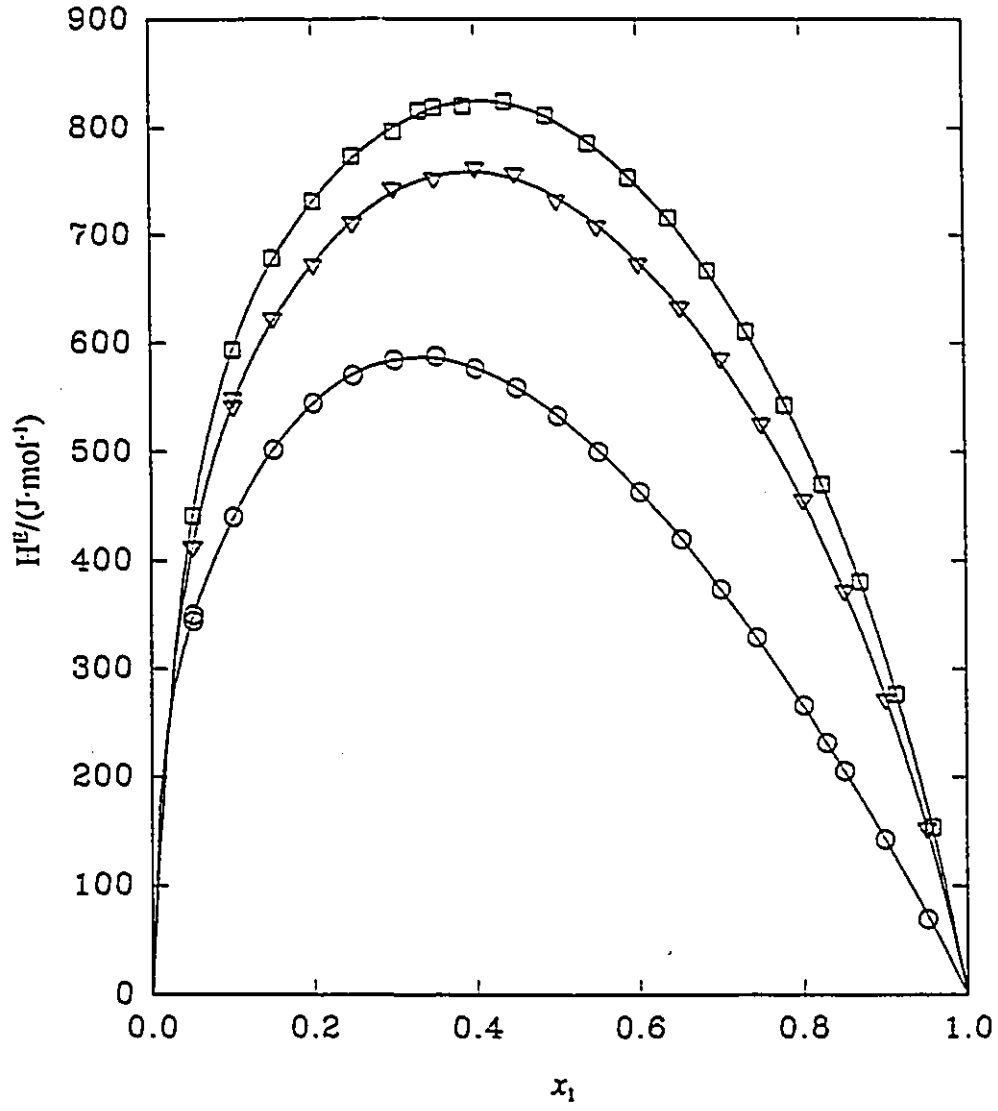
Table 4.8 Parameters h_j and root mean square deviations (RMSD) for the representations of H_m^E by Equation 4.11

System	h_0	h_1	h_2	h_3	h_4	h_5	RMSD
ethanol+n-hexane	-0.9699	2198.6	-1507.5	388.6	-412.8	-	3.7
ethanol+n-decane	-0.9399	2741.5	-1868.3	896.1	-1757.2	1170.4	2.9
ethanol+n-dodecane	-0.6923	2932.4	-1567.7	952.7	-1015.5	2397.8	4.9
propanol+n-hexane	-0.9839	2134.1	-941.2	-339.8	-243.2	-	1.5
propanol+n-decane	-0.9205	2941.0	-1853.0	312.1	-689.0	705.2	2.9
propanol+n-dodecane	-0.8809	3221.1	-2034.6	472.7	-632.6	925.3	2.1
ethanol+2,2,4-TMP	-0.9299	2330.2	-1451.9	493.0	-703.5	405.8	0.9
ethanol+2,3-DMB	-0.9931	2020.8	-1346.7	446.7	-495.4	-149.9	1.3
propanol+2,2,4-TMP	-0.9619	2306.2	-1062.8	-232.5	-198.2	75.0	0.7
propanol+2,3-DMB	-0.9474	1913.8	-668.0	-338.4	-	-	2.2



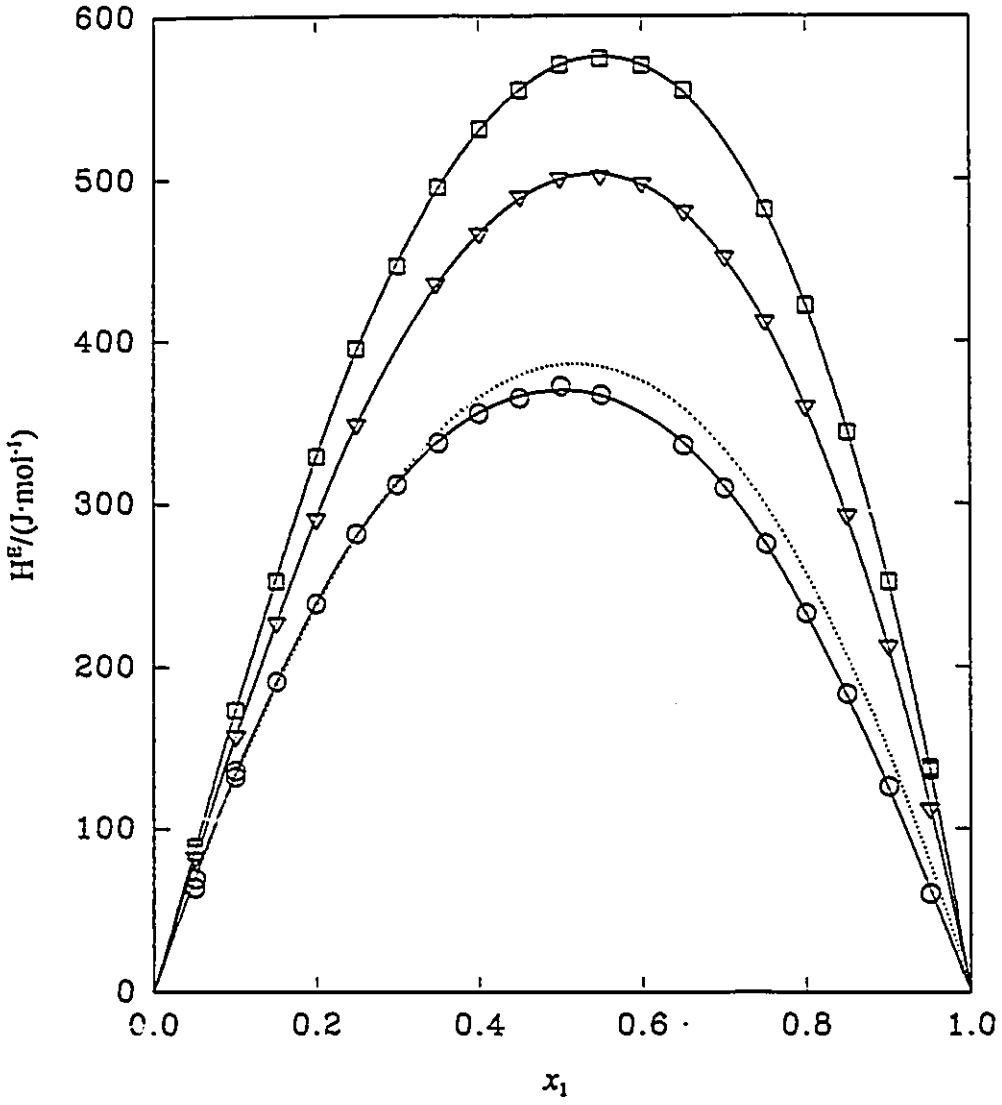
Experimental results: ○, n-hexane; ▽, n-decane; □, n-dodecane; ——, correlated with the experimental data by means of Equation 4.11.

Figure 4.7 Binary H_m^E data for the mixtures of ethanol(1)+normal alkane(2) at 298.15 K



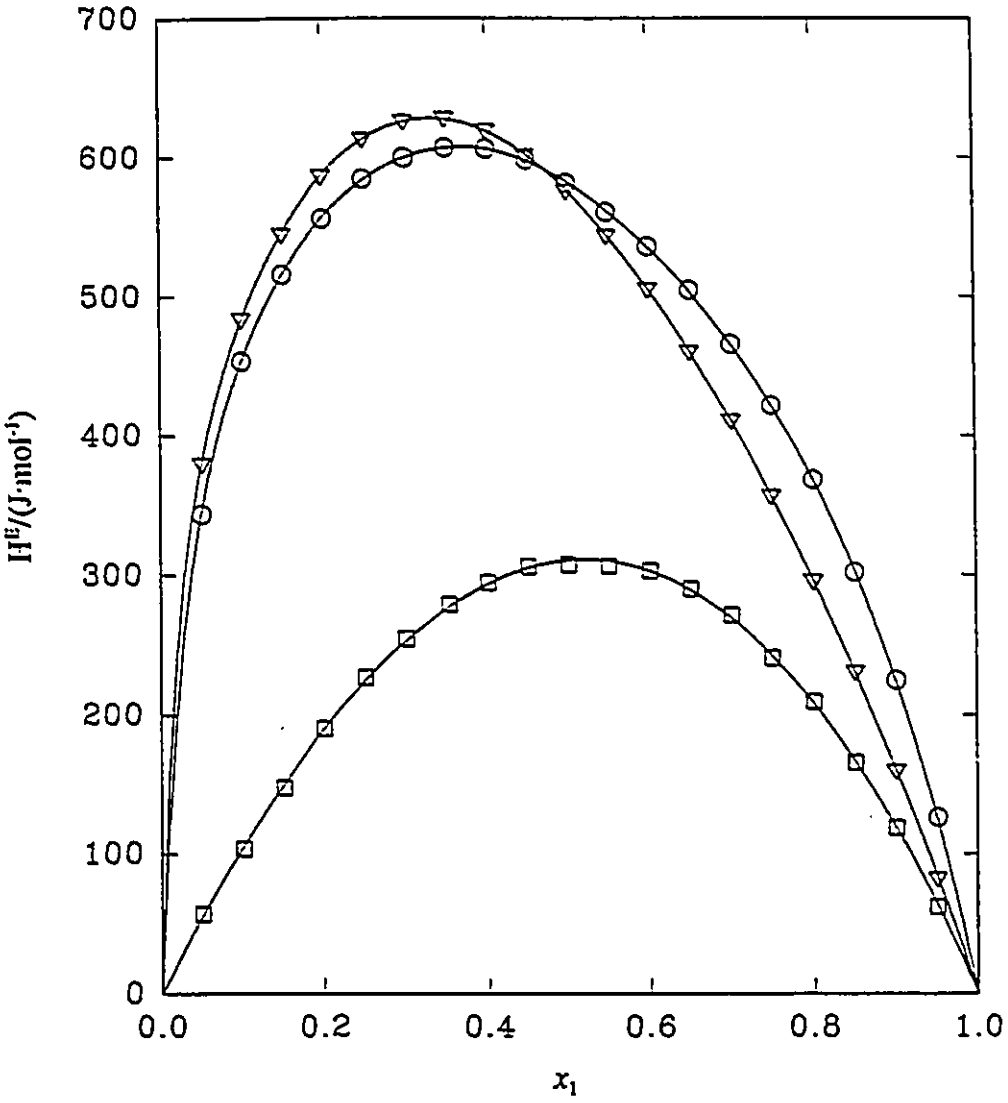
Experimental results: ○, n-hexane; ▽, n-decane; □, n-dodecane; ——, correlated with the experimental data by means of Equation 4.11.

Figure 4.8 Binary H_m^E data for the mixtures of 1-propanol(1)+normal alkane(2) at 298.15 K



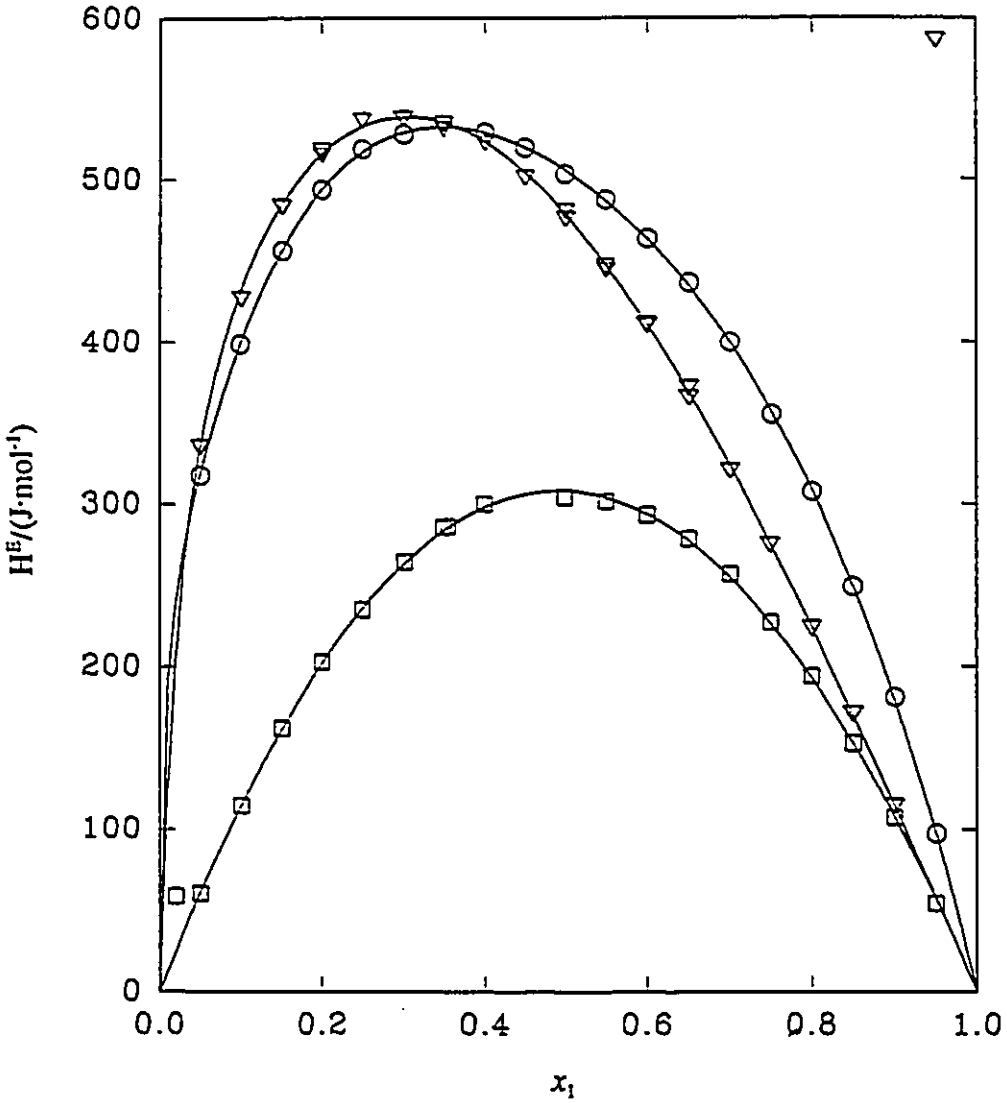
Experimental results: ○, n-hexane; ▽, n-decane; □, n-dodecane; ···, n-heptane, Tusel-Langer *et al.* (1991); ——, correlated with the experimental data by means of Equation 4.10.

Figure 4.9 Binary H_m^E data for the mixtures of MTBE(1) + normal alkane(2) at 298.15 K



Experimental results: ○, ethanol; ▽, 1-propanol; □, MTBE; ——, correlated with the experimental data by means of Eqs. 4.10 and 4.11.

Figure 4.10 Binary H_m^E data for the mixtures of (ethanol or 1-propanol or MTBE)(1) + 2,2,4-TMP(2) at 298.15 K

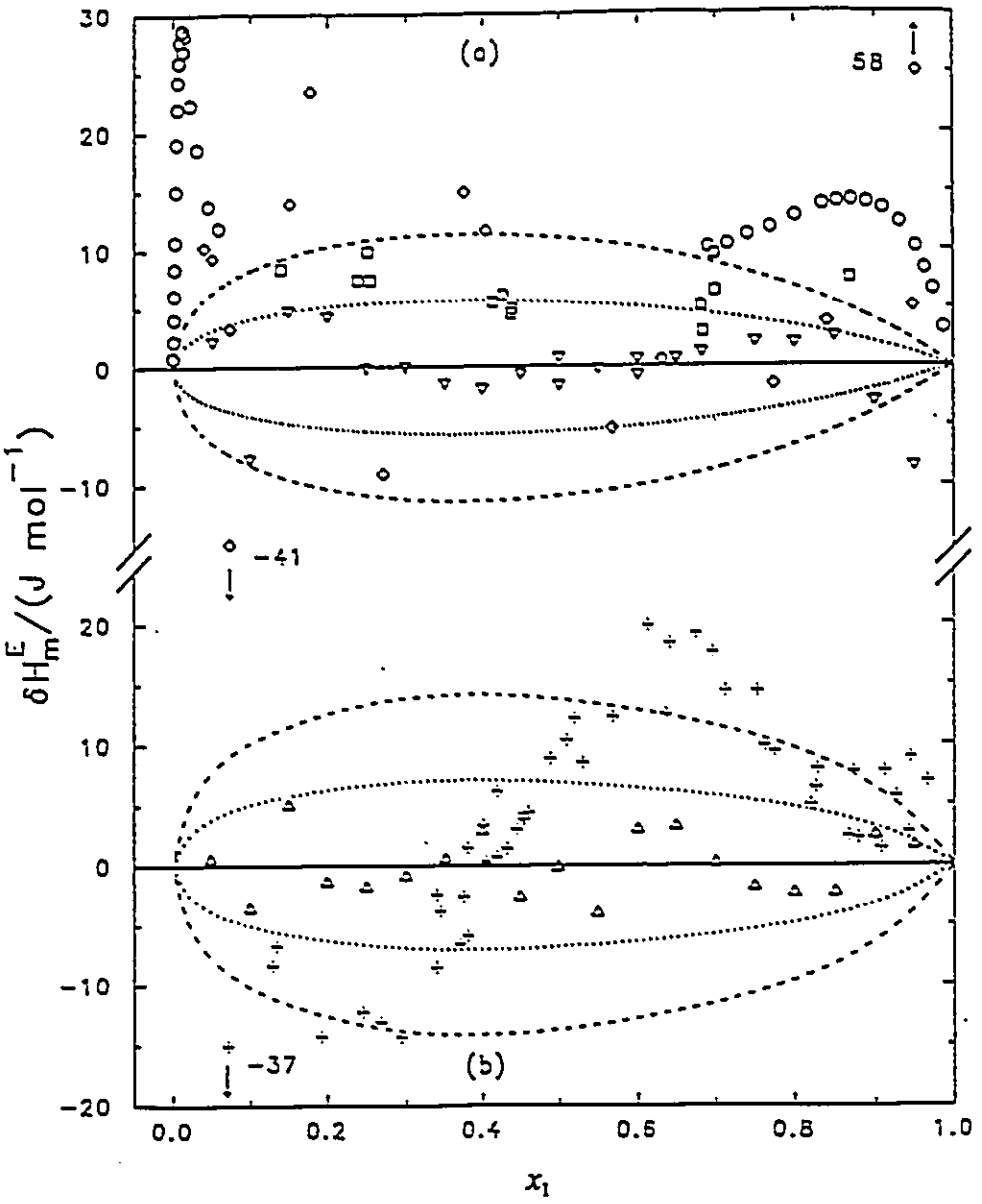


Experimental results: ○, ethanol; ▽, 1-propanol; □, MTBE; ——, correlated with the experimental data by means of Eqs. 4.10 and 4.11.

Figure 4.11 Binary H_m^E data for the mixtures of (ethanol or 1-propanol or MTBE)(1) + 2,3-DMB(2) at 298.15 K

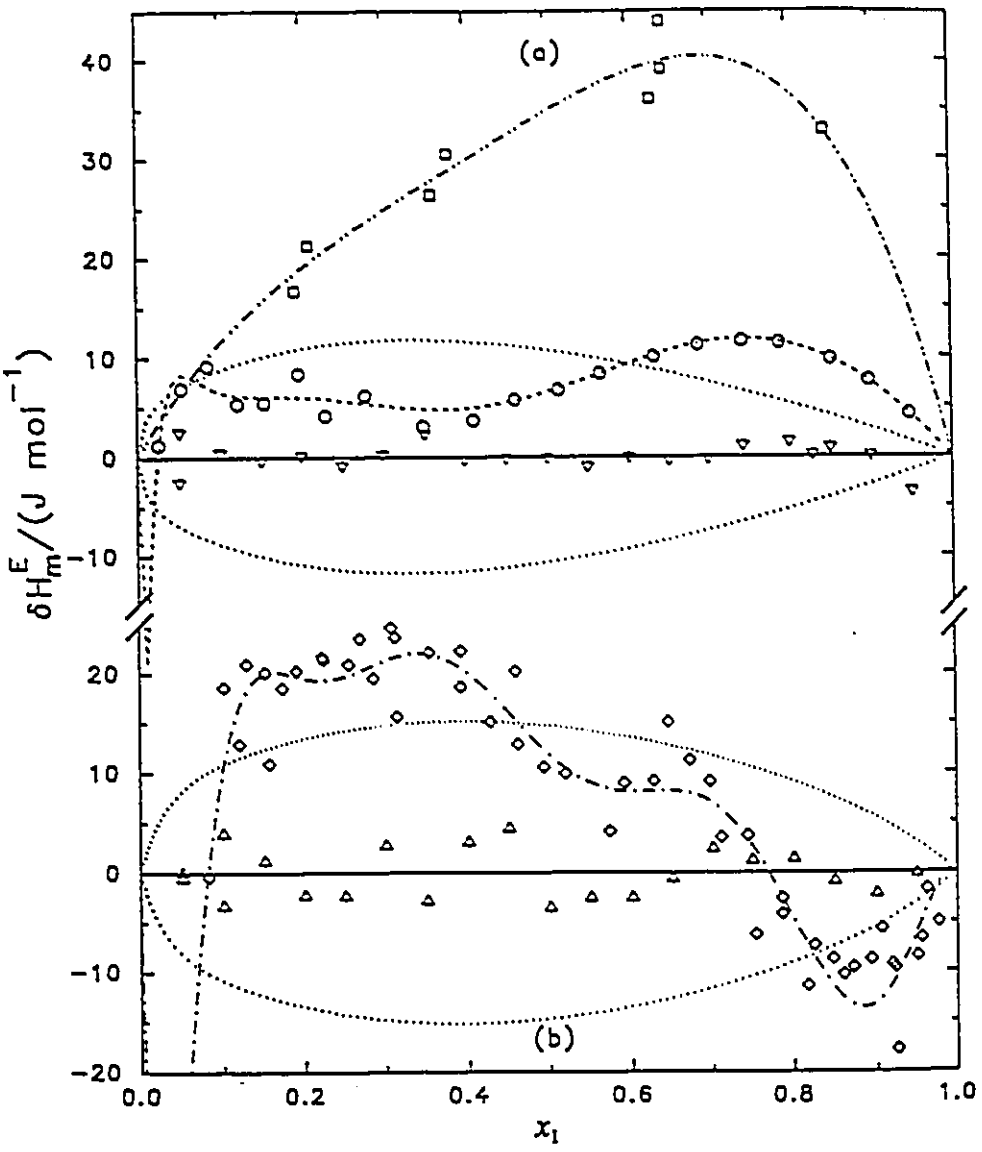
The H_m^E values for the mixtures of ethanol or 1-propanol or MTBE with n-alkanes, as shown in Figures 4.7 to 4.9, increase fairly regularly with increasing chain length of the n-alkane. The curves are approximately symmetrical about $x_1=0.5$, but show a slight skew towards $x_1=1$ for the mixtures of MTBE with n-alkanes and towards $x_1=0$ for the mixtures of n-alkanes with alcohols. For the mixtures with branched alkanes, as shown in Figures 4.10 and 4.11, the curves for the alcohols skew toward low alcohol mole fractions, with maxima occurring in the range of $0.3<x_1<0.4$. For the same branched alkane, both the maximum and skew of the 1-propanol curve are greater than that for the ethanol curve, leading to a crossing of the two alcohol curves in both figures. It appears that the replacement of 2,2,4-trimethylpentane by 2,3-dimethylbutane involves only minor changes in the molecular interaction, since the general characteristics of the curves in these two figures are very similar. This is particularly true for the MTBE mixtures, where the changes in H_m^E are relatively small.

Although there have been several other investigations of n-hexane with both ethanol and 1-propanol, as reviewed previously, the excess enthalpies of these two binary systems were re-investigated in this study. Deviations of those earlier results from the representations of the data obtained in this work are plotted in Figures 4.12 and 4.13. For the system of ethanol and n-hexane, as shown in Figure 4.12(a), there was agreement within a few per cent over most of the mole-fraction range; large discrepancies occurred near both ends of the concentration range.



(a) ethanol+n-hexane: this work, (▽); Brown *et al.* (1964), (□); Jones and Lu (1966), (◇); Stokes and Burfitt (1973), (○); (b) ethanol+n-decane: this work, (△); Christensen *et al.* (1979), (+). For both (a) and (b): (···), ±1% and (- - -), ±2% deviation from Eq. 4.11.

Figure 4.12 Deviations of δH_m^E {$=(H_m^E(exp)-H_m^E(cal)$} for the mixtures of ethanol(1) + (n-hexane or n-decane)(2)



(a) 1-propanol+n-hexane: this work, (▽); Brown *et al.* (1964), (□), (——), our smoothing of data), Veselý *et al.* (1982), (○), (- - -); (b) 1-propanol+n-decane: this work, (△); Christensen *et al.* (1979), (◇), (— · —); For both (a) and (b): (···), ±2% deviation from Equation 4.11.

Figure 4.13 Deviations of δH_m^E {=(H_m^E(exp)-H_m^E(cal)} for the mixtures of 1-propanol(1) + (n-hexane or n-decane)(2)

Apart from the relatively large deviations of the values from Brown *et al.* (1964) for the system of 1-propanol and n-hexane, there is agreement between the previously published data and the experimental results of this study within ~ 3 per cent over most of the mole fraction range, as shown in Figure 4.13(a). As mentioned in the previous section, Christensen *et al.* (1979) have studied the systems of n-hexane + ethanol/1-propanol at a pressure of 170KPa. A comparison of their data and the results from this work are also included in Figures 4.12(b) and 4.13(b).

Although there were no previous studies reported in the literature for the mixtures of MTBE with n-hexane, n-decane, and n-dodecane, a similar system of MTBE and n-heptane has been investigated by Tusel-Langer *et al.* (1991). The dotted curve shown in Figure 4.9 was calculated from the smoothing equation reported by those authors. It lies somewhat closer to the curve for n-hexane obtained in this work than might be expected from the results for the other n-alkanes.

Subsequently, all the experimental excess enthalpy data obtained in this study were used to serve various purposes. First of all, they were published as valuable data sources for industrial or academic usage. They were also used, as essential information about the constituent binary mixtures, in determining the excess enthalpy values of the related ternary mixtures. In addition, they played a key role in producing reliable parameters of the new model proposed in this study for predicting H_m^E values of the ternary mixtures.

4.5 Determination of ternary excess enthalpy

In studying the ternary mixtures, the excess enthalpy $H^E_{m,123}$ was obtained by means of Equation 3.13

$$H^E_{m,123} = H^E_{m,1-23} + (1-x_1)H^E_{m,23} \qquad (3.13)$$

where the $H^E_{m,1+23}$ was measured for pseudo-binary mixtures in which alcohol or ether, as component 1, was added to binary mixtures of component 2 (n-hexane) and 3 (n-decane or n-dodecane) having a fixed composition, and $H^E_{m,23}$ was the molar excess enthalpy of the particular binary mixture of components 2 and 3.

It can be seen from the above equation that the experimental values of the ternary excess enthalpy H^E_{m123} were obtained mainly by measuring $H^E_{m,1+23}$ values for pseudo-binary mixtures. The values of $H^E_{m,23}$ for the binary systems of n-hexane with n-decane, and n-hexane with n-dodecane were taken from the literature (Marsh *et al.*, 1980; Ott *et al.*, 1981).

The following section will explain how the specific binary mixtures were prepared and how the experimental data of $H^E_{m,1+23}$ were represented.

4.5.1 Preparation of the binary mixtures

For each ternary system studied, three binary mixtures of component 2 (n-hexane)

and 3 (n-decane/n-dodecane) were prepared at the concentrations of $x_2^b \approx 0.25$, ≈ 0.50, and ≈ 0.75, by weighing. The superscript b denotes the binary mixture.

A Mettler analytical balance with ± 0.02mg accuracy was used for preparing the mixtures. The measurements were carried out at room temperature. There were two important things to watch for during the weighing operation. One was proper closure of the weighing container, which assured no vapour leakage so that a steady balance reading could be reached. The other one was to prevent any component liquid from contacting the opening of the weighing container, which would cause errors in determining the mixture composition.

The prepared binary mixture was stored in a glass flask with a magnetic stirrer and then placed on a magnetic stirrer device, as shown in Figure 4.3, which drove the stirrer in the flask so that the two component liquids could be well mixed. This mixing process took about ten minutes.

There were three more stages in the preparation of the mixture. They were pre-estimation, weight correction, and calculation of the mixture densities.

Estimations of weight ratio and volume ratio

Estimations were carried out before the mixture preparation to decide the proper amount of each component liquid required for a specific mixture. The following, as an example, shows how an estimation was achieved for making a mixture of n-hexane and

n-decane with $x_2^b \approx 0.50$.

The molecular weights M_2 and M_3 are 86.17716 and 142.28468 for n-hexane, and n-decane, respectively. The mole fractions of x_2^b and x_3^b can be expressed by

$$x_2^b = \frac{\frac{W_2}{M_2}}{\frac{W_2}{M_2}+\frac{W_3}{M_3}} \quad \text{and} \quad x_3^b = 1 - x_2^b = \frac{\frac{W_3}{M_3}}{\frac{W_2}{M_2}+\frac{W_3}{M_3}} \tag{4.12}$$

where W_2 and W_3 are the expected quantities of the two components. Letting $x_2^b = x_3^b = 0.5$ leads to

$$\frac{W_2}{M_2} = \frac{W_3}{M_3} \quad \text{or} \quad W_3 = \frac{M_3}{M_2} W_2 \tag{4.13}$$

Introducing the values of the molecular weights, Equation 4.13 becomes

$$W_3 = \frac{M_3}{M_2} W_2 = \frac{142.28468}{86.17716} W_2 = 1.65107 W_2 \tag{4.14}$$

Equation 4.14 determines the weight ratio of the two components.

The densities of the two pure components, measured at the temperature 298.15 K, were $d_2 = 0.65512 g \cdot cm^{-3}$ and $d_3 = 0.72629 g \cdot cm^{-3}$. The W_2 can then be expressed in terms of the volume of n-hexane, V_2, by

$$W_2 = d_2 V_2 = 0.65512 V_2 \qquad (4.15)$$

With Equations 4.14 and 4.15, the volume ratio of the two components was then determined as

$$V_3 = \frac{W_3}{d_3} = \frac{1.65107 W_2}{0.72629} = \frac{1.65107 \times 0.65512}{0.72629} V_2 = 1.48928 V_2 \qquad (4.16)$$

Equations 4.14 and 4.16 provide guidance in preparing a selected binary mixture. Similar estimations were carried out for each binary mixture used in this study.

Weight corrections

It has been suggested that in order to obtain a relatively high accuracy on weighing, the effect of buoyancy in air of the objects on the balance pans must be taken into account (Bauer, 1952). In our mixture preparations, there was not only a buoyancy effect involved, but also air in the flask above the liquid mixture. Therefore, the measured weights of the component liquids were corrected to their values in vacuum, thereby eliminating errors caused by the involvement of air.

All of the data on weights of the component liquids listed in Appendix A-3 are the "vacuum-corrected" values.

The details of the correction procedure are explained in Appendix B.

Determination of the mixture densities

The densities of the binary mixtures, calculated on the assumption that the excess volume V_m^E cannot be neglected, are shown in Appendix A-3. Since the molar quantity of the excess volume V_m^E at constant temperature and pressure is only a function of the materials involved, two Redlich-Kister representations of V_m^E from the literature (Marsh and Ott, 1983 a,b) were adopted for the mixtures of n-hexane + n-decane, and n-hexane + n-dodecane. The density, d_m, of the mixture prepared is expressed by

$$d_m = \frac{M_m}{v_m} = \frac{M_m}{V_m^E + x_2^b v_2 + x_3^b v_3} \qquad (4.17)$$

where M_m and v_m are the molecular weight and molar volume of the mixture; x_2^b and x_3^b are the mole fractions of components 2 and 3; and v_2 and v_3 represent the molar volumes of the pure components.

The details of the R-K representations of V_m^E are presented in Appendix C.

4.5.2 Measurement of $H_{m,1+23}^E$ for the pseudo-binary mixtures

Pure component 1 (ethanol or 1-propanol or MTBE) was pumped into the calorimeter through pump A, while a prepared binary mixture of components 2 (n-hexane) and 3 (n-

decane or n-dodecane) was transferred, as a pseudo-pure component, to the mixing ceil through pump B.

All prepared binary mixtures were calibrated with pump B. The calibration procedure is the same as outlined for pure substances in section 4.3.2. The calibration results and their numerical representations are listed in Appendix A-3. Similar to Equations 4.8 and 4.9, the calibration constant for the pseudo-binary mixture, ϵ_m, was obtained from the flow rates and calibration constants of pure component 1, ϵ_1, and of the specific binary mixture of components 2 and 3, ϵ_b, as

$$\epsilon_m = \Phi_1\epsilon_1 + \Phi_b\epsilon_b \tag{4.18}$$

where Φ_1 and Φ_b are the volume fractions of component 1 and the specific binary mixture of components 2 and 3, defined as

$$\Phi_1 = \frac{f_1}{f_1+f_b} \quad \text{and} \quad \Phi_b = \frac{f_b}{f_1+f_b} \tag{4.19}$$

The experimental results of $H^E_{m,1+23}$ for ternary systems of ethanol + n-hexane + n-decane/n-dodecane are plotted in Figures 14 and 15, as examples, along with the results for the binary mixtures having $x_2=0$ or $x_3=0$. In all cases, the maximum values of $H^E_{m,1+23}$ occur near $x_1=0.4$, and for comparable values of $x_2/(1-x_1-x_2)$ the values at the maxima are larger for the mixture containing dodecane. For both mixtures at a constant

value of x_1, the enthalpies increase as the ratio $x_2/(1-x_1-x_2)$ decreases.

The details of experimental results of $H^E_{m,1+23}$ and the corresponding excess enthalpy $H^E_{m,123}$, obtained from Equation 3.13, for the six ternary systems are presented in Appendix A-4.

The values of experimental $H^E_{m,1+23}$ data were represented as a sum of binary terms (Tsao and Smith, 1953) with an added ternary contribution:

$$H^E_{m,1-23} = \left(\frac{x_2}{1-x_1}\right)H^E_{m,12} + \left(\frac{x_3}{1-x_1}\right)H^E_{m,13} + H^E_{m,T} \qquad (4.20)$$

Following Morris *et al.*(1975), the relation:

$$H^E_{m,T} = x_1x_2x_3(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + c_6x_1^3 + c_7x_1^2x_2 + c_8x_1x_2^2 + c_9x_2^3) \qquad (4.21)$$

was adopted for the ternary term $H^E_{m,T}$, where the parameters c_i were determined by fitting Equations 4.20 and 4.21 to the values of the experimental $H^E_{m,1+23}$ data, by means of the least-squares analyses. Although there are a number of $H^E_{m,T}$ expressions available in the literature, such as the expressions proposed by Rastogi *et al.* (1977), Kratochvila *et al.* (1980), and Pando *et al.* (1987), we have found that the Morris expression has the simplest form and is able to represent our data well.

For the six ternary systems studied, the parameters in their $H^E_{m,T}$ expression (Equation 4.21) are listed in Table 4.9, where the root mean square deviations (RMSD) of the

representations are also indicated. In some cases, experimental data fitting indicated that adequate representations of the present results were obtained with fewer adjustable parameters c_i. Curves obtained from these representations are shown in Figures 4.14 and 4.15, as well as in Appendix A-4.

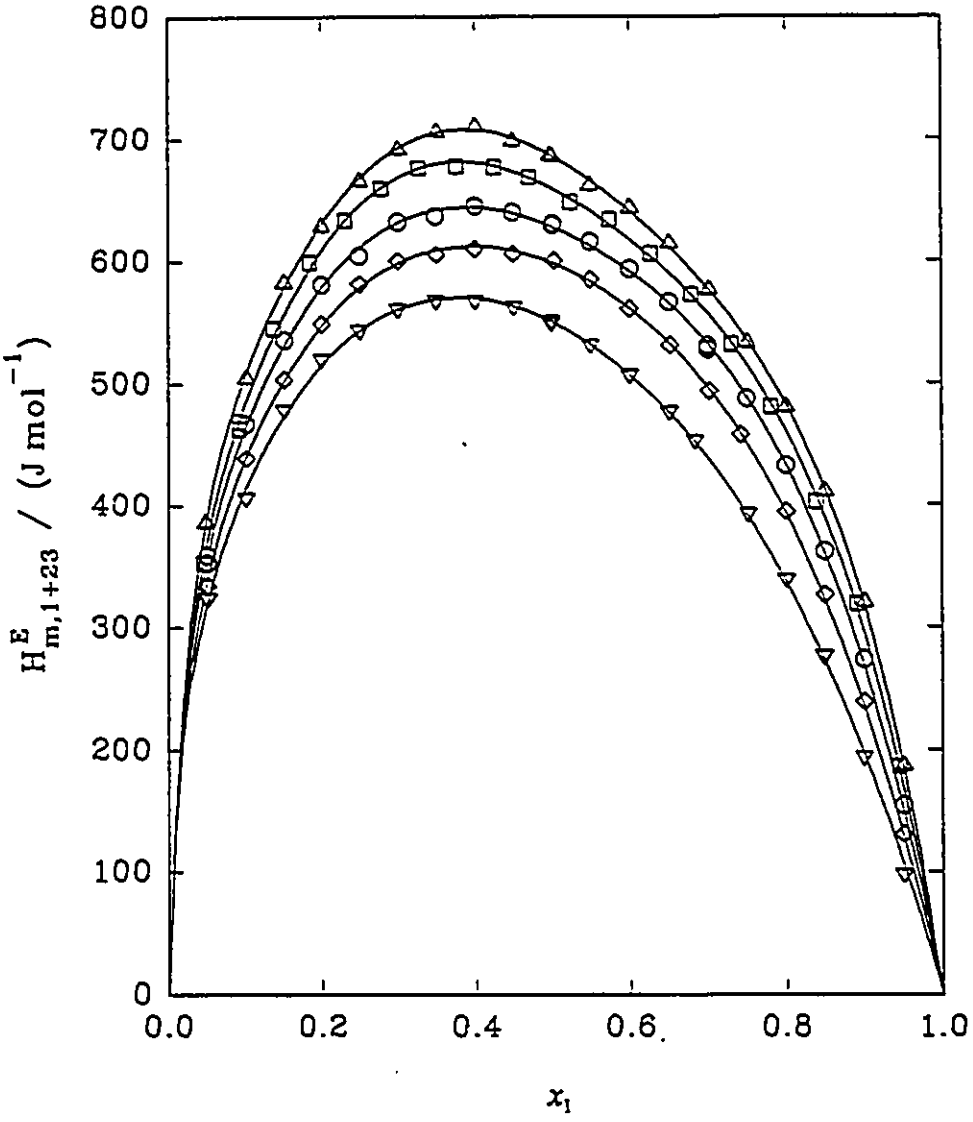
To illustrate, some constant $H^E_{m,123}$ contours, calculated for the ternary mixtures are plotted in the triangular diagrams of Figure 4.16 for the ethanol+n-hexane+n-decane mixtures and Figure 4.17 for the 1-propanol+n-hexane+n-dodecane mixtures. The general characteristics of the contours for all six ternary mixtures are very similar, except for the occurrence of a maximum located inside the triangular plot for the 1-propanol+n-hexane+n-dodecane system. Similar plottings for all the ternary mixtures involved are presented in Appendix A-4.

Table 4.9 Adjustable parameters c_i in the expression of the ternary term $H^E_{m,T}$

parameter	system 1*	system 2*	system 3*	system 4*	system 5*	system 6*
c_1	-1943.6	322.8	1855.1	-1252.7	651.9	1522.2
c_2	20825.6	15484.1	-5997.2	33198.2	-2783.5	-6710.2
c_3	6315.8	-6686.2	-4936.3	8596.7	-24.9	-1893.3
c_4	-51217.5	-58851.6	4747.0	-78880.3	3607.8	7079.7
c_5	-48958.5	19339.0	10166.1	-112649.7	-	5467.8
c_6	-4905.2	6351.4	3964.8	-9200.4	-	-
c_7	39563.1	49577.5	-	51959.0	-	-
c_8	57995.2	13076.1	-	129996.0	-	-
c_9	29130.4	-36714.0	-	88705.0	-	-
RMSD	3.2	6.7	3.7	4.9	2.6	3.4

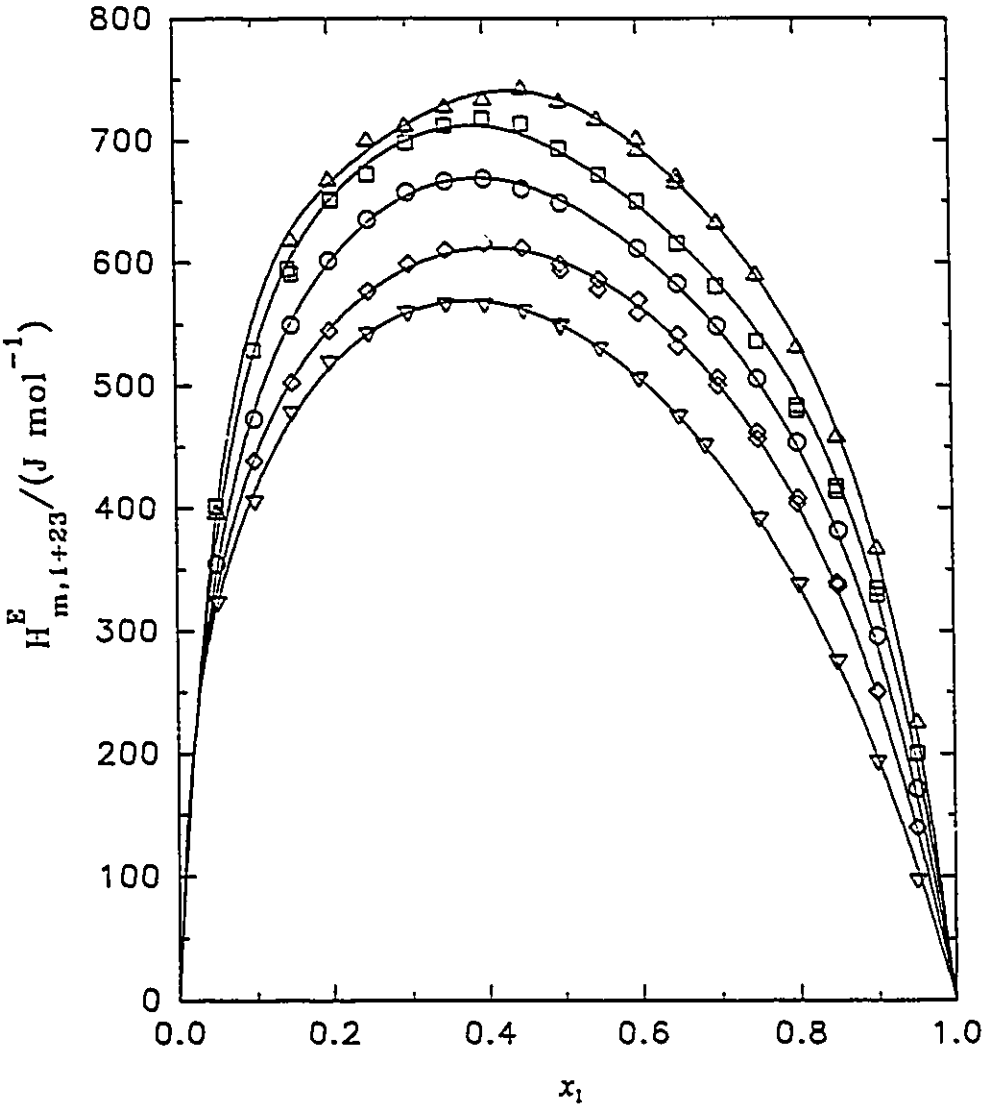
* Systems:

1. Ethanol+n-hexane+n-decane
2. Ethanol+n-hexane+n-dodecane
3. 1-Propanol+n-hexane+n-decane
4. 1-Propanol+n-hexane+n-dodecane
5. MTBE+n-hexane+n-decane
6. MTBE+n-hexane+n-dodecane



Experimental results: ▽, $x_1+x_2=1$; ◇, $x_2/(1-x_1-x_2)=2.9841$; ○, $x_2/(1-x_1-x_2)=0.9912$; □, $x_2/(1-x_1-x_2)=0.3339$; △, $x_2=0$. Curves: ——, calculated from the representation of the results by Equations 4.20 and 4.21.

Figure 4.14 Excess molar enthalpies $H^E_{m,1+23}$ of x_1(ethanol)+x_2(n-hexane)+x_3(n-decane) at 298.15 K



Experimental results: ▽, $x_1+x_2=1$; ◇, $x_2/(1-x_1-x_2)=2.9526$; ○, $x_2/(1-x_1-x_2)=1.0296$; □, $x_2/(1-x_1-x_2)=0.3328$; △, $x_2=0$. Curves: ——, calculated from the representation of the results by Equations 4.20 and 4.21.

Figure 4.15 Excess molar enthalpies $H^E_{m,1+23}$ of x_1(ethanol)+x_2(n-hexane)+x_3(n-dodecane) at 298.15 K

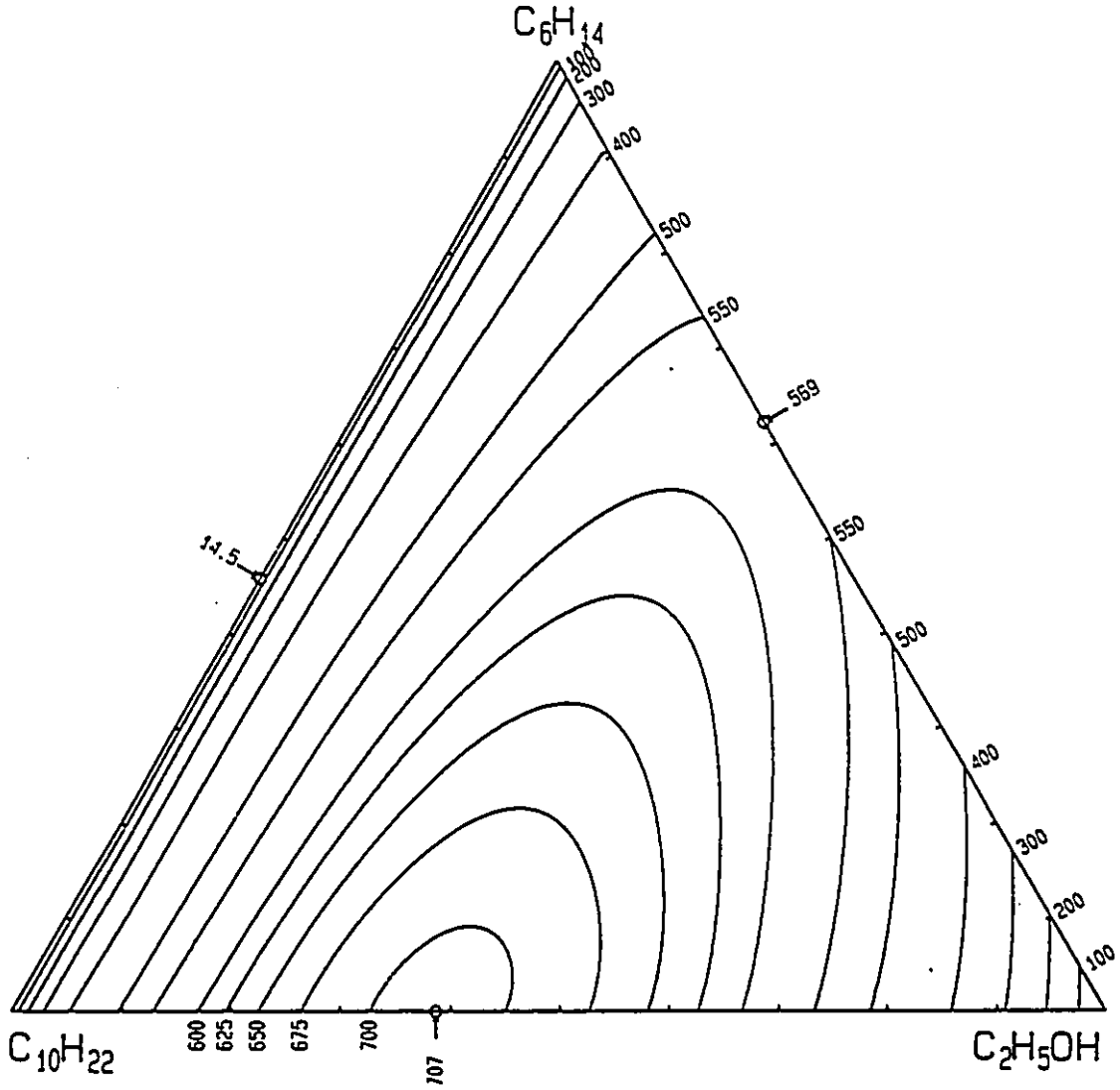


Figure 4.16 Contours for constant values of $H^{E}_{m,123}/(J \cdot mol^{-1})$ for $\{x_1C_2H_5OH + x_2CH_3(CH_2)_4CH_3 + x_3CH_3(CH_2)_8CH_3\}$ calculated from the representation of the experimental results by Equations 4.20 and 4.21.

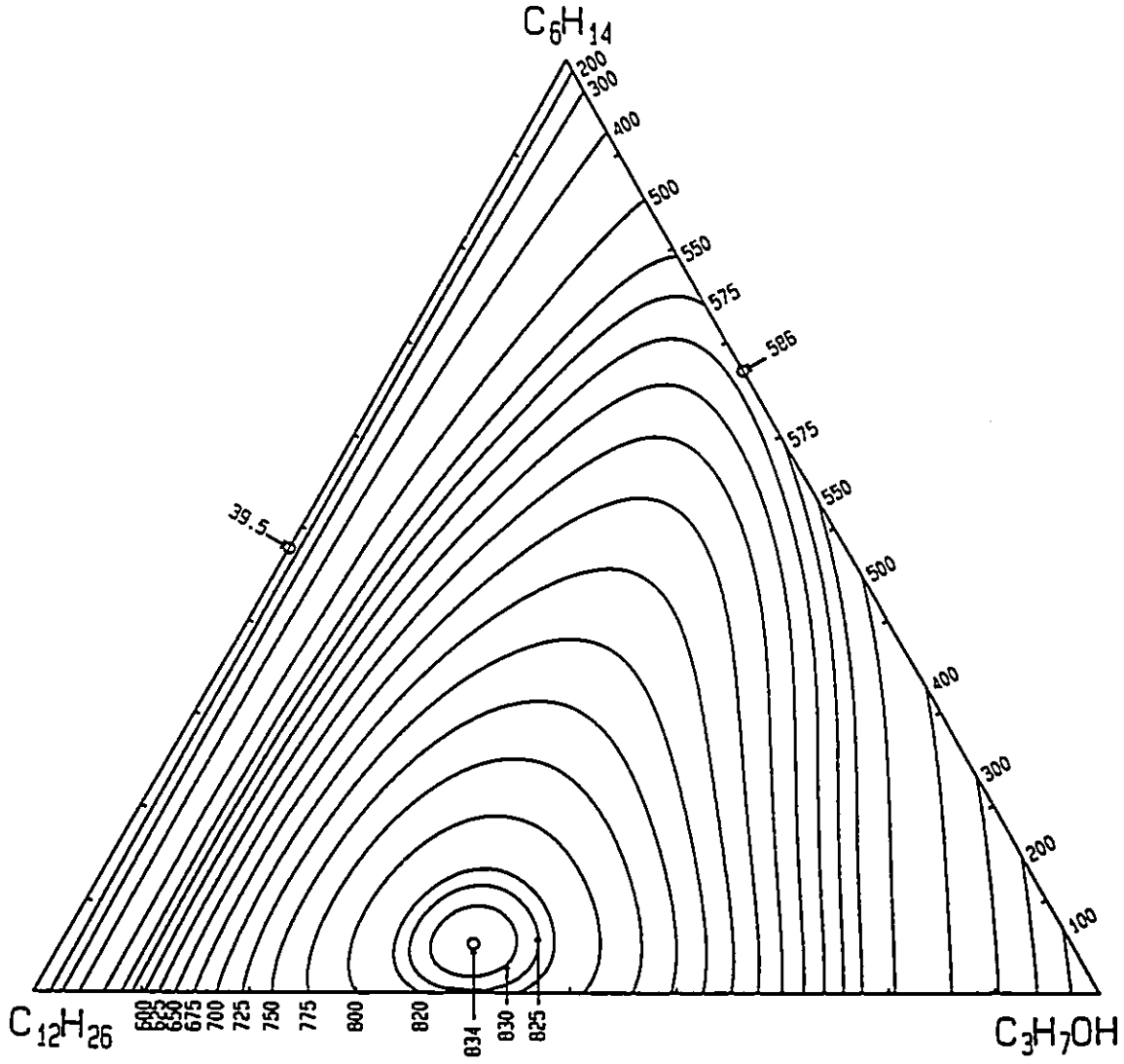


Figure 4.17 Contours for constant values of $H^{E}_{m,123}/(J \cdot mol^{-1})$ for $\{x_1C_3H_7OH + x_2CH_3(CH_2)_4CH_3 + x_3CH_3(CH_2)_{10}CH_3\}$ calculated from the representation of the experimental results by Equations 4.20 and 4.21.

Chapter 5

Correlation and prediction of binary and ternary excess enthalpy data

Analyses of experimental results were carried out with several solution models, such as the Flory theory model, the association model with a Flory contribution term, and the DISQUAC, NRTL and UNIQUAC models. They were fitted to the experimental results. The values of the model parameters were determined by the least-square method with all points weighted equally.

The first section of this chapter describes how the new model was developed in this study. The reason for having various models involved is that some existing models work well for certain types of systems, but provide large discrepancies when used for other systems. That was also one of the main concerns for developing a new model with an expectation that it can well represent all types of the systems studied.

The second part of this chapter presents the correlations of experimental H_m^E results by means of the different models investigated in this study, including the proposed model.

The last section of the chapter is focused on the prediction of the ternary excess enthalpies from the binary H^E data by means of the proposed model and a comparison with the NRTL and UNIQUAC models.

5.1 Development of a new model

Based on principles of statistical thermodynamics, a new model has been proposed for representing and predicting the excess enthalpies of a ternary mixture from correlations of the enthalpies of its constituent binaries.

This section describes the development and verification of the model. It includes the local composition expression employed, the expressions for calculations of binary and ternary excess enthalpies, and a comparison with the results from the molecular dynamic simulation (Nakanishi *et al.*, 1982) and the NRTL and UNIQUAC models. The treatment was based on an approximation of the radial distribution function and the quasi-lattice two-liquid theory. It should be suitable for a relatively wide range of solution types.

5.1.1 Local composition expression

In general, the interaction between a pair of molecules depends strongly on their separation. Within a mixture, this leads to a distribution of the molecules which is locally non-random. The local species-species coordination number, N_{ji}, is defined as the number of j molecules interacting with a central i molecule, and is related to the radial distribution function, $g_{ji}(r)$, by the equation (Lee and Sandler, 1987)

$$N_{ji} = 4\pi\frac{N_j}{V}\int_{\sigma_{ji}}^{R_w\sigma_{ji}} g_{ji}(r)\, r^2 dr \qquad (5.1)$$

where r is the separation of the molecules, σ_{ji} is the collision diameter, R_w is the reduced well width ($R_w\sigma_{ji}$ represents the first coordination shell) and N_j is the number of j molecules in volume V.

According to the radial distribution function theory (Lee, 1988), at low densities

$$g_{ji}(r) = \exp(-u_{ji}(r)/kT) \qquad (5.2)$$

where $u_{ji}(r)$ is the potential function for the interaction between a pair of j and i molecules, and k stands for Boltzmann constant. This relation can not be adopted directly, since the mixtures considered here are liquids with appreciable densities. For the present work, the radial distribution function for a j-i pair in a liquid mixture is assumed to have the following simple form in the range $\sigma_{ji} \le r \le R_w\sigma_{ji}$:

$$g_{ji}(r) = \exp(-\alpha_i \epsilon_{ji} / RT) \qquad (5.3)$$

where ϵ_{ji} denotes the molar value of the potential function $u_{ji}(r)$ at the lowest potential level. The α_i is a correction factor which is introduced to compensate for two effects in the environment of the i molecule. One is the correction to an average value of the potential function in the range $\sigma_{ji} \leq r \leq R_w \sigma_{ji}$. The other is to allow for the finite density of the liquid in comparison with the infinitesimal density required in Equation 5.2. In this regard, α_i should be a function of the density, and consequently the temperature. However, in the present work which is concerned with liquid mixtures whose densities vary in a relatively small range, α_i is assumed to be a function only of the temperature.

Substituting Equation 5.3 into Equation 5.1 (Lee and Sandler, 1987) then yields

$$N_{ji} = \frac{4\pi}{3} \frac{N_j}{V} (R_w^3 - 1) \sigma_{ji}^3 \exp(-\alpha_i \epsilon_{ji} / RT) \qquad (5.4)$$

Assuming a constant reduced well width for the first coordination shell of all molecular pairs, the expression for the local composition

$$x_{ji} = \frac{N_{ji}}{\sum_k N_{ki}} \qquad (5.5)$$

becomes

$$x_{ji} = \frac{x_j \sigma_{ji}^3 \exp\left(-\alpha_i \epsilon_{ji} / RT\right)}{\sum_k x_k \sigma_{ki}^3 \exp\left(-\alpha_i \epsilon_{ki} / RT\right)} \qquad (5.6)$$

where x_j is the mole fraction of component j in the mixture. Equation 5.6 is the local composition expression used in this work.

5.1.2 Representation of binary excess enthalpy H_m^E

Using the quasi-lattice two-liquid theory and neglecting long range interactions, the configurational molar internal energy of a binary system can be expressed (Prausnitz *et al.*, 1986) as

$$U_{config,m} = \frac{Z}{2}\left[x_1(x_{21}\epsilon_{21} + x_{11}\epsilon_{11}) + x_2(x_{12}\epsilon_{12} + x_{22}\epsilon_{22})\right] \qquad (5.7)$$

where Z denotes the coordination number. For the first coordination shell in liquids, Z=10 is assumed.

Similarly, for the pure component liquids

$$U^{(j)}_{config,m} = \frac{Z}{2}\epsilon_{jj} \qquad (j=1,2) \qquad (5.8)$$

Assuming that changes in the internal energy of the mixture are primarily due to configurational effects and that the difference between the excess molar enthalpy and excess molar energy is negligible (i.e. PV_m^E is small), then

$$H_m^E = U_m^E = \frac{Z}{2}(x_1 x_{21} \Delta\epsilon_{21} + x_2 x_{12} \Delta\epsilon_{12}) \qquad (5.9)$$

where

$$x_{21} = x_2\left(\frac{\sigma_{21}}{\sigma_{11}}\right)^3 \exp\left(\frac{-\alpha_1 \Delta\epsilon_{21}}{RT}\right) \Big/ \left[x_1 + x_2\left(\frac{\sigma_{21}}{\sigma_{11}}\right)^3 \exp\left(\frac{-\alpha_1 \Delta\epsilon_{21}}{RT}\right)\right] \qquad (5.10)$$

and

$$x_{12} = x_1\left(\frac{\sigma_{12}}{\sigma_{22}}\right)^3 \exp\left(\frac{-\alpha_2 \Delta\epsilon_{12}}{RT}\right) \Big/ \left[x_2 + x_1\left(\frac{\sigma_{12}}{\sigma_{22}}\right)^3 \exp\left(\frac{-\alpha_2 \Delta\epsilon_{12}}{RT}\right)\right] \qquad (5.11)$$

In these equations, the notation $\Delta\epsilon_{ji}=\epsilon_{ji}-\epsilon_{ii}$ has been adopted for the molar potential differences.

It can be seen from Equations 5.9-5.11 that the expression for H_m^E contains four parameters ($\Delta\epsilon_{21}$, $\Delta\epsilon_{12}$, α_2 and α_1), which must be adjusted to fit the binary enthalpy data. Practical application of the model indicates that it is generally adequate to impose the further constraint $\alpha_2=\alpha_1=\alpha$, where α is characteristic of the particular binary system. As a consequence, the number of adjustable parameters is reduced to three. Equations 5.9-5.11 formally resemble the expressions obtained in the NRTL (Renon and Prausnitz, 1968a) and UNIQUAC (Abrams and Prausnitz, 1975) treatments of mixtures.

5.1.3 Calculation of H_m^E for multicomponent systems

With the assumption of pairwise additivity, the expression for H_m^E, given in Equation 5.9, can be extended directly to multicomponent systems as follows:

$$H_m^E = \frac{Z}{2}\sum_i\sum_j x_i x_{ji}\,\Delta\epsilon_{ji} \qquad (j \neq i) \qquad (5.12)$$

where

$$x_{ji} = \frac{x_j\left(\frac{\sigma_{ji}}{\sigma_{ii}}\right)^3 \exp\left(\frac{-\alpha_i\Delta\epsilon_{ji}}{RT}\right)}{\sum_k x_k\left(\frac{\sigma_{ki}}{\sigma_{ii}}\right)^3 \exp\left(\frac{-\alpha_i\Delta\epsilon_{ki}}{RT}\right)} \qquad (5.13)$$

5.1.4 Comparison with computer-simulation results

In non-ideal fluid mixtures, the local composition around each kind of central molecule generally differs from the overall composition. Information about this can be obtained from statistical mechanical ensemble data in molecular dynamics (MD) calculations (Nakanishi and Toukubo, 1979) or Monte Carlo (MC) calculations (Nakanishi *et al.*, 1982).

Computer simulations are based on the assumption of some specific potential energy model, such as the Lennard-Jones potential. Theoretically, the thermodynamic properties of such a fluid can be obtained from computer-aided numerical calculations through strict

statistical thermodynamic relations. Comparison of the calculated results with those obtained from a particular solution theory model can serve as a test of the feasibility of the model. In Table 5.1, results calculated from Equation 5.9 are compared with excess molar internal energies obtained for the three kinds of Lennard-Jones mixtures in the computer-simulation work of Nakanishi *et al.* (1982). Also included in the table for further comparison are the results of calculations with the NRTL (Renon and Prausnitz, 1968a) and UNIQUAC (Abrams and Prausnitz, 1975) models.

It is evident from Table 5.1 that the present model with an assumed value of α=0.1 gives molar excess internal energy values which are fairly close to the computer-simulation results for the three different types of fluids. The NRTL and UNIQUAC models provide poorer predictions. When α is adjusted, the NRTL model reproduces the MD result for the weak non-ideal LB-2 mixture, but is unable to reproduce the behaviors of the fluids with strong non-ideality, such as the A-2 mixture with a large positive deviation, and the S-2 mixture with a large negative deviation.

The utility of the present model was investigated through calculations for the ternary systems studied, plus six more ternaries selected. It was carried out through the correlation of binary excess enthalpy data and the prediction of ternary H_m^E with the binary system parameters. The details of the investigation are described in the following sections.

Table 5.1 Comparison of results from solution theories with MD computer simulations

Fluid model	$\epsilon_{22}/\epsilon_{11}$	$\epsilon_{12}/\epsilon_{11}$	$U_m^E/(J\cdot mol^{-1})$				
			MD[d]	This work[e]	NRTL		UNIQUAC
					(α=0.4)[f]	(α fitted)[g]	
LB-2[a]	2	$\sqrt{2}$	184	135	4.7	184 (α=-2.879)	-1.4
A-2[b]	2	1	791	849	129	387 (α=-3.359)	116
S-2[c]	2	2	-1105	-991	-225	-387 (α=3.375)	-236

[a] Lorentz-Berthelot mixture.

[b] Association model.

[c] Solvation model.

[d] Conditions for MD simulations: T=120 K, $x_1=x_2=0.5$, $\rho=0.75$, $\sigma_{11}=\sigma_{22}=\sigma_{12}=3.405$ Å and $(\epsilon_{11}\epsilon_{22})^{1/2}/k=119.8$ K (Nakanishi *et al.*, 1982).

[e] Equation 5.9 with $\alpha_1=\alpha_2=0.1$.

[f] Following Nakanishi and Toukubo (1979).

[g] α is adjusted for the best fit of the computer-simulation results.

5.2 Representation of experimental results with various models

The Flory theory, the association model with a Flory contribution term, the DISQUAC, NRTL and UNIFAC models, and the proposed model were investigated for H_m^E data correlation. In this section, a brief discussion will be presented on the capabilities of these models in terms of representing the binary and ternary experimental H_m^E data.

5.2.1 Estimation from the Flory theory

In the past, we have found the Flory theory (Flory, 1965; Abe and Flory, 1965) to be useful in correlating the excess molar enthalpies of a number of (ether + n-alkane) binary mixtures (see Wang *et al.*, 1989a, where references to earlier work may be found). In this regard, the possibility of predicting the behaviour of a ternary system from analyses of its constituent binaries was particularly attractive.

The Flory theory was applied to the two ternary systems containing MTBE. The extension of the theory to multicomponent systems has been outlined by Brostow and Sochanski (1975). Here, only the equations needed for application to the present ternary systems are summarized; the notation is essentially the same as in the reference.

$$H^{E}_{m\,123} = \left(\sum x_i V_i^*\right)\left[\sum \phi_i P_i^*\left(\tilde{v}_i^{-1} - \tilde{v}^{-1}\right) + \tilde{v}^{-1}\psi\right] \tag{5.14}$$

$$T^* = \left(\sum \phi_i P_i^* - \psi\right)/\left(\sum \phi_i P_i^*/T_i^*\right) \tag{5.15}$$

where

$$\psi = \phi_1\theta_2 X_{12} + \phi_2\theta_3 X_{23} + \phi_3\theta_1 X_{13}(s_3/s_1) \tag{5.16}$$

and the sums are taken over the three components i (i=1,2,3). The asterisk is used to indicate characteristic values of the pressure P, volume V, and temperature T; the tilde indicates their reduced values obtained by dividing by the corresponding characteristic values. The segment fractions ϕ_j and site fractions θ_j are defined by the relations

$$\phi_j = \frac{x_j V_j^*}{\sum x_i V_i^*} \tag{5.17}$$

and

$$\theta_j = \frac{\phi_j}{\sum \phi_i (s_i/s_j)} \tag{5.18}$$

where s_i is the number of contact sites per segment of a molecule of species i. The quantities X_{ij} in Equation 5.16 denote the mixed-pair interchange interaction energies

between sites on species i and j. The factor s_j/s_i in the last term of Equation 5.16 has been introduced to allow for the asymmetry in Flory's definition of X_{ij} because, in the present usage, the convention $i<j$ has been adopted. The reduced form of the equation of state is

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3}-1)-1/\tilde{v}\tilde{T} \qquad (5.19)$$

which for zero pressure becomes

$$\tilde{v}^{4/3}\tilde{T}-\tilde{v}^{1/3}+1 = 0 \qquad (5.20)$$

Values of V_i^* and P_i^* for the pure components are obtained from

$$\tilde{v}^{1/3} = (V_{m,i}/V_i^*)^{1/3} = 1+\alpha_{p,i}T/3(1+\alpha_{p,i}T) \qquad (5.21)$$

and

$$P_i^* = (\alpha_{p,i}/\kappa_{T,i})T\tilde{v}_i^2 \qquad (5.22)$$

where $V_{m,i}$, $\alpha_{p,i}$, and $\kappa_{T,i}$ are the molar volume, isobaric expansivity, and isothermal compressibility, respectively. The value of T_i^* can then be calculated from Equation 5.15.

The component properties and parameters used in the present calculations are given in Table 5.2. In the case of MTBE, α_p at 298.15K has been reported by Obama *et al.* (1985), but it appears that a value of κ_T is not available in the literature. The value given

in Table 5.2 was derived from a group contribution estimate of the thermal pressure coefficient (Manzini and Crescenzi, 1974). The data for the n-alkanes are the same as in our previous work (Wang *et al.* 1989a).

Values of X_{12} and X_{13} were obtained from the least-squares calculations in which Equation 3.36 was fitted to the representations of $H^E_{m,1j}$ given in Table 4.7. Values of X_{23} were obtained from similar treatments of $H^E_{m,23}$ for (n-hexane + n-decane) mixtures (Marsh *et al.*, 1980), and (n-hexane + n-dodecane) mixtures (Ott *et al.*, 1981). In all of these calculations, it was assumed that the segments were approximately spherical, and the relation

$$s_i / s_j = (V_j^* / V_i^*)^{1/3} \qquad (5.23)$$

was used to estimate the site ratios.

The dashed curves in Figures 5.1-5.3 were calculated from Equation 5.14, using the parameters from Table 5.2. The agreement between these estimates and the experimental results is very good, in view of the fact that only data for the pure components and their binary mixtures were used. For the 96 points of the n-decane systems, the root mean square deviation (RMSD) between the estimated and experimental values of $H^E_{m,123}$ is 5.7 $J \cdot mol^{-1}$, and the average absolute percentage deviation (AAPD) is only 2.0 per cent. For the 99 points of the n-dodecane systems, the corresponding deviations are 6.7 $J \cdot mol^{-1}$ and 2.1 per cent. Thus the Flory theory provides useful estimates of $H^E_{m,123}$ for systems of

the present type. It should also be noted that X_{1j} is nearly linear in the carbon chain length of the second component (n-hexane, or n-decane, or n-dodecane), which could be used to provide estimates of $H^{E}_{m,1j}$ for mixtures of MTBE with other n-alkanes.

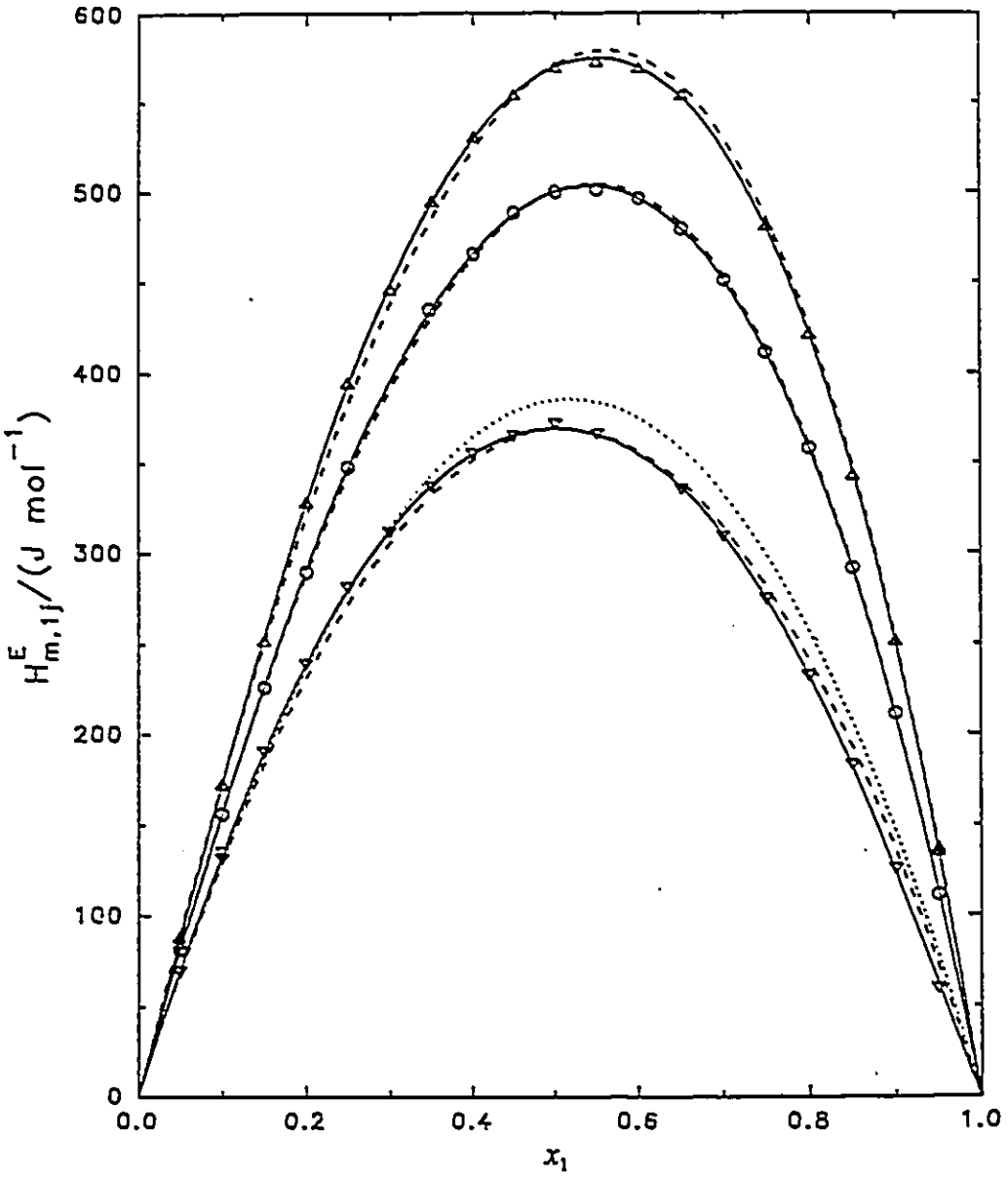
Table 5.2 Component properties and parameters used in the Flory calculations for the systems $x_1C_5H_{12}O+x_2C_6H_{14}+x_3C_{10}H_{22}$[a] and $x_1C_5H_{12}O+x_2C_6H_{14}+x_3C_{12}H_{26}$[b] at 298.15 K

Com-ponent	V_m/ ($cm^3 \cdot mol^{-1}$)	α_p/ (kK^{-1})	κ_T/ (TPa^{-1})	p*/ ($J \cdot cm^{-3}$)	V*/ ($cm^3 \cdot mol^{-1}$)	T*/ (K)
$C_5H_{12}O$	119.82	1.423	1690.6	442.9	90.20	4385.0
C_6H_{14}	131.57	1.387	1703.9	424.2	99.52	4436.1
$C_{10}H_{22}$	195.94	1.051	1109.6	447.0	155.75	5091.4
$C_{12}H_{26}$	228.55	0.960	987.6	445.2	184.40	5351.4

Interchange interaction energy parameters $X_{ij}/(J \cdot cm^{-3})$

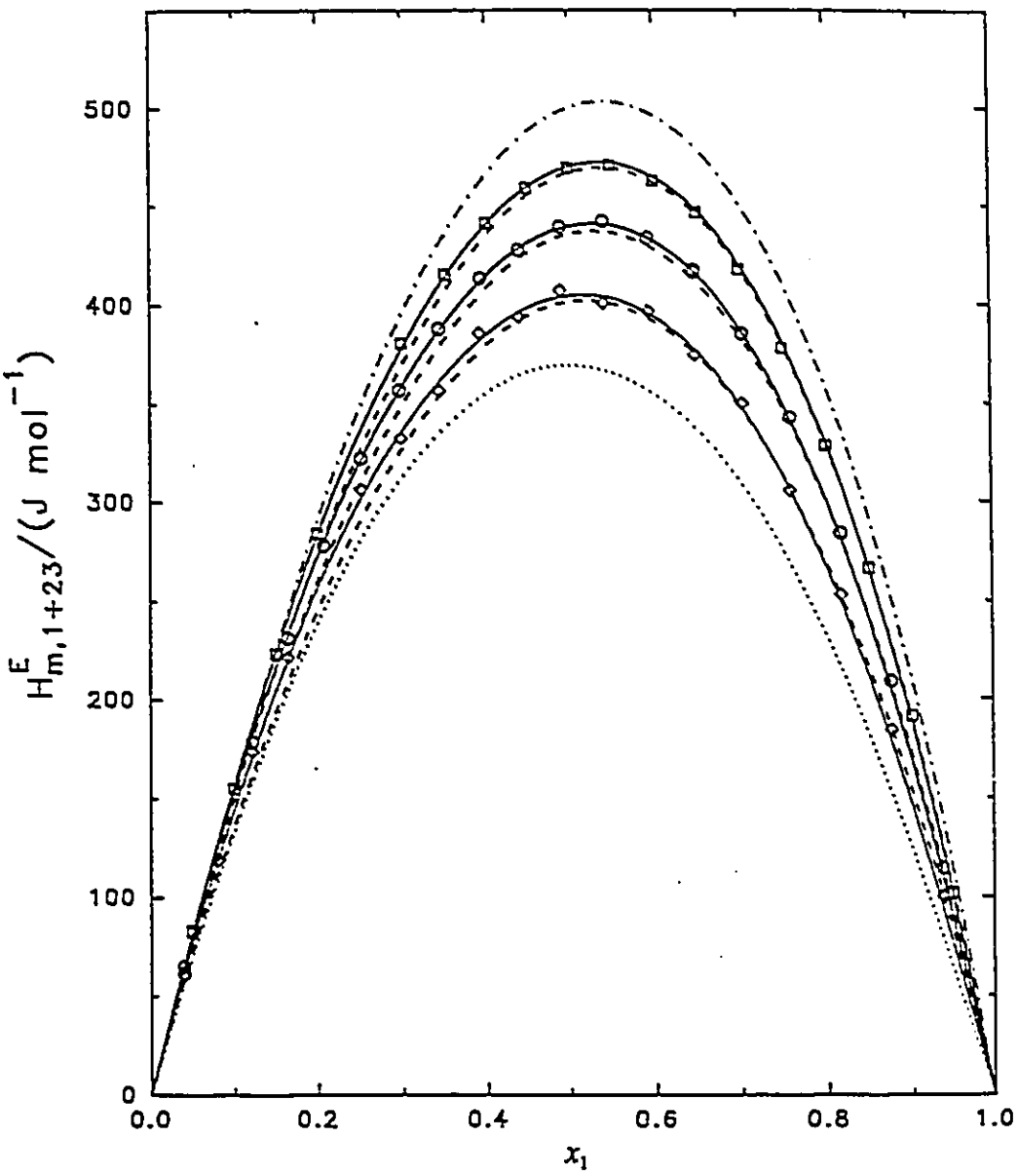
[a] $X_{12}=14.7950$; $X_{13}=18.7764$; $X_{23}=1.2208$.

[b] $X_{12}=14.7950$; $X_{13}=21.1118$; $X_{23}=2.5204$.



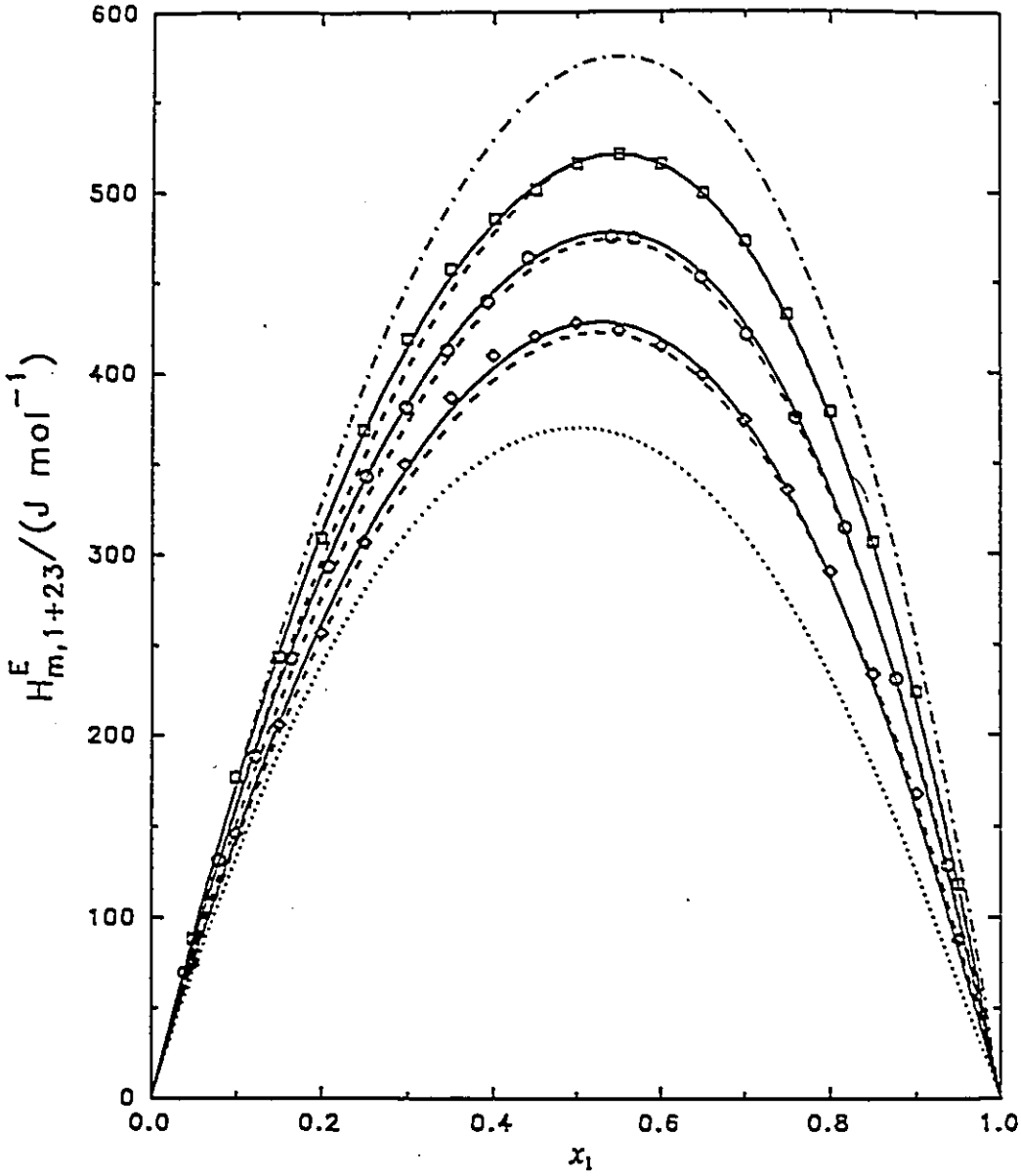
Experimental results: △, ν=6; ○, ν=10; ▽, ν=12. Curves: ···, ν=7, Tusel-Langer *et al.* (1991); ——, calculated from Equation 4.10 using the representations in Table 4.7; - - -, calculated from the Flory theory.

Figure 5.1 Excess molar enthalpies $H^E_{m,1j}$ for $x_1C_5H_{12}O+x_jC_\nu H_{2\nu+2}$ mixtures at 298.15K



Experimental results: ▫, x_2/x_3=0.3477; ○, x_2/x_3=0.9984; ◇, x_2/x_3=3.1408. Curves: — · —, x_2=0, and ···, x_1+x_2=1, both calculated from Equation 4.10 using the representation in Table 4.7; ———, calculated from Equations 4.7, 4.20 and 4.21 using the representations in Tables 4.7 and 4.9; - - -, calculated from the Flory theory.

Figure 5.2 Excess molar enthalpies $H^E_{m,1+23}$ for $x_1C_5H_{12}O+x_2C_6H_{14}+x_3C_{10}H_{22}$ mixtures at 298.15K



Experimental results: ▫, x_2/x_3=0.3738; ○, x_2/x_3=0.9845; ◇, x_2/x_3=2.8956. Curves: — · —, x_2=0, and ···, x_1+x_2=1, both calculated from Equation 4.10 using the representation in Table 4.7; ———, calculated from Equations 4.7, 4.20 and 4.21 using the representations in Tables 4.7 and 4.9; - - -, calculated from the Flory theory.

Figure 5.3 Excess molar enthalpies $H^E_{m,1+23}$ for $x_1C_5H_{12}O+x_2C_6H_{14}+x_3C_{12}H_{26}$ mixtures at 298.15K

5.2.2 Estimation from an association model with a Flory contribution term

In agreement with the findings from this work for (MTBE + n-alkane) systems (Wang *et al.*, 1993), exploratory calculations showed that the results for the systems of (MTBE + a branched alkane) could also be fitted quite well by the Flory theory. However, large discrepancies occurred when the mixtures containing the alkanols were treated in a similar manner, and it was evident that specific recognition of the self-association must be included in formulating a model for these mixtures.

As mentioned in chapter 3, it was found previously that the excess molar volumes could be correlated quite well by an association model of the Mecke-Kempter type with an added Flory-contribution term, for the mixtures formed from an alkan-1-ol with either a normal (Treszczanowicz and Benson, 1985) or a branched (Treszczanowicz and Benson, 1988) alkane. An extension of this treatment to excess enthalpy was carried out in this study for the binary systems of an alcohol or MTBE with some branched alkanes.

Equations 3.37 to 3.39 were used in this calculation. The values of the characteristic pressure P^*, molar volume V_i^*, and temperature T^* needed for its evaluation are tabulated for the alkan-1-ol and the branched alkanes in the literature (Treszczanowicz and Benson, 1988), and for MTBE in Table 5.2.

In the present use of Equation 3.37, the values of ΔH_H^*=-24.4kJ·mol^{-1} and ΔS_H^*=-33.0J·K^{-1}·mol^{-1}, used previously (Treszczanowicz and Benson, 1985; 1988), were adopted for the mixtures containing ethanol or 1-propanol. For the MTBE mixtures, $H^E_{m,MK}$=0 was used, correponding to no self-association. Table 5.3 summarizes the results of the two sets of calculations. In calculation A, the Flory exchange interaction parameter X_{12} was adjusted to obtain a least-squares fit of the experimental results as represented by Equation 4.11 for each mixture. These values of X_{12} can be represented fairly well by the empirical relation:

$$X_{12} = (V_1^*/V_2^*)^{1/3}(0.0130 - 0.0636\,\alpha_{OH} + 0.3253\,\alpha_{OH}^2)\times 10^3 \qquad (5.24)$$

where α_{OH} is the volume fraction of the OH group in component 1 of the binary systems: α_{OH} =0.2517, 0.1907 (Treszczanowicz and Benson, 1985), and 0, for ethanol, 1-propanol, and MTBE, respectively. In calculation B, estimates of H^E_m were obtained from Equations 3.37 to 3.40 using the values of X_{12} calculated from Equation 5.24. Plots of these values of H^E_m are shown in Figures 5.4 and 5.5 for comparison with the experimental results. It can be seen that the model reproduces the general behaviour of the experimental findings but fails to duplicate the crossing of the ethanol and 1-propanol curves.

The absolute average percentage deviations given in Table 5.3 are all in the range of 2 to 7 per cent and it is evident that no significant difference is introduced by using

Equation 5.24 instead of an individual adjustment of X_{12}.

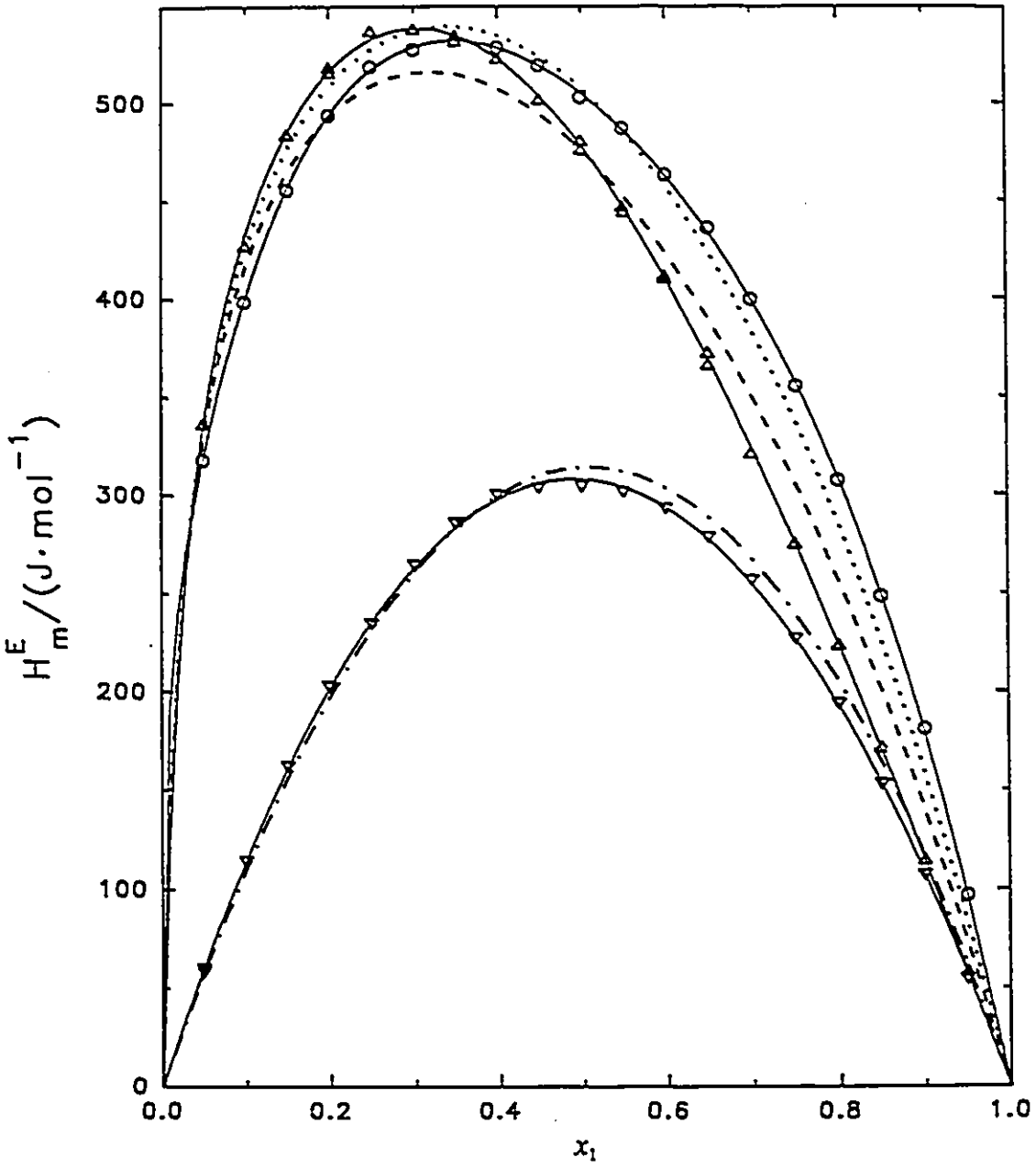
Table 5.3 Summary of the Flory exchange interaction parameters X_{12}, and deviations, RMSD and AAPD, for calculations with Equations 3.37 to 3.40 and Equation 5.24

Mixture	Calculation A[a]			Calculation B[b]		
	X_{12} J·cm^{-3}	RMSD J·mol^{-1}	AAPD	X_{12} J·cm^{-3}	RMSD J·mol^{-1}	AAPD
$x_1$ethanol+$x_2$2,3-dimethylbutane	13.826	15.0	4.4	13.658	15.3	4.5
$x_1$ethanol+$x_2$2,2,4-trimethylpentane	12.394	27.8	6.7	12.508	27.8	6.6
$x_1$1-propanol+$x_2$2,3-dimethylbutane	10.591	20.0	6.1	10.760	20.0	6.3
$x_1$1-propanol+$x_2$2,2,4-trimethylpentane	10.070	10.5	2.9	9.855	11.0	2.7
x_1MTBE+$x_2$2,3-dimethylbutane	12.351	6.3	3.6	12.596	7.6	3.7
x_1MTBE+$x_2$2,2,4-trimethylpentane	11.841	5.0	3.0	11.536	7.8	3.7

[a] X_{12} fitted to the results for each mixture.
[b] X_{12} estimated from Equation 5.24.

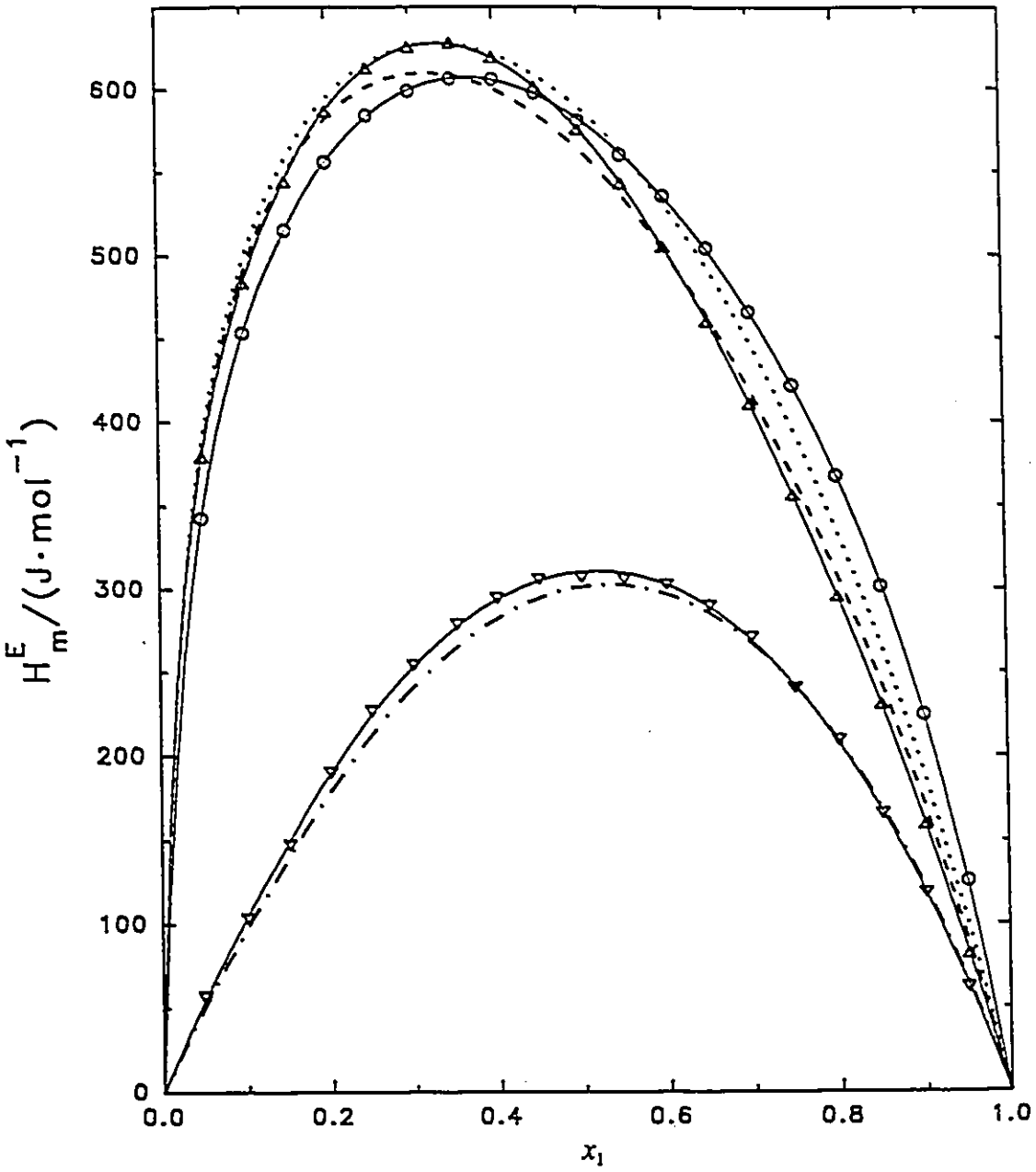
It is probable that Equations 3.37 to 3.40 along with Equation 5.24 could be used to estimate H_m^E for mixtures of ethanol, or 1-propanol, or MTBE with other (similar) branched alkanes such as 2,2-dimethylbutane and 2,3,4-trimethylpentane. However, Equation 5.24 may not be suitable for mixtures with an n-alkane which might involve different interstitial or conformational effects.

The AAPDs shown in Table 5.3 indicate that this model can provide reasonable representations for the present systems.



Experimental results and model estimates: O and ···, C_2H_5OH; ▵ and ---, C_3H_7OH; ▿ and —· —, $(CH_3)_3COCH_3$. Curves: ———, calculated from Equation 4.10 or 4.11

Figure 5.4 Binary H^E_m data and corresponding model estimates for the mixtures of $x_1\{C_2H_5OH$ or C_3H_7OH or $(CH_3)_3COCH_3\}+x_2(CH_3)_2CHCH(CH_3)_2$ at 298.15K



Experimental results and model estimates: O and ···, C_2H_5OH; △ and ---, C_3H_7OH; ▽ and —· —, $(CH_3)_3COCH_3$. Curves: ———, calculated from Equation 4.10 or 4.11

Figure 5.5 Binary H^E_m data and corresponding model estimates for the mixtures of $x_1\{C_2H_5OH$ or C_3H_7OH or $(CH_3)_3COCH_3\}+x_2(CH_3)_2CHCH_2C(CH_3)_3$ at 298.15K

5.2.3 Estimation from the DISQUAC model

Recently, González *et al.* (1990) have applied the DISQUAC group-contribution model (Kehiaian, 1983; Tiné and Kehiaian, 1987) to some ternary mixtures containing ethanol. In their treatment, values of the interchange energy coefficients $C^{dis}_{ah,i}$ and $C^{quac}_{ah,i}$ (i=1,2,3), describing the interactions between the hydroxy group (-OH in ethanol) and aliphatic hydrocarbon groups (>CH_2 and -CH_3) were obtained from an analysis of the excess molar Gibbs energies and excess molar enthalpies of selected binary mixtures (Gonzalez *et al.*, 1990).

Since the DISQUAC group-contribution model has been recommended for the systems containing alcohols, its application to the ternary systems of ethanol with normal alkanes was investigated in this study. The average absolute percentage deviations are 6.5% for the 103 points of the ethanol + n-hexane + n-decane system and 7.9% for the 114 points of the ethanol + n-hexane + n-dodecane system. In all cases, the model overestimated the values of $H^E_{m,1+23}$ in the central range of x_1, with negative deviations occuring at lower and higher values of x_1. This agreement seems reasonable, since Tiné and Kehiaian (1987) have pointed out that the treatment of contacts formed by a strongly associating group and a non-polar group as in (alcohol + alkane) "may well be at, if not beyond, the limits of accurate applicability of quasi-chemical models, including the DISQUAC, especially in the dilute-solution range". It should also be noted that the

present analysis does not differentiate between the interactions of the $>CH_2$ and $-CH_3$ groups, and that $H^E_{m,123}=H^E_{m,1+23}$ since $H^E_{m,23}$ is zero at all compositions.

5.2.4 Correlation by means of the proposed model

In order to investigate the validity of the proposed model, a correlation of the experimental data for all six ternary mixtures and their constituent binaries was carried out. For the purpose of comparison, the three-parameter NRTL and the two-parameter UNIQUAC models were also used for the same calculation. Furthermore, six more ternary systems were selected to involve a variety of molecular species, including alcohol, ketone, ether, n-alkane, chloroalkane, amine, organic acid, aliphatic nitrile, and aromatic types.

Since values of the collision diameter, σ_{ii}, are not usually available in the literature, the pure component parameter, r_i, from the UNIQUAC model was introduced to represent the molecular size, and $\sigma_{ii}^3 \propto r_i$ was assumed. In the case of an unlike pair of molecules, an average size $r_{ij}=(r_i+r_j)/2$ was adopted. Values of r_i (and also q_i required in the UNIQUAC calculations) were taken from the compilation by Gmehling *et al.* (1982).

For the calculation of the 12 ternary systems, correlations of their 29 constituent binary systems are required. The results are summarized in Table 5.4 which also includes the results of similar calculations for the NRTL and UNIQUAC models. Also

listed in Table 5.4 are the average absolute deviation (AAD), the average absolute percent deviation (AAPD) and the root mean square deviation (RMSD) for each fit of the data. The Bi in the table stands for ith binary system. In most cases, the use of the proposed model (Equation 5.9) provides a better representation of the binary excess enthalpy data than the NRTL and UNIQUAC treatments.

It is also evident that the representations of experimental H_m^E data with the proposed model is comparable with those from the Flory model for the ether-containing systems, yet better than those from the Flory and the other models investigated in this study when the model was used individualy to deal with different types of systems.

The corresponding computer programs used for these calculations are presented in Appendix D.

Table 5.4 Summary of least-squares analyses of binary H_m^E data

System	Component 1	Component 2	T/(K)	Model	model parameters*		α	AAD/(J·mol⁻¹)	AAPD/%	RMSD/(J·mol⁻¹)
B1[a]	Ethanol	n-Hexane	298.15	Eqn.5.9	2300.3	351.1	3.6861	4.6	1.5	9.2
				NRTL	461.1	723.0	-4.2494	12.0	3.5	22.7
				UNIQUAC	1900.5	-417.2		49.2	11.9	75.5
B2[a]	Ethanol	n-Decane	298.15	Eqn.5.9	2133.8	726.6	3.9466	7.5	1.5	13.2
				NRTL	585.8	771.6	-4.6558	10.6	2.1	21.3
				UNIQUAC	2059.2	-490.0		83.3	17.1	116.7
B3[b]	n-Hexane	n-Decane	298.15	Eqn.5.9	-353.1	506.6	0.5792	0.05	0.56	0.07
				NRTL	822.2	-679.4	0.1875	0.16	2.26	0.21
				UNIQUAC	372.5	-313.6		0.03	0.45	0.05
B4[a]	Ethanol	n-Dodecane	298.15	Eqn.5.9	2642.9	972.7	3.4799	5.3	0.8	7.3
				NRTL	647.0	778.2	-4.5250	10.1	2.0	19.6
				UNIQUAC	2179.0	-566.3		71.8	14.2	106.6
B5[c]	n-Hexane	n-Dodecane	298.15	Eqn5.9	-167.9	275.6	0.4088	0.01	0.06	0.02
				NRTL	204.2	-30.1	1.0593	0.33	1.56	0.47
				UNIQUAC	504.3	-394.0		0.11	0.46	0.14
B6[d]	1-Propanol	n-Hexane	298.15	Eqn.5.9	1627.0	129.0	3.7927	10.1	2.8	19.3
				NRTL	308.9	830.2	-3.8292	16.5	4.2	28.6
				UNIQUAC	10237.0	268.6		29.0	7.7	42.8
B7[d]	1-Propanol	n-Decane	298.15	Eqn.5.9	2335.5	492.3	3.3857	8.7	1.6	13.4
				NRTL	588.5	942.8	-3.4786	19.9	3.6	34.1
				UNIQUAC	2224.0	-549.8		84.2	17.1	116.6
B8[d]	1-Propanol	n-Dodecane	298.15	Eqn.5.9	2825.0	584.2	3.0195	9.0	1.3	13.8
				NRTL	677.5	1000.7	-3.1111	16.4	2.7	30.0
				UNIQUAC	2146.5	-542.7		76.7	13.9	114.0

Table 5.4 (continued)

System	Component 1	Component 2	T/(K)	Model	model parameters*		α	AAD/(J·mol^{-1})	AAPD/%	RMSD/(J·mol^{-1})
B9[e]	MTBE	n-Hexane	298.15	Eqn.5.9	692.4	-397.9	0.2146	2.0	1.7	3.1
				NRTL	437.6	994.9	-0.0850	2.0	1.7	3.1
				UNIQUAC	339.2	78.2		2.0	1.7	3.1
B10[e]	MTBE	n-Decane	298.15	Eqn.5.9	566.3	-289.5	0.0477	1.5	0.5	2.3
				NRTL	1552.9	132.6	-0.3225	1.5	0.5	2.2
				UNIQUAC	418.0	51.1		1.4	0.5	2.0
B11[e]	MTBE	n-Dodecane	298.15	Eqn.5.9	526.8	-207.5	0.1322	3.3	1.1	4.9
				NRTL	1428.4	381.1	-0.5411	3.1	1.2	4.6
				UNIQUAC	528.2	-13.6		3.1	1.1	4.4
B12[f]	Ethanol	1-Propanol	298.15	Eqn5.9	202.5	-198.5	0.9843	0.3	2.7	0.5
				NRTL	310.0	-291.2	-0.8261	0.3	3.1	0.5
				UNIQUAC	-38.0	75.4		0.3	2.4	0.4
B13[g]	Ethanol	Cyclohexane	298.15	Eqn.5.9	2306.7	475.5	3.5394	8.0	1.9	14.8
				NRTL	599.4	830.2	-3.0391	13.2	3.8	30.6
				UNIQUAC	1456.9	-35.3		37.6	9.8	67.6
B14[g]	1-Propanol	Cyclohexane	298.15	Eqn.5.9	1718.2	175.0	3.5478	10.9	3.2	25.1
				NRTL	384.6	958.9	-2.6820	14.5	4.8	37.5
				UNIQUAC	2030.8	-418.0		31.5	9.8	60.3
B15[h]	2-Propanol	Benzene	298.15	Eqn.5.9	2823.6	524.8	1.9361	28.2	3.2	38.5
				NRTL	944.9	1907.0	-1.4207	38.1	5.2	55.2
				UNIQUAC	5213.8	1213.1		21.2	3.1	25.9
B16[i]	2-Propanol	Cyclohexane	298.15	Eqn.5.9	1215.3	246.2	3.4390	15.2	4.1	32.4
				NRTL	621.3	1319.1	-1.6063	18.3	4.7	35.8
				UNIQUAC	2211.0	-192.6		27.4	7.7	49.4

Table 5.4 (continued)

System	Component 1	Component 2	T/(K)	Model	model parameters*		α	AAD/(J·mol^{-1})	AAPD/%	RMSD/(J·mol^{-1})
B17[g]	Benzene	Cyclohexane	298.15	Eqn.5.9	457.2	175.3	0.1651	3.3	0.7	4.2
				NRTL	1511.4	1132.0	-0.3886	1.1	0.2	1.4
				UNIQUAC	915.4	438.3		1.9	0.3	2.2
B18[j]	Pyridine	Acetic acid	293.15	Eqn.5.9	1277.9	-3579.1	0.4360	82.5	2.9	113.6
				NRTL	-36082.0	4318.6	-0.0228	64.6	2.2	92.0
				UNIQUAC	-1945.2	-3750.0		252.1	7.6	299.3
B19[j]	Pyridine	Trichloro-methane	293.15	Eqn5.9	-364.0	-1014.4	0.6809	25.0	1.6	34.6
				NRTL	-1412.7	-5526.3	0.0585	24.1	1.5	33.0
				UNIQUAC	-985.2	-1632.0		35.1	2.4	47.8
B20[j]	Acetic acid	Trichloro-methane	293.15	Eqn.5.9	-287.7	202.0	-0.1519	8.8	2.3	11.2
				NRTL	-1694.4	-587.6	0.1411	8.8	2.3	11.3
				UNIQUAC	-478.6	-523.2		9.4	2.3	11.6
B21[k]	Acetonitrile	Trichloro-methane	298.15	Eqn.5.9	-7067.3	5199.5	-0.1676	13.6	3.6	18.5
				NRTL	-11042.0	5017.5	-0.0512	15.4	3.9	21.1
				UNIQUAC	1257.4	-1742.9		42.1	13.8	52.6
B22[k]	Acetonitrile	2-Propanone	298.15	Eqn.5.9	-549.2	414.0	-1.3255	0.2	0.5	0.3
				NRTL	-1823.1	2319.0	0.2708	1.7	2.6	2.3
				UNIQUAC	545.4	-618.1		4.4	8.7	5.3
B23[k]	Trichloro-methane	2-Propanone	298.15	Eqn.5.9	1870.7	-4058.9	-0.2287	44.3	4.6	58.7
				NRTL	3201.7	-13238.0	-0.0383	42.9	4.4	56.9
				UNIQUAC	-1879.5	-375.4		57.9	6.1	74.3
B24[l]	Acetonitrile	Benzene	318.15	Eqn.5.9	102.9	412.8	3.2136	3.8	1.2	5.3
				NRTL	494.7	2219.4	0.4210	3.9	1.2	5.5
				UNIQUAC	232.0	896.0		3.8	1.2	5.0

Table 5.4 (continued)

System	Component 1	Component 2	T/(K)	Model	model parameters*		α	AAD/(J·mol⁻¹)	AAPD/%	RMSD/(J·mol⁻¹)
B25[l]	Acetonitrile	Tetrachloro-methane	318.15	Eqn.5.9	1126.2	530.1	4.0712	8.9	1.2	14.4
				NRTL	5148.4	3306.6	0.3691	9.1	1.2	14.6
				UNIQUAC	2754.7	112.0		28.7	4.0	36.8
B26[l]	Benzene	Tetrachloro-methane	318.15	Eqn5.9	-254.4	356.1	-0.4096	4.1	3.3	9.0
				NRTL	456.2	426.8	2.6281	2.8	2.1	7.5
				UNIQUAC	449.1	-202.3		4.2	3.4	7.3
B27[m]	Diethylamine	Ethanol	293.15	Eqn.5.9	-548.9	-581.1	4.4409	89.6	6.3	185.1
				NRTL	-2139.1	-2900.1	0.6754	89.7	6.6	181.7
				UNIQUAC	-1446.6	-1418.6		107.4	7.1	175.2
B28[m]	Diethylamine	Triethylamine	293.15	Eqn.5.9	198.7	179.8	5.2926	3.8	1.4	7.2
				NRTL	844.7	537.6	-0.4120	4.1	1.4	7.4
				UNIQUAC	470.7	-4.77		3.9	1.5	6.7
B29[m]	Ethanol	Triethylamine	293.15	Eqn.5.9.	280.6	-2306.1	-0.3780	56.4	21.8	93.2
				NRTL	17520.0	-31292.0	-0.0151	60.9	19.3	90.2
				UNIQUAC	-794.6	-959.9		76.9	22.8	109.6

[a] Wang *et al.* (1992a). [b] Marsh *et al.* (1980). [c] Ott *et al.* (1981). [d] Wang *et al.* (1992b). [e] Wang *et al.* (1993). [f] Pflug *et al.* (1968). [g] Nagata and Kazuma (1977). [h] Nagata *et al.* (1977). [i] Nagata *et al.* (1978). [j] Abramov *et al.* (1972). [k] Nagata *et al.* (1981). [l] Lien and Missen (1974). [m] Ratkovics *et al.* (1973).

* The model parameters: for the proposed model, $\Delta\epsilon_{21}$/(J·mol^{-1}), $\Delta\epsilon_{12}$(J·mol^{-1}); for the NRTL model, Δg_{21}/(J·mol^{-1}), Δg_{12}(J·mol^{-1}); for the DISQUAC model, X(1), X(2), as defined in Eq. (3.54).

5.3 Prediction of ternary excess enthalpy with the proposed model

As mentioned in previous sections, prediction of excess enthalpy values for multicomponent systems from limited binary data is very much in demand and obviously economic. It would be extremely beneficial if a model well representing binary data can produce reasonable predictions of H_m^E values for the corresponding ternary systems based only on binary data.

The capability of the proposed model for prediction of ternary excess enthalpies was investigated. The H_m^E was calculated from Equation 5.12 using the parameters obtained from the previous analyses of the constituent (1-2, 1-3, 2-3) binary systems. The results of the calculations are summarized in Table 5.5, where the deviations AAD, AAPD, and RMSD are listed. In the table, Ti stands for the ith ternary system. As in the case of the binary systems, similar calculations were also carried out for the NRTL and UNIQUAC models.

It can be seen from Table 5.5 that the overall agreement between the predictions of the present model and the experimental results is within 5 per cent in most cases. It also appears that the model usually provides a somewhat better prediction of the ternary excess enthalpies than both the NRTL and the UNIQUAC treatments.

Table 5.5 Summary of predictions of H_m^E for ternary systems

System	Component 1	Component 2	Component 3	T/(K)	Binary parameter from Table 5.4 1-2	1-3	2-3	Model	AAD/ (J·mol^{-1})	AAPD/ %	RMSD/ (J·mol^{-1})
T1[a]	Ethanol	n-Hexane	n-Decane	298.15	B1	B2	B3	Eqn.5.12	7.2	1.5	10.4
								NRTL	15.6	3.4	24.4
								UNIQUAC	72.8	16.6	107.3
T2[a]	Ethanol	n-Hexane	n-Dodecane	298.15	B1	B4	B5	Eqn.5.12	8.7	1.8	12.7
								NRTL	16.4	3.3	26.1
								UNIQUAC	73.7	16.4	105.6
T3[d]	1-Propanol	n-Hexane	n-Decane	298.15	B6	B7	B3	Eqn.5.12	10.8	2.4	17.4
								NRTL	16.4	3.1	26.7
								UNIQUAC	78.7	14.3	101.0
T4[d]	1-Propanol	n-Hexane	n-Dodecane	298.15	B6	B8	B5	Eqn.5.12	13.7	2.8	20.3
								NRTL	23.5	4.7	39.6
								UNIQUAC	85.0	15.0	110.1
T5[e]	MTBE	n-Hexane	n-Decane	298.15	B9	B10	B3	Eqn.5.12	8.0	3.8	11.2
								NRTL	7.2	6.5	31.6
								UNIQUAC	7.3	3.6	10.3
T6[e]	MTBE	n-Hexane	n-Dodecane	298.15	B9	B10	B5	Eqn.5.12	5.6	2.0	7.6
								NRTL	8.2	2.6	11.3
								UNIQUAC	7.4	2.5	8.9

Table 5.5 (Continued)

System	Component 1	Component 2	Component 3	T/(K)	Binary paramter from Table 5.4 1-2	1-3	2-3	Model	AAD/ (J·mol^{-1})	AAPD/ %	RMSD/ (J·mol^{-1})
T7[g]	Ethanol	1-Propanol	Cyclohexane	298.15	B12	B13	B14	Eqn.5.12	3.1	1.0	5.5
								NRTL	5.2	1.6	7.3
								UNIQUAC	12.1	4.4	14.7
T8[i]	2-Propanol	Benzene	Cyclohexane	298.15	B15	B16	B17	Eqn.5.12	25.8	2.8	38.1
								NRTL	137.6	12.6	182.0
								UNIQUAC	37.6	3.7	57.2
T9[j]	Pyridine	Acetic acid	Trichloro-methane	293.15	B18	B19	B20	Eqn.5.12	205.8	6.8	337.2
								NRTL	344.2	10.6	537.8
								UNIQUAC	386.0	11.7	496.4
T10[k]	Acetonitrile	Trichloro-methane	2-Propanone	298.15	B21	B22	B23	Eqn.5.12	25.5	3.0	43.5
								NRTL	41.4	8.6	52.8
								UNIQUAC	46.2	9.9	55.6
T11[l]	Acetonitrile	Benzene	Tetrachloro-methane	318.15	B24	B25	B26	Eqn.5.12	33.0	5.7	55.7
								NRTL	40.1	7.0	62.3
								UNIQUAC	29.2	5.3	42.1
T12[m]	Diethylamin	Ethanol	Triethylamin	293.15	B27	B28	B29	Eqn.5.12	100.3	4.5[a]	216.5
								NRTL	394.5	17.9[a]	890.0
								UNIQUAC	350.3	15.9[a]	462.9

[g,i,j,k,l,m] See footnotes to Table 5.4 for sources of ternary H^E_m data.

[a] Since the excess enthalpy of this system changes sign, the following expression is used to calculate the average absolute percentage deviation: $AAPD=(100/2210.6n)\sum_{i=1}^{n}|H^E_m(expt)_i - H^E_m(calc)_i|$ where 2210.6 J·mol^{-1} is the maximum value of $H^E_m(expt)$ for the system.

For the systems involving alcohols, a lattice coordination number less than that used in the present work might be anticipated. Nevertheless, in calculations for system T1 in which the coordination number was varied between 6 and 12, the lowest value of the AAPD was obtained with $Z=10$.

In conclusion, the present model provides a well-defined excess enthalpy expression which contains a fixed number of parameters. Values of these parameters can be obtained from analyses of binary enthalpy data alone. Although the expression for H_m^E is somewhat similar to the forms used in the NRTL and UNIQUAC theories, it leads to better estimates of the ternary excess enthalpies for many of the systems considered.

The computer programs related to this calculation are also presented in Appendix D.

It should be mentioned that an attempt was also made to represent vapour-liquid equilibrium (VLE) and excess enthalpies H^E simultaneously by means of cubic equations of state. Some preliminary results of these calculations are presented in Appendix E.

Chapter 6

Conclusions

The experimental determination of excess enthalpy values at 25°C for 15 binary and six ternary mixtures has been satisfactorily carried out with an LKB flow microcalorimeter. The results indicate that for all of the systems experimentally investigated in this study, the heat effects produced by mixing the two or three constituent components are significant enough to contribute to any other processes accompanying the mixing process. These results are of considerable importance for the design of mixing or separation processes in the chemical and petroleum industries. Especially for the systems involved in this work, the experimental investigation has enriched the increasingly attention-drawing research on alternative transportation fuels, aiming at reducing our dependence on crude oil supply and improving air quality.

A theoretical study on various approaches of representing experimental H^E data has been carried out with a focus on the solution theory-related models. Some existing solution theory models, such as the Flory theory model, the association model, the

DISQUAC model, the NRTL and UNIQUAC models, were used to represent the experimental results. It has been found that in some cases, a model worked well only for a certain type of system. Some of the models were not able to provide satisfactory representations of the experimental findings for almost all of the systems studied. The association model reduces to the Flory model while being used for the systems containing ether. Our study shows that the Flory model provides better representation of H^E for the systems with n-alkane than the ones with branched-alkane. It is consistent with the chain-molecule assumption of the Flory model.

A new model, based on statistical thermodynamic principles, has been developed in this study. Its applicability has been investigated. It was found that the proposed model is comparable with the Flory model for the representation of H^E data for the ether-containing systems, yet better than the Flory model and any other models studied when used for the other types of mixtures. It is evident that the proposed model has the ability of representing binary and ternary excess enthalpies for all of the systems involved, with the lowest overall deviation in comparison with the other models studied.

In developing the model, the model parameter α has been assumed as a function of temperature. To represent excess enthalpy values at different temperatures by using this model, a set of α is required through the regression of experimental H^E results at the corresponding temperatures.

The new model was also used successfully for predicting ternary H^E values from the

H^E data of its constituent binaries. This successful attempt allows the possible extension of the model to predict ternary excess enthalpies for systems composed of similar components.

For further study, it is desirable to examine the applicability of the proposed model in correlating and predicting the excess enthalpies of multicomponent systems of other types.

It would be also interesting to explore the applicability of our model to equations of state (EOS) through the mixing rules, which couples with EOS and excess Gibbs energy models, to represent vapour-liquid equilibrium and excess enthalpies simultaneously.

References

Abdoul, W., Rauzy, E., and Péneloux, A., "Group-contribution equation of state for correlating and predicting the thermodynamic properties of weakly polar and non-associating mixtures. Binary and multicomponent systems", Fluid Phase Equilib., **68**, 47-102 (1991).

Abe, A. and Flory, P.J., "The thermodynamic properties of mixtures of small, nonpolar molecules", J. Am. Chem. Soc., **87**, 1838-1846 (1965).

Abello, L., J. Chim. Phys. Phys.-Chim. Biol., **70**, 1355 (1973).

Abramov, E.V., Mizayan, A.S., and Fedorova, J.I., "Heats of formation of ternary systems. 1. Acetic acid-pyridine-chloroform system", Akad. Nauk Kaz. SSR, Ser. Khim., **22**, 26-32 (1972).

Abrams, D.S. and Prausnitz, J.M., "Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems", AIChE. J., **21**, 116-128 (1975).

Adachi, Y., Lu, B.C.-Y., and Sugie, H., "A four-parameter equation of state", Fluid Phase Equilib., **11**, 29-48 (1983).

Adachi, Y. and Sugie, H., "Effects of mixing rules on phase equilibrium calculatoins", Fluid Phase Equilib., **24**, 353-362 (1985).

Adachi, Y. and Sugie, H., "A new mixing rule-modified conventional mixing rule", Fluid Phase Equilib., **28**, 103-118 (1986).

Alonso, R., Guerrero R., and Corrales, J.A., "Excess molar enthalpies of (methylcyclo-hexane+an alkanol) at 323.15K. I. Results for *n*-butanol, *n*-pentanol, and *n*-hexanol" J. Chem. Thermodyn., **19**, 1271-1273 (1987)

Armitage, D.A. and Morcom, K.W., "Thermodynamic behaviour of mixtures of hexafluoro-benzene with amines. I. Enthalpies of mixing", Trans. Faraday Soc., **65**, 688-695 (1969).

Ashraf, F.A. and Vera, J.H., "A simplified group method analysis", Fluid Phase Equilib., **4**, 211-228 (1980).

Artal, M., Fernández, J., Muñoz Embid, J., Velasco, I., Otin, S., and Kehiaian, H.V., "Excess enthalpies and molecular interactions in solutions of 1-fluoroalkanes in alkanes, benzene or tetrachloromethane. A group contribution (DISQUAC) study", J. Solution Chem., **20**, 3-16 (1991).

Atkins, P.W., "Physical chemistry", Oxford, New York: Oxford University Press, 5th Ed. (1994).

Bauer, N. "Determination of density", Chapter VI in "Physical methods of organic chemistry", Part I, Ed. by A. Weissberger, Second Ed. (1952).

Benson, G.C., Luo, B., and Lu, B.C.-Y., "Excess enthalpies of dibutyl ether + n-alkane mixtures at 298.15K", Can. J. Chem., **66**, 531-534 (1988).

Bissell, T.G. and Williamson, A.G., "Vapour pressures and excess Gibbs energies of n-

hexane + and of n-heptane + carbon tetrachloride and + chloroform at 298.15 K", J. Chem. Thermodyn., 7, 131-136 (1975).

Bissell, T.G., Okafor, G.E., and Williamson, A.G., "Enthalpies and volumes of mixing of alkanes with carbon tetrachloride, chloroform, and methylene chloride at 25°C", J. Chem. Thermodyn., 3, 393-399 (1971).

Bondi, A., "Physical properties of molecular crystals, liquids and gases", Wiley, New York, (1968), p502 .

Brandani, V. and Evangelista, F., "The UNIQUAC associated-solution theory: vapor-liquid equilibria of binary systems containing one associating and one inert or active component", Fluid Phase Equilib., 17, 281-303 (1984).

Brandani, V. and Evangelista, F., "Correlation and prediction of enthalpies of mixing for systems containing alcohols with the UNIQUAC associated-solution theory", Ind. Eng. Chem. Res., 26, 2423-2430 (1987).

Brostow, W. and Sochanski, J.S., "Prediction of thermodynamic properties of ternary liquid solutions including metal alloys", J. Mater. Sci., 10, 2134-2145 (1975).

Brown, I., Fock, W., and Smith, F., "Heat of mixing. V. Systems of alcohols with hexane", Aust. J. Chem., 17, 1106-1118 (1964).

Brownlee, K.A., "Statistical theory and methodolory in science and engineering", Wiley, Second Ed. (1965).

Bulletin of Thermodynamics and Thermochemistry, 13, 507 (1970).

Chao, K.C. and Greenkorn, R.A., "Thermodynamics of fluids", Chemical Processing and Engineering - An International Series, Vol. 4, (1975).

Chen, C.C., Britt, H.I., Boston, J.K., and Evans, L.B., "Local composition model of excess Gibbs energy of electrolyte systems", AIChE J., 28, 588-596 (1982).

Chen, G., Wu, Z., Chen, Z., and Hou, Y., "Correlation of excess enthalpies and prediction of vapour-liquid equilibria from excess enthalpies by means of an equation of state", Fluid Phase Equilib., 65, 145-157 (1991).

Christensen, J.J., Izatt, R.M., Stitt, B.D., Hanks, R.W., "The excess enthalpies of seven *n*-decane + alcohol mixtures at 298.15 K", J. Chem. Thermodyn., 11, 261-266 (1979).

Christensen, C., Gmehling, J., Rasmussen, P., and Weidlich, U., "Heats of mixing data collection", DECHEMA Chemistry Data Series, Vol. III, Part 1. DECHEMA, Frankfurt (1984).

Cruz, J.C. and Renon, H., "A new thermodynamic representation of binary electrolyte solution nonideality in the whole range of concentration", AIChE. J., 24, 817- 830 (1978).

Dahl, S., Fredenslund, Aa., and Rasmussen, P., "The MHV2 model. A UNIFAC based model for prediction of gas solubility and vapor-liquid equilibria at low and high pressures", Institutet for Kemiteknik Danmarks Tekniske Hojskole, Lyngby, Danmark, Report SEP 9023 (1990).

Daniel, C., Wood, F.S., and Gorman, J.W., "Fitting equations to data", Wiley-Interscience, a division of John Wiley & Sons, Inc. (1971).

Delmas, G., de Saint-Romain, P., and Purves, P., "Excess volumes of mixtures of tetra-

butyltin with branced and linear alkanes", J. Chem. Soc., Faraday Trans., I, 71, 1181-1187 (1975).

Derr, E.L. and Deal, C.H., Je., "Analytical solutions of groups. Correlation of activity coefficients through structural group parameters", Inst. Chem. Eng. Symp. Ser. (Lond.), 3, 40-51 (1969).

Draper, N.R. and Smith, H., "Applied regression analysis", John Wiley & Sons, Inc. (1966).

Ewing, M.B., Marsh, K.N., Stokes, R.H., and Tuxford, C.W., "The isothermal displacement calorimeter: Design refinements", J. Chem. Thermodyn., 2, 751-756 (1970).

Fenby, D.V., Khurma, J.R., Konner, Z.S., Block, T.E., Knobler, C.M., Reeder, J., and Scott, R.L., "Isomer effects in mixtures of hydrocarbons: some experimental excess volumes and enthalpies", Aust. J. Chem., 33, 1927-1941 (1980).

Flory, P.J., "Thermodynamics of high-polymer solutions", J. Chem. Phys., 9, 660-661 (1941).

Flory, P.J., "Thermodynamics of high-polymer solutions", J. Chem. Phys., 10, 51-61 (1942).

Flory, P.J., "Statistical thermodynamics of liquid mixtures", J. Am. Chem. Soc., 87, 1833-1838 (1965).

Fredenslund, Aa., Jones, R.L., and Prausnitz, J.M., "Group-contribution estimation of activity coefficients in nonideal liquid mixtures", AIChE J., 21, 1086-1099 (1975).

Fredenslund, Aa., Gmehling, J., Michelsen, M.L., Rasmussen, P., and Prausnitz, J.M., "Computerized design of multicomponent distillation columns using the UNIFAC group contribution method for calculation of activity coefficients", Ind. Eng. Chem. Process Des. Develop., 16, 450-462 (1977a).

Fredenslund, Aa., Gmehling, J., and Rasmussen, P., "Vapor-liquid equilibria using UNIFAC a group-contribution method", Elsevier Scientific Publishing Company, Amsterdam/Oxford/New York (1977b).

Gani, R., Tzouvaras, N., Rasmussen, P., and Fredenslund, Aa., "Prediction of gas solubility and VLE by group contribution", Fluid Phase Equilib., 47, 133-152 (1989).

García-Lisbona, N., García Vicente, I., Muñoz Embid, J., Velasco, I., Otin, S., and Kehiaian, H.V., "Thermodynamics of mixtures containing bromoalkanes. II. Excess enthalpies of mixtures of 1-bromoalkane with cyclohexane, with benzene, or with tetrachloromethane. Measurement and analysis in terms of group contributions (DISQUAC)", Fluid Phase Equilib., 45, 191-203 (1989).

García Vicente, I., García-Lisbona, N., Velasco, I., Otin, S., Muñoz Embid, J., and Kehiaian, H.V., "Excess enthalpies of 1-chloroalkanes + benzene. Measurement and analysis in terms of group contributions (DISQUAC)", Fluid Phase Equilib., 49, 251-262 (1989).

Gierycz, P., "New local composition model for Gibbs energy. I. Application for the correlation of isothermal VLE data", Phys. Chem. Liq., 22, 177-190 (1990).

Ginnings, D.C., Douglas, T.B., and Ball, A.B., "Heat capacity of sodium between 0°

and 900°, the triple point, and heat of fusion", J. Research Natl. Bur. Standards, 45, 23-33 (1950).

Gmehling, J., Onken, U., and Arlt, W., "Vapor-liquid equilibrium data collection", DECHEMA Chemistry Data Series, Vol. 1, Prt 2c, DECHEMA, Frankfurt (1982).

Gomez-Ibanez, J.D. and Shieh, J.J.C., "The excess free energy of mixtures of cyclohexane and *n*-hexadecane", J. Phys. Chem., **69**, 1660-1966 (1965).

González, J.A., Cobos, J.C., Garcia, I., and Casanova, C., "Prediction of excess functions of some ternary organic mixtures containing ethanol with a group contribution model", Thermochim. Acta, **171**,153-167 (1990).

González, J.A., Garcia, I., Cobos, J.C., and Casanova, C., "Prediction of excess enthalpies of some ternary systems involving a binary mixture with a miscibility gap using group contribution model", Thermochim. Acta, **189**, 115-127 (1991).

González, J.A., García, I., Cobos, J.C., and Casanova, C., "Characterization of the alkanol/alkanol contacts and prediction of excess functions of ternary systems of two n-alkan-1-ols and one n-alkane using DISQUAC", Fluid Phase Equilib., **78**, 61-80 (1992).

Grolier, J.-P.E. and Inglese, A., Int. Data Serries, Sel. Data Mixtures Ser. A, 71 (1975)

Gupte, P.A. and Daubert, T., "Extension of UNIFAC to high pressure VLE using vidal mixing rules", Fluid Phase Equilib., **28**, 155-170 (1986).

Gupte, P.A., Rasmussen, P., and Fredenslund, Aa., "A new group-contribution equation of state for vapor-liquid equilibria", Ind. Eng. Chem. Fundam., 25, 636-645 (1986).

Hála, E., Pick, J., Fried, V. and Vilim, O., "Vapour-liquid equilibrium", Pergamon Press (1956).

Hammerl, I. and Raetzsch, M.T., "Enthalpies of mixing of normal paraffins with aromatics", Wiss. Z. Tech. Hochsxch. Chem. Leuna-Merseburg, **15**, 175-178 (1973).

Harsted, B.S. and Thomsen, E.S., "Excess enthalpies from flow microcalorimetry. 1. Experimental method and excess enthalpies for carbon tetrachloride + cyclohexane, + benzene, and + octamethyl-cyclotetrasiloxane, and of *n*-hexane + cyclohexane", J. Chem. Thermodyn., **6**, 549-555 (1974).

Hill, R.J. and Swinton, F.L., "The thermodynamic properties of binary mixtures containing carbon disulphide. II. Excess enthalpies", J. Chem. Thermodyn., 12, 383-385 (1980a).

Hill, R.J. and Swinton, F.L., "The excess enthalpies of some mixtures containing carbon disulphide", J. Chem. Thermodyn., 12, 489-492 (1980b).

Hu, Y., Lüdecke, D., and Prausnitz, J.M., "Molecular thermodynamics of fluid mixtures containing molecules differing in size and potential energy", Fluid Phase Equilib., 7, 217-241 (1984).

Huggins, M.L., "Solutions of long-chain compounds", J. Phy. Chem., 9, 440-449 (1941).

Hunt, V.D., "The gasohol handbook", Industrial Press Inc., New York, N.Y., (1982).

Huron, M.J. and Vidal, J., "New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures", Fluid Phase

Equilib., 3, 255-271 (1979).
IUPAC, Notification for the 13th IUPAC conference on chemical thermodynamics, Clermont-Ferrand, France, July 17-22, 1994.
Jain, D.V.S., Gupta, V.K., and Lark, B.S., "Thermodynamics of n-alkane mixture. V. Vapour pressure and excess Gibbs energies of n-heptane + benzene and n-octane + benzene", J. Chem. Thermodyn., 5, 451-454 (1973).
Jones, H.K.De Q. and Lu, B.C.-Y., "Heats of mixing of liquids for the system ethanol-benzene-n-hexane", J. Chem. Eng. Data, 11, 488-492 (1966).
Karbalai, G.M.H. and Grolier, J.-P.E., Int. Data Series, Sel. Data Mixtures Ser. A., 188 (1975).
Kehiaian, H.V., "Group contribution methods for liquid mixtures: a critical review", Fluid Phase Equilib., 13, 243-252 (1983).
Kehiaian, H.V. and Velasco, I., "Thermodynamics of mixtures containing bromoalkanes. I. Estimation of DISQUAC interchange energy parameters for 1-bromoalkane + n-alkane mixtures. Comparison with other haloalkanes", Fluid Phase Equilib., 38, 227-244 (1987).
Kehiaian, H.V. and Marongiu, B., "A comparative study of thermodynamic properties and molecular interactions in mono- and polychloroalkane + n-alkane or + cyclohexane mixtures", Fluid Phase Equilib., 40, 23-78 (1988a).
Kehiaian, H.V. and Marongiu, B., "Thermodynamics of 1-chloroalkanes or α, ω-dichloroalkanes + tetrachloromethane mixtures", Fluid Phase Equilib., 42, 141-163 (1988b).
Kempter, H. and Mecke, R., "Spectroscopic determination of association equilibrium", Phys. Chem., B46, 229-241 (1940).
Kim, H., Lin, H.M., and Chao, K.C., "Cubic chain-of-rotators equation of state", Ind. Eng. Chem. Fundam., 25, 75-84 (1986).
Kimura, F., Benson, G.C., and Halpin, C.J., "Excess enthalpies of binary mixtures of *n*-heptane with hexane isomers", Fluid Phase Equilib., 11, 245-250 (1983).
Kojima, K. and Tochigi, K., "Prediction of vapor-liquid equilibria by the ASOG method", Tokyo: Kodansha Ltd./Amsterdam: Elsevier/North-Holland (1979).
Kratochvila, J., Cibulka, I., and Holub, R., "Excess volume of benzene-methanol-acetonitrile ternary mixture at temperatures of 25 and 40°C and correlation of its concentration dependence", Collect. Czech. Chem. Commun.,45, 3241-3248 (1980).
Kretschmer, C.B., Nowakowska, J., and Wiebe, R., "Densities and liquid-vapor eequilibria of the system ethanol-isoöctane (2,2,4-trimethylpentane) between 0° and 50°", J. Am. Chem. Soc., 70, 1785-1790 (1948).
Kubic, Jr.W.L., "A modification of the martin equation of state for calculating vapour-liquid equilibria", Fluid Phase Equilib., 9, 79-97 (1982).
Lai, T.T., Nguyen, H.T.D., Vera, J.H., and Ratcliff, C.A., "Prediction of heats of mixing of liquid mixtures containing alkane, chloroalkane and alcohols by an analytical group solution model", Can. J. Chem. Eng., 56, 358-363 (1978).
Langmuir, I., "The distribution and orientation of molecules", Third Colloid Symposium Monograph, The Chemical Catalog Company, Inc., New York (1925).

Larkin, J.A. and McGlashan, M.L., "A new calorimeter for heats of mixing. The heat of mixing of benzene with carbon tetrachloride", J. Chem. Soc., 3425-3432 (1961).
Larsen, B.L., Rasumussen, P., and Fredenslund, A.a., "A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing", Ind.Eng. Chem. Res., 26, 2274-2286 (1987).
Lee, K.-H. and Sandler, S.I., "The generalized van der Waals partition function-IV. Local composition models for mixtures of unequal-size molecules", Fluid Phase Equilib., 34, 113-147 (1987).
Lee, L.L. "Molecular thermodynamics of non-ideal fluids", Butterworths, Boston (1988).
Lermite, C. and Vidal, J., "A group contribution equation of state for polar and non-polar compounds", Fluid Phase Equilib., 72, 111-130 (1992).
Lien, T.R. and Missen, R.W., "Excess enthalpis at 45°C for ternary system acetonitrile-benzene-carbon tetrachloride", J. Chem. Eng. Data, 19, 84-86 (1974).
Lim, K.-H., Whiting, W.B., and Smith, D.H., "Excess enthalpies and liquid-liquid equilibrium phase compositions of the nonionic amphiphile 2-butoxyethanol and water", J. Chem. Eng. Data, 39, 399-403 (1994).
Lin, H.M., Kim,H., Guo, T.M., and Chao, K.C., "Cubic chain-of-rotators equation of state and VLE calculations", Fluid Phase Equilib., 13, 143-152 (1983).
Luo, B., Benson, G.C., and Lu, B.C.-Y., "Excess enthalpies for (diethyl ether + n-alkane) at 298.15K", J. Chem. Thermodyn., 20, 267-271 (1988).
Mączyński, A., Biliński, A., Oracz, P., and Treszczanowicz, T., "Verified vapor-liquid equilibrium data", Thermodynamic Data for Technology Series A, Vol. 6, Binary systems of C_{3+} hydrocarbons and alcohols, PWN-Polish Scientific Publishers (1982).
Mann, W.B., "Use of callendar's 'radio balance' for the measurement ot the energy emission from radioactive sources", J. Research Natl. Bur. Standards, 52, 177-184 (1954).
Manzini, G. and Crescenzi, V., "Simple, accurate method of calculation of the thermal pressure coefficient of nonpolar liquids and a possible estimate of their excess volumes of mixing", Gazz. Chim. Ital., 104 51-61 (1974).
Margerum, M.R., "Equation of state for polar fluids", PhD thesis, University of Ottawa, Canada (1989).
Margerum, M.R. and Lu, B.C.-Y., "VLE correlaton for binary 1-alkanol + n-alkane mixtures", Fluid Phase Equilib., 56, 106-118 (1990).
Marquardt, D.W. and Baumeister, T., "Least-squares estimation of non-linear parameters", IBM Share Program No. 1428 (1962).
Marquardt, D.W., "An algorithm for least-squares estimation of non-linear parameters", J. Soc. Ind. Appl. Math., 11, No.2, 431-441 (1963).
Marsh, K.N., and Ott, J.B., Int. Data Ser., Selec. Data Mixtures, Ser. A, 209 (1983).
Marsh, K.N., and Ott, J.B., Int. Data Ser., Selec. Data Mixtures, Ser. A, 213 (1983).
Marsh, K.N., Ott, J.B., and Costigan, M.J., "Excess enthalpies, excess volumes, and excess Gibbs free energies for (n-hexane + n-decane) at 298.15 and 308.15 K", J. Chem. Thermodyn., 12, 343-348 (1980).

McCullough, J.P. and Scott, D.W. (Ed.), "Experimental thermodynamics", London, Vol.1,2, (1968).

McGlashan, M.L., Williamson, A.G., "Thermodynamics of mixtures of n-hexane + n-hexadecane. Part 2.-Vapour pressures and activity coefficients", Trans. Faraday Soc., 57, 588--600 (1961).

Miller, R.C. and Williamson, A.G., "Excess molar enthalpies of (n-hexane + n-hexadecane) and for three- and four- component alkane mixtures simulating this binary mixtures", J. Chem. Thermodyn., **16**, 793-799 (1984).

Miltenburg, J.C.van, Berg, G.J.K. van den, and Bommel, M.J.van, "Construction of an adiabatic calorimeter. Measurements of the molar heat capacity of synthetic sapphire and of n-heptane", J. Chem. Thermodyn., **19**, 1129-1137 (1987).

Moorthi, K., Gierycz, P., and Nagata, I., "Prediction and correlation of excess enthalpy and excess Gibbs energy of the 1-alkanol + n-alkane systems", Fluid Phase Equilib., **64**, 13-32 (1991).

Morris, J.W., Mulvey, P.J., Abbott, M.M., and Van Ness, H.C., "Excess thermodynamic functions for ternary systems. I. Acetone-chloroform-methanol at 50°C", J. Chem. Eng. Data, **20**, 403-405 (1975).

Mrazek, R.V. and Van Ness, H.C., "Heats of mixing: Alcohol-aromatic binary systems at 25°C, 35°C and 45°C", AIChE J., 7, 190-195 (1961).

Muñoz Embid, J., Otin, S., Velasco, I., Gutiérrez Losa, C., and Kehiaian, H.V., "Excess enthalpies of 1-iodoalkane + n-alkane mixtures. Measurement and analysis in terms of group contributions (DISQUAC)", Fluid Phase Equilib., 38, 1-17 (1987).

Murakami, S. and Benson, G.C., "An isothermal delution calorimeter for measuring enthalpies of mixing", J. Chem. Thermodyn., 1, 559-572 (1969).

Nagata, I., Asano, H., and Fujiwara, K., "Excess enthalpies for systems of 2-propanol-benzene-methylcyclohexane", Fluid Phase Equilib., 1, 211-217 (1977).

Nagata, I., Fujiwara, K., and Ogasawara, Y., "Excess enthalpies of 2-propanol+cyclohexane and 2-propanol+benzene+cyclohexane at 298.15 K", J. Chem. Thermodyn., **10**, 1201-1203 (1978).

Nagata, I. and Kawamura, Y., "Thermodynamics of alcohol - unassociated active component liquid mixtures", Chem. Eng. Sci., 34, 601-611 (1979).

Nagata, I. and Kazuma, K., "Heats of mixing for the ternary system ethanol-1-propanol-cyclohexane at 25°C", J. Chem. Eng. Data, 22, 79-84 (1977).

Nagata, I. and Miyamoto, K., "Correlation of the spectroscopic and thermodynamic properties of solutions of propanols or butanols with non-associating components using the UNIQUAC associated-solution model", Fluid Phase Equilib., **56**, 203-218 (1990).

Nagata, I. and Miyazaki, K., "Correlation of the spectroscopic and thermodynamic properties of solutions of ethanol with non-associating components by means of the UNIQUAC associated-solution model", Thermochim. Acta, 118, 237-252 (1987).

Nagata, I. and Tamura, K., "Thermodynamics of solutions of ethanol in non-associating components", Thermochim. Acta, 77, 281-297 (1984).

Nagata, I. and Tamura, K., "Thermodynamics of solutions of propanols in non-

associating components", Thermochim. Acta, 87, 129-140 (1985).
Nagata, I. and Tamura, K., "Thermodynamics of solutions of butanols in hydrocarbons", Thermochim. Acta, 121, 447-462 (1987).
Nagata, I., Tamura, K., and Tokuriki, S., "Excess enthalpies and complex formation of acetonitrile with acetone, chloroform, and benzene", Thermochim. Acta, 47, 315-331 (1981).
Nagata, I. and Yamada, T., "Correlation and prediction of excess thermodynamic functions of strong nonideal liquid mixtures", Ind. Eng. Chem., Process Des. Dev., 13, 47-53 (1974).
Nakanishi, K., Okazaki, S., Ikari, K., Higuchi, T., and Tanaka, H., "Free energy of mixing, phase stability, and local composition in Lennard-Jones liquid mixtures", J. Chem. Phys., 76, 629-636 (1982).
Nakanishi, K. and Toukubo, K., "Molecular dynamics studies of Lennard-Jones liquid mixtures. V. Local composition in several kinds of equimolar mixtures with different combining rule", J. Chem. Phys., 70, 5848-5850 (1979).
Obama, M., Oodera,Y., Kohama,N., Yanase, T., Saito,Y., and Kusano, K., "Densities, molar volumes, and cubic expansion coefficients of 78 apiphatic ethers", J. Chem. Eng. Data, 30, 1-5 (1985).
Ott, J.B., Marsh, K.N., and Stokes, R,H., "Excess enthalpies, excess volumes, and excess Gibbs free energies for (n-hexane + n-dodecane) at 298.15 and 308.15 K", J. Chem. Thermodyn., 13, 371-376 (1981).
Pando, C., Renuncio, J.A.R., Calzon, J.A.G., Christensen, J.J., and Izatt, R.M., "Correlation and prediction of ternary excess enthalpy data", J. Solution Chem., 16, 503-527 (1987).
Patel, N.C. and Teja, A.S., "A new cubic equation of state for fluids and fluid mixtures", Chem. Eng. Sci., 37, 463-473 (1982).
Peng, D.Y. and Robinson, D., "A new two-constant equation of state", Ind. Eng. Chem. Fundam., 15, 59-64 (1976).
Pflug, H.D., Pope, A.E., and Benson, G.C., "Heats of mixing of normal alcohols at 25°C", 13, 408-410 (1968).
Prausnitz, J.M., Lichtenthaler, R.N., and Gomes de Azevedo, E., "Molecular thermodynamics of fluid-phase equilibria", 2nd Ed., Prentice-Hall Inc., Englewood Cliffs, N.J. 07632 (1986).
Prigogine, I., "The molecular theory of solution", Amsterdam, North-Holland Pub. Co. (1957).
Rastogi, R.P., Nath, J., and Das, S.S., "Thermodynamic properties of ternary mixtures. 2. The excess volumes of mixing of ternary mixtures of cyclohexane, aromatics, and halomethanes", J. Chem. Eng. Data, 22, 249-252 (1977).
Ratkovics, F., Liszi, J., László, M., Szeiler, B., and Dévay, J., "Mixing properties of the ethanol-diethylamine-triethylamine system", Acta Chim. Acad. Sci. Hung., 77, 249-265 (1973).
Redlich, O. and Kister, T., "Thermodynamics of nonelectrolytic solutions. Algebraic representation of thermodynamic properties and the classification of solutions", Ind.

Eng. Chem., 40, 345-348 (1948).
Renon, H., "NRTL: an empirical equation or an inspiring model for fluids mixtures properties?", Fluid Phase Equilib., 24, 87-114 (1985).
Renon, H. and Prausnitz, J.M., "Local composition thermodynamic excess functions for liquid mixtures", AIChE J., 14, 135-144 (1968a).
Renon, H. and Prausnitz, J.M., "Liquid-liquid and vapor-liquid equilibria from binary and ternary systems with dibutylketone, dimethyl sulfoxide, n-hexane and 1-hexane", Ind. Eng. Chem., Process Res. Develop., 7, 220-225 (1968b).
Renon, H. and Prausnitz, J.M., "Estimation of parameters for the NRTL equation for excess Gibbs energies of strongly nonideal liquid mixtures", Ind. Eng. Chem., Process Res. Develop., 8, 413-419 (1969).
Riddick, J., Bunder, W.B., and Sakano, T.K., "Organic solvents; Physical properties and methods of purification", 4th Ed. (1986), p73.
Rossini, F.D. (Ed.), "Experimental Thermochemistry", Vol. 1, Interscience, New York (1956), p239, 297.
Rowlinson, J.S. and Swinton, F.L., "Liquid and liquid mixtures",3rd Ed., Butterworths (1982), p139.
Savini, C.G., Winterhalter, D.R., Kovach, L.H., and Van Ness, H.C., "Endothermic heats of mixing by isothermal dilution calorimetry", J. Chem. Eng. Data, 11, 40-43 (1966).
Scatchard, G. and Satkifwicz, F.G., "Vapor-liquid equilibrium XII. The system ethanol-cyclohexane from 5° to 65°", J. Am. Chem. Soc., 86, 130-133 (1964).
Schmidt, G. and Wenzel, H., "A modified van der Waals type equation of state", Chem. Eng. Sci., 35, 1503-1512 (1980).
Schwartzentruber, J., Galiver-Solastriouk, F, and Renon, H., "Representation of the vapour-liquid equilibrium of the ternary system Carbon dioxide - propane - methanol and its binaries with a cubic equation of state: A new mixing rule", Fluid Phase Equilib., 38, 217-226 (1987).
Schwartzentruber, J. and Renon, H., "Extension of UNIFAC to high pressures and temperatures by the use of a cubic equation of state", Ind. Eng. Chem. Res., 28, 1049-1055 (1989).
Smith, V.C. and Robinson, R.L.Jr., "Vapor-liquid equilibriums at 25° in the binary mixtures formed by hexane, benzene, and ethanol", J. Chem. Eng. Data, 15, 391-395 (1970).
Soave, G., "Equilibrium constants from a modified Redlich-Kwong equation of state", Chem. Eng. Sci., 27, 1197-1203 (1972).
Soriano, M. J., Velasco, I., Otin, S., and Kehiaian, H.V., "Thermodynamics of mixtures containing iodoalkanes. II. Excess enthalpies of mixtures of 1-iodoalkane + cyclohexane, + benzene, or + tetrachloromethane. Measurement and analysis in terms of group contributions (DISQUAC)", Fluid Phase Equilib., 45, 205-216 (1989).
Stathis, P. J. and Tassios, D. P., "Prediction of enthalpies of mixing for systems containing alcohols with a UNIFAC/association model", Ind. Eng. Chem. Process

Des. Develop., 24, 701-707 (1985).
Stokes, R.H. and Burfitt, C., "Enthalpies of dilution and transfer of ethanol in non-polar solvents", J. Chem. Thermodyn., 5, 623-631 (1973).
Stokes, R. H., Marsh, K. N., and Tomlins, R. P., "An isothermal displacement calorimeter for endothermic enthalpies of mixing", J. Chem. Thermodyn., 1, 211-221 (1969).
Stryjek, R. and Vera, J.H., "PRSV: An improved Peng-Robinson equation of state for pure compounds and mixtures", Can. J. Chem. Eng., 64, 323-333 (1986a).
Stryjek, R. and Vera, J.H., "PRSV - An improved Peng-Robinson equation of state with new mixing rules for strongly nonideal mixtures", Can. J. Chem. Eng., 64, 334-340 (1986b).
Tanaka, R., D'Arcy, P.J., and Benson, G.C., "Application of a flow microcalorimeter to determine the excess enthalpies of binary mixtures of non-electrolytes",Thermochim. Acta, 11, 163-175 (1975).
Tasic, A., Djordjevic, B., Grozanic, D., Afgan, N., and Malic, D., "Vapor-liquid equilibriums of the systems acetone-benzene, benzene-cyclohexane, and acetone-cyclohexane at 250°C", Chem. Eng. Sci., 33, 189-197 (1978).
Tiné, M.R. and Kehiaian, H.V., "A comparative study of thermodynamic properties of n-alkane or cycloalkane mixtures with aliphatic, linear or heterocyclic, molecules containing the same functional groups", Fluid Phase Equilib., 32, 211-248 (1987).
Tochigi, K., Kurihara, K., and Kojima, K., "Prediction of high pressure vapor-liquid equilibria with mixing rule using ASOG group contribution method", J. Chem. Eng. Jpn., 18, 60-65 (1985).
Tochigi, K., Kurihara, K., and Kojima, K., "Prediction of high pressure vapor liquid equilibria using the Soave-Redlich-Kong group contribution method", Ind. Eng. Chem. Res., 29, 2142-2149 (1990).
Toop, G.W., "Predicting ternary activities using binary data", Trans. AIME, 233, 850-855 (1965).
Treszczanowicz, A.J. and Benson, G.C., "Excess volumes of alkanol + alkane binary systems in terms of an association model with a Flory contribution term", Fluid Phase Equilib., 23, 117-135 (1985).
Treszczanowicz, A.J. and Benson, G.C., "Prediction of excess volumes of 1-alkanol + branched aliphatic hydrocarbon binary system in terms of an association model with a Flory contribution term", Fluid Phase Equilib., 41, 31-42 (1988).
Treszczanowicz, A.J., Kiyohara, O., and Benson, G.C., "Interpretation of the excess volume in alcohol+saturated hydrocarbon binary systems", Bull. Acad. Polon. Sci., Ser. Sci. Chim., 29, 103-110 (1981).
Tsao, C.C. and Smith, J.M., "Heats of mixing of liquids", Chem. Eng. Prog. Symp. Ser., No.7, 49, 107-117 (1953).
Tusel-Langer, E., Garcia Alonso, J.M., Villamanan Olfos, M.A., and Lichtenthaler, R.N., "Excess enthalpies of mixtures containing n-heptane, methanol and methyl-tertiary butyl ether", J. Solution Chem., 20, 153-163 (1991).
van der Waals, J.D., "Over de continuiteit van den gas-en Vloeistoftoe-stand", PhD thesis, University of Leiden (1873).

van Laar, J.J, "Theory of vapor pressure of binary mixtures", Z. Physik. Chem., 83, 599-608 (1913).

Vera, J.H. and Prausnitz, J.M., "Vapor-liquid equilibria in binary aromatic-olefin system", J. Chem. Eng. Data, 16, 149-154 (1971).

Vera, J.H. and Vidal, J., "An improved group method for hydrocarbon-hydrocarbon systems arising from a comparative study of ASOG and UNIFAC", Chem. Eng. Sci., 39(4), 651-661 (1984).

Veselý, F., Dohnal, V., and Prchal, M., "Enthalpy data of liquids. XXVI. Heats of mixing of the ternary system 1-propanol-n-alkane-cyclohexane", Collect. Czech. Chem. Commun., 47, 1045-1059 (1982).

Walas, S.M., "Phase equilibria in chemical engineering", Butterworth Publishers (1985).

Wang, L., Benson, G.C., and Lu, B.C.-Y., "Excess enthalpies for (di-n-propyl ether + n-alkane) at 298.15K", J. Chem. Thermodyn., 20, 975-979 (1988).

Wang, L., Benson, G.C., and Lu, B.C.-Y., "Excess enthalpies of binary mixtures of di-n-pentyl ether with n-alkanes at 298.15K", Fluid Phase Equilib.,46, 211-221 (1989a)

Wang, L., Benson, G.C., and Lu, B.C.-Y., "Excess enthalpies and excess volumes for (di-n-propyl ether + a cycloalkane)", J. Chem. Thermodyn., 21, 67-71 (1989b).

Wang, L., "Excess enthalpies and excess volumes for n-butyl methyl ether + n-alkane systems at 298.15K", Master thesis (1990a)

Wang, L., Benson, G.C., and Lu, B.C.-Y., "Excess enthalpies for (n-butyl methyl ether + n-alkane) at 298.15K", J. Chem. Thermodyn., 22, 173-179 (1990b).

Wang, L., Benson, G.C., and Lu, B.C.-Y., "Excess enthalpies of (ethanol + hexane + decane or dodecane) at the temperature 298.15 K", J. Chem. Thermodyn., 24, 1135-1143 (1992a).

Wang, L., Benson, G.C., and Lu, B.C.-Y., "Excess enthalpies of 1-propanol+n-hexane +n-decane or n-dodecane at 298.15 K", J. Chem. Eng. Data, 37, 403-406 (1992b).

Wang, L., Benson, G.C., and Lu, B.C.-Y., "Excess enthalpies of {(ethanol or propan-1-ol or methyl 1,1-dimethylethyl ether) + (2,3-dimethylbutane or 2,2,4-trimethylpentane)}", J. Chem. Thermodyn., 24, 1305-1310 (1992c).

Wang, L., Benson, G.C., and Lu, B.C.-Y., "Excess molar enthalpies of methyl tert-butyl ether + n-hexane + (n-decane or n-dodecane) ternary mixtures at 298.15 K", Thermochimi. Acta, 213, 83-93 (1993).

Wilson, G.M., "A new expression for the excess free energy of mixing", J. Am. Chem. Sco., 86, 127-130 (1964).

Wilson, G.M. and Deal, C.H., "Activity coefficient and molecular structure activity coefficients in changing environment - solutions of groups", Ind. Eng. Chem. Fundam., 1, 20-23 (1962).

Wohl. K., "Thermodynamic evaluation of binary and ternary liquid systems", Trans. Amer. Inst. Chem. Eng., 42, 215-249 (1946).

Wohl. K., "Thermodynamic evaluation of binary and ternary liquid systems", Chem. Eng. Progr., 49, 218-219 (1953).

Wong, D.S.H. and Sandler, S.I., "A theoretically correct mixing rule for cubic equations of state", AIChE J., 38, 671-680 (1992).

Appendix A

Experimental data

The experimental data included in appendix A are presented in the following four groups:

1. The calibration results for the pure components.

2. The excess enthalpy data for binary mixtures.

3. The calibration results for the prepared binary mixtures.

4. The ternary excess enthalpy data (the experimental results for $H^{E}_{m,1+23}$ and the corresponding $H^{E}_{m,123}$ for the six ternary mixtures).

A-1 Calibration results for the pure components

Table A-1 Calibration results of ethanol with pump A (R=49.520Ω)

Flow rate (counts·s^{-1})	Gear ratio	$V^{\circ}(f)$ (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
300.35	0.1	-0.0019796	-0.4147054	-0.4127258	0.1140	15.5929
500.85	0.1	-0.0017094	-0.4135442	-0.4118348	0.1140	15.6267
701.60	0.1	-0.0020580	-0.4125333	-0.4104753	0.1140	15.6784
900.20	0.1	-0.0020013	-0.4113582	-0.4093569	0.1140	15.7212
1099.90	0.1	-0.0021699	-0.4102624	-0.4080925	0.1141	15.7976

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5067 + 2.52 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.013115 J·s^{-1}·V^{-1}.

Table A-2 Calibration results of 1-propanol with pump A (R=49.520Ω)

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
302.05	0.1	-0.0018483	-0.4445497	-0.4427014	0.1180	15.5752
499.90	0.1	-0.0017344	-0.4301613	-0.4284269	0.1153	15.6338
701.10	0.1	-0.0018497	-0.4308120	-0.4289623	0.1165	15.6680
899.70	0.1	-0.0018312	-0.4358585	-0.4340273	0.1174	15.7253
1101.80	0.1	-0.0017321	-0.4063467	-0.4046146	0.1135	15.7663

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5076 + 2.37 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.006698 J·s^{-1}·V^{-1}.

Table A-3 Calibration results of MTBE with pump A (R=49.520Ω)

Flow rate (counts·s^{-1})	Gear ratio	$V^{o}(f)$ (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
299.90	0.1	-0.0027652	-0.3986785	-0.3959133	0.1117	15.6058
500.50	0.1	-0.0029571	-0.3966680	-0.3937109	0.1115	15.6370
700.00	0.1	-0.0026282	-0.3944810	-0.3918528	0.1114	15.6830
900.90	0.1	-0.0025342	-0.3982715	-0.3957373	0.1121	15.7248
1100.60	0.1	-0.0025786	-0.3984685	-0.3958899	0.1122	15.7468

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5501 + 1.85 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.007213 J·s^{-1}·V^{-1}.

Table A-4 Calibration results of n-hexane with pump B (R=49.520Ω)

Flow rate (counts·s^{-1})	Gear ratio	$V^c(f)$ (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
302.95	0.1	-0.0018381	-0.4110472	-0.4092041	0.1134	15.5618
499.50	0.1	-0.0018769	-0.4104010	-0.4085241	0.1134	15.5879
500.40	0.1	-0.0014829	-0.4248292	-0.4233463	0.1155	15.6044
696.00	0.1	-0.0017302	-0.4213632	-0.4196330	0.1151	15.6336
900.40	0.1	-0.0016392	-0.4159086	-0.4142694	0.1145	15.6714
1005.75	0.1	-0.0017222	-0.4117936	-0.4100714	0.1140	15.6938
1100.80	0.1	-0.0016920	-0.4185928	-0.4169008	0.1150	15.7088

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5036 + 1.87 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.00534 J·s^{-1}·V^{-1}.

Table A-5 Calibration results of n-decane with pump B (R=49.520Ω)

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
302.20	0.1	-0.0012766	-0.4067194	-0.4054428	0.1129	15.5682
498.20	0.1	-0.0015355	-0.4043774	-0.2028419	0.1128	15.6410
691.65	0.1	-0.0013029	-0.4034160	-0.4021140	0.1128	15.6693
898.90	0.1	-0.0014771	-0.4047138	-0.4032367	0.1131	15.7089
1099.05	0.1	-0.0015089	-0.4027116	-0.4012027	0.1130	15.7606

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5113 + 2.27\times10^{-4}F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.012319 J·s^{-1}·V^{-1}.

Table A-6 Calibration results of n-dodecane with pump B (R=49.520Ω)

Flow rate (counts·s^{-1})	Gear ratio	$V^c(f)$ (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
268.20	0.1	-0.0017313	-0.4273671	-0.4256358	0.1158	15.6013
503.30	0.1	-0.0018156	-0.4120060	-0.4101904	0.1138	15.6343
701.60	0.1	-0.0014412	-0.4100823	-0.4086411	0.1137	15.6661
900.00	0.1	-0.0015197	-0.4080140	-0.4064943	0.1135	15.6934
1101.00	0.1	-0.0015290	-0.4039577	-0.4024287	0.1131	15.7404

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5490 + 1.68 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.005564 J·s^{-1}·V^{-1}.

Table A-7 Calibration results of 2,2,4-trimethylpentane with pump B (R=49.520Ω)

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
301.05	0.1	-0.0028705	-0.4120900	-0.4092185	0.1135	15.5889
501.10	0.1	-0.0029065	-0.4262915	-0.4233850	0.1156	15.6301
700.60	0.1	-0.0024756	-0.4063810	-0.4039054	0.1130	15.6552
900.65	0.1	-0.0020305	-0.4023435	-0.4003130	0.1126	15.6840
1101.10	0.1	-0.0018005	-0.4008480	-0.3990475	0.1126	15.7338

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5379 + 1.72 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.007461 J·s^{-1}·V^{-1}.

Table A-8 Calibration results of 2,3-dimethylbutane with pump B (R=49.520Ω)

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
301.05	0.1	-0.0026356	-0.4142133	-0.4115777	0.1138	15.5816
501.60	0.1	-0.0024320	-0.4103673	-0.4079353	0.1134	15.6105
700.00	0.1	-0.0018969	-0.4113080	-0.4094111	0.1137	15.6366
900.00	0.1	-0.0021354	-0.4009773	-0.3988419	0.1124	15.6860
1100.00	0.1	-0.0021800	-0.3968820	-0.3947020	0.1119	15.7098

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5284 + 1.66 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.006933 J·s^{-1}·V^{-1}.

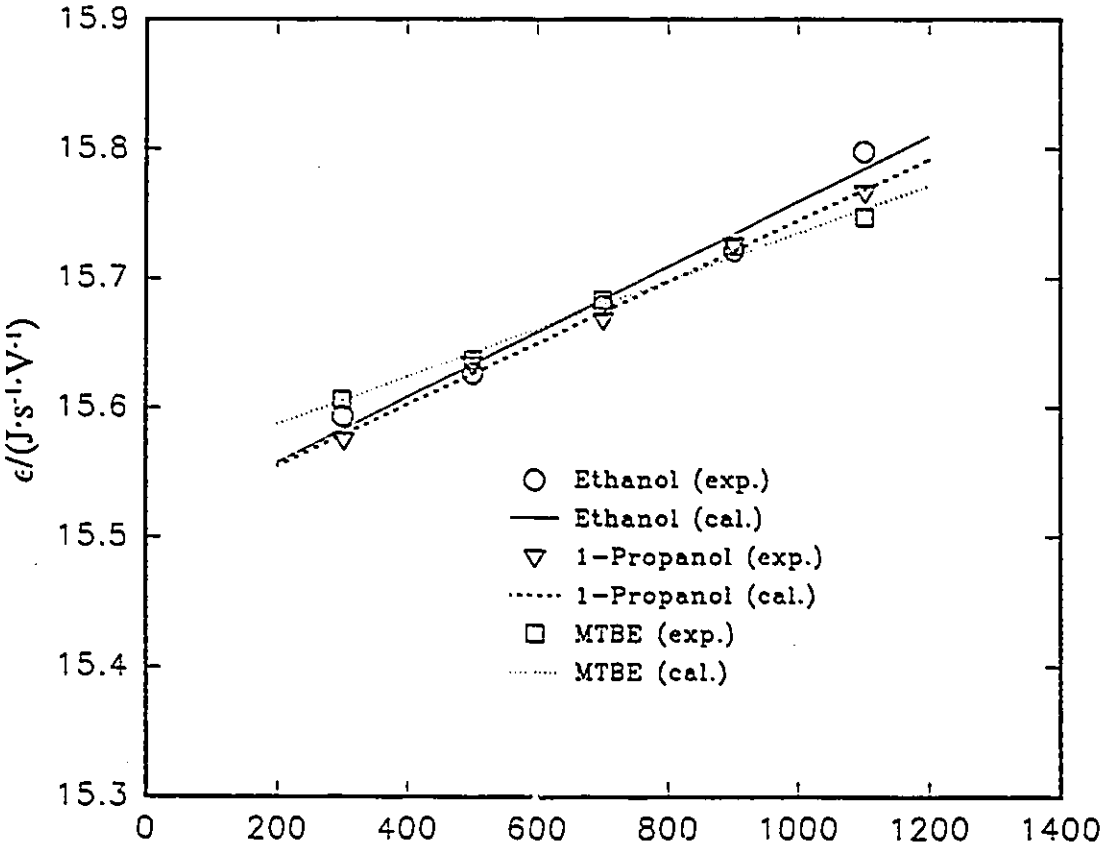


Figure A-1 Calibration results of pure components with pump A

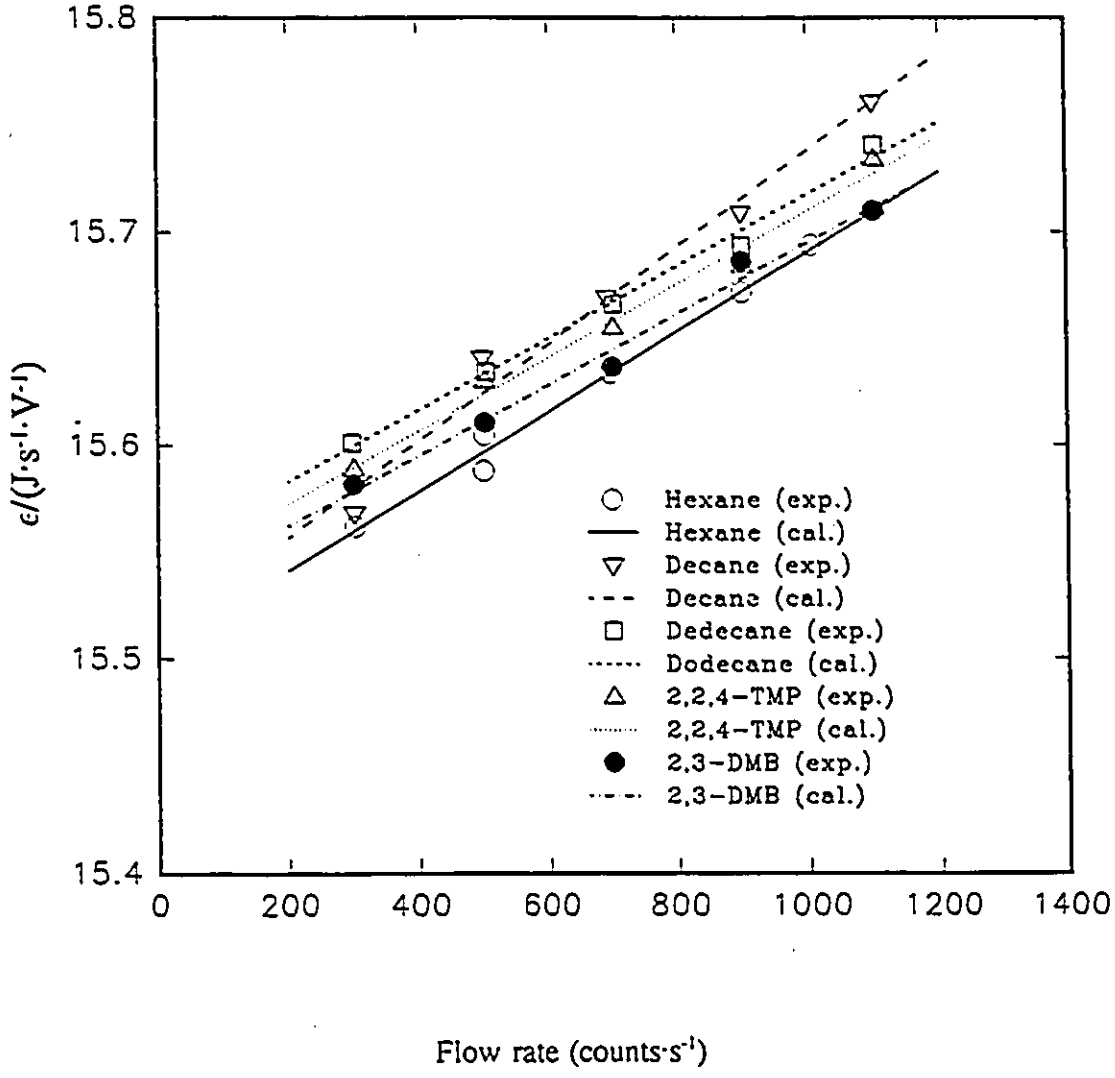


Figure A-2 Calibration results of pure components with pump B

A-2 Excess enthalpy data for binary mixtures

Table A-9 H_m^E data for the mixture of ethanol + n-hexane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05050	323.23
2	0.09994	405.80
3	0.15001	478.19
4	0.20013	519.07
5	0.25002	542.44
6	0.30006	559.71
7	0.34990	566.49
8	0.40013	566.57
9	0.45096	561.38
10	0.50003	550.34
11	0.49992	548.01
12	0.55043	530.64
13	0.60013	506.82
14	0.60048	505.29
15	0.65019	475.74
16	0.68311	452.07
17	0.75160	391.96
18	0.80084	337.89
19	0.84937	275.63
20	0.89958	193.51
21	0.94997	97.29

Table A-10 H_m^E data for the mixture of ethanol + n-decane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.04790	385.87
2	0.10013	504.67
3	0.14993	583.22
4	0.19994	628.05
5	0.24990	665.02
6	0.30015	690.89
7	0.35070	705.33
8	0.40005	709.83
9	0.44983	697.44
10	0.49759	686.14
11	0.50016	685.34
12	0.54934	661.37
13	0.60021	642.78
14	0.64988	613.83
15	0.70079	575.89
16	0.75043	532.76
17	0.80015	480.18
18	0.85001	411.01
19	0.90011	320.30
20	0.94990	187.27

Table A-11 H_m^E data for the mixture of ethanol + n-dodecane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05000	396.14
2	0.14990	617.74
3	0.20002	667.29
4	0.24998	699.73
5	0.29895	711.26
6	0.29894	711.83
7	0.35042	727.36
8	0.40019	733.29
9	0.44972	742.27
10	0.50008	731.50
11	0.54876	717.02
12	0.60009	691.91
13	0.59975	701.25
14	0.64995	665.42
15	0.64971	669.93
16	0.69961	631.38
17	0.70001	632.28
18	0.69998	632.92
19	0.74916	589.99
20	0.79996	531.25
21	0.85036	458.59
22	0.90019	367.11
23	0.95001	225.57

Table A-12 H_m^E data for the mixture of 1-propanol + n-hexane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05018	344.05
2	0.05021	349.15
3	0.10008	439.79
4	0.15009	501.58
5	0.19994	544.62
6	0.25007	570.43
7	0.29994	584.49
8	0.35085	587.82
9	0.39924	576.61
10	0.44983	558.82
11	0.50076	532.89
12	0.54986	500.38
13	0.60049	462.86
14	0.65022	419.56
15	0.69898	373.18
16	0.74302	328.99
17	0.80011	265.74
18	0.82811	231.35
19	0.84996	205.39
20	0.89880	142.22
21	0.94998	68.95

Table A-13 H_m^E data for the mixture of 1-propanol + n-decane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.04998	411.14
2	0.04998	411.65
3	0.09997	548.40
4	0.09998	541.19
5	0.15005	621.53
6	0.20029	671.52
7	0.25004	710.16
8	0.30004	741.99
9	0.35012	751.71
10	0.40010	761.68
11	0.44952	756.55
12	0.50023	731.78
13	0.54950	707.35
14	0.60000	672.72
15	0.65012	632.14
16	0.69995	584.96
17	0.74965	525.14
18	0.80050	454.80
19	0.84998	371.19
20	0.89996	270.94
21	0.94994	151.49

Table A-14 H_m^E data for the mixture of 1-propanol + n-dodecane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05002	441.10
2	0.09981	593.56
3	0.15008	678.14
4	0.19996	731.15
5	0.24997	773.00
6	0.30039	796.00
7	0.33200	815.56
8	0.34992	818.54
9	0.38562	819.61
10	0.43719	824.02
11	0.48779	811.26
12	0.53900	785.36
13	0.58863	753.22
14	0.63660	715.71
15	0.68371	667.07
16	0.73130	610.40
17	0.77818	543.03
18	0.82335	469.59
19	0.86862	380.44
20	0.91302	276.03
21	0.95683	153.28

Table A-15 H_m^E data for the mixture of MTBE + n-hexane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05005	63.39
2	0.05007	68.95
3	0.10001	131.53
4	0.10001	135.19
5	0.15005	190.32
6	0.20001	238.95
7	0.25006	281.16
8	0.29975	311.46
9	0.35007	337.10
10	0.39981	355.07
11	0.44991	364.28
12	0.50015	371.82
13	0.55026	366.25
14	0.64981	335.47
15	0.69972	309.11
16	0.75061	274.69
17	0.80007	232.49
18	0.84992	182.84
19	0.90014	125.92
20	0.94998	59.67

Table A-16 H_m^E data for the mixture of MTBE + n-decane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.04999	81.54
2	0.10016	156.27
3	0.15006	226.26
4	0.20011	289.75
5	0.24995	347.90
6	0.34736	434.91
7	0.40034	465.90
8	0.45057	488.46
9	0.50018	500.01
10	0.54958	501.35
11	0.59988	496.61
12	0.65008	479.48
13	0.70032	451.21
14	0.74945	411.41
15	0.79966	358.55
16	0.84999	291.77
17	0.89986	211.87
18	0.95001	111.54

Table A-17 H_m^E data for the mixture of MTBE + n-dodecane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05004	85.17
2	0.05004	88.50
3	0.09992	172.89
4	0.15002	252.28
5	0.19984	328.63
6	0.24981	394.83
7	0.29995	446.29
8	0.35005	494.91
9	0.40091	530.77
10	0.45012	554.23
11	0.49980	569.75
12	0.54945	573.28
13	0.59992	569.59
14	0.65025	554.05
15	0.75010	481.17
16	0.79968	421.68
17	0.85024	343.25
18	0.89999	252.15
19	0.95001	135.59
20	0.95002	137.54

Table A-18 H_m^E data for the mixture of ethanol + 2,2,4-trimethylpentane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05008	342.89
2	0.10007	453.68
3	0.14997	515.56
4	0.20012	556.08
5	0.25014	584.25
6	0.30003	599.40
7	0.35022	606.66
8	0.40018	606.11
9	0.45003	598.24
10	0.50056	581.19
11	0.54976	560.84
12	0.60024	535.96
13	0.65025	504.81
14	0.70023	466.06
15	0.74998	421.60
16	0.80010	367.66
17	0.84993	301.75
18	0.89970	224.62
19	0.94995	125.87

Table A-19 H_m^E data for the mixture of ethanol + 2,3-dimethylbutane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05000	317.93
2	0.09859	398.58
3	0.14999	455.67
4	0.20002	493.66
5	0.25019	518.64
6	0.30031	527.70
7	0.39996	528.91
8	0.45034	519.48
9	0.49973	503.09
10	0.54975	487.17
11	0.60013	463.43
12	0.64989	436.26
13	0.69995	399.70
14	0.75169	355.28
15	0.80014	307.35
16	0.84984	248.79
17	0.89999	181.00
18	0.95002	97.22

Table A-20 H_m^E data for the mixture of 1-propanol + 2,2,4-trimethylpentane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05097	379.59
2	0.10000	484.06
3	0.15010	544.61
4	0.20010	586.65
5	0.25005	613.16
6	0.30020	625.80
7	0.35028	628.30
8	0.39997	619.41
9	0.44899	601.67
10	0.50017	575.89
11	0.55006	543.73
12	0.60005	505.52
13	0.65012	460.59
14	0.70044	410.55
15	0.74960	356.26
16	0.80022	295.46
17	0.84998	230.72
18	0.89999	159.60
19	0.95001	82.14

Table A-21 H_m^E data for the mixture of 1-propanol + 2,3-dimethylbutane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.04987	336.50
2	0.09989	427.45
3	0.14983	483.76
4	0.15002	484.31
5	0.19999	518.58
6	0.20017	515.86
7	0.24994	537.32
8	0.29998	538.46
9	0.34998	532.33
10	0.35001	535.17
11	0.39994	523.31
12	0.45051	502.08
13	0.49996	481.04
14	0.50044	476.36
15	0.54971	447.33
16	0.55029	444.97
17	0.59920	412.16
18	0.59981	410.79
19	0.64981	372.64
20	0.65010	366.51
21	0.69993	321.33
22	0.74968	275.34
23	0.79991	224.19
24	0.84989	171.70
25	0.89994	115.29
26	0.94999	86.60

Table A-22 H_m^E data for the mixture of MTBE + 2,2,4-trimethylpentane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05005	56.26
2	0.05006	57.08
3	0.10000	103.65
4	0.14995	147.43
5	0.20004	189.97
6	0.25006	226.50
7	0.30019	254.04
8	0.35230	278.68
9	0.39992	294.47
10	0.45000	305.88
11	0.50005	307.24
12	0.55003	306.22
13	0.60023	302.67
14	0.65020	289.80
15	0.69946	270.85
16	0.74971	240.49
17	0.80022	209.29
18	0.85000	165.91
19	0.89999	118.50
20	0.95001	61.76

Table A-23 H_m^E data for the mixture of MTBE + 2,3-dimethylbutane at 298.15K

Point	x_1	H_m^E/J·mol^{-1}
1	0.05001	58.37
2	0.05002	60.11
3	0.09996	114.22
4	0.15008	161.80
5	0.19993	202.68
6	0.25023	234.58
7	0.30114	264.13
8	0.34969	285.41
9	0.35565	286.01
10	0.39911	299.86
11	0.49954	303.51
12	0.50035	304.13
13	0.55022	301.46
14	0.59973	292.92
15	0.64971	278.27
16	0.69995	256.72
17	0.75017	226.86
18	0.79974	193.72
19	0.85005	152.86
20	0.90001	107.16
21	0.95006	54.29

A-3 Calibration results for the prepared binary mixtures

There were eighteen specific binary mixtures required for the six ternary systems studied, nine of them were from n-hexane and n-decane and the others were from n-hexane and n-dodecane. Among the mixtures of n-hexane and n-decane, #4 was the same as #1, and #9 was the same as #6. For the mixtures of n-hexane and n-dodecane, #3 and #5, #4 and #7, and #6 and #9 were the same. This was because the quantities of some prepared mixtures were sufficient for making two sets of measurements.

Table A-24 Preparation of #1 mixture of n-hexane+n-decane

Room temperature: 23.90°C			
Relative humidity: 66.8%			
Pressure: 754.3 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-decane	142.28468	0.72629
In #1 mixture		Weight/(g)	Mole fraction
	n-hexane	89.98689	0.49775
	n-decane	149.92086	0.50225
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	144.35743		0.69881

Table A-25 Calibration results of #1 mixture of n-hexane+n-decane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
301.50	0.1	-0.0016898	-0.4162333	-0.4145435	0.1142	15.5791
499.25	0.1	-0.0018675	-0.4218430	-0.4199755	0.1151	15.6209
704.35	0.1	-0.0017507	-0.4100113	-0.4082606	0.1136	15.6531
897.45	0.1	-0.0017381	-0.4122297	-0.4104916	0.1141	15.7054
1096.60	0.1	-0.0017815	-0.4082943	-0.4065128	0.1137	15.7481

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5127 + 2.12 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.005929 J·s^{-1}V^{-1}.

Table A-26 Preparation of #2 mixture of n-hexane+n-decane

Room temperature: 23.95°C			
Relative humidity: 56.4%			
Pressure: 757.2 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-decane	142.28468	0.72629
In #2 mixture		Weight/(g)	Mole fraction
	n-hexane	35.51923	0.25034
	n-decane	175.61759	0.74966
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	128.23883		0.71404

Table A-27 Calibration results of #2 mixture of n-hexane+n-decane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
299.10	0.1	-0.0016652	-0.4182760	-0.4166108	0.1145	15.5834
501.45	0.1	-0.0018481	-0.4117223	-0.4098742	0.1137	15.6189
699.00	0.1	-0.0015024	-0.4121053	-0.4106029	0.1140	15.6736
899.40	0.1	-0.0019000	-0.4103813	-0.4084813	0.1138	15.6998
1095.00	0.1	-0.0017358	-0.4090927	-0.4073569	0.1138	15.7431

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5232 + 2.01 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.006865 J·s^{-1}V^{-1}.

Table A-28 Preparation of #3 mixture of n-hexane+n-decane

Room temperature: 23.95°C			
Relative humidity: 58.0%			
Pressure: 765.2 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-decane	142.28468	0.72629
In #3 mixture		Weight/(g)	Mole fraction
	n-hexane	122.77431	0.74904
	n-decane	67.91715	0.25096
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	100.25806		0.67949

Table A-29 Calibration results of #3 mixture of n-hexane+n-decane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}·V^{-1})
301.35	0.1	-0.0024791	-0.4360185	-0.4335394	0.1167	15.5559
497.15	0.1	-0.0024856	-.04234975	-0.4210119	0.1152	15.6096
701.50	0.1	-0.0016411	-0.4180615	-0.4164205	0.1147	15.6450
902.65	0.1	-0.0016905	-0.4067765	-0.4050860	0.1133	15.6925
1101.25	0.1	-0.0017551	-0.4067270	-0.4049719	0.1134	15.7247

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.4986 + 2.10 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.006465 J·s^{-1}·V^{-1}.

Table A-30 Preparation of #5 mixture of n-hexane+n-decane

Room temperature: 25.20°C			
Relative humidity: 63.2%			
Pressure: 760.8 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-decane	142.28468	0.72629
In #5 mixture		Weight/(g)	Mole fraction
	n-hexane	35.77105	0.24724
	n-decane	179.82337	0.75276
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	128.41291		0.71421

Table A-31 Calibration results of #5 mixture of n-hexane+n-decane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
299.70	0.1	-0.0021797	-0.4335785	-0.4313988	0.1165	15.5795
499.30	0.1	0.0021748	-0.4510108	-0.4488360	0.1190	15.6238
700.00	0.1	-0.0018954	-0.4372060	-0.4353106	0.1174	15.6790
900.10	0.1	-0.0020283	-0.4204004	-0.4183721	0.1152	15.7081
1100.60	0.1	-0.0019718	-0.4293668	-0.4273950	0.1166	15.7525

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5182 + 2.15 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.006769 J·s^{-1}V^{-1}.

Table A-32 Preparation of #6 mixture of n-hexane+n-decane

Room temperature: 25.00°C			
Relative humidity: 63.2%			
Pressure: 753.0 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-decane	142.28468	0.72629
In #6 mixture		Weight/(g)	Mole fraction
	n-hexane	97.06803	0.75846
	n-decane	51.03748	0.24154
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	99.72915		0.67868

Table A-33 Calibration results of #6 mixture of n-hexane+n-decane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
302.35	0.1	-0.0021548	-0.4419845	-0.4398297	0.1176	15.5708
501.30	0.1	-0.0019804	-0.4471240	-0.4451436	0.1185	15.6213
700.00	0.1	-0.0019432	-0.4250585	-0.4231153	0.1157	15.6671
900.00	0.1	-0.0021227	-0.4292235	-0.4271008	0.1164	15.7093
1099.70	0.1	-0.0020754	-0.4353013	-0.4332259	0.1174	15.7544

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5046 + 2.28 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.002738 J·s^{-1}V^{-1}.

Table A-34 Preparation of #7 mixture of n-hexane+n-decane

Room temperature: 24.70°C			
Relative humidity: 63.4%			
Pressure: 759.0 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-decane	142.28468	0.72629
In #7 mixture		Weight/(g)	Mole fraction
	n-hexane	63.79206	0.49956
	n-decane	105.50883	0.50044
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	114.25535		0.69869

Table A-35 Calibration results of #7 mixture of n-hexane+n-decane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
301.10	0.1	-0.0031908	-0.3982760	-0.3950852	0.1115	15.5826
500.90	0.1	-0.0029491	-0.3975575	-0.3946084	0.1116	15.6294
700.10	0.1	-0.0024280	-0.3996925	-0.3972645	0.1121	15.6643
900.20	0.1	-0.0026697	-0.3998295	-0.3971598	0.1122	15.6964
1099.5	0.1	-0.0026787	-0.4008300	-0.3981513	0.1125	15.7412

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5280 + 1.92 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.004644 J·s^{-1}V^{-1}.

Table A-36 Preparation of #8 mixture of n-hexane+n-decane

Room temperature: 24.50°C			
Relative humidity: 68.2%			
Pressure: 754.5 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-decane	142.28468	0.72629
In #8 mixture		Weight/(g)	Mole fraction
	n-hexane	34.58175	0.25803
	n-decane	164.18564	0.74197
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	127.80741		0.71362

Table A-37 Calibration results of #8 mixture of n-hexane+n-decane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
301.20	0.1	-0.0032337	-0.4238310	-0.4205973	0.1150	15.5708
500.60	0.1	-0.0030017	-0.3974540	-0.3944523	0.1115	15.6076
699.35	0.1	-0.0030038	-0.4024360	-0.3994322	0.1124	15.6628
900.80	0.1	-0.0029681	-0.4063700	-0.4034019	0.1131	15.7025
1100.00	0.1	-0.0024896	-0.3925050	-0.3900154	0.1113	15.7286

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5106 + 2.05 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.008567 J·s^{-1}V^{-1}.

Table A-38 Preparation of #1 mixture of n-hexane+n-dodecane

Room temperature: 24.50°C			
Relative humidity: 68.7%			
Pressure: 761.2 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-dodecane	170.33844	0.74535
In #1 mixture		Weight/(g)	Mole fraction
	n-hexane	63.05876	0.50728
	n-decane	121.06594	0.49272
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	127.64528		0.71318

Table A-39 Calibration results of #1mixture of n-hexane+n-dodecane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
300.90	0.1	-0.0019495	-0.4116683	-0.4097188	0.1135	15.5699
499.20	0.1	-0.0016473	-0.4184380	-0.4167907	0.1146	15.6039
698.95	0.1	-0.0017402	-0.4265617	-0.4248215	0.1159	15.6582
900.15	0.1	-0.0016970	-0.4110363	-0.4093393	0.1139	15.6944
1100.15	0.1	-0.0017169	-0.4162587	-0.4145418	0.1148	15.7433

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5009 + 2.19 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.005246 J·s^{-1}V^{-1}.

Table A-40 Preparation of #2 mixture of n-hexane+n-dodecane

Room temperature: 25.85°C			
Relative humidity: 65.5%			
Pressure: 757.1 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-dodecane	170.33844	0.74535
In #2 mixture		Weight/(g)	Mole fraction
	n-hexane	114.95829	0.74701
	n-decane	76.95340	0.25299
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	107.46876		0.69000

Table A-41 Calibration results of #2 mixture of n-hexane+n-dodecane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
297.65	0.1	-0.0019642	-0.4585887	-0.4566245	0.1198	15.5645
500.10	0.1	-0.0017914	-0.4276853	-0.4258939	0.1159	15.6187
700.85	0.1	-0.0019365	-0.4277755	-0.4258390	0.1161	15.6747
899.90	0.1	-0.0020306	-0.4121090	-0.4100784	0.1141	15.7212
1098.70	0.1	-0.0018487	-0.4111645	-0.4093158	0.1142	15.7781

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.4864 + 2.65 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.002616 J·s^{-1}V^{-1}.

Table A-42 Preparation of #3 mixture of n-hexane+n-dodecane

Room temperature: 25.80°C			
Relative humidity: 58.4%			
Pressure: 757.0 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-dodecane	170.33844	0.74535
In #3 mixture		Weight/(g)	Mole fraction
	n-hexane	34.93020	0.24973
	n-decane	207.42614	0.75027
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	149.32066		0.73163

Table A-43 Calibration results of #3 mixture of n-hexane+n-dodecane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
301.20	0.1	-0.0014633	-0.5139770	-0.5125137	0.1268	15.5351
501.70	0.1	-0.0015418	-0.4921944	-0.4906526	0.1243	15.5937
700.50	0.1	-0.0015795	-0.4991208	-0.4975413	0.1254	15.6512
900.70	0.1	-0.0013605	-0.4636520	-0.4622915	0.1211	15.7092
1098.90	0.1	-0.0016675	-0.4427795	-0.4411120	0.1185	15.7641

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.4492 + 2.88 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.001013 J·s^{-1}V^{-1}.

Table A-44 Preparation of #4 mixture of n-hexane+n-dodecane

Room temperature: 24.70°C			
Relative humidity: 66.8%			
Pressure: 762.8 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-dodecane	170.33844	0.74535
In #4 mixture		Weight/(g)	Mole fraction
	n-hexane	70.18394	0.49614
	n-decane	140.88723	0.50386
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	128.58304		0.71409

Table A-45 Calibration results of #4 mixture of n-hexane+n-dodecane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
301.00	0.1	-0.0031906	-0.4163845	-0.4131939	0.1141	15.6026
500.00	0.1	-0.0026983	-0.4281780	-0.4254797	0.1159	15.6339
700.50	0.1	-0.0027264	-0.4297935	-0.4270671	0.1162	15.6566
899.60	0.1	-0.0028112	-0.4307645	-0.4279533	0.1164	15.6780
110.00	0.1	-0.0027138	-0.4325550	-0.4298412	0.1168	15.7166

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5622 + 1.36 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.005181 J·s^{-1}V^{-1}.

Table A-46 Preparation of #6 mixture of n-hexane+n-dodecane

Room temperature: 24.75°C			
Relative humidity: 66.3%			
Pressure: 756.6 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-dodecane	170.33844	0.74535
In #6 mixture		Weight/(g)	Mole fraction
	n-hexane	105.97229	0.74326
	n-decane	72.35321	0.25674
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	107.78444		0.69042

Table A-47 Calibration results of #6 mixture of n-hexane+n-dodecane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
300.90	0.1	-0.0027023	-0.4437340	-0.4410317	0.1177	15.5548
500.95	0.1	-0.0023522	-0.4433620	-0.4410098	0.1179	15.6085
699.90	0.1	-0.21491	-0.4377460	-0.4355969	0.1174	15.6687
899.90	0.1	-0.0023600	-0.4322950	-0.4299350	0.1168	15.7132
1100.00	0.1	-0.0027339	-0.4438455	-0.4411116	0.1185	15.7641

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.4784 + 2.62 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.004561 J·s^{-1}V^{-1}.

Table A-48 Preparation of #8 mixture of n-hexane+n-dodecane

Room temperature: 24.62°C			
Relative humidity: 70.0%			
Pressure: 760.4 mmHg			
Pure components		Mol. weight	Density/(g·cm^{-3})
	n-hexane	86.17716	0.65512
	n-dodecane	170.33844	0.74535
In #8 mixture		Weight/(g)	Mole fraction
	n-hexane	27.71994	0.27206
	n-decane	146.60009	0.72794
Mixture prepared	Molecular weight		Density/(g·cm^{-3})
	147.44116		0.73023

Table A-49 Calibration results of #8 mixture of n-hexane+n-dodecane with pump B

Flow rate (counts·s^{-1})	Gear ratio	V°(f) (mV)	V(f) (mV)	ΔV (mV)	E (V)	ϵ (J·s^{-1}V^{-1})
300.15	0.1	-0.0028188	-0.3972225	-0.3944037	0.1115	15.6095
499.80	0.1	-0.0029399	-0.4011825	-0.3982426	0.1122	15.6538
699.80	0.1	-0.0028708	-0.3990267	-0.3961559	0.1120	15.6802
900.60	0.1	-0.0025232	-0.3975593	-0.3950361	0.1120	15.7246
1100.50	0.1	-0.0028251	-0.3991860	-0.3963609	0.1123	15.7561

The data representation by Equation (4.5) has a form of

$$\epsilon = 15.5575 + 1.82 \times 10^{-4} F$$

where F is the flow rate. The root mean square deviation of calculated ϵ from the experimental value is 0.004835 J·s^{-1}V^{-1}.

A-4 Ternary excess enthalpy data

The experimental results of $H^E_{m,1+23}$ and the corresponding excess enthalpy $H^E_{m,123}$ for the six ternary systems are presented in this section.

The values of experimental $H^E_{m,1+23}$ data were represented by means of Tsao and Smith's (1953) expression (Equation 4.20) with the ternary contribution term represented by the Morris's relation (Equation 4.21).

The ternary excess enthalpy $H^E_{m,123}$ was calculated from Equation 3.13. Some contours, corresponding to constant values of $H^E_{m,123}$, are plotted in triangular diagrams (Figures A-9 to A-14).

The Morris's expressions for the six ternary systems are expressed as follows:

For the (ethanol(1)+n-hexane(2)+n-decane(3)) systems

$$H^E_{m,T}=x_1x_2(1-x_1-x_2)(-1943.6+20825.6x_1+6315.8x_2-51217.5x_1^2$$
$$-48958x_1x_2-4905.2x_2^2+39563.1x_1^3+57995.2x_1^2x_2+29130.4x_1x_2^2)$$

For the (ethanol(1)+n-hexane(2)+n-dodecane(3)) systems

$$H^E_{m,T}=x_1x_2(1-x_1-x_2)(322.8+15484.1x_1-6686.2x_2-58851.6x_1^2+19339.0x_1x_2$$
$$+6351.4x_2^2+49577.5x_1^3+13076.1x_1^2x_2-36714.0x_1x_2^2)$$

For the (1-propanol(1)+n-hexane(2)+n-decane(3)) systems

$$H^{E}_{m,T}=x_1x_2(1-x_1-x_2)(1855.1-5997.2x_1-4936.3x_2+4747.0x_1^2+10166.1x_1x_2+3964.8x_2^2)$$

For the (1-propanol(1)+n-hexane(2)+n-dodecane(3)) systems

$$H^{E}_{m,T}=x_1x_2(1-x_1-x_2)(-1252.7+33198.2x_1+8596.7x_2-78880.3x_1^2-112649.7x_1x_2$$
$$-9200.4x_2^2+51959.0x_1^3+129996.0x_1^2x_2+88705.0x_1x_2^2)$$

For the (methyl *tert*-butyl ether(1)+n-hexane(2)+n-decane(3)) systems

$$H^{E}_{m,T}=x_1x_2(1-x_1-x_2)(651.9-2783.5x_1-24.9x_2+3607.8x_1^2)$$

For the (methyl *tert*-butyl ether(1)+n-hexane(2)+n-dodecane(3)) systems

$$H^{E}_{m,T}=x_1x_2(1-x_1-x_2)(1522.2-6710.2x_1-1893.3x_2+7079.7x_1^2+5467.8x_1x_2)$$

Table A-50 Experimental excess molar enthalpies $H^E_{m,1+23}$ for the addition of ethanol to (n-hexane+n-decane) to form $\{x_1$(ethanol)$+x_2$(n-hexane)$+x_3$(n-decane)$\}$ and values of $H^E_{m,123}$ calculated from Equation 3.13 using $H^E_{m,23}$ provided by Marsh *et al.*(1980).

x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}
			$x_2/(1-x_1-x_2)=0.3339$, $H^E_{m,23}/(J\cdot mol^{-1})=11.5$					
0.0453	352.4	363.4	0.3267	675.1	682.9	0.6782	571.4	575.1
0.0912	468.6	479.1	0.3761	676.8	684.0	0.7300	531.0	534.1
0.0912	462.5	472.9	0.4252	675.9	682.5	0.7811	480.2	482.7
0.1365	544.4	554.3	0.4711	667.8	673.9	0.8363	409.5	411.4
0.1840	598.3	607.7	0.5245	647.1	652.6	0.8395	401.9	403.7
0.2314	632.2	641.1	0.5745	632.9	637.8	0.8902	318.5	319.7
0.2787	658.4	666.7	0.6264	605.0	609.3	0.9448	186.2	186.8
			$x_2/(1-x_1-x_2)=0.9912$, $H^E_{m,23}/(J\cdot mol^{-1})=14.4$					
0.0499	352.5	366.2	0.3998	644.0	652.6	0.6995	529.9	534.2
0.0499	358.6	372.2	0.4493	638.6	646.5	0.6995	526.8	531.2
0.0998	466.4	479.3	0.5004	628.2	635.3	0.7498	486.8	490.4
0.1501	535.1	547.3	0.5013	629.9	637.1	0.8000	431.6	434.5
0.1998	579.9	591.4	0.5495	614.8	621.3	0.8500	361.1	363.3
0.2498	603.7	614.5	0.6001	592.4	598.2	0.8998	273.5	274.9
0.2999	631.0	641.1	0.6498	565.3	570.3	0.9499	154.2	154.9
0.3488	635.8	645.1						
			$x_2/(1-x_1-x_2)=2.9841$, $H^E_{m,23}/(J\cdot mol^{-1})=9.6$					
0.0499	333.9	343.0	0.3999	609.0	614.8	0.7014	492.9	495.8
0.1001	438.4	447.0	0.4501	605.0	610.2	0.7417	457.0	459.5
0.1500	503.2	511.3	0.5031	599.5	604.2	0.8004	393.7	395.6
0.2000	548.1	555.7	0.5498	584.0	588.3	0.8499	325.8	327.3
0.2499	580.4	587.6	0.5999	560.0	563.9	0.9000	238.8	239.7
0.3000	599.3	606.0	0.6510	530.1	533.4	0.9499	130.1	130.6
0.3501	604.5	610.7						

Table A-51 Experimental excess molar enthalpies $H^E_{m,1+23}$ for the addition of ethanol to (n-hexane+ n-dodecane) to form $\{x_1$(ethanol)$+x_2$(n-hexane)$+x_3$(n-dodecane)$\}$ and values of $H^E_{m,123}$ calculated from Equation 3.13 using $H^E_{m,23}$ provided by Ott *et al.*(1981).

x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}
			$x_2/(1-x_1-x_2)=0.3328$, $H^E_{m,23}/(J\cdot mol^{-1})=30.6$					
0.0500	401.3	430.4	0.3990	717.9	736.3	0.7997	483.7	489.8
0.0997	528.9	556.4	0.4499	713.5	730.3	0.7999	480.1	486.2
0.1460	594.7	620.8	0.4994	693.3	708.6	0.8499	417.8	422.4
0.1498	590.9	616.9	0.5509	671.6	685.4	0.8501	414.0	418.6
0.2032	651.0	675.4	0.5995	650.1	662.3	0.8999	334.6	337.7
0.2502	671.8	694.7	0.6501	615.5	626.2	0.9003	329.5	332.6
0.2998	698.5	719.9	0.6987	580.9	590.2	0.9500	199.8	201.3
0.3498	712.1	732.0	0.7500	536.5	544.2	0.9505	200.7	202.2
			$x_2/(1-x_1-x_2)=1.0296$, $H^E_{m,23}/(J\cdot mol^{-1})=39.4$					
0.0500	354.4	391.8	0.3999	667.0	691.7	0.7504	505.8	515.6
0.0998	473.0	508.5	0.4503	660.0	681.7	0.8000	453.9	461.8
0.1500	549.3	582.8	0.5003	648.7	668.4	0.8519	382.3	388.1
0.2001	601.9	633.4	0.6000	611.8	627.6	0.8519	381.5	387.4
0.2501	634.9	664.5	0.6500	583.2	597.0	0.9001	296.1	300.0
0.3000	657.4	684.9	0.6995	548.9	560.8	0.9500	171.3	173.2
0.3499	666.3	691.9						
			$x_2/(1-x_1-x_2)=2.9526$, $H^E_{m,23}/(J\cdot mol^{-1})=27.8$					
0.1001	439.0	464.0	0.5007	574.2	608.0	0.7502	462.4	469.4
0.1498	502.3	525.9	0.5494	578.5	591.0	0.7503	456.6	463.5
0.1998	544.9	567.1	0.5500	586.3	598.8	0.7998	403.8	409.3
0.2499	576.7	597.5	0.5998	559.5	570.6	0.8001	408.3	413.8
0.3019	598.9	618.3	0.6002	569.9	581.0	0.8496	339.5	343.7
0.3500	610.2	628.2	0.6498	542.0	551.8	0.8501	336.7	340.9
0.4000	615.4	632.1	0.6500	532.1	541.8	0.9000	251.6	254.4
0.4501	611.7	627.0	0.7000	506.5	514.8	0.9001	250.1	252.9
0.4995	599.0	612.9	0.7000	500.4	508.8	0.9499	139.5	140.9

Table A-52 Experimental excess molar enthalpies $H^E_{m,1+23}$ for the addition of 1-propanol to (n-hexane+n-decane) to form $\{x_1$(1-propanol)+x_2(n-hexane)+x_3(n-decane)$\}$ and values of $H^E_{m,123}$ calculated from Equation 3.13 using $H^E_{m,23}$ provided by Marsh *et al.*(1980).

x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}
			$x_2/(1-x_1-x_2)=0.3284$, $H^E_{m,23}/(J\cdot mol^{-1})=11.5$					
0.0500	399.6	410.5	0.3997	719.5	726.4	0.7503	470.8	473.6
0.1000	518.2	528.5	0.4518	706.5	712.8	0.8000	403.5	405.7
0.1500	600.0	609.7	0.5008	686.3	692.1	0.8501	322.8	324.5
0.2002	653.8	663.0	0.5500	658.0	663.2	0.9000	233.0	234.2
0.2499	690.2	698.8	0.6000	621.9	626.4	0.9500	124.8	125.4
0.2998	712.0	720.0	0.6501	578.8	582.8			
0.3499	723.2	730.6	0.7005	529.7	533.1			
			$x_2/(1-x_1-x_2)=0.9912$, $H^E_{m,23}/(J\cdot mol^{-1})=14.4$					
0.0399	350.4	364.2	0.4001	679.1	687.7	0.7501	430.3	433.9
0.1000	499.3	512.2	0.4513	663.2	671.1	0.7999	365.6	368.5
0.1500	567.4	579.7	0.4996	642.8	650.0	0.8501	290.2	292.3
0.1999	620.4	631.9	0.5502	614.3	620.7	0.8984	210.1	211.6
0.2500	651.9	662.7	0.6006	579.6	585.4	0.9500	109.2	109.9
0.3001	675.7	685.8	0.6505	536.8	541.8			
0.3499	682.4	691.7	0.7000	488.4	492.7			
			$x_2/(1-x_1-x_2)=2.9841$, $H^E_{m,23}/(J\cdot mol^{-1})=9.3$					
0.0501	366.5	375.3	0.3501	643.8	649.8	0.6999	437.1	439.9
0.1001	473.0	481.3	0.4018	632.5	638.0	0.7501	381.9	384.2
0.1001	472.2	480.6	0.4505	618.0	623.0	0.7997	320.5	322.3
0.1489	538.6	546.5	0.5002	595.5	600.1	0.8497	250.7	252.1
0.1999	588.2	595.6	0.5494	567.3	571.5	0.8992	177.3	178.2
0.2500	621.8	628.7	0.5996	525.0	528.7	0.9501	92.2	92.7
0.3000	640.4	646.9	0.6495	482.5	485.7			

Table A-53 Experimental excess molar enthalpies $H^E_{m,1+23}$ for the addition of 1-propanol to (n-hexane+n-dodecane) to form $\{x_1$(1-propanol)+x_2(n-hexane)+x_3(n-dodecane)$\}$ and values of $H^E_{m,123}$ calculated from Equation 3.13 using $H^E_{m,23}$ provided by Ott *et al.*(1981).

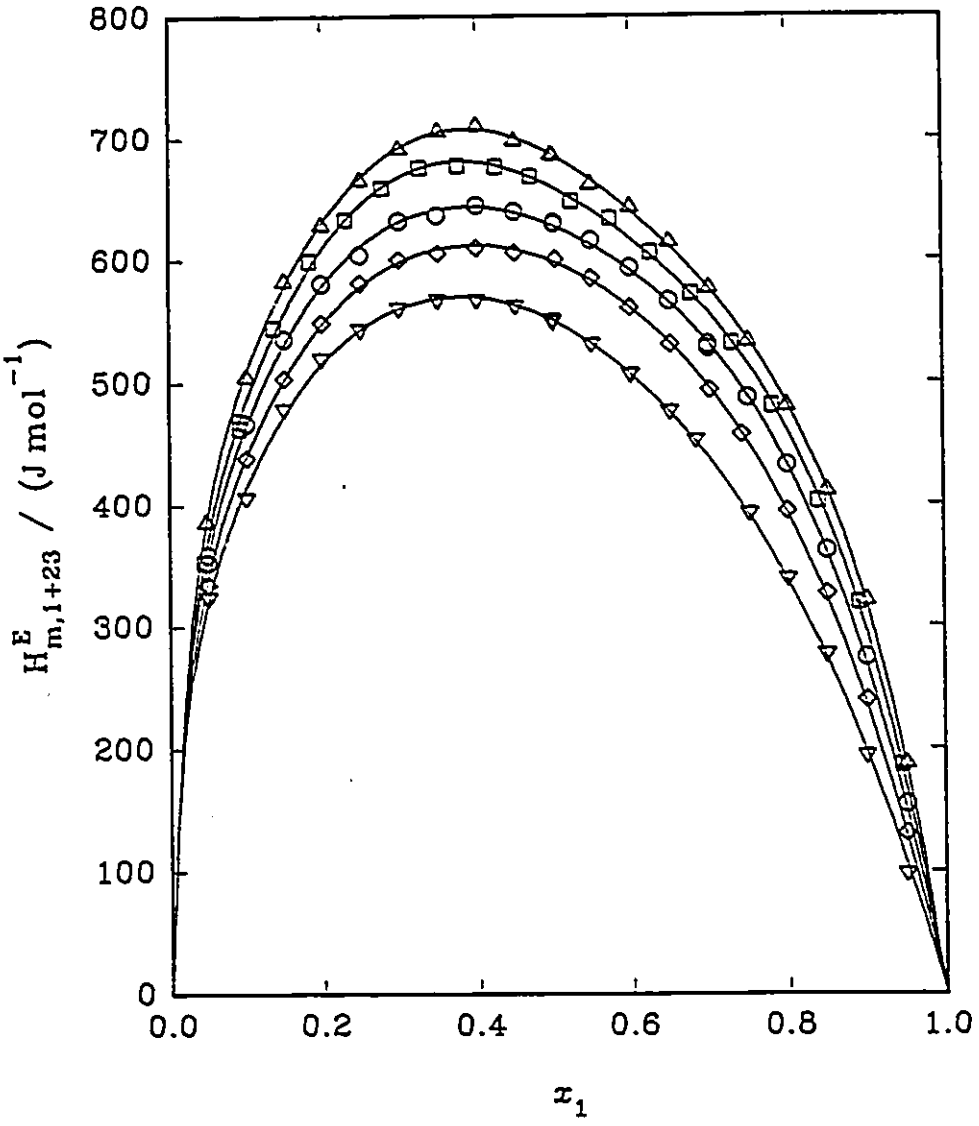
x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}
			$x_2/(1-x_1-x_2)=0.3328$, $H^E_{m,23}/(J\cdot mol^{-1})=30.6$					
0.0500	430.5	459.6	0.3502	791.6	811.5	0.7498	830.4	538.1
0.0500	438.8	467.8	0.4500	781.6	798.4	0.8001	454.4	460.5
0.0999	567.6	595.2	0.5002	755.5	770.8	0.8498	368.6	373.2
0.1502	651.9	677.9	0.5515	725.2	738.9	0.9001	266.0	269.0
0.1999	708.5	733.0	0.6000	690.6	702.8	0.9499	145.8	147.3
0.2499	750.4	773.3	0.6500	645.1	655.9			
0.2998	780.0	801.5	0.7000	592.3	601.5			
			$x_2/(1-x_1-x_2)=0.9845$, $H^E_{m,23}/(J\cdot mol^{-1})=39.5$					
0.0500	410.6	448.1	0.3998	720.0	743.7	0.7504	473.1	482.9
0.1001	521.1	556.7	0.4508	702.5	724.2	0.7994	407.2	415.1
0.1501	602.4	635.9	0.4997	683.3	703.0	0.8499	327.1	333.0
0.2000	655.9	687.5	0.5498	655.9	673.6	0.9002	237.5	241.4
0.2501	689.9	719.5	0.5990	620.1	635.9	0.9501	128.1	130.0
0.3000	716.0	743.7	0.6503	577.9	591.7			
0.3500	719.5	745.1	0.7002	528.3	540.1			
			$x_2/(1-x_1-x_2)=2.8956$, $H^E_{m,23}/(J\cdot mol^{-1})=28.1$					
0.0495	369.4	396.1	0.3499	665.6	683.9	0.7001	479.6	488.0
0.0495	365.7	392.4	0.3998	660.8	677.6	0.7499	412.2	419.2
0.1000	486.3	511.6	0.4514	654.6	670.0	0.8001	348.3	353.9
0.1501	553.8	577.6	0.5004	634.8	648.8	0.8501	275.0	279.2
0.2001	608.3	630.7	0.5494	607.4	620.1	0.9000	195.7	198.5
0.2502	639.8	660.9	0.5999	571.0	582.3	0.9499	104.2	105.6
0.3000	659.2	678.9	0.6512	525.4	535.2			

Table A-54 Experimental excess molar enthalpies $H^E_{m,1+23}$ for the addition of MTBE to (n-hexane+n-decane) to form $\{x_1$(MTBE)+x_2(n-hexane)+x_3(n-decane)$\}$ and values of $H^E_{m,123}$ calculated from Equation 3.13 using $H^E_{m,23}$ provided by Marsh *et al.*(1980).

x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}
			$x_2/(1-x_1-x_2)=0.3477$, $H^E_{m,23}$/(J·mol^{-1})=11.8					
0.0500	83.4	94.6	0.4004	441.3	448.3	0.6997	417.7	421.2
0.0500	82.3	93.5	0.4500	459.2	465.6	0.7500	377.9	380.8
0.1000	155.2	165.8	0.5000	469.6	475.4	0.8002	328.4	330.7
0.1499	223.6	233.6	0.5502	471.0	476.3	0.8501	266.5	268.3
0.1999	284.6	294.0	0.6007	463.0	467.7	0.9007	191.6	192.8
0.2999	380.6	388.9	0.6502	446.7	450.8	0.9500	102.2	102.8
0.3515	415.1	422.7						
			$x_2/(1-x_1-x_2)=0.9984$, $H^E_{m,23}$/(J·mol^{-1})=14.4					
0.0397	61.6	75.3	0.3438	388.1	397.5	0.6467	417.3	422.4
0.0398	64.8	78.6	0.3933	413.1	421.8	0.7029	385.2	389.5
0.1218	178.7	191.3	0.4402	427.7	435.7	0.7587	342.8	346..3
0.1642	231.7	243.7	0.4901	439.3	446.7	0.8167	284.2	286.8
0.2073	278.4	289.8	0.5412	442.2	448.8	0.8761	209.4	211.2
0.2519	322.5	333.2	0.5932	433.8	439.6	0.9372	114.9	115.8
0.2975	357.2	367.3	0.6465	416.1	421.1			
			$x_2/(1-x_1-x_2)=3.1408$, $H^E_{m,23}$/(J·mol^{-1})=9.3					
0.0397	59.9	68.8	0.3915	385.6	391.2	0.7027	349.8	352.6
0.0804	119.0	127.5	0.4402	393.7	398.9	0.7588	305.4	307.6
0.1217	173.8	181.9	0.4901	407.1	411.8	0.8168	252.8	254.5
0.1644	221.9	229.6	0.5408	400.7	405.0	0.8762	184.4	185.5
0.2520	306.8	313.7	0.5934	396.7	400.4	0.9373	100.6	101.2
0.2987	332.5	339.0	0.6472	374.5	377.8	0.9374	100.1	100.7
0.3440	356.6	362.7						

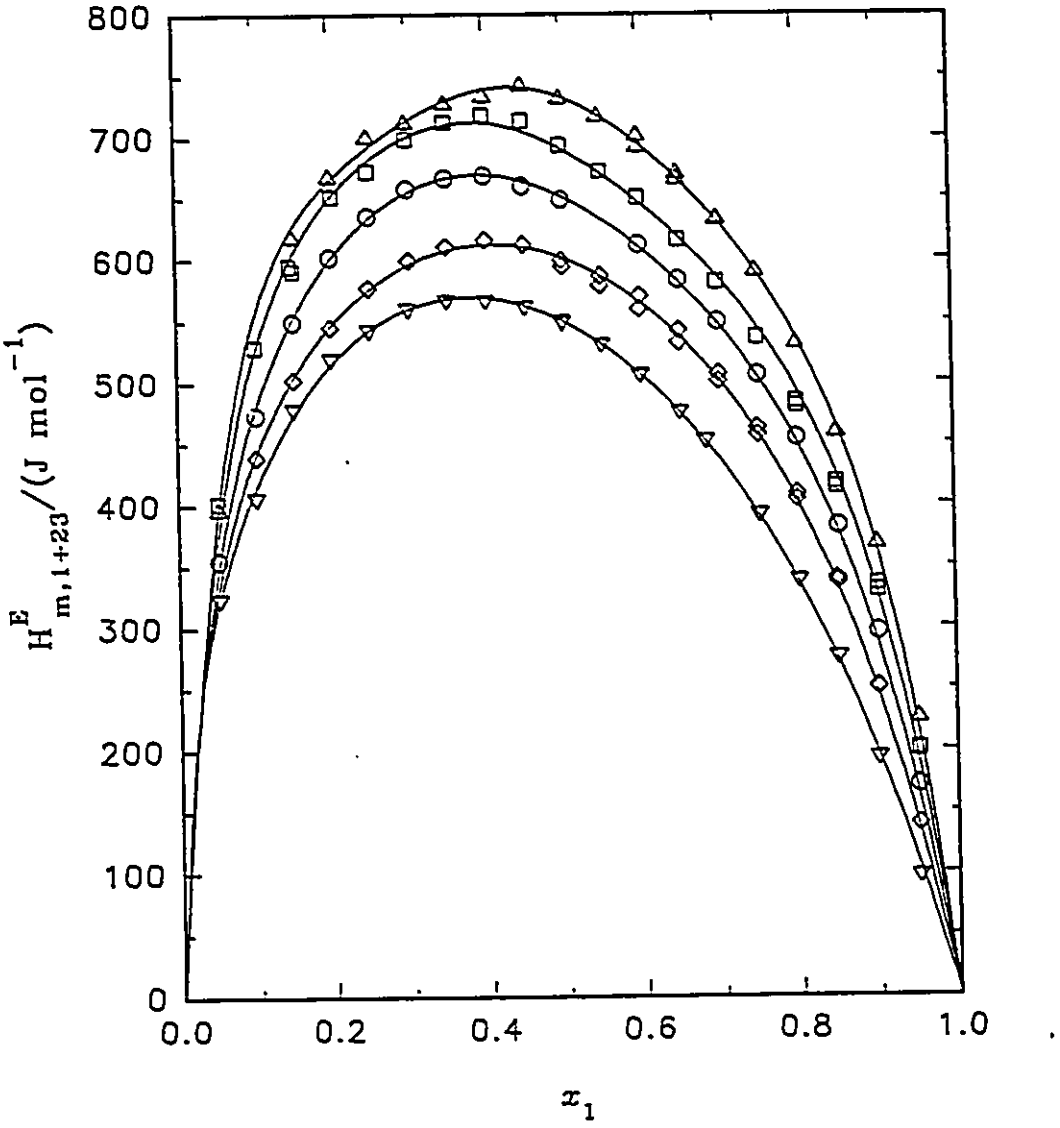
Table A-55 Experimental excess molar enthalpies $H^E_{m,1+23}$ for the addition of MTBE to (n-hexane+ n-dodecane) to form $\{x_1(\text{MTBE})+x_2(\text{n-hexane})+x_3(\text{n-dodecane})\}$ and values of $H^E_{m,123}$ calculated from Equation 3.13 using $H^E_{m,23}$ provided by Ott *et al.*(1981).

x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	$H^E_{m,1+23}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}
			$x_2/(1-x_1-x_2)=0.3738$, $H^E_{m,23}/(\text{J·mol}^{-1})=32.3$					
0.0500	89.1	119.8	0.3502	457.1	478.1	0.7003	472.5	482.2
0.0500	88.2	118.9	0.4015	485.2	504.5	0.7499	432.0	440.1
0.1002	177.0	206.0	0.4503	501.5	519.3	0.8002	378.2	384.7
0.1501	243.7	271.1	0.4999	515.8	531.9	0.8500	306.6	311.4
0.2000	308.9	334.8	0.5501	520.8	535.4	0.9000	224.0	227.3
0.2500	368.6	392.9	0.5999	515.5	528.4	0.9499	118.3	120.0
0.2998	418.8	441.4	0.6505	499.3	510.6			
			$x_2/(1-x_1-x_2)=0.9845$, $H^E_{m,23}/(\text{J·mol}^{-1})=39.5$					
0.0397	69.6	107.5	0.2982	381.0	408.7	0.6483	452.7	466.6
0.0805	131.7	168.0	0.3460	412.6	438.4	0.7028	421.0	432.7
0.1221	188.6	223.3	0.3923	439.5	463.5	0.7597	375.3	384.8
0.1646	242.8	275.8	0.4405	463.4	485.5	0.8173	314.4	321.6
0.2079	293.5	324.8	0.5414	475.2	493.3	0.8765	231.2	236.1
0.2524	343.2	372.7	0.5680	474.1	491.2	0.9374	128.8	131.2
			$x_2/(1-x_1-x_2)=2.8956$, $H^E_{m,23}/(\text{J·mol}^{-1})=28.1$					
0.0500	74.3	101.0	0.3505	386.3	404.6	0.6999	373.6	328.1
0.0500	76.5	103.1	0.3999	409.7	426.5	0.7505	335.1	342.1
0.1000	146.2	171.5	0.4501	419.9	435.3	0.8000	290.1	295.7
0.1501	206.2	230.1	0.4995	427.3	441.4	0.8500	233.7	238.0
0.2002	256.6	279.1	0.5499	423.4	436.1	0.9007	167.8	170.5
0.2499	307.0	328.1	0.6001	414.5	425.7	0.9502	87.7	89.0
0.2972	349.7	369.5	0.6597	398.8	408.6	0.9502	88.0	89.4



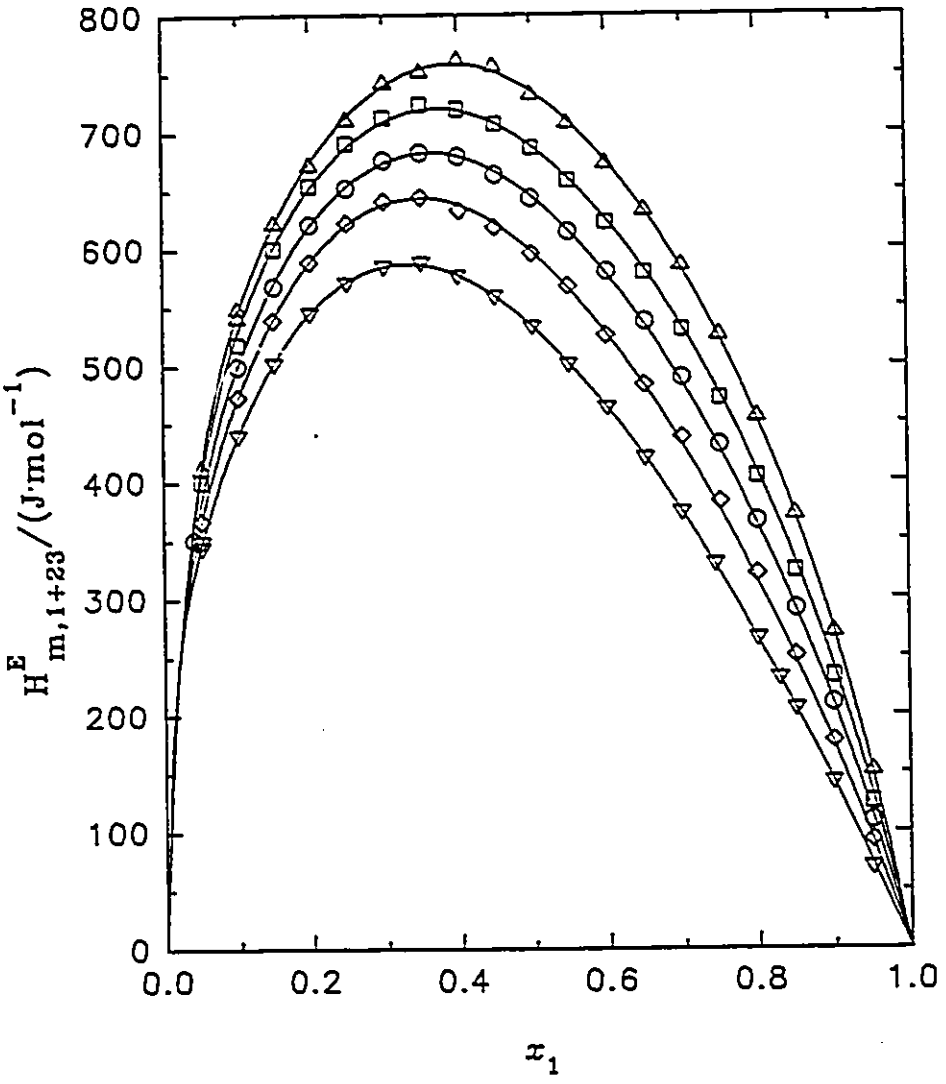
Experimental results: ▽, $x_1+x_2=1$; ◇, $x_2/(1-x_1-x_2)=2.9841$; ○, $x_2/(1-x_1-x_2)=0.9912$; □, $x_2/(1-x_1-x_2)=0.3339$; △, $x_2=0$. Curves: ——, calculated from the representation of the results by Equations 4.20 and 4.21.

Figure A-3 Excess molar enthalpies $H^E_{m,1+23}$ of x_1(ethanol)+x_2(n-hexane)+x_3(n-decane) at 298.15 K



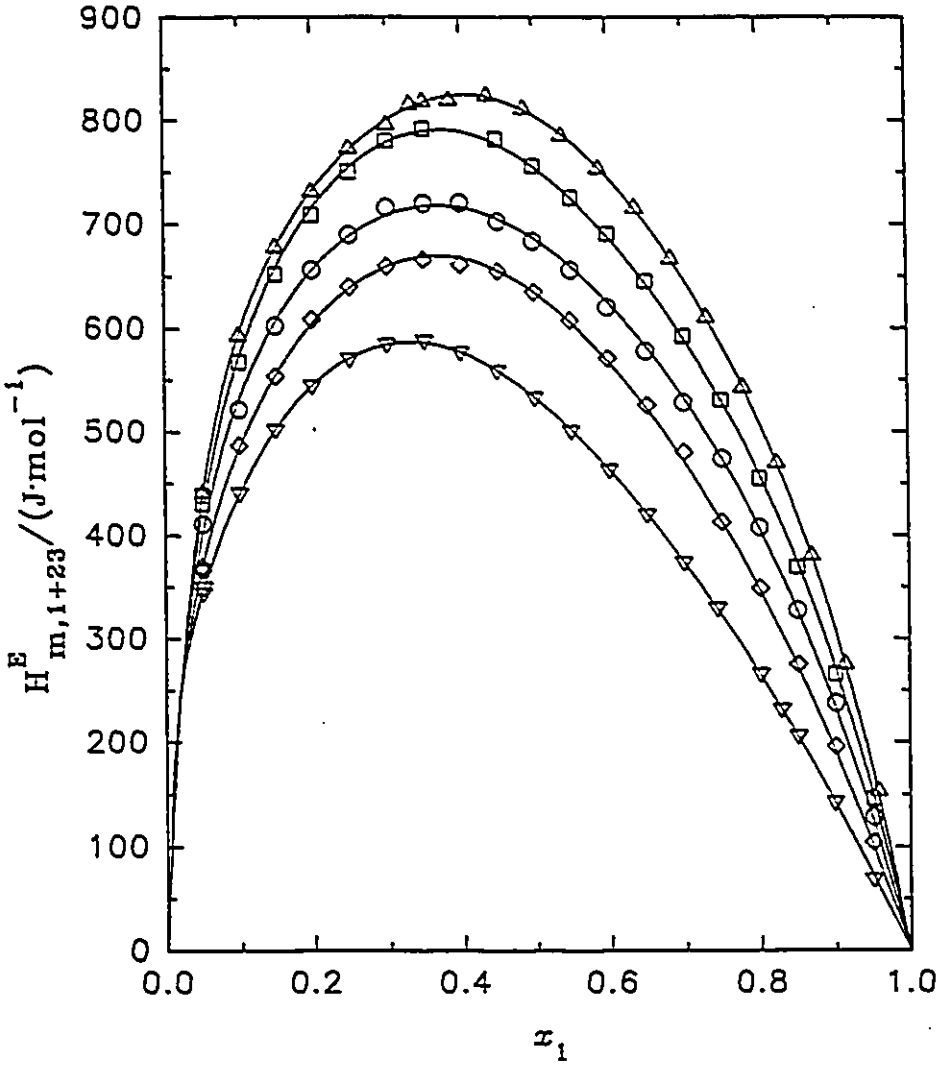
Experimental results: ▽, $x_1+x_2=1$; ◇, $x_2/(1-x_1-x_2)=2.9526$; ○, $x_2/(1-x_1-x_2)=1.0296$; □, $x_2/(1-x_1-x_2)=0.3328$; △, $x_2=0$. Curves: ——, calculated from the representation of the results by Equations 4.20 and 4.21.

Figure A-4 Excess molar enthalpies $H^E_{m,1+23}$ of x_1(ethanol)+x_2(n-hexane)+x_3(n-dodecane) at 298.15 K



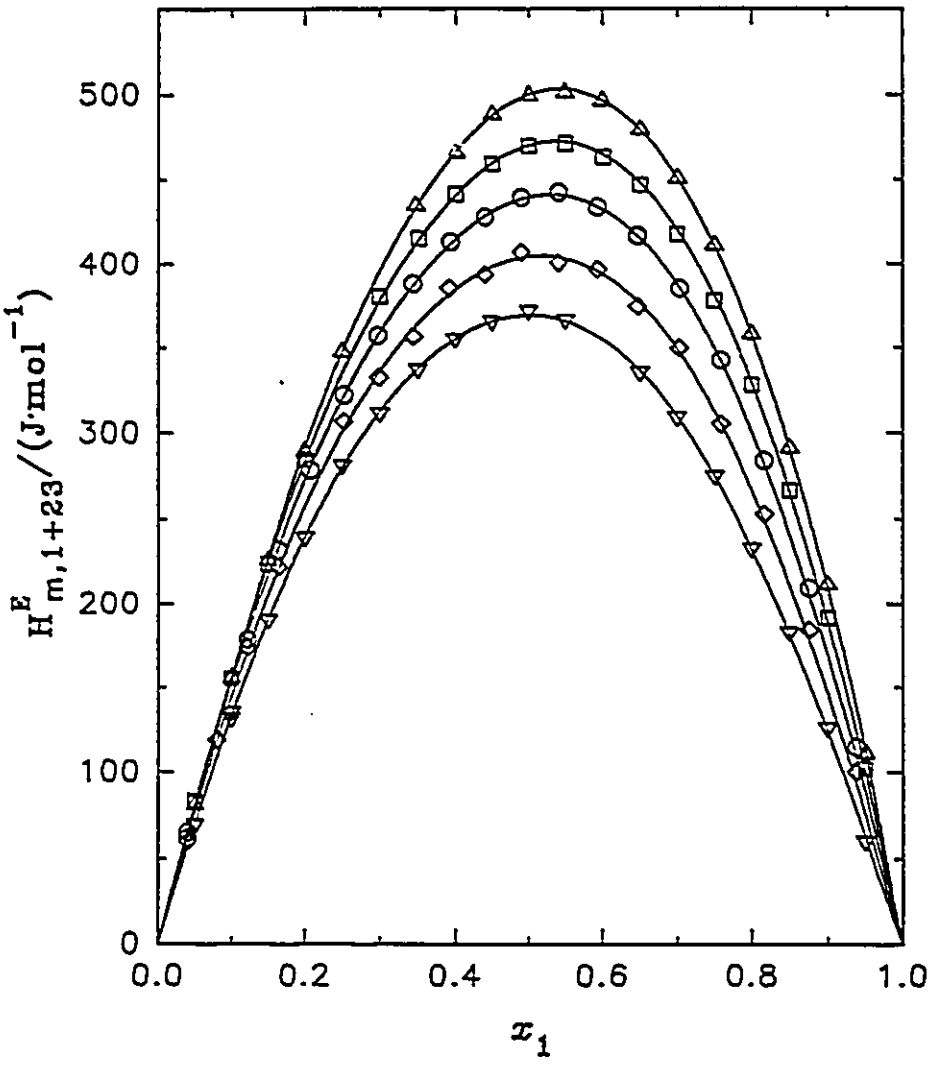
Experimental results: ▽, $x_1+x_2=1$; ◇, $x_2/(1-x_1-x_2)=3.1408$; ○, $x_2/(1-x_1-x_2)=0.9912$; □, $x_2/(1-x_1-x_2)=0.3284$; △, $x_2=0$. Curves: ——, calculated from the representation of the results by Equations 4.20 and 4.21.

Figure A-5 Excess molar enthalpies $H^E_{m,1+23}$ of x_1(1-propanol)+x_2(n-hexane)+x_3(n-decane) at 298.15 K



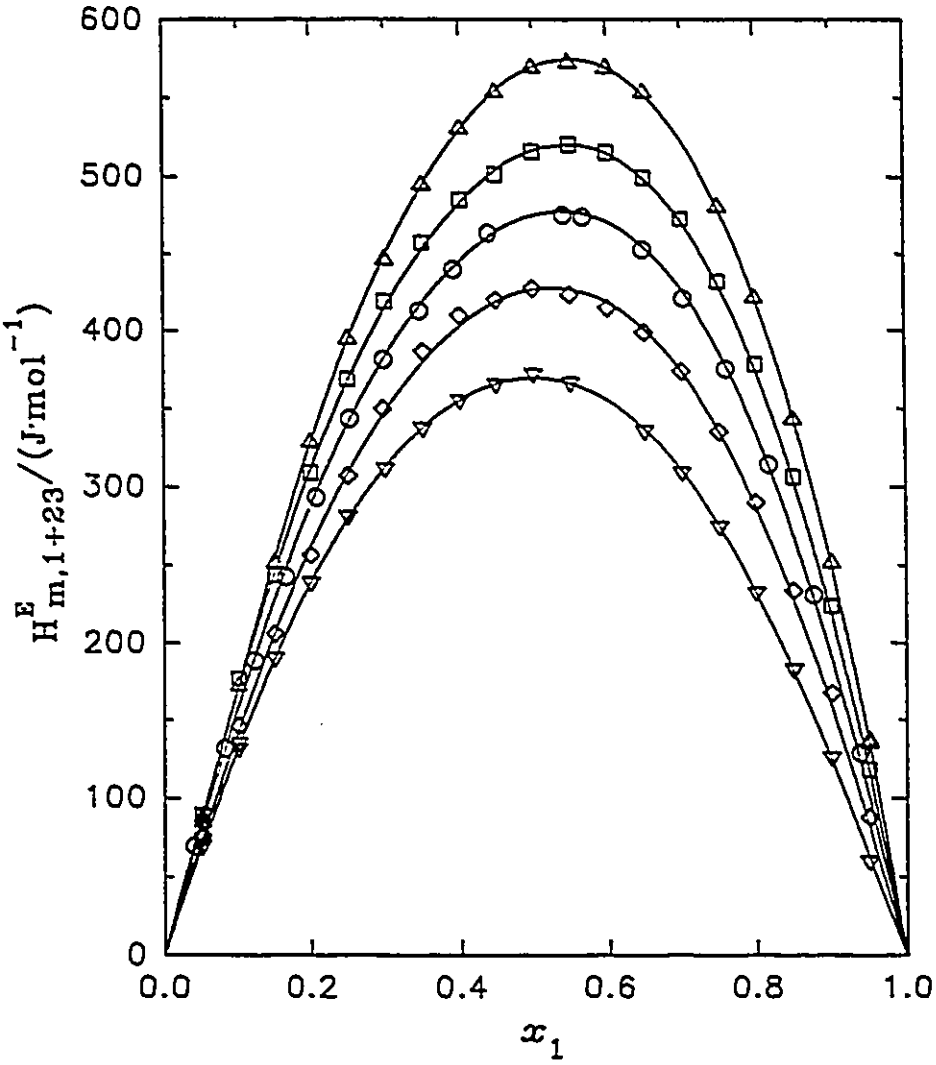
Experimental results: ▽, $x_1+x_2=1$; ◇, $x_2/(1-x_1-x_2)=2.8956$; ○, $x_2/(1-x_1-x_2)=0.9845$; □, $x_2/(1-x_1-x_2)=0.3328$; △, $x_2=0$. Curves: ——, calculated from the representation of the results by Equations 4.20 and 4.21.

Figure A-6 Excess molar enthalpies $H^E_{m,1+23}$ of x_1(1-propanol) + x_2(n-hexane) + x_3(n-dodecane) at 298.15 K



Experimental results: ▽, $x_1+x_2=1$; ◇, $x_2/(1-x_1-x_2)=3.1408$; ○, $x_2/(1-x_1-x_2)=0.9984$; □, $x_2/(1-x_1-x_2)=0.3477$; △, $x_2=0$. Curves: ——, calculated from the representation of the results by Equations 4.20 and 4.21.

Figure A-7 Excess molar enthalpies $H^E_{m,1+23}$ of x_1(MTBE)+x_2(hexane)+x_3(n-decane) at 298.15 K



Experimental results: ▽, $x_1+x_2=1$; ◇, $x_2/(1-x_1-x_2)=2.8956$; ○, $x_2/(1-x_1-x_2)=0.9845$; □, $x_2/(1-x_1-x_2)=0.3738$; △, $x_2=0$. Curves: ——, calculated from the representation of the results by Equations 4.20 and 4.21.

Figure A-8 Excess molar enthalpies $H^E_{m,1+23}$ of x_1(MTBE)+x_2(n-hexane)+x_3(n-dodecane) at 298.15 K

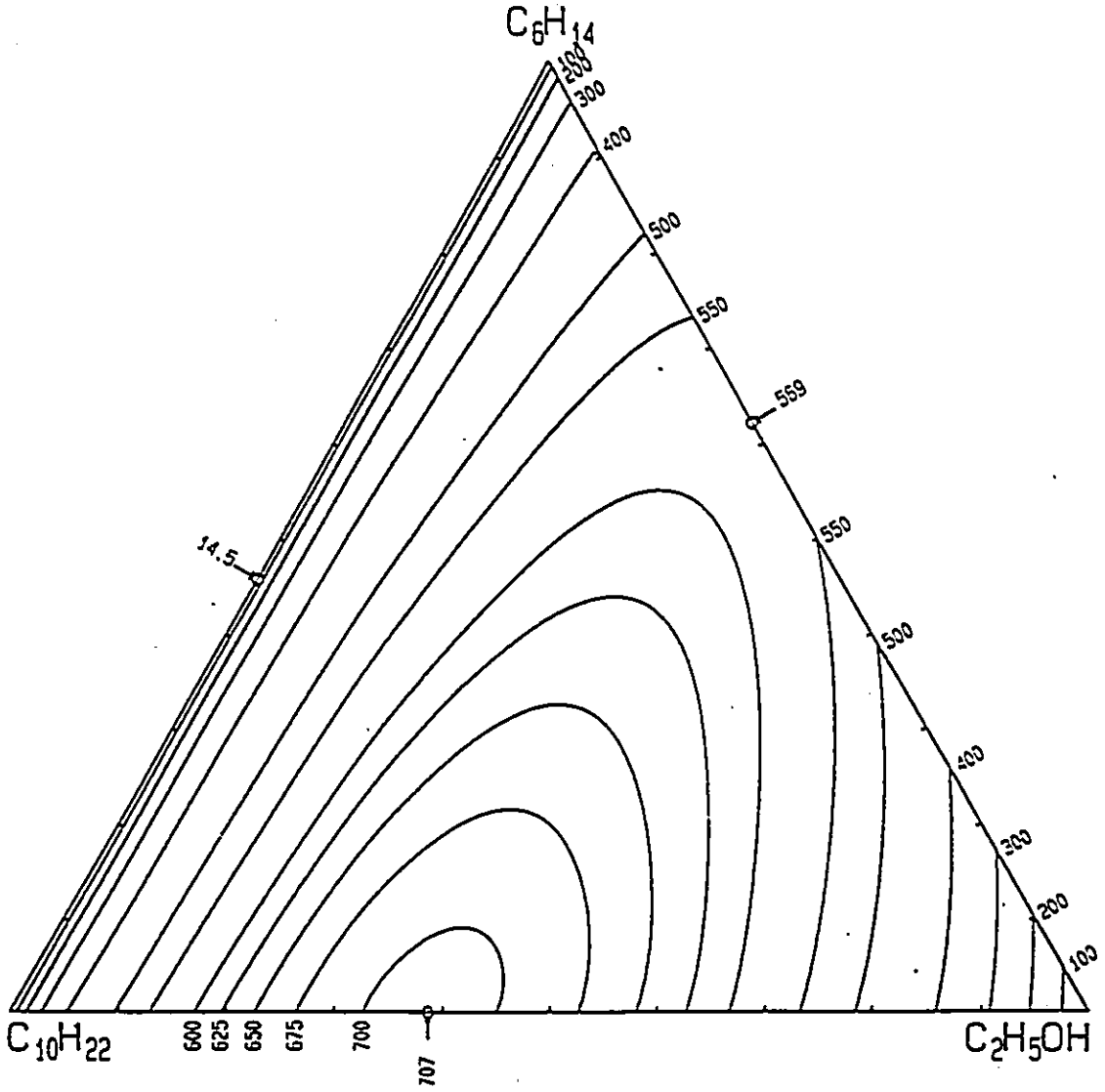


Figure A-9 Contours for constant values of $H^{E}_{m,123}/(J \cdot mol^{-1})$ for $\{x_1C_2H_5OH + x_2CH_3(CH_2)_4CH_3 + x_3CH_3(CH_2)_8CH_3\}$, calculated from the representation of the experimental results by Equations 4.20 and 4.21.

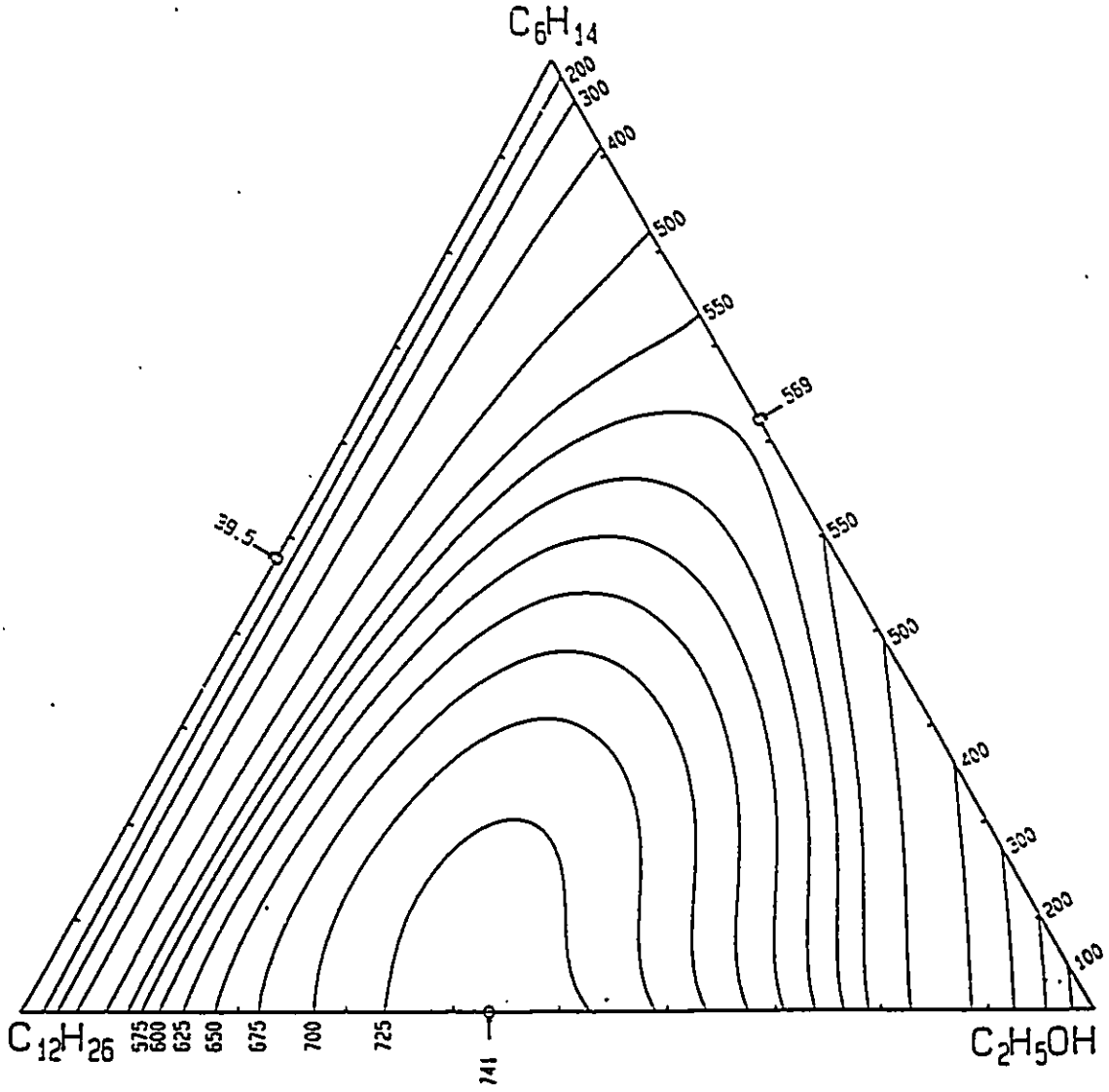


Figure A-10 Contours for constant values of $H^{E}_{m,123}/(J \cdot mol^{-1})$ for $\{x_1C_2H_5OH + x_2CH_3(CH_2)_4CH_3 + x_3CH_3(CH_2)_{10}CH_3\}$, calculated from the representation of the experimental results by Equations 4.20 and 4.21.

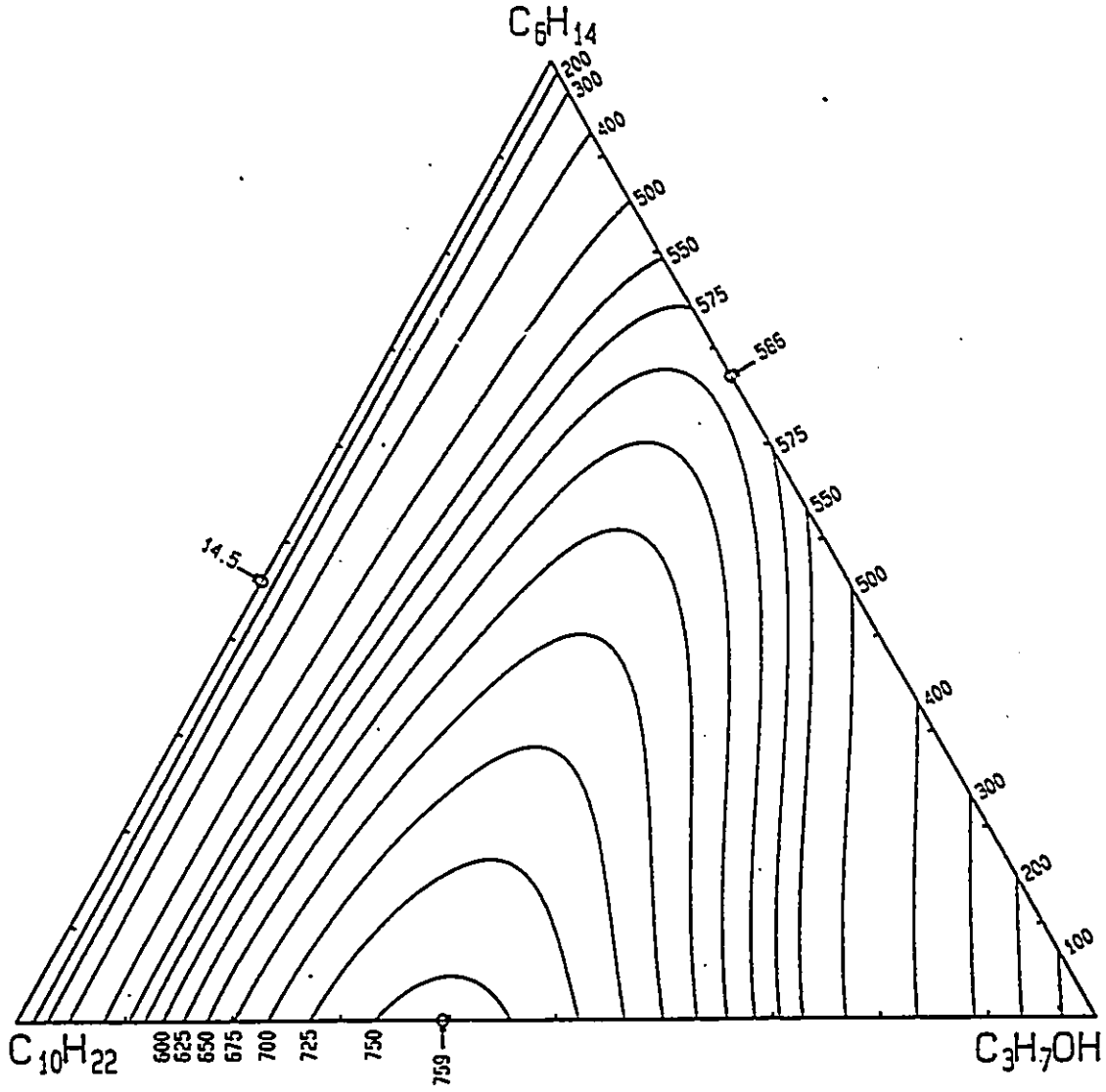


Figure A-11 Contours for constant values of $H^{E}_{m,123}/(J \cdot mol^{-1})$ for $\{x_1C_3H_7OH + x_2CH_3(CH_2)_4CH_3 + x_3CH_3(CH_2)_8CH_3\}$, calculated from the representation of the experimental results by Equations 4.20 and 4.21.

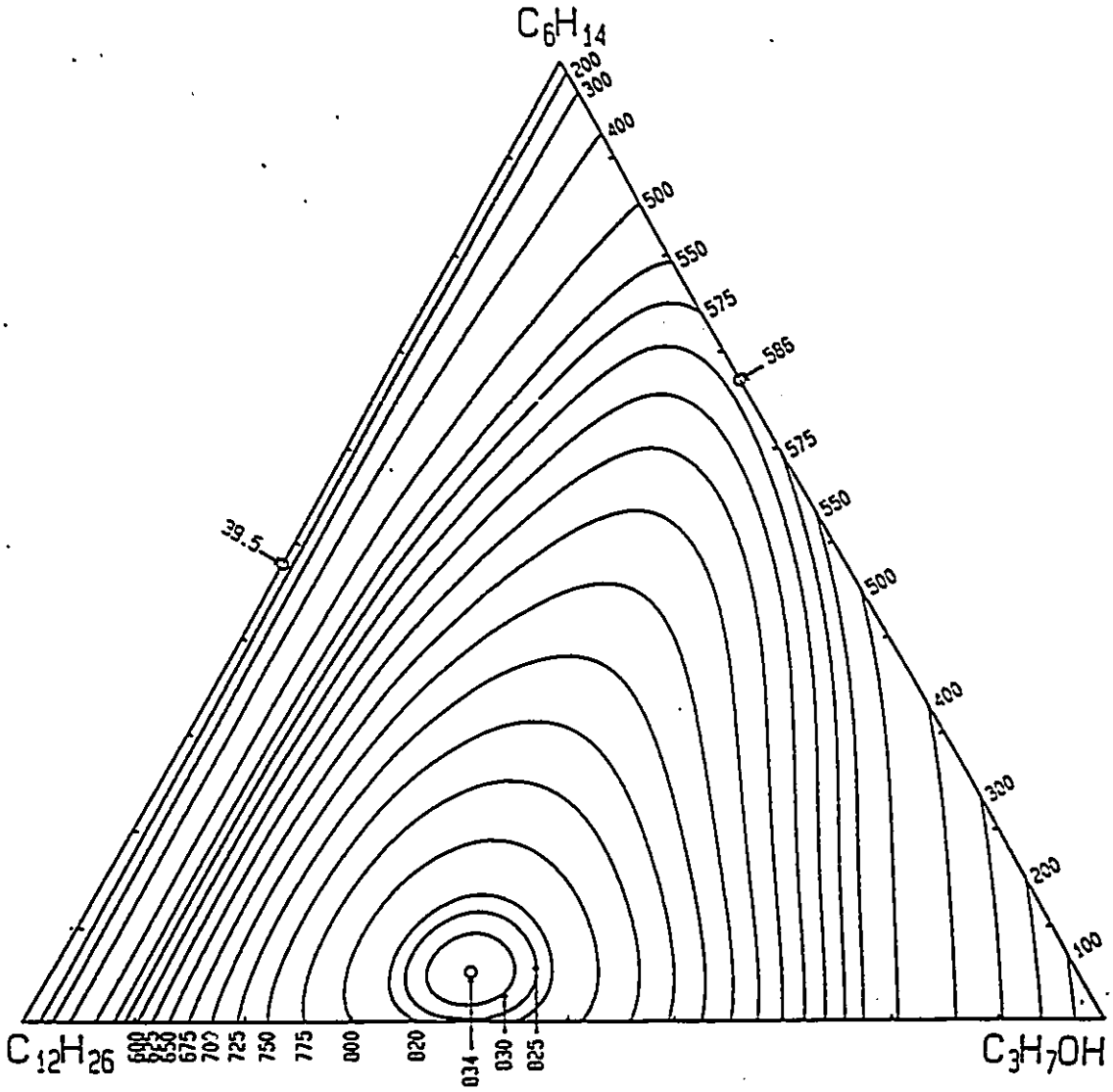


Figure A-12 Contours for constant values of $H^{E}_{m,123}/(J \cdot mol^{-1})$ for $\{x_1C_3H_7OH + x_2CH_3(CH_2)_4CH_3 + x_3CH_3(CH_2)_{10}CH_3\}$, calculated from the representation of the experimental results by Equations 4.20 and 4.21.

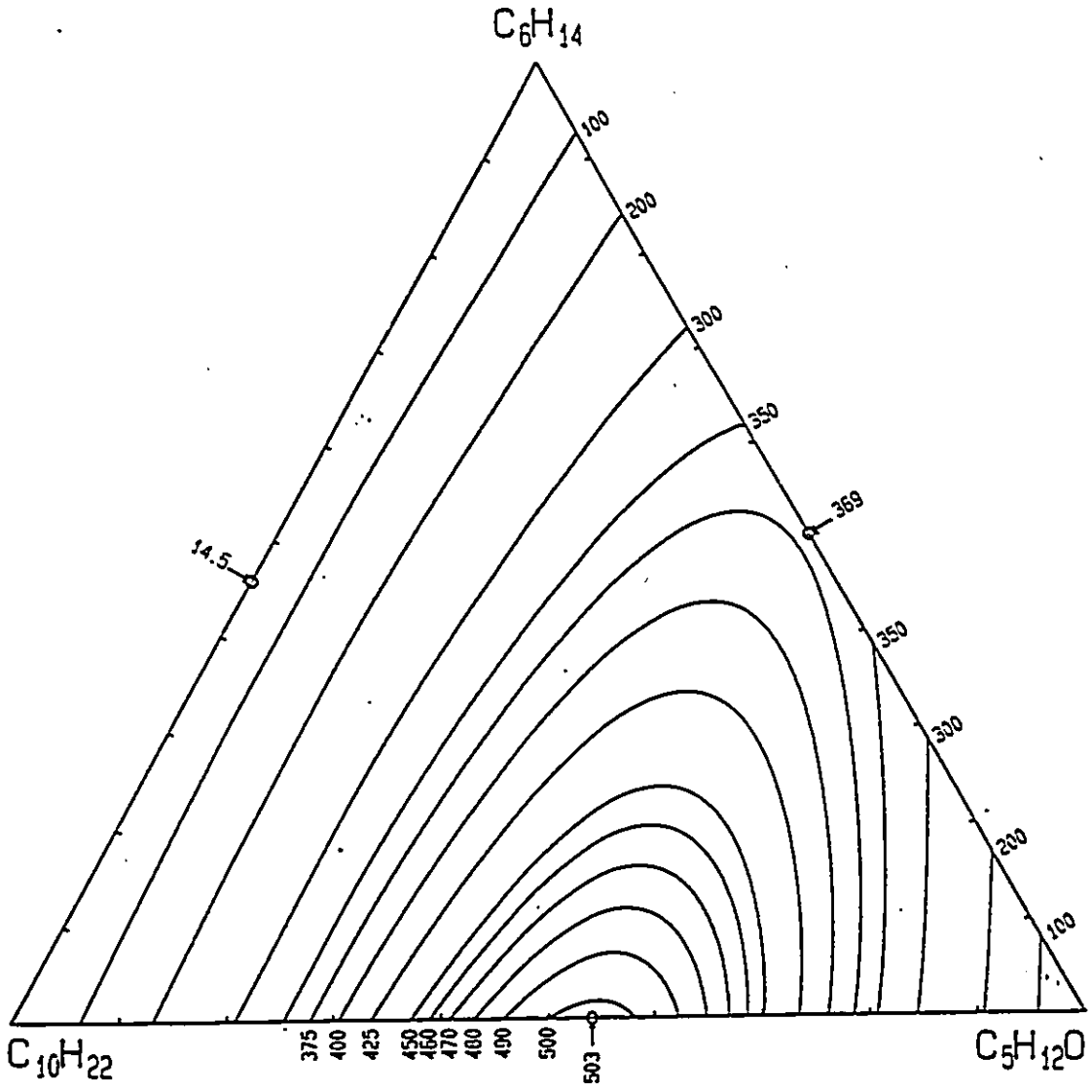


Figure A-13 Contours for constant values of $H^{E}_{m,123}/(J \cdot mol^{-1})$ for $\{x_1C_5H_{12}O + x_2CH_3(CH_2)_4CH_3 + x_3CH_3(CH_2)_8CH_3\}$, calculated from the representation of the experimental results by Equations 4.20 and 4.21.

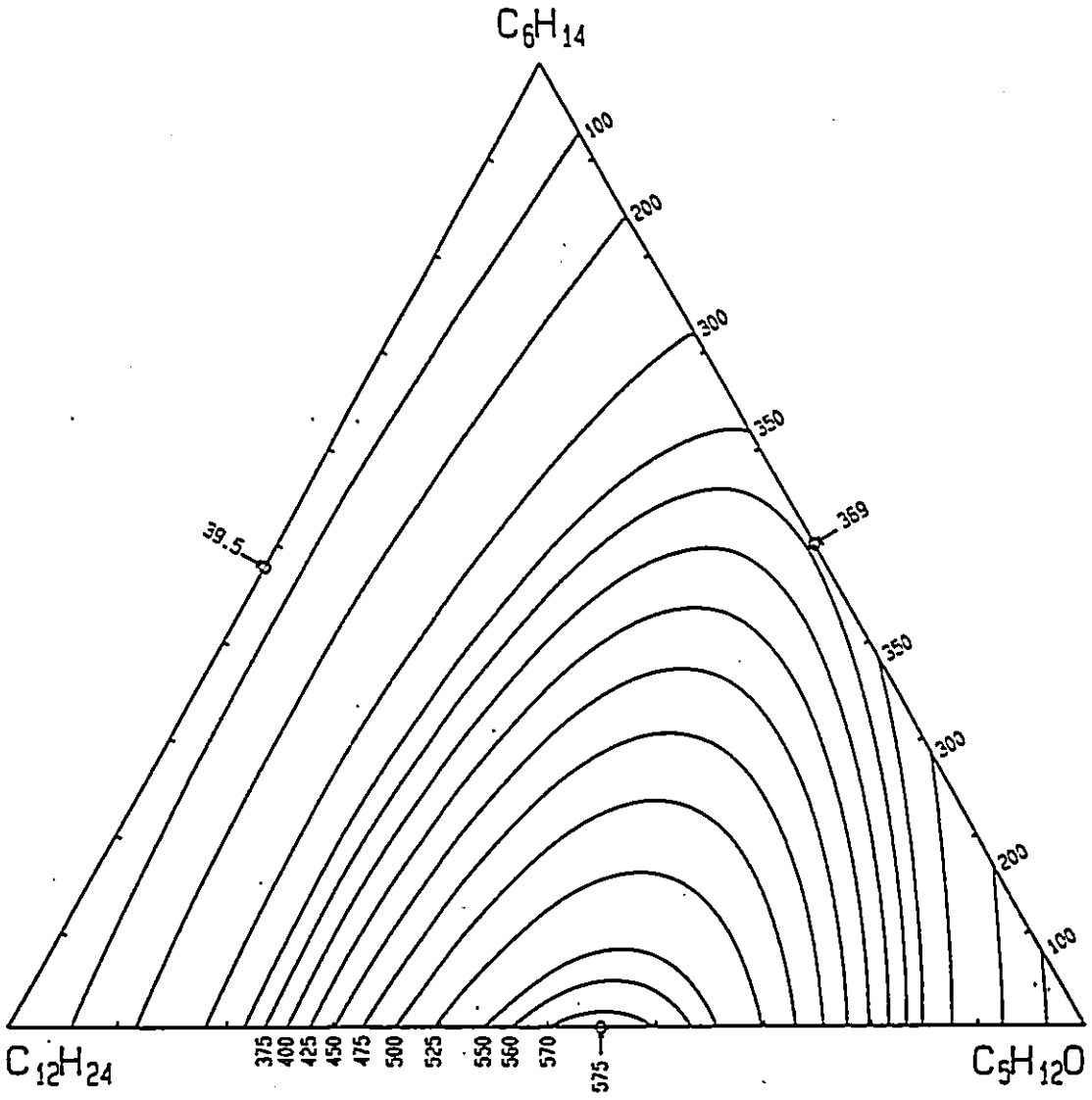


Figure A-14 Contours for constant values of $H^{E}_{m,123}/(J \cdot mol^{-1})$ for $\{x_1C_5H_{12}O + x_2CH_3(CH_2)_4CH_3 + x_3CH_3(CH_2)_{10}CH_3\}$, calculated from the representation of the experimental results by Equations 4.20 and 4.21.

Appendix B

Correction of weight to vacuum

For weighing of liquid L, according to Bauer (1952), the basic formula for obtaining the true ("vacuum-corrected") weight W_L from the weights W_{obs} which are needed to balance the liquid of volume V_L should be expressed by

$$W_L = W_{obs} + V_L d_{air} - V_w d_{air} \qquad \text{(B-1)}$$

where $V_w = W_{obs}/d_w$ is the volume occupied by the W_{obs} weights consisting of a material having a density d_w; d_{air} is the density of air at the time and place of weighing. The Mettler analytical balance employed in this study uses steel weights, but manufacturer has calibrated it to give readings which correspond to using brass weights. Therefore, in our case, d_w is the density of brass which has a value of 8.4 $g \cdot cm^{-3}$.

Rearranging Equation B-1 yields

$$W_L\left(1 - \frac{d_{air}}{d_L}\right) = W_{obs}\left(1 - \frac{d_{air}}{d_w}\right) \qquad \text{(B-2)}$$

or

$$W_L = W_{obs}\left(1-\frac{d_{air}}{d_w}\right)/\left(1-\frac{d_{air}}{d_L}\right) \qquad \text{(B-3)}$$

The density of air, d_{air}, was determined by means of the following equation (Bauer, 1952)

$$d_{air} = \frac{0.001293(P-k)}{(1+0.00367t)760} = \frac{1.701\times10^{-6}(P-k)}{1+0.00367t} \qquad \text{(B-4)}$$

where P and t are the pressure (mmHg) and temperature (°C) at the balance room condition; k is a parameter related to moisture content in the air,

$$k = 0.0038H\ p^t_{H_2O} \qquad \text{(B-5)}$$

where H is the relative humidity (%) at the same condition and p^t_{H2O} represents the vapour pressure of water at temperature of t, which can be obtained by using Antoine equation

$$\log_{10}(P^t_{H_2O}/mmHg) = A-\frac{B}{C+t(°C)} \qquad \text{(B-6)}$$

with the parameters, A=8.184254, B=1791.3, and C=238.1, taken from the literature (Riddick *et al.*, 1986).

Appendix C

Determination of the mixture densities

Considering a binary mixture of components 2 and 3, the density of the mixture, d_m, is expressed in terms of its molecular weight, M_m, and its molar volume, v_m:

$$d_m = \frac{M_m}{v_m} \qquad (C\text{-}1)$$

where

$$M_m = \sum x_i^b M_i = x_2^b M_2 + x_3^b M_3 \qquad (C\text{-}2)$$

and

$$v_m = \sum x_i^b M_i / d_i + V_m^E = \frac{x_2^b M_2}{d_2} + \frac{x_3^b M_3}{d_3} + V_m^E \qquad (C\text{-}3)$$

In above equations, x_i^b is the mole fraction of the component i in the mixture; M_i and d_i are the molecular weight and density of pure component i, respectively; and V_m^E is the

molar excess volume of the mixture.

At constant temperature and pressure, molar excess volume V_m^E is a function of the materials involved, and can be expressed by means of the Redlich-Kister formula as

$$V_m^E = x_i x_{i+1} \sum_{j=1}^{n} \nu_j (x_{i+1} - x_i)^{j-1} \qquad \text{(C-4)}$$

or in our case

$$V_m^E = x_2^b x_3^b \sum_{j=1}^{n} \nu_j (x_3^b - x_2^b)^{j-1} \qquad \text{(C-5)}$$

For the binary mixtures of (n-hexane + n-decane/n-dodecane), the equation coefficients, ν_j, were taken from the literature (Marsh and Ott, 1983 a,b) and listed in Table C-1.

Table C-1 Coefficients of the Redlich-Kister representations of molar excess volume V_m^E

Binary system	ν_1	ν_2	ν_3	ν_4
n-hexane + n-decane	-0.9005	-0.2715	-0.0780	-
n-hexane + n-dodecane	-1.4035	0.5563	-0.2195	0.0624

Appendix D

H^E calculations by the proposed model

This section contains two computer programs in the FORTRAN language. They were used in this study for H^E calculations by means of the proposed model, as well as the UNIQUAC and NRTL models for the purpose of comparison.

The first program (p228-236) was used to correlate the excess enthalpy data for binary systems. The second program (p237-245) was for the prediction of ternary H^E values. There is a switch parameter called "ICO", which was designed to allow the program to have two different functions. When ICO=0, the program would calculate ternary H^E values from given binary parameters, which means a calculation for predicting ternary H^E values. When ICO=1, all the given binary parameters would serve as initial values in order to generate parameter values for the ternary H^E representation, which means a calculation for ternary H^E correlation.

All the calculations included in this section were carried out in main-frame environment. The FORTRAN programs presented here were run in a CMS system.

```
C     ******************************************************
C       THIS PROGRAM IS USED TO CORRELATE THE EXCESS
C              ENTHALPY DATA FOR BINARY SYSTEMS
C           WITH DIFFERENT SOLUTION THEORY MODELS
C     ******************************************************
C
C     AAD - AVERAGE ABSOLUTE DEVIATION
C     ARD - AVERAGE RELATIVE DEVIATION
C     IC - SWITCH PARAMETER
C       IC = 1, THIS WORK
C       IC = 2, UNIQUAC MODEL
C       IC = 3, NRTL MODEL
C       IC = 4, PURE EMPIRICAL EXPRESSION FROM CHRISTENSEN
C     HE - EXPERIMENTAL EXCESS ENTHALPY DATA, HE(EXP)
C     HEC - EXCESS ENTHALPY VALUES FROM CORRELATION, HE(CAL)
C     N - NUMBER OF PARAMETERS
C     NP - NUMBER OF DATA POINTS IN DATA SST
C     NS - NUMBER OF DATA SETS (UP TO 10)
C     RMSH - ROOT MEAN SQUARE
C     RM,Q,V - MOLECULAR VOLUME PARAMETER, MOLECULAR AREA PARAMETER,
C              AND VOLUME OF SATURATED LIQUID AT 20 C, RESPECTIVELY
C     X(N) - ADJUSTABLE PARAMETERS
C     X1,X2 - MOLE FRACTIONS OF COMPONENT 1 AND 2, RESPECTIVELY
C
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER*70 AAA
      CHARACTER*70 BBB
      DIMENSION X(10),G(10),H(10),DX(10),OLDX(10),FP(40),FM(40),F(40),
     1 DFDX(40,10),AA(10,10),XH(10),XL(10)
      DIMENSION AAD(10),ARD(10),RMSH(10)
      DIMENSION XO(10,10),HO(10,10),XHO(10,10),XLO(10,10)
      EXTERNAL FUN
      COMMON /DATA1/R1,R2,Q1,Q2,V1,V2,R
      COMMON /DATA2/X1(10,40),HE(10,40)
      COMMON /DATA3/NP(10),T(10),X2(10,40)
      COMMON /DATA4/NS
      COMMON /RESULT/HEC(10,40),FF(10,40)
      COMMON /SWITCH/IC,I,ICO(10)
      COMMON P3
      LDER=0
      EPS=1.D-10
      READ(5,*)NSYS
```

```
      DO 999 INSYS=1,NSYS
      WRITE(6,*)INSYS
      READ(5,*)AAA
C     THE NAME OF THE BINARY SYSTEM
      READ(5,*)BBB
C     DATA SOURCE
      READ(5,*)R1,Q1,V1,R2,Q2,V2
C     THE PARAMETERS OF PURE SUBSTANCES
      READ(5,*)NS
C     THE NUMBER OF DATA SET
      NPSUM=0
      DO 10 I=1,NS
      READ(5,*)T(I),NP(I)
      NPSUM=NPSUM+NP(I)
      DO 11 J=1,NP(I)
      READ(5,*)X1(I,J),HE(I,J)
      X2(I,J)=1.-X1(I,J)
   11 CONTINUE
   10 CONTINUE
      IC=1
C     DO 20 IC=1,4
      READ(5,*)N
C     THE NUMBER OF ADJUSTABLE PARAMETERS
      DO 30 I=1,N
      READ(5,*)XO(IC,I),ICO(I)
   30 CONTINUE
C  20 CONTINUE
      R=8.314
      WRITE(6,*)AAA
      WRITE(6,*)BBB
      WRITE(6,*)'THE PARAMETERS FOR THE MODEL OF'
      IC=1
C     DO 50 IC=1,4
      DO 55 J=1,N
      X(J)=XO(IC,J)
   55 CONTINUE
      CALL MARQS(N,NPSUM,FUN,X,ICO,F,EPS)
      WRITE(6,*)IC
      DO 40 I=1,NS
      WRITE(6,100)(X(M),M=1,N)
  100 FORMAT(2X,3G14.7)
      WRITE(6,*)' THE TOTAL OBJECTIVE FUNCTION =  ',P3
      WRITE(6,*)
```

```
      WRITE(6,200)T(I),NP(I)
200   FORMAT(2X,'T=',G10.5,'K',4X,'NP=',I2)
      WRITE(6,*)
      WRITE(6,300)
300   FORMAT(7X,'X1',13X,'HE',11X,'HEC',10X,'HE-HEC',8X,'1-HEC/HE')
      AADS=0.
      ARDS=0.
      RMSHS=0.
      DO 80 J=1,NP(I)
      DHE=HE(I,J)-HEC(I,J)
      AADS=AADS+DABS(DHE)
      RATIO=HEC(I,J)/HE(I,J)
      ARDS=ARDS+DABS(1.-RATIO)
      RMSHS=RMSHS+(HE(I,J)-HEC(I,J))**2
      WRITE(6,500)X1(I,J),HE(I,J),HEC(I,J),DHE,1.-RATIO
500   FORMAT(2X,5G14.7)
   80 CONTINUE
      AAD(I)=AADS/NP(I)
      ARD(I)=ARDS/NP(I)
      RMSH(I)=DSQRT(RMSHS)/(NP(I)-N)
      WRITE(7,400)AAD(I),ARD(I),RMSH(I)
      WRITE(6,400)AAD(I),ARD(I),RMSH(I)
400   FORMAT(2X,'AAD=',G14.7,'ARD=',G12.7,3X,'RMSH=',G12.7)
      WRITE(7,*)'KEY = ',KEY
      WRITE(6,*)'KEY = ',KEY
C  50 CONTINUE
 40   CONTINUE
 999  CONTINUE
      STOP
      END

      SUBROUTINE FUN(N,M,X,F)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION X(N),F(M)
      COMMON /DATA1/R1,R2,Q1,Q2,V1,V2,R
      COMMON /DATA2/X1(10,40),HE(10,40)
      COMMON /DATA3/NP(10),T(10),X2(10,40)
      COMMON /DATA4/NS
      COMMON /RESULT/HEC(10,40),FF(10,40)
      COMMON /SWITCH/IC,I,ICO(10)
      DO 30 I=1,NS
      DO 10 J=1,NP(I)
      GOTO(61,62,63,64),IC
```

```
  61  CONTINUE
C     THIS MODEL
      R12=0.5*(V1+V2)
      R21=R12
      HEC(I,J)=5.*X1(I,J)*X2(I,J)*(X(1)*(R21/V1)*DEXP(-X(1)*X(3)/R/T(I
     1 /(X1(I,J)+X2(I,J)*(R21/V1)*DEXP(-X(1)*X(3)/R/T(I)))+X(2)*(R12/V
     2 *DEXP(-X(2)*X(3)/R/T(I))/(X2(I,J)+X1(I,J)*(R12/V2)*
     3 DEXP(-X(2)*X(3)/R/T(I))))
C     WRITE(7,*)X1(I,J),HE(I,J),HEC(I,J)
      GOTO 70
  62  CONTINUE
C     UNIQUAC MODEL
      TAO21=DEXP(-X(1)/R/T(I))
      TAO12=DEXP(-X(2)/R/T(I))
      THETA1=X1(I,J)*Q1/(X1(I,J)*R1+X2(I,J)*Q2)
      THETA2=X2(I,J)*Q2/(X1(I,J)*Q1+X2(I,J)*Q2)
      HEC(I,J)=X1(I,J)*Q1*THETA2*TAO21/(THETA1+THETA2*TAO21)*X(1)
     1 +X2(I,J)*Q2*THETA1*TAO12/(THETA2+THETA1*TAO12)*X(2)
      GOTO 70
  63  CONTINUE
C     NRTL MODEL
      TAO21=X(1)/R/T(I)
      TAO12=X(2)/R/T(I)
      G21=DEXP(-X(3)*TAO21)
      G12=DEXP(-X(3)*TAO12)
      HEC(I,J)=R*T(I)*X1(I,J)*X2(I,J)*(G21*TAO21/(X1(I,J)+G21*X2(I,J))
     1  G12*TAO12/
     1  (X2(I,J)+G12*X1(I,J))-X(3)*(G21*X1(I,J)*TAO21**2/(X1(I,J)+
     2  G21*X2(I,J))**2+G12*X2(I,J)*TAO12**2/(X2(I,J)+G12*X1(I,J))**2)
      GOTO 70
  64  CONTINUE
C     PURE EMPIRICAL EXPRESSION FROM CHRISTENSEN
      Z=1.-2.*X1(I,J)
      HEC(I,J)=X1(I,J)*X2(I,J)*(X(1)+X(2)*Z+X(3)*Z**2)/(1.+X(4)*Z)
   70 CONTINUE
      FF(I,J)=DSQRT(DABS((HE(I,J)-HEC(I,J))/HE(I,J)/0.01))
      F(J)=FF(I,J)
C     WRITE(7,*)F(J)
   10 CONTINUE
  30  CONTINUE
      RETURN
      END
C
```

```
C     NONLINEAR LEAST SQUARE METHOD OF MARQUARDT
      SUBROUTINE MARQS(N,M,FUN,X,ICO,F,EPS)
      IMPLICIT REAL*8(A-H,O-Z)
C     N - THE NUMBER OF INDEPENDENT VARIABLES, <20
C     M - THE NUMBER OF EQUATIONS <200
C     FUN - OBJECT FUNCTION SUBROUTINE FUN(N,M,X,F)
C     X(N) - THE INDEPENDENT VARIABLES
C     ICO(N) - ICO(I)=0 => I VARIABLE WILL NOT CHANGE
C              ICO(I)=1 => I VARIABLE WILL CHANGE
C     F(M) - THE OBJECT FUNCTION FOR EACH I
C     EPS - ACCURACY
      DIMENSION P1(20),RMO(20),DOF(20),GOF(20),AO(20,21),A1(20,21)
      DIMENSION A2(200,20),F(M),X(N),XO(200),ICO(N)
      COMMON P3
      L=0
      NO=N+1
      T=0.000001
      A9=10
      D4=0.1
      RLO=0.01
      I3=0
      IO=0
      VO=0.0001
      Z=EPS
      CALL FUN(N,M,X,F)
      P2=0.0
      DO 20 J=1,M
      P2=P2+F(J)**2
 20   CONTINUE
      I3=I3+1
      IC8=0
      DO 30 I=1,N
      IC8=IC8+ICO(I)
 30   CONTINUE
      IF(IC8.EQ.0)GOTO 200
 300  CONTINUE
      IO=IO+1
      RLO=RLO*D4
      IF(RLO.LT.T)RLO=T
      P3=P2
C     WRITE(7,1000)IO,I3,RLO,P3
C1000 FORMAT(2X,'IO=',I4,' I3=',I4,' RLO=',G12.4,' P3=',G12.5)
      DO 40 J=1,N
```

```
      P1(J)=X(J)
40    CONTINUE
      DO 50 J=1,M
      XO(J)=F(J)
50    CONTINUE
      DO 60 K=1,N
      IF(ICO(K).EQ.0)GOTO 60
      D9=(DABS(X(K))+VO)*VO
      X(K)=X(K)+D9
      CALL FUN(N,M,X,F)
      DO 65 I=1,M
      A2(I,K)=(F(I)-XO(I))/D9
65    CONTINUE
      X(K)=X(K)-D9
60    CONTINUE
      DO 70 I=1,N
      IF(ICO(I).NE.0)THEN
       RHO(I)=0
       DO 72 J=1,M
       RHO(I)=RHO(I)+A2(J,I)*XO(J)
72     CONTINUE
       DO 74 J=1,N
       A1(I,J)=0
       IF(ICO(J).EQ.0)GOTO 74
       DO 76 K=1,M
       A1(I,J)=A1(I,J)+A2(K,I)*A2(K,J)
76     CONTINUE
74        CONTINUE
      ELSE
       DO 78 J=1,N
       A1(I,J)=0.0
78     CONTINUE
       A1(I,I)=1.0
       RHO(I)=0.0
      ENDIF
70    CONTINUE
      DO 80 I=1,N
      GOF(I)=A1(I,I)**0.5
      IF(DABS(GOF(I)).LT.1.D-5)GOF(I)=1
80    CONTINUE
      DO 90 I=1,N
      RHO(I)=RHO(I)/GOF(I)
     DO 90 J=1,N
```

```
      A1(I,J)=A1(I,J)/(GOF(I)*GOF(J))
90    CONTINUE
400   CONTINUE
      DO 100 I=1,N
      AO(I,NO)=-RMO(I)
      DO 105 J=1,N
      AO(I,J)=A1(I,J)
105   CONTINUE
      AO(I,I)=AO(I,I)+RLO
100   CONTINUE
      CALL GAUSS(N,AO)
      DO 110 I=1,N
      DOF(I)=AO(I,NO)/GOF(I)
      X(I)=P1(I)+DOF(I)
110   CONTINUE
      CALL FUN(N,M,X,F)
      I3=I3+1
      P2=0.0
      DO 120 J=1,M
      P2=P2+F(J)**2
120   CONTINUE
      IF(P2.LT.EPS)GOTO 200
      IF(P2.LT.P3)GOTO 150
      RLO=RLO*A9
      IF(RLO.GT.100000.)THEN
       WRITE(7,*)'RLO>1.E10'
       GOTO 200
      ELSE
C      WRITE(7,*)'RLO=',RLO
       GOTO 400
      ENDIF
150   CONTINUE
      IW=0
      DO 160 J=1,N
      IF(DABS(DOF(J))/DABS(X(J))+VO.GT.Z)IW=IW+1
160   CONTINUE
      IF(L.EQ.0)GOTO 180
      DO 170 I=1,N
      WRITE(7,2000)I,X(I)
2000  FORMAT(2X,'X(',I1,')=',G12.5)
170   CONTINUE
180   CONTINUE
      IF(IW.EQ.0)GOTO 200
```

```
      GOTO 300
200   CONTINUE
      RETURN
      END
C
      SUBROUTINE GAUSS(N,AO)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION AO(20,21)
      NO=N+1
      DO 10 I=1,N
      DO 20 J=I+1,NO
      AO(I,J)=AO(I,J)/AO(I,I)
20    CONTINUE
      DO 30 J=1,N
      IF(I.EQ.J)GOTO 30
      DO 40 K=I+1,NO
      AO(J,K)=AO(J,K)-AO(I,K)*AO(J,I)
40    CONTINUE
30    CONTINUE
10    CONTINUE
      RETURN
      END
```

```
C     ************************************************
C       THIS PROGRAM IS USED TO CALCULATE THE EXCESS
C             ENTHALPY FOR TERNARY SYSTEMS
C           WITH DIFFERENT SOLUTION THEORY MODELS
C     ************************************************
C
C     AAD - AVERAGE ABSOLUTE DEVIATION
C     ARD - AVERAGE RELATIVE DEVIATION
C     IC - SWITCH PARAMETER
C       IC = 1, THIS WORK
C       IC = 2, UNIQUAC MODEL
C       IC = 3, NRTL MODEL
C       IC = 4, PURE EMPIRICAL EXPRESSION FROM CHRISTENSEN
C     HE - EXPERIMENTAL EXCESS ENTHALPY DATA, HE(EXP)
C     HEC - EXCESS ENTHALPY VALUES FROM CORRELATION, HE(CAL)
C     NN - NUMBER OF PARAMETERS
C     NP - NUMBER OF DATA POINTS
C     RMSH - ROOT MEAN SQUARE
C     R,Q,V - MOLECULAR VOLUME PARAMETER, MOLECULAR AREA PARAMETER,
C             AND VOLUME OF SATURATED LIQUID AT 20 C, RESPECTIVELY
C     X(NN) - ADJUSTABLE PARAMETERS
C     X1,X2 - MOLE FRACTIONS OF COMPONENT 1 AND 2, RESPECTIVELY
C
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER*70 AAA
      CHARACTER*70 BBB
      DIMENSION F(100),X(40),XO(20,40),ICO(20)
      EXTERNAL FUN
      COMMON /DATA1/R1,R2,Q1,Q2,V1,V2,R3,Q3,V3,R
      COMMON /DATA2/X1(100),X2(100),X3(100),HE(100)
      COMMON /DATA3/T,NN(14),NP
      COMMON /RESULT/HEC(100),FF(100)
      COMMON /SWITCH/IC,I
      LDER=0
      EPS=1.D-10
      WRITE(6,*)'MODEL (1) - THIS WORK (1) WITH 9 PARAMETERS'
C     WRITE(6,*)'MODEL (2) - THIS WORK (2) WITH 12 PARAMETERS'
C     WRITE(6,*)'MODEL (3) - UNIQUAC MODEL WITH 6 PARAMETERS'
C     WRITE(6,*)'MODEL (4) - NRTL MODEL WITH 12 PARAMETERS'
      READ(5,*)NSYS
      DO 999 INSYS=1,NSYS
      WRITE(6,111)INSYS
```

```
C     THE NUMBER OF SYSTEMS
 111  FORMAT(2X,'SYSTEM',2X,I2)
      READ(5,*)AAA
C     THE NAME OF THE TERNARY SYSTEM
      READ(5,*)BBB
C     DATA SOURCE
      READ(5,*)R1,Q1,V1,R2,Q2,V2,R3,Q3,V3
C     THE PARAMETERS OF PURE SUBSTANCES
      READ(5,*)T,NP
      DO 11 J=1,NP
      READ(5,*)X1(J),X2(J),HE(J)
      X3(J)=1.-X1(J)-X2(J)
   11 CONTINUE
      IC=1
      READ(5,*)NN(IC)
C     THE NUMBER OF ADJUSTABLE PARAMETERS
      DO 30 I=1,NN(IC)
      READ(5,*)XO(IC,I),ICO(I)
   30 CONTINUE
C     DO 20 IC=1,5
      R=8.314
      WRITE(6,*)AAA
      WRITE(6,*)BBB
      WRITE(6,*)'THE PARAMETERS FOR THE MODEL OF'
      DO 55 J=1,NN(IC)
      X(J)=XO(IC,J)
   55 CONTINUE
      CALL MARQS(NN(IC),NP,FUN,X,ICO,F,EPS)
      CALL FUN(NN(IC),NP,X,F)
      WRITE(6,*)IC
      FT=0.0
      DO 70 J=1,NP
      FT=FT+(F(J))**2
   70 CONTINUE
      FT=FT/NP
      WRITE(6,222)FT
  222 FORMAT(2X,'THE TOTAL OBJECTIVE FUNCTION = ',G12.7)
      WRITE(6,100)(X(M),M=1,NN(IC))
  100 FORMAT(2X,3G14.7)
      WRITE(6,*)
      WRITE(6,200)T,NP
  200 FORMAT(2X,'T=',G10.5,'K',4X,'NP=',I2)
          WRITE(6,*)
```

```
      WRITE(6,300)
  300 FORMAT(7X,'X1',13X,'X2',12X,'HE',
     1 11X,'HEC',10X,'HE-HEC',8X,'1-HEC/HE')
      AADS=0.
      ARDS=0.
      RMSHS=0.
      DO 80 J=1,NP
      DHE=HE(J)-HEC(J)
      AADS=AADS+DABS(DHE)
      RATIO=HEC(J)/HE(J)
      ARDS=ARDS+DABS(1.-RATIO)
      RMSHS=RMSHS+(HE(J)-HEC(J))**2
      WRITE(6,500)X1(J),X2(J),HE(J),HEC(J),DHE,1.-RATIO
  500 FORMAT(2X,6G14.5)
   80 CONTINUE
      AAD=AADS/NP
      ARD=ARDS/NP
C     RMSH=DSQRT(RMSHS/NP)
      RMSH=DSQRT(RMSHS/(NP-NN(IC)))
      WRITE(7,400)AAD,ARD,RMSH
      WRITE(6,400)AAD,ARD,RMSH
  400 FORMAT(2X,'AAD=',G14.5,'ARD=',G12.5,3X,'RMSH=',G12.5)
C 20      CONTINUE
  999 CONTINUE
      STOP
      END

      SUBROUTINE FUN(N,M,X,F)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION X(N),F(M),SUM(100)
      COMMON /DATA1/R1,R2,Q1,Q2,V1,V2,R3,Q3,V3,R
      COMMON /DATA2/X1(100),X2(100),X3(100),HE(100)
      COMMON /DATA3/T,NN(14),NP
      COMMON /RESULT/HEC(100),FF(100)
      COMMON /SWITCH/IC,I
      DO 10 J=1,NP
      GOTO(61,62,63,64,65),IC
   61 CONTINUE
C     THIS WORK -- MODEL (1)
      R12=0.5*(R1+R2)
      R21=R12
             R13=0.5*(R1+R3)
      R31=R13
```

```
      R23=0.5*(R2+R3)
      R32=R23
      X(3)=X(4)
      X(7)=X(8)
      X(11)=X(12)
      X21=X2(J)*(R21/R1)*DEXP(-X(3)*X(1)/R/T)
     1    /(X1(J)+X2(J)*(R21/R1)*DEXP(-X(3)*X(1)/R/T)
     2    +X3(J)*(R31/R1)*DEXP(-X(7)*X(5)/R/T))
      X12=X1(J)*(R12/R2)*DEXP(-X(4)*X(2)/R/T)
     1    /(X2(J)+X1(J)*(R12/R2)*DEXP(-X(4)*X(2)/R/T)
     2    +X3(J)*(R32/R2)*DEXP(-X(11)*X(9)/R/T))
      X31=X3(J)*(R31/R1)*DEXP(-X(7)*X(5)/R/T)
     1    /(X1(J)+X2(J)*(R21/R1)*DEXP(-X(3)*X(1)/R/T)
     2    +X3(J)*(R31/R1)*DEXP(-X(7)*X(5)/R/T))
      X13=X1(J)*(R13/R3)*DEXP(-X(8)*X(6)/R/T)
     1    /(X3(J)+X1(J)*(R13/R3)*DEXP(-X(8)*X(6)/R/T)
     2    +X2(J)*(R23/R3)*DEXP(-X(12)*X(10)/R/T))
      X23=X2(J)*(R23/R3)*DEXP(-X(12)*X(10)/R/T)
     1    /(X3(J)+X1(J)*(R13/R3)*DEXP(-X(8)*X(6)/R/T)
     2    +X2(J)*(R23/R3)*DEXP(-X(12)*X(10)/R/T))
      X32=X3(J)*(R32/R2)*DEXP(-X(11)*X(9)/R/T)
     1    /(X2(J)+X1(J)*(R12/R2)*DEXP(-X(4)*X(2)/R/T)
     2    +X3(J)*(R32/R2)*DEXP(-X(11)*X(9)/R/T))
      HEC(J)=5.0*(X1(J)*X21*X(1)+X1(J)*X31*X(5)
     1          +X2(J)*X12*X(2)+X2(J)*X32*X(9)
     2          +X3(J)*X13*X(6)+X3(J)*X23*X(10))
      GOTO 70
   62 CONTINUE
C     THIS WORK -- MODEL (2)
      ALFA=0.1
      X21=X2(J)*(X(3)/R1)*DEXP(-ALFA*X(1)/R/T)
     1    /(X1(J)+X2(J)*(X(3)/R1)*DEXP(-ALFA*X(1)/R/T)
     2    +X3(J)*(X(7)/R1)*DEXP(-ALFA*X(5)/R/T))
      X12=X1(J)*(X(4)/R2)*DEXP(-ALFA*X(2)/R/T)
     1    /(X2(J)+X1(J)*(X(4)/R2)*DEXP(-ALFA*X(2)/R/T)
     2    +X3(J)*(X(11)/R2)*DEXP(-ALFA*X(9)/R/T))
      X31=X3(J)*(X(7)/R1)*DEXP(-ALFA*X(5)/R/T)
     1    /(X1(J)+X2(J)*(X(3)/R1)*DEXP(-ALFA*X(1)/R/T)
     2    +X3(J)*(X(7)/R1)*DEXP(-ALFA*X(5)/R/T))
      X13=X1(J)*(X(8)/R3)*DEXP(-ALFA*X(6)/R/T)
     1    /(X3(J)+X1(J)*(X(8)/R3)*DEXP(-ALFA*X(6)/R/T)
     2    +X2(J)*(X(12)/R3)*DEXP(-ALFA*X(10)/R/T))
      X23=X2(J)*(X(12)/R3)*DEXP(-ALFA*X(10)/R/T)
```

```
     1    /(X3(J)+X1(J)*(X(8)/R3)*DEXP(-ALFA*X(6)/R/T)
     2    +X2(J)*(X(12)/R3)*DEXP(-ALFA*X(10)/R/T))
      X32=X3(J)*(X(11)/R2)*DEXP(-ALFA*X(9)/R/T)
     1    /(X2(J)+X1(J)*(X(4)/R2)*DEXP(-ALFA*X(2)/R/T)
     2    +X3(J)*(X(11)/R2)*DEXP(-ALFA*X(9)/R/T))
      HEC(J)=5.0*(X1(J)*X21*X(1)+X1(J)*X31*X(5)
     1          +X2(J)*X12*X(2)+X2(J)*X32*X(9)
     2          +X3(J)*X13*X(6)+X3(J)*X23*X(10))
      GOTO 70
   63 CONTINUE
C     UNIQUAC MODEL
      SUM(J)=0.
      SUM(J)=X1(J)*Q1+X2(J)*Q2+X3(J)*Q3
      SATA1=X1(J)*Q1/SUM(J)
      SATA2=X2(J)*Q2/SUM(J)
      SATA3=X3(J)*Q3/SUM(J)
      TAO21=DEXP(-X(1)/R/T)
      TAO12=DEXP(-X(2)/R/T)
      TAO31=DEXP(-X(3)/R/T)
      TAO13=DEXP(-X(4)/R/T)
      TAO32=DEXP(-X(5)/R/T)
      TAO23=DEXP(-X(6)/R/T)
      HEC(J)=Q1*X1(J)*(SATA2*TAO21*X(1)+SATA3*TAO31*X(3))
     1       /(SATA1+SATA2*TAO21+SATA3*TAO31)+
     2       Q2*X2(J)*(SATA1*TAO12*X(2)+SATA3*TAO32*X(5))
     3       /(SATA2+SATA1*TAO12+SATA3*TAO32)+
     4       Q3*X3(J)*(SATA1*TAO13*X(4)+SATA2*TAO23*X(6))
     5       /(SATA3+SATA1*TAO13+SATA2*TAO23)
C
      GOTO 70
   64 CONTINUE
C     NRTL MODEL
      ALFA21=X(3)
      ALFA12=X(4)
      ALFA31=X(7)
      ALFA13=X(8)
      ALFA32=X(11)
      ALFA23=X(12)
      TAO21=X(1)/R/T
      TAO12=X(2)/R/T
      TAO31=X(5)/R/T
      TAO13=X(6)/R/T
      TAO32=X(9)/R/T
```

```
      TAO23=X(10)/R/T
      G21=DEXP(-X(3)*TAO21)
      G12=DEXP(-X(4)*TAO12)
      G31=DEXP(-X(7)*TAO31)
      G13=DEXP(-X(8)*TAO13)
      G32=DEXP(-X(11)*TAO32)
      G23=DEXP(-X(12)*TAO23)
      HEC(J)=R*T*(X1(J)*((X2(J)*G21*TAO21+X3(J)*G31*TAO31)/
     1                   (X1(J)+X2(J)*G21+X3(J)*G31)-
     2  X1(J)*(X2(J)*ALFA21*G21*TAO21**2+X3(J)*ALFA31*G31*TAO31**2)/
     3                   (X1(J)+X2(J)*G21+X3(J)*G31)**2-
     4  X2(J)*X3(J)*G21*G31*(TAO31-TAO21)*(ALFA31*TAO31-ALFA21*TAO21)/
     5                   (X1(J)+X2(J)*G21+X3(J)*G31)**2)+
     6            X2(J)*((X1(J)*G12*TAO12+X3(J)*G32*TAO32)/
     7                   (X1(J)*G12+X2(J)+X3(J)*G32)-
     8  X2(J)*(X1(J)*ALFA12*G12*TAO12**2+X3(J)*ALFA32*G32*TAO32**2)/
     9                   (X1(J)*G12+X2(J)+X3(J)*G32)**2-
     1  X1(J)*X3(J)*G12*G32*(TAO32-TAO12)*(ALFA32*TAO32-ALFA12*TAO12)/
     2                   (X1(J)*G12+X2(J)+X3(J)*G32)**2)+
     3            X3(J)*((X1(J)*G13*TAO13+X2(J)*G23*TAO23)/
     4                   (X1(J)*G13+X3(J)+X2(J)*G23)-
     5  X3(J)*(X1(J)*ALFA13*G13*TAO13**2+X2(J)*ALFA23*G23*TAO23**2)/
     6                   (X1(J)*G13+X3(J)+X2(J)*G23)**2-
     7  X1(J)*X2(J)*G13*G23*(TAO23-TAO13)*(ALFA23*TAO23-ALFA13*TAO13)/
     8                   (X1(J)*G13+X3(J)+X2(J)*G23)**2))
       GOTO 70
   65  CONTINUE
C     PURE EMPIRICAL EXPRESSION FROM CHRISTENSEN
C
   70 CONTINUE
      FF(J)=DSQRT(DABS((HE(J)-HEC(J))/HE(J)/0.01))
      F(J)=FF(J)
C
   10 CONTINUE
      RETURN
      END
C
C     NONLINEAR LEAST SQUARE METHOD OF MARQUARDT
      SUBROUTINE MAROS(N,M,FUN,X,ICO,F,EPS)
      IMPLICIT REAL*8(A-H,O-Z)
C     N - THE NUMBER OF INDEPENDENT VARIABLES, <20
C     M - THE NUMBER OF EQUATIONS <200
C     FUN - OBJECT FUNCTION SUBROUTINE FUN(N,M,X,F)
```

```
C     X(N) - THE INDEPENDENT VARIABLES
C     ICO(N) - ICO(I)=0 => I VARIABLE WILL NOT CHANGE
C              ICO(I)=1 => I VARIABLE WILL CHANGE
C     F(M) - THE OBJECT FUNCTION FOR EACH I
C     EPS - ACCURACY
      DIMENSION P1(20),RHO(20),DOF(20),GOF(20),AO(20,21),A1(20,21)
      DIMENSION A2(200,20),F(M),X(N),XO(200),ICO(N)
      L=0
      NO=N+1
      T=0.000001
      A9=10
      D4=0.1
      RLO=0.01
      I3=0
      IO=0
      VO=0.0001
      Z=EPS
      CALL FUN(N,M,X,F)
      P2=0.0
      DO 20 J=1,M
      P2=P2+F(J)**2
 20   CONTINUE
      I3=I3+1
      IC8=0
      DO 30 I=1,N
      IC8=IC8+ICO(I)
 30   CONTINUE
      IF(IC8.EQ.0)GOTO 200
 300  CONTINUE
      IO=IO+1
      RLO=RLO*D4
      IF(RLO.LT.T)RLO=T
      P3=P2
C     WRITE(7,1000)IO,I3,RLO,P3
C1000  FORMAT(2X,'IO=',I4,' I3=',I4,' RLO=',G12.4,' P3=',G12.5)
      DO 40 J=1,N
      P1(J)=X(J)
 40   CONTINUE
      DO 50 J=1,M
      XO(J)=F(J)
 50   CONTINUE
      DO 60 K=1,N
      IF(ICO(K).EQ.0)GOTO 60
```

```
      D9=(DABS(X(K))+V0)*V0
      X(K)=X(K)+D9
      CALL FUN(N,M,X,F)
      DO 65 I=1,M
      A2(I,K)=(F(I)-X0(I))/D9
65    CONTINUE
      X(K)=X(K)-D9
60    CONTINUE
      DO 70 I=1,N
      IF(ICO(I).NE.0)THEN
       RMO(I)=0
       DO 72 J=1,M
       RMO(I)=RMO(I)+A2(J,I)*X0(J)
72     CONTINUE
       DO 74 J=1,N
       A1(I,J)=0
       IF(ICO(J).EQ.0)GOTO 74
       DO 76 K=1,M
       A1(I,J)=A1(I,J)+A2(K,I)*A2(K,J)
76     CONTINUE
74     CONTINUE
      ELSE
       DO 78 J=1,N
       A1(I,J)=0.0
78     CONTINUE
       A1(I,I)=1.0
       RMO(I)=0.0
      ENDIF
70    CONTINUE
      DO 80 I=1,N
      GOF(I)=A1(I,I)**0.5
      IF(DABS(GOF(I)).LT.1.D-5)GOF(I)=1
80    CONTINUE
      DO 90 I=1,N
      RMO(I)=RMO(I)/GOF(I)
      DO 90 J=1,N
      A1(I,J)=A1(I,J)/(GOF(I)*GOF(J))
90    CONTINUE
400   CONTINUE
      DO 100 I=1,N
      A0(I,N0)=-RMO(I)
      DO 105 J=1,N
      A0(I,J)=A1(I,J)
```

```
105   CONTINUE
      AO(I,I)=AO(I,I)+RLO
100   CONTINUE
      CALL GAUSS(N,AO)
      DO 110 I=1,N
      DOF(I)=AO(I,NO)/GOF(I)
      X(I)=P1(I)+DOF(I)
110   CONTINUE
      CALL FUN(N,M,X,F)
      I3=I3+1
      P2=0.0
      DO 120 J=1,M
      P2=P2+F(J)**2
120   CONTINUE
      IF(P2.LT.EPS)GOTO 200
      IF(P2.LT.P3)GOTO 150
      RLO=RLO*A9
      IF(RLO.GT.100000.)THEN
       WRITE(7,*)'RLO>1.E10'
       GOTO 200
      ELSE
C      WRITE(7,*)'RLO=',RLO
       GOTO 400
      ENDIF
150   CONTINUE
      IW=0
      DO 160 J=1,N
      IF(DABS(DOF(J))/DABS(X(J))+VO.GT.Z)IW=IW+1
160   CONTINUE
      IF(L.EQ.0)GOTO 180
      DO 170 I=1,N
      WRITE(7,2000)I,X(I)
2000  FORMAT(2X,'X(',I1,')=',G12.5)
170   CONTINUE
180   CONTINUE
      IF(IW.EQ.0)GOTO 200
      GOTO 300
200   CONTINUE
      RETURN
      END
C
      SUBROUTINE GAUSS(N,AO)
      IMPLICIT REAL*8(A-H,O-Z)
```

```
      DIMENSION AO(20,21)
      NO=N+1
      DO 10 I=1,N
      DO 20 J=I+1,NO
      AO(I,J)=AO(I,J)/AO(I,I)
20    CONTINUE
      DO 30 J=1,N
      IF(I.EQ.J)GOTO 30
      DO 40 K=I+1,NO
      AO(J,K)=AO(J,K)-AO(I,K)*AO(J,I)
40    CONTINUE
30    CONTINUE
10    CONTINUE
      RETURN
      END
```

Appendix E

Simultaneous representation of VLE and H^E values by means of cubic EOS

An attempt was made in this study to represent vapour-liquid equilibrium (VLE) and excess enthalpies simultaneously by means of cubic equations of state (EOS). It is presented in this section in three parts: the equations of state and the mixing rules considered, the preliminary results and some evaluation comments, and the computer programs used in the calculations.

E-1 The cubic equations of state and the mixing rules

There were five simple cubic equations of state and five commonly used mixing rules studied in this work. Their general expressions are presented as follows:

A. Simple cubic equations of state

The simplest useful analytical equation of state is explicit in pressure P and cubic in molar volume v. In its general form, pressure can be expressed as the sum of two parts,

a repulsive term, P_R, and an attractive part, P_A, as

$$P = P_R + P_A \qquad \text{(E-1)}$$

where

$$P_R = \frac{RT}{v-b}, \quad P_A = -\frac{a}{g(v)} \qquad \text{(E-2)}$$

In Equation E-2, g(v) is a function of the molar volume "v" and co-volume parameter "b" which is related to the size of the hard spheres. The cohesion parameter "a" can be regarded as a measure of the intermolecular attraction forces.

In the five equations of state used in this study, the parameter "a" was treated temperature dependent and the function g(v) was expressed in different forms.

The SRK equation of state (Soave, 1972)

This is a modified R-K equation proposed by Soave. It is expressed by

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \qquad \text{(E-3)}$$

where $b=0.08664RT_c/P_c$ and is temperature independent. The energy parameter "a" is proportional to a dimensionless scaling factor α, which is treated as a function of the reduced temperature T_r. ω is the acentric factor of the related compounds. Thus, $a(T)=a(T_c)\alpha(T_r)$, $a(T_c)=0.42747R^2(T_c)^2/P_c$, $\alpha=[1+m(1-T_r^{0.5})]^2$, and $m=0.480+1.547\omega-0.176\omega^2$.

The PR equation of state (Peng and Robinson, 1976)

The PR equation is of the following form:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \qquad (E-4)$$

where $b=0.07780RT_c/P_c$, $a(T)=a(T_c)\alpha(T_r,\omega)$ and $a(T_c)=0.45724R^2(T_c)^2/P_c$. The dimensionless scaling factor α for the energy parameter was treated as a function of acentric factor in addition to reduced temperature, $\alpha(T_r,\omega)=[1+k(1-T_r^{0.5})]^2$ with k considered as a function of the acentric factor, $k=0.37464+1.54226\omega-0.26992\omega^2$.

The PRSV equation of state (Stryjek and Vera, 1986)

This is a modified PR equation proposed by Stryjek and Vera. The core part of the modification is the functional dependence of k. In this equation, $k=k_0+k_1(1+T_r^{0.5})(0.7-T_r)$, with $k_0=0.378893+1.4897153\omega-0.17131848\omega^2+0.0196554\omega^3$, a function of the acentric factor the same as in the PR equation, and k_1 is an adjustable parameter characteristic of each pure compound.

The SW equation of state (Schmidt and Wenzel, 1980)

With the introduction of a third parameter and a quadratic form of g(v), the SW equation of state is expressed by

$$P=\frac{RT}{v-b}-\frac{a(T)}{v^2+ubv+wb^2} \qquad (E-5)$$

where u, w, and b are independent of temperature. The SW equation reduces to the SRK

equation when u=1 and w=0, and to the PR equation when u=2 and w=-1. For the SW equation, u+w=1 and w=-3ω were suggested. A similar form of the temperature dependence "a" was expressed by $a(T)=a_c\alpha(T_r,k)$, where $\alpha(T_r,k)$ was given as a function of the reduced temperature T_r by $\alpha(T_r,k)=[1+k(T_r,k_0)(1-T_r^{0.5})]^2$ with $k(T_r,k_0)=k_0+(5T_r-3k_0-1)^2/70$ for $T_r\leq 1$ and $k(T_r,k_0)=k(1,k_0)$ for $T>1$, and $k_0=0.465+1.347\omega-0.528\omega^2$. Unlike that in the SRK equation, k in the SW equation is temperature dependent. A substance-dependent critical compressibility factor ζ_c was introduced to calculate equation parameters b and a_c, which made the equation somewhat more complicated.

The PT equation of state (Patel and Teja, 1982)

As an extension of the works of Soave, Peng and Robinson, and Schmidt and Wenzel, PT equation was proposed especially for polar substances. In addition to the critical temperature T_c and critical pressure P_c, the PT equation uses two substance dependent parameters ζ and F as the input parameters.

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)+c(v-b)} \qquad (E-6)$$

B. Mixing rules

Mixing rules required by equations of state in the calculation of thermodynamic properties of mixtures are at least equally important as equations of state themselves. Most of the existing mixing rules can fairly well represent VLE or thermal behaviour, such as heat of mixing, with a reasonable accuracy. However, when being used for

simultaneous representation of VLE and H^E values, their performance will be affected by the nature of the mixing rules themselves and the systems involved.

The conventional mixing rules

The mixing rule of the van der Waals one-fluid model is referred to in this work as the conventional mixing rule

$$a = \sum_i \sum_j x_i x_j a_{ij} , \qquad b = \sum_i \sum_j x_i x_j b_{ij} \tag{E-7}$$

Generally, a geometric mean is used to calculate a_{ij}, and an arithmetic mean to calculate b_{ij}:

$$a_{ij} = (a_i a_j)^{1/2}, \qquad b_{ij} = (b_i + b_j)/2 \tag{E-8}$$

where a_i, b_i and a_j, b_j are the parameters for pure components i and j respectively.

The conventional mixing rule can be improved considerably by adding a binary interaction coefficient to the mixing rule of the parameter "a"

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \tag{E-9}$$

where k_{ij} ($=k_{ji}$) is the binary interaction coefficient between components i and j. k_{ij} is determined normally by fitting binary vapour liquid equilibrium data, and is usually found to be weakly dependent on temperature.

The A-S mixing rule (Adachi and Sugie, 1985,1986)

Adachi and Sugie first proposed their Redlich-Kister (1948) type A-S mixing rule in 1985 and then further simplified it (1986) to

$$a_{ij} = (a_i a_j)^{1/2}[1 - k_{ij} - l_{ij}(x_i - x_j)] \qquad \text{(E-10)}$$

where k_{ij} (= k_{ji}) and l_{ij} (= $-l_{ji}$) are the two system dependent binary interaction coefficients.

The S-G-R mixing rule (Schwartzentruber *et al.*, 1987)

The S-G-R mixing rule for a_{ij} was developed to overcome the false liquid phase splitting problem which often happens in the VLE calculations of alcohol-hydrocarbon mixtures. This mixing rule has three binary interaction coefficients, k_{ij}, l_{ij}, and m_{ij}.

$$a_{ij} = (a_j a_j)^{1/2}\left[1 - k_{ij} - l_{ij}\frac{m_{ij}x_i - m_{ji}x_j}{m_{ij}x_i + m_{ji}x_j}(x_i + x_j)\right] \qquad \text{(E-11)}$$

where $k_{ij} = k_{ji}$, $l_{ij} = -l_{ji}$, and $m_{ij} = 1 - m_{ji}$.

The Stryjek-Vera mixing rule of van Laar type (Stryjek and Vera, 1986b)

The Stryjek-Vera (S-V) mixing rule was proposed with a Margules-type expression and a van Laar-type expression. Since the former one is identical to the A-S mixing rule, only the van Laar type of the S-V mixing rule, as shown below, was considered in this study and denoted as S-V2 mixing rule.

$$a_{ij} = (a_i a_j)^{1/2}\left[1 - \frac{k_{ij}\, k_{ji}}{x_i k_{ij} + x_j k_{ji}}\right] \qquad \text{(E-12)}$$

It contains two adjustable binary interaction coefficients, k_{ij} and k_{ji}, and reduces to the conventional one parameter mixing rule when the parameters are equal, $k_{ij}=k_{ji}$.

The mixing rules coupling with cubic EOS and excess Gibbs energy models

Huron and Vidal (1979) first coupled cubic EOS with a G^E model. They matched G^E values predicted from activity coefficient models with those from a cubic equation of state. Although the resulting H-V mixing rules cannot take advantage of the correlated interaction parameters for activity coefficient models in the DECHEMA chemistry data series, their method provides a very flexible framework for the correlation of VLE and LLE data. However, as indicated by Wong and Sandler (1992), H-V mixing rules do not satisfy the requirement that the second virial coefficient be a quadratic function of composition, and therefore are inconsistent with the statistical mechanics theory.

The mixing rules coupling the cubic EOS and excess Gibbs energy models used in this work were proposed by Wong and Sandler (1992). Being considered theoretically correct, the Wong-Sandler (W-S) mixing rules are based on two conditions:

(1). The excess Helmholtz free energy, A^E, at infinite pressure was assumed equal to the excess Gibbs free energy at low pressures.

$$G^E(T,x,P=\text{low}) = A^E(T,x,p=\text{low}) = A^E(T,x,p=\infty) \qquad \text{(E-13)}$$

This assumption makes the excess Gibbs free energy models or the activity coefficient models applicable to equations of state. The A^E is a weak function of pressure, so that the mixing rule can be used at high pressures.

(2). The composition dependence of the second virial coefficient is quadratic.

$$B_m(T) = \sum_i \sum_j x_i x_j B_{ij}(T) \qquad \text{(E-14)}$$

This condition satisfies the theoretical requirement.

The following mixing rules were introduced to satisfy these two conditions

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 + \frac{A_\infty^E(x)}{RT} - \sum_i x_i \left(\frac{a_i}{b_i RT}\right)} \qquad \text{(E-15)}$$

and

$$a_m = b_m \left[\sum_i x_i \frac{a_i}{b_i} - \frac{A_\infty^E(x)}{C}\right] \qquad \text{(E-16)}$$

where

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \qquad \text{(E-17)}$$

The value of the quantity, C, depends on the equation of state used. For the Peng-Robinson equation,

$$C=\ln\left(2^{1/2}-1\right)/2^{1/2} \qquad \text{(E-18)}$$

The W-S mixing rules can be used together with different activity coefficient models, two of which were considered in this study:

(1). NRTL model (Renon and Prausnitz, 1968a):

$$\frac{A_\infty^E}{RT}=\sum_i x_i\left(\frac{\sum_j x_j\tau_{ji}g_{ji}}{\sum_k x_k g_{ki}}\right) \qquad \text{(E-19)}$$

where

$$g_{ij}=\exp(-\alpha_{ij}\tau_{ij}) \ , \quad (\alpha_{ij}=\alpha_{ji}) \qquad \text{(E-20)}$$

(2). van Laar model (1910, 1913). For binary systems:

$$\frac{G^E}{RT}=\frac{2\alpha_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2} \qquad \text{(E-21)}$$

To avoid confusion, W-S1 was used to represent the W-S mixing rule with the van Laar model in this work, while W-S2 was for the W-S mixing rule with the NRTL model.

E-2 The calculation results

Ten systems with available experimental data of both VLE and H^E were selected. They are listed on the following page along with the data source. The calculation was carried out for four times aiming at optimizing different properties, such as P (vapour

pressure) only, P + y (vapor composition), P + H^E, or P + y + H^E.

Systems studied and the data source

No.	Systems	VLE data source	H^E data source
1	carbon tetrachloride+n-heptane	Bissell&Williamson (1975)	Grolier&Inglese (1975)
2	chloroform+n-hexane	Bissell&Williamson (1975)	Bissell *et al.* (1971)
3	cyclohexane+n-hexadecane	Gomez-Ibanez&Shieh (1965)	Fenby *et al.* (1980)
4	n-hexane+n-hexadecane	McGlashan&Williamson(1961)	Miller&Williamson (1984)
5	benzene+cyclohexane	Tasic *et al.* (1978)	Abello (1973)
6	benzene+n-heptane	Jain *et al.* (1973)	Hammerl&Raetzsch (1973)
7	benzene+1-octene	Vera&Prausnitz (1971)	Karbalai&Grolier (1975)
8	n-hexane+ethanol	Smith&Robinson (1970)	Brown *et al.* (1964)
9	ethanol+cyclohexane	Scatchard&Satkifwicz (1964)	Nagata&Yamada (1974)
10	ethanol+2,2,4-trimethylpentane	Kretschmer *et al.*(1948)	Wang *et al.* (1992c)

The calculation results will be presented in the sequence of the systems listed above. In some of the case, only two calculations were involved instead of four, due to the validility of vapour pressure data. In these situations, the calculation was carried out by optimizing vapor pressure, P, or both P and excess enthalpy, H^E.

It needs to be mentioned that, in this study, the PT equation was applied only to system #8 due to the lack of information in equation parameters and that the use of the W-S mixing rule was restricted to the PR and PRSV equations with the available expressions given by Wong and Sandler (1992).

System 1. Carbon tetrachloride + n-heptane

Table E-1 System 1 with the SW equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	0.66	0.65	4.73	1.92
	Δy×100	0.39	0.37	0.75	0.11
	ΔH^E%	71.71	69.92	2.74	47.04
A-S	Δp%	0.63	0.63	4.67	1.89
	Δy×100	0.38	0.35	0.74	0.04
	ΔH^E%	71.71	69.50	2.97	47.15
S-G-R	Δp%	0.60	0.42	4.79	1.80
	Δy×100	1.45	0.25	0.77	0.03
	ΔH^E%	63.12	72.72	1.94	48.74
S-V2	Δp%	3.24	3.95	4.76	1.84
	Δy×100	6.30	1.39	0.78	0.03
	ΔH^E%	60.81	9.79	2.13	47.94

Table E-2 System 1 with the SRK equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	0.36	0.36	1.73	1.10
	Δy×100	0.28	0.26	0.67	0.11
	ΔH^E%	26.64	29.97	1.25	40.75
A-S	Δp%	0.36	0.36	1.72	1.14
	Δy×100	0.27	0.24	0.66	0.05
	ΔH^E%	26.62	27.91	1.28	41.10
S-G-R	Δp%	0.33	0.33	1.75	1.31
	Δy×100	0.28	0.27	0.68	0.04
	ΔH^E%	26.78	27.39	1.23	44.23
S-V2	Δp%	0.32	0.36	1.71	1.17
	Δy×100	0.85	0.25	0.65	0.05
	ΔH^E%	32.08	27.78	1.28	41.69

Table E-3 System 1 with the PR equation of state

Mixing rules		P	P+y	P+H^E	P+y+H^E
Conventional	Δp%	1.35	1.36	6.77	4.15
	Δy×100	0.79	0.77	0.67	0.07
	ΔH^E%	89.10	87.89	4.02	42.22
A-S	Δp%	1.35	1.36	6.73	4.13
	Δy×100	0.80	0.74	0.67	0.03
	ΔH^E%	88.83	85.79	4.27	42.37
S-G-R	Δp%	1.17	0.98	6.84	4.02
	Δy×100	0.73	0.66	0.74	0.04
	ΔH^E%	91.45	92.42	3.20	44.16
S-V2	Δp%	1.36	1.32	6.69	4.12
	Δy×100	0.86	0.79	0.61	0.03
	ΔH^E%	91.92	87.83	43.1	42.62
W-S1	Δp%	1.36	-	1.14	-
	Δy×100	0.84	-	0.63	-
	ΔH^E%	93.79	-	1.98	-
W-S2	Δp%	1.29	-	1.34	-
	Δy×100	0.79	-	0.83	-
	ΔH^E%	36.99	-	1.06	-

Table E-4 System 1 with the PRSV equation of state

Mixing rules		P	P+y	P+H^E	P+y+H^E
Conventional	Δp%	0.12	0.12	2.69	0.12
	Δy×100	0.07	0.07	0.70	0.08
	ΔH^E%	42.64	42.84	0.82	41.99
A-S	Δp%	0.10	0.10	2.66	0.10
	Δy×100	0.04	0.04	0.69	0.04
	ΔH^E%	42.95	42.85	2.00	42.20

(Continued)

Mixing rules		P	P+y	P+H^E	P+y+H^E
S-G-R	Δp%	0.10	0.10	2.71	0.13
	Δy×100	0.05	0.05	0.75	0.04
	ΔH^E%	43.41	43.59	1.68	44.71
S-V2	Δp%	0.10	0.09	2.65	0.09
	Δy×100	0.04	0.04	0.67	0.04
	ΔH^E%	42.99	42.96	2.01	42.50
W-S1	Δp%	0.09	0.09	0.29	0.26
	Δy×100	0.05	0.04	0.27	0.06
	ΔH^E%	104.30	85.00	1.66	22.96
W-S2	Δp%	0.09	0.09	0.19	0.11
	Δy×100	0.05	0.04	0.13	0.03
	ΔH^E%	90.83	42.46	1.00	2.71

System 2. Chloroform + n-hexane

Table E-5 System 2 with the SW equation of state

Mixing rules		P	P+y	P+H^E	P+y+H^E
Conventional	Δp%	0.66	0.66	2.17	0.66
	Δy×100	0.71	0.71	0.97	0.71
	ΔH^E%	17.87	17.83	7.61	17.33
A-S	Δp%	0.17	0.18	2.00	0.43
	Δy×100	0.14	0.13	0.44	0.10
	ΔH^E%	16.14	15.89	1.83	13.72
S-G-R	Δp%	0.24	0.32	2.15	0.22
	Δy×100	0.93	0.48	0.96	0.09
	ΔH^E%	25.46	21.36	5.58	15.87
S-V2	Δp%	0.52	0.53	2.00	1.96
	Δy×100	0.57	0.52	0.34	0.19
	ΔH^E%	14.44	13.34	2.37	3.84

Table E-6 System 2 with the SRK equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	0.77	0.74	0.82	2.12
	Δy×100	0.91	0.87	0.94	0.66
	ΔH^E%	7.31	7.49	7.19	16.10
A-S	Δp%	0.45	0.45	0.49	1.88
	Δy×100	0.46	0.42	0.46	0.09
	ΔH^E%	1.55	1.73	1.33	12.72
S-G-R	Δp%	0.56	0.67	0.72	3.26
	Δy×100	1.52	0.86	0.94	0.37
	ΔH^E%	10.94	6.18	5.33	27.28
S-V2	Δp%	0.35	0.40	0.37	0.94
	Δy×100	0.28	0.17	0.30	0.17
	ΔH^E%	1.65	2.03	1.52	4.56

Table E-7 System 2 with the PR equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	0.92	0.91	3.68	1.28
	Δy×100	0.87	0.86	1.12	0.80
	ΔH^E%	27.33	26.76	7.43	20.50
A-S	Δp%	0.45	0.45	3.51	1.52
	Δy×100	0.38	0.34	0.54	0.16
	ΔH^E%	25.39	24.70	2.53	16.72
S-G-R	Δp%	0.35	0.44	3.66	0.65
	Δy×100	0.79	0.46	1.14	0.40
	ΔH^E%	34.75	30.99	5.96	33.43
S-V2	Δp%	0.87	0.89	3.48	3.05
	Δy×100	0.79	0.72	0.41	0.19
	ΔH^E%	24.31	22.65	2.29	6.12

Table E-8 System 2 with the PRSV equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	0.76	0.74	1.61	1.29
	Δy×100	0.89	0.87	1.51	0.80
	ΔH^E%	11.93	12.75	7.24	20.25
A-S	Δp%	0.22	0.21	1.34	0.99
	Δy×100	0.24	0.23	0.58	0.16
	ΔH^E%	10.14	10.47	1.63	16.42
S-G-R	Δp%	0.39	0.47	1.47	2.64
	Δy×100	1.39	0.72	1.25	0.40
	ΔH^E%	20.34	15.29	6.50	33.15
S-V2	Δp%	0.34	0.33	5.10	0.82
	Δy×100	0.28	0.25	1.31	0.19
	ΔH^E%	26.87	26.89	4.78	23.30
W-S1	Δp%	0.24	0.24	0.64	1.58
	Δy×100	0.26	0.25	0.80	0.16
	ΔH^E%	76.17	69.96	3.69	37.03
W-S2	Δp%	0.24	0.21	0.24	1.13
	Δy×100	0.25	0.11	0.24	0.15
	ΔH^E%	14.07	106.95	0.86	3.78

System 3. Cyclohexane + n-hexadecane

Table E-9 System 3 with the SW equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	1.37	17.78
	Δy×100	-	-
	ΔH^E%	172.79	25.52
A-S	Δp%	1.30	16.97
	Δy×100	-	-
	ΔH^E%	172.95	20.38
S-G-R	Δp%	0.68	17.18
	Δy×100	-	-
	ΔH^E%	176.11	22.27
S-V2	Δp%	1.29	14.34
	Δy×100	-	-
	ΔH^E%	102.43	22.62

Table E-10 System 3 with the SRK equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	1.40	9.25
	Δy×100	-	-
	ΔH^E%	105.20	16.14
A-S	Δp%	0.34	9.10
	Δy×100	-	-
	ΔH^E%	105.20	15.03
S-G-R	Δp%	0.33	9.46
	Δy×100	-	-
	ΔH^E%	105.00	14.63
S-V2	Δp%	0.33	8.62
	Δy×100	-	-
	ΔH^E%	76.18	21.38

Table E-11 System 3 with the PR equation of state

Mixing rules		P	$P+H^E$
Conventional	Δp%	1.85	14.78
	Δy×100	-	-
	ΔH^E%	138.24	21.83
A-S	Δp%	1.88	14.54
	Δy×100	-	-
	ΔH^E%	138.23	21.63
S-G-R	Δp%	1.78	16.15
	Δy×100	-	-
	ΔH^E%	137.16	9.42
S-V2	Δp%	1.87	14.55
	Δy×100	-	-
	ΔH^E%	138.29	21.80
W-S1	Δp%	1.69	3.99
	Δy×100	-	-
	ΔH^E%	100.76	32.98
W-S2	Δp%	1.19	2.67
	Δy×100	-	-
	ΔH^E%	172.74	3.79

Table E-12 System 3 with the PRSV equation of state

Mixing rules		P	$P+H^E$
Conventional	Δp%	2.35	8.18
	Δy×100	-	-
	ΔH^E%	96.27	15.57
A-S	Δp%	0.91	8.09
	Δy×100Δy	-	-
	ΔH^E%	95.56	14.69

(Continued)

Mixing rules		P	P+H^E
S-G-R	Δp%	0.75	8.16
	Δy×100	-	-
	ΔH^E%	91.33	14.65
S-V2	Δp%	1.08	7.55
	Δy×100	-	-
	ΔH^E%	97.63	19.69
W-S1	Δp%	0.6	4.35
	Δy×100	-	-
	ΔH^E%	105.29	37.46
W-S2	Δp%	0.81	4.25
	Δy×100	-	-
	ΔH^E%	126.59	3.98

System 4. n-hexane + n-hexadecane

Table E-13 System 4 with the SW equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	1.28	9.27
	Δy×100	-	-
	ΔH^E%	395.13	51.32
A-S	Δp%	0.15	9.09
	Δy×100	-	-
	ΔH^E%	332.90	64.31
S-G-R	Δp%	0.13	9.08
	Δy×100	-	-
	ΔH^E%	328.29	44.66
S-V2	Δp%	0.16	9.53
	Δy×100	-	-
	ΔH^E%	187.03	47.13

Table E-14 System 4 with the SRK equation of state

Mixing rules		P	$P+H^E$
Conventional	$\Delta p\%$	1.87	3.31
	$\Delta y \times 100$	-	-
	$\Delta H^E\%$	120.89	35.25
A-S	$\Delta p\%$	0.64	3.26
	$\Delta y \times 100$	-	-
	$\Delta H^E\%$	81.84	37.20
S-G-R	$\Delta p\%$	0.45	3.46
	$\Delta y \times 100$	-	-
	$\Delta H^E\%$	128.73	19.73
S-V2	$\Delta p\%$	0.94	4.10
	$\Delta y \times 100$	-	-
	$\Delta H^E\%$	72.74	34.47

Table E-15 System 4 with the PR equation of state

Mixing rules		P	$P+H^E$
Conventional	$\Delta p\%$	0.92	4.82
	$\Delta y \times 100$	-	-
	$\Delta H^E\%$	199.37	36.47
A-S	$\Delta p\%$	0.12	4.69
	$\Delta y \times 100$	-	-
	$\Delta H^E\%$	157.44	44.29
S-G-R	$\Delta p\%$	0.11	4.83
	$\Delta y \times 100$	-	-
	$\Delta H^E\%$	159.75	36.55
S-V2	$\Delta p\%$	0.12	4.96
	$\Delta y \times 100$	-	-
	$\Delta H^E\%$	111.37	44.29

Table E-16 System 4 with the PRSV equation of state

Mixing rules		P	$P+H^E$
Conventional	$\Delta p\%$	1.69	3.91
	$\Delta y\times 100$	-	-
	$\Delta H^E\%$	147.68	36.22
A-S	$\Delta p\%$	0.52	3.78
	$\Delta y\times 100$	-	-
	$\Delta H^E\%$	92.47	41.74
S-G-R	$\Delta p\%$	0.39	3.96
	$\Delta y\times 100$	-	-
	$\Delta H^E\%$	122.17	33.98
S-V2	$\Delta p\%$	0.72	3.62
	$\Delta y\times 100$	-	-
	$\Delta H^E\%$	83.12	44.48
W-S1	$\Delta p\%$	0.66	4.24
	$\Delta y\times 100$	-	-
	$\Delta H^E\%$	164.36	104.58
W-S2	$\Delta p\%$	0.76	5.03
	$\Delta y\times 100$	-	-
	$\Delta H^E\%$	201.23	6.56

System 5. Benzene + cyclohexane

Table E-17 System 5 with the SW equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	$\Delta p\%$	0.86	0.86	6.53	2.15
	$\Delta y\times 100$	0.53	0.51	1.64	0.18
	$\Delta H^E\%$	47.64	47.21	2.42	35.89
A-S	$\Delta p\%$	0.83	0.84	6.53	2.18
	$\Delta y\times 100$	0.63	0.52	1.61	0.13
	$\Delta H^E\%$	48.71	47.04	2.24	35.53

(Continued)

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
S-G-R	Δp%	0.69	0.62	6.38	1.97
	Δy×100	0.46	0.30	1.59	0.11
	ΔH^E%	48.75	48.29	3.44	37.25
S-V2	Δp%	0.88	0.84	12.89	2.32
	Δy×100	0.62	0.52	3.86	0.13
	ΔH^E%	66.00	64.90	6.92	56.55

Table E-18 System 5 with the SRK equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	0.24	0.25	4.31	0.48
	Δy×100	0.23	0.21	1.80	0.17
	ΔH^E%	34.03	34.57	1.72	37.46
A-S	Δp%	0.09	0.12	4.31	0.45
	Δy×100	0.19	0.16	1.76	0.12
	ΔH^E%	33.83	34.37	1.51	37.12
S-G-R	Δp%	1.09	0.12	4.25	0.64
	Δy×100	1.04	0.09	1.79	0.11
	ΔH^E%	25.67	33.55	2.13	38.64
S-V2	Δp%	0.10	0.12	4.28	0.21
	Δy×100	0.19	0.15	1.75	0.12
	ΔH^E%	33.85	34.36	1.71	35.08

Table E-19 System 5 with the PR equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	1.80	1.78	9.88	4.72
	Δy×100	1.24	1.09	1.89	0.25
	ΔH^E%	66.20	62.80	3.71	39.77

(Continued)

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
A-S	Δp%	1.79	1.75	9.89	4.77
	Δy×100	1.31	1.14	1.85	0.17
	ΔH^E%	62.94	63.44	3.52	39.31
S-G-R	Δp%	1.37	1.35	10.01	4.12
	Δy×100	0.82	0.74	2.01	0.03
	ΔH^E%	66.68	65.60	2.73	43.91
S-V2	Δp%	1.82	1.76	9.82	4.90
	Δy×100	1.32	1.12	1.83	0.17
	ΔH^E%	66.94	63.47	3.99	38.30
W-S1	Δp%	1.59	-	1.22	-
	Δy×100	1.07	-	1.10	-
	ΔH^E%	60.28	-	2.43	-
W-S2	Δp%	1.74	-	1.75	-
	Δy×100	1.17	-	1.25	-
	ΔH^E%	44.26	-	0.72	-

Table E-20 System 5 with the PRSV equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	0.72	0.70	3.13	2.30
	Δy×100	0.75	0.65	1.88	0.14
	ΔH^E%	23.29	25.36	1.31	38.13
A-S	Δp%	0.68	0.70	3.15	2.28
	Δy×100	0.72	0.62	1.84	0.10
	ΔH^E%	23.18	25.19	0.99	37.86
S-G-R	Δp%	0.63	0.68	0.37	2.61
	Δy×100	1.05	0.61	1.88	0.03
	ΔH^E%	23.70	24.92	1.67	40.43
S-V2	Δp%	0.68	0.70	3.10	2.14
	Δy×100	0.72	0.62	1.82	0.10
	ΔH^E%	23.15	25.20	1.29	36.72

(Continued)

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
W-S1	Δp%	0.68	0.68	1.56	2.58
	Δy×100	0.72	0.63	1.63	0.15
	ΔH^E%	77.28	76.00	2.47	56.35
W-S2	Δp%	0.41	0.49	0.66	2.28
	Δy×100	0.46	0.44	0.68	0.10
	ΔH^E%	15.57	8.25	0.58	1.34

System 6. Benzene + n-heptane

Table E-21 System 6 with the SW equation of state

Mixing rules		P	$P+H^E$
Conventional	Δp%	1.89	5.62
	Δy×100	-	-
	ΔH^E%	34.21	2.07
A-S	Δp%	0.82	5.47
	Δy×100	-	-
	ΔH^E%	27.37	2.27
S-G-R	Δp%	1.07	5.64
	Δy×100	-	-
	ΔH^E%	83.31	1.43
S-V2	Δp%	1.62	5.39
	Δy×100	-	-
	ΔH^E%	25.97	2.61

Table E-22 System 6 with the SRK equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	1.01	2.78
	Δy×100	-	-
	ΔH^E%	16.98	0.82
A-S	Δp%	0.50	2.74
	Δy×100	-	-
	ΔH^E%	13.06	1.12
S-G-R	Δp%	0.76	2.89
	Δy×100	-	-
	ΔH^E%	17.25	0.41
S-V2	Δp%	0.33	2.71
	Δy×100	-	-
	ΔH^E%	15.20	1.21

Table E-23 System 6 with the PR equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	2.87	8.48
	Δy×100	-	-
	ΔH^E%	47.38	3.22
A-S	Δp%	1.57	8.28
	Δy×100	-	-
	ΔH^E%	38.53	3.45
S-G-R	Δp%	1.42	8.98
	Δy×100	-	-
	ΔH^E%	67.45	0.60
S-V2	Δp%	2.69	8.12
	Δy×100	-	-
	ΔH^E%	38.42	4.11

Table E-24 System 6 with the PRSV equation of state

Mixing rules		P	$P+H^E$
Conventional	Δp%	0.58	1.82
	Δy×100	-	-
	ΔH^E%	11.63	0.63
A-S	Δp%	0.55	1.82
	Δy×100	-	-
	ΔH^E%	9.57	0.63
S-G-R	Δp%	0.62	1.78
	Δy×100	-	-
	ΔH^E%	11.59	0.79
S-V2	Δp%	0.51	1.79
	Δy×100	-	-
	ΔH^E%	8.98	0.77
W-S1	Δp%	0.56	1.46
	Δy×100	-	-
	ΔH^E%	71.75	2.09
W-S2	Δp%	0.28	0.61
	Δy×100	-	-
	ΔH^E%	24.16	0.18

System 7. Benzene + 1-octene

Table E-25 System 7 with the SW equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	1.07	7.37
	Δy×100	-	-
	ΔH^E%	55.78	4.29
A-S	Δp%	0.69	7.29
	Δy×100	-	-
	ΔH^E%	53.98	4.35
S-G-R	Δp%	0.44	7.80
	Δy×100	-	-
	ΔH^E%	59.20	1.63
S-V2	Δp%	0.58	7.20
	Δy×100	-	-
	ΔH^E%	55.74	4.60

Table E-26 System 7 with the SRK equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	0.93	4.36
	Δy×100	-	-
	ΔH^E%	31.14	2.81
A-S	Δp%	0.91	4.39
	Δy×100	-	-
	ΔH^E%	30.43	2.69
S-G-R	Δp%	0.95	4.42
	Δy×100	-	-
	ΔH^E%	30.90	2.08
S-V2	Δp%	0.76	4.37
	Δy×100	-	-
	ΔH^E%	40.64	2.81

Table E-27 System 7 with the PR equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	1.64	9.21
	Δy×100	-	-
	ΔH^E%	62.04	5.50
A-S	Δp%	1.28	9.17
	Δy×100	-	-
	ΔH^E%	61.26	5.52
S-G-R	Δp%	0.56	9.34
	Δy×100	-	-
	ΔH^E%	70.65	4.41
S-V2	Δp%	0.96	9.08
	Δy×100	-	-
	ΔH^E%	66.82	5.90

Table E-28 System 7 with the PRSV equation of state

Mixing rules		P	P+H^E
Conventional	Δp%	5.26	7.58
	Δy×100	-	-
	ΔH^E%	37.65	3.50
A-S	Δp%	3.64	7.62
	Δy×100	-	-
	ΔH^E%	44.41	3.52
S-G-R	Δp%	3.52	7.54
	Δy×100	-	-
	ΔH^E%	49.69	3.14
S-V2	Δp%	3.60	7.89
	Δy×100	-	-
	ΔH^E%	61.90	1.79

(Continued)

Mixing rules		P	$P+H^E$
W-S1	$\Delta p\%$	3.58	5.51
	$\Delta y\times 100$	-	-
	$\Delta H^E\%$	36.73	6.12
W-S2	$\Delta p\%$	3.58	5.68
	$\Delta y\times 100$	-	-
	$\Delta H^E\%$	162.47	1.26

System 8. n-hexane + ethanol

Table E-29 System 8 with the SW equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	$\Delta p\%$	10.98	11.20	38.15	11.82
	$\Delta y\times 100$	6.25	6.21	16.50	6.18
	$\Delta H^E\%$	525.39	517.60	34.95	501.75
A-S	$\Delta p\%$	2.41	2.44	36.99	2.70
	$\Delta y\times 100$	1.84	1.82	15.70	1.80
	$\Delta H^E\%$	553.07	552.37	7.92	540.19
S-G-R	$\Delta p\%$	1.11	1.19	36.53	1.49
	$\Delta y\times 100$	1.67	1.63	16.72	1.53
	$\Delta H^E\%$	561.56	562.89	4.74	565.36
S-V2	$\Delta p\%$	12.24	12.36	37.12	13.27
	$\Delta y\times 100$	5.06	5.00	15.40	4.71
	$\Delta H^E\%$	432.57	432.61	9.96	432.54

Table E-30 System 8 with the SRK equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	12.46	12.59	38.75	14.62
	Δy×100	4.78	4.78	14.22	4.65
	ΔH^E%	476.50	472.78	24.61	418.74
A-S	Δp%	3.78	3.88	37.77	9.07
	Δy×100	2.28	1.94	13.96	0.98
	ΔH^E%	515.21	507.31	9.13	452.91
S-G-R	Δp%	0.96	1.29	37.89	7.06
	Δy×100	1.62	1.44	14.50	0.38
	ΔH^E%	524.91	522.02	4.46	473.80
S-V2	Δp%	3.85	3.88	37.86	7.18
	Δy×100	3.18	1.86	13.73	2.06
	ΔH^E%	532.81	551.55	10.49	499.17

Table E-31 System 8 with the PT equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	10.52	10.61	36.46	11.96
	Δy×100	5.04	5.03	14.47	4.95
	ΔH^E%	441.53	439.13	25.13	406.37
A-S	Δp%	2.51	2.56	35.41	4.69
	Δy×100	1.45	1.38	14.06	1.14
	ΔH^E%	473.49	469.79	9.19	441.15
S-G-R	Δp%	0.34	0.39	35.73	2.79
	Δy×100	0.47	0.42	14.73	0.30
	ΔH^E%	481.52	480.72	3.30	461.30
S-V2	Δp%	3.13	3.16	35.52	4.06
	Δy×100	3.14	2.42	13.81	1.99
	ΔH^E%	488.50	489.27	10.71	491.15

Table E-32 System 8 with the PR equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	10.17	10.20	35.85	11.23
	Δy×100	5.31	5.30	14.62	5.24
	ΔH^E%	434.67	432.61	24.72	408.33
A-S	Δp%	2.46	2.49	34.85	3.17
	Δy×100	1.45	1.44	14.07	1.37
	ΔH^E%	463.99	462.36	9.16	443.43
S-G-R	Δp%	0.57	0.62	34.98	1.17
	Δy×100	0.66	0.64	14.64	0.68
	ΔH^E%	471.91	472.24	4.69	465.85
S-V2	Δp%	2.99	2.94	34.96	3.49
	Δy×100	3.07	2.57	13.82	1.85
	ΔH^E%	478.98	481.35	10.77	504.38
W-S1	Δp%	1.31	-	1.84	-
	Δy×100	0.81	-	0.95	-
	ΔH^E%	34.36	-	7.84	-
W-S2	Δp%	0.54	-	1.41	-
	Δy×100	0.55	-	0.70	-
	ΔH^E%	124.89	-	2.49	-

Table E-33 System 8 with the PRSV equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	10.42	10.48	35.90	11.85
	Δy×100	5.20	5.19	14.29	5.11
	ΔH^E%	431.67	430.10	24.80	397.11
A-S	Δp%	2.36	2.40	34.90	4.30
	Δy×100	1.52	1.48	13.77	1.26
	ΔH^E%	464.71	461.94	9.22	432.96

(Continued)

Mixing rules		P	P+y	P+H^E	P+y+H^E
S-G-R	Δp%	0.09	0.18	35.23	2.50
	Δy×100	0.42	0.39	14.25	0.46
	ΔH^E%	473.35	472.67	3.25	453.84
S-V2	Δp%	2.80	2.77	35.00	3.27
	Δy×100	3.10	2.45	13.51	1.88
	ΔH^E%	480.92	481.29	10.85	488.43
W-S1	Δp%	1.03	1.09	1.70	1.66
	Δy×100	0.88	0.58	1.05	0.50
	ΔH^E%	34.98	30.11	7.90	28.23
W-S2	Δp%	0.08	0.22	1.17	1.12
	Δy×100	0.38	0.28	0.57	0.23
	ΔH^E%	156.62	71.55	3.05	31.03

System 9. Ethanol + cyclohexane

Table E-34 System 9 with the SW equation of state

Mixing rules		P	P+y	P+H^E	P+y+H^E
Conventional	Δp%	7.91	8.00	31.95	7.98
	Δy×100	6.64	6.52	15.07	6.55
	ΔH^E%	313.60	306.35	37.82	308.00
A-S	Δp%	2.49	2.55	31.44	3.07
	Δy×100	2.17	2.08	14.30	1.81
	ΔH^E%	328.88	330.60	11.72	338.10
S-G-R	Δp%	4.20	1.94	28.05	3.83
	Δy×100	9.41	1.64	11.73	1.45
	ΔH^E%	365.13	338.99	33.62	357.82
S-V2	Δp%	2.34	2.39	31.75	4.50
	Δy×100	1.95	1.75	13.74	1.34
	ΔH^E%	343.71	347.13	17.99	366.72

Table E-35 System 9 with the SRK equation of state

Mixing rules		P	P+y	P+H^E	P+y+H^E
Conventional	Δp%	8.11	8.21	32.56	9.95
	Δy×100	5.34	5.26	13.09	4.79
	ΔH^E%	291.43	286.26	26.78	257.83
A-S	Δp%	2.07	2.15	32.08	5.15
	Δy×100	2.15	1.94	12.86	1.62
	ΔH^E%	314.94	309.55	13.37	284.97
S-G-R	Δp%	3.69	1.28	28.01	8.25
	Δy×100	8.93	1.07	10.96	2.99
	ΔH^E%	379.55	319.34	26.33	245.72
S-V2	Δp%	1.28	1.29	32.43	4.18
	Δy×100	1.21	1.08	12.46	0.46
	ΔH^E%	322.41	319.72	18.12	300.08

Table E-36 System 9 with the PR equation of state

Mixing rules		P	P+y	P+H^E	P+y+H^E
Conventional	Δp%	6.60	6.85	29.50	7.06
	Δy×100	5.74	5.36	13.18	5.26
	ΔH^E%	274.68	252.21	26.85	246.55
A-S	Δp%	2.20	2.28	29.07	2.45
	Δy×100	1.76	1.76	12.74	1.76
	ΔH^E%	270.95	270.65	13.71	271.95
S-G-R	Δp%	1.29	1.25	29.19	2.30
	Δy×100	0.75	0.76	13.59	0.33
	ΔH^E%	278.15	278.50	2.98	288.94
S-V2	Δp%	1.26	1.33	29.41	2.14
	Δy×100	0.73	0.70	12.43	0.34
	ΔH^E%	278.72	279.75	18.35	286.93

Table E-37 System 9 with the PRSV equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	7.23	7.48	30.72	8.79
	Δy×100	6.39	5.79	12.99	5.45
	ΔH^E%	298.74	261.58	26.94	241.27
A-S	Δp%	1.75	1.70	30.32	3.41
	Δy×100	1.91	1.87	12.39	1.81
	ΔH^E%	287.08	283.49	13.49	266.53
S-G-R	Δp%	0.77	4.36	26.57	9.22
	Δy×100	0.99	6.29	10.54	5.33
	ΔH^E%	292.87	307.10	26.44	234.49
S-V2	Δp%	0.85	0.82	30.68	2.32
	Δy×100	0.75	0.67	12.29	0.69
	ΔH^E%	294.76	293.65	18.57	283.01
W-S1	Δp%	1.32	1.27	1.80	1.51
	Δy×100	1.54	0.79	1.81	0.77
	ΔH^E%	21.46	47.99	11.62	46.91
W-S2	Δp%	0.76	1.00	2.80	1.32
	Δy×100	0.96	0.44	1.97	0.41
	ΔH^E%	90.11	29.08	1.34	12.17

System 10. Ethanol + 2,2,4-trimethylpentane

Table E-38 System 10 with the SW equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	14.72	14.72	34.68	14.72
	Δy×100	9.24	9.24	21.79	9.39
	ΔH^E%	490.23	490.54	47.20	503.74

(Continued)

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
A-S	Δp%	3.19	3.24	34.47	4.95
	Δy×100	3.42	3.34	20.93	3.05
	ΔH^E%	547.23	550.78	14.61	567.70
S-G-R	Δp%	10.06	11.02	-	14.72
	Δy×100	10.75	9.13	-	9.39
	ΔH^E%	556.69	597.58	-	504.01
S-V2	Δp%	9.64	9.83	34.61	15.01
	Δy×100	7.47	7.22	20.85	8.30
	ΔH^E%	502.67	503.65	17.44	594.45

Table E-39 System 10 with the SRK equation of state

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
Conventional	Δp%	14.91	15.02	38.12	15.99
	Δy×100	9.07	8.91	20.82	8.33
	ΔH^E%	473.43	467.86	34.73	430.29
A-S	Δp%	4.15	3.95	37.89	6.24
	Δy×100	3.57	3.35	20.44	2.72
	ΔH^E%	539.41	532.63	17.91	501.53
S-G-R	Δp%	10.06	9.33	36.88	16.89
	Δy×100	8.40	6.65	18.34	8.32
	ΔH^E%	595.07	561.43	49.82	407.64
S-V2	Δp%	10.37	11.13	37.99	13.73
	Δy×100	12.28	7.14	20.33	7.60
	ΔH^E%	567.35	541.51	19.27	474.92

Table E-40 System 10 with the PR equation of state

Mixing rules		P	P+y	P+H^E	P+y+H^E
Conventional	Δp%	13.08	13.10	33.77	13.10
	Δy×100	8.47	8.33	20.65	8.33
	ΔH^E%	421.51	409.42	34.83	409.42
A-S	Δp%	3.52	3.56	33.54	3.77
	Δy×100	3.15	2.99	20.01	2.90
	ΔH^E%	464.20	468.95	17.93	477.26
S-G-R	Δp%	8.98	9.76	33.05	1.81
	Δy×100	9.13	8.20	20.80	0.61
	ΔH^E%	542.62	517.97	4.68	482.45
S-V2	Δp%	11.00	11.00	33.65	11.19
	Δy×100	7.33	7.18	19.91	6.95
	ΔH^E%	476.46	482.94	19.38	505.57

Table E-41 System 10 with the PRSV equation of state

Mixing rules		P	P+y	P+H^E	P+y+H^E
Conventional	Δp%	13.25	13.25	34.51	13.68
	Δy×100	8.61	8.59	20.43	8.34
	ΔH^E%	423.82	422.18	34.92	401.33
A-S	Δp%	3.20	3.13	34.29	2.73
	Δy×100	3.25	3.11	19.77	2.86
	ΔH^E%	474.48	474.83	17.91	467.80
S-G-R	Δp%	0.96	1.02	35.69	1.57
	Δy×100	0.57	0.52	18.56	0.59
	ΔH^E%	479.89	479.34	38.73	472.90
S-V2	Δp%	9.43	10.22	34.40	10.34
	Δy×100	11.50	6.92	19.68	7.06
	ΔH^E%	505.50	516.04	19.40	493.98

(Continued)

Mixing rules		P	P+y	$P+H^E$	$P+y+H^E$
W-S1	Δp%	0.86	0.87	2.02	1.12
	Δy×100	1.28	1.22	1.09	1.14
	ΔH^E%	26.22	27.13	14.60	27.41
W-S2	Δp%	0.35	0.46	1.55	0.92
	Δy×100	0.65	0.51	1.21	0.46
	ΔH^E%	77.53	86.81	3.00	75.56

Evaluation remarks

It was found that the PRSV equation of state, with an additional adjustable parameter characteristic of each pure component, provided a better simultaneous representation of VLE and H^E. Yet it is fair to say that all the equations investigated in this work performed with a similar degree of reliability.

Comparing to EOS, mixing rules have a much stronger effect on simultaneous representation of VLE and H^E, especially for the systems containing a polar component. For example, for the system of n-hexane + ethanol, all the equations with respectively the conventional, A-S, S-V2 mixing rules, and even three-parameter S-G-R mixing rule were unable to produce reasonable results for simultaneous representation of VLE and H^E. The deviations of vapour pressure produced by these calculations were above 34 per cent in all the cases. However, when W-S1 and W-S2 mixing rules were employed (with, for example, PR and PRSV equations of state), a dramatic improvement was observed on not only vapor pressure, but H^E as well. With the van Laar model, the W-S1 mixing rule bought the deviations down to 1.70 per cent for vapour pressure and 7.90 per cent for H^E, while with the NRTL model for the W-S2 mixing rule, the deviations

were 1.17 per cent for vapor pressure and 3.05 per cent for H^E. This is probably due to the theoretical background of the mixing rule and the temperature function involved in its parameter determination.

The following conclusions are reached for the simultaneous representation of VLE and H^E:

1. Simple cubic equations of state are capable of performing the studied simultaneous representation with a reasonable accuracy.

2. A better representation of vapor pressure at a given temperature by means of an equation of state cannot guarantee a better fitting of H^E, because the variation of the equation parameters with temperature contributes a more important factor in the H^E calculations than in the VLE calculations.

3. Mixing rules have stronger effect on simultaneous representation of VLE and H^E than equations of state.

4. It has been proven that the Wong-Sandler mixing rule could be used for simultaneous representation of VLE and H^E values even for the systems containing a strong polar component.

E-3 Computer programs used in simultaneous representation of VLE and H^E values by means of cubic equations of state

Some computer programs used in simultaneous representation of VLE and H^E values are presented in this section. They are the ones for PR and PRSV equations of state, for Wong-Sandler mixing rule with the NRTL and van Laar activity coefficient models, and for bubble point calculations.

```
*****************************************************************
*  This program is used to calculate thermodynamic properties by *
*  using Peng-Robinson equation.                                 *
*   N - Number of components                                     *
*   T - Temperature K                                            *
*   P - Pressure Pa                                              *
*   X(N) - Composition mol                                       *
*   V - Volume m^3/mol                                           *
*   FU(N) - Fugacity coefficients                                *
*   H - Enthalpy J/mol                                           *
*   S - Entropy J/mol K                                          *
*   IP - IP =1 Gas phase                                         *
*           =2 Liquid phase                                      *
*   IFU - IFU =1 Calculate V and FU                              *
*             =2 Calculate V, H and S                            *
*             =3 Calculate C1,C2 AND C3 ONLY FOR CRITICAL POINT  *
*****************************************************************
      SUBROUTINE EOSPR(N,T,P,X,V,FU,H,S,IP,IFU)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),FU(N),RX(3)
      DIMENSION AP(20),BP(20),BP2(20),BP3(20)
      COMMON/CONST1/TC(20),PC(20),VC(20),W(20),U(20),WM(20)
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      COMMON/ABT/DAI(20),DBI(20),DB2I(20),DB3I(20)
      COMMON/ABT1/ATI,BTI,BT2I,BT3I
      COMMON/KIJ1/RK(3,20,20),ID(20)
      COMMON/VEOR/IVR
      COMMON/LEOR/ILR
      COMMON/LC/LC
      COMMON/RT/R,T0
      LC=1
      IF(IFU.NE.2)LC=0
      IF(IP.EQ.1)IVR=0
      IF(IP.EQ.2)ILR=0
      RT=R*T
      DO 10 I=1,N
      TR=T/TC(I)
      QAC=0.45724
      AL=0.37464+1.54226*W(I)-0.26992*W(I)**2
      ALF=(1.0+AL*(1.0-DSQRT(TR)))**2
      AP(I)=QAC*ALF*R*R*TC(I)**2/PC(I)
      QBC=0.0778
```

```
      QB2C=-QBC*(1.0-DSQRT(2))
      QB3C=-QBC*(1.0+DSQRT(2))
      BP(I)=QBC*R*TC(I)/PC(I)
      BP2(I)=QB2C*R*TC(I)/PC(I)
      BP3(I)=QB3C*R*TC(I)/PC(I)
      IF(LC.EQ.0)GOTO 10
      DALF=2.0*DSQRT(ALF)*(-0.5*AL*TR**(-0.5)/TC(I))
      DAI(I)=QAC*DALF*R*R*TC(I)**2/PC(I)
      DBI(I)=0.0
      DB2I(I)=0.0
      DB3I(I)=0.0
10    CONTINUE
      CALL MIXT(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      AEO=AE
      AE=AE*P/(RT*RT)
      BEO=BE
      BE=BE*P/RT
      BE2=BE2*P/RT
      BE3=BE3*P/RT
      C1=-(1.0+BE+BE2+BE3)
      C2=AE+BE2+BE3+BE*BE2+BE*BE3+BE2*BE3
      C3=-(AE*BE+BE2*BE3+BE*BE2*BE3)
      IF(IFU.EQ.3)RETURN
      CALL RTCUB(C1,C2,C3,RX,NR,NG)
      IF(NR.EQ.1)THEN
       ZG=RX(1)
       ZL=RX(1)
       IF(IP.EQ.1)IVR=1
       IF(IP.EQ.2)ILR=1
      ELSE
       IF(NG.NE.0)THEN
        ZG=RX(3)
        ZL=RX(3)
       ELSE
        ZL=RX(1)
        ZG=RX(3)
       ENDIF
      ENDIF
C      WRITE(*,*)'C1,C2,C3',C1,C2,C3
C      WRITE(*,*)'ZG,ZL',ZG,ZL
      IF(IP.EQ.1)Z=ZG
      IF(IP.EQ.2)Z=ZL
      IF(DABS(Z).LT.1.E-8)THEN
```

```
      V=0.0
      H=0.0
      S=0.0
      DO 20 I=1,N
      FU(I)=0.0
20    CONTINUE
      RETURN
     ENDIF
     V=Z*R*T/P
     DO 30 I=1,N
     AEI(I)=AEI(I)*P/(R*R*T*T)
     BEI(I)=BEI(I)*P/R/T
     BE2I(I)=BE2I(I)*P/R/T
     BE3I(I)=BE3I(I)*P/R/T
30   CONTINUE
     GOTO(100,200),IFU
100  CONTINUE
     CALL FUGGEN(N,Z,AE,BE,BE2,BE3,FU)
     RETURN
200  CONTINUE
     ATI=T*ATI*P/(R*R*T*T)
     BTI=T*BTI*P/R/T
     BT2I=T*BT2I*P/R/T
     BT3I=T*BT3I*P/R/T
     CALL HSGEN(N,T,P,X,Z,AE,BE,BE2,BE3,ATI,BTI,BT2I,BT3I,H,S)
     RETURN
     END
```

```
*****************************************************************
*  This program is used to calculate thermodynamic properties by *
*  using PRSV equation                                           *
*  (Stryjek,R. Can. J. Chem. Eng. 64, 323(1986)                  *
*  (Mathias, P.M. Ind.Eng.Chem.Process Des.Dev.1983,22,385-391)  *
*   N - Number of components                                     *
*   T - Temperature K                                            *
*   P - Pressure Pa                                              *
*   X(N) - Composition mol                                       *
*   V - Volume m^3/mol                                           *
*   FU(N) - Fugacity coefficients                                *
*   H - Enthalpy J/mol                                           *
*   S - Entropy J/mol K                                          *
*   IP - IP =1 Gas phase                                         *
*           =2 Liquid phase                                      *
*   IFU - IFU =1 Calculate V and FU                              *
*             =2 Calculate V, H and S                            *
*             =3 Calculate C1,C2 AND C3 ONLY FOR CRITICAL POINT  *
*****************************************************************
      SUBROUTINE EOSPRSV(N,T,P,X,V,FU,H,S,IP,IFU)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),FU(N),RX(3)
      DIMENSION AP(20),BP(20),BP2(20),BP3(20)
      COMMON/CONST1/TC(20),PC(20),VC(20),W(20),U(20),WM(20)
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      COMMON/ABT/DAI(20),DBI(20),DB2I(20),DB3I(20)
      COMMON/ABT1/ATI,BTI,BT2I,BT3I
      COMMON/KIJ1/RK(3,20,20),ID(20)
      COMMON/VEOR/IVR
      COMMON/LEOR/ILR
      COMMON/MPR/EP1(20),EP2(20)
      COMMON/LC/LC
      COMMON/RT/R,TO
      LC=1
      IF(IFU.NE.2)LC=0
      IF(IP.EQ.1)IVR=0
      IF(IP.EQ.2)ILR=0
      RT=R*T
      DO 10 I=1,N
      TR=T/TC(I)
C --  MATHIAS EXPRESSION
```

```
C      QAC=0.45724
C      QBC=0.0778
C      AL=0.37464+1.54226*W(I)-0.26992*W(I)**2
C      ALF=(1.0+AL*(1.0-DSQRT(TR))-EP1(I)*(1.0-TR)*(0.7-TR))**2
C      DALF=2.0*DSQRT(ALF)*(-0.5*AL*TR**(-0.5)/TC(I)+
C     1 EP1(I)*((0.7-TR)+(1.0-TR))/TC(I))
C ---------------------
C --  STRYJEK-VERA EXPRESSION
      QAC=0.457235
      QBC=0.077796
      AK0=0.378893+1.4897153*W(I)-0.17131848*W(I)**2+0.0196554*W(I)**3
      AK=AK0+EP1(I)*(1.0+DSQRT(TR))*(0.7-TR)
      ALF=(1.0+AK*(1.0-DSQRT(TR)))**2
      DAK=EP1(I)*(0.5*TR**(-0.5)*(0.7-TR)-(1.0+DSQRT(TR)))/TC(I)
      DALF=2.0*DSQRT(ALF)*(DAK*(1.0-DSQRT(TR))+
     1 AK*(-0.5*TR**(-0.5)/TC(I)))
C ---------------------
      AP(I)=QAC*ALF*R*R*TC(I)**2/PC(I)
      QB2C=-QBC*(1.0-DSQRT(2))
      QB3C=-QBC*(1.0+DSQRT(2))
      BP(I)=QBC*R*TC(I)/PC(I)
      BP2(I)=QB2C*R*TC(I)/PC(I)
      BP3(I)=QB3C*R*TC(I)/PC(I)
      IF(LC.EQ.0)GOTO 10
      DAI(I)=QAC*DALF*R*R*TC(I)**2/PC(I)
      DBI(I)=0.0
      DB2I(I)=0.0
      DB3I(I)=0.0
10    CONTINUE
      CALL MIXT(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      AEO=AE
      AE=AE*P/(RT*RT)
      BEO=BE
      BE=BE*P/RT
      BE2=BE2*P/RT
      BE3=BE3*P/RT
      C1=-(1.0+BE+BE2+BE3)
      C2=AE+BE2+BE3+BE*BE2+BE*BE3+BE2*BE3
      C3=-(AE*BE+BE2*BE3+BE*BE2*BE3)
C      C1=-(1.0-BE)
C      C2=(AE-3.0*BE**2-2.0*BE)
C      C3=-(AE*BE-BE**2-BE**3)
      IF(IFU.EQ.3)RETURN
```

```
      CALL RTCUB(C1,C2,C3,RX,NR,NG)
      IF(NR.EQ.1)THEN
       ZG=RX(1)
       ZL=RX(1)
       IF(IP.EQ.1)IVR=1
       IF(IP.EQ.2)ILR=1
      ELSE
       IF(NG.NE.0)THEN
        ZG=RX(3)
        ZL=RX(3)
       ELSE
        ZL=RX(1)
        ZG=RX(3)
       ENDIF
      ENDIF
C      WRITE(*,*)'C1,C2,C3',C1,C2,C3
C      WRITE(*,*)'ZG,ZL',ZG,ZL
      IF(IP.EQ.1)Z=ZG
      IF(IP.EQ.2)Z=ZL
      IF(DABS(Z).LT.1.E-8)THEN
       V=0.0
       H=0.0
       S=0.0
       DO 20 I=1,N
       FU(I)=0.0
20     CONTINUE
       RETURN
      ENDIF
      V=Z*R*T/P
      DO 30 I=1,N
      AEI(I)=AEI(I)*P/(R*R*T*T)
      BEI(I)=BEI(I)*P/R/T
      BE2I(I)=BE2I(I)*P/R/T
      BE3I(I)=BE3I(I)*P/R/T
30    CONTINUE
      GOTO(100,200),IFU
100   CONTINUE
      DO 110 I=1,N
C      FU1=-DLOG(Z-BE)
C      FU2=BEI(I)/BE*(Z-1.0)
C      FU3=0.5/DSQRT(2.0)*AE/BE*((AEI(I)+AE)/AE-BEI(I)/BE)
C      FU4=DLOG((Z+BE*(1.0-DSQRT(2.0)))/(Z+BE*(1.0+DSQRT(2.0))))
C      FU(I)=DEXP(FU1+FU2+FU3*FU4)
```

```
110   CONTINUE
      CALL FUGGEN(N,Z,AE,BE,BE2,BE3,FU)
      RETURN
200   CONTINUE
      ATI=T*ATI*P/(R*R*T*T)
      BTI=T*BTI*P/R/T
      BT2I=T*BT2I*P/R/T
      BT3I=T*BT3I*P/R/T
C      H1=Z-1.0
C      H2=(ATI-AE)/(2.0*DSQRT(2.0)*BE)
C      H3=DLOG((Z+2.414*BE)/(Z-0.414*BE))
C      H=R*T*(H1+H2*H3)
C      WRITE(*,*)'RT,Z,BE=',RT,Z,BE
C      WRITE(*,*)'AE,ATI=',AE,ATI
C      WRITE(*,*'H1,2,3=',RT*H1,RT*H2,RT*H3
      CALL HSGEN(N,T,P,X,Z,AE,BE,BE2,BE3,ATI,BTI,BT2I,BT3I,H,S)
      RETURN
      END
```

```
************************************************************************
*   FUGMSL SUBROUTINE IS USED TO CALCULATE THE FUGACITY OF MSL TYPE *
*   EQUATION   1=1/(Z-B)-A/((Z-B2)(Z-B3))                          *
************************************************************************
      SUBROUTINE FUGGEN(N,Z,AE,BE,BE2,BE3,FU)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION FU(N)
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      IF(Z-BE.LE.0.DO)THEN
      WRITE(*,*)' Z<BE AT FUGGEN'
      RETURN
      ENDIF
      DO 100 I=1,N
      FU1=BEI(I)/(Z-BE)-DLOG(Z-BE)
      IF(DABS(BE2-BE3).GT.1.D-8)THEN
       FU2=AE/(BE2-BE3)*((BE2I(I)-BE3I(I))/(BE2-BE3)-1.0-AEI(I)/AE)*
     1  DLOG((Z-BE3)/(Z-BE2))
       FU3=-AE/(BE2-BE3)*(BE2I(I)/(Z-BE2)-BE3I(I)/(Z-BE3))
      ELSE
       FU2=-(AE+AEI(I))/(Z-BE2)
       FU3=-AE*BE2I(I)/(Z-BE2)**2
      ENDIF
      IF(FU1+FU2+FU3.GT.140.0.OR.FU1+FU2+FU3.LT.-140.0)THEN
       WRITE(*,*)' FU IS WRONG'
       RETURN
      ENDIF
      FU(I)=DEXP(FU1+FU2+FU3)
100   CONTINUE
      RETURN
      END
************************************************************************
*   HSGEN SUBROUTINE IS USED TO CALCULATE THE ENTHALPY AND ENTROPY  *
*   OF GENERAL TYPE EQUATION   1=1/(Z-B)-A/((Z-B2)(Z-B3))          *
************************************************************************
      SUBROUTINE HSGEN(N,T,P,X,Z,AE,BE,BE2,BE3,ATI,BTI,BT2I,BT3I,H,S)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N)
      COMMON/RT/R,TO
      RT=R*T
C      ACM=0.0
C      BCM=0.0
C      CCM=0.0
```

```
C      DCM=0.0
C      DO 10 I=1,N
C      ACM=ACM+X(I)*AC(I)
C      BCM=BCM+X(I)*BC(I)
C      CCM=CCM+X(I)*CC(I)
C      DCM=DCM+X(I)*DC(I)
C10    CONTINUE
C      H01=ACM*(T-T0)+BCM*(T**2-T0**2)/2+CCM*(T**3-T0**3)/3+
C     1 DCM*(T**4-T0**4)/4
       H01=0.0
       DH1=-BTI/(Z-BE)
       DH2=AE/(BE2-BE3)*(BT2I/(Z-BE2)-BT3I/(Z-BE3))
       DH31=DLOG((Z-BE2)/(Z-BE3))/(BE2-BE3)*(AE-ATI)
       DH32=DLOG((Z-BE2)/(Z-BE3))/(BE2-BE3)*AE*(BT2I-BT3I)/
      1 (BE2-BE3)
       DH3=DH31+DH32
       DH4=Z-1
C      WRITE(*,*)'H1,2=',DH1*RT,DH2*RT
C      WRITE(*,*)'H3,4=',DH3*RT,DH4*RT
       H=H01+RT*(DH1+DH2+DH3+DH4)
C      S0=ACM*DLOG(T/T0)+BCM*(T-T0)+CCM*(T**2-T0**2)/2+
C     1 DCM*(T**3-T0**3)/3
       S0=0.0
       DS1=DLOG((Z-BE)/Z)
       DS2=-BTI/(Z-BE)
       DS3=-ATI/(BE2-BE3)*DLOG((Z-BE2)/(Z-BE3))
       DS41=AE*BT2I/(BE2-BE3)
       DS421=1.0/(Z-BE2)
       DS422=1.0/(BE2-BE3)*DLOG((Z-BE2)/(Z-BE3))
       DS4=DS41*(DS421+DS422)
       DS51=AE*BT3I/(BE3-BE2)
       DS52=(1.0/(Z-BE3)+
      1 1.0/(BE3-BE2)*DLOG((Z-BE3)/(Z-BE2)))
       DS5=DS51*DS52
       DS6=0.0
       DO 20 I=1,N
       IF(DABS(X(I)).LT.1.D-6)GOTO 20
       DS6=DS6-X(I)*DLOG(X(I))
 20    CONTINUE
       DS7=-DLOG(P/Z)
 1000  FORMAT(2X,A,3G12.5)
       S=S0+R*(DS1+DS2+DS3+DS4+DS5+DS6+DS7)
       RETURN
```

```
      END
*****************************************************************
*     MACT IS A SUBROUTINE FOR CALCULATING EXCESS GIBBS FREE ENERGY  *
*     BY USING DIFFERENT ACTIVITY MODELS                             *
*     LA - CODE OF ACTIVITY MODEL                                    *
*          LA=1 VAN LAAR                                             *
*             =2 NRTL                                                *
*     N - THE NUMBER OF COMPONENTS                                   *
*     X(N) - COMPOSITIONS OF COMPONENTS                              *
*     T - TEMPERATURE K                                              *
*     GEXC - EXCESS GIBBS FREE ENERGY                                *
*     DGEXC - DIFFERENTIAL OF EXCESS GIBBS FREE ENERGY d(nG)/dni     *
*     DGEXCT - DIFFERENTIAL OF EXCESS GIBBS FREE ENERGY WITH T       *
*              d(G/RT)/dT                                            *
*     CONACT - ENERGY COEFFICIENTS                                   *
*****************************************************************
      SUBROUTINE MACT(N,X,T,GEXC,DGEXC,DGEXCT)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),DGEXC(N)
      COMMON/ACT/CONACT(5,10,10),LA
      COMMON/RT/R,T0
      RT=R*T
      GEXC=0.0
      DO 5 I=1,N
      DGEXC(I)=0.0
5     CONTINUE
      GOTO(10,20),LA
10    CONTINUE
C --  VAN LAAR MODEL(ONLY FOR BINARY SYSTEM)
C     CONACT - PARAMETERS
C              1,I,J=Aij
      GEXC=R*T*X(1)*X(2)*CONACT(1,1,2)*CONACT(1,2,1)/
     1 (X(1)*CONACT(1,1,2)+X(2)*CONACT(1,2,1))
      DGEXC(1)=R*T*CONACT(1,1,2)*((CONACT(1,2,1)*X(2))/
     1 (CONACT(1,1,2)*X(1)+CONACT(1,2,1)*X(2)))**2
      DGEXC(2)=R*T*CONACT(1,2,1)*((CONACT(1,1,2)*X(1))/
     1 (CONACT(1,1,2)*X(1)+CONACT(1,2,1)*X(2)))**2
      RETURN
20    CONTINUE
C --  NRTL MODEL
C     CONACT - PARAMETERS
C              1,I,J=ALFij
C              2,I,J=TOij
```

```
      DO 200 I=1,N
      GS1=0.0
      GS2=0.0
      DO 210 J=1,N
      TOJI=CONACT(2,J,I)/RT
      GJI=DEXP(-CONACT(1,J,I)*CONACT(2,J,I)/RT)
      GS1=GS1+X(J)*TOJI*GJI
      GS2=GS2+X(J)*GJI
210   CONTINUE
      GEXC=GEXC+R*T*X(I)*(GS1/GS2)
      DGS=0.0
      DO 220 J=1,N
      DGS1=0.0
      DGS2=0.0
      DO 222 K=1,N
      GKJ=DEXP(-CONACT(1,K,J)*CONACT(2,K,J)/RT)
      DGS1=DGS1+X(K)*CONACT(2,K,J)/RT*GKJ
      DGS2=DGS2+X(K)*GKJ
222   CONTINUE
      GIJ=DEXP(-CONACT(1,I,J)*CONACT(2,I,J)/RT)
      DGS=DGS+X(J)*GIJ/DGS2*(CONACT(2,I,J)/RT-DGS1/DGS2)
220   CONTINUE
      DGEXC(I)=R*T*(GS1/GS2+DGS)
200   CONTINUE
      DGEXCT=0.0
      DO 240 I=1,N
      GS1=0.0
      GS2=0.0
      DGS1T=0.0
      DGS2T=0.0
      DO 250 J=1,N
      TOJI=CONACT(2,J,I)/RT
      GJI=DEXP(-CONACT(1,J,I)*CONACT(2,J,I)/RT)
      GS1=GS1+X(J)*TOJI*GJI
      GS2=GS2+X(J)*GJI
      DTOJIT=-CONACT(2,J,I)/(R*T**2)
      DGJIT=GJI*(-CONACT(1,J,I)*DTOJIT)
      DGS1T=DGS1T+X(J)*(DTOJIT*GJI+DGJIT*TOJI)
      DGS2T=DGS2T+X(J)*DGJIT
250   CONTINUE
      DGEXCT=DGEXCT+X(I)*(DGS1T*GS2-DGS2T*GS1)/GS2**2
240   CONTINUE
      RETURN
      END
```

```
*****************************************************************
*     1 - CONVENTIONAL MIXING RULE                              *
*     2 - ADACHI-SUGIE MIXING RULE                              *
*     3 - S. G. R. MIXING RULE                                  *
*     4 - STRYJEK-VERA MIXING RULE 1: MARGULES-TYPE             *
*     5 - STRYJEK-VERA MIXING RULE 2: VAN LAAR-TYPE             *
*     6 - WONG-SANDLER MIXING RULE                              *
*****************************************************************
      SUBROUTINE MIXT(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),AP(N),BP(N),BP2(N),BP3(N)
      COMMON/MIX/LMIX
      GOTO(1,2,3,4,5,6,7,8),LMIX
1     CONTINUE
      CALL MIXC(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      RETURN
2     CONTINUE
      CALL MIXAS(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      RETURN
3     CONTINUE
      CALL MIXSGR(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      RETURN
4     CONTINUE
      CALL MIXSV1(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      RETURN
5     CONTINUE
      CALL MIXSV2(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      RETURN
6     CALL MIXWS(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      RETURN
      END
*****************************************************************
*  MIXC SUBROUTINE IS USED TO CALCULATE MIXTURE PARAMETERS BY USING  *
*  CONVENTIONAL MIXING RULE                                     *
*     AIJ=(AI*AJ)^0.5(1-KAIJ)                                   *
*     BIJ=(BI+BJ)/2                                             *
*     A=sum.XI*XJ*AIJ                                           *
*     B=sum.XI*XJ*BIJ                                           *
*****************************************************************
      SUBROUTINE MIXC(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),AP(N),BP(N),BP2(N),BP3(N)
```

```
      COMMON/CONST1/TC(20),PC(20),VC(20),W(20),U(20),WM(20)
      COMMON/KIJ1/RK(3,20,20),ID(20)
      COMMON/ABT/DAI(2),DBI(2),DB2I(2),DB3I(2)
      COMMON/ABT1/ATI,BTI,BT2I,BT3I
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      COMMON/LC/LC
      COMMON/RT/R,T0
      T=T
      P=P
      DO 10 I=1,N
      RK(1,I,I)=0.D0
10    CONTINUE
      DO 20 I=1,N-1
      DO 20 J=I+1,N
      RK(1,J,I)=RK(1,I,J)
20    CONTINUE
      AE=0.D0
      BE=0.D0
      BE2=0.D0
      BE3=0.D0
      DO 100 I=1,N
      AEI(I)=0.0
      BEI(I)=0.0
      BE2I(I)=BP2(I)
      BE3I(I)=BP3(I)
      BE2=BE2+X(I)*BP2(I)
      BE3=BE3+X(I)*BP3(I)
      DO 100 J=1,N
      AIJ=DSQRT(AP(I)*AP(J))*(1.D0-RK(1,I,J))
      BIJ=(BP(I)+BP(J))/2.0
      AE=AE+X(I)*X(J)*AIJ
      BE=BE+X(I)*X(J)*BIJ
      AEI(I)=AEI(I)+X(J)*AIJ
      BEI(I)=BEI(I)+X(J)*BIJ
100   CONTINUE
      DO 110 I=1,N
      AEI(I)=2.0*AEI(I)-AE
      BEI(I)=2.0*BEI(I)-BE
110   CONTINUE
      RETURN
      END
```

```
************************************************************************
*  THIS SUBROUTINE IS USED TO CALCULATE MIXTURE PARAMETERS BY USING *
*  ADACHI AND SUGIE MIXING RULE                                      *
*  AIJ=(AI*AJ)^0.5(1-KIJ-LIJ(XI-XJ))                                 *
************************************************************************
      SUBROUTINE MIXAS(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),AP(N),BP(N),BP2(N),BP3(N)
      COMMON/CONST1/TC(20),PC(20),VC(20),W(20),U(20),WM(20)
      COMMON/KIJ1/RK(3,20,20),ID(20)
      COMMON/ABT/DAI(2),DBI(2),DB2I(2),DB3I(2)
      COMMON/ABT1/ATI,BTI,BT2I,BT3I
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      COMMON/LC/LC
      COMMON/RT/R,T0
      T=T
      P=P
      DO 10 I=1,N
      RK(1,I,I)=0.D0
      RK(2,I,I)=0.D0
      I1=I+1
      IF(I.EQ.N)GOTO 10
      DO 20 J=I+1,N
      RK(1,J,I)=RK(1,I,J)
      RK(2,J,I)=-RK(2,I,J)
20    CONTINUE
10    CONTINUE
      AE=0.D0
      BE=0.D0
      BE2=0.D0
      BE3=0.D0
      DO 100 I=1,N
      BE=BE+X(I)*BP(I)
      BE2=BE2+X(I)*BP2(I)
      BE3=BE3+X(I)*BP3(I)
      DO 100 J=1,N
      IF(I.EQ.J)THEN
      AIJ=AP(I)
      ELSE
      AIJ=DSQRT(AP(I)*AP(J))*(1.D0-RK(1,I,J)-RK(2,I,J)*
     1 (X(I)-X(J)))
      ENDIF
```

```
      AE=AE+X(I)*X(J)*AIJ
100   CONTINUE
      AEO=0.DO
      DO 110 I=1,N
      DO 110 J=1,N
      AEO=AEO+X(I)*X(J)*DSQRT(AP(I)*AP(J))*RK(2,I,J)*(X(I)-X(J))
110   CONTINUE
      AEO=AEO-AE
      DO 120 I=1,N
      BEI(I)=BP(I)
      BE2I(I)=BP2(I)
      BE3I(I)=BP3(I)
      AE1=0.DO
      AE2=0.DO
      DO 130 J=1,N
      IF(I.EQ.J)THEN
      AIJ=AP(I)
      ELSE
      AIJ=DSQRT(AP(I)*AP(J))*(1.DO-RK(1,I,J)-RK(2,I,J)*
     1 (2.0*X(I)-X(J)))
      ENDIF
      AE1=AE1+X(J)*AIJ
130   CONTINUE
      AE1=AE1*2.DO
      AEI(I)=AE1+AEO
120   CONTINUE
      IF(LC.EQ.0)RETURN
      ATI=0.0
      BT1=0.0
      BT2I=0.0
      BT3I=0.0
      DO 140 I=1,N
      BT2I=BT2I+X(I)*DB2I(I)
      BT3I=BT3I+X(I)*DB3I(I)
      DO 140 J=1,N
      IF(I.EQ.J)THEN
       DAIJ=DAI(I)
       DBIJ=DBI(I)
      ELSE
       AIJ=DSQRT(AP(I)*AP(J))
       DAIJ=0.5*(1.0-RK(1,I,J)-RK(2,I,J)*(X(I)-X(J)))/AIJ*
     1 (AP(J)*DAI(I)+AP(I)*DAI(J))
       DBIJ=0.5*(DBI(I)+DBI(J))
```

```
      ENDIF
      ATI=ATI+X(I)*X(J)*DAIJ
      BTI=BTI+X(I)*X(J)*DBIJ
  140 CONTINUE
      RETURN
      END
*************************************************************************
*  MIXSGR SUBROUTINE IS USED TO CALCULATE MIXTURE PARAMETERS BY USING *
*  SGR MIXING RULE. KIJ AND LIJ ARE INDEPENDENT OF TEMPERATURE        *
*     AIJ=(AI*AJ)^0.5(1-KIJ-LIJ(MIJXI-MJIXJ)/(MIJXI+MJIXJ))          *
*************************************************************************
      SUBROUTINE MIXSGR(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),AP(N),BP(N),BP2(N),BP3(N)
      COMMON/CONST1/TC(20),PC(20),VC(20),W(20),U(20),WM(20)
      COMMON/KIJ1/RK(3,20,20),ID(20)
      COMMON/ABT/DAI(2),DBI(2),DB2I(2),DB3I(2)
      COMMON/ABT1/ATI,BTI,BT2I,BT3I
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      COMMON/RT/R,T0
      COMMON/LC/LC
      T=T
      P=P
      DO 10 I=1,N
      RK(1,I,I)=0.D0
      RK(2,I,I)=0.D0
      RK(3,I,I)=1.D0
      I1=I+1
      IF(I.EQ.N)GOTO 10
      DO 20 J=I+1,N
      RK(1,J,I)=RK(1,I,J)
      RK(2,J,I)=-RK(2,I,J)
      RK(3,J,I)=1.-RK(3,I,J)
20    CONTINUE
10    CONTINUE
      AE=0.D0
      BE=0.D0
      BE2=0.D0
      BE3=0.D0
      DO 100 I=1,N
      BE=BE+X(I)*BP(I)
      BE2=BE2+X(I)*BP2(I)
      BE3=BE3+X(I)*BP3(I)
```

```
      DO 100 J=1,N
      IF(I.EQ.J)THEN
       AIJ=AP(I)
      ELSE
       AIJ=DSQRT(AP(I)*AP(J))*(1.DO-RK(1,I,J)-RK(2,I,J)*
     1 (RK(3,I,J)*X(I)-RK(3,J,I)*X(J))/(RK(3,I,J)*X(I)+
     2 RK(3,J,I)*X(J))*(X(I)+X(J)))
      ENDIF
      AE=AE+X(I)*X(J)*AIJ
  100 CONTINUE
      AEO=0.DO
      DO 110 I=1,N
      DO 110 J=1,N
      AEO=AEO+X(I)*X(J)*DSQRT(AP(I)*AP(J))*(1.DO-RK(1,I,J))
  110 CONTINUE
      AEO=AEO-2.DO*AE
      DO 120 I=1,N
      BEI(I)=BP(I)
      BE2I(I)=BP2(I)
      BE3I(I)=BP3(I)
      AE1=0.DO
      AE2=0.DO
      DO 130 J=1,N
      IF(I.EQ.J)THEN
       AIJ=AP(I)
       AIJ1=0.DO
      ELSE
       AIJ=DSQRT(AP(I)*AP(J))*(1.DO-RK(1,I,J)-RK(2,I,J)*
     1 (RK(3,I,J)*X(I)-RK(3,J,I)*X(J))/(RK(3,I,J)*X(I)+
     2 RK(3,J,I)*X(J))*(X(I)+X(J)))
       AIJ1=X(I)*X(J)*DSQRT(AP(I)*AP(J))*RK(2,I,J)*((RK(3,I,J)*X(I)-
     1 RK(3,J,I)*X(J))/(RK(3,I,J)*X(I)+RK(3,J,I)*X(J))+2.*RK(3,I,J)*
     2 RK(3,J,I)*X(J)*(X(I)+X(J))/(RK(3,I,J)*X(I)+RK(3,J,I)*X(J))**2)
      ENDIF
      AE1=AE1+X(J)*AIJ
      AE2=AE2+AIJ1
  130 CONTINUE
      AE1=AE1*2.DO
      AE2=AE2*2.DO
      AEI(I)=AE1+AEO-AE2
  120 CONTINUE
      IF(LC.EQ.0)RETURN
      ATI=0.0
```

```
      BTI=0.0
      BT2I=0.0
      BT3I=0.0
      K(3,I,J)=CONSTANT
      DO 140 I=1,N
      BTI=BTI+X(I)*DBI(I)
      BT2I=BT2I+X(I)*DB2I(I)
      BT3I=BT3I+X(I)*DB3I(I)
      DO 140 J=1,N
      IF(I.EQ.J)THEN
       DAIJ=DAI(I)
      ELSE
       AIJ=DSQRT(AP(I)*AP(J))
       RK3=(RK(3,I,J)*X(I)-RK(3,J,I)*X(J))/(RK(3,I,J)*X(I)+
     1 RK(3,J,I)*X(J))*(X(I)+X(J))
       DAIJ=0.5/AIJ*(AP(J)*DAI(I)+AP(I)*DAI(J))*
     1 (1.D0-RK(1,I,J)-RK(2,I,J)*RK3)
      ENDIF
      ATI=ATI+X(I)*X(J)*DAIJ
140   CONTINUE
      RETURN
      END
*************************************************************************
*  THIS SUBROUTINE IS USED TO CALCULATE MIXTURE PARAMETERS BY USING *
*  STRYJEK AND VERA MIXING RULE 1: MARGULES-TYPE                    *
*       AIJ=(AI*AJ)^0.5(1-XI*KIJ-XJ*KJI)                            *
*************************************************************************
      SUBROUTINE MIXSV1(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),AP(N),BP(N),BP2(N),BP3(N)
      COMMON/CONST1/TC(20),PC(20),VC(20),W(20),U(20),WM(20)
      COMMON/ABT/DAI(2),DBI(2),DB2I(2),DB3I(2)
      COMMON/ABT1/ATI,BTI,BT2I,BT3I
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      COMMON/KIJ1/RK(3,20,20),ID(20)
      COMMON/RT/R,T0
      COMMON/LC/LC
      T=T
      P=P
      DO 10 I=1,N
      RK(1,I,I)=0.D0
      RK(2,I,I)=0.D0
      RK(3,I,I)=0.D0
```

```
      I1=I+1
      IF(I.EQ.N)GOTO 10
      DO 20 J=I+1,N
      RK(1,J,I)=RK(2,I,J)
20    CONTINUE
10    CONTINUE
      AE=0.D0
      BE=0.D0
      BE2=0.D0
      BE3=0.D0
      AE2=0.0
      DO 100 I=1,N
      BEI(I)=BP(I)
      BE2I(I)=BP2(I)
      BE3I(I)=BP3(I)
      BE=BE+X(I)*BP(I)
      BE2=BE2+X(I)*BP2(I)
      BE3=BE3+X(I)*BP3(I)
      DO 100 J=1,N
      AIJ=DSQRT(AP(I)*AP(J))*(1.D0-RK(1,I,J)*X(I)-RK(1,J,I)*X(J))
      AIJ2=DSQRT(AP(I)*AP(J))*(X(I)*RK(1,I,J)+X(J)*RK(1,J,I))
      AE=AE+X(I)*X(J)*AIJ
      AE2=AE2+X(I)*X(J)*AIJ2
100   CONTINUE
      DO 110 I=1,N
      AE1=0.0
      DO 120 J=1,N
      AIJ1=DSQRT(AP(I)*AP(J))*(1.D0-2.0*RK(1,I,J)*X(I)-RK(1,J,I)*
     1 X(J))
      AE1=AE1+X(J)*AIJ1
120   CONTINUE
      AE1=AE1*2.D0
      AEI(I)=AE1+AE2-AE
110   CONTINUE
      IF(LC.EQ.0)RETURN
      ATI=0.0
      BTI=0.0
      BT2I=0.0
      BT3I=0.0
      DO 140 I=1,N
      BT2I=BT2I+X(I)*DB2I(I)
      BT3I=BT3I+X(I)*DB3I(I)
      DO 140 J=1,N
```

```
      IF(I.EQ.J)THEN
       DAIJ=DAI(I)
       DBIJ=DBI(I)
      ELSE
       AIJ=DSQRT(AP(I)*AP(J))
       DAIJ=0.5*(1.D0-RK(1,I,J)*X(I)-RK(1,J,I)*X(J))
     1  /AIJ*(AP(J)*DAI(I)+AP(I)*DAI(J))
       DBIJ=0.5*(DBI(I)+DBI(J))
      ENDIF
      ATI=ATI+X(I)*X(J)*DAIJ
      BTI=BTI+X(I)*X(J)*DBIJ
140   CONTINUE
      RETURN
      END
*************************************************************************
*  THIS SUBROUTINE IS USED TO CALCULATE MIXTURE PARAMETERS BY USING *
*  STRYJEK AND VERA MIXING RULE 2: VAN LAAR-TYPE                    *
*     AIJ=(AI*AJ)^0.5(1-KIJ*KJI/(XI*KIJ+XJ*KJI))                    *
*************************************************************************
      SUBROUTINE MIXSV2(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),AP(N),BP(N),BP2(N),BP3(N)
      COMMON/CONST1/TC(20),PC(20),VC(20),W(20),U(20),WM(20)
      COMMON/ABT/DAI(2),DBI(2),DB2I(2),DB3I(2)
      COMMON/ABT1/ATI,BTI,BT2I,BT3I
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      COMMON/KIJ1/RK(3,20,20),ID(20)
      COMMON/RT/R,T0
      COMMON/LC/LC
      T=T
      P=P
      DO 10 I=1,N
      RK(1,I,I)=0.D0
      RK(2,I,I)=0.D0
      RK(3,I,I)=0.D0
      I1=I+1
      IF(I.EQ.N)GOTO 10
      DO 20 J=I+1,N
      RK(1,J,I)=RK(2,I,J)
20    CONTINUE
10    CONTINUE
      AE=0.D0
      AE2=0.0
```

```
      BE=0.D0
      BE2=0.D0
      BE3=0.D0
      DO 100 I=1,N
      BE1(I)=BP(I)
      BE2I(I)=BP2(I)
      BE3I(I)=BP3(I)
      BE=BE+X(I)*BP(I)
      BE2=BE2+X(I)*BP2(I)
      BE3=BE3+X(I)*BP3(I)
      DO 100 J=1,N
      IF(I.EQ.J)THEN
       AIJ=AP(I)
       AIJ2=0.0D0
      ELSE
       AIJ=DSQRT(AP(I)*AP(J))*(1.D0-RK(1,I,J)*RK(1,J,I)/
     1  (X(I)*RK(1,I,J)+X(J)*RK(1,J,I)))
       AIJ2=DSQRT(AP(I)*AP(J))*(RK(1,I,J)*RK(1,J,I)/(X(I)*RK(1,I,J)+
     1  X(J)*RK(1,J,I)))
      ENDIF
      AE=AE+X(I)*X(J)*AIJ
      AE2=AE2+X(I)*X(J)*AIJ2
  100 CONTINUE
      DO 110 I=1,N
      AE1=0.0
      AE3=0.0
      DO 120 J=1,N
      IF(I.EQ.J)THEN
      AIJ=AP(I)
      AIJ3=0.0
      ELSE
      AIJ=DSQRT(AP(I)*AP(J))*(1.D0-RK(1,I,J)*RK(1,J,I)/
     1 (X(I)*RK(1,I,J)+X(J)*RK(1,J,I)))
      AIJ3=DSQRT(AP(I)*AP(J))*(RK(1,I,J)**2*RK(1,J,I)/(X(I)*RK(1,I,J)+
     1 X(J)*RK(1,J,I))**2)
      ENDIF
      AE1=AE1+X(J)*AIJ
      AE3=AE3+X(I)*X(J)*AIJ3
  120 CONTINUE
      AE1(I)=2.0*AE1-AE2+2.0*AE3-AE
  110 CONTINUE
      IF(LC.EQ.0)RETURN
      ATI=0.0
```

```
      BTI=0.0
      BT2I=0.0
      BT3I=0.0
      DO 140 I=1,N
      BT2I=BT2I+X(I)*DB2I(I)
      BT3I=BT3I+X(I)*DB3I(I)
      DO 140 J=1,N
      IF(I.EQ.J)THEN
       DAIJ=DAI(I)
       DBIJ=DBI(I)
      ELSE
       AIJ=DSQRT(AP(I)*AP(J))
       DAIJ=0.5*(1.D0-RK(1,I,J)*RK(1,J,I)/
     1 (X(I)*RK(1,I,J)+X(J)*RK(1,J,I)))
     2  /AIJ*(AP(J)*DAI(I)+AP(I)*DAI(J))
       DBIJ=0.5*(DBI(I)+DBI(J))
      ENDIF
      ATI=ATI+X(I)*X(J)*DAIJ
      BTI=BTI+X(I)*X(J)*DBIJ
140   CONTINUE
      RETURN
      END
*************************************************************************
*  MIXWS SUBROUTINE IS USED TO CALCULATE MIXTURE PARAMETERS BY USING  *
*  WONG-SANDLER MIXING RULE                                           *
*     ABIJ=((BI-AI/RT)+(BJ-AJ/RT))/2.0*(1.0-KIJ)                      *
*     BIJ=(BI+BJ)/2                                                   *
*     Q=sum.XI*XJ*(BIJ-AIJ/RT)                                        *
*     D=sum.XI*AI/(BI*RT) + AEinf/CRT                                 *
*     C=1/SQRT(2)*ALOG(SQRT(2)-1) (for PR equation of state           *
*     A=RT*Q*D/(1-D)                                                  *
*     B=Q/(1-D)                                                       *
*************************************************************************
      SUBROUTINE MIXWS(N,X,T,P,AE,BE,BE2,BE3,AP,BP,BP2,BP3)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),AP(N),BP(N),BP2(N),BP3(N),DAEXC(20)
      COMMON/CONST1/TC(20),PC(20),VC(20),W(20),U(20),WM(20)
      COMMON/KIJ1/RK(3,20,20),ID(20)
      COMMON/ABT/DAI(2),DBI(2),DB2I(2),DB3I(2)
      COMMON/ABT1/ATI,BTI,BT2I,BT3I
      COMMON/ABE/AEI(20),BEI(20),BE2I(20),BE3I(20)
      COMMON/RT/R,TO
      COMMON/ACT/CONACT(5,10,10),LA
```

```
      COMMON/LC/LC
      COMMON/SIGMA/SIGMA
C     LC=0 DON'T CALCULATE ENTHALPY
C       =1 CALCULATE ENTHALPY
C     LA=1 VAN LAAR MODEL
C       =2 NRTL MODEL
C -------------------------
C --  FOR P-R EQUATION ONLY
      CONB2=BP2(1)/BP(1)
      CONB3=BP3(1)/BP(1)
      SIGMA=DLOG(DSQRT(2.0)-1.0)/DSQRT(2.0)
C --------------------------------
      P=P
      DO 10 I=1,N
      RK(1,I,I)=0.D0
      I1=I+1
      IF(I.EQ.N)GOTO 10
      DO 20 J=I+1,N
      RK(1,J,I)=RK(1,I,J)
20    CONTINUE
10    CONTINUE
      AE=0.D0
      AES=0.0
      BE=0.D0
      BES=0.0
      QE=0.0
      BE2=0.D0
      BE3=0.D0
      DO 100 I=1,N
      AEI(I)=0.0
      BEI(I)=0.0
      BE2I(I)=0.0
      BE3I(I)=0.0
      BES=BES+X(I)*AP(I)/(BP(I)*R*T)
      AES=AES+X(I)*AP(I)/BP(I)
      DO 100 J=1,N
      ABIJ=0.5*((BP(I)-AP(I)/R/T)+(BP(J)-AP(J)/R/T))*(1.0-RK(1,I,J))
      QE=QE+X(I)*X(J)*ABIJ
100   CONTINUE
      CALL MACT(N,X,T,AEXC,DAEXC,DAEXCT)
      DE=BES+AEXC/(SIGMA*R*T)
      BE=QE/(1.0-DE)
      AE=R*T*QE*DE/(1.0-DE)
```

```
      BE2=BE*CONB2
      BE3=BE*CONB3
      DO 110 I=1,N
      DDE=AP(I)/(BP(I)*R*T)+DAEXC(I)/(SIGMA*R*T)
      DQES=0.0
      DO 112 J=1,N
      ABIJ=0.5*((BP(I)-AP(I)/R/T)+(BP(J)-AP(J)/R/T))*(1.0-RK(1,I,J))
      DQES=DQES+2.0*X(J)*ABIJ
112   CONTINUE
      BEI(I)=DQES/(1.0-DE)-QE/(1.0-DE)**2*(1.0-DDE)
      AEI(I)=R*T*(DE*BEI(I)+BE*DDE)-AE
      BE2I(I)=CONB2*BEI(I)
      BE3I(I)=CONB3*BEI(I)
110   CONTINUE
      IF(LC.EQ.0)RETURN
      DQDT=0.0
      DDDT=0.0
      DO 140 I=1,N
      DDDT=DDDT+X(I)/(R*(BP(I)*T)**2)*(T*DAI(I)*BP(I)-
     1 AP(I)*(T*DBI(I)+BP(I)))
      DO 140 J=1,N
      DABIJ=0.5*((DBI(I)-(T*DAI(I)-AP(I))/(R*T**2))+
     1 (DBI(J)-(T*DAI(J)-AP(J))/(R*T**2)))*(1.0-RK(1,I,J))
      DQDT=DQDT+X(I)*X(J)*DABIJ
140   CONTINUE
      DDDT=DDDT+DAEXCT/SIGMA
      ATI=R*(QE*DE/(1.0-DE)+T*((1.0-DE)*(DE*DQDT+QE*DDDT)+QE*DE*DDDT)/
     1 (1.0-DE)**2)
      BTI=(DDDT*QE+(1.0-DE)*DQDT)/(1.0-DE)**2
C     FOR PR EOS ONLY
      BT2I=BTI*CONB2
      BT3I=BTI*CCNB3
      RETURN
      END
```

```
*************************************************************************
*  This pogram is used for VLE calculation (bubble point pressure       *
*  calculation). The program normally returns to IERR=0, but to IEER=-2 *
*  if bad data(T and X) was used, to IEER=1 if it run 20 step and still *
*  cannot find the root, to IEER=-1 when K value is over the range and  *
*  to IEER=-3 while no VLE exisist.                                     *
*  The program needs to call subroutine EOS Which form is:              *
*  EOS(N,T,P,X,V,FU,H,S,IP,IFU)                                         *
*  In EOS fugacity coeffients FU(N) are calculated by Equation of state *
*************************************************************************
      SUBROUTINE VLEB(N,T,P,X,Y,IEER)
      IMPLICIT REAL*8(A-H,O-Z)
      EXTERNAL FBUBP
      DIMENSION X(N),Y(N),FK(20)
      COMMON/FBU/XCOM(20),YCOM(20),TCOM,NCOM
      COMMON/VEOR/IVR
      COMMON/LEOR/ILR
      COMMON/IEOR/IEOR
      COMMON/DV/DVGL
      COMMON/QQE/QQE
      TCOM=T
      NCOM=N
      IEER=0
      EPS1=1.D-8
      EPS2=1.D-8
      IF(N.GT.20)THEN
       WRITE(7,*)' N GREATER THAN 20'
       IEER=-2
       RETURN
      ENDIF
      IF(T.LE.20.D0.OR.T.GT.700.D0)THEN
       WRITE(7,*)' T DATA IS WRONG'
       IEER=-2
       RETURN
      ENDIF
      S=0.0
      SS=0.0
      NRX=N
      DO 5 I=1,N
      IF(DABS(X(I)).LT.1.D-6)NRX=NRX-1
      XCOM(I)=X(I)
      YCOM(I)=Y(I)
```

```
      S=S+X(I)
      SS=SS+Y(I)
5     CONTINUE
      IF(DABS(S-1.D0).GT.0.01D0)THEN
       WRITE(7,*)' X DATA IS WRONG'
       IEER=-2
       RETURN
      ENDIF
      IF(DABS(SS-1.D0).GT.1.E-4)THEN
       CALL IDVLE(3,N,T,P,X,Y,FK,IEER)
       IF(IEER.EQ.-2)THEN
        WRITE(7,*)' PSAT DATA WRONG'
        RETURN
       ENDIF
      ENDIF
      CALL KCALC(N,T,P,X,Y,FK)
      IF(DABS(DVGL).LT.0.75)GOTO 100
      P1=P
      P2=P*0.98
      P=RTSEC(FBUBP,P1,P2,1.D-10)
      DO 10 I=1,N
      Y(I)=YCOM(I)
10    CONTINUE
      RETURN
100   CONTINUE
      WRITE(*,*)'N,T,P=',N,T,P
      WRITE(*,*)'X1,Y1,DVGL=',X(1),Y(1),DVGL
      DL=0.2
      ND=10
      PO=P
      Y1O=YCOM(1)
105   CONTINUE
      P=PO*DL
      DT=T*DL/ND
      P1O=P
      P1=P
      P2=P1*QQE
      TCOM=T-ND*DT
      P=RTSEC(FBUBP,P1,P2,1.D-10)
      IF(NRX.EQ.1)THEN
       IF(IVR.NE.0.OR.ILR.NE.0)THEN
        DL=DL*1.2
        ND=ND*1.2
```

```
        GOTO 105
       ENDIF
      ELSE
       IF(DABS(YCOM(1)-XCOM(1)).LT.1.D-4)THEN
        DL=DL*1.2
        ND=ND*1.2
        YCOM(1)=Y10
        YCOM(2)=1.0-YCOM(1)
        GOTO 105
       ELSE
       ENDIF
      ENDIF
      ND1=ND
      P100=P10
      Y100=Y10
107   CONTINUE
      ND=ND1
      DO 110 I=1,ND
      I1=ND-I
      TCOM=T-I1*DT
      P1=P10
      P2=P1*0.992
      YCOM(1)=Y10
      YCOM(2)=1.0-Y10
      P=RTSEC(FBUBP,P1,P2,1.D-10)
      IF(NRX.EQ.1)THEN
       IF(IVR.NE.0.OR.ILR.NE.0)THEN
        ND1=(ND-I+1)*2
        DT=DT/2.0
        P10=P100
        GOTO 107
       ENDIF
      ELSE
       IF(DABS(YCOM(1)-XCOM(1)).GT.1.D-4)THEN
       ELSE
        ND1=(ND-I+1)*2
        IF(ND1.GT.5000)THEN
         WRITE(*,*)' NONCONV. IN ',I,' ND=',ND,' TCOM=',TCOM
         WRITE(*,*)' T=',T,' IEOR=',IEOR
         P=P10
         YCOM(1)=Y10
         YCOM(2)=1.0-Y10
         GOTO 130
```

```
        ENDIF
        DT=DT/2.0
        P10=P100
        Y10=Y100
        GOTO 107
       ENDIF
      ENDIF
      P100=P10
      P10=P
      Y100=Y10
      Y10=YCOM(1)
110   CONTINUE
130   CONTINUE
      DO 120 I=1,N
      Y(I)=YCOM(I)
120   CONTINUE
      RETURN
      END
      DOUBLE PRECISION FUNCTION FBUBP(P)
      IMPLICIT REAL*8(A-H,O-Z)
      LOGICAL FLAG
      DIMENSION X(20),Y(20),FK(20),YTEMP(20)
      COMMON/FBU/XCOM(20),YCOM(20),TCOM,NCOM
      T=TCOM
      N=NCOM
      DO 5 I=1,N
      X(I)=XCOM(I)
      Y(I)=YCOM(I)
5     CONTINUE
      ITER=0
10    CONTINUE
      CALL KCALC(N,T,P,X,Y,FK)
      YSUM=0.0
      DO 20 I=1,N
      YTEMP(I)=X(I)*FK(I)
      YSUM=YSUM+YTEMP(I)
20    CONTINUE
      FLAG=.TRUE.
      DO 30 I=1,N
      YTEMP(I)=YTEMP(I)/YSUM
      FLAG=FLAG.AND.DABS(YTEMP(I)-Y(I)).LT.1.D-6
      Y(I)=YTEMP(I)
30    CONTINUE
```

```
      ITER=ITER+1
      IF(ITER.GE.20)FLAG=.TRUE.
      IF(.NOT.FLAG)GOTO 10
      FBUBP=0.0
      DO 40 I=1,N
      YCOM(I)=Y(I)
      FBUBP=FBUBP+X(I)*FK(I)
40    CONTINUE
      FBUBP=DLOG(FBUBP)
      RETURN
      END
      SUBROUTINE KCALC(N,T,P,X,Y,FK)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),Y(N),FG(20),FL(20),FK(N)
      COMMON/DV/DVGL
      CALL EOS(N,T,P,X,VL,FL,H,S,2,1)
      CALL EOS(N,T,P,Y,VG,FG,H,S,1,1)
      IF(VL.LE.0.0.OR.VG.LE.0.0)THEN
       WRITE(*,*)'N,T,P=',N,T,P
       WRITE(*,*)'X=',(X(I),I=1,N)
       WRITE(*,*)'Y=',(Y(I),I=1,N)
      ENDIF
      DVGL=(VG-VL)/VL
      DO 10 I=1,N
      FK(I)=FL(I)/FG(I)
10    CONTINUE
      RETURN
      END
      SUBROUTINE IDVLE(ITP,N,T,P,X,Y,K,IER)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 X(N),Y(N),K(N)
      COMMON/PS/PSA(20),PSB(20),PSC(20)
      PV(T,I)=DEXP(PSA(I)-PSB(I)/(T+PSC(I)))
      IF(ITP.EQ.5)GOTO 50
      IER=0
      DO 5 I=1,N
      IF(DABS(PSA(I)).LE.1.D-10)THEN
       IER=-2
       RETURN
      ENDIF
5     CONTINUE
      IF(ITP.GT.2) GOTO 30
      T=0.DO
```

```
      DO 10 I=1,N
      IF(ITP.EQ.1) Z=X(I)
      IF(ITP.EQ.2) Z=Y(I)
10    T=T+Z*(-PSC(I)+PSB(I)/(PSA(I)-DLOG(P)))
      IT=1
13    SS=0.D0
      DO 15 I=1,N
      K(I)=PV(T,I)/P
      IF (ITP.EQ.1) SS=SS+K(I)*X(I)
15    IF (ITP.EQ.2) SS=SS+Y(I)/K(I)
      F=SS-1.
      IF (DABS(F).LE.5.D-6) GOTO 20
      IF (IT.EQ.1) GOTO 14
      BFF=F*(T-TO)/(F-FO)
      IF(DABS(BFF).GT.T*0.3)BFF=DSIGN(T*0.3,BFF)
      TO=T
      T=T-BFF
      FO=F
      DO 16 I=1,N
      BBK=PSA(I)-PSB(I)/(T+PSC(I))
      IF(BBK.GT.120.D0.AND.BBK.LT.-120.D0)GOTO 17
16    CONTINUE
      GOTO 13
17    T=TO
      GOTO 20
14    TO=T
      T=T*1.01D0
      FO=F
      IT=IT+1
      GOTO 13
20    DO 25 I=1,N
      IF (ITP.EQ.2) GOTO 26
      Y(I)=K(I)*X(I)/SS
      GOTO 25
26    X(I)=Y(I)/K(I)/SS
25    CONTINUE
      RETURN
30    IF(ITP.GT.3) GOTO 40
      P=0.D0
      DO 35 I=1,N
35    P=P+X(I)*PV(T,I)
      DO 37 I=1,N
      K(I)=PV(T,I)/P
```

```
37    Y(I)=X(I)*K(I)
      RETURN
40    P=0.D0
      QQ=0.9D0
      DO 41 I=1,N
41    P=P+Y(I)*PV(T,I)
      IT=1
42    SS=0.D0
      DO 43 I=1,N
      K(I)=PV(T,I)/P
43    SS=SS+Y(I)/K(I)
      F=DLOG(SS)
      IF (DABS(F).LT.0.00001D0) GOTO 47
      IF (IT.EQ.1) GOTO 45
      P=(P-F*(P-P0)/(F-F0))*(1.-QQ)+P*QQ
      QQ=QQ*QQ
      GOTO 42
45    P0=P
      F0=F
      P=P*1.01D0
      IT=IT+1
      GOTO 42
47    DO 48 I=1,N
48    X(I)=Y(I)/K(I)/SS
      RETURN
50    CONTINUE
      DO 55 I=1,N
      K(I)=PV(T,I)/P
55    CONTINUE
      RETURN
      END
*************************************************************************
* Use the secant method to find the root of a function FUNC,
* thought to lie near X1 and X2, to an accuracy XACC.
* Taken from "Numerical Recipes".
*************************************************************************
      DOUBLE PRECISION FUNCTION RTSEC(FUNC,X1,X2,XACC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/IEOR/IEOR
      XACC=XACC
      IEOR=0
      MAXIT=200
      QQ=0.0
```

```
      FL=FUNC(X1)
      F=FUNC(X2)
      IF(DABS(FL).LT.DABS(F)) THEN
       RTSEC=X1
       XL=X2
       SWAP=FL
       FL=F
       F=SWAP
      ELSE
       XL=X1
       RTSEC=X2
      ENDIF
20    CONTINUE
      DO 11 J=1,MAXIT
       DF=F-FL
       IF(J.GE.MAXIT-1)THEN
       WRITE(*,*)'F=',F,FL
       WRITE(*,*)'X=',RTSEC,XL
       ENDIF
       IF(DABS(DF).LT.1.D-16)DF=DSIGN(1.D-16,DF)
       DX=(XL-RTSEC)*F/DF
       XL=RTSEC
       FL=F
13     CONTINUE
       IF(DABS(DX).GT.DABS(XL*0.1))THEN
        DX=DX*0.5
        GOTO 13
       ENDIF
       RTSEC=RTSEC+DX*(1.0-QQ)
15     CONTINUE
       F=FUNC(RTSEC)
       IF(DABS(F).LT.1.0D-5) RETURN
   11 CONTINUE
      IF(MAXIT.LT.202)THEN
       MAXIT=300
       QQ=0.99
       GOTO 20
      ENDIF
12    CONTINUE
      WRITE(*,*)' *** MAXIT EXCEEDED IN RTSEC'
      IEOR=1
      RETURN
      END
```