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EXCESS ENTHALPIES AND EXCESS VOLUMES FOR n-BUTYL METHYL ETHER + n-ALKANE SYSTEMS AT 298.15 K

by

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ABSTRACT

Research on excess properties plays an important role in solution thermodynamics. The experimental excess properties of liquid mixtures provide essential information for testing and developing solution theories. They also provide the data required for process design in chemical and petroleum industries. In addition excess properties are useful for testing thermodynamic consistency for vapor-liquid equilibrium data.

Both excess enthalpies H^E and excess volumes V^E were determined in this study for six binary systems consisting of n-butyl methyl ether and an n-alkane at 298.15 K.

Flory theory with an interaction parameter, which was found to be a quadratic function of the carbon number of the n-alkane molecules, was used to correlate the experimental H^E data and then to predict V^E values which were subsequently compared with the experimental V^E data.

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NOMENCLATURE

A	constant of densimeter in equation 4.13 and 4.14
A_0, A_1	constants for equation 4.4
A_{11}, A_{12}, A_{22}	the numbers of contact pairs in Flory model
B	constant of densimeter in equation 4.13 and 4.14
c	the external degree of freedom in Flory model
c	the spring constant in chapter 4
E	electrical potential
E_0	the mean intermolecular energy in Flory model
f	vibration frequency
f_i	volumetric flow rate of component i
G^E	excess Gibbs energy
H^E	excess enthalpy
$H_m^E(cal)$	the representation of H_m^E by equation 4.9
$H_m^E(exp)$	experimental value of H_m^E
h_j	coefficient of smoothing equation 4.9
I	current
k	velocity constant
M	mass
M	an actual property in chapter 1
$M^{(id)}$	the property for an ideal solution

M^E	excess property
ΔM	property change
ΔM^E	the property change of mixing
$\Delta M^{(id)}$	the property change for an ideal solution
M_i	molar mass
N	the mole number of mixture produced in mixing cell per second
N	the number of molecules in Flory model
N_i	the number of molecules of component i
n_{pt}	the number of experimental points
n_{coeff}	the number of coefficients in equation 4.9
P	electrical power
p^*	characteristic pressure in Flory model
p_i^*	characteristic pressure for component i in Flory model
Q_{comb}	combinatorial factor in partition function
Q_p	partition function
R	calibration resistance in equation 4.2 and 4.3;
R	gas constant
R_c	standard resistance
r_i	segment number of component i
s	standard deviation
S^E	excess entropy
s_i	molecular surface area of contact per segment for component i

T	temperature
T	vibration period in equation 4.12 and 4.14
T^*	characteristic temperature in Flory model
V	the volume of vibrating tube in chapter 4
v	the volume of a spherical segment in Flory model
$\tilde{v}$	reduced volume in Flory model
v_i	the volume of a spherical segment in Flory model for component i
v_i	molar volume of component i in chapter 4
v_i^*	molar core volume in Flory model for component i
v_j	constant for smoothing equation 4.16
V_m^E	molar excess volume
$V_m^E(cal)$	the representaton of V_m^E by equation 4.16
$V_m^E(exp)$	experimental value of V_m^E
V^E	excess volume
VLE	vapor-liquid equilibrium
$V_l(f)$	voltage reading at flow rate f
$V_l^\circ(f)$	baseline voltage reading at flow rate f
W	electrical power
x	mole fraction
X	flow rate in equation 4.4

GREEK LETTERS

γ	geometric factor
γ_i	activity coefficient of component i
ε	thermopile calibration constant
$\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{12}$	energies associated with each contact pair
θ_i	contacted surface area fraction
ρ	density of sample
ρ_i	density of component i
ϕ_i	volume fraction
X_{12}	interchange energy parameter in Flory model

Chapter 1

INTRODUCTION

It seems definitely right that one plus one equals two, but not always. Driving a car during the winter, for example, antifreeze is certainly needed, which is mainly composed of water and ethylene glycol. If one liter of water is mixed with one liter of ethylene glycol, can we obtain two liters of the mixture? The answer is "no". We can not expect to understand mixing behavior as simple as 1+1=2, mathematically, because the excess volume V^E has to be considered here. In other words, mixing process brings to the system some changes. Not only in volume, the change is also found in temperature. For example, if one mole of n-hexane is mixed adiabatically with the same amount of cyclohexane at 25°C, the temperature of the mixture must be lower than the original one, because the mixing process is endothermic and about 432 Joules of heat must be added to bring the temperature back to 25°C. We call this amount of heat excess enthalpy, H^E. Both H^E and V^E in these two examples are called excess properties.

In thermodynamics, an excess property of a solution or mixture is, by definition, the difference between the actual property, M, and the property, $M^{(id)}$, which would be obtained for the same conditions of temperature, pressure and composition for an ideal solution as shown in equation (1.1) or (1.2).

$$M^E = M - M^{(id)} \tag{1.1}$$

or

$$\Delta M^E = \Delta M - \Delta M^{(id)} \tag{1.2}$$

where M^E represents the excess property and ΔM^E is the property change of mixing. Since

$$\begin{aligned} \Delta M^E &= \Delta M - \Delta M^{(id)} \\ &= (M - \Sigma x_i M_i) - (M^{(id)} - \Sigma x_i M_i) \qquad (1.3) \\ &= \mathrm{M} - M^{(id)} \\ &= M^E \end{aligned}$$

the general equation can be written as

$$M^E = \Delta M^E = \Delta M - \Delta M^{(id)} \tag{1.4}$$

Excess properties include the excess enthalpy H^E, excess volume V^E, excess entropy S^E and excess Gibbs energy G^E, etc. The research on these properties occupies an important place in thermodynamics.

Why is it true? Why are people interested in excess properties? There are several reasons. First, the experimental excess properties of liquid mixtures provide essential data to test solution theories. Up to date, many successful solution theories have been developed, such as the regular solution theory, cell theory, Flory theory, associated solution theory and so on. The feasibility of these solution theories can be tested by excess properties. For example, in 1965, Flory proposed his solution theory based on the study of mixtures of chain molecules. In his study, Flory suggested a semi-empirical partition function and derived a liquid equation of state, which is related to the excess functions of mixture. To test the Flory theory, experimental excess enthalpy H^E data can be used to obtain the interaction parameter X_{12} in the model. Then the theory can be applied to predict the excess volume V^E of the same system using the X_{12} obtained from H^E. Comparing the results of such calculations with experimental V^E data frequently gives a satisfactory agreement. Secondly, excess properties can serve as a guide for formulating a new solution theory. Also, the experimental excess property data provide the data required for process design in the chemical and petroleum industries. In addition, excess properties are useful for testing the thermodynamic consistency of vapor-liquid equilibrium (VLE) data by means of the following equations.

For isothermal data,

$$\int_{x_1=0}^{x_1=1} ln\frac{\gamma_1}{\gamma_2}dx_1 = -\int_{P_{(x_1=0)}}^{P_{(x_1=1)}} \frac{V^E}{RT}dP \tag{1.5}$$

and for isobaric data,

$$\int_{x_1=0}^{x_1=1} ln\frac{\gamma_1}{\gamma_2}dx_1 = \int_{T_{(x_1=0)}}^{T_{(x_1=1)}} \frac{H^E}{RT^2}dT \tag{1.6}$$

Among excess properties, the excess enthalpy H^E and excess volume V^E can be measured directly from experiments. Values of H^E are measured by means of a calorimeter. Adiabatic calorimeters, isothermal calorimeters and flow calorimeters are some popular ones which are widely used today. To determine excess volume

V^E, there are two methods used. One is the precision measurement of density using a densimeter, and the other is the direct measurement of volume change with a dilatometer.

The excess Gibbs energy G^E, unlike H^E and V^E, can not be measured directly. It can be derived from experimental VLE data by using the following equation

$$G^E = RT \sum x_i ln \gamma_i \tag{1.7}$$

The methods from which G^E can be derived include: the measurement of VLE data at a fixed temperature, gas-liquid chromatography, isobaric VLE measurement, light-scattering measurement and freezing temperature determination combined with excess enthalpies measured over a temperature range [25].

The excess entropy S^E can be only derived from other excess properties

$$S^E = \frac{H^E - G^E}{T} \tag{1.8}$$

Because H^E and V^E are the only excess properties which can be measured directly, they are especially interesting to chemists and chemical engineers. In this study, both H^E and V^E were measured for six binary systems.

Ethers are widely used in chemists' laboratories and in chemical industry especially as a solvent, because many organic substances are soluble in ethers. A product of vaccum distillation, for example, may contain a large proportion of water which is difficult to be separated from the desired product by ordinary distillation. Adding a proper ether as an extractant, however, makes the separation much easier. Recent papers [4,16,22,46,47] from our laboratory have reported the measurements of excess enthalpies for mixtures of a symmetrical di-n-alkyl ether $(C_pH_{2p+1})_2O$ (p=2,3,4,5), with an n-alkane C_nH_{2n+2} (n=6,7,8,10,12,16). As an extension to these studies, we have chosen to measure binary mixtures of n-butyl methyl ether with n-alkanes and thus to investigate the effect of ether asymmetry on the excess properties of n-alkyl ether + n-alkane systems.

Chapter 2

METHODOLOGY

The determination of H^E and V^E should be based on experiments, as mentioned in the introduction. Different experimental methods are reviewed in this chapter.

2.1 Calorimetric measurements of excess enthalpy

In principle, the excess enthalpy H^E may be derived from the temperature dependence of the excess Gibbs free energy. From the definitions of Gibbs energy and enthalpy

$$G = H - ST \tag{2.1}$$

and

$$H = U + PV \tag{2.2}$$

and the fundamental equation for a closed system

$$dU = TdS - PdV \tag{2.3}$$

the following thermodynamic equation is obtained

$$dG = -SdT + VdP \tag{2.4}$$

Taking the derivatives of both sides of equation 2.4 with respect to T at constant pressure gives

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{2.5}$$

From equation 2.1,

$$-S = \frac{G-H}{T} \tag{2.6}$$

Combining equations 2.5 and 2.6 yields

$$\left(\frac{\partial G}{\partial T}\right)_P = \frac{G-H}{T} \tag{2.7}$$

Dividing T on both sides of equation 2.7 yields

$$\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P = \frac{G-H}{T^2} = \frac{G}{T^2} - \frac{H}{T^2} \tag{2.8}$$

Rearranging equation 2.8 leads to the Helmholtz equation

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} \tag{2.9}$$

For the excess properties, the Helmholtz equation remains in the same form

$$\left(\frac{\partial G^E/T}{\partial T}\right)_P = -\frac{H^E}{T^2} \tag{2.10}$$

Therefore,

$$H^E(T,P,x) = G^E(T,P,x) - T\left([\frac{\partial G^E(T,P,x)}{\partial T}]_P\right) \tag{2.11}$$

In practice, however, to obtain precise values of H^E, it is necessary to measure H^E directly using a calorimeter rather than derive it from G^E, because measurements of G^E rarely extend over a temperature range of more than 15 per cent of the temperature [25] and the error in evaluation of the variation of G^E with temperatures is relatively large. Williamson [52] has discussed the case where G^E is determined at two temperatures 30 K apart in the region of 300 K. If G^E is assumed independent of temperature then an error of $\pm\delta$ in G^E will lead to an error of $\pm$ 15 δ in H^E.

Nowadays, many types of calorimeters are used for different needs. Usually, calorimeters may be classified according to which physical variables are kept constant [26].

2.1.1 Adiabatic calorimeter

The type of adiabatic batch calorimeter designed originally by McGlashan is one of the most successful ones and has been used to obtain results over a wide range of temperature [3,11,20]. In an adiabatic calorimeter, the two liquid components are mixed in a calorimetric vessel which is thermally isolated from its surroundings. Strictly speaking, the term adiabatic is used in a vague sense because 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 done by

(i) minimizing the temperature difference between the calorimetric vessel and its surroundings. If H^E is positive (endothermic) then there will be a lowering of the temperature. In practice, electrical energy is usually supplied to the calorimeter partially to compensate the temperature drop. If H^E is negative (exothermic) then the temperature of the calorimeter rises on mixing. A second equipment is necessary to determine the amount of energy required to produce the same temperature rise. Alternatively two identical calorimeters can be used [3]. 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.

(ii) Minimizing the heat transfer coefficient, or

(iii) Minimizing the time for the heat exchange.

It should be noticed that the basic definition of adiabatic refers to heat, not any other form of energy. The accepted meaning of an adiabatic calorimeter permits measured electric energy to enter the calorimeter and be transformed into heat, as in 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.

2.1.2 Isothermal calorimeter

The isothermal calorimeter originally developed by Van Ness [27,37] has been further improved by Marsh and his colleagues [7,38] and is capable of producing highly precise and accurate results. An isothermal calorimeter, as the name implies, is one in which no temperature change occurs during the experiment. There are two ways to keep the temperature of the calorimeter constant. One is based on solid-liquid or liquid-vapor phase change. For example, the solid-liquid phase change is used in the ice calorimeter [10], the resulting volume change being used as a measure of the heat added or removed. The major disadvantage of this method is that measurements can only be made at the phase change temperature of the calorimeter fluid. The other way to keep constancy of temperature during the experiments is to use electrical heating to balance the removal of heat and electrical cooling (Peltier effect) to balance the addition of heat [23,35]. The isothermal dilution calorimeter [25] uses this principle. For an endothermic system, one component is slowly injected into the second component with the simultaneous addition of electrical energy sufficient to maintain the calorimeter isothermal. The excess enthalpy is determined from the initial amount of substance of component 1 in the vessel, the amount of substance of component 2 injected, and the electrical energy added to maintain isothermal conditions. The apparatus is normally designed so that the entire composition range can be covered in two experimental runs. For exothermic systems, a thermoelectric cooling device can be used. Energy is removed from the calorimeter at a constant rate and the calorimeter is maintained isothermal, at the thermostat temperature.

The isothermal calorimeter has an advantage that its heat capacity does not affect the results since its temperature does not change. Also the problem of minimizing uncertainty in heat leakage is frequently made easier. The isothermal calorimeter offers excellent heat leakage control without elaborate instruments.

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. Since the name is somewhat cumbersome to use, this calorimeter has sometimes loosely and erroneously been called an isothermal calorimeter. As an alternative name for this calorimeter, the term isoperibol has been suggested by Kubaschewki and Hultgren [17]

This type of calorimeter has also been used extensively for determining heats of mixing. During an experiment, the calorimeter may change temperature while the shield is kept at a constant temperature. One obvious advantage of this method is the simplicity of the operation of the shield. Another advantage may be the relative independence from variable thermal constant in the shield, since it is at constant temperature. The use of isothermal jacket calorimeters at higher temperatures depends on successfully keeping heat leaks down to a reasonable value. With special treatment, it is even possible to use an isothermal shield at room temperature and still measure heat effects at a higher temperature with minimized error caused by heat leakage [45].

2.1.4 Flow calorimeter

A flow calorimeter is one used with two fluid samples flowing through a mixing cell at steady and known rates. This type of calorimeter is particularly interesting in that 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 [36]. The effect of the mixing process is compared with the electrical power P needed to produce the same thermal effect in the mixing cell. The excess molar enthalpy and the mole fraction x_1 of component 1 are given by

$$H_m^E = P/(f_1 + f_2) \tag{2.12}$$

and

$$x_1 = f_1/(f_1 + f_2) \tag{2.13}$$

where f_1 and f_2 are the molar flow rates of the two components. The major advantage of flow calorimeters is that they are adaptable for measurements over wide temperature and pressure ranges. Relatively large quantities, typically one mole, of each of the pure components are required to produce a complete set of results.

2.2 Measurements of excess volume

Among the various thermodynamic functions for mixing processes, the volume change on mixing at constant pressure is one of the most interesting, simply because the experiments are relatively easy to perform with great precision and because the volume change on mixing is a sensitive indicator of the accuracy of solution theories. Comparing with H^E, the measurements of excess volume are more demanding. Usually, the values of V^E are quite small. The accuracy of measurement, therefore, appears to be more important. Excess volume V^E data can be determined by two principle methods: directly by mixing the liquids and observing the volume changes in dilatometers, and indirectly by precisely measuring the density of liquid mixtures.

2.2.1 Determination of V^E from density measurements

The excess volume V^E of a mixture can be obtained from the measurement of the density at known composition. The fundamental equation used for calculating V^E from densities is

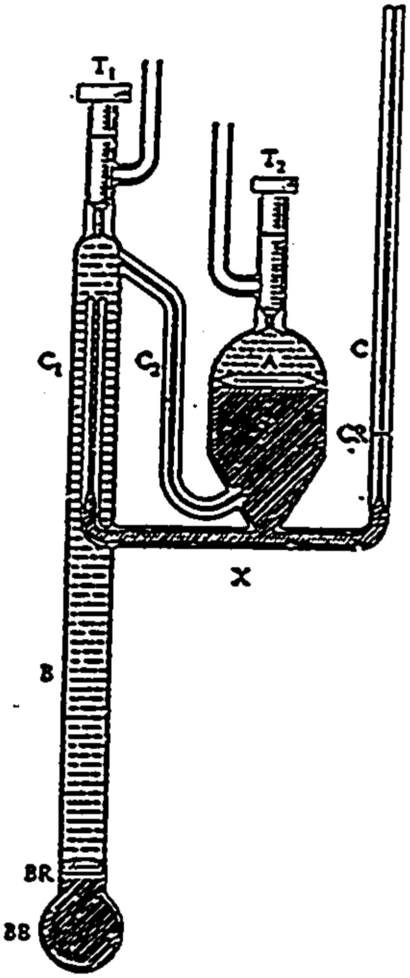
$$V^E = (x_1 M_1 + x_2 M_2)/\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2 \tag{2.14}$$

where x_1, x_2, M_1, M_2 and ρ_1, ρ_2 represent the mole fractions, molar masses and densities of the pure components 1 and 2, respectively, and ρ is the density of the liquid mixture. This equation gives the relationship between V^E and densities. Once the value of ρ is known, V^E can be calculated easily from this equation for the same mixture.

The advantages of this method include the simple procedure, easy operation and short experimental period. Its major advantage is that this method avoids using mercury which usually has to be involved in direct measurement of volume change by a dilatometer. This method has been widely used to determine V^E, although it is difficult to obtain satisfactory accuracy for mixtures with a volatile component.

2.2.2 Dilution dilatometer

A dilution dilatometer is an apparatus which is especially designed to determine excess volume. With a successive dilution dilatometer, V^E can be measured for a given pair of liquids over the whole range of mole fraction in two dilution runs which overlap through some range of x values, the particular range of overlapping depending on the relative molar volumes of the two pure liquids. Such overlapping provides a sensitive check on the quality of the measurements. In fact, the direct measurement of V^E is the simplest and best method for obtaining the density of mixtures containing volatile materials. The improved tilting dilution dilatometer reported by Kumaran and McGlashan [18], is shown in Figure 2.1. Before mixing, the pure liquid components are kept in the mixing bulb A and burette B and are separated by mercury. The burette B and the mixing bulb A are well sealed by the needle valves T_1 and T_2 in the measurement. The capillary C remains open to the atmosphere. During a run, the liquid component in B is introduced into the mixing bulb A, where the other liquid component resides, through the mercury in steps by anticlockwise tilting of the dilatometer. The volume change is observed on the change of the mercury meniscus in the calibrated capillary C. Some previous V^E measurements for di-n-propyl ether + n-alkanes or cycloalkanes systems were done in our laboratory by using this dilatometer.[48,49]



A – mixing bulb, B – burette, BB – bulb, BR,CR – reference marks, C, C_1, C_2 – capillaries, T_1, T_2 – needle valves, X – a fixed horizontal axis in a thermostat bath

Figure 2.1: Tilting dilution dilatometer

Chapter 3

SOLUTION THEORIES

In principle, understanding the behavior of solutions should be based on experimental work. Actually, however, experiments are usually restricted by many factors such as equipment, materials, experimental conditions and finances. This has stimulated scientists to study solution theory.

The purpose of studying solution theory is to represent the behavior of real solutions by means of the theories of intermolecular forces and the physical makeup of solutions. A perfect solution theory should be based on well understood theories of intermolecular forces and the structure of solutions. Hopefully a solution theory can be used to predict the properties of the solution from the parameters of molecules, or to predict the behaviors of mixtures only from the properties of the pure components. Although many solution theories have been developed to date, due to limited understanding of intermolecular forces, they are still in an empirical or semi-empirical level. Usually, some of the parameters of these models have to be determined by fitting the experimental data. Then the solution theories can be used to correlate the other experimental data and to predict the behavior of the solutions concerned.

Traditional theories of solutions represent exclusively two aspects of liquid mixtures. One of them is the entropy associated with dispersion of the two molecular species, or of their constituent elements in the case of complex molecules, among one another. A lattice model often serves as the device for estimating this "combinatorial" entropy. The other aspect relates to the interactions between neighboring molecules and, in particular, to the difference in the interactions between unlike and like neighbor pairs [8]. Since van der Waals and his colleagues started theoretical quantitative studies of the properties of liquid mixtures, many solution theories have been developed, such as strictly regular solution theory, cell theory, associated solution theory, Flory theory, etc. As an example, the Flory theory is outlined in more detail.

In the 1960's, Flory [1,8] proposed his solution theory based on liquid mixtures of chain molecules. In his study, Flory suggested a semi-empirical partition function and derived a liquid equation of state which is related to the excess functions of mixtures.

According to Flory, a chain molecule can be divided into several elements, or segments. 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, the partition function Q_p can be expressed as follows:

$$Q_p = Q_{comb}[\gamma(v^{1/3} - v^{-1/3})^3]^{rNc} exp(-E_0/kT) \qquad (3.1)$$

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 neighbor. γ is a geometric factor, v is the volume per segment and v^* is the hard core volume of a segment. 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.

$$\frac{r_1}{r_2} = \frac{v_1^*}{v_2^*} \tag{3.2}$$

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

$$E_0 = -(A_{11}\varepsilon_{11} + A_{22}\varepsilon_{22} + A_{12}\varepsilon_{12})/v \tag{3.3}$$

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

$$\theta_i = \mathrm{N}_i r_i s_i / \sum_{j=1}^{2} \mathrm{N}_j r_j s_j \tag{3.4}$$

and the volume fraction ϕ_i, by

$$\phi_i = \mathrm{N}_i r_i / \sum_{j=1}^{2} \mathrm{N}_j r_j \tag{3.5}$$

Hence, A_{11}, A_{22} and A_{12} can be expressed by

$$A_{11} = \frac{1}{2}\mathrm{N}_1 r_1 s_1 \theta_1 \tag{3.6}$$

$$A_{22} = \frac{1}{2}N_2 r_2 s_2 \theta_2 \tag{3.7}$$

$$A_{12} = N_1 r_1 s_1 \theta_2 = N_2 r_2 s_2 \theta_1 \tag{3.8}$$

Putting equations 3.6-3.8 into equation 3.3 gives

$$E_0 = -\frac{1}{2v}(N_1 r_1 s_1 \theta_1 \varepsilon_{11} + N_2 r_2 s_2 \theta_2 \varepsilon_{22} + 2N_1 r_1 s_1 \theta_2 \varepsilon_{12}) \tag{3.9}$$

or

$$E_0 = -\frac{1}{2v}(N_1 r_1 s_1 + N_2 r_2 s_2)(\theta_1^2 \varepsilon_{11} + \theta_2^2 \varepsilon_{22} + 2\theta_1 \theta_2 \varepsilon_{12}) \tag{3.10}$$

Defining the interchange energy parameter X_{12} as

$$X_{12} = \frac{s_1(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})}{2v^{*2}} \tag{3.11}$$

and dividing equation 3.10 by $(N_1 r_1 + N_2 r_2)$ with X_{12} from equation 3.11 yields

$$\begin{aligned} \frac{E_0}{N_1 r_1 + N_2 r_2} &= -\frac{1}{2v}(\phi_1 s_1 \varepsilon_{11} + \phi_2 s_2 \varepsilon_{22} - 2\phi_1 \theta_2 X_{12} v^{*2}) \\ &= -\frac{v^*}{\tilde{v}}(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}) \end{aligned} \tag{3.12}$$

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

$$p_1^* = s_1 \varepsilon_{11}/2v^{*2} \tag{3.13}$$

$$p_2^* = s_2 \varepsilon_{22}/2v^{*2} \tag{3.14}$$

By definition,

$$p^* v^* / T^* = ck \tag{3.15}$$

where T^* is the characteristic temperature and c is a parameter which represents the external degree of freedom proposed by Prigogine [32]. Two of the three solution parameters, c, p^* and T^* are independent. The quantities p^* and c are defined by

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_1 X_{12} \tag{3.16}$$

and

$$c = \phi_1 c_1 + \phi_2 c_2 \tag{3.17}$$

Rearranging equation 3.15 yields

$$\begin{aligned} \frac{1}{T^*} &= \frac{ck}{p^* v^*} = \frac{1}{p^*}\left(\phi_1 \frac{c_1 k}{v^*} + \phi_2 \frac{c_2 k}{v^*}\right) \\ &= \frac{\phi_1 p_1^*/T_1^* + \phi_2 p_2^*/T_2^*}{\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}} \end{aligned} \tag{3.18}$$

Ignoring the difference between the energy and enthalpy of a condensed system at low pressures, the excess enthalpy H^E can be expressed by

$$H^E = \Delta H^E = E_0(mixture) - E_0(1) - E_0(2) \tag{3.19}$$

Equation 3.12 may be expressed as follows:

$$E_0 = -\frac{v^*}{\tilde{v}}(N_1 r_1 p_1^* + N_2 r_2 p_2^* - N_1 r_1 \theta_2 X_{12}) \tag{3.20}$$

For the two pure components,

$$E_0(1) = -\frac{v^*}{\tilde{v}_1} N_1 r_1 p_1^* = -\frac{v_1^*}{\tilde{v}_1} N_1 p_1^* \tag{3.21}$$

and

$$E_0(2) = -\frac{v^*}{\tilde{v}_2} N_2 r_2 p_2^* = -\frac{v_2^*}{\tilde{v}_2} N_2 p_2^* \tag{3.22}$$

Thus, an equation for excess enthalpy is obtained:

$$H^E = N_1 p_1^* v_1^* \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + N_2 p_2^* v_2^* \left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right) + \frac{N_1 v_1^* \theta_2}{\tilde{v}} X_{12} \tag{3.23}$$

All parameters in this equation can be derived from the properties of the pure components 1 and 2, which are usually available in the literature, except the interchange energy parameter X_{12}.

There are two ways to obtain the value of X_{12}. One is from a calculation using a statistical thermodynamic model and equation 3.11. The reliability of the calculated results depends on how well the intermolecular forces and structure of the solution are understood. The other way to find X_{12} is from regression of experimental data. In this work, the values of X_{12} were obtained from least-squares analyses with experimental data.

Chapter 4

EXPERIMENTAL

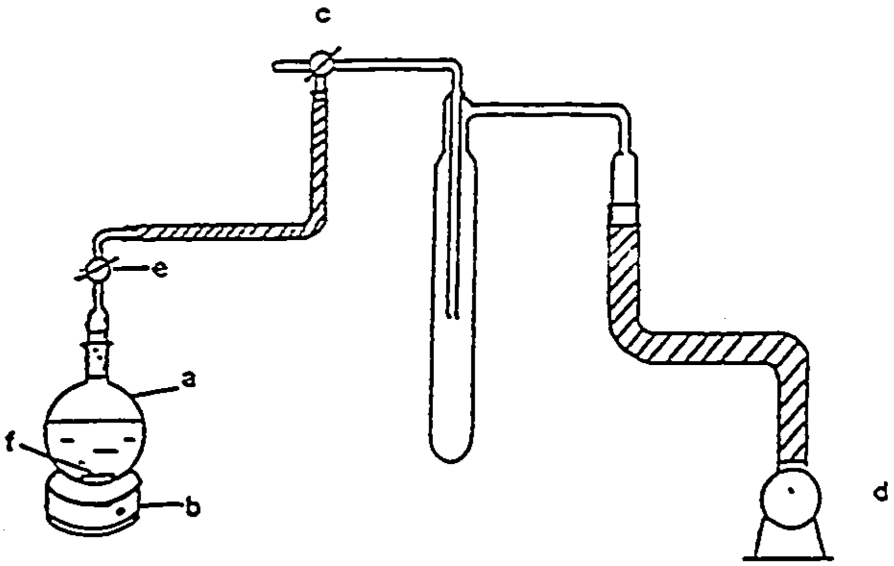
4.1 Materials

In this study, n-butyl methyl ether, n-hexane, n-heptane, n-octane, n-decane, n-dodecane and n-hexadecane were used. Among them, n-butyl methyl ether, n-decane and n-hexadecane, all with stated purities exceeding 99 moles per cent, were obtained from the Aldrich Chemical Co. The Research Grade n-hexane and the Pure Grade n-dodecane were obtained from the Phillips Petroleum Co. The n-heptane was obtained from Eastman Organic Chemicals Co. Apart from storing the n-butyl methyl ether over Type 4A molecular-sieve beads, the component liquids were used without further purification. Densities $\rho(T=298.15K)$ measured in an Anton-Paar digital densimeter (DMA 02C), were compared with the values from the literature [41,43,44] and are shown in Table 4.1.

Before being used, all component liquids were degassed in the way shown in Figure 4.1. The flask (a) with each pure component liquid was placed on a

Table 4.1: Densities of component liquids at 298.15K

Component	Density (kg/m^3)	
	measured	literature
n-Butyl methyl ether	742.28	739.3[43] 744.1[44]
n-Hexane	655.58	654.84[41]
n-Heptane	681.16	679.46[41]
n-Octane	698.79	698.62[41]
n-Decane	726.31	726.35[41]
n-Dodecane	745.40	745.18[41]
n-Hexadecane	770.15	769.94[41]



a – flask, b – magnetic stirrer, c – three-way valve,
d – vaccum pump, e – two-way valve, f – stirrer

Figure 4.1: Degassing of the component liquids

magnetic stirrer (b) which drives 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 about 10 minutes for each sample.

4.2 Experimental measurement of excess enthalpy

Excess enthalpies were measured in this study for six binary systems consisting of n-butyl methyl ether and n-alkanes, which have the carbon number from 6 to 16, at 298.15K. Over most of the mole-fraction range, the errors of the excess molar enthalpy H_m^E and mole fraction x are estimated to be less than 0.5 per cent and 5 × 10^{-4}, respectively.

4.2.1 Equipment

An LKB flow microcalorimeter(Model 10700-1), shown in Figure 4.2, was used to measure H^E data in this study. As shown in this figure, the calorimeter unit is immersed in a water bath where the temperature is controlled by both a temperature controller for heating and a proportional temperature control (NESLAB model RTE-110) mainly for cooling. In this work, the temperature of the system was maintained at 25.000 ± 0.002°C, which was indicated on a quartz thermometer (HEWLETT-PACKARD model 2804 A). As shown in figure 4.2, this calorimeter unit consists of a heat sink (b), in which two reaction cells (e1) and (e2), thermopiles (d1) and (d2), and other equipment required for the temperature control are housed. These two cells are of different designs which make it possible to carry out two types of flow calorimetric experiments in the same calorimeter. The cell (e1) is a mixing cell. The two liquids to be mixed are pumped through two tubes into the mixing cell and mixed there. The flow-through cell (e2) is used for relatively slow reactions such as biological processes. The thermal signal from the cells is transformed into electrical signal by thermopiles and then transported to the amplifier and the recording system. In this study, liquids flowed only through the mixing cell; the other cell was empty and the inlet and outlet were connected.

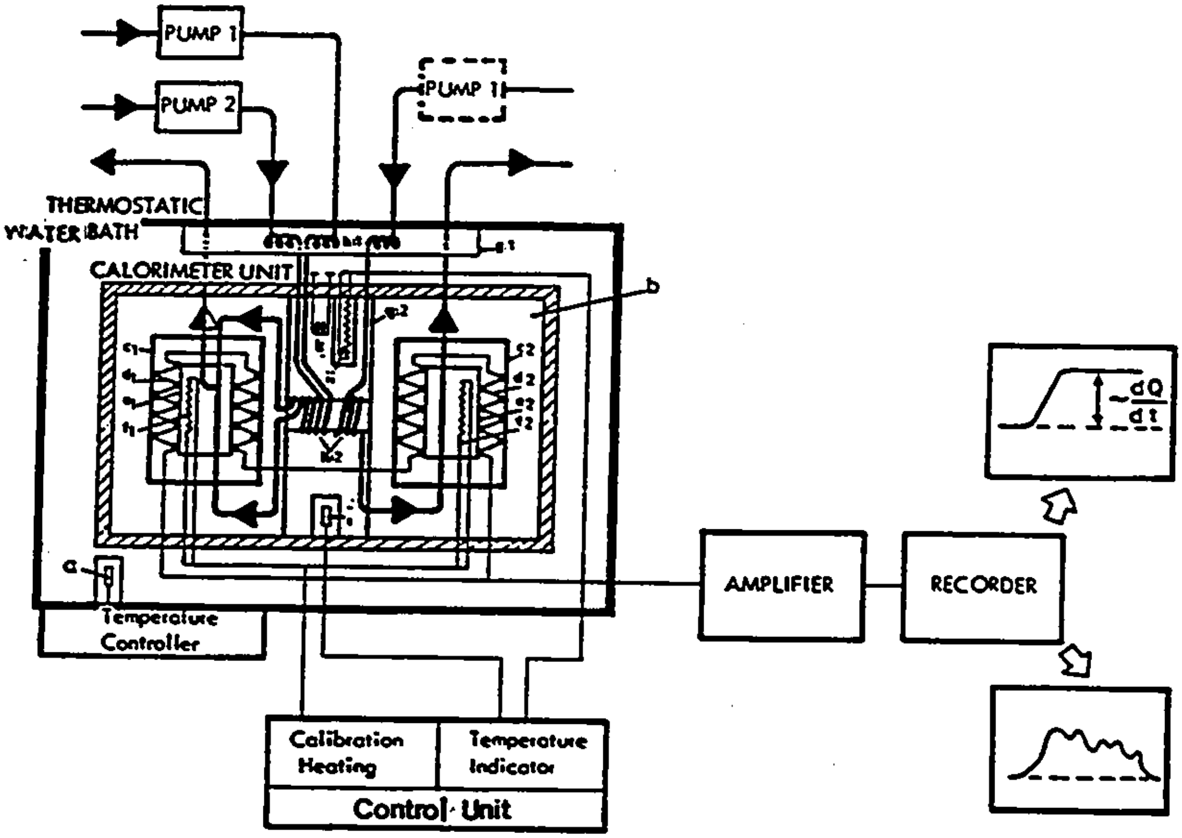
There are two groups of heat exchanger coils (h1) and (h2), located in heat exchanger I (g1) and heat exchanger II (g2), respectively. These bring the liquid(s) to the working temperature before reaching the reaction cell.

Two syringe pumps were used to transport the component liquids into the mixing cell.

4.2.2 Verification of calorimeter

There are two possible sources of uncertainties in the experimentally determined H^E values. One is from errors in the calorimeter itself (energy, temperature, mass etc.). The other one is from the uncertainties in the purity and state of the materials to be measured. In order to minimize the errors in the calorimeter, researchers usually check the reliability of the calorimetric measurements with a "reference" material, or a standard system, whose state is reproducible and well known, before they start to work on their systems. If the thermal properties of this reference material are known, this check yields evidence on the reliability of the calorimetric measurements [26].

Since the benzene + cyclohexane system is an acceptable reference system, its H^E values were measured at 298.15K in this work, so as to test the accuracy of our calorimeter. This system has been frequently used as a standard endothermic mixture. The component liquids, obtained from Phillips Petroleum Co., were used without further purification. Table 4.2. gives the densities of component liquids at



a – sensor, b – heat sink, c1,c2 – detectors, d1,d2 – thermopiles, e1 – mixing cell,

e2 – flow-through cell, f1,f2 – heaters, g1,g2 – heat exchangers,

h1,h2 – heat exchanger coils, i – sensor, k – cooler

Figure 4.2: LKB Flow Microcalorimeter

Table 4.2: Densities of component liquids for the reference system at 298.15K

Component	Density (g/cm^3)	
	observed	literature [42]
benzene (Phillips Petro. Co. Research Grade)	0.87358	0.87370
cyclohexane (Phillips Petro. Co. Research Grade)	0.77295	0.77389

298.15K along with the data reported in the literature for comparison [42]. The excess molar enthalpy values obtained in this work are compared with the literature values [38] and shown in Table 4.3. The same comparison is depicted in Figure 4.3. From the comparison we can see that the equipment used in this study is capable of yielding acceptable results.

Table 4.3: Excess enthalpies of benzene + cyclohexane system at 298.15K

this work		literature [38]	
x^*	H_m^E(J/mol)	x^*	H_m^E(J/mol)
0.0991	273.13	0.1000	280.98
0.1995	504.61	0.2000	500.98
0.3004	659.63	0.3000	660.46
0.3999	759.07	0.4000	759.70
0.4996	796.75	0.5000	798.44
0.5995	771.16	0.6000	775.59
0.6998	680.28	0.7000	688.93
0.8000	519.92	0.8000	534.77
0.8999	285.07	0.9000	307.64

* mole fraction of benzene

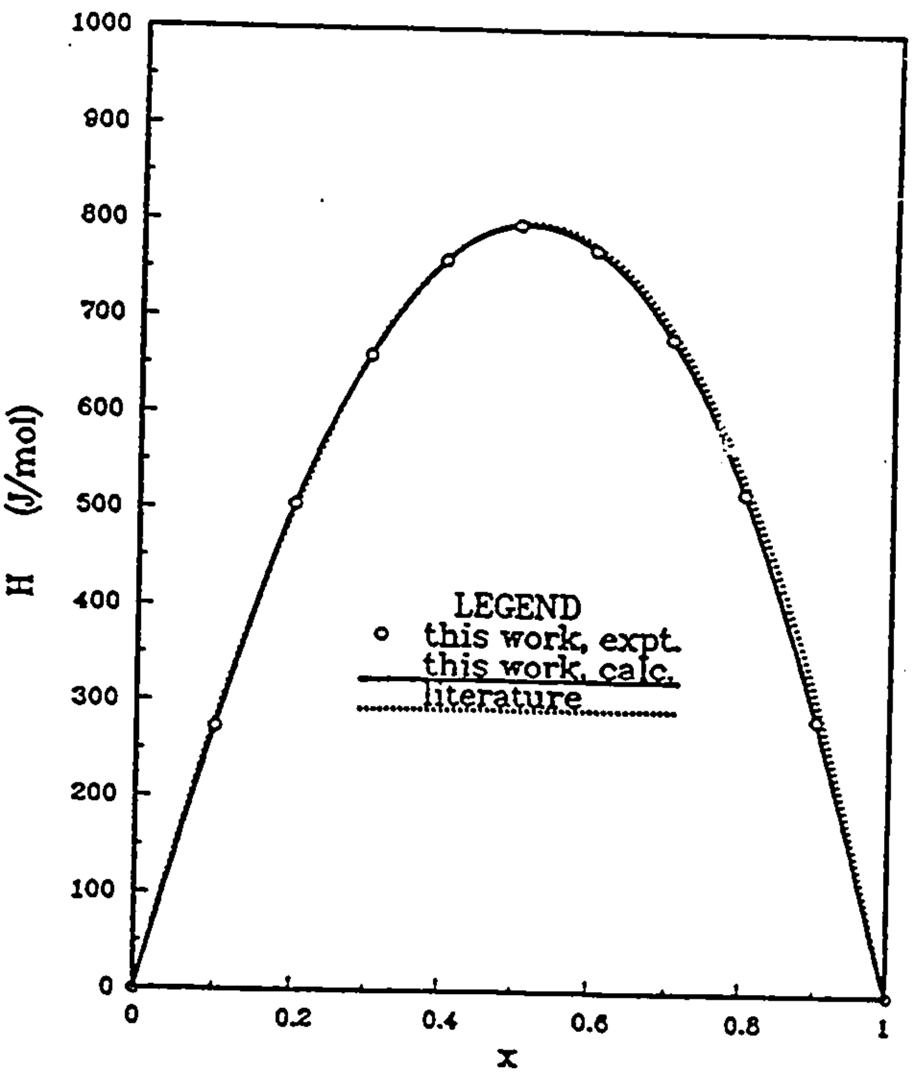


Figure 4.3: H^E of reference system with benzene and cyclohexane at 298.15K

x = mole fraction of benzene

4.2.3 Calibration

A calorimeter can be used to measure the heat effect by comparison either directly with a known electrical energy or indirectly with materials which have the thermal properties known. This comparison is called calibration. In a direct calibration, it usually involves a known amount of electrical energy in the form of heat, because electrical energy can be measured more accurately and conveniently than other forms of energy. The thermal properties of some standard systems have already been well measured electrically. By utilizing these known thermal properties, the use of electrical energy measurements can be avoided in an indirect measurement.

Electrical calibration of the calorimeter was used in this study to find the values on a digital voltmeter corresponding to a known dissipation of power in the cell when a known current from the control unit passed through the calibration heater (f1) in Figure 4.2. Since the base line voltage is related to the flows, the calibration was carried out as the blank liquid, corresponding to the solution used during the experiment, was pumped through the cell at different flow rates. The relationship among the zero line, the base lines and the mixing heat curve is shown in Figure 4.4.

Before a known current was introduced, a pure component liquid was pumped through the cell at a steady flow rate. The voltage value $V_i^{\circ}(f)$, the baseline voltage associated with the flow alone, was recorded when the system was steady. Then a known electrical potential E was applied to the calibration circuit through a standard resistance $R_c (= 10.0\Omega)$. In other words, a known current $I(=E/R_c)$ was sent into the heater. It made the voltage curve have a deflection V_i(f) from the

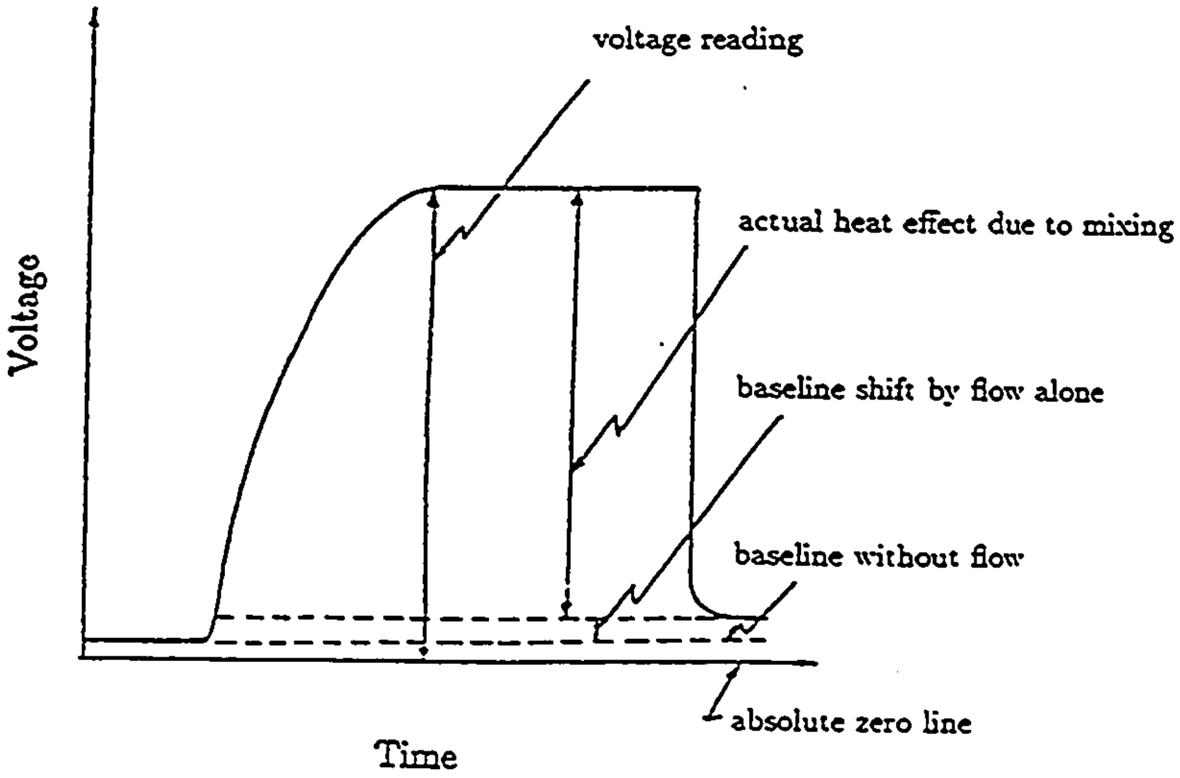


Figure 4.4: The relationship between voltage reading and baselines

baseline, as shown in Figure 4.4. The actual heat effect by electricity can be written as $\Delta V(= V_l(f) - V_l^{\circ}(f))$. The basic equation for a steady state, in which a power, W, is released within the calorimetric cell by electrical heating or as the result of a mixing process, is

$$W = \varepsilon[V_l(f) - V_l^{\circ}(f)] = \varepsilon \Delta V \tag{4.1}$$

The value of the thermopile calibration constant, ε, can be obtained from the change in thermopile voltage corresponding to the dissipation of a known electrical power in the heater.

As mentioned above, W is an electrical power in our calibration, therefore, it can be written as

$$W = \mathrm{I}^2\mathrm{R} \tag{4.2}$$

Combining equation 4.1 and equation 4.2 gives

$$\varepsilon = \mathrm{I}^2\mathrm{R}/\Delta V \tag{4.3}$$

where R(=49.520 Ω) is the calibration resistance in our calibration.

Setting a new flow rate by adjusting the pump (counts/sec.), the same procedure was then repeated. By doing so, the calibration curves(ε vs. counts/sec.) could be made.

During all the measurements, n-butyl methyl ether was pumped by pump A all along. Pump B was used to feed alkanes for different systems. Therefore, the calibration of pump A was done with n-butyl methyl ether only and pump B with alkanes.

The results of calibration were correlated with a linear equation

$$\varepsilon = \mathrm{A}_0\mathrm{X} + \mathrm{A}_1 \tag{4.4}$$

where A_0 and A_1 are constants for a given component, and X represents flow rate (counts/sec.). The results of calibration for pump A and pump B with different component liquids are reported in Table 4.4-5. The same results are also depicted in Figure 4.5.

Both syringe pumps were calibrated by determining the time required to fill a calibrated volume.

The values of the coefficients for equation 4.4 for all component liquids are listed in Table 4.6.

Table 4.4: The calibration results for pump A

count/sec = X	ε(exp)	ε(cal)
n-butyl methyl ether		
300.20	15.6147	15.6175
499.95.	15.6567	15.6531
698.45	15.6875	15.6886
898.50.	15.7269	15.7243
1099.80	15.7579	15.7602

Table 4.5: The calibration results for pump B

count/sec = X	ε(exp)	ε(cal)
n-Hexane		
305.55	15.5712	15.5707
500.75	15.6162	15.6184
700.40	15.6715	15.6672
900.00	15.7119	15.7160
1099.90	15.7663	15.7648
n-Heptane		
305.50	15.5928	15.5938
501.20	15.6350	15.6316
700.00	15.6707	15.6690
900.30	15.6968	15.7067
1099.90	15.7499	15.7442
n-Octane		
300.65	15.6851	15.6809
500.05	15.7183	15.7240
700.10	15.7665	15.7673
900.30	15.8124	15.8159
1100.30	15.8543	15.8538
n-Decane		
301.90	15.6648	15.6769
499.10	15.7339	15.7207
699.00	15.7693	15.7651
902.00	15.8102	15.8102
1100.00	15.8488	15.8542
n-Dodecane		
299.85	15.5144	15.5161
499.20	15.5886	15.5885
699.95	15.6665	15.6614
901.35	15.7306	15.7345
1101.10	15.8074	15.8071
n-Haxanedecane		
304.65	15.6346	15.6293
499.75	15.6596	15.6695
700.10	15.7143	15.7108
899.10	15.7534	15.7519
1099.00	15.7926	15.7930

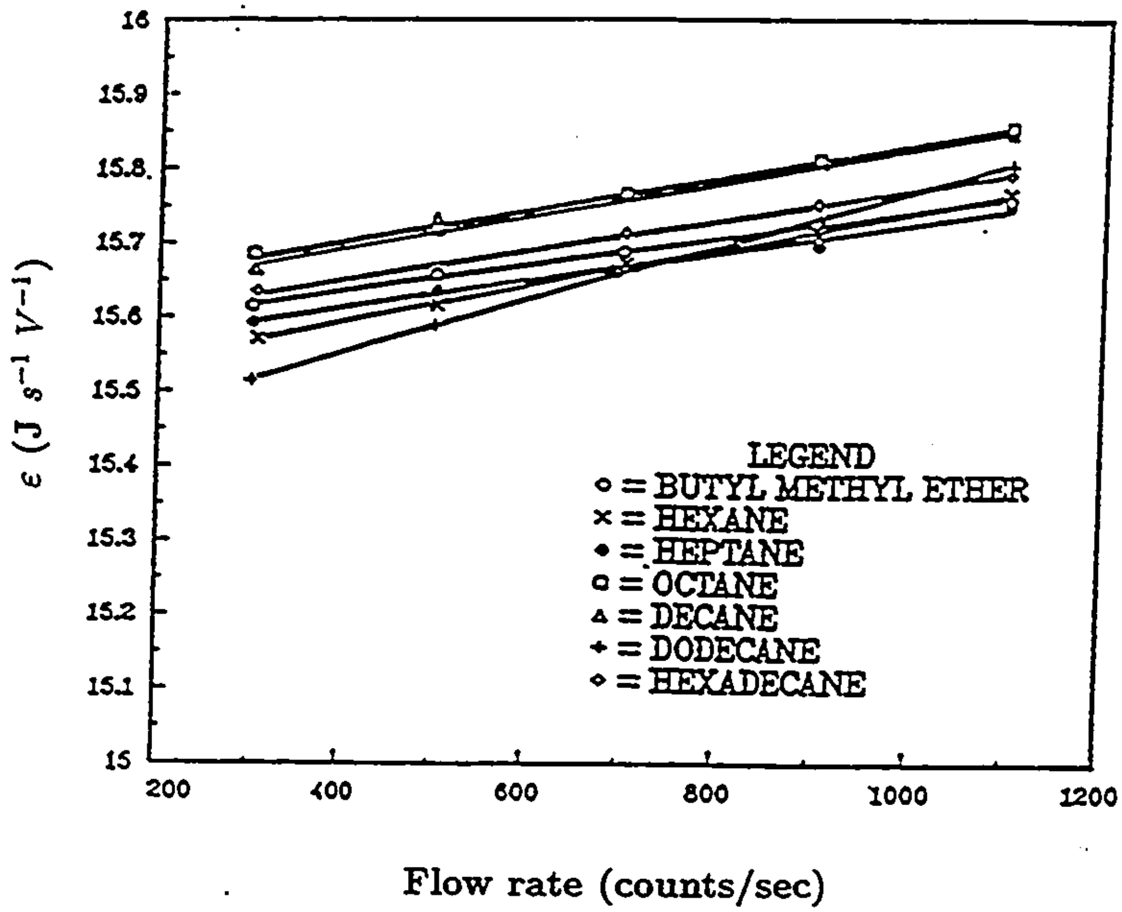


Figure 4.5: Calibration lines for pure components

Table 4.6: The values of coefficients of equation 4.4

component	$A_o \times 10^3$	A_1
n-Butyl methyl ether	0.1785	15.5639
n-Hexane	0.2444	15.4960
n-Heptane	0.1882	15.5372
n-Octane	0.2163	15.6159
n-Decane	0.2222	15.6098
n-Dodecane	0.3631	15.4072
n-Hexadecane	0.2061	15.5665

4.2.4 Measurements of H_m^E

All the auxiliary equipment, such as amplifier, digital voltmeter, pumping control system, recorder, printer and a computer used to collect simultaneously the signals from an amplifier, were turned on when the temperature of the system was steady at 25.000 ± 0.002°C. The time needed for warming up the amplifier and voltameter was about an hour.

The n-butyl methyl ether in pump A and the n-alkane in pump B were, after being degassed, pumped into the calorimeter at certain flow rates f_1 and f_2, and mixed in the mixing cell. The deflection of voltage curve due to the mixing process was recorded by the recorder (HEWLETT-PACKARD model 7133 A) as well as the computer (COMMODORE model 4032) through an instrument coupler (ICS model 4880). When the recorder began to indicate that the voltage curve had reached a steady stage, the computer was started to take the voltage readings, once every second. Usually, 500 voltage readings were needed. For the relatively low excess molar enthalpies, such as in the low concentration range, up to 1000 voltage readings were required to be taken. The deflection of voltage curve $V(f)$ from the baseline voltage $V^\circ(f)$ due to the heat of mixing was obtained by taking an average of the voltage readings. The values of the excess molar enthalpies of the mixtures were calculated by using following equations:

$$H_m^E = \frac{W}{N}, \qquad \frac{[J/sec]}{[mol/sec]} = [J/mol] \tag{4.5}$$

$$W = \varepsilon[V - V^\circ] \tag{4.6}$$

$$N = N_1 + N_2 = \frac{f_1}{v_1} + \frac{f_2}{v_2} \tag{4.7}$$

$$H_m^E = \frac{\varepsilon[V - V^\circ]}{\frac{f_1}{v_1} + \frac{f_2}{v_2}} \tag{4.8}$$

where f_1 and f_2 are the volumetric flow rates of component 1 and 2, respectively; v_1 and v_2 are the molar volumes of the corresponding components and X is the number of moles of the mixture produced per second.

Repeating the same procedure at different flow rates, H_m^E values were obtained over the entire concentration range.

4.2.5 Experimental results for H_m^E

The experimental results of excess molar enthalpies H_m^E for six binary mixtures $[xC_4H_9OCH_3 + (1\text{-}x)C_nH_{2n+2}]$ determined at 298.15K are listed in Table 4.7. The smoothing equation

$$H_m^E(J/mol) = x_1(1 - x_1)\sum_{j=1}^{m} h_j(1 - 2x_1)^{j-1} \tag{4.9}$$

was fitted to each set of results. Values of the coefficients h_j, determined by the method of least-squares with all points weighted equally, are given in Table 4.8 along with the standard deviations s of the representations. The following form for the standard deviation was employed:

$$s = \sqrt{\frac{\sum_{i=1}^{n_{pt}} (H_m^E(exp) - H_m^E(cal))_i^2}{n_{pt} - n_{coeff.}}} \tag{4.10}$$

where $H_m^E(cal)$ is the value obtained from equation 4.9; n_{pt} is the number of the experimental points and $n_{coeff.}$ is the number of coefficients in equation 4.9.

Plots of the experimental results and their representations by equation 4.9 are shown in Figure 4.6. The H_m^E values obtained for $[xC_4H_9OCH_3 + (1\text{-}x)C_nH_{2n+2}]$, as

Table 4.7: Excess molar enthalpies for [xC$_4$H$_9$OCH$_3$ + (1-x)C$_n$H$_{2n+2}$] at 298.15K

x	$\frac{H_m^E}{\mathrm{J\cdot mol^{-1}}}$	x	$\frac{H_m^E}{\mathrm{J\cdot mol^{-1}}}$	x	$\frac{H_m^E}{\mathrm{J\cdot mol^{-1}}}$	x	$\frac{H_m^E}{\mathrm{J\cdot mol^{-1}}}$	x	$\frac{H_m^E}{\mathrm{J\cdot mol^{-1}}}$
$x\mathrm{C_4H_9OCH_3}+(1-x)\mathrm{C_6H_{14}}$									
0.0500	57.3	0.2998	248.0	0.4493	287.4	0.6499	261.4	0.7999	177.0
0.0998	108.3	0.3501	266.7	0.4993	288.6	0.6996	238.4	0.8499	138.2
0.1500	154.1	0.3502	266.6	0.5496	287.7	0.7497	211.0	0.9000	93.4
0.1999	192.6	0.4000	279.2	0.5993	277.5	0.7998	177.8	0.9500	43.5
0.2496	224.6								
$x\mathrm{C_4H_9OCH_3}+(1-x)\mathrm{C_7H_{16}}$									
0.0500	59.2	0.3021	261.4	0.5005	306.6	0.6500	278.8	0.8498	154.5
0.1000	111.8	0.3507	281.8	0.5008	308.2	0.6997	258.7	0.8996	107.4
0.1501	159.3	0.3509	279.6	0.5504	304.0	0.7504	229.9	0.9001	108.5
0.1998	199.6	0.4004	295.7	0.6005	294.8	0.8000	196.3	0.9500	53.0
0.2498	233.2	0.4500	304.9						
$x\mathrm{C_4H_9OCH_3}+(1-x)\mathrm{C_8H_{18}}$									
0.0503	62.1	0.2508	251.5	0.4509	330.8	0.6507	313.9	0.8506	180.5
0.1002	118.1	0.3005	281.7	0.5012	338.0	0.7004	292.0	0.9002	127.7
0.1505	169.2	0.3506	303.0	0.5508	336.7	0.7513	262.1	0.9502	66.9
0.2006	213.7	0.4001	320.7	0.6006	328.6	0.8014	224.3		
$x\mathrm{C_4H_9OCH_3}+(1-x)\mathrm{C_{10}H_{22}}$									
0.0499	70.4	0.2500	274.2	0.4501	373.6	0.6004	375.4	0.7999	267.6
0.1000	130.8	0.2999	309.4	0.5003	382.4	0.6493	361.7	0.8501	217.0
0.1499	185.1	0.3499	339.0	0.5495	382.0	0.6999	339.0	0.9033	150.2
0.2001	231.4	0.3999	358.0	0.5500	381.7	0.7491	308.4	0.9499	82.6
$x\mathrm{C_4H_9OCH_3}+(1-x)\mathrm{C_{12}H_{26}}$									
0.0499	68.6	0.2996	336.2	0.4496	412.1	0.6010	424.6	0.7995	312.2
0.1001	134.0	0.2997	335.8	0.4500	413.0	0.6502	411.4	0.8499	255.0
0.1487	190.4	0.3498	370.1	0.4992	424.1	0.7002	388.6	0.9000	185.4
0.2000	246.3	0.3499	370.3	0.5503	428.0	0.7497	355.7	0.9500	100.0
0.2500	294.0	0.3958	392.4	0.5992	423.7				
$x\mathrm{C_4H_9OCH_3}+(1-x)\mathrm{C_{16}H_{34}}$									
0.0499	93.5	0.2504	372.6	0.4002	509.3	0.6001	555.7	0.7998	420.1
0.1002	176.8	0.3003	428.2	0.4478	533.8	0.6500	542.5	0.8504	347.0
0.1503	245.2	0.3501	472.8	0.5011	549.8	0.7004	512.8	0.9001	256.0
0.2000	309.6	0.4002	508.6	0.5504	558.3	0.7499	474.5	0.9499	139.9

Table 4.8: Coefficients h_j and standard deviations s for least-squares representations of H_m^E for [$x\mathrm{C_4H_9OCH_3} + (1\text{-}x)\mathrm{C_nH_{2n+2}}$] at 298.15K by equation 4.9

n	h_1	h_2	h_3	h_4	h_5	h_6	s
6	1157.1	29.3	63.6	136.8	−194.8		1.0
7	1228.0	2.7	65.2	50.2	−126.5		0.9
8	1348.6	−74.6	116.4	16.5	−138.7		0.8
10	1526.7	−175.6	98.6				1.0
12	1698.9	−299.1	173.9	−98.5	−108.1		0.9
16	2208.8	−463.6	148.2	−445.3	201.7	450.3	1.6

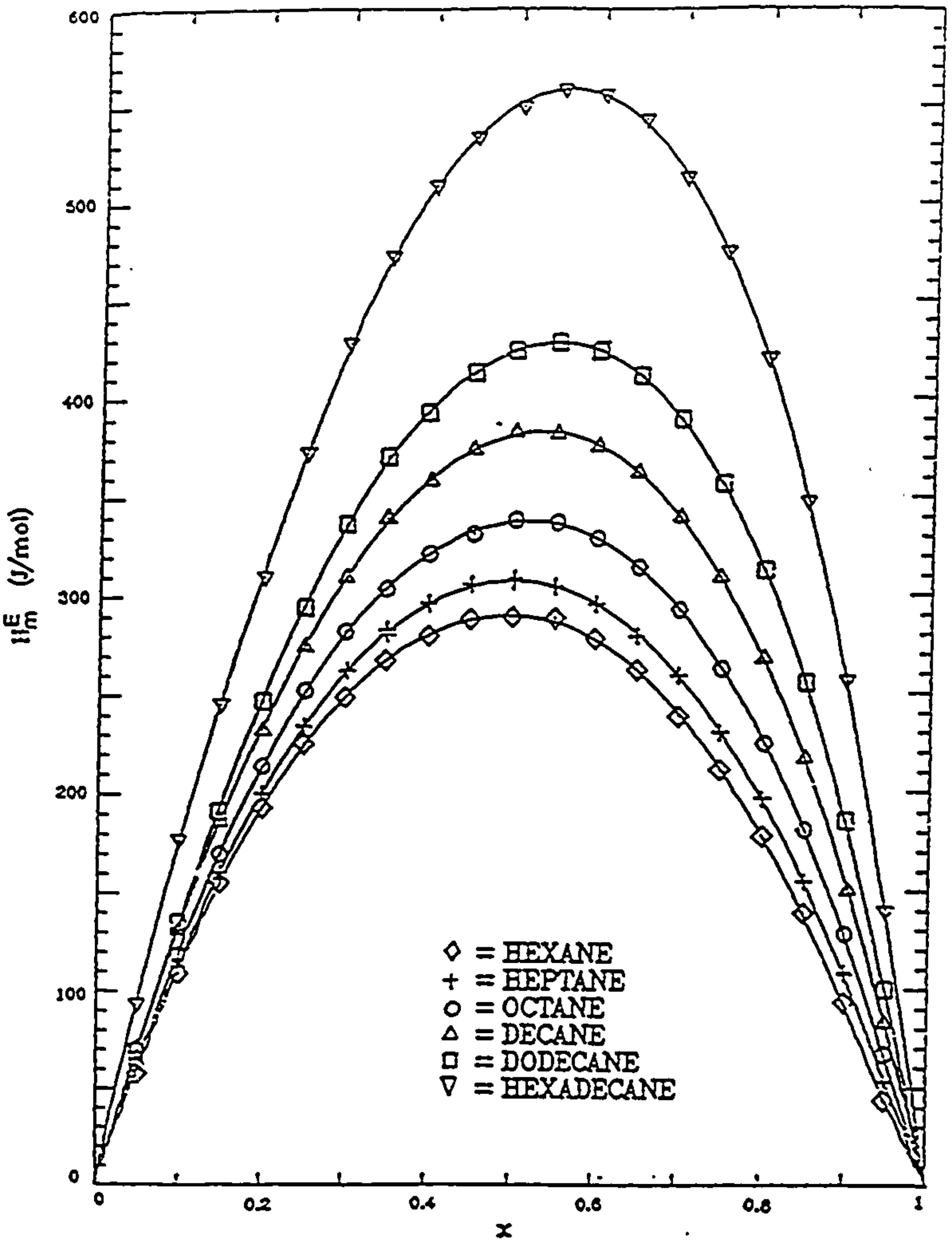


Figure 4.6: Experimental results of excess molar enthalpies, H_m^E, for $[xC_4H_9OCH_3 + (1\text{-}x)C_nH_{2n+2}]$ at 298.15K

shown in this figure, are positive at all mole fractions, and increase fairly regularly with increasing chain length of the n-alkane. The curves are approximately symmetrical about x=0.5, but show a slight skew towards x=1, which becomes more evident for the larger n-alkanes. Over most of the mole-fraction range, the errors of the excess molar enthalpy H_m^E and mole fraction x are estimated to be less than 0.5 per cent and 5×10^{-4}, respectively.

4.3 Experimental measurement of excess volume

Excess molar volumes for the same six systems were determined from the accurate density measurements at the same temperature, 298.15K.

4.3.1 Equipment

A Sodev vibrating tube densimeter (Model 02D), originally designed by P. Picker *et al* [30], was applied to measure the densities of the pure components and the liquid mixtures. The principle of this kind of densimeter is that the accurate determination of the density of fluids is simplified to the electronic measurement of frequency f (or, in fact, the period T, which equals $1/f$). The variation of the natural frequency of a hollow oscillator can be detected when it is filled with fluids having different densities. Considering an equivalent system represented by a hollow body of mass M which is suspended on a spring with a spring constant c, its volume V is filled with a sample of density ρ, the natural frequency of this system will be

$$f = \frac{1}{2\pi}\sqrt{\frac{c}{\rho V + M}} \tag{4.11}$$

therefore, the period of vibration

$$T = 2\pi\sqrt{\frac{\rho V + M}{c}} \tag{4.12}$$

Taking the square of this expression yields

$$T^2 = A\rho + B \tag{4.13}$$

where

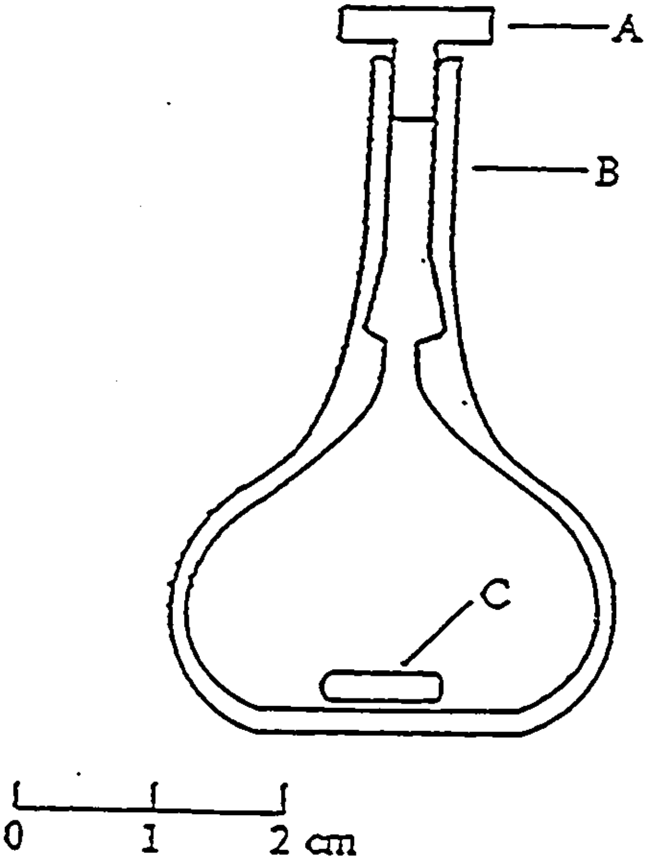
$$A = \frac{4\pi^2 V}{c}; \qquad B = \frac{4\pi^2 M}{c} \tag{4.14}$$

Both A and B are constants for a given mechanical system which can be determined from frequency measurements on two liquids of accurately known densities.

To obtain precise values of V^E from density measurements, the composition of mixtures must be determined accurately. Since the error in composition is produced mainly from the imperfect control of the vapor phase in the vessel used to prepare the mixtures, a special kind of cell, shown in Figure 4.7, was used for the mixture preparation. This cell is called an onion cell, because of its shape. It is made of Pyrex glass with a capacity of 10 cm^3. As shown in this figure, a small magnetic stirrer C sealed in glass is contained within the cell. The opening of the capillary B can be sealed with a Teflon plug A.

4.3.2 Preparation of the mixtures

A Multi-Dosimat (Model 645) was used to load the liquids into onion cell. The mass of liquid component was obtained by weighing the onion cell before and after being charged. A number of mixtures in the whole composition range were made for each system.



A – Teflon plug, B – capillary, C – magnetic stirrer

Figure 4.7: Onion cell (total capacity about 10 cm^3)

4.3.3 Density measurement

A static mode was employed for the liquid loading. Liquid mixtures were introduced into the densimeter by using a hypodermic syringe. During a run, the inside of the vibrating tube was never dry, which was charged with the liquid mixtures of different mole fractions beginning from a pure component. For each system, the calibration of the densimeter was based on measurements using the pure components. The density measurements were done in the order of the mixture concentration from x_1=0 to x_1=1 for each system. The results of measurement were indicated on a Newport counter (Model 700).

The error in the mole fraction is estimated to be less than 1×10^{-4} [51].

4.3.4 Determination of excess molar volume

Excess molar volumes, V_m^E, were calculated from densities measured for each system. The fundamental equation used for calculating V_m^E is

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (4.15)$$

where M_1, M_2 and ρ_1, ρ_2 represent the molar masses and densities of pure components 1 and 2, respectively, and ρ is the density of the liquid mixture. The experimental results for the excess molar volume V_m^E are shown in Table 4.9 and in Figure 4.8 as well. In all cases, x is the mole fraction of n-butyl methyl ether.

The error in the V_m^E determination is estimated to be less than 5×10^{-4} cm^3/mol [51].

Table 4.9: Experimental results for the excess molar volumes, V_m^E, of n-butyl methyl ether + n-alkane (C_nH_{2n+2}) mixtures as a function of the mole fraction, x, of ether

x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}
n = 6					
0.0500	0.0645	0.2990	0.2619	0.6990	0.2420
0.0991	0.1184	0.3995	0.2955	0.7995	0.1830
0.1495	0.1653	0.5020	0.3031	0.8997	0.0991
0.1995	0.2045	0.6001	0.2855	0.9494	0.0495
n = 7					
0.1002	0.1421	0.4043	0.3370	0.6996	0.2844
0.1500	0.1906	0.5013	0.3453	0.8493	0.1670
0.2036	0.2358	0.5992	0.3287	0.8989	0.1115
0.3003	0.2977				
n = 8					
0.0498	0.0566	0.3998	0.3051	0.7999	0.2145
0.0997	0.1076	0.4995	0.3239	0.8966	0.1205
0.1500	0.1571	0.5999	0.3160	0.9470	0.0616
0.2995	0.2625	0.6990	0.2808		
n = 10					
0.0500	0.0441	0.3009	0.2330	0.6992	0.2655
0.0997	0.0893	0.4007	0.2725	0.7991	0.2112
0.1499	0.1280	0.4991	0.2927	0.8992	0.1227
0.1995	0.1688	0.6000	0.2907		
n = 12					
0.0519	0.0349	0.2995	0.1874	0.6999	0.2315
0.1002	0.0722	0.3993	0.2257	0.7994	0.1908
0.1502	0.1048	0.4992	0.2463	0.8991	0.1154
0.2001	0.1349	0.6008	0.2509	0.9493	0.0624
n = 16					
0.0510	0.0254	0.3066	0.1191	0.6991	0.1252
0.0998	0.0449	0.3993	0.1372	0.7996	0.0999
0.1490	0.0678	0.5000	0.1468	0.8992	0.0617
0.1992	0.0877	0.6002	0.1404	0.9504	0.0354

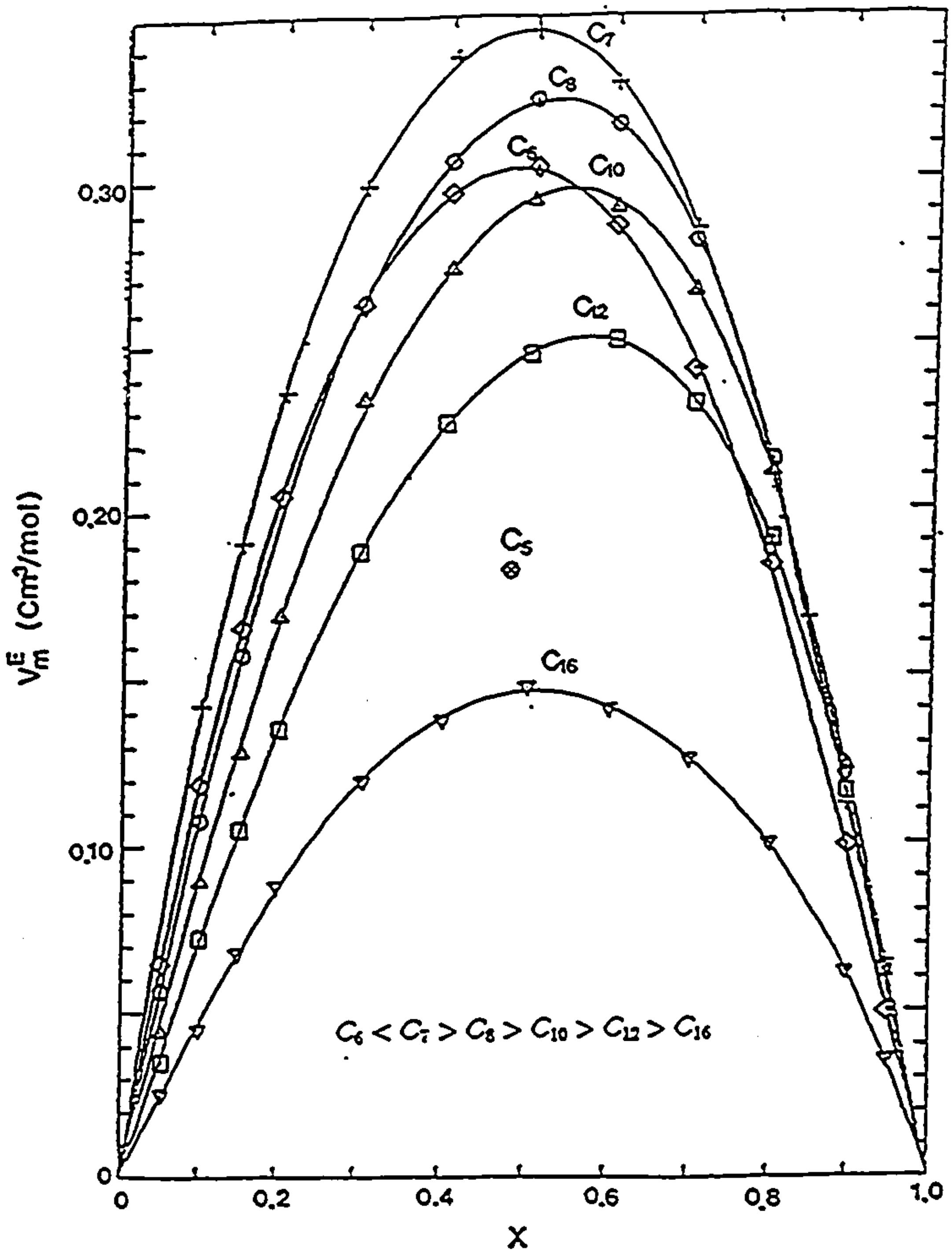


Figure 4.8: Experimental results of excess molar volumes, V_m^E, for [$xC_4H_9OCH_3$ + (1-x)C_nH_{2n+2}] at 298.15K

The smoothing equation

$$V_m^E(cm^3/mol) = x(1-x)\sum_{j=1}^{m} v_j(1-2x)^{j-1} \tag{4.16}$$

was fitted to each set of results by the method of least squares with all points weighted equally. The values of the coefficients, v_j, and the standard deviations, s, defined by

$$s = \sqrt{\frac{\sum_{i=1}^{p}[V_m^E(exp) - V_m^E(cal)]_i^2}{p-m}} \tag{4.17}$$

are reported in Table 4.10. In equation 4.17, p is the number of experimental points in a particular set; m is the number of coefficients in equation 4.16 and $V_m^E(cal)$ is the calculated value of V_m^E obtained from equation 4.16. The calculated values for all the systems investigated are shown in Figure 4.8.

The V_m^E values are positive at all mole fractions. Some of the curves in Figure 4.8 cross, having maxima which increase and then decrease in the following order:

$$C_6 < C_7 > C_8 > C_{10} > C_{12} > C_{16} \tag{4.18}$$

This is in contrast of the excess molar enthalpies which increase successively with increasing size of the n-alkane. However, similar behavior has been reported for the excess molar volumes [48] and enthalpies [46] of binary mixtures of di-propyl ether with n-alkanes, but the change from increasing to decreasing maxima occurred at a point higher in the n-alkane series. In order to verify the trend, one point was measured for the mixture of n-butyl methyl ether with n-pentane. The result shown in Figure 4.8 conferms the validity of the order as expressed in equation 4.18.

Table 4.10: Coefficients v_j and standard deviations s for least squares representations of V_m^E for [n-butyl methyl ether + n-alkane (C_nH_{2n+2}) mixtures at 298.15K by equation 4.16

n	v_1	v_2	v_3	v_4	v_5	s
6	-1.2089	0.1023	-0.0061	0.0675		0.0014
7	1.3817	0.0407	0.0267	0.2338		0.0019
8	1.2929	-0.1225	0.0476	0.1117	-0.1791	0.0009
10	1.1765	-0.2162				0.0021
12	0.9892	-0.2541	0.0648	-0.0766		0.0013
16	0.5825	-0.0213	-0.0405	-0.1292	0.1132	0.0011

Chapter 5

CORRELATION AND DISCUSSION

During the literature review, we have noted that the values of H_m^E for n-butyl methyl ether + n-heptane have been reported previously by Kehiaian *et al.*[12] and more recently by Marongiu *et al.* [24]. The deviation plot in Figure 5.1 shows that several of the results in reference [12] differ from this investigation by 5 per cent or more. However, in the middle mole-fraction range, there is an agreement within ± 1 per cent. Most of the results of Marongiu *et al.* are higher, but for $x < 0.7$, their deviations are less than 2.5 per cent.

The experimental results of H_m^E for present systems were correlated with different models. The prediction of excess volumes V_m^E for the same systems was carried out by the Flory theory with the values of interchange energy parameter X_{12} obtained from the H_m^E correlation. The experimental phenomena of mixing processes are discussed in terms of the concept of intermolecular forces.

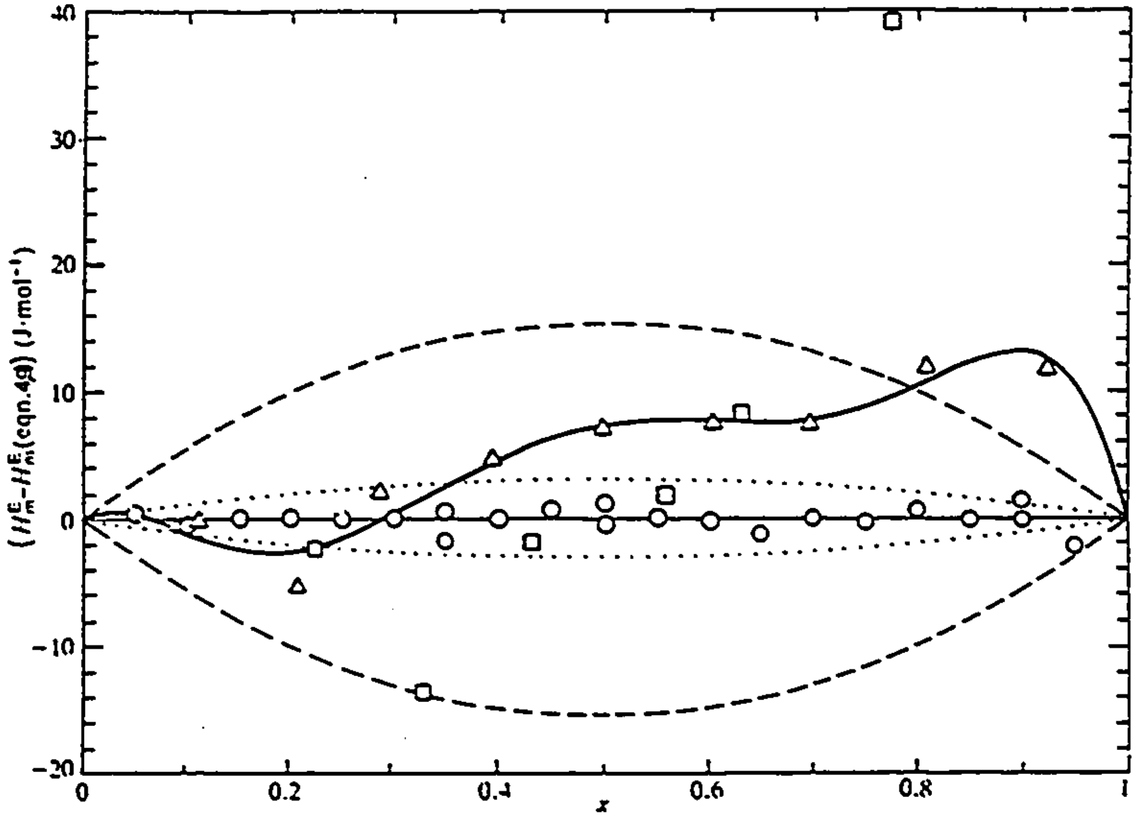


Figure 5.1: Comparison of H_m^E results for $[xC_4H_9OCH_3 + (1\text{-}x)C_7H_{16}]$ system at 298.15K.

Points and curves represent deviations of the excess molar enthalpy H_m^E from equation 4.9 : ○, present work; □, Kehiaian *et al.* [12]; △ and — Marongiu *et al.* [24]; ····, ± 1 per cent deviation; - - -, ± 5 per cent deviation

5.1 Group contribution models

The thermodynamic excess functions of organic liquid mixtures depend on the chemical nature, size and shape of the constituent molecules. For molecules of similar chemical nature, e.g., alkanes, the size and shape factors yield the main contributions, viz., the free volume contribution and the combinatorial entropy of mixing. For molecules of dissimilar molecular nature but nearly the same size and shape, the differences in force fields produce the main contribution to the thermodynamic excess functions. Orientational effects, conditioned by the energy differences and molecular nonhomogeneity, become quite important and also need to be taken into account. Therefore, the thermodynamic properties can be usually separated into two parts: one part provides the contribution due to differences in molecular size and the other provides the contribution due to molecular interaction. Based on this idea, group contribution models have been developed.

Estimation of thermodynamic properties of liquid mixtures from group contributions was first suggested by Langmuir [19]. This suggestion, however, received little attention until Derr and co-workers [5,33] used group contributions to correlate heats of mixing, followed by Wilson and Deal [53] who developed the solution-of-groups method for activity coefficients. This work was expanded by Derr and Deal [6] with their Analytical-Solution-of-Group (ASOG) method and by Ratcliff and co-workers [34].

The group contribution models give a method to predict thermodynamic properties of liquid mixtures from limited experimental data on reference systems. In this work, two group contribution models, UNIFAC (Universal Quasi-Chemical

Functional Group Activity Coefficient model) and DISQUAC (Dispersive Quasi-Chemical model), have been applied to the excess enthalpies of the present systems.

5.1.1 UNIFAC model

In the original formulation of UNIFAC [9], the interaction parameters were assumed to be independent of temperature. Their values were obtained from analyses of vapor-liquid equilibria, and generally are not useful for estimating excess enthalpies. Nagata and Ohta [28] used experimental H_m^E results to redetermine UNIFAC parameters which were more suitable for estimating the excess enthalpies of binary mixtures of an n-alkane with an n-alkanol, ketone, ester, or ether.

The expressions for excess enthalpy in UNIFAC model are given as follows.

$$\Delta H_m^E = \sum_i x_i \Delta \bar{H}_i \tag{5.1}$$

$$\Delta \bar{H}_i = \sum_k N_{ki}(H_k - H_{ki}^*) \tag{5.2}$$

$$H_k = f(X_1, X_2, ..., X_k, T, P) \tag{5.3}$$

$$X_k = \frac{\sum_i x_i N_{ki}}{\sum_k \sum_i x_i N_{ki}} \tag{5.4}$$

where X_k is the fraction of group k in the mixture; N_{ki} is the number of groups of type k in molecular species i; and the group excess enthalpy of group k, H_k, is a function of the group fraction, temperature and pressure. H_{ki}^* is the group excess enthalpy of group k in a reference solution containing only molecules of type i.

The group activity coefficient Γ_k is used to evaluate the group excess enthalpies.

$$ln\Gamma_k = Q_k[1 - ln(\sum_m \Theta_m \psi_{mk}) - \sum_m(\Theta_m \psi_{km} / \sum_n \Theta_n \psi_{nm})] \tag{5.5}$$

where Q_k is the group area parameter of group k, which can be obtained from the work of Fredenslund *et al.* [9]. ψ_{mn} is the group UNIFAC parameter between groups m and n ($\psi_{mm} = \psi_{nn}$=1). The area fraction of group m, Θ_m, is calculated by

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{5.6}$$

The group excess enthalpies are related to the group activity coefficients by using the Gibbs-Helmholtz relation.

$$H_k = -RT^2 \left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{P,x} \tag{5.7}$$

From equation 5.5 and 5.7, the analytical expression for H_k is given by

$$-\frac{H_k}{RT^2} = Q_k[-\frac{\sum_m \Theta_m \psi'_{mk}}{\sum_m \Theta_m \psi_{mk}} - \sum_m \frac{\sum_m \Theta_m \psi'_{km}}{\sum_n \Theta_m \psi_{nm}} + \sum_m \frac{\Theta_m \psi_{km} \sum_n \Theta_n \psi'_{nm}}{(\sum_n \Theta_n \psi_{nm})^2}] \tag{5.8}$$

where $\psi'_{mk} = \frac{\partial(\psi_{mk})}{\partial T}$. In the case of (ether + n-alkane), only two types of group surfaces were distinguished: etheric O and hydrocarbon CH_2 or CH_3. Thus the treatment involved four parameters $\psi(O, CH_2)$, and $\psi(CH_2, O)$, and their temperature derivatives $\psi'(O, CH_2)$, and $\psi'(CH_2, O)$. Using the values of those given in reference [28] along with the group-area parameters [9], H_m^E was estimated for the present mixtures. Mean absolute deviations Δ_1, root-mean-square deviations Δ_2, and percentage root-mean-square deviations Δ_3 of the predicted values from the experimental results for each mixture are listed in Table 5.1. The estimates for n=6 and 7 are reasonable, but the deviations become progressively larger for the longer alkanes. This behavior is probably due to the use by Nagata and Ohta[28] of (n-butyl methyl ether + n-heptane) as a reference mixture in adjusting the UNIFAC parameters.

More recently, Larsen *et al.* [21] have formulated a modified UNIFAC group-contribution model for the prediction of both phase equilibria and enthalpies of mixing. In this model, the interaction parameters are explicit functions of the temperature, and experimental excess enthalpies as well as (vapor + liquid) equilibria were used in establishing their values. However, as shown in Table 5.1, this model grossly overestimates H_m^E for the present mixtures.

5.1.2 DISQUAC model

Kehiaian *et al.*[15] have treated the thermodynamic properties of binary (oxaalkane + n-alkane) mixtures on the basis of DISQUAC [14]. In this approach, the group contributions are sums of dispersive and quasi-chemical terms, with the quasi-chemical parameters for monoethers depending on the nature of the groups attached to the oxygen atom. According to the DISQUAC model, n-alkyl ether + n-alkane systems are regarded as possessing two types of surfaces: (i) type a (CH_3, CH_2, and CH groups in n-alkanes and in alkyl ethers); (ii) type e (O, in alkyl ethers).

The analytical expressions for excess enthalpy in the DISQUAC model can be written as the sum of the dispersive contribution $H^{E,dis}$ and the quasichemical contribution $H^{E,quac}$, thus

$$H^E = H^{E,dis} + H^{E,quac} \tag{5.9}$$

The $H^{E,dis}$ term is given by

$$H^{E,dis} = (q_1x_1 + q_2x_2)\xi_1\xi_2h_{12}^{dis} \tag{5.10}$$

where

$$h_{12}^{dis} = -\frac{1}{2}\sum_s\sum_t(\alpha_{s1}-\alpha_{s2})(\alpha_{t1}-\alpha_{t2})h_{st}^{dis} \qquad (5.11)$$

h_{st}^{dis} is the dispersive interchange parameter of the $s-t$ contact. α_{si} is the molecular surface fraction of surface type s ($s = a$ and e) on a molecule of type i. q_i is the total relative molecular area of a molecule of type i and $\xi_i = q_ix_i/(q_1x_1+q_2x_2)$ is the surface fraction of component i in the mixture (i=1.2).

For a binary system. $H^{E,quac}$ is given by the known quasichemical equation [14]

$$H^{E,quac} = \frac{1}{2}(q_1x_1+q_2x_2)\sum_s\sum_t[X_sX_t-(\xi_1X_{s1}X_{t1}+\xi_2X_{s2}X_{t2})]\eta_{st}h_{st}^{quac} \qquad (5.12)$$

where

$$\eta_{st} = exp\left(-\frac{g_{st}^{quac}}{zRT}\right) \qquad (5.13)$$

h_{st}^{quac} is the quasichemical interchange parameter of the $s-t$ contact and z is the lattice coordination number whose 'reference' value is z=4 [40].

The quantities X_s and X_t are obtained by solving the system of λ equations (λ is the number of contact surfaces).

$$X_s(X_s+\sum_t X_t\eta_{st}) = \alpha_{s.} = \sum_i \xi_i\alpha_{si} \qquad s,t = a \;\; and \;\; e \qquad (5.14)$$

X_{si} and X_{ti} (i=1.2) are the solutions of equation 5.14 for $x_i = 1$ (pure component i). Equation 5.10 is obtained from the quasichemical equation 5.12 when z→ ∞ [13], and represents the so-called random mixing (or zero) approximation of the model.

The various mean deviations between the present experimental results and their DISQUAC estimates calculated with values of the parameters from reference[15] are given in Table 5.1. The agreement is best for (n-butyl methyl ether + n-decane), with the deviations increasing for both longer and shorter n-alkanes. Kehiaian *et al.* [15] also noted that for (di-n-alkyl ether + long-chain n-alkane) mixtures the experimental H_m^E are much higher than their DISQUAC estimates, which neglect contributions arising from changes in orientational order in the long-chain n-alkanes.

5.2 Flory model

5.2.1 The correlation of H_m^E data

It was found, previously [4,22,46,47], that H^E for mixtures of a symmetrical di-n-alkyl ether with n-alkane could be correlated by the Flory theory [1,8]. A similar investigation of the present mixtures was carried out in this study [50].

A semi-empirical configurational partition function was introduced in and an equation for liquids was derived from the Flory theory, which was advanced during the 1960's.

According to the Flory model, the excess molar enthalpy for binary liquid mixture is represented by

$$H_{Flory}^E = x_1 p_1^* v_1^* \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + x_2 p_2^* v_2^* \left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right) + \frac{x_1 v_1^* \theta_2}{\tilde{v}} X_{12} \qquad (5.15)$$

All parameters in this equation are related to the properties of pure components 1 and 2 only, which are usually available in the literature. What is left to do is to estimate the interchange energy parameter X_{12}. In this work, the values of X_{12} were obtained from least-squares analyses in which the Flory formula for H_m^E was fitted to the representations of the experimental results by equation 5.15.

For the present systems, characteristic properties, p^*, V_m^*, and T^*, of the pure components are listed in Table 5.2. The values for the n-alkanes were reported earlier[47]. Those for n-butyl methyl ether were derived from the primary thermodynamic values indicated in the footnote of the table. Also listed in Table 5.2 is the ratio s_{12} of (ether-to-alkane) molecular surface areas of contact per segment, and the interaction parameter X_{12} for each mixture. The values of s_{12} are based on the simple assumption that the molecules are spherical.

In the previous work [4,22,46,47], the Flory theory was successfully applied with X_{12} taken to be a linear function of n, the number of carbon atoms in the alkane molecules. A similar treatment was done in this study. It can be seen that X_{12} for the present systems also varies nearly linearly with n. However, the quadratic form

$$X_{12}(J/cm^3) = 8.700 + 0.3487n - 0.02089n^2 \tag{5.16}$$

provides a significantly better representation. Curves calculated from the Flory theory with values of X_{12} given by equation 5.16 are plotted in Figure 5.2, and the corresponding values of the various mean deviations are listed in Table 5.1. The agreement with the experimental results is good, although the Flory curves are slightly more skewed towards x=1.

Of the treatments investigated, the Flory theory with X_{12} given by equation 5.16 provides the most reasonable correlation of the results, with Δ_3 less than 10 per cent for all mixtures. This method can be used to estimate H_m^E for mixtures of n-butyl methyl ether with any n-alkane having a chain length between 6 and 16.

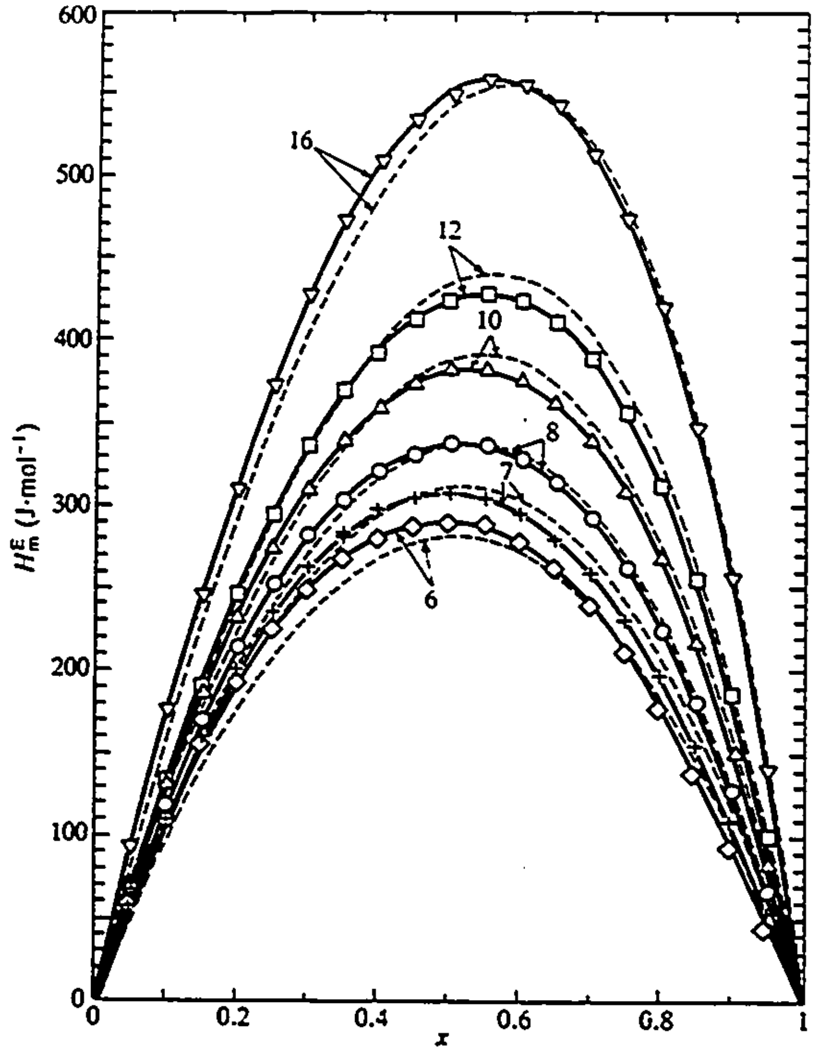


Figure 5.2: Excess molar enthalpies, H_m^E, of n-butyl methyl ether + n-alkane(C_nH_{2n+2}) mixtures as a function of the mole fraction, x, of ether at 298.15K

Experimental results: ◇, n=6; +, n=7; ○, n=8; △, n=10; □, n=12; ▽, n=16. —, calculated from equation(4.9); - - -, calculated from the Flory theory with X_{12} from equation(5.16). Curves labelled with values of n.

Table 5.1: Mean deviations between estimated and experimental H_m^E for $[xC_4H_9OCH_3 + (1\text{-}x)C_nH_{2n+2}]$ at 298.15K

	$\Delta_1/(Jmol^{-1})^a$			
n	UNIFAC Ref.28	UNIFAC Ref.21	DISQUAC Ref.15	FLORY Ref.8
6	6.3	173.0	16.1	9.3
7	7.0	185.4	17.6	7.9
8	13.9	183.5	8.0	6.1
10	25.8	195.4	5.6	8.4
12	42.1	202.5	13.4	7.2
16	105.7	158.6	73.7	11.4
	$\Delta_2/(Jmol^{-1})^b$			
n	UNIFAC Ref.28	UNIFAC Ref.21	DISQUAC Ref.15	FLORY Ref.8
6	7.0	183.5	16.6	10.3
7	7.9	198.0	18.6	8.8
8	16.0	196.6	9.0	7.0
10	28.8	209.9	6.2	8.9
12	45.7	215.3	15.4	8.9
16	113.8	173.3	79.6	13.6
	Δ_3^c			
n	UNIFAC Ref.28	UNIFAC Ref.21	DISQUAC Ref.15	FLORY Ref.8
6	6.7	87.5	10.7	8.2
7	5.5	86.4	9.5	6.8
8	7.0	77.1	3.8	4.0
10	11.3	70.3	3.7	4.5
12	14.2	64.0	5.0	2.7
16	27.9	40.1	19.9	5.2

[a] $\Delta_1 = (1/p)\sum_{i=1}^{p} |H_m^E(\mathrm{estd})_i - H_m^E(\mathrm{expt})_i|$;

[b] $\Delta_2 = \left[\sum_{i=1}^{p} \{H_m^E(\mathrm{estd})_i - H_m^E(\mathrm{expt})_i\}^2/p\right]^{1/2}$;

[c] $\Delta_3 = 100\left(\sum_{i=1}^{p} [\{H_m^E(\mathrm{estd})_i - H_m^E(\mathrm{expt})_i\}/H_m^E(\mathrm{expt})_i]^2/p\right)^{1/2}$

where p is the number of points.

Table 5.2: Parameters used in the calculations for [x$C_4H_9OCH_3$ + (1-x)C_nH_{2n+2}] systems by the Flory theory

Component	$\frac{p^*}{J \cdot cm^{-3}}$	$\frac{V^*_m}{cm^3 \cdot mol^{-1}}$	$\frac{T^*}{K}$	s_{12}	X_{12} ($J \cdot cm^{-3}$)	
					Fit of H^E_m	Eqn. 5.16
$C_4H_9OCH_3$	469.1[a]	90.28[a]	4476.3[a]			
C_6H_{14}	424.2	99.52	4436.1	1.0330	11.615	11.544
C_7H_{16}	431.9	113.60	4648.1	1.0796	11.960	12.165
C_8H_{18}	436.8	127.70	4827.0	1.1225	12.959	12.827
$C_{10}H_{22}$	447.0	155.75	5091.4	1.1993	14.339	14.276
$C_{12}H_{26}$	445.2	184.40	5351.4	1.2688	15.819	15.893
$C_{16}H_{34}$	457.0	240.41	5614.7	1.3860	19.641	19.628

[a] Calculated from the following properties at 298.15K: isobaric thermal expansivity $\alpha_p/kK = 1.360$[29], molar isobaric heat capacity $C_{p,m}(J.K^{-1}.mol^{-1}) = 192.7$[2] and speed of ultrasound transmission $u(m.s^{-1})$=1078.77 measured in our laboratory.

5.2.2 The prediction of V_m^E

Because of the satisfactory utilization of Flory theory in correlating the excess enthalpies in this work, the prediction of excess molar volumes V_m^E was carried out for the same systems by the Flory theory. As recommended by Flory[1], the interchange energy parameter X_{12} can be calculated from the observed excess enthalpy for the given mixture and then the other excess quantities can be predicted with the value of X_{12} thus obtained. According to Flory model, the excess molar volume for binary liquid mixture is represented by

$$V^E_{Flory} = v^*(\tilde{v} - \tilde{v}^\circ) \tag{5.17}$$

where

$$v^* = x_1 v_1^* + x_2 v_2^* \tag{5.18}$$

$$\tilde{v}^\circ = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 \tag{5.19}$$

As mentioned previously, $\tilde{v}_1, \tilde{v}_2, v_1^*$ and v_2^* are the properties of pure component 1 and 2, respectively. For a mixture, $\tilde{v}$ can be obtained by solving the following equation with the Newton method:

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}} \tag{5.20}$$

Since

$$\tilde{T} = \frac{T}{T^*} \tag{5.21}$$

and

$$T^* = \frac{\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_1 X_{12}}{\phi_1 p_1^*/T_1^* + \phi_2 p_2^*/T_2^*} \tag{5.22}$$

the reduced temperature $\tilde{T}$ can be also written as

$$\tilde{T} = \frac{\phi_1 p_1^* \tilde{T}_1 + \phi_2 p_2^* \tilde{T}_2}{\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}} \tag{5.23}$$

By solving these equations with the same values of X_{12} obtained from H_m^E correlation, the excess molar volume V_m^E can be predicted for the same systems. The calculated results are plotted in Figure 5.3 as broken curves. As shown in this figure, the Flory curves are more skewed toward x=1 than those found experimentally. The theory predicts increasing maxima of V_m^E followed by successive decreases, although the latter do not occur until after n-octane instead of after n-heptane as observed. Despite these discrepancies, it appears that the theory provides a reasonable description of the volume behavior of the present systems, bearing in mind that the V_m^E data was not used in adjusting the parameters.

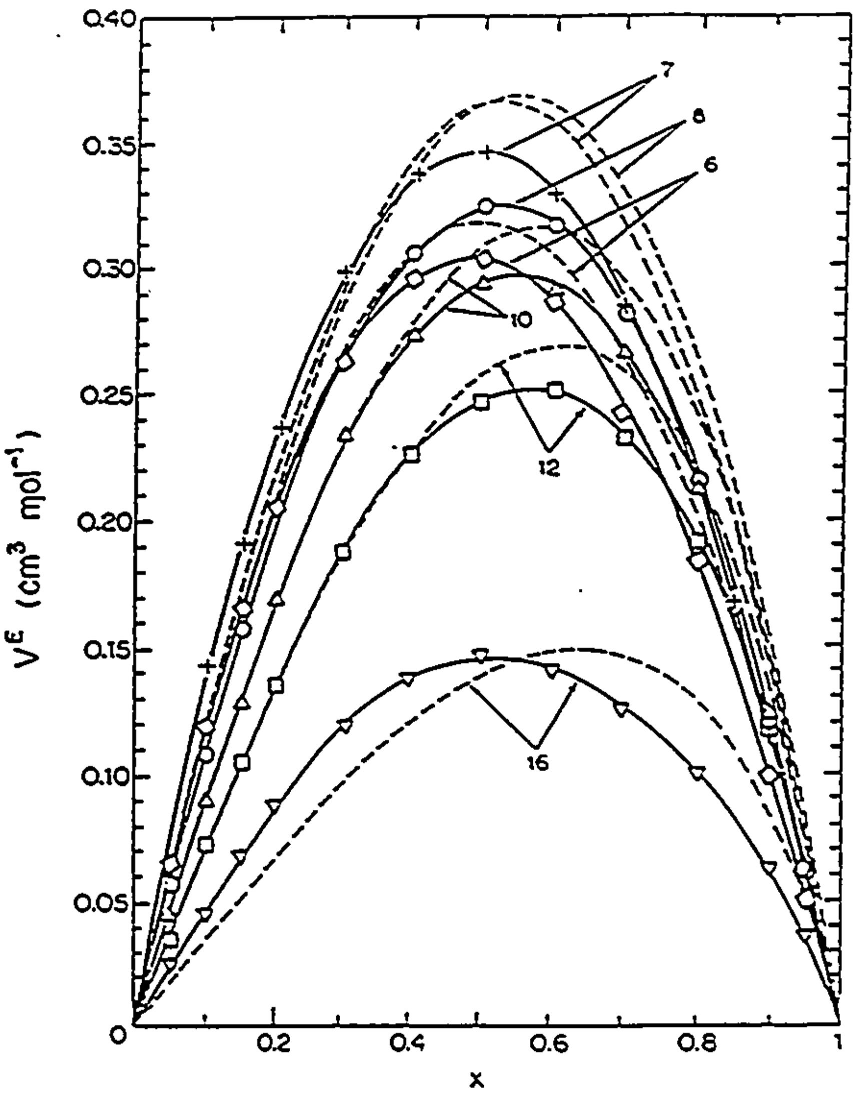


Figure 5.3: Excess molar volumes, V_m^E, of n-butyl methyl ether + n-alkane(C_nH_{2n+2}) mixtures as a function of the mole fraction, x, of ether at 298.15K

Experimental results: ◇, n=6; +, n=7; ○, n=8; △, n=10; □, n=12; ▽, n=16. —, calculated from equation(4.16); - - -, calculated from the Flory theory with X_{12} from equation(5.16). Curves labelled with values of n.

5.2.3 The effect of molecular structure of ether on H_m^E

In addition to the correlation of experimental H_m^E data by means of the solution theory, a comparison with our previous work [4,21,46,47] gives some revelation of the effect of molecular structure of alkyl ether on the excess enthalpies for alkyl ether mixtures with n-alkanes.

The chemical structures of n-alkanes are fairly symmetrical. The interaction of atoms and molecules in n-alkanes, therefore, cannot be accounted for by either dipole-dipole interaction, or dipole-induced dipole interaction. The dominant attractive force between nonpolar molecules is the London dispersion force. Instantaneously, the electrons will be at particular positions in the orbital and unless they are exactly opposite each other, the center of negative charge will not be situated at the nucleus and there will be an instantaneous orbital dipole. This instantaneous dipole can induce a dipole in an orbital of another molecule. Even though a single interaction of this type lasts only an instant, the combined effect of many of these instantaneous interactions results in a net attractive force, i.e. London dispersion force. This type of intermolecular force strongly relates to the amount and the size of function groups in molecules. Therefore, the more CH_2 groups are in the n-alkane molecules, the larger the heat effect of mixing is. The experimental results show that the excess enthalpy values for ether + n-alkane systems increase with the size of n-alkane molecules, as expected.

The ethers which have been studied in our laboratory previously include diethyl ether, di-n-propyl ether, di-n-butyl ether and di-n-pentyl ether. There is an oxygen atom in the middle of each ether molecule. In addition to the dispersion force as that exists in n-alkanes, the dipole-dipole force exists in the ethers as well. When the second component liquid, n-alkane, was introduced into the ether, a positive heat of mixing was produced. This is due to the change of intermolecular forces from that of the same molecules to that of the different molecules. In other words, the attraction between two ether molecules is stronger than that between an ether molecule and an n-alkane molecule, because the same ether molecules have the same frequencies of electron movement at high speed, which makes more chances for producing dipole-dipole attraction. With introduction of n-alkane, some of the dipole-dipole interaction between the same ether molecules are replaced by the intermolecular force between ether and n-alkane molecules. For doing so, extra energy is needed. That might be the reason why the heat of mixing for this kind of systems shows the positive sign. The oxygen atom in ether plays an important role in mixing process. With increasing of carbon chain, however, its effect reduces. The experimental results show that the excess enthalpy values decrease with increasing of carbon number in ether molecules. Table 5.3 shows the experimental data of H_m^E for hexadecane mixtures with each ether used in the previous work [4,21,46,47].

In the present systems, the ether contains both the methyl and butyl groups. The experimental result shows that H_m^E for n-butyl methyl ether mixture with n-alkanes is in between the H_m^E values for di-ethyl ether and di-n-butyl ether mixtures with the same alkanes, as expected.

Table 5.3: Excess enthalpy H_m^E for the mixtures of hexadecane with different ethers

x	H_m^E	x	H_m^E	x	H_m^E	x	H_m^E
(x)Diethyl ether + (1-x)n-Hexadeca[22]							
0.0500	130.0	0.2999	476.5	0.5997	618.7	0.9000	293.2
0.1000	197.2	0.3999	561.0	0.6996	578.0	0.9500	163.5
0.1995	347.8	0.4999	615.9	0.8000	472.2		
(x)Di-n-propyl ether + (1-x)n-Hexadece[46]							
0.0499	77.3	0.3002	383.2	0.6001	480.3	0.9001	208.1
0.0998	152.4	0.3998	451.2	0.7002	437.1	0.9500	113.1
0.2001	280.9	0.5002	482.3	0.7988	351.2		
(x)Di-n-butyl ether + (1-x)n-Hexadecane[4]							
0.0500	60.7	0.3000	288.2	0.6000	346.6	0.9000	145.3
0.1000	117.8	0.3997	332.8	0.7002	311.6	0.9500	78.6
0.2000	214.3	0.5001	354.2	0.8001	246.2		
(x)Di-n-pentyl ether + (1-x)n-Hexadecane[47]							
0.0999	105.1	0.3989	275.6	0.6997	246.7	0.9499	58.4
0.2000	158.8	0.4997	287.9	0.8003	190.9		
0.3000	245.0	0.6003	277.3	0.9001	109.1		

Chapter 6

CONCLUSION

In conclusion, the following points have been made:

1. H_m^E values increase fairly regularly with increasing chain length of the n-alkane.

2. H_m^E values increase with decreasing the number of CH_2 groups in ether.

3. Flory theory can be used to estimate H_m^E and V_m^E for the mixtures of alkyl ether, having two to ten carbon atoms, with any n-alkanes having a chain length between 6 and 16.

4. For present systems, the interaction parameter X_{12} in Flory theory varies quadratically with n, the number of carbon atoms in the alkane molecules.

5. V_m^E data are not suitable to be used to adjust the parameters in Flory theory for the present systems.

Chapter 7

RECOMMENDATIONS FOR FUTURE WORK

A lot of experimental measurements on excess enthalpy and excess volume have been done in our laboratory previously. The correlation of experimental data with different solution theories have been tried as well. Some further works are worth trying, such as the prediction of other excess properties from the experimental excess enthalpy or excess volume data. By doing so, we can get more useful information from the finite experimental data we have obtained. With the equipments available in our laboratory, the excess enthalpy can also be determined for some ternary systems based on our previous work.

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