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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE

Interfacial Tension Characteristics of Pure Oil and Crude Oil Systems

by

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ABSTRACT

The present work relates to the recovery of oil from partially-depleted underground petroleum reservoirs by means of aqueous solution injection. In particular, it is concerned with developing a better understanding of the interfacial activity of Canadian crude oils when in contact with aqueous solutions. Of special importance in this context is the prevailing interfacial tension as oil recovery efficiency is known to be inversely proportional to this parameter.

In the first part of this study, the interfacial tension behaviour of binary mixtures of pure component oils against water is examined experimentally and theoretically. For all binary hydrocarbon mixtures, the excess interfacial tensions are computed from the ideal solution and show negative deviations. In the second part, the interfacial activity of real crude oils, and crude oils diluted with pure component oils, is investigated. The dilution of three Canadian crude oils (Cold Lake, Lloydminster and Chatham) with hexadecane, toluene and hexadecane/toluene mixtures results in higher IFT values than those for the pure crude oils, when in contact with alkaline solutions. However, the opposite trend is observed when no alkali solution is present in aqueous phase.

In the third part of the study, the dynamic interfacial tension behaviour of crude oils, and diluted crude oils, against aqueous alka-

line solutions is examined. These systems, which are encountered frequently in practice, are characterized by chemical reactions between the alkali and the various acidic components in the crude oil, which generate surfactants in-situ at the interface and which lead to drastically lowered interfacial tensions. A dynamic minimum IFT is observed in all cases.

In the fourth and final part of this study, the effects of clay particles on interfacial tension are investigated. Real petroleum reservoirs contain various natural clays and it is important to know how they can influence the interfacial tension and hence the oil recovery efficiency. It is found that bentonite has some effect on the IFT of crude oils and pure oils. When a small amount of clay is present in the aqueous phase, the reduction in IFT is accompanied by clay adsorption at the interface.

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NOMENCLATURE

The symbols used in the text, unless otherwise stated, have the following meaning:

C_j	coefficient in Redlich-Kister equation
H^E	excess enthalpy (J/mol)
k	Boltzmann constant
M_i	molecular weight of component i (c.u)
n	number of fitting constants
n_{obs}	number of data points
P	pressure (atm)
R	gas constant
T	temperature (°C)
V^E	excess molar volume (cm^3/mole)
W_i	weight of component i (gm)
X_i	mole fraction of component i
X_{12}	interaction parameter

Greek Alphabet

α	coefficient of thermal expension
β	isothermal compressibility
γ^E	excess interfacial tension (mN/m)
γ_i	interfacial tension of component i (mN/m)

γ_{12}	interfacial tension of solution (mN/m)
$\gamma^{E(o)}$	excess surface tension (mN/m)
γ_i^o	surface tension of component i'(mN/m)
γ_{12}^o	surface tension of solution (mN/m)
$\Delta\rho$	density difference (g/cm^3)
ρ_i	density of pure component i,(g/cm^3)
ρ_m	density of mixture (g/cm^3)
σ_r	standard deviation
Σ	summation

CONTENTS

FIGURES

TABLES

Chapter I

INTRODUCTION

(1) Alkaline Flooding in Enhanced Oil Recovery.

Recent advances in enhanced oil recovery (EOR) have shown that interfacial forces have important, and often dominant, effects on oil recovery processes. The meaning of enhanced oil recovery is to use a chemical flood to displace additional oil. The method in this area of using mixtures of sodium hydroxide and sodium chloride is called alkaline flooding and is quite widespread, especially for crude oils. The advantage of this method is that it is cheap and efficient for lowering interfacial tension (IFT) compared to other methods, such as surfactant flooding, steam flooding, polymer flooding and co-surfactant flooding.

However, the success or failure of alkaline flooding may be controlled, to a large extent, by alkali adsorption on to the reservoir rock and the amount of acid in the crude oil. It is important to note that alkali reacts with crude oil only within a certain concentration range to give an ultralow interfacial tension favorable for oil displacement.

There are two major factors causing alkali consumption, i.e.,

(a) alkali and oil reaction.

(b) alkali adsorption on reservoir rock.

Alkali and oil reaction is useful and necessary for oil recovery. In contrast, alkali adsorption on rock is usually detrimental. In recent years, many observations on reservoir rocks have shown that most

of the rock surface is covered by clay particles [51]. Thus, studies of the effects of clay on interfacial tension between crude oil and alkaline solutions are necessary.

The ultimate goal of the first part of the present work is to examine the effects of alkali, bentonite (clay) and solution dilution on the interfacial tension behaviour of various pure oil and crude oil systems, in particular:

(a) to generalize the effects of alkali on the IFT of crude oils.

(b) to examine the effects of clay on the IFT of crude oils.

(c) to study the effects of acidity of crude oils on IFT.

(2) Binary Mixtures of Pure oils

It should be noted that interfacial tension can affect such basic chemical engineering processes as mass and heat transfer. In many cases, the interfacial tension driving forces result from concentration gradients in solutions. Thus, an understanding of the interfacial tension of solutions is basic to solving many chemical engineering problems.

Liquid-liquid systems are characterized by the presence of strong intermolecular forces. The non-ideality of a liquid mixture is usually described by excess thermodynamic functions, like the excess enthalpy H^E, the excess volume V^E, the excess surface tension $\gamma^{E(o)}$, and so on. However, most of the reports in the literature give the excess properties against the vapor phase. Clearly, important information could be derived by studying excess properties for systems in which liquid water replaces the vapor phase. This is the main objective of the second part of the present work. The systems chosen for this investigation are shown in Table 1.

Table 1: Oils for Binary Mixture Study

Aromatic	Hydrocarbon
Benzene	Octane
Toluene	Decane
O-Xylene	Hexadecane

(with fifteen binary combinations)

This approach allows us to study the important classes of system, namely hydrocarbon+hydrocarbon, aromatic+aromatic and aromatic+hydrocarbon mixtures. Such mixtures are of technical interest because they frequently occur in petroleum processing. These mixtures are non-polar and are essentially insoluble in water, except for benzene.

Because of the complex physical interactions which are possible in solutions, the excess interfacial tension can be used as a quantitative measure of the non-ideality of the solutions. For interfacial properties, a more realistic expectation would be to start from a knowledge of bulk phase interactions and the pure component interfacial properties. A less ambitious, but still valuable, goal would be a widely-applicable correlative technique. This would allow reliable extrapolation from limited experimental data and would provide a concise method of reporting and evaluating experimental data.

In terms of bulk thermodynamic properties, the excess volume is also studied for the binary systems hexadecane+decane, +octane, +benzene, +toluene and +o-xylene. Flory [16] developed a theory based on a cell model which is not restricted to spherical molecules and which will therefore be used in the present work to correlate excess volume data.

In addition, the above calculated excess results from ideal solutions are fitted using the Redlich-Kister [43] equation.

Chapter II

LITERATURE REVIEW

A great deal of work has been carried out on interfacial tension and its application to EOR in the last decades. The effects of many variables on interfacial tension have been investigated, such as temperature, pressure, chemical additive etc. However, there are some aspects of interfacial tension behaviour that are still not clearly understood.

2.1 Thermodynamics of Liquid-Liquid Systems

(1) Thermodynamics of the Bulk Liquid

(a) Description of the theory

Flory [16] proposed a theory for mixtures of non-spherical molecules. Only a brief discussion will be given here; the original paper may be consulted for further details.

Flory assumes that the forces between polyatomic molecules effectively arise from the surface of adjoining molecules. Each molecule is divided into r segments, each of which has s contact sites. The number of segments per molecule is proportional to the volume of the molecule. The total number of contact sites per molecule, rs, is proportional to the surface area of the molecule. The mean intermolecular energy of the liquid, E, is assumed to be inversely proportional to the volume per segment,

$$E \leq -Nrs\varepsilon/2v \qquad (1)$$

where N is the number of molecules, v is the volume of a segment, and ε is a constant energy of interaction for a pair of neighboring sites. Starting from these assumptions, Flory derives a reduced equation of state:

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T} \qquad (2)$$

The reduced quantities $\tilde{v}$, $\tilde{T}$, and $\tilde{p}$ are defined as:

$$\tilde{v} = v/v^{*} \qquad (3)$$

$$\tilde{p} = p/p^{*} \qquad (4)$$

$$\tilde{T} = T/T^{*} \qquad (5)$$

v denotes the molar volume, and v^{*}, p^{*} and T^{*} are the characteristic quantities for each liquid.

The theory is extended to a binary mixture by introducing a parameter X_{12} which characterizes the difference in the energy of interaction between neighboring molecules of different species from the average of the interactions in the pure component liquids:

$$X_{12} = s_1(\varepsilon_{11}+\varepsilon_{22}-2\varepsilon_{12})/2v^{*2} \qquad (6)$$

The quantity v^{*} is defined as

$$v^{*} = v/\tilde{v} \qquad (7)$$

and is the same for all species. Flory has shown that the reduced temperature of a binary mixture is given by the expression:

$$\tilde{T} = (\phi_1 p_1^* \tilde{T}_1 + \phi_2 p_2^* \tilde{T}_2)/(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \hat{\theta}_2 X_{12}) \quad (8)$$

where the segment fraction, ϕ_1 and ϕ_2, are defined by:

$$\phi_2 = 1-\phi_1 = X_2/(X_2 + X_1 r_1/r_2) \quad (9)$$

and the site fraction θ_2 by:

$$\theta_2 = \phi_2/(\phi_2 + \phi_1 s_1/s_2) \quad (10)$$

The molar excess enthalpy and volume are:

$$H^E = X_1 p_1^* v_1^* (\tilde{v}_1^{-1} - v^{-1}) + X_2 p_2^* v_2^* (\tilde{v}_2^{-1} - v^{-1}) + X_1 v_1^* \theta_2 X_{12} \tilde{v}^{-1} \quad (11)$$

$$V^E = (X_1 v_1^*) + (X_2 v_2^*)(\tilde{v} - \phi_1 \tilde{v}_1 - \phi_2 \tilde{v}_2) \quad (12)$$

(b) Parameters for the pure components

At zero pressure, the reduced equation of state becomes:

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (13)$$

Equation (13) is differentiated with respect to temperature and rearranged to give:

$$\tilde{v} = [(1+4\alpha T/3)/(1+\alpha T)]^3 \quad (14)$$

Equation (14) permits the determination of v if the thermal expansion coefficient, α, is known at the same temperature. If the molar volume, v^*, can be computed from Equation (3), Equation (13) serves to determine the corresponding value of $\tilde{T}$, which is inserted into Equation (5) to determine T^*.

Differentiation of Equation (2) with respect to pressure yields for the limit of zero pressure:

$$p^* = T\tilde{v}^2\alpha/\beta \tag{15}$$

This equation allows us to determine the characteristic pressure, p^*, from the isothermal compressibility, β.

(c) Determination of interaction parameter

The interaction parameter X_{12} can be determined according to Abe and Flory [1]. They applied this theory to a wide variety of binary mixtures of non-polar molecules and determined the interaction parameter X_{12} by fitting the experimental excess enthalpy and then other excess functions from the X_{12}. This procedure was adopted here.

Since the number of segments, r, was chosen proportional to the volume of the molecules it follows that:

$$r_1/r_2 = v_1^*/v_2^* \tag{16}$$

The number of contact sites, rs, was assumed to be proportional to the surface area of the molecules. For spherical molecules, this leads to the relation:

$$s_1/s_2 = (v_2^*/v_1^*)^{1/3} \tag{17}$$

Thus the quantities ϕ_1, ϕ_2, and θ can be determined from the Equations (9) and (10).

Equations (8), (11), and (13) contain three unknown quantities, X_{12}, v, and T. Equations (8) and (13) can be combined to give:

$$X_{12} = -(\phi_1 p_1^* \tilde{T}_1 + \phi_2 p_2^* \tilde{T}_2)/[\phi_1 \theta_2 (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3}]$$

$$+ (\phi_1 p_1^* + \phi_2 p_2^*)/\phi_1 \theta_2 \tag{18}$$

Equation (11) is arranged to yield:

$$X_{12} = [H^E - X_1 p_1^* v_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) - X_2 p_2^* v_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1})]$$

$$/X_1 v_1^* \theta_2 \tilde{v}^{-1} \tag{19}$$

The values of X_{12} were determined by minimizing the integral:

$$\sigma_v^2 = \int_0^1 (V^E_{exptl} - V^E_{Flory})^2 \, dX_1 \tag{20}$$

(2) Thermodynamics of the liquid interface

The equation for the interfacial tension is usually given in terms of the surface tension of the two phases. A well-known relation called Antonoff's rule [15] applies to two mutual saturated phases:

$$\gamma_{12} = \gamma_1^{o} - \gamma_2^{o} \tag{21}$$

which has never been theoretically derived in any fashion, but which from time to time appears in the literature.

A similar relation was given by Good:

$$\gamma_{12} = [(\gamma_1^{o})^{1/2} - (\gamma_2^{o})^{1/2}]^2 \tag{22}$$

and is sometimes [50] referred to as the unmodified Good equation. This represents the standard Good equation with a value of unity for the interaction parameter, Φ.

Neumann and Good [36] proposed an equation of state for interfacial tension, based on strictly thermodynamic arguments as follows:

$$\gamma_{12}^{\#} = [(\gamma_1^{o})^{1/2} - (\gamma_2^{o})^{1/2}]^2/[1-0.015(\gamma_1^{o}\gamma_2^{o})] \tag{23}$$

They used this equation in combination with Young's equation for evaluating the surface tension of a solid phase. However, this equation is never used for calculating the interfacial tension of liquid-liquid systems.

Another equation for predicting interfacial tension was given by Legrand et al. [29] as:

$$\gamma_{12} = \gamma_1^{o} + \gamma_2^{o} - \Delta \qquad (24)$$

in which they treated Δ as being molecular weight independent.

In these equations γ_{12} is the interfacial tension between phases 1 and 2. γ_1^{o} is the surface tension of phase 1, and γ_2^{o} is the surface tension of phase 2. It is obvious that all equations for estimating interfacial tension are expressed in terms of the surface tensions of both phases.

The theoretical treatment of surface tension as opposed to interfacial tension of pure components and their mixtures is well documented in the literature, due to Guggenheim [19], Hoar and Melford [21], Shereshefeky [49], and Brock and Bird [10].

Patterson and Rastogi [38], in their extension of the corresponding states principle, started with Prigogine's [40] result and used as the reduction parameter the quantity

$$\gamma^{*} = K^{1/3} p^{*1/3} T^{*1/3} \qquad (25)$$

where K is the Boltzmann constant. Furthermore, they formulated a reduced surface tension equation which in the case of a van der Waals liquid can be written:

$$\tilde{\gamma}(\tilde{v}) = N\tilde{v}^{-5/3} - (\tilde{v}^{1/3} - 1)/\tilde{v}^{2} N[(\tilde{v}^{1/3} - 0.5)/(\tilde{v}^{1/3} - 1)] \qquad (26)$$

In this equation N represents the fractional reduction in nearest neighbors for a cell at the surface compared with one in the bulk of the liquid. Therefore, theoretical estimates of the surface tensions of the pure component liquids at a given temperature can be obtained from the relation:

$$\gamma = \gamma^* \tilde{\gamma}(\tilde{v}) \tag{27}$$

The values of the characteristic and reduced surface tension can be determined following Flory's theory, if the values of V, α, and β are known. Therefore, for the mixtures, $\langle v^* \rangle$, $\langle p^* \rangle$, and $\langle T^* \rangle$ also can be calculated from the following equations:

$$\langle v^* \rangle = X_1 v_1^* + X_2 v_2^* \tag{28}$$

$$\langle T^* \rangle = \langle p^* \rangle / (\phi_1^*/T_1^* + \phi_2^*/T_2^*) \tag{29}$$

$$\langle p^* \rangle = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \phi_2 X_{12} / (\phi_2 + S_{12}\phi_1) \tag{30}$$

which are the same as in Flory's theory. The surface tension of the pure components and mixture can be expressed as:

$$\gamma_i = \gamma_i^* \tilde{\gamma}(\tilde{v}_i) \tag{31}$$

$$\gamma_{12}^{o} = \langle \gamma^* \rangle \tilde{\gamma}(\tilde{v}) \tag{32}$$

Using Antonoff's rule, the interfacial tension, in the case of water as the lower phase, can be written:

$$\gamma_{12} = \gamma_w^* \tilde{\gamma}(\tilde{v}_w) - \langle \gamma^* \rangle \tilde{\gamma}(\tilde{v}) \tag{33}$$

The excess interfacial tension can then be expressed as:

$$\gamma^E = \gamma_{12} - X_1 \gamma_1 - X_2 \gamma_2$$

$$= \gamma_w^* \tilde{\gamma}(\tilde{v}_w) - \langle \gamma^* \rangle \tilde{\gamma}(\tilde{v}) - X_1 [\gamma_w^* \tilde{\gamma}(\tilde{v}_w) - \gamma_1^* \tilde{\gamma}(\tilde{v}_1)]$$

$$- (1-X_1) [\gamma_w^* \tilde{\gamma}(\tilde{v}_w) - \gamma_2^* \tilde{\gamma}(\tilde{v}_2)] \qquad (34)$$

Therefore, the excess interfacial tension may be determined theoretically, provided the equation of state for calculating interfacial tension is explicit, such as Equation (22).

2.2 Dynamic Interfacial Tension of Crude Oils

The lowering of IFT at crude oil-caustic interfaces was observed by Atkinson [2] and Nutting [37] a long time ago. This led to the use of caustic solutions as EOR agents. Since then, many researchers have studied crude oil-caustic interfacial tensions and elucidated the mechanisms of such processes. It is now well established that the acidic components of the crude oil diffuse out from the interface, where they react with the caustic to generate surface active species, which cause a lowering of the IFT.

Jennings [23] studied the effect of caustic solutions on the IFT of 164 crude oils from 78 different fields. He concluded that 131 of these crude oils showed surface activity against caustic solutions and observed the change in IFT with interfacial age. A minimum IFT was observed in most cases, often after only a short time.

Rubin and Radke [45] suggested that the minimum IFT attained was accompanied by a maximum adsorption of active species at the interface. This behaviour also was observed by Bansal et al. [4]. Their results showed that a maximum in charge density corresponded to the minimum IFT at the crude oil-caustic interface. To satisfy this charge accumulation

at the interface, the convective diffusion from the oil to aqueous phase should be less than from the aqueous to oil phase [45].

Due to the variability of oil-field conditions, it is very difficult to determine which IFT values are representive of alkaline flooding in actual reservoirs. Moreover, the alkali can adsorb on, or react with, the clays in the reservoir rock , and can combine with the divalent ions (principally Mg^{++} and Ca^{++}) naturally present in the reservoir water. These factors may adversely affect the ability of the alkaline flooding process and make it difficult to mobilize the trapped oil [22]. McCaffery [33] observed that in the presence of calcium and magnesium ions, it was necessary to have a higher concentration of alkali to reduce the IFT to ultralow values.

Recently, Borwankar and Wasan [8,9], based on previous work of Ramakrishnan and Wasan [41], developed a chemical diffusion kinetic model for the case of acidic oil recovery by alkaline flooding. This model reveals that the occurrence of a dynamic IFT minimum is a function of the rate constants of the adsorption and desorption barriers, and is independent of the composition of the aqueous phase.

Chapter III

EXPERIMENTAL

3.1 Materials

The crude oil samples employed in this work were obtained from the following sources and were used as received:

(1). COLD LAKE OIL: this came directly from the Cold Lake deposit (Well No. 13) in Alberta, and was supplied by ESSO Resources Canada Ltd., Calgary. It possessed an acid number of 1.2 mg.KOH/g.oil.

(2). LLOYDMINSTER OIL: this came directly from the Lloydminster deposit (Well No. A2-12-49-23 W3) in Saskatchewan, and was also supplied by ESSO Resources Canada Ltd., Calgary. Its acid number was 0.9 mg.KOH/g.oil.

(3). CHATHAM OIL: this came directly from the Gosfield South Field in Chatham, Ontario, and was supplied by Gaiswinkler Enterprises, Chatham. This oil possessed a much lower acid number of 0.2 mg.KOH/g.oil.

The properties of the Lloydminster and Chatham oils are displayed in Tables 2 [55] and 3 [25].

Table 2: Properties of Lloydminster Crude Oil

°API	16.7
Viscosity (°C), cSt	330(40)
	23(100)
Pour Point, °C	-10
Flash Point, °C	34
Asphaltenes, Wt.%	8.7
BS+W, Wt.%	3.4
CCR, Wt.%	9.2
Ash, Wt.%	0.14
Carbon, Wt.%	83.9
Hydrogen, Wt.%	11.4
Nitrogen, Wt.%	-
Sulphur, Wt.%	3.40
V, ppm	79
Ni, ppm	41
Fe, ppm	6
Salt, Ptb	147

Table 3: Properties of Chatham Crude Oil

°API	39.4
Color	Greenish-black
Carbon,% by weight	85.70
Hydrogen,% by weight	13.39
Nitrogen,% by weight	0.4
Sulfur,% by weight	0.18
ASh,% by weight	0.007
Water,% by weight	Nil

Other chemicals used in this study were ordered from Fisher Scientific and T.J. Baker Companies, namely Benzene, Toluene, O-xylene, Octane, Decane, Hexadecane, Bentonite, Fuller's Earth, Sodium hydroxide and Sodium Chloride (see Table 4).

Table 4: Manufacturers and Purities of Chemical Compounds.

Material	Manufacturer	Grade
Benzene	Fisher	99 mol%
Toluene	Fisher	99 mol%
O-xylene	Fisher	Reagent
Octane	Fisher	Reagent
Decane	Fisher	Certified
Hexadecane	Fisher	Reagent
Bentonite	Fisher	Purified
Fuller's Earth	Fisher	Technical
Sodium Chloride	Fisher	Certified
Sodium Hydroxide	T.J.Baker	Baker Analyzed

3.2 Preparation of Solutions

The desired binary hydrocarbon mixtures were prepared using the following steps:

(1) In order to cover the whole concentration range, the first step is to calculate the required weight of each component from the equation:

$$X_j = W_j/M_j/(\Sigma_i W_i/M_i) \tag{35}$$

(2) Assuming one component weight is known (e.g. W_2), the other (W_1) can be easily determined from the following equation:

$$X_1 = W_1/M_1/(W_1/M_1 + W_2/M_2) \tag{36}$$

where X_1 , X_2 are mole fractions of components 1 and 2, M_1 , M_2 are molecular weights of components 1 and 2 and W_1 , W_2 are weights of components 1 and 2.

The molecular weights of the pure components are listed in [56] are listed in Table 5.

(3) The weights of the pure components (W_1 and W_2) were determined by using an analytical balance (Mettler H64). For each binary mixture, three weighings were necessary (i.e., firstly the empty bottle, then with added component 1, and finally with added component 2).

(4) A 25-ml glass tube was used to introduce the liquid components into the bottle, which was capped with a glass stopper in order to minimize any evaporation.

Table 5: Molecular Weight of Pure Organic Compounds.

Compounds	Formula	Molecular Weight
Benzene	C_6H_6	78.12
Toluene	C_7H_8	92.00
O-xylene	C_8H_{11}	106.70
Octane	C_8H_{18}	114.23
Decane	$C_{10}H_{22}$	142.29
Hexadecane	$C_{16}H_{32}$	226.45
Bentonite	-	62.42*

* from reference [42]

The binary hydrocarbon mixtures were prepared using the above steps and they were stored overnight in order to allow an equilibrium condition to become established [26].

A similar procedure was used to prepare the diluted crude oil mixtures. All dilutions were performed on a weight basis so that throughout this work the units of concentration are weight percent. All the solutions were degassed for 3 hours using vacuum before each measurement.

3.3 Interfacial and Surface Tension Measurements

3.3.1 Ring Method

Interfacial and surface tensions of pure liquids and their binary mixtures were measured by the ring technique originally developed by Wilhemy and du Nouy [15]. Details of its operational procedure have already been listed elsewhere [3], including the method of cleaning the ring and glass-ware. The instrument used was the Autotensiomat, supplied by Fisher Scientific Ltd.

In this study, the apparent values of interfacial and surface tension were recorded on a chart. A typical calibration chart is shown in Figure 1. This calibration was done every two months, due to changes in the condition of the equipment.

For all interfacial tension measurements the volume ratio of distilled water to oil phase was controlled at 2:1. All the experiments were performed under the same conditions with the Autotensiomat and recorder speeds set at 0.08 in/min and 0.4 in/min respectively.

In order to minimize temperature effects, all solutions were pre-equilibrated in a water bath at 25 0.2°C for at least two hours before measurement.

The measurements of interfacial and surface tensions were made using the following procedure:

(1) Calibrate the instrument for the selected readout (usually 1 gm , for which recorder reads out 81.6 mN/m).

(2) Pour more dense liquid into vessel (80 ml), which has been cleaned previously.

(3) Check temperature to ensure that it is 25°C.

(4) Turn elevator direction switch (0.08 in/min.), until elevator platform reaches maximum height.

(5) Release vertical carriage lock and submerge ring in liquid by lowering transducer-balance assembly.

(6) Pour less dense liquid carefully onto the surface of the more dense liquid. The layer of the less dense liquid is about 2 inch which is deep enough for the ring to break through the interface film before its upper surface ruptures.

(7) Turn elevator speed selector to 0.08 in/min. for measurements.

(8) Turn recorder chart speed switch to 0.4 in/min. for measurements.

(9) Turn recorder power switch on and adjust recorder pen to baseline.

(10) Turn elevator direction switch down, and observe apparent interfacial or surface tension on recorder.

Figure 2 shows the correction factor as a function of P/(D-d), where P is the apparent value of interfacial or surface tension, D is density of upper phase and d is density of lower phase. The absolute value of the tension can be calculated from the equation:

$$S = F \cdot P \tag{37}$$

where S is the absolute value of tension and F is the correction factor.

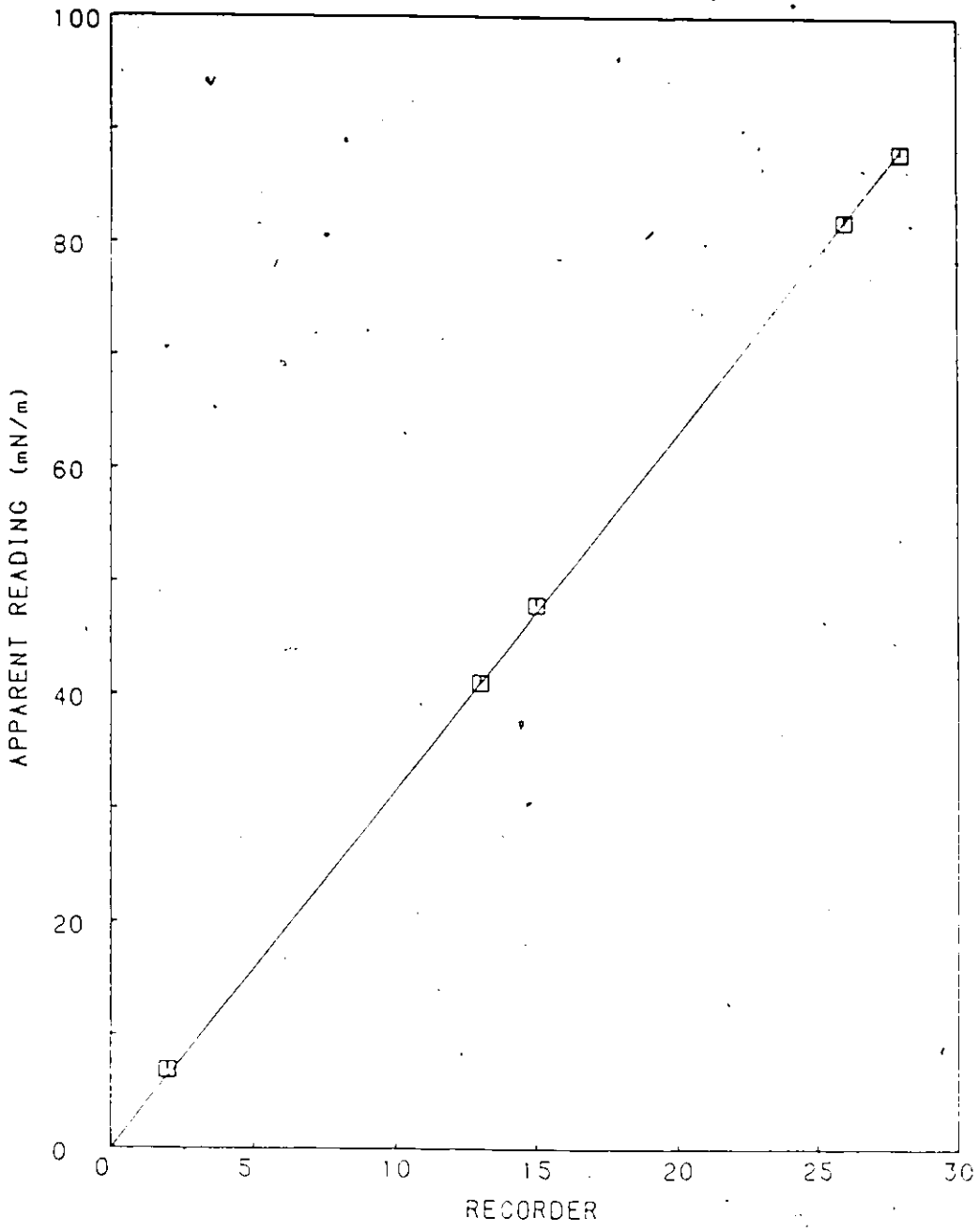

Figure 1: Apparent IFT value vs. recorder value for Autotensiomat at 25°C

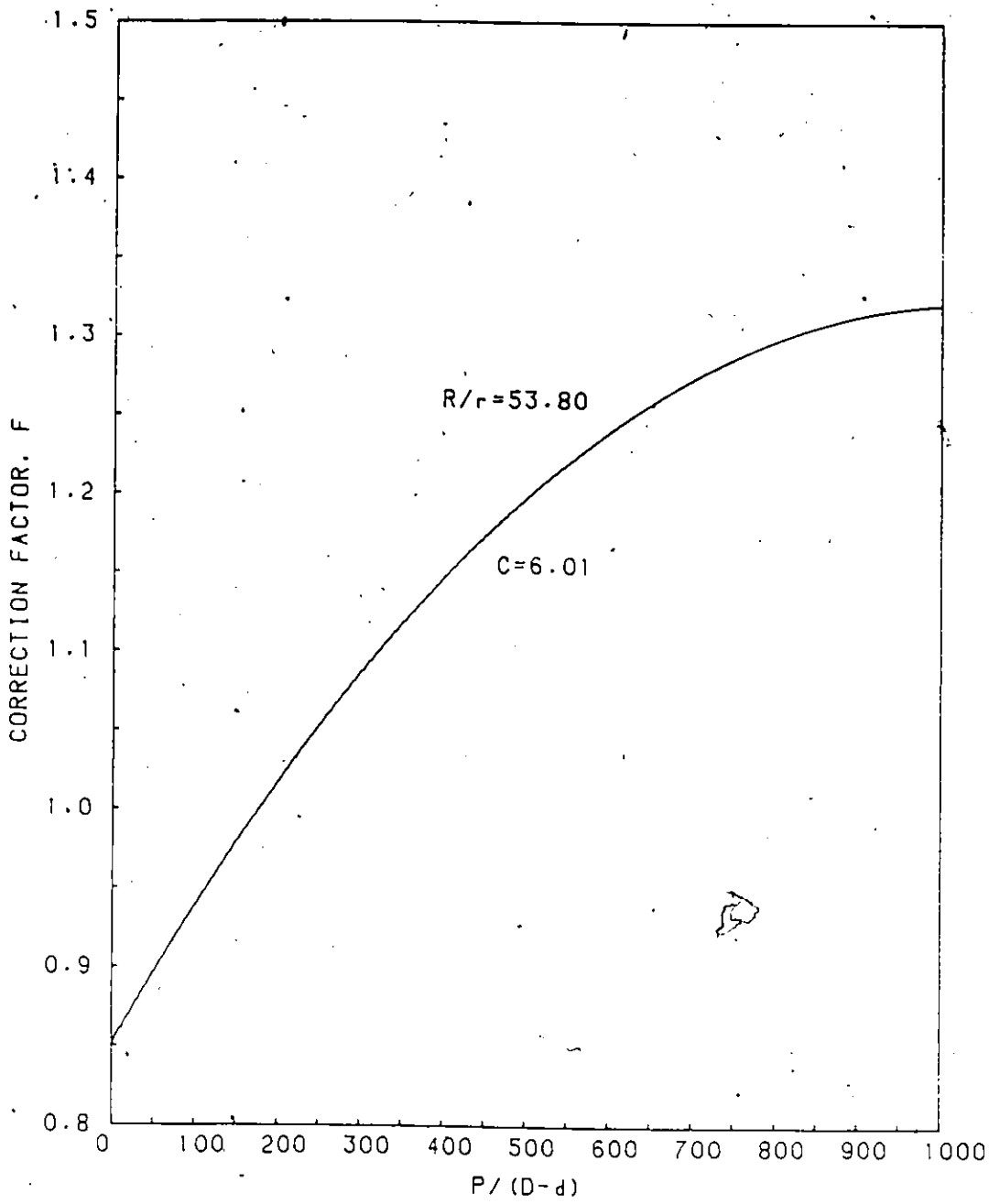

Figure 2: Correction factor F vs. P/(D-d) for Autotensiomat

3.3.2 Spinning Drop Method.

The IFT of crude oils against different alkaline solutions was measured on the Spinning Drop Interfacial Tensiometer (University of Texas model 500). The description of measurements as well as the cleaning procedure are discussed elsewhere [17,44].

In the spinning drop tensionmeter, a small droplet of oil (2-3 µl in volume) [44] was injected, by using Hamilton microliter syringes (50 µl in volume), into a capillary tube approximately 2mm in diameter and 10 cm long, which had been filled with alkaline solution. Then a cap was pushed completely into the end of the capillary tube. The entire assembly was screwed into the rotating sleeve of the spinning drop tensiometer for the measurement. Usually this took about 90 seconds from the initial oil-aqueous contact. The time was recorded for the dynamic IFT measurements from the instant the spinning commenced. The diameter of the rotating drop was measured at regular intervals up to a time of 4000 seconds. The temperature was controlled at $29 \pm 0.2°C$, by means of air circulation during the measurements. The rotating speed was set at 9.0 ± 0.2 msec/rev, which is about 6700 RPM. After each measurement the capillary tube was cleaned by using toluene, followed by acetone, and then distilled water. Then the capillary tube was placed in an oven to dry at 100°C.

The equation for calculating IFT is given [17] as follows:

$$\gamma = 0.522 \cdot \Delta\rho \cdot d^3/T^2 \qquad (38)$$

where γ is IFT (mN/m), $\Delta\rho$ is density difference between the two phases (g/cm^3), d is diameter of the droplet (cm), and T is rotating speed (msec/rev).

3.4 Density Measurements

The densities of the organic and aqueous phases were measured on a Density Meter Model (MA-602) at 25.0±0.1 °C. The procedure described in the manual was followed using dry air and distilled water as the calibration standards.

The densities of the pure organic components are listed in Table 8 and are compared with the literature values. Good agreement is observed in all cases.

The densities of pure organic binary mixtures for the systems of hexadecane+benzene, +toluene, +o-xylene, +octane and +decane were determined experimentally. The results are shown in Table 9 and were used to calculate excess molar volume from the equation:

$$V^E = X_1 M_1 (\rho_m^{-1} - \rho_1^{-1}) + X_2 M_2 (\rho_m^{-1} - \rho_2^{-1}) \qquad (39)$$

The obtained values are listed in Table 10 and have been fitted by the Redlich-Kister equation (discussed in next chapter) as shown in Figure 3. The values of the fitting constants and the standard deviations are displayed in Table 11. In Figure 3, the longer dotted line is the excess molar volume of Hexadecane+Benzne from the literature [20] and the results are compared with this study. There is a small difference between the two experimental results. Figure 4 shows the deviation between the two systems, where the broken line is obtained from :

$$\Delta V^E = V^E_{cal} - V^E_{theory} \qquad (40)$$

$$\Delta V^E = V^E_{cal} - V^E_{ref} \qquad (41)$$

while the solid line represents ± 10% deviation from this system. It can be seen that the dotted line lies within the ± 10% deviation envelope except at very low or very high hexadecane concentrations.

The Flory theory [16] has been adopted here to analyze the experimental results, and is shown in Figure 3 (dashed line). It can be seen that the Flory theory provides estimates of the excess molar volume of binary mixtures which are of the right order of magnitude and which exhibit very nearly the same relative order as the experimental results. In the case of hexadecane+decane and +octane, there is a tendency for the theoretical values to be higher than the experimental, while hexadecane+benzene and +toluene binary mixtures are vice versa. The system of hexadecane+O-Xylene has not been predicted, due to the unavailability of heat-of-mixing data in the literature. Since the prediction of excess molar volume from the Flory theory depends on using available heat-of-mixing data [14], any errors present in this data would affect the estimation of excess molar volume. In fact for the systems hexadecane+benzene and +decane, the differences between theoretical and experimental values of excess enthalpy are 473 and -200 (J/mol) respectively.

Tables 6 and 7 display component properties and parameters used in the Flory theory. The interchange-energy parameter was adjusted to give a fit between the experimental and theoretical excess volume curves. For the present mixtures used the isobaric thermal expansivities α, and isothermal compressibilities β are shown in Table 6, from references [6,27]. The characteristic pressure p^*, molar volume V^* and temperature T^*, obtained from the Flory theory, are also listed in Table 6. Table 7

gives the ratio S_{12} of molecular surface areas of contact and the interchange energy parameter X_{12} for each mixture. The values of S_{12} are based on the assumption that the molecules are spherical; the values X_{12} were obtained by fitting the Flory theory for the excess molar enthalpies [14].

Table 6: Component Properties Used in Calculation by Flory Theory

Component	V (cm^3/mol)	α (K^{-1})	β (atm^{-1})	v^* (cm^3/mol)	T^* K	p^* (J/cm^3)
Hexadecane	294.088	0.883	73.53	240.422	5614.7	542.8
Toluene	106.740	0.829	95.00	88.107	5831.0	396.7
Benzene	89.440	0.913	98.12	72.736	5505.6	425.2
Octane	162.71	1.164	105.62	127.078	4827.0	548.8
Decane	195.570	1.015	91.64	156.359	5188.5	523.5

Table 7: Parameters and Excess Molar Volume Used in Calculation by Flory Theory

System	S_{12} (Mole fraction=0.5) Theory	Expt.	X_{12}
Hexadcane +	(cm /mol)		(J/CC)
Benzene	0.6713	0.7224	1.111	0.7766
Toluene	0.7151	0.5569	0.598	17.0351
O-Xylene	-	-	0.504	-
Octane	0.8085	0.1107	0.037	2.4145
Decane	0.8664	0.0691	0.079	0.9517

Since the excess molar volumes of these systems are quite small [45], the densities of other binary organic mixtures could be calculated quite accurately based on the assumption of ideal solutions [32].

The densities of diluted crude oils and either Bentonite in distilled water or in Chatham crude oil, were measured using the density meter, but pure Cold Lake, Lloydminster as well as of their 10% dilutions were determined using the 25-ml density flask. The results of these experiments are listed through Tables 12 to 16.

Table 8: Densities of Organic Component Liquids at 25°C

Component	Period	Density (g/cm^3)	Lit.	Ref.
Benzene	754309	0.8734	0.8736	(53)
Toluene	752017	0.8619	0.8623	(53)
O-Xylene	754666	0.8752	0.8760	(53)
Octane	719808	0.7006	0.7026	(53)
Decane	724997	0.7250	0.7261	(53)
Hexadecane	733864	0.7710	0.7776	(53)
Air	558736	-	-	
Water	778090	-	0.99707	

Table 9: Densities of Binary Organic Component Liquid at 25°C

Component	Mole Fraction X_1	Period	Density (g/cm^3)
Hexadcane + Benzene	0.77247	735182	0.77660
	0.42088	739819	0.75953
	0.28630	742834	0.81496
	0.11604	747083	0.83649
	0.02736	752180	0.86252
+ Toluene	0.80911	753084	0.77719
	0.45050	739206	0.79673
	0.27740	742268	0.81211
	0.13694	745941	0.83069
	0.00801	748092	0.84414
+ O-Xylene	0.77873	735926	0.78025
	0.49621	739687	0.79910
	0.29621	743783	0.81971
	0.15154	748095	0.84163
	0.04536	752332	0.86372
+ Octane	0.83760	732512	0.76331
	0.57070	729780	0.74972
	0.35950	726895	0.73540
	0.18696	723962	0.72100
	0.04670	720971	0.70631
+ Decane	0.87630	733042	0.76592
	0.61711	731321	0.75731
	0.36053	729560	0.74857
	0.22500	727748	0.73960
	0.04215	724245	0.72890

Table 10: Excess Molar Volume of Binary Mixtures at 25°C

Component	Mole Fraction X_1	Excess Molar Volume V^E
Hexadcane + Benzene	0.77247	0.608
	0.42088	1.148
	0.28630	1.015
	0.11604	0.7659
	0.02736	0.2369
+ Toluene	0.78930	0.3038
	0.43600	0.6350
	0.27840	0.5304
	0.13704	0.5010
	0.00801	0.393
+ O-Xylene	0.77873	0.2730
	0.49621	0.5300
	0.29621	0.5400
	0.15154	0.3362
	0.04536	0.1800
+ Octane	0.83760	-0.0117
	0.57070	-0.0371
	0.35950	-0.0340
	0.18696	-0.0265
	0.04670	-0.0126
+ Decane	0.87630	-0.03200
	0.61711	-0.06330
	0.36053	-0.08790
	0.22500	-0.05160
	0.04215	-0.02200

Table 11: Values of coefficients determined from Redlich-Kister equation

Excess Molar Volume of Binary Mixtures

Systems	C_1	C_2	σ_r
Hexadecane +			
Benzene	4.444	2.224	0.1030
Toluene	2.590	1.889	0.0800
O-Xylene	2.124	0.936	0.0160
Octane	-0.147	0.0056	0.0056
Decane	-0.316	0.0095	0.0095

Table 12: Densities of Diluted Chatham crude oil at 25°C

Component	Period T	Density (g/cm^3)	Dilution (wt.%)
Toluene	744834	0.8252	0%
	745364	0.8278	10%
	746623	0.8342	30%
	747648	0.8410	50%
	749047	0.8464	60%
	750755	0.8552	85%
	751631	0.8597	95%
	752071	0.8619	100%
Hexadecane + Toluene	744834	0.8252	0%
	744029	0.8210	10%
	743768	0.8197	20%
	743468	0.8182	30%
	743066	0.8161	50%
	742401	0.8128	70%
	742156	0.8154	90%
	741995	0.8107	95%
	741688	0.8084	100%
Hexadecane	746006	0.8311	0%
	743030	0.8159	10%
	740986	0.8056	30%
	739462	0.7980	40%
	739139	0.7963	50%
	736391	0.7826	70%
	734819	0.7747	90%
	733864	0.7700	100%

Toluene+Hexadecane = 50% wt. Toluene/Hexadecane

Table 13: Densities of Diluted Lloydminster Crude Oil at 25°C

Component	Period T	Density (g/cm^3)	Dilution (wt.%)
Toluene	*	0.9680	0%
	*	0.9443	10%
	765866	0.9330	30%
	762423	0.9151	50%
	758438	0.8946	70%
	754198	0.8728	90%
	752071	0.8619	100%
Hexadecane	*	0.9680	0%
+	*	0.9215	10%
Toluene	761423	0.9099	30%
	755488	0.8794	50%
	749803	0.8503	70%
	745725	0.8300	85%
	744357	0.8226	90%
	742974	0.8157	95%
	741688	0.8084	100%
Hexadecane	*	0.9680	0%
	*	0.9312	10%
	768696	0.9144	30%
	756642	0.8853	50%
	742400	0.8128	70%
	735472	0.7780	85%
	735433	0.7778	90%
	735133	0.7763	95%
	733864	0.7700	100%

* denotes desities measured in 25-ml density flask

Table 14: Densities of Diluted Cold Lake Crude Oil at 25°C

Component	Period T	Density (g/cm^3)	Dilution (wt.%)
Toluene	*	0.9864	0%
	*	0.9652	10%
	771341	0.9616	20%
	763489	0.9207	50%
	757643	0.8905	75%
	754609	0.8749	80%
	753167	0.8675	95%
	752071	0.8619	100%
Hexadecane + Toluene	*	0.9864	0%
	*	0.9460	10%
	765557	0.9314	30%
	757967	0.8975	50%
	754807	0.8759	70%
	746506	0.8335	85%
	744918	0.8255	90%
	743426	0.8180	95%
	741688	0.8064	100%
Hexadecane	*	0.9864	0%
	*	0.9132	10%
	768696	0.9144	30%
	755722	0.8805	50%
	745492	0.8284	70%
	744574	0.8237	75%
	737171	0.7865	90%
	733864	0.7700	100%

* denotes desities measured in 25-ml density flask

Table 15: Densities of Bentonite in Distilled Water at 25°C

Component	Period T	Density (g/cm^3)	Dilution (wt.%)
Bentonite	778090	0.99707	0%
	778105	0.9972	0.01%
	778153	0.9974	0.05%
	778190	0.9976	0.1%
	778679	1.0003	0.5%
	778920	1.0015	1.0%
	781645	1.0159	5.0%

Table 16: Densities of Bentonite in Chatham Crude Oil at 25°C

Component	Period T	Density (g/cm^3)	Dilution (wt.%)
Bentonite	746323	0.8304	0.0%
	746420	0.8317	0.01%
	746516	0.8325	0.05%
	746621	0.8343	0.1%
	746734	0.8368	0.25%
	746890	0.8412	0.5%

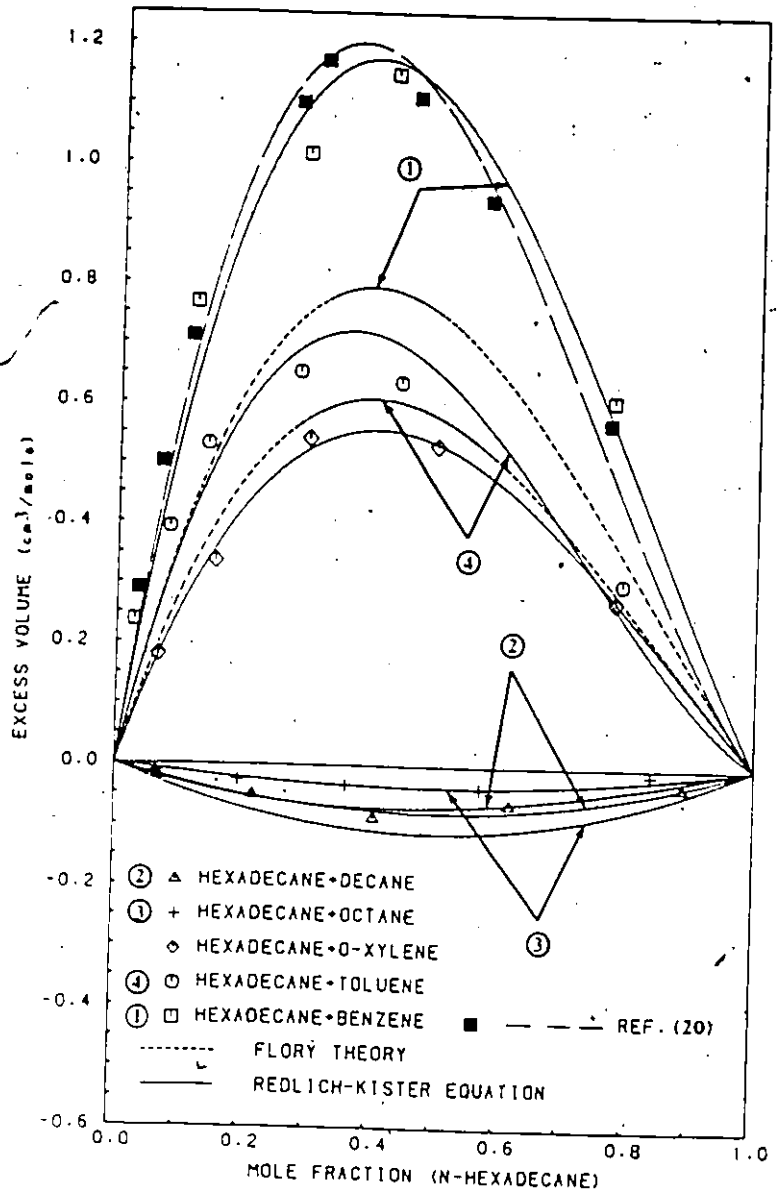

Figure 3: Excess Molar Volume of Binary Mixtures at 25°C

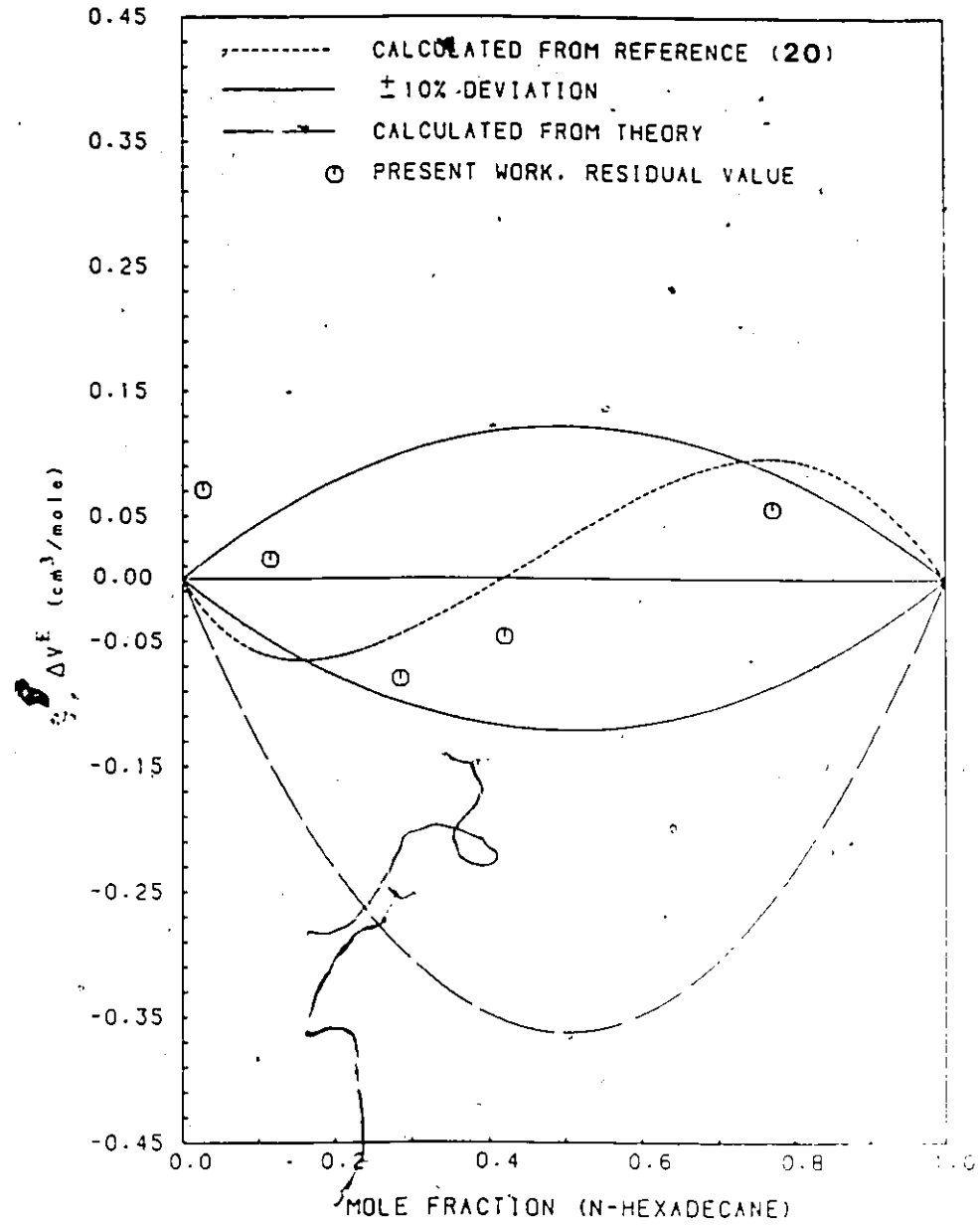

Figure 4: Plot of Deviation for Hexadecane+Benzene at 25°C

Chapter IV

RESULTS AND DISCUSSION

4.1 Interfacial Tension of Binary Mixtures

4.1.1 Reproducibility of Interfacial Tension Measurements

Figures 5 and 6 show the reproducibility of measurement for interfacial tensions of binary mixtures of Benzene+O-Xylene. The maximum deviation is about 5% and averages about 3% throughout the measurements.

The solubilities of these organic components in water are insignificant except for Benzene [56], which has minimal solubility in water. Figure 6 shows the result for benzene-O-Xylene binary mixtures. All the solutions were carefully equilibrated for about two hours before the measurements. It can be seen that there is an appreciable difference between systems with and without equilibrium. The maximum variability for this case is about 8%, compared to that without equilibration. This is probably due to the finite solubility of Benzene in water (0.07g Benzene/100g water) [28].

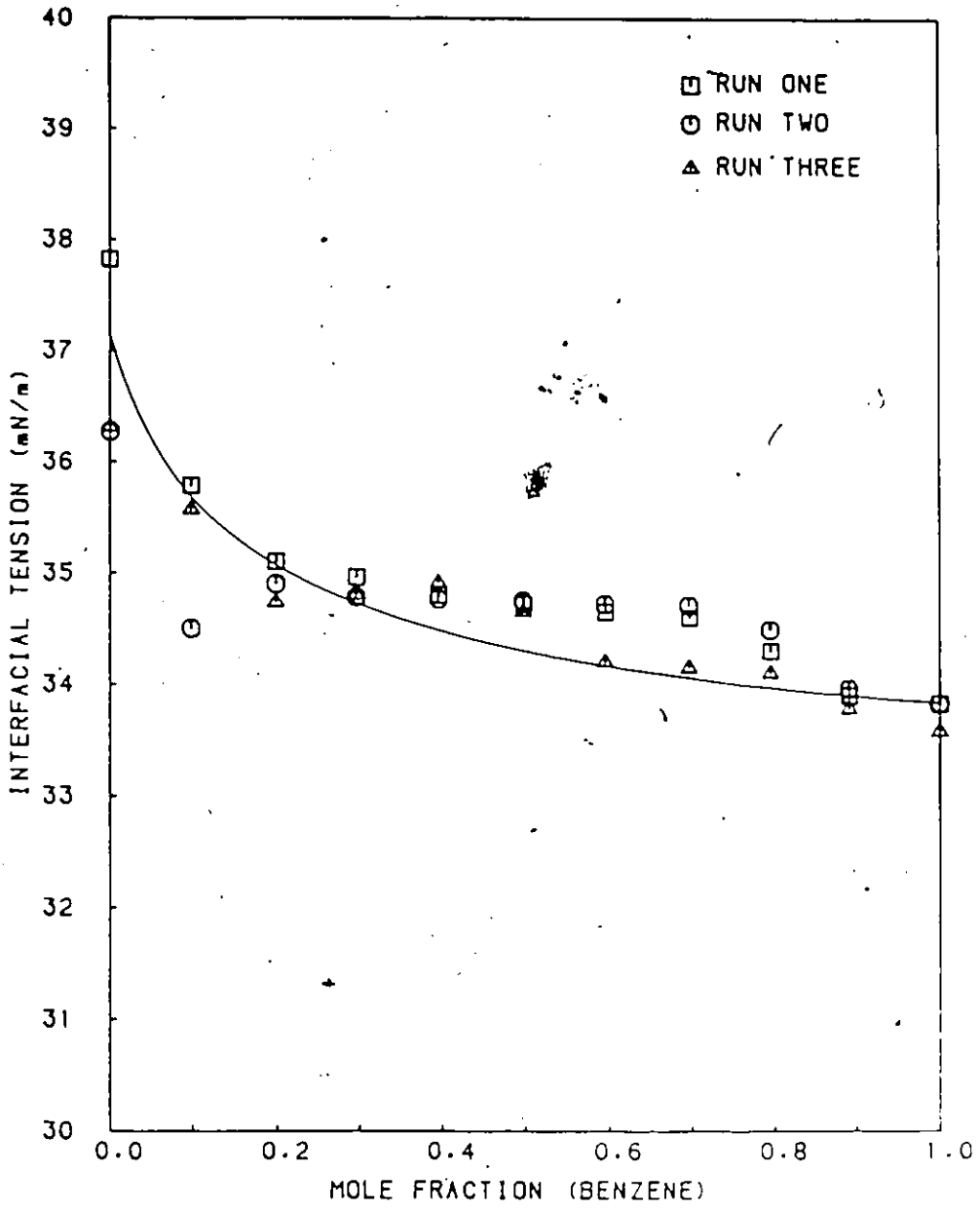

Figure 5: Reproducibility of IFT Measurements for Benzene-p-xylene at 25°C

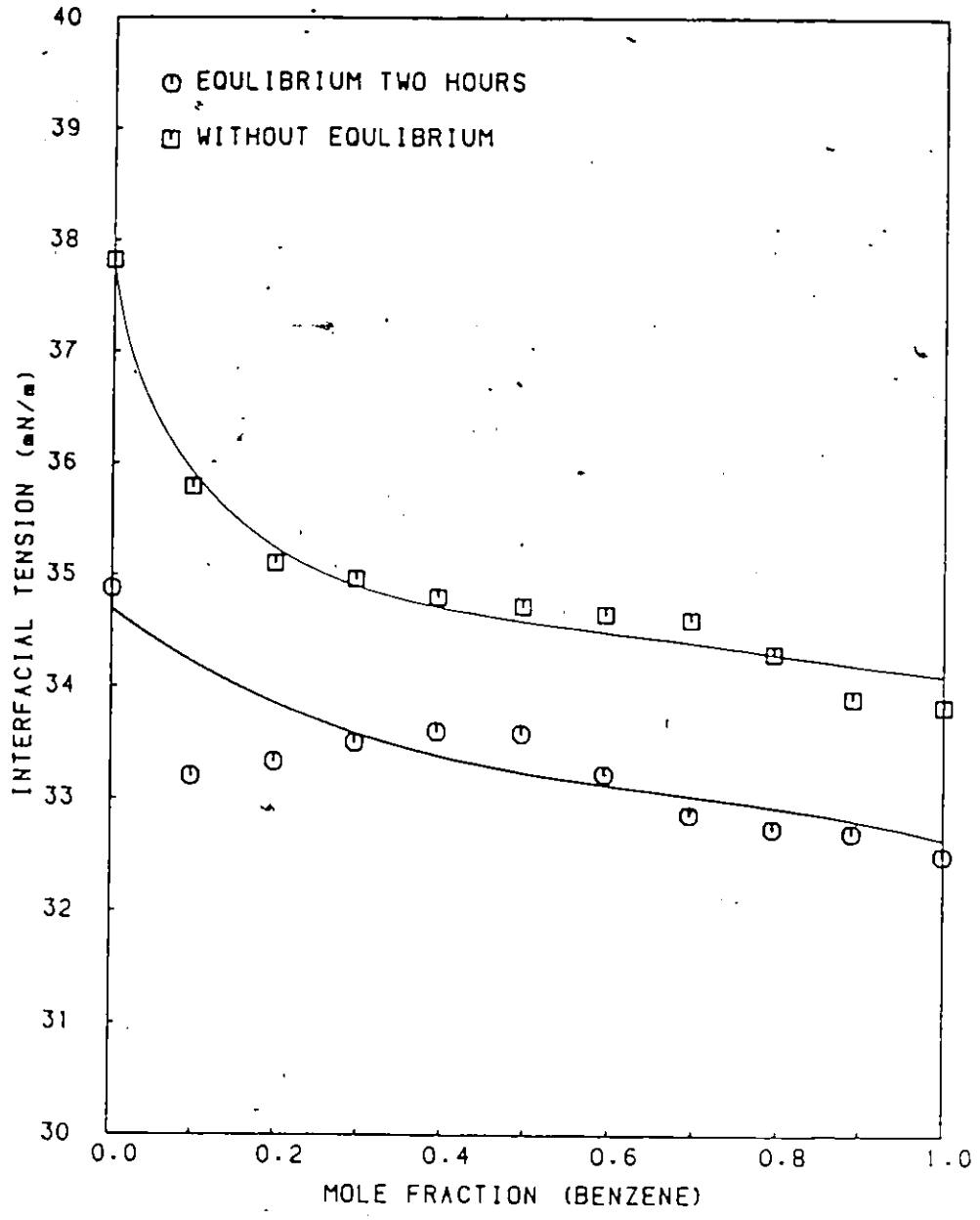

Figure 6: Equilibrium IFT Results for Benzene+O-xylene at 25°C

4.2 Interfacial Tensions of Binary Mixtures and Their Excess Properties

The interfacial and surface tensions of pure components have already been reported in Tables 17 and 18, along with observed values from this study for comparison. In general, the experimental results in this study agree fairly well with the literature values.

The experimental results (X_1, γ^E) for the fifteen binary systems are listed in Table 19 which also contains the values of excess interfacial tension. The excess interfacial tension is defined as :

$$\gamma^E = \gamma_{12} - (X_1 \gamma_1 + X_2 \gamma_2) \qquad (42)$$

where γ_1 and γ_2 are the interfacial tensions of the pure components, and X_i is the mole fraction of component i in the mixture.

In all cases the experimental results for the pure components were used in computing the ideal values for the mixtures. However, any systematic errors in determination of interfacial tension will tend to cancel in the evaluation of excess interfacial tension.

Table 17: Surface Tensions for Component Liquids at 25°C

Component	Observed	Literature	Reference
Benzene	28.27	28.20	(53)
Toluene	27.24	27.92	(53)
O-xylene	29.40	29.48	(53)
N-Octane	21.13	21.45	(53)
N-Decane	23.00	23.37	(53)
N-Hexadecane	26.87	27.32	(53)

Table 18: Interfacial Tensions for Component Liquids at 25°C

Component	Observed	Literature	Reference
Benzene	33.40	34.71	(34)
Toluene	35.15	35.00	(2)
O-xylene	36.60	-	-
N-Octane	48.00	-	-
N-Decane	47.40	-	-
N-Hexadecane	42.00	-	-

Table 19: Interfacial Tension of Binary mixtures at 25°C

Benzene+O-Xylene

X_1	γ_{12}	γ^E
0.0	37.82	0.0
0.0980	35.76	-1.644
0.1981	35.10	-1.926
0.2962	34.96	-1.680
0.3951	34.80	-1.544
0.4970	34.72	-1.117
0.5950	34.65	-0.896
0.6964	34.60	-0.441
0.7950	34.30	-0.267
0.8910	33.90	-0.167
1.0	33.83	0.0

Toluene+Benzene

X_1	γ_{12}	γ^E
0.0	32.85	0.0
0.0987	33.02	-0.062
0.2831	33.35	-0.183
0.4964	33.69	-0.302
0.6970	34.05	-0.403
0.8987	34.60	-0.320
1.0	35.15	0.0

Toluene+O-Xylene

X_1	γ_{12}	γ^E
0.0	34.24	0.0
0.0982	34.30	-0.080
0.2958	34.27	-0.240
0.4995	34.31	-0.377
0.6958	34.35	-0.523
0.8982	34.75	-0.304
1.0	33.83	0.0

Octane+Benzene

X_1	γ_{12}	γ^E
0.0	32.85	0.0
0.0747	33.28	-0.698
0.2554	33.35	-2.707
0.4446	35.50	-4.069
0.6513	39.00	-3.691
0.8867	44.45	-1.982
1.0	47.96	0.0

Octane+Toluene

X_1	γ_{12}	γ^E
0.0	35.15	0.0
0.0766	35.30	-1.644
0.2581	37.10	-1.356
0.4481	39.25	-1.643
0.6545	41.85	-1.684
0.8881	45.32	-1.207
1.0	47.96	0.0

Octane+O-Xylene

X_1	γ_{12}	γ^E
0.0	34.16	0.0
0.0892	34.20	-1.191
0.2543	35.50	-2.169
0.4431	36.87	-3.405
0.6499	39.00	-4.129
0.8775	43.07	-3.199
1.0	47.96	0.0

Octane+Decane

X_1	γ_{12}	γ^E
0.0	47.37	0.0
0.0970	47.25	-0.186
0.2929	47.23	-0.313
0.4915	47.27	-0.390
0.6929	47.37	-0.403
0.8969	37.53	-0.370
1.0	47.96	0.0

Octane+Hexadecane

X_1	γ_{12}	γ^E
0.0	41.85	0.0
0.0856	42.25	-0.125
0.2819	43.20	-0.378
0.4779	44.33	-0.445
0.6811	45.70	-0.313
0.8995	47.23	-0.113
1.0	47.96	0.0

Table 19: (Concluded)

Decane+Benzene

X_1	γ_{12}	γ^E
0.0	32.85	0.0
0.0843	33.20	-0.873
0.2619	34.60	-2.053
0.4530	36.43	-3.000
0.6590	39.45	-2.979
0.8817	44.30	-1.323
1.0	47.37	0.0

Decane+Toluene

X_1	γ_{12}	γ^E
0.0	35.16	0.0
0.0843	33.20	-0.873
0.2619	34.60	-2.053
0.4530	36.43	-3.000
0.6590	39.45	-2.979
0.8871	44.33	-1.323
1.0	47.37	0.0

Decane+O-Xylene

X_1	γ_{12}	γ^E
0.0	34.24	0.0
0.0838	34.87	-0.470
0.2608	35.90	-1.764
0.4515	37.60	-2.527
0.6929	40.78	-2.093
0.8969	45.12	-0.645
1.0	47.96	0.0

Decane+Hexadecane

X_1	γ_{12}	γ^E
0.0	41.85	0.0
0.0883	42.13	-0.212
0.2887	42.88	-0.568
0.4864	43.76	-0.772
0.6885	44.82	-0.830
0.9025	46.30	-0.530
1.0	47.96	0.0

Hexadecane+Benzene

X_1	γ_{12}	γ^E
0.0	32.85	0.0
0.0821	33.47	-0.120
0.2726	34.90	-0.404
0.4665	36.50	-0.550
0.6711	38.14	-0.753
0.8953	40.44	-0.466
1.0	41.85	0.0

Hexadecane+Toluene

X_1	γ_{12}	γ^E
0.0	35.15	0.0
0.1023	35.58	-0.258
0.2745	36.29	-0.695
0.4700	37.32	-0.979
0.6742	38.60	-1.067
0.8966	40.87	-0.287
1.0	41.85	0.0

Hexadecane+O-Xylene

X_1	γ_{12}	γ^E
0.0	35.20	0.0
0.1005	35.66	-0.224
0.3188	36.47	-0.851
0.5220	37.55	-1.128
0.7181	38.90	-1.074
0.9144	40.95	-0.332
1.0	41.85	0.0

Note: all the X_1 assigned to name the first component

The method of least squares was used to fit each set of experimental results for excess interfacial tension with an equation which was derived by Redlich-Kister [43]. It takes the form :

$$\gamma^E = X_1(1-X_1)\Sigma_j C_j(1-2X_1)^j \qquad (43)$$

which contains n adjustable coefficients, C_j. By convention, the subscripts 1 and 2 were assigned to the two components in the order used to name the system and the minimum number of coefficients was selected to represent the results adequately. In this way the corresponding standard errors of estimate, σ_r, were calculated from the equation:

$$\sigma_r = \{\Sigma(\gamma^E_{obs} - \gamma^E_{cal})^2/(n_{obs}-n)\}^{1/2} \qquad (44)$$

Values of the coefficients obtained in this way are given in Table 20, along with the corresponding values of σ_r.

The experimental results for excess interfacial tension and of their least squares representations by Equation (44) are plotted and shown in Figures 7 to 10.

There are almost no other determinations of the interfacial tension of the present systems in the literature.

Table 20: Values of coefficients determined from Redlich-Kister equation

Excess Interfacial Tensions of binary mixtures

Systems	C_1	C_2	C_3	C_4	σ_r
(4)+(1)	-16.380	2.936	3.328		0.223
(4)+(2)	- 6.457	1.799	-7.191	-1.556	0.122
(4)+(3)	-14.800	12.170	-7.140		0.311
(4)+(5)	- 1.453	0.304	-2.310	1.423	0.046
(4)+(6)	- 1.171	0.458	0.430		0.022
(5)+(1)	-12.340	2.179	1.094		0.126
(5)+(2)	- 8.468	- 5.489	3.467		0.054
(5)+(3)	-11.020	- 0.691	6.331		0.020
(5)+(6)	- 3.091	1.724	-1.866		0.036
(6)+(1)	- 2.457	1.929	-1.629	0.187	0.052
(6)+(2)	- 4.280	- 2.166	1.694	-3.262	0.090
(6)+(3)	- 4.622	1.982	1.492	-1.177	0.077
(2)+(1)	- 1.202	1.477	-1.414		0.028
(2)+(3)	- 1.604	1.581	-0.990		0.030
(1)+(3)	- 4.373	- 6.383	-7.379	-6.391	0.110

Assigned Systems:
(1)- Benzene, (2)- Toluene, (3)- O-Xylene,
(4)- Octane, (5)- Decane, (6)- Hexadecane.

Table 21: Comparison Values of Coefficients

Excess Surface Tension of Binary Mixtures

Systems	C_1	σ_r	Note
O-Xylene+Benzene	-0.8280	0.042	(Present Work)
O-Xylene+Benzene	-0.4380	0.027	(Calculated from Ref. (26))
O-Xylene+Benzene	-0.4400	0.026	(G.C.Benson Ref. (26))

It appears that only the surface tension of benzene + O-xylene mixtures has been measured previously [26]. Values of excess surface tension of this system obtained at 25°C are included in Figure 11 and Table 22 for comparison with this study. The excess surface tensions at 25°C measured in the present work, and Benson's values [26], possess appreciable differences. This may indicate different excess surface free energies or entropies for both systems. The dotted line in Figure 11 is calculated from the corresponding states theory and results are taken from reference [26]. Figure 12 shows the deviation for both systems. The dotted and solid curves are obtained as following:

$$\Delta\gamma^E = \gamma^E_{exptl} - \gamma^E_{theory} \tag{45}$$

$$\Delta\gamma^E = \gamma^E_{cal} - \gamma^E_{cal(ref)} \tag{46}$$

where the theory agrees with this study within $\pm 10\%$. However, Benson's results exhibit an approximate deviation of 10%.

The excess interfacial tension of Benzene+O-Xylene in Figure 11 is almost ten times larger than the excess surface tension. The computed parameters and standard errors for this system are compared with the published data [26] in Table 21. An almost consistent agreement is reached between the calculations.

Table 22: Comparison Results for Surface Tension of Binary Mixtures at 25 °C

Benzene+O-Xylene (Present Work)			Benzene+O-Xylene (G.C. Benson. (26))		
X_1	γ_{12}	γ^E	X_1	γ_{12}	γ^E
0.0000	29.35	0.0	0.0000	29.44	0.0
0.0980	29.32	-0.158	0.0955	29.32	-0.01
0.1981	29.00	-0.192	0.1973	29.11	-0.09
0.2962	28.85	-0.178	0.3083	28.94	-0.12
0.3951	28.73	-0.177	0.4053	28.84	-0.10
0.4970	28.64	-0.168	0.4975	28.72	-0.10
0.5950	28.53	-0.143	0.6121	28.58	-0.10
0.6964	28.42	-0.180	0.6847	28.53	-0.06
0.7950	28.30	-0.135	0.7905	28.35	-0.11
0.8910	28.23	-0.076	-	-	-
1.0000	28.27	0.0	1.0000	28.20	0.0

Plots of the experimental results for excess interfacial tension and of their Redlich-Kister representations for the systems of hexadecane+aromatic compounds, decane+hydrocarbons or aromatic compounds, octane+hydrocarbons or aromatic compounds and toluene+aromatic compounds are shown in Figures 7 to 10.

It is observed that for all the binary systems, Aromatic compound+Aromatic compound and Aromatic compound+hydrocarbon give higher excess interfacial tension than that of hydrocarbon+hydrocarbon. Negative deviations from interfacial ideality occurred in all binary systems. The simple application of qualitative argument based on weak or strong molecular energies of interaction leads to the view of negative deviations from interfacial ideality [7].

Benson et al. [5] observed positive excess surface tension only for those systems involving polar molecules, such as mixtures of alcohols.

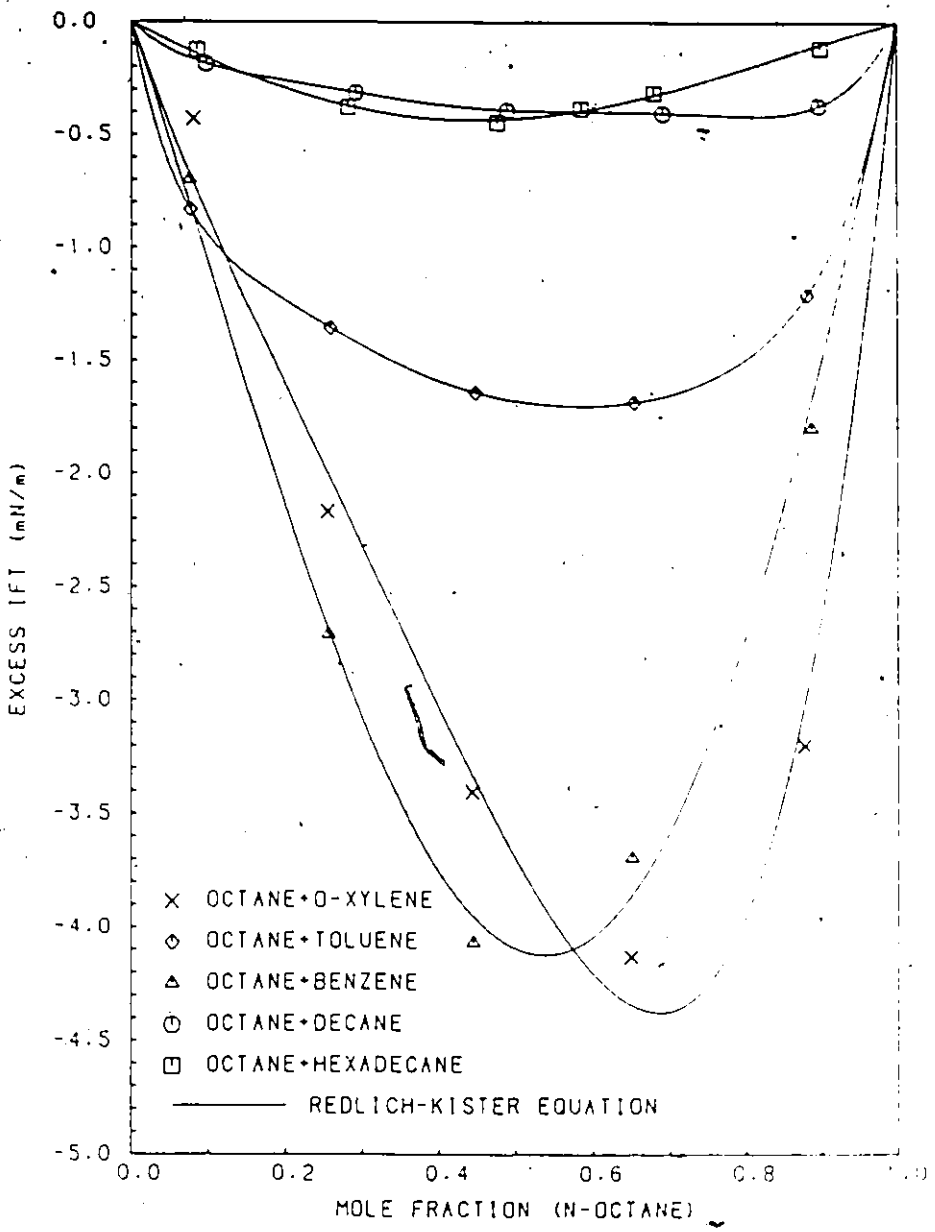

Figure 7: Excess Interfacial Tension of Binary Mixtures at 25°C

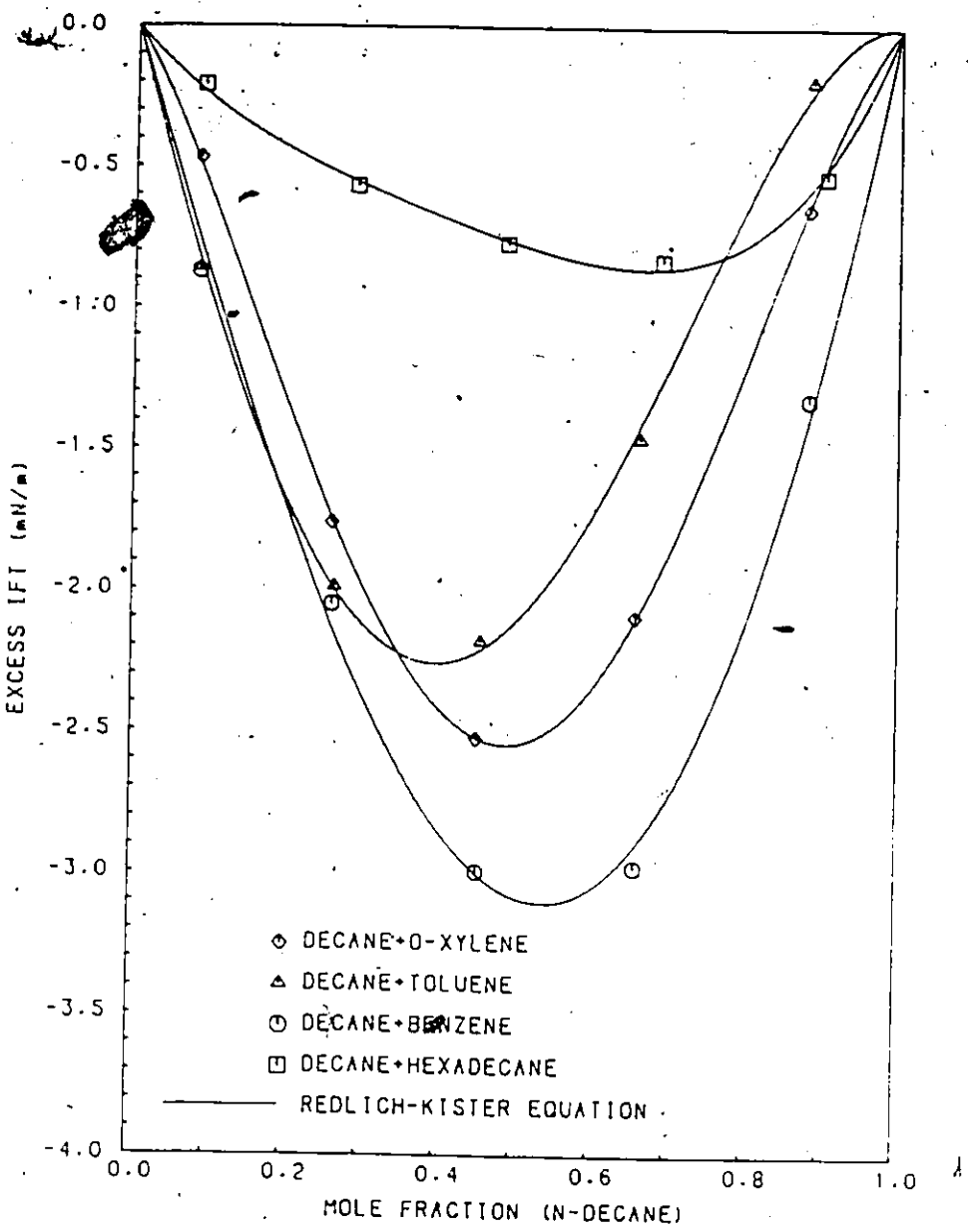

Figure 8: Excess Interfacial Tension of Binary Mixtures at 25°C

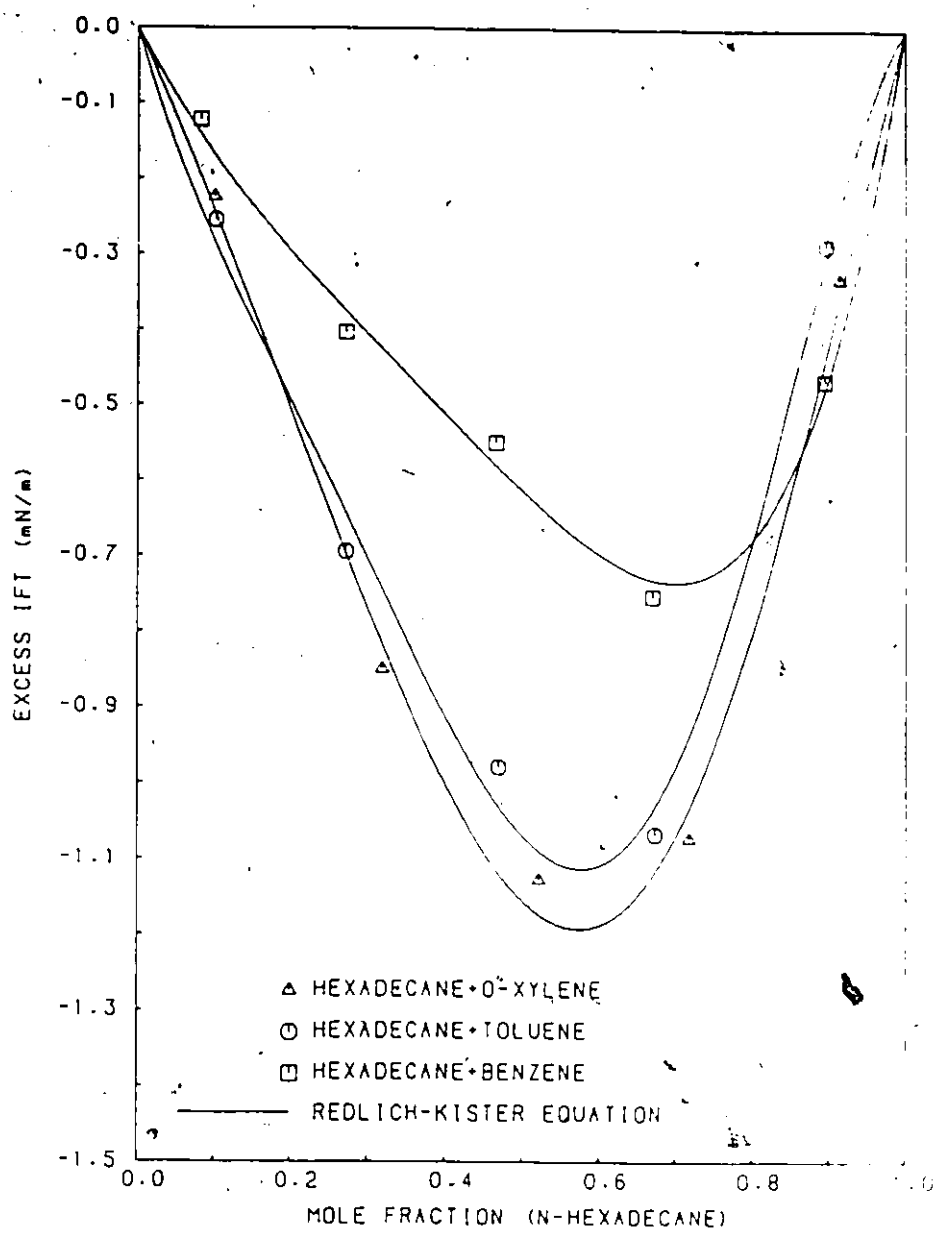

Figure 9: Excess Interfacial Tension of Binary Mixtures at 25°C

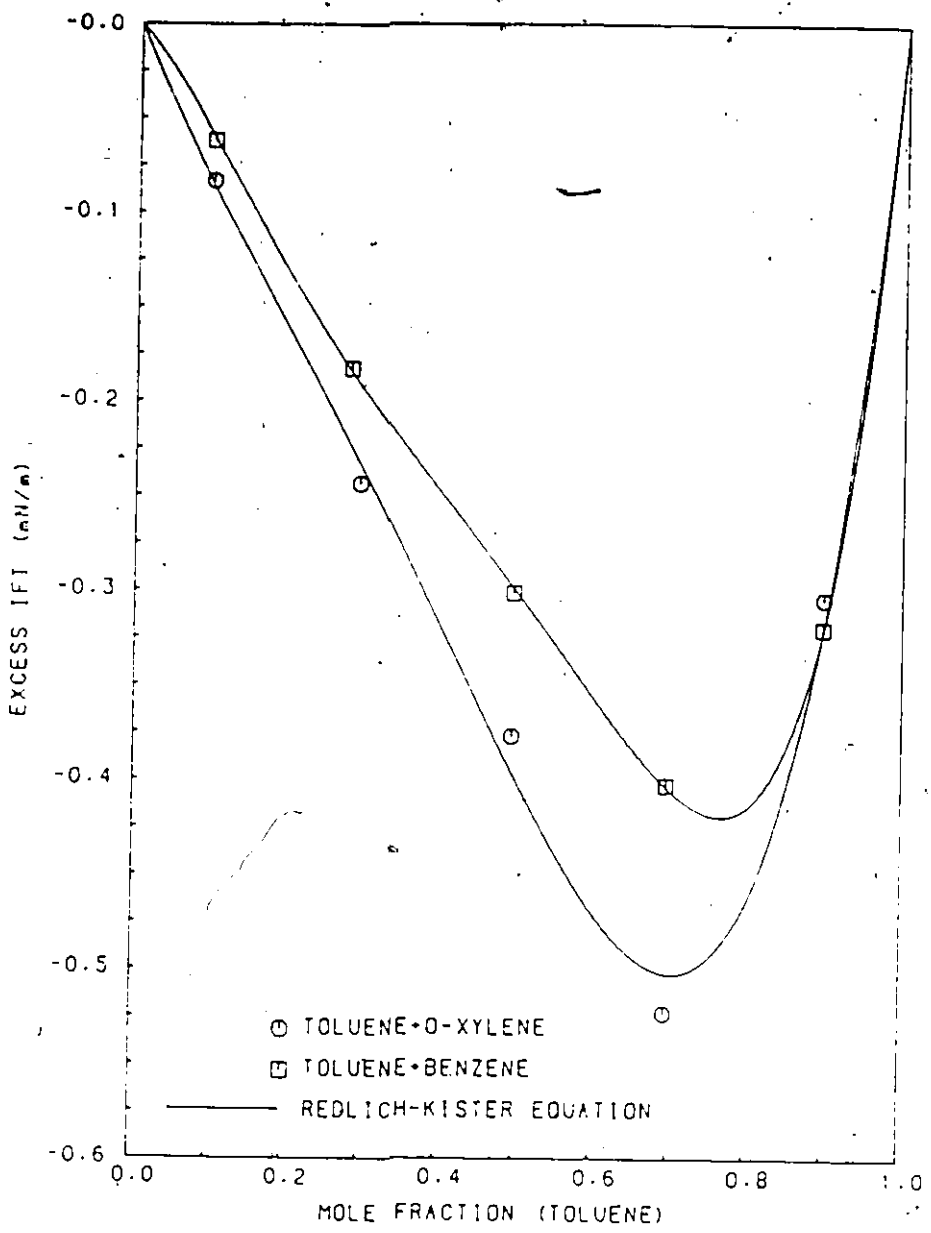

Figure 10: Excess Interfacial Tension of Binary Mixtures at 25°C

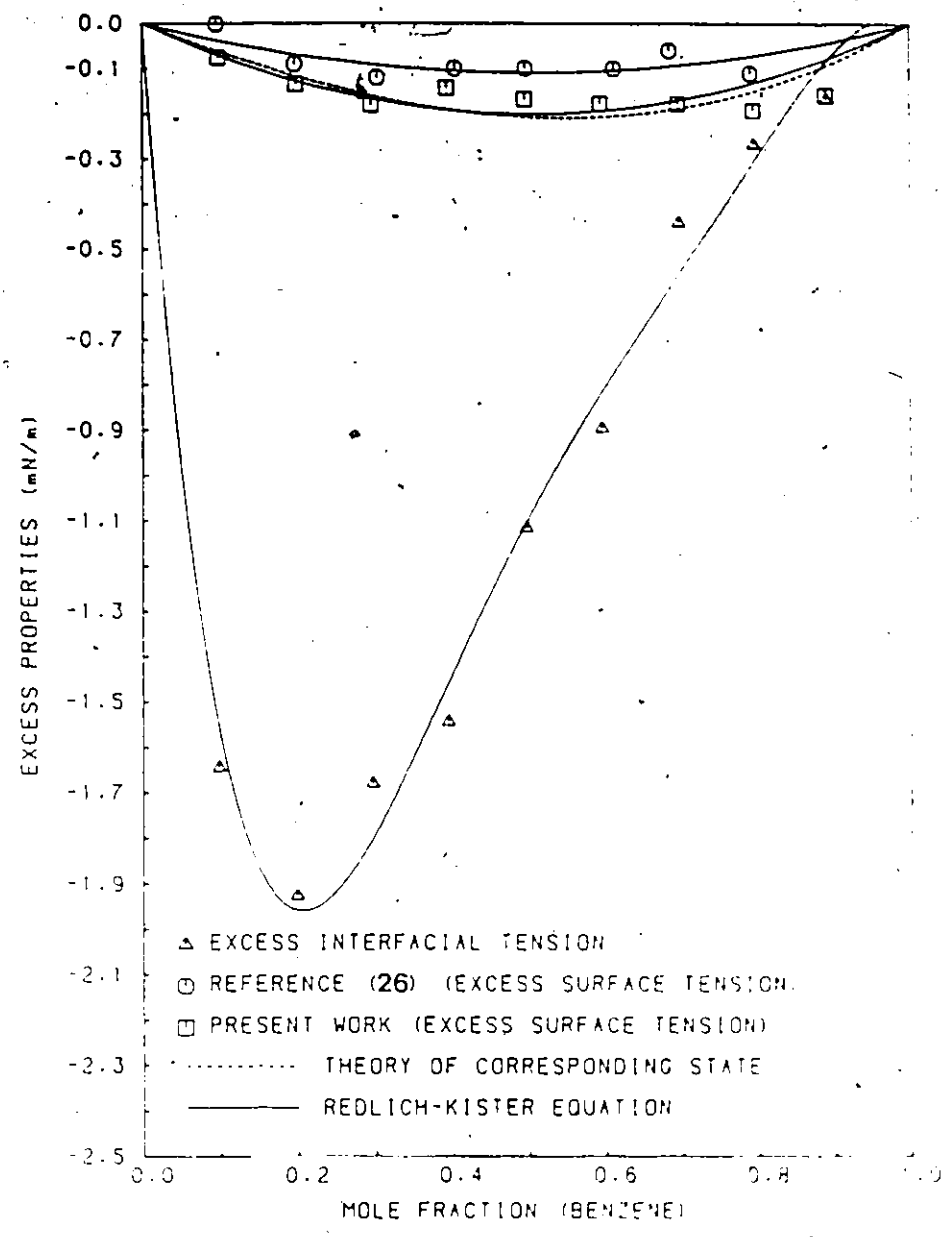

Figure 11: Excess Interfacial and surface tensions at 25°C

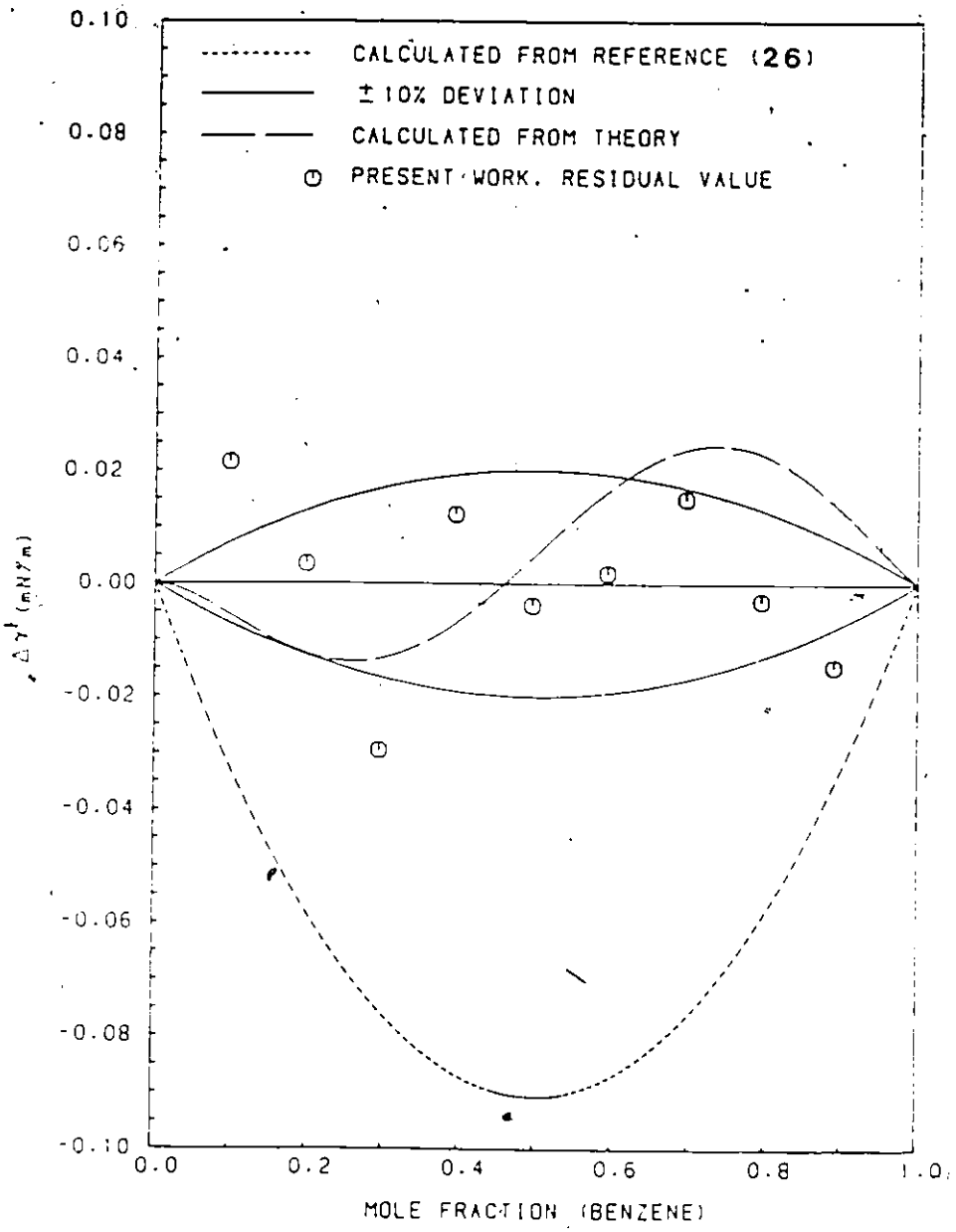

Figure 12: Plot of Deviation for Benzene+O-Xylene at 25°C

Chapter V

RESULTS AND DISCUSSION

5.1 Interfacial Tension of Crude Oil Systems

5.1.1 Reproducibility of Interfacial Tension Measurements

Figures 13 to 15 show the reproducibility of measurement of IFT vs. time for Cold Lake, Lloydminster and Chatham crude oils against alkaline solutions. The maximum variability is 15% for Cold Lake, 20% for Lloydminster and 20% for Chatham crude oils at any specific time. This is consistent with the findings of other researchers [44,33].

The IFT vs. time data are compared with those of other researchers [35,44] in Figure 16. It can be seen that the variability between the present work and previously published work [35,44] is less than 20%, which is within the experimental error of this study. However, at the beginning of the measurements, it shows the largest difference. There is one major reason for this. The time is measured from the start of spinning of the tensiometer, usually about 80 seconds after injecting the oil droplet into the capillary tube filled with caustic solution. Since a sharp reduction in IFT occurs at short times, a small difference in the time of introduction of the capillary tube into the spinning drop tensiometer could make an appreciable difference during the early stages of IFT measurement, but this effect becomes negligible with increasing time of contact.

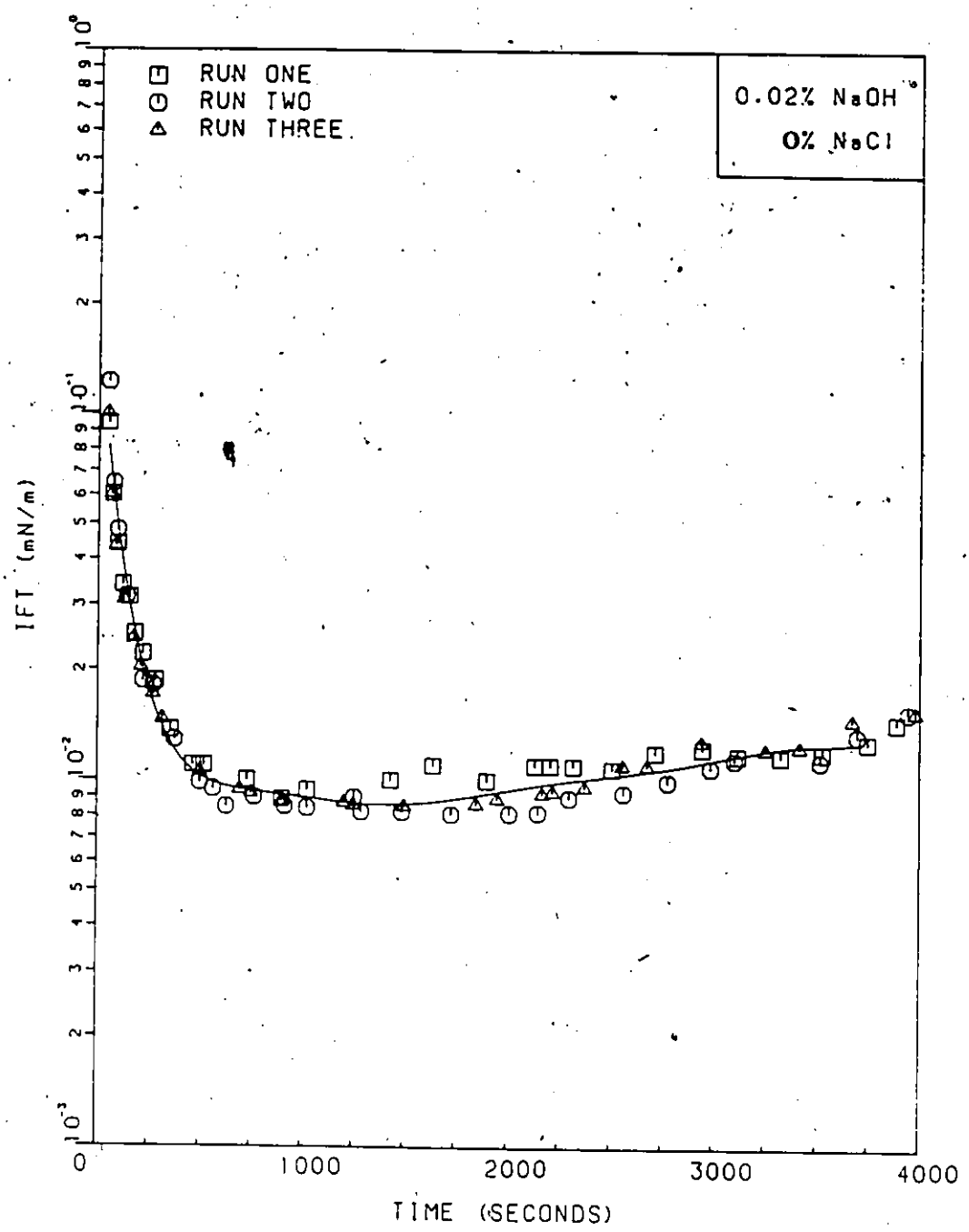

Figure 13: Reproducibility for Lloydminster crude oil 6700 RPM and 29°C

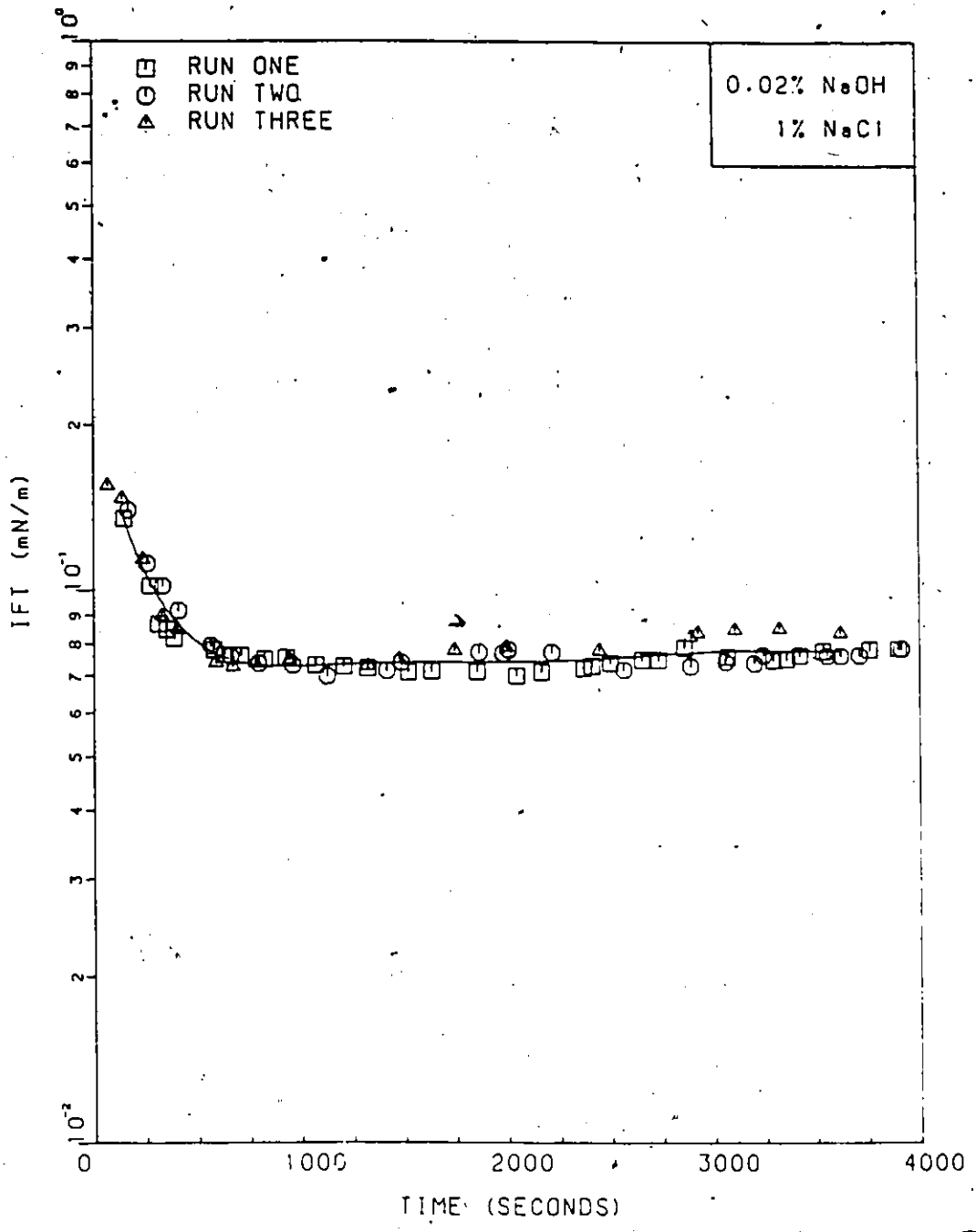

Figure 14: Reproducibility for Cold Lake crude oil at 6700 RPM and temperature 29°C

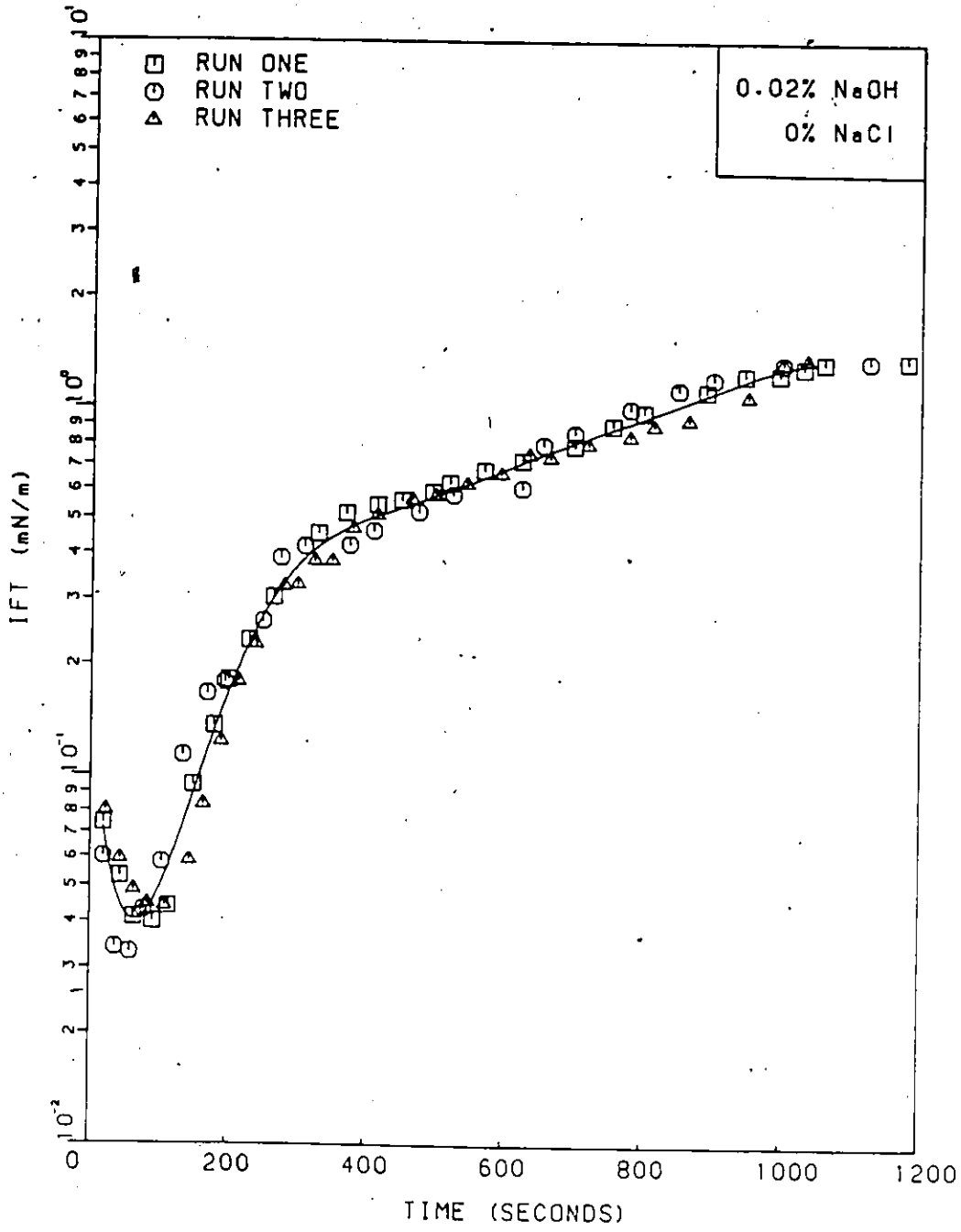

Figure 15: Reproducibility for Chatham crude oil at 6700 RPM and 29°C

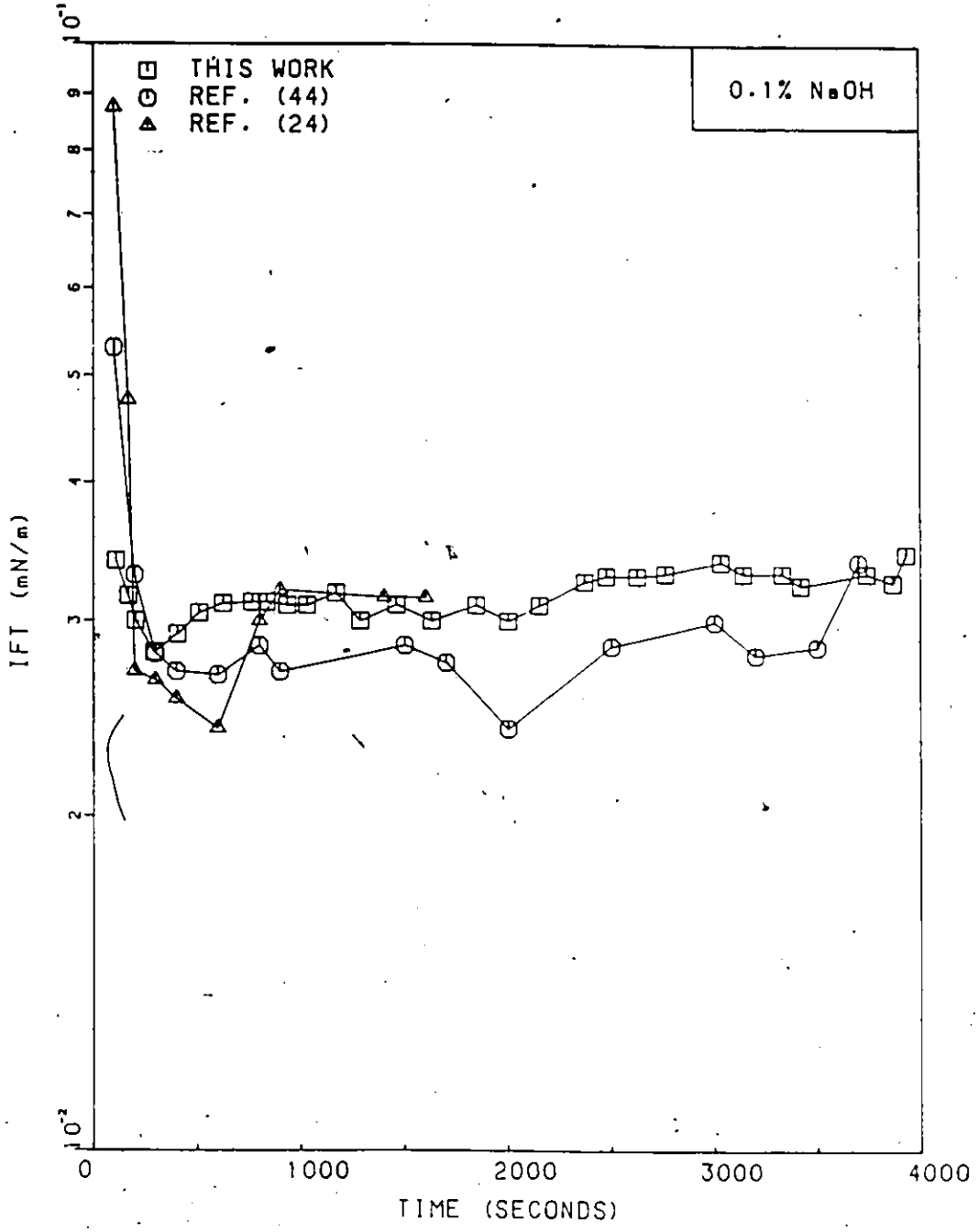

Figure 16: Comparison result for Lloydminster crude oil at 7000 RPM and 25°C

5.2 Effect of Alkalinity and Salinity

The effects of NaOH, NaCl and their mixtures on the interfacial tension behaviour of three crude oils were determined experimentally. The results are shown in Figures 17 to 20. From Figure 17 it is seen that adding NaCl has almost no effect on the interfacial tension of Cold Lake and Lloydminster crude oils. This is because the pH value of these aqueous solutions (pH 4.9) remains about the same as that of distilled water. This suggests that little or no chemical reaction takes place at all at the oil/aqueous interface. However, Chan [11] found minimum IFT of Seeligsoil crude oil (Texas) at a NaCl concentration of 3.5% (wt). He further observed a minimum IFT corresponding to a maximum electrophoretic mobility at the interface.

Figures 19 and 20 show the effects of NaOH as well as NaCl on IFT of these crude oils. In the absence of any NaCl, IFTs are very low and emulsions are formed spontaneously. At high NaOH concentrations, IFT increases rapidly. A possible reason for such a phenomenon is due to chemical reactions which produce surface active agents (surfactants) at the interface, which are responsible for lowering IFT. However, chemical reaction between organic acids and alkaline solution largely depends on the pH of the aqueous solution.

The minimum IFTs for the Lloydminster (10^{-3} mN/m), Cold lake (10^{-3} mN/m) and Chatham (10^{-2} mN/m) crude oils correspond to pH values of 11.7, 12.0 and 12.4 respectively. This may indicate that the sudden decrease in IFT is due to the bulk pH value of NaOH solution reaching pK_a value in these crude oils. Interfacial tension increase is probably due to the desorption of the surface active species (surfactant) from

the interface into the aqueous phase. When additional NaCl is present in the aqueous phase, the minimum IFTs of these crude oils is shifted to the left in the Figures, where the pH values are lower (low NaOH concentration). Therefore, it may indicate that NaCl can raise the pH value at the interface relative to the bulk phase.

The observed same behaviour in IFT was explained [4] on the basis of charge density at the crude oil interface. As NaOH concentration further increases, undissociated soaps of organic acids will be formed due to increasing ionic interaction, which will eventually decrease the charge density at the crude oil/caustic interface.

The dynamic IFT of Lloydminster crude against different alkaline solutions is shown in Figure 21. The experimental results in Figure 21 show that 0.02% NaOH concentration gave the lowest interfacial tension. At this alkaline concentration the minimum IFT takes a much longer time to become established. This seems to indicate formation of the critical micellar concentration (CMC) at about 500 seconds. Interfacial tension of Lloydminster crude oil decreased from 22 to 0.009 (mN/m) (a factor of 2,450 times) when 0.02% NaOH was present in the aqueous phase. The presence of salt (1% by weight) in the aqueous phase increases the IFT slightly as shown in Figures 21 and 22. This observation agrees with previous work by [44] and other researchers [35].

Figures 23 and 24 show the effects of alkaline solutions on interfacial tension of Chatham oil. In all cases, IFT increases suddenly after reaching the minimum value at short times. This is possible because the pK_a value of Chatham oil is lower than the others. After contact with alkaline solution, the chemical reactions seem to decay very quickly.

However, the gradually increasing IFT is due to diffusion control at the interface. A typical curve for 0.02% NaOH is given in Figure 23. It should be noted that increase in NaOH concentration raises the IFT slowly after a certain time. The effect of salinity on interfacial tension of Chatham oil shows almost the same behaviour as for Lloydminster and Cold Lake, i.e., the presence of NaCl significantly reduces the amount of NaOH required to achieve low IFT.

Figures 25 and 26 indicate the IFT behaviour of Cold Lake/alkaline systems as functions of the age of the interface. The 0.02% NaOH system gives much higher IFTs than when 1% NaCl is present in the solution. This again indicates that NaCl increases pH value at the interface relative to that of the bulk phase.

The observed shape of these curves is similar to that found in the literature for a large number of crude oils in contact with NaOH solutions [23,33,45]. The times taken for Chatham and Lloydminster crude oils to reach the IFT minima in these experiments are virtually the same as those observed in the literature, except for the Cold Lake oil. These observations also agree with Rubin et al. [45] that the dynamic lowering of IFT is a function of the rates of adsorption and desorption of surface active species at the interface. The increase of the IFTs also depends on the water-oil ratio in the tensiometer [45]. As this ratio decreases, the measured IFT increases.

It is found in some cases that it takes a much longer time for a drop of Cold Lake crude oil to separate from the capillary tube than the others. This is probably due to the very high viscosity of Cold Lake crude oil, so it takes a longer time to reach the minimum interfacial

tension. Irregular and transient drop shapes for the Cold Lake oil were observed during the beginning of the measurements. These irregular shapes are evidence of low and nonuniform interfacial tension due to lack of diffusion and chemical equilibrium during generation of surface active species at the viscous Cold Lake /aqueous interface.

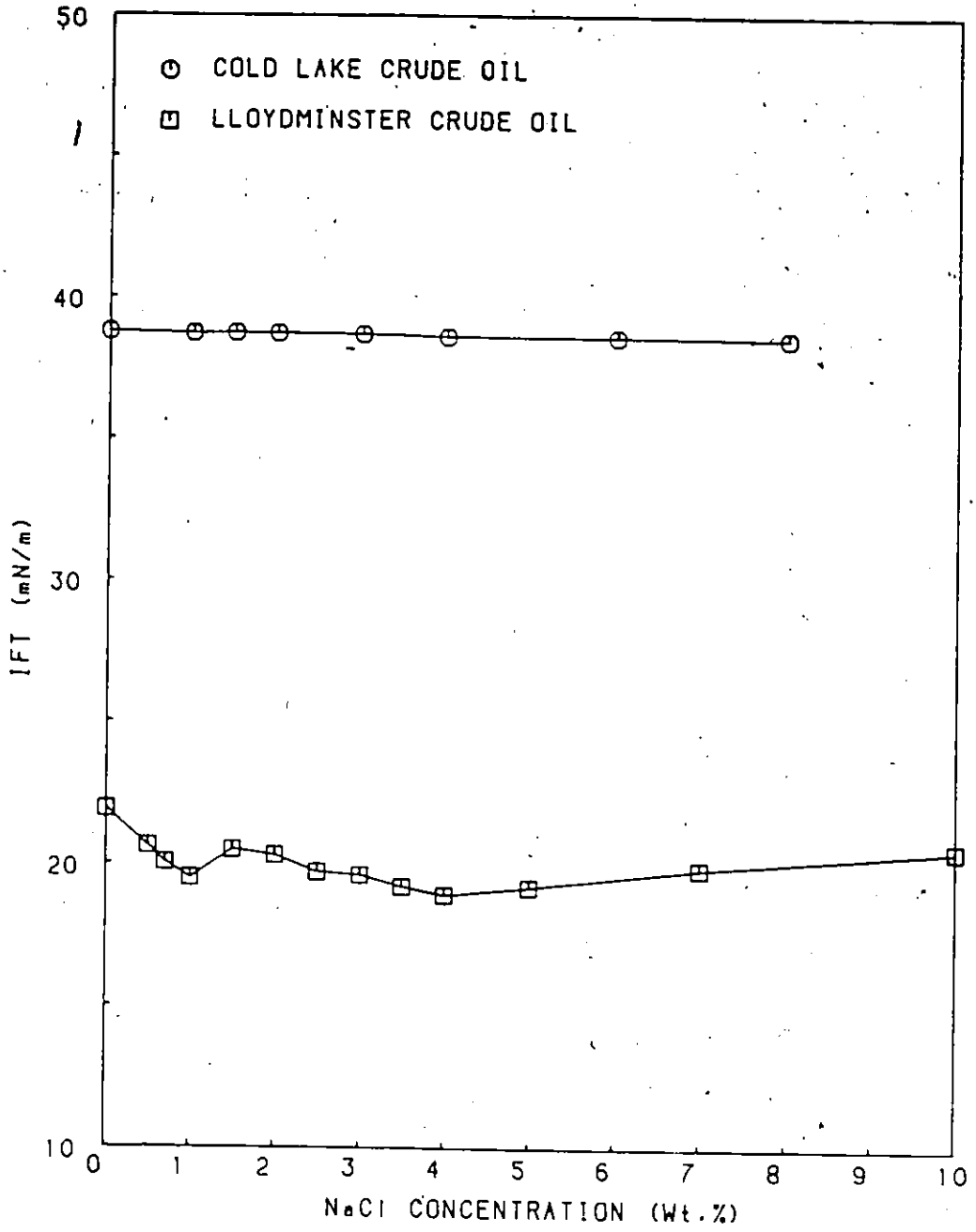

Figure 17: Effect of salinity on IFT of Lloydminster and Cold Lake crude oils at 6700 RPM and 29 °C

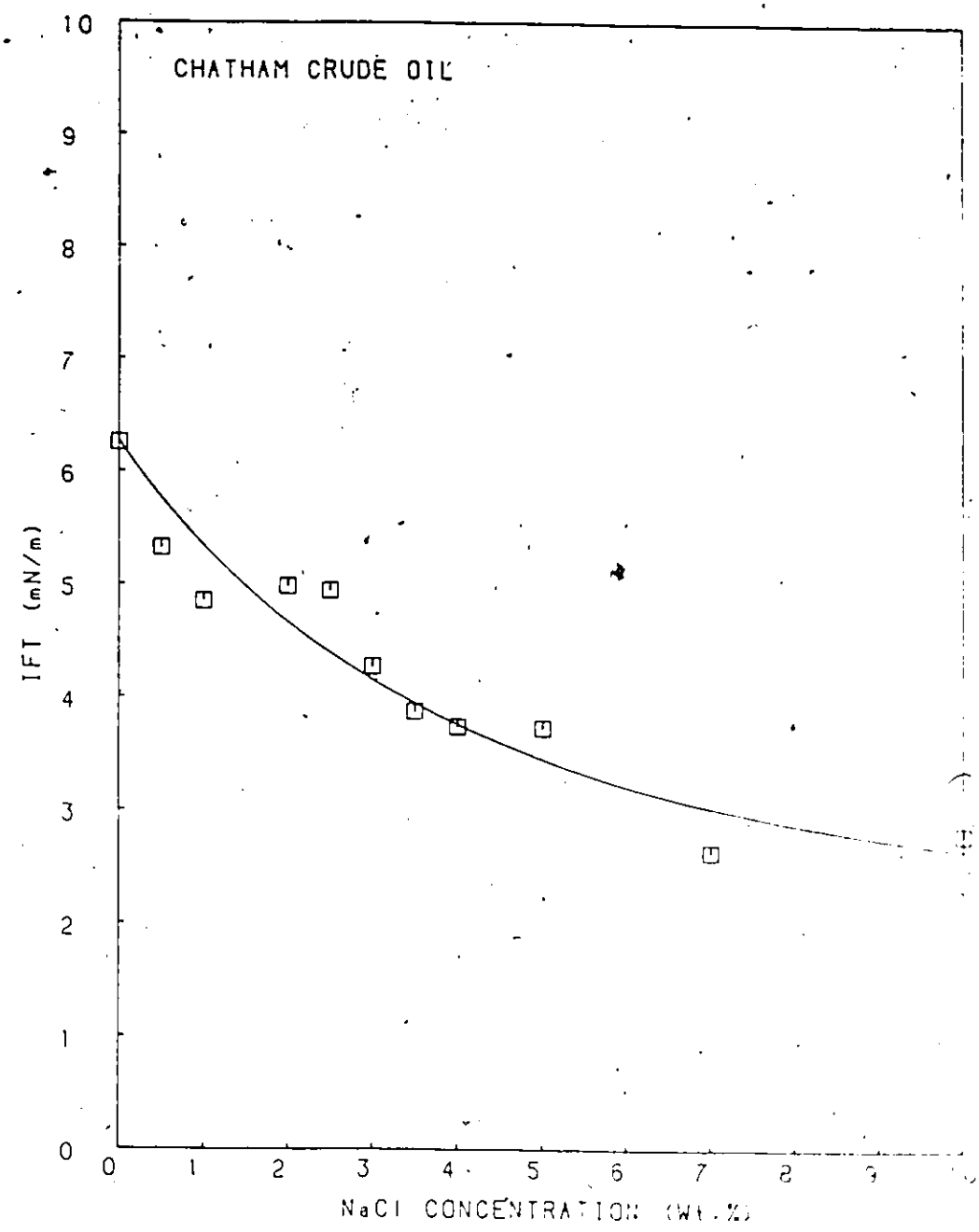

Figure 18: Effect of salinity on IFT of Chatham crude oil at 6700 RPM and 29°C

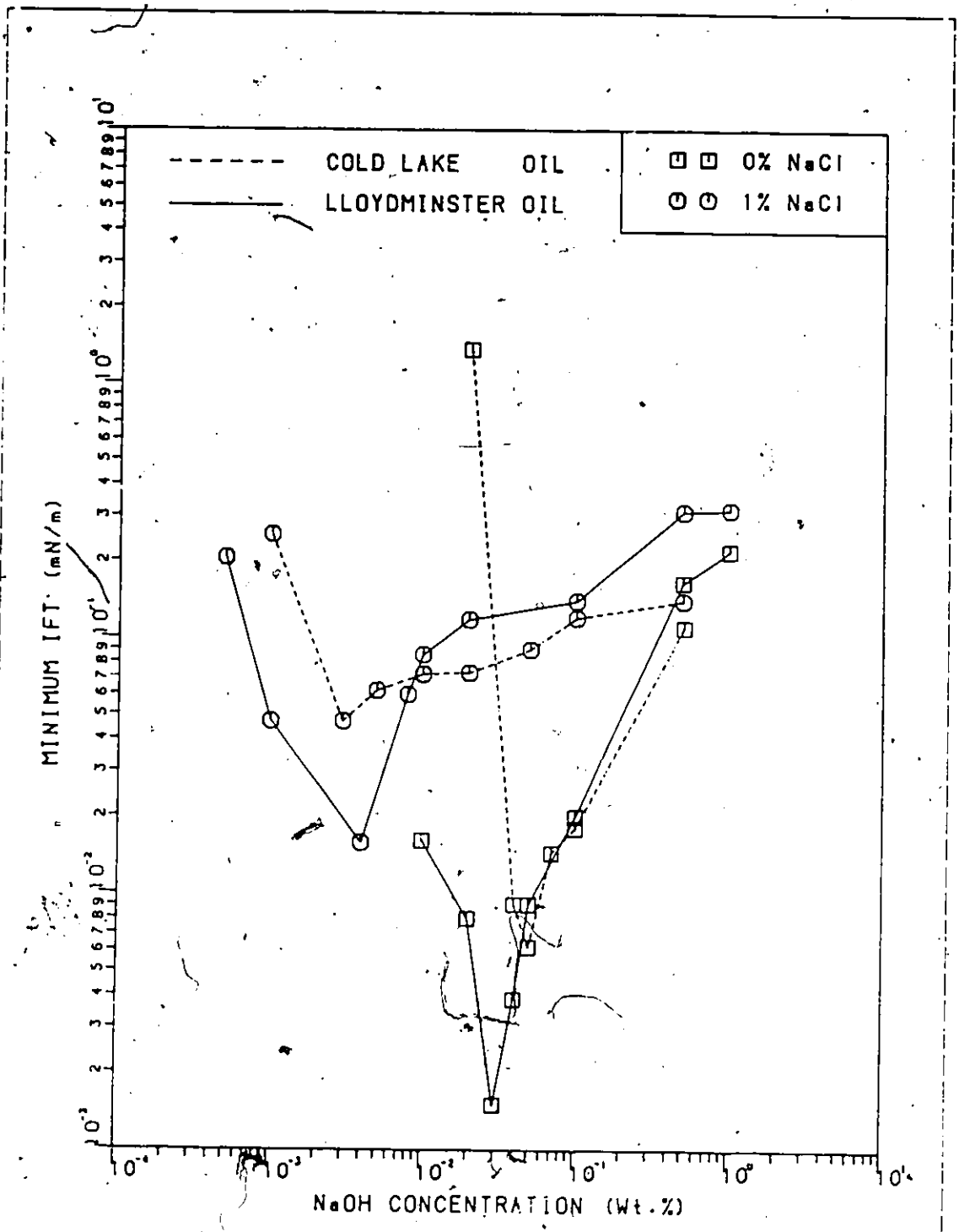

Figure 19: Plot of minimum IFT of Lloydminster and Cold Lake oils against alkaline solutions, at 6700 RPM and 29°C

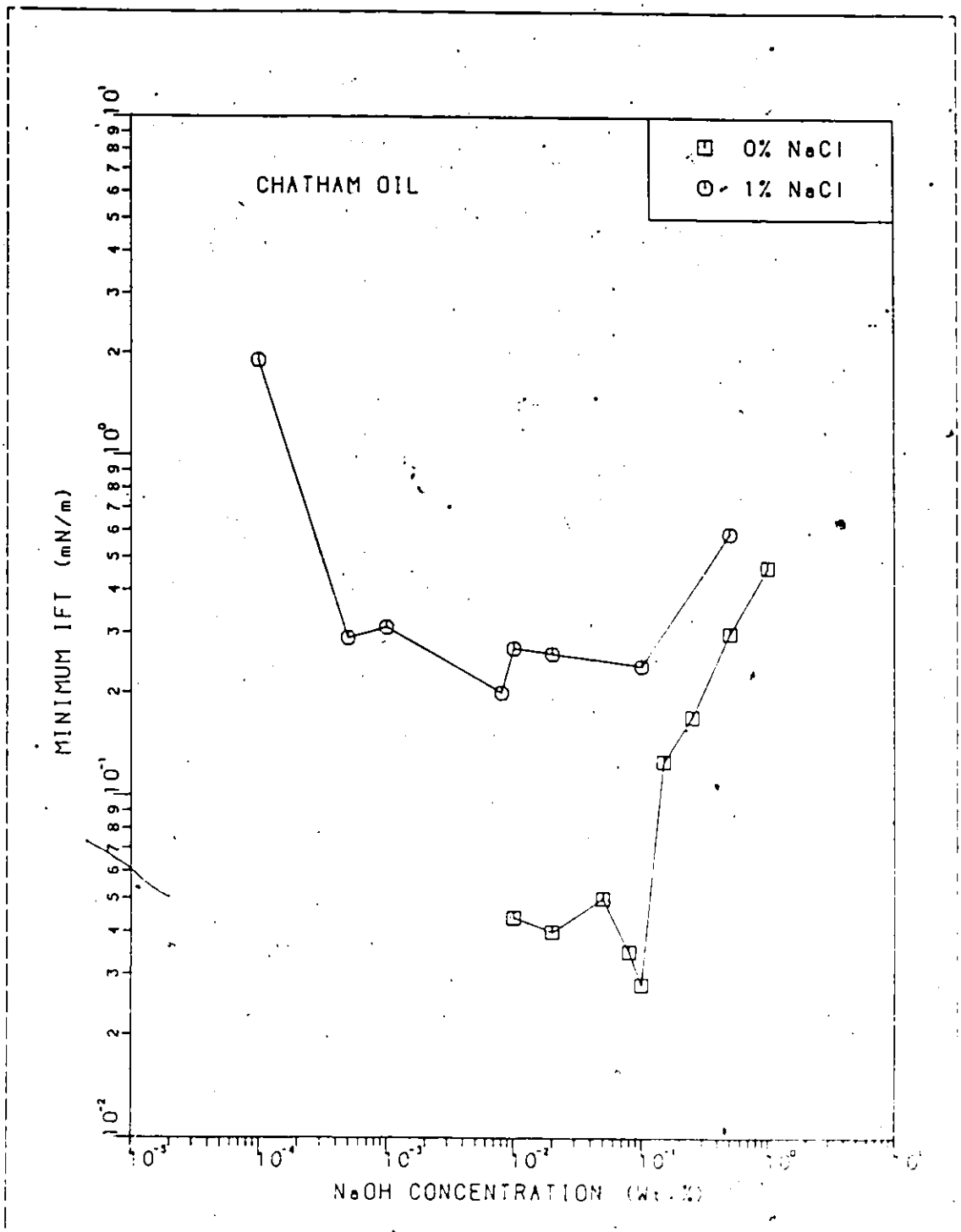

Figure 20: Plot of minimum IFT of Chatham crude oil against alkaline solutions at 700 RPM and 29°C

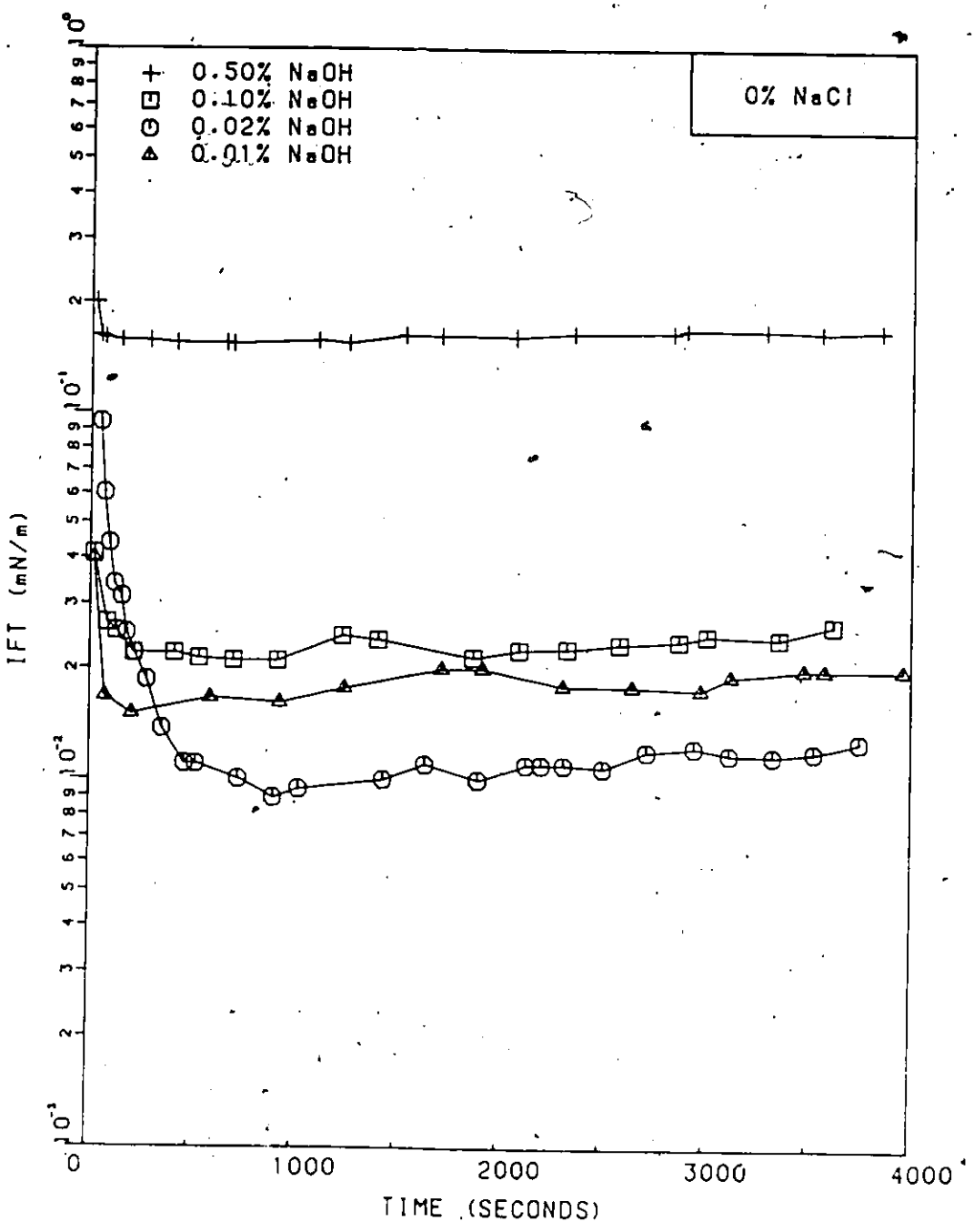

Figure 21: Effect of alkaline solution (0% NaCl) on IFT of Lloydminster crude oil at 6700 RPM and 29°C

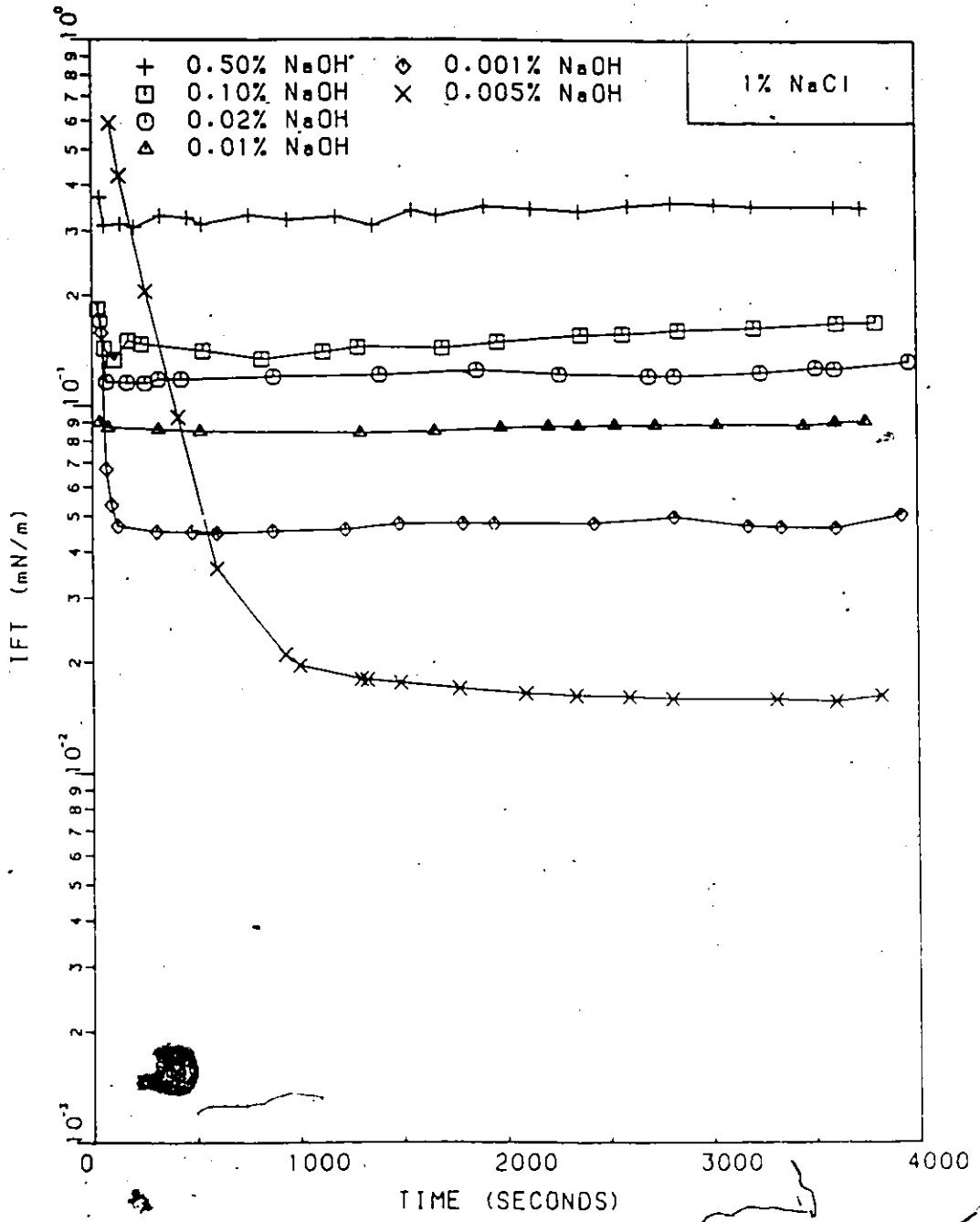

Figure 22: Effect of alkaline solution (1% NaCl) on IFT of Lloydminster crude oil at 6700 KPM and 29°C

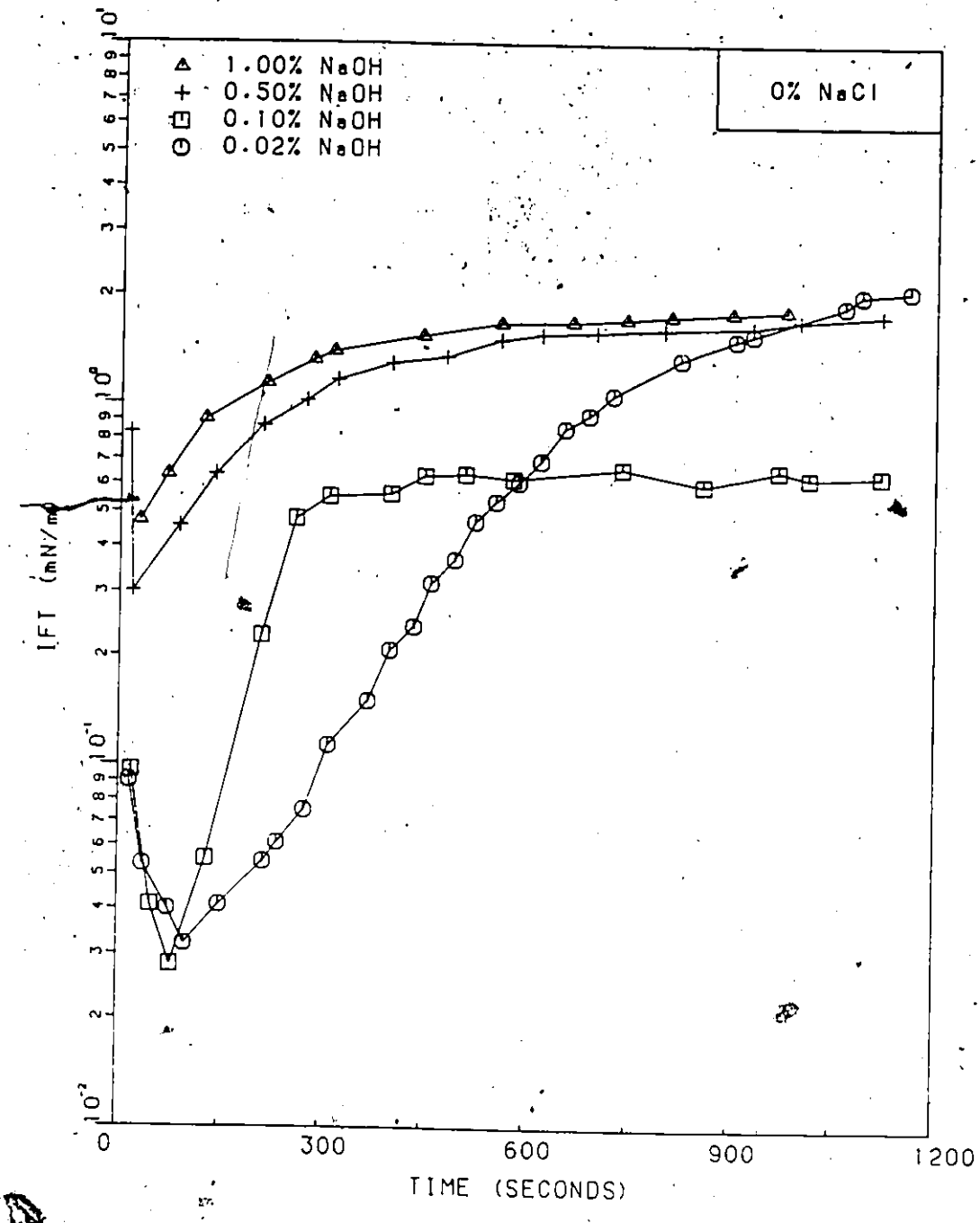

Figure 23: Effect of alkaline solution (0% NaCl) on IFT of Chatham crude oil at 6700 RPM and 29°C

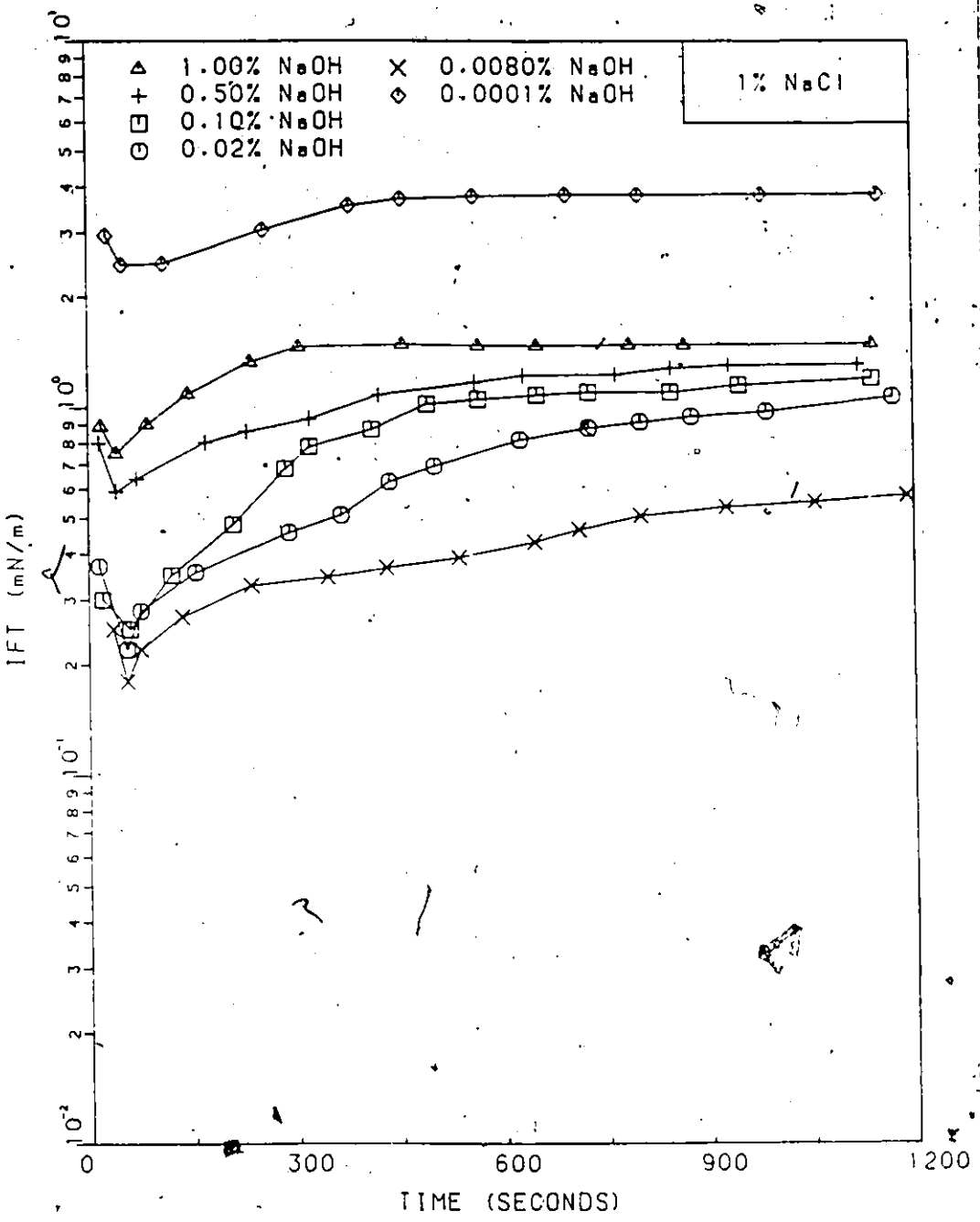

Figure 24: Effect of alkaline solution (1% NaCl) on IFT of Chatham crude oil, at 6700 RPM and 29°C

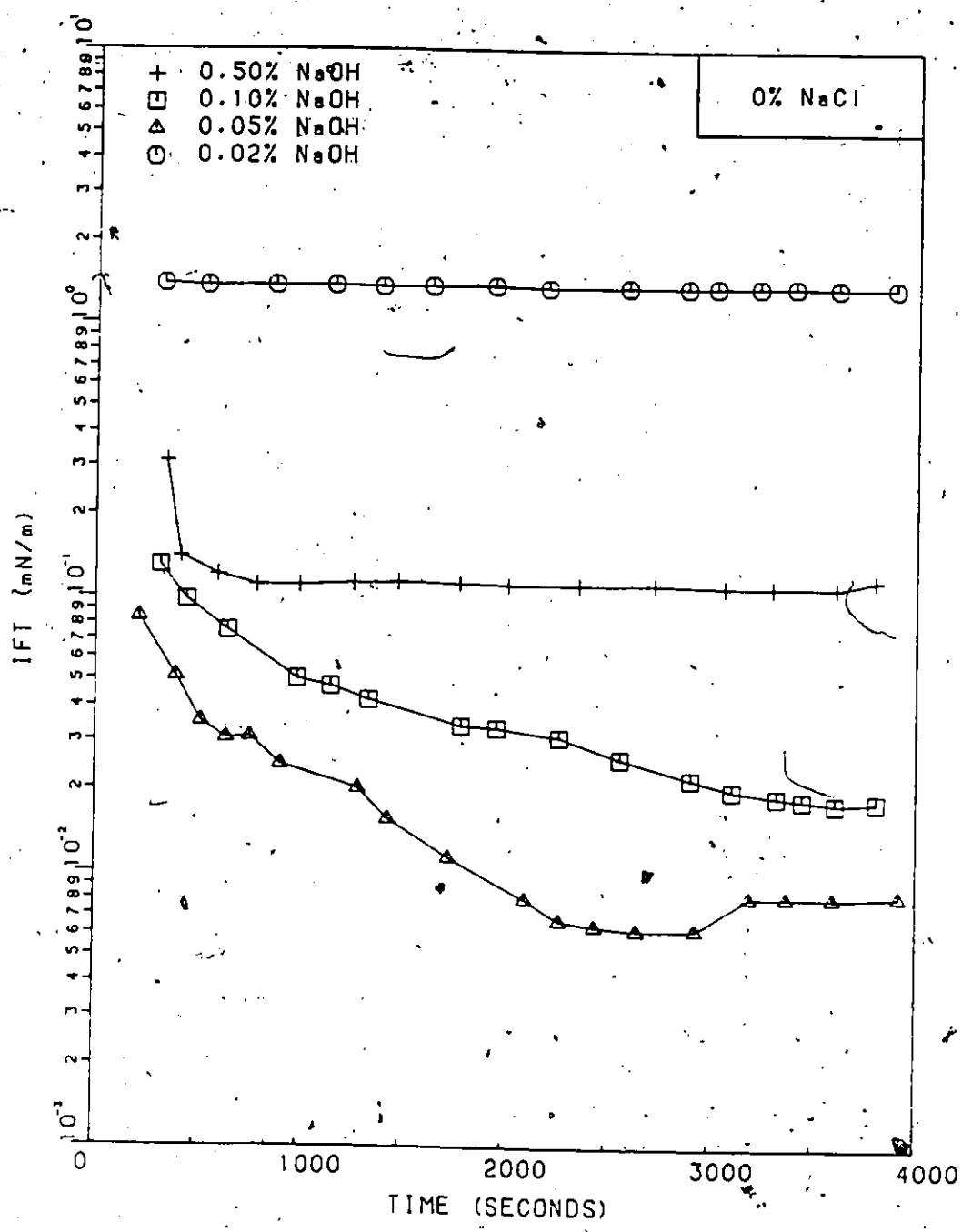

Figure 25: Effect of alkaline solution (0% NaCl) on IFT of Cold Lake crude oil, at 6700 RPM and 29°C

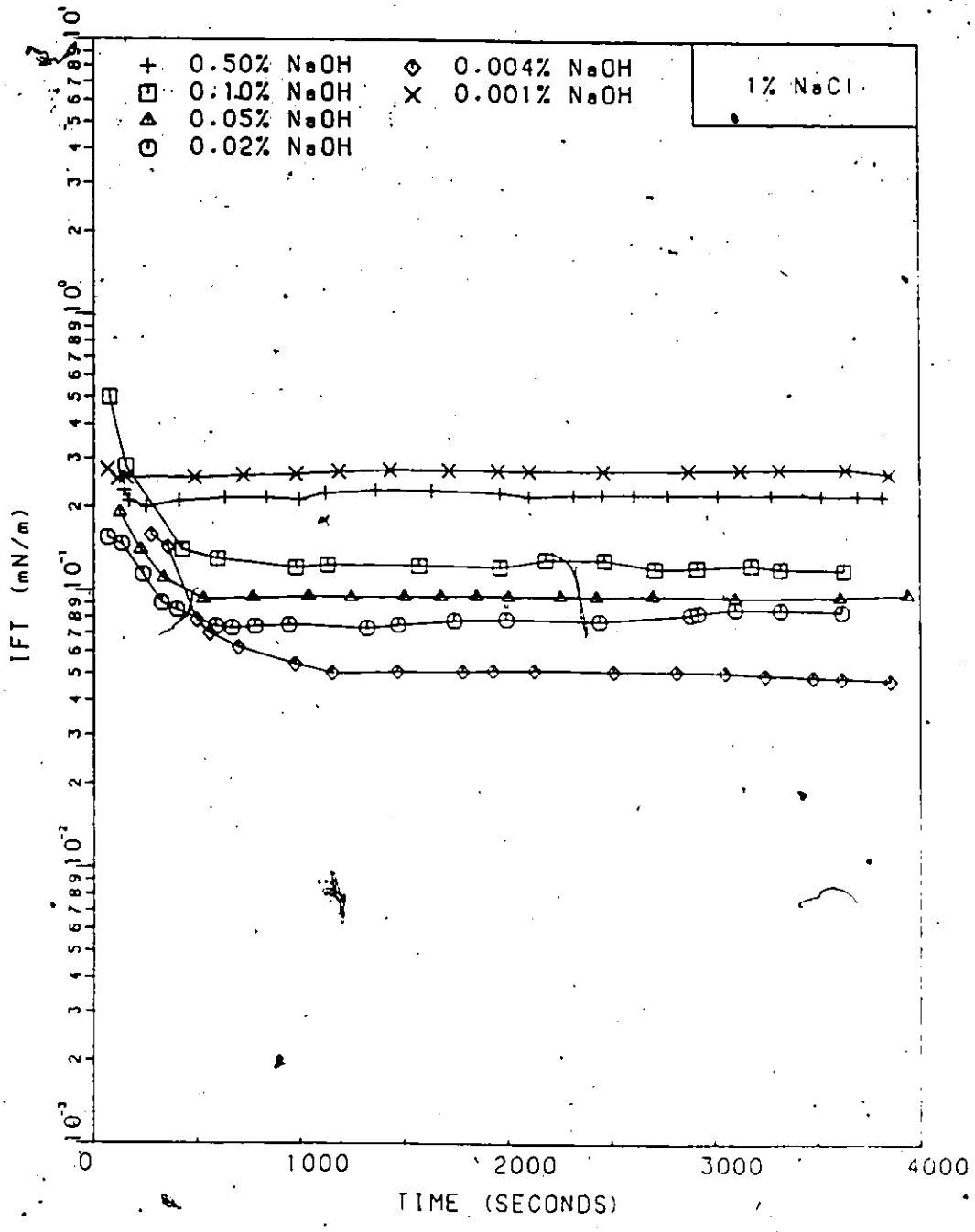

Figure 26: Effect of alkaline solution (1% NaCl) on IFT of Cold Lake crude oil at 6700 RPM and 29°C

Chapter VI

RESULTS AND DISCUSSION

6.1 Interfacial Tension of Crude oil Systems

6.1.1 Effect of Oil Acidity

Three crude oils, Lloydminster, Cold Lake and Chatham, were chosen and diluted with hexadecane, toluene and a 50% wt. hexadecane/toluene solution to examine the effects of acidity on IFT of diluted crude oils. Hexadecane was used as a diluent based on the assumption that the equivalent alkane carbon number [32,44] for Cold Lake oil would be approximately sixteen. For comparison purposes, hexadecane was also chosen as a diluent for both Lloydminster and Chatham oils. Toluene was selected because it is a widely used solvent [39] for dissolving crude oils. In order to compare all results, the transient IFT behavior of the three crude oils was recorded experimentally under similar conditions (see Figures 21 to 30).

It is evident that the shape of the IFT curves is dependent upon the degree of dilution. For diluted Lloydminster crude oil, no minimum IFT is observed in the case of 30% toluene, 50% toluene, 30% toluene/hexadecane or 50% toluene/hexadecane (see Figures 35 to 37). However, for the case of dilution with hexadecane, a minimum IFT is reached, even with 50% hexadecane (see Figure 33).

Similar behavior concerning the effects of dilution on IFT of Cold Lake oil is observed. Comparing Figures 37 and 38, a minimum IFT is observed for Cold Lake oil diluted with hexadecane/toluene mixtures. This is possible because Cold Lake contains more acid than Lloydminster oil.

Figures 30 to 32 show the effects of dilution on IFT of light Chatham oil. It seems that the behavior of Chatham oil has little similarity with the two heavy oils, in which the dilution with hexadecane/toluene gives high IFT, and no minimum IFT is observed for the case of 50% (hexadecane/toluene). In Figure 30 the transient IFT behavior of Chatham oil diluted with hexadecane shows slightly lower minimum IFT than pure Chatham crude.

It may be concluded that dilution with hexadecane has less effect (lower IFT) than dilution with toluene on the IFT of oils against alkaline solutions. However for oil against distilled water dilution with hexadecane gives lower IFT than with toluene (Figures 27 and 28). A possible explanation for such phenomena is because toluene can dissolve high molecular weight components in crude oils (such as asphaltenes and resins) more efficiently [24] than can hexadecane. Moreover, these high molecular weight components are usually polar [24]. When crude oil is diluted with toluene or hexadecane at very dilute concentrations of crude oil (about 10 wt.% in Figures 27 to 29), IFT decreases very sharply in all cases. It is likely that these crude oils contain some surface active components which reduce the IFT of pure toluene, hexadecane and a 50% hexadecane/toluene mixture substantially. For the cases of Cold Lake and Lloydminster heavy oils, the IFT increases slightly as the

oil concentration increases. This is due to these polar compounds associating and dissociating, leading to a gradual increase in IFT. However, this is not the case with the Chatham light oil, which does not contain such large polar molecules.

For comparison purposes, Figures 27 and 29 also display the effects of bentonite (clay) on IFT of the three crude oils. With 0.5 wt.% clay concentration in the aqueous phase, the IFT decreases in all cases. These phenomena are discussed in the next chapter.

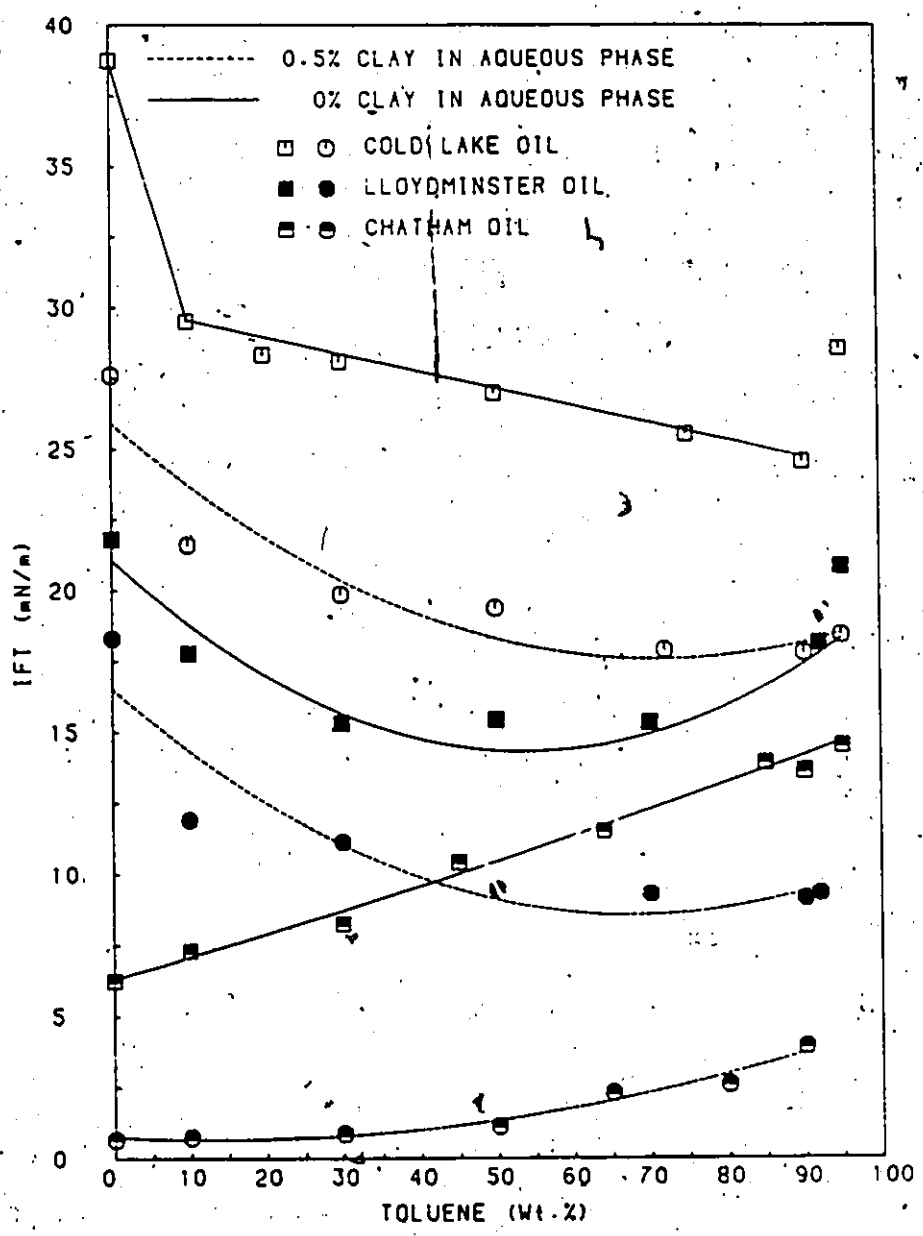

Figure 27: Effect of Dilution On IFT of Crude Oils at 6700 RPM and 29°C

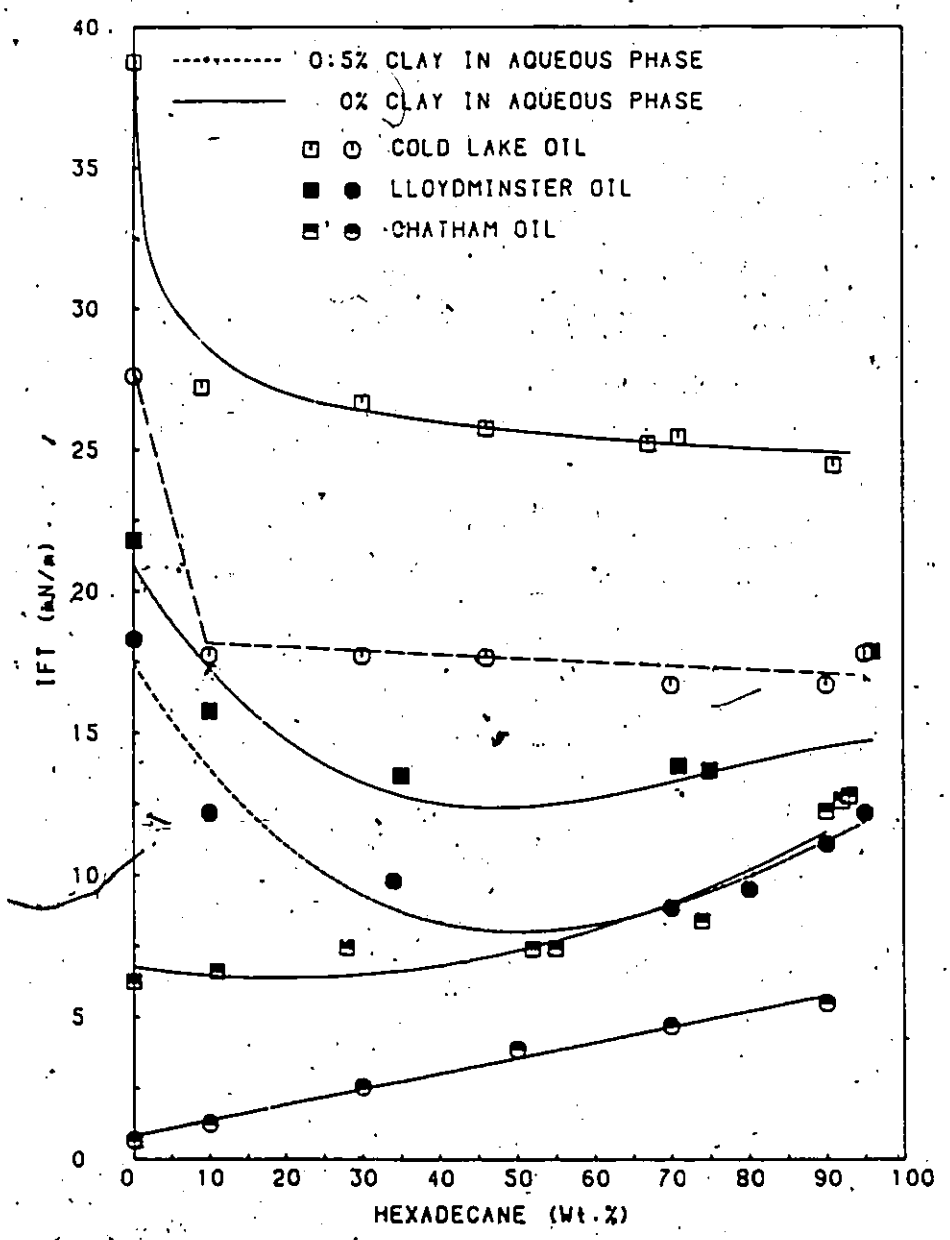

Figure 28: Effect of Dilution On IFT of Crude Oils at 6700 RPM and 29°C

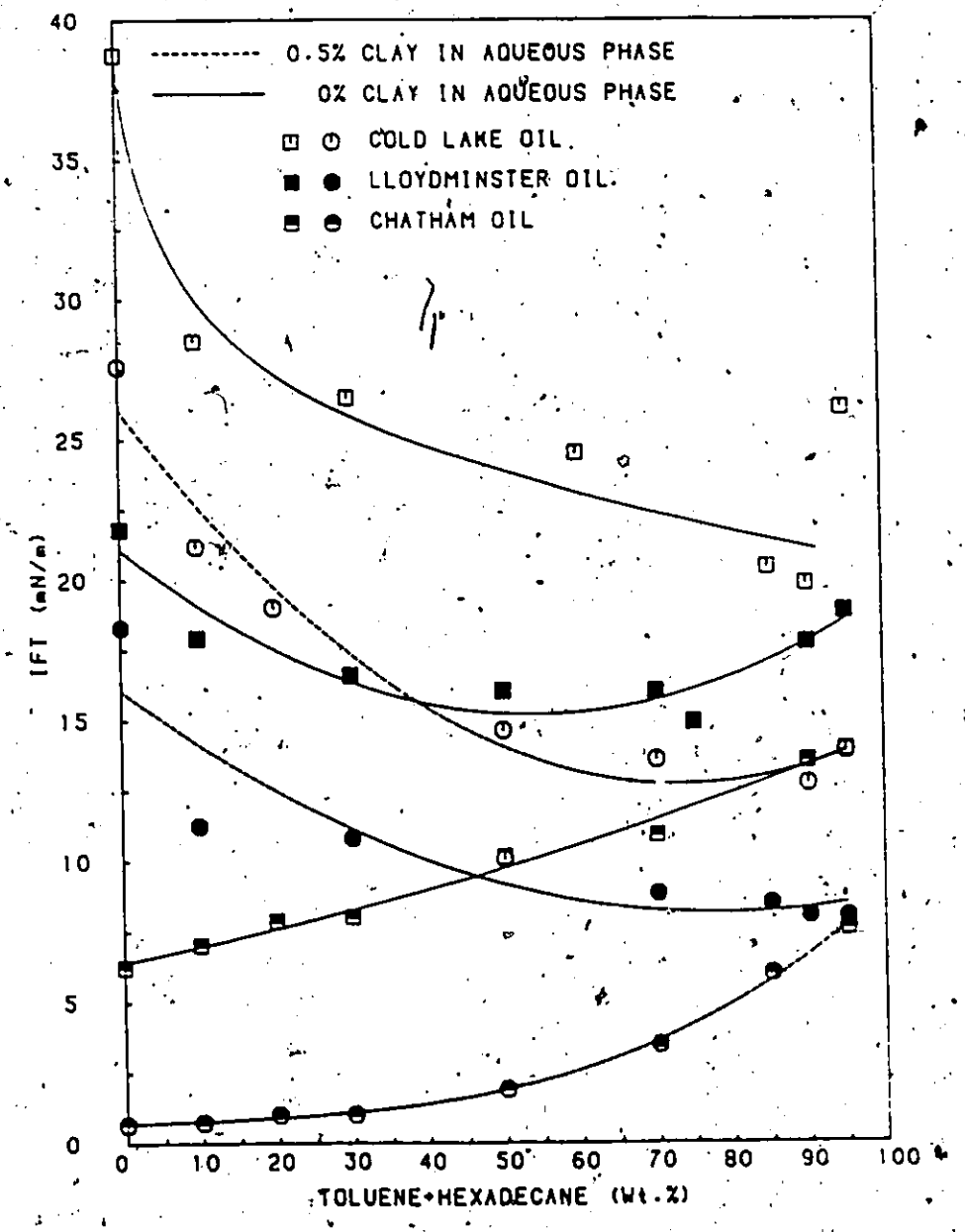

Figure 29: Effect of Dilution On IFT of Crude Oils at 2700 RPM and 29°C

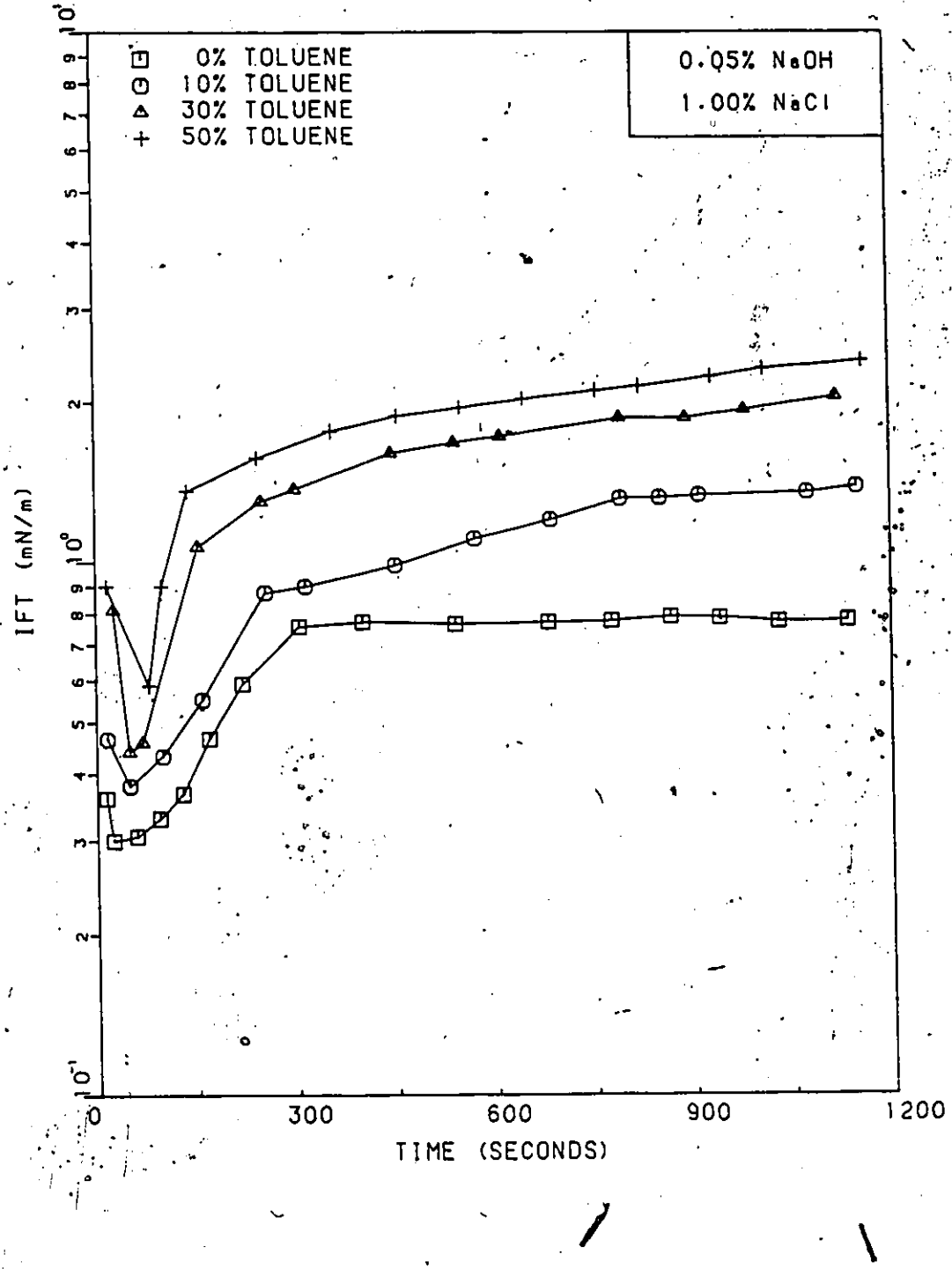

Figure 30: Transient Behavior of IFT of Chatham crude oil at 6700 RPM and 29°C

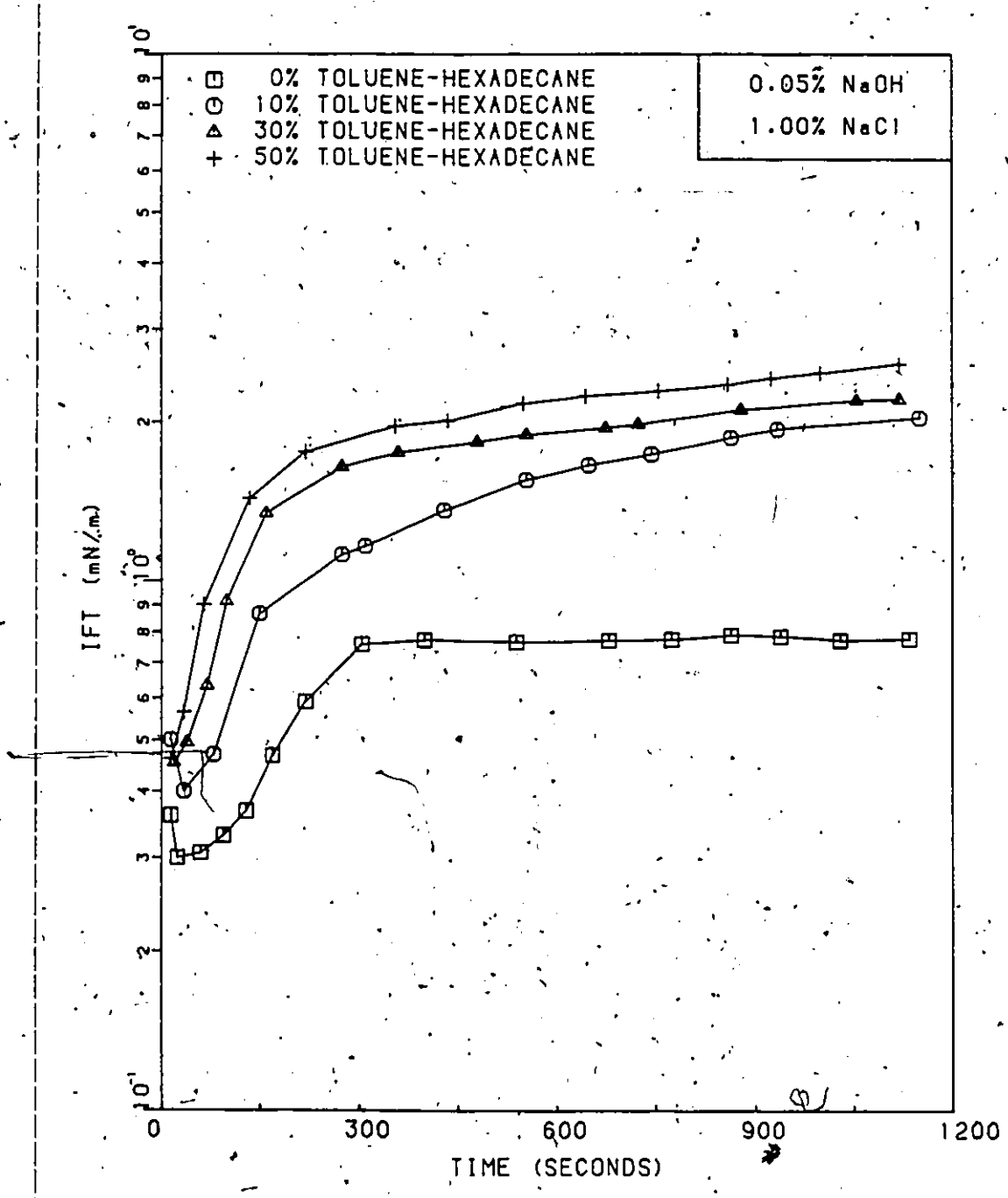

Figure 31: Transient Behavior of IFT of Chatham Crude Oil at 6700 RPM and 29°C

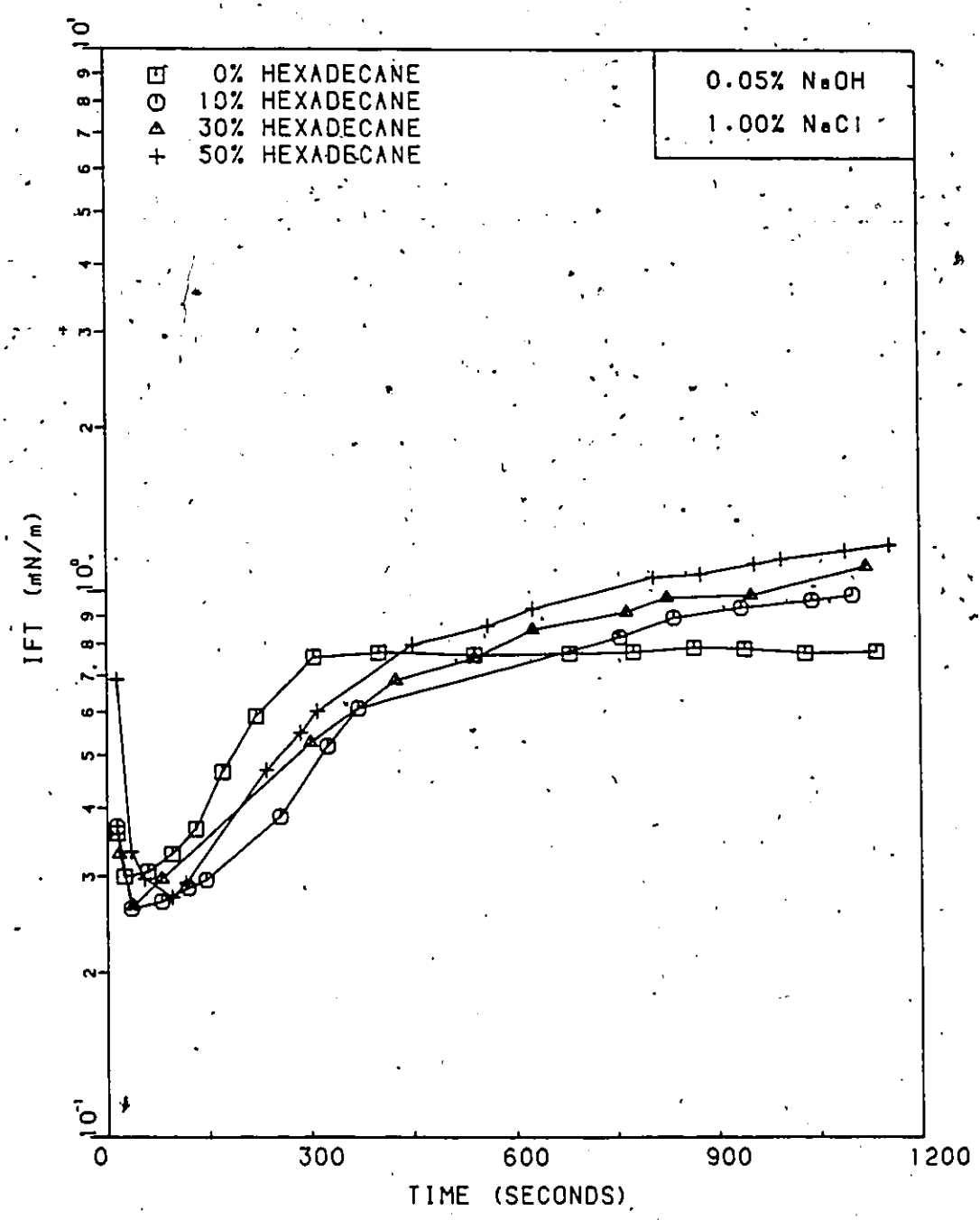

Figure 32: Transient Behavior of IFT of Chatham Crude Oil at 6700 RPM and 29°C

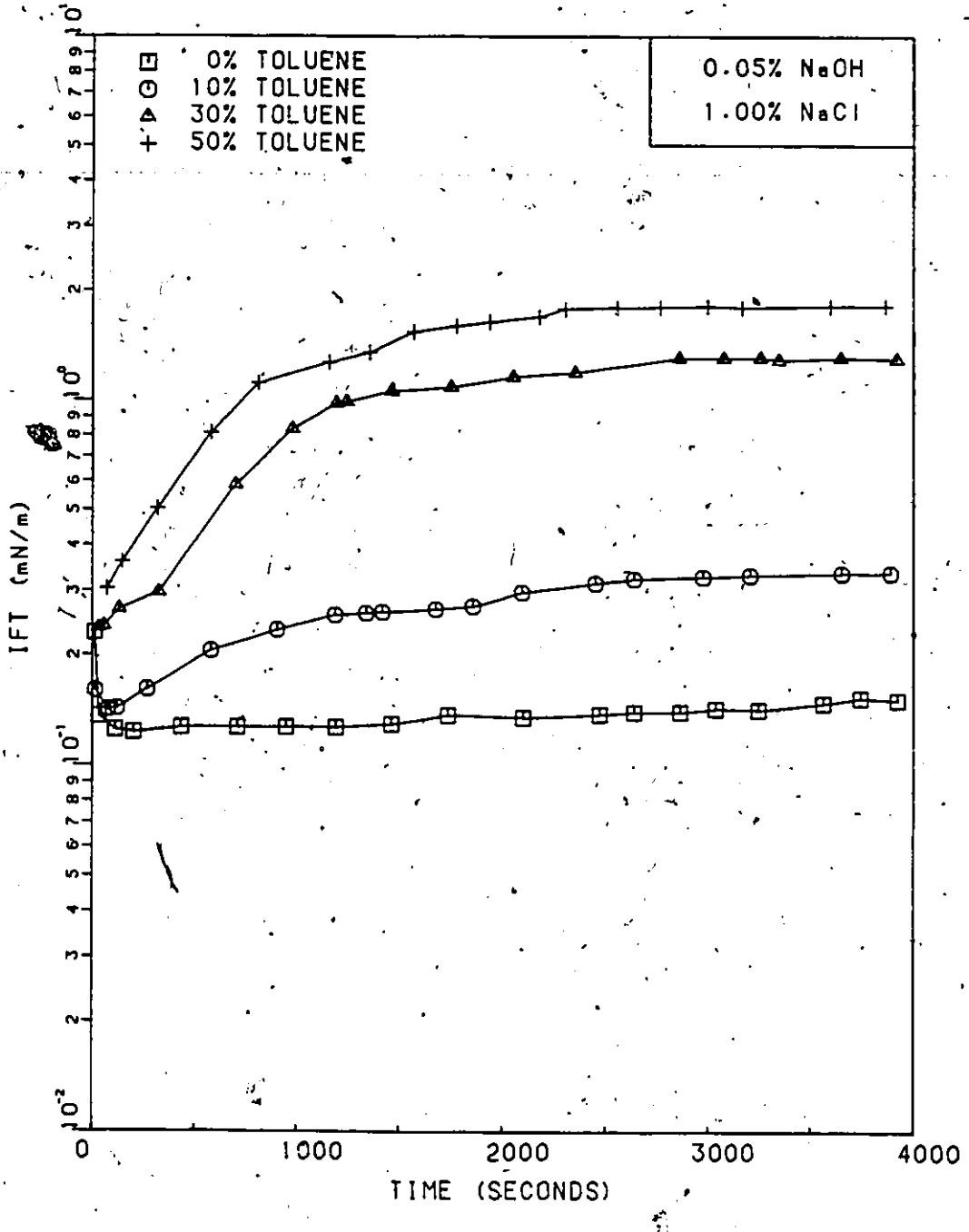

Figure 33: Transient Behavior of IFT of Lloydminster Crude Oil at 6700 RPM and 29°C

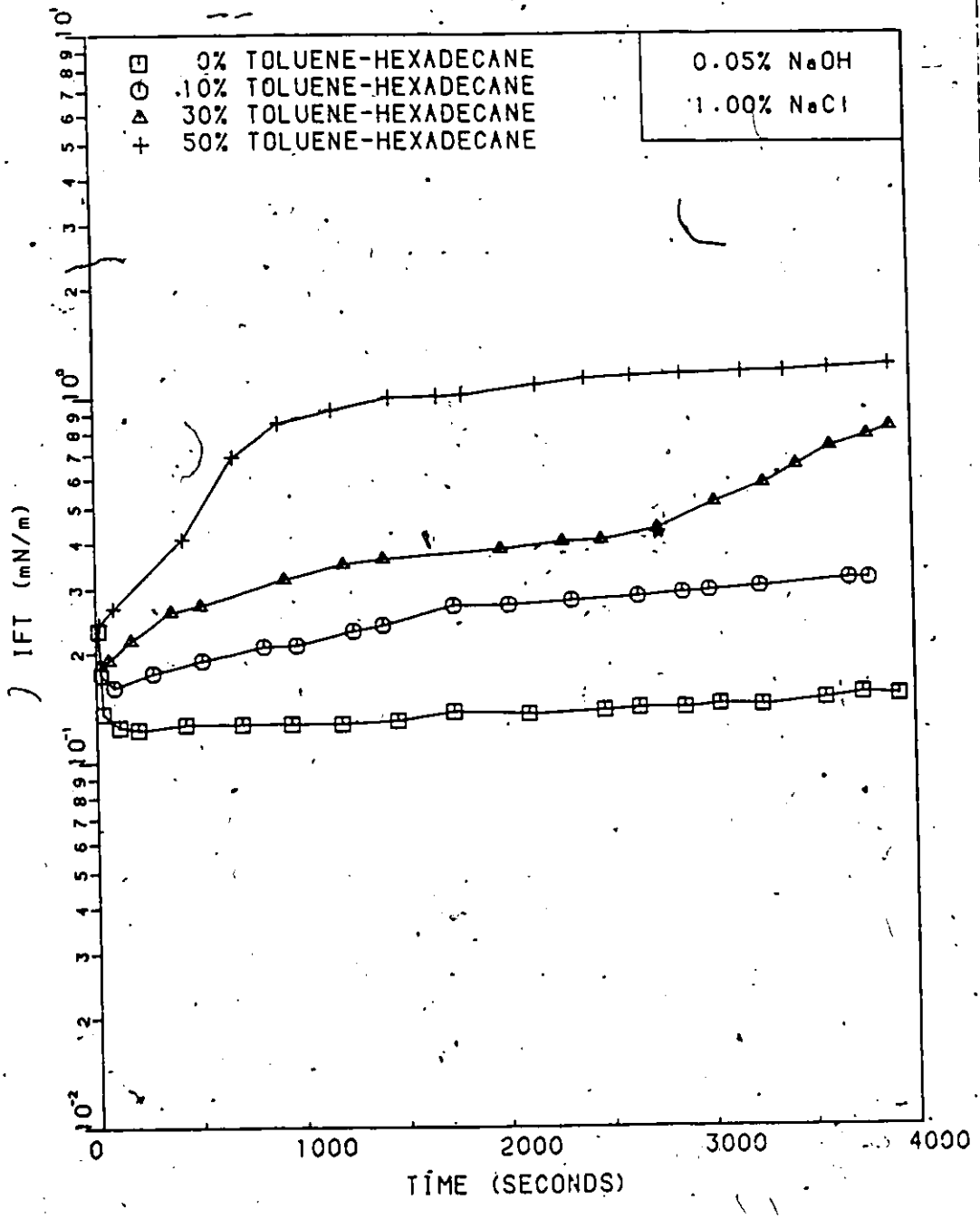

Figure 34: Transient Behavior of IFT of Cold Lake Crude Oil At 29°C

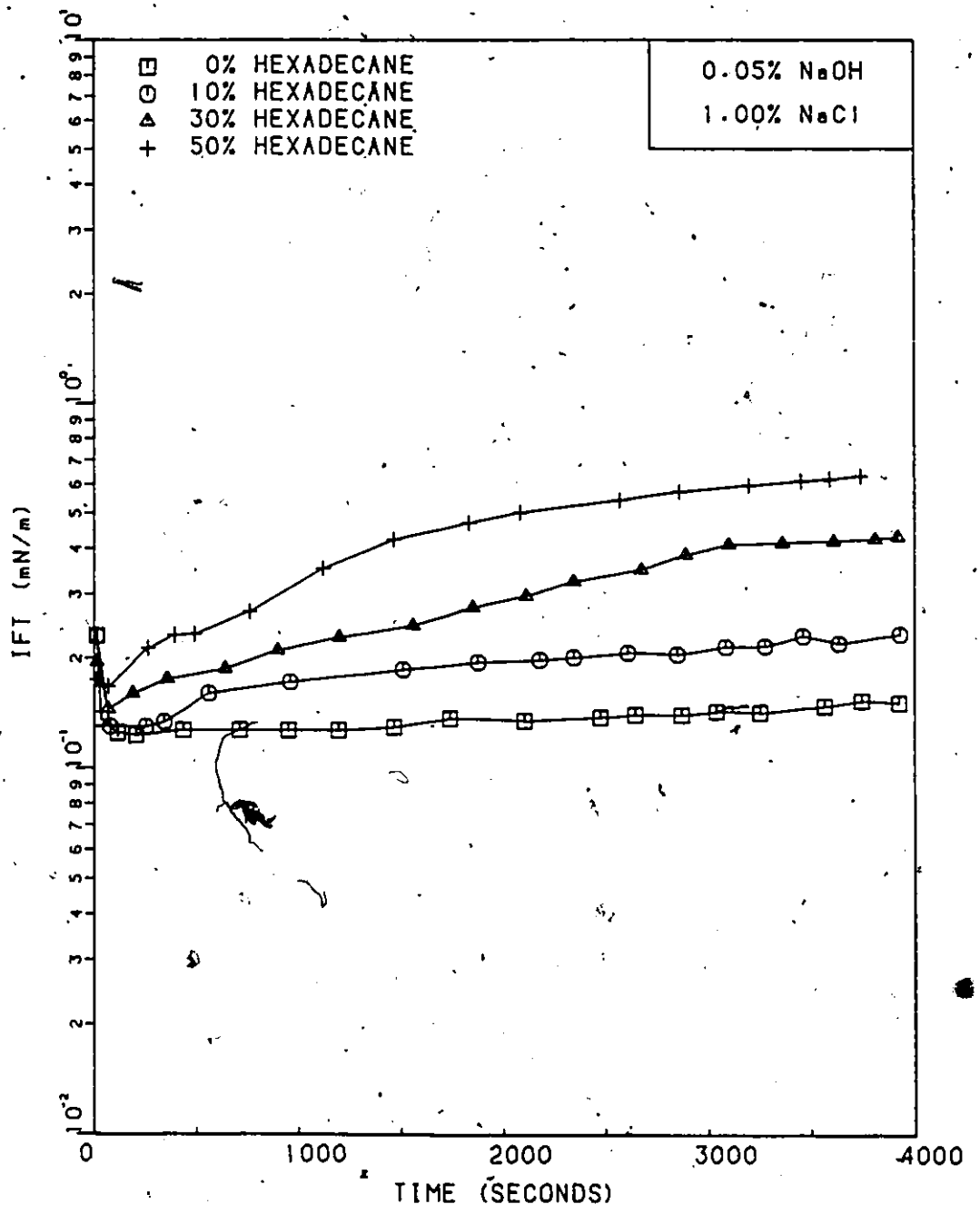

Figure 35: Transient Behavior of IFT of Lloydminster Crude Oil at 6700 RPM and 29°C

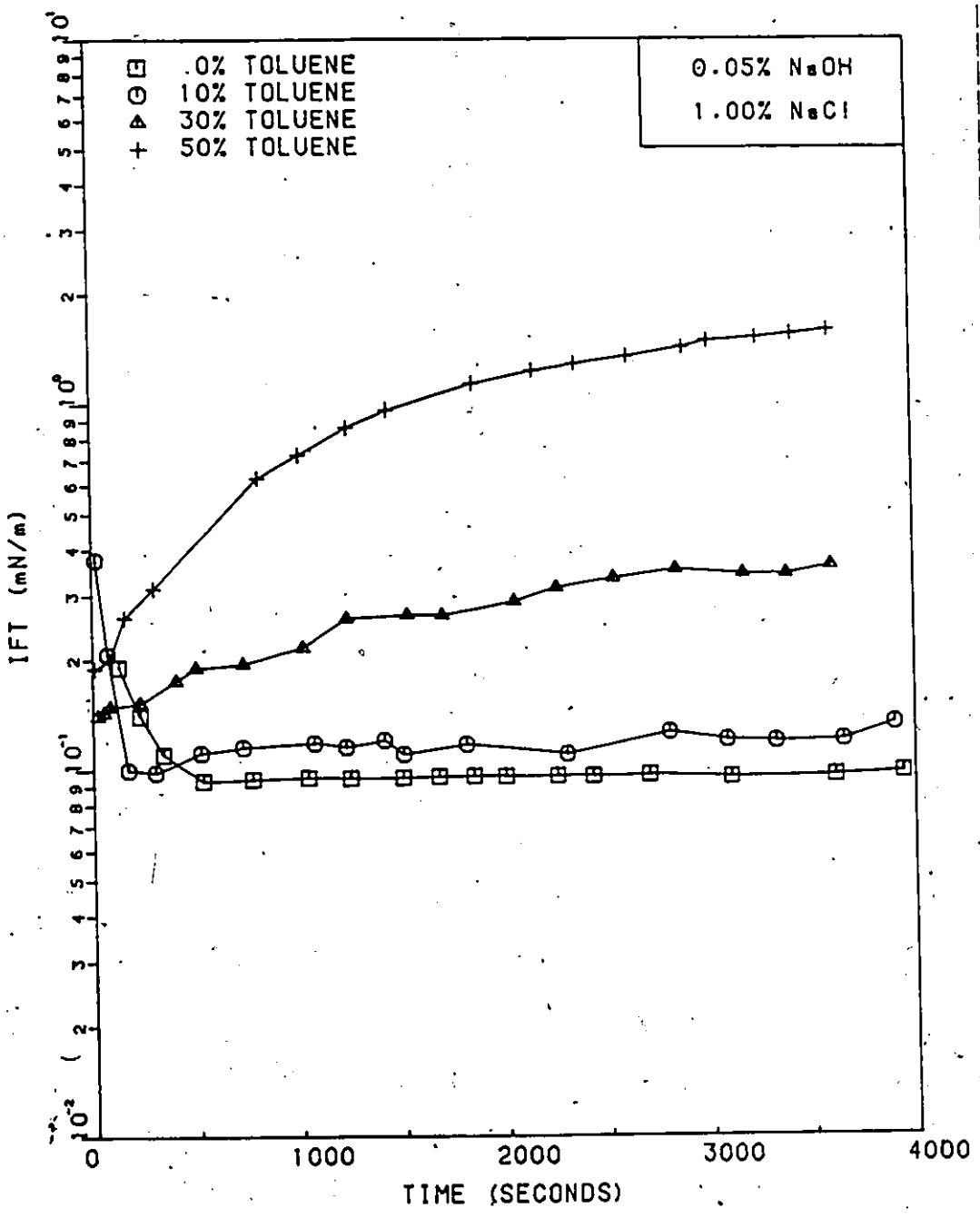

Figure 36: Transient Behavior of IFT of Cold Lake Crude Oil at 6700 RPM and 29°C

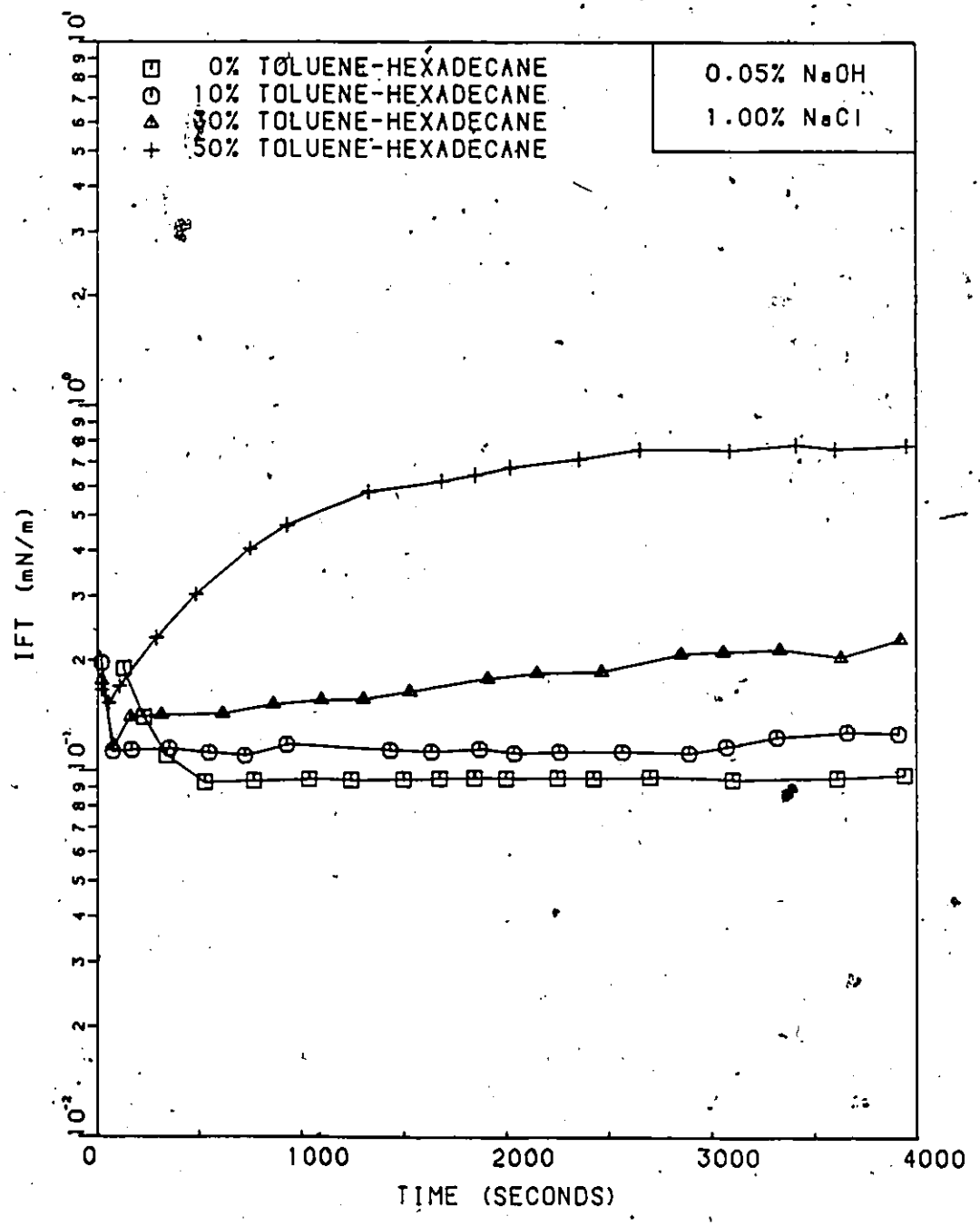

Figure 37: Transient Behavior of IFT of Lloydminster Crude Oil at 6700 RPM and 29°C

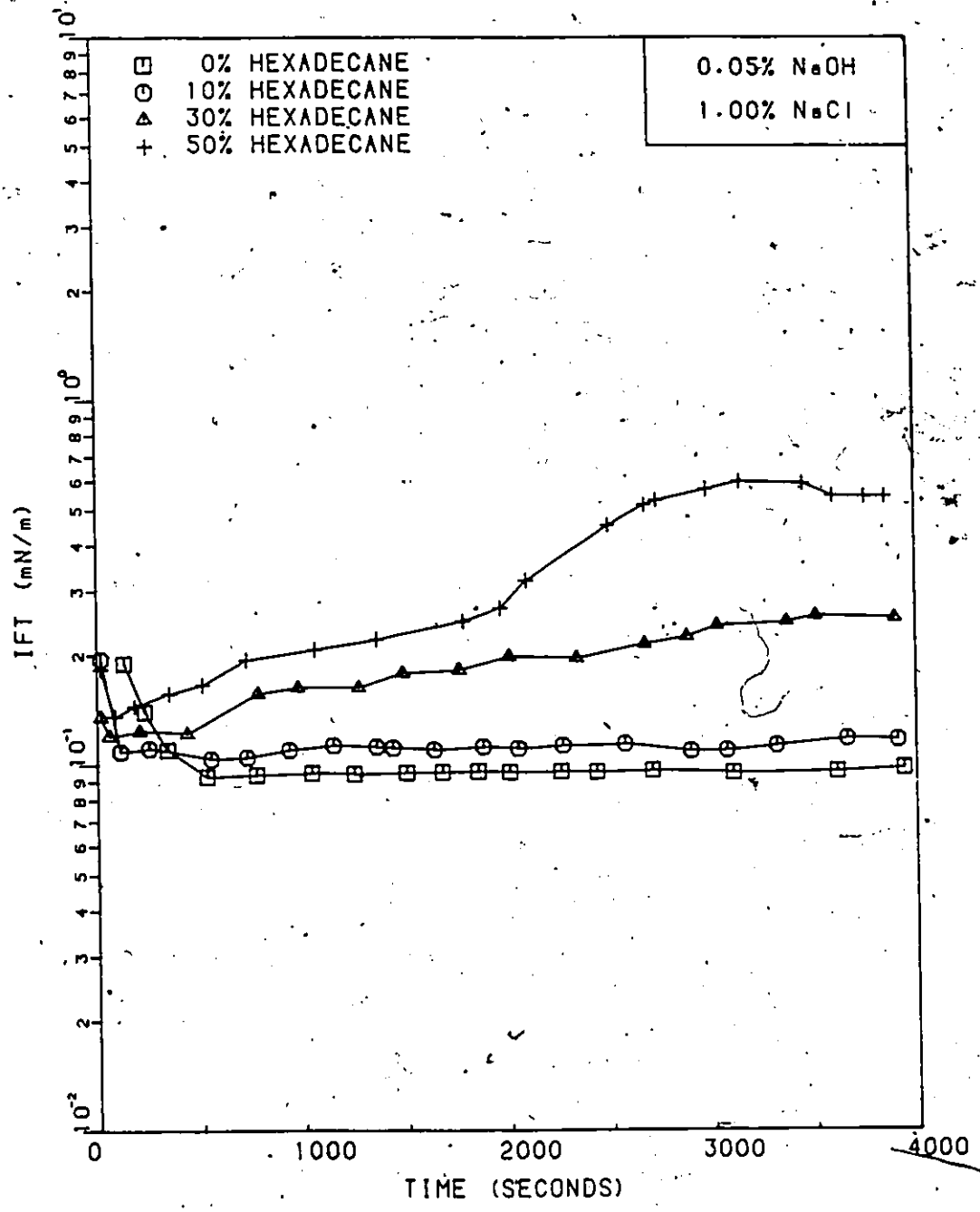

Figure 38: Transient Behavior of IFT of Cold Lake Crude Oil at 6700 RPM and 29°C

Chapter VII

RESULTS AND DISCUSSION

7.1 Interfacial Tension of Crude Oil Systems

7.1.1 The Effects of Clay Fines On IFT of Crude Oils.

Figure 39 shows the effects of clay fines on the IFT of hexadecane against distilled water. The upper curve is calculated from Gibbs' adsorption equation [15] to determine the amount of clay adsorbing at the interface assuming dilute solution (activity coefficient f=1), i.e.,

$$\Gamma = - C/RT \cdot (\partial\gamma/\partial C) \qquad (47)$$

This equation states that IFT lowering is accompanied by interfacial adsorption of clay, while IFT raising is accompanied by interface depletion of clay. The maximum adsorption corresponds to the sharp reduction in IFT.

The results for the effect of clay on IFT of Cold Lake, Lloydminster, and Chatham oils are shown in Figure 40. When there is 0.5 wt.% clay in the aqueous phase, IFT decreases from 38 to 27 for Cold Lake, 22 to 18 for Lloydminster and 6.5 to 0.6 for Chatham oils. These decreases in IFT could be due to either clay adsorption, or to interaction between active agents in the oil phase and silicates and aluminates in the clay [18]. At very low clay concentrations (0.01-0.05 wt.%), the IFT increases slightly in Figure 40. Such small amounts of clay are prob-

ably not enough to saturate the interface, and sedimentation of clay occurs which possibly carries positive charges which require net compensating negative charges at the interface [30]. These effects may increase the IFT slightly. Experimental results for the surface tension of clay in distilled water (which are not given here) show that small amounts of clay (0.01-0.05 wt.%) actually increase surface tension from 71.2 to 72.8 mN/m. This may indicate that the clay is sedimenting from the surface of the water. Recently Jennings et al. [23] have studied the effects of clay on oil/water dispersions. They found that the addition of 0.04 wt.% of pure Kaolinite had a large effect on hexane, little effect on paraffin, and very little effect on Alberta bitumen oil in oil-water dispersion.

Figures 41 and 42 show the effects of additional clay on the three different crude oils against alkaline solutions. For Chatham light oil, the effects of clay in both the oil phase and aqueous phase were studied. The results in Figures 43 and 44 show that the minimum IFT decreases in most cases, whether the clay is in the oil or the aqueous phase. Clay in the oil phase gives higher IFT than when it is in the aqueous phase. Verma and Farouq Ali [55] have noticed that oil often contains small amounts of extremely fine clay, which increases its viscosity and makes its flow behavior in the porous medium complex.

Figures 45 and 46 show the effects of clay concentration on IFT of Chatham oil for different alkaline solutions. It can be seen that clay in the oil phase has less effect than when in the aqueous phase. This is consistent with the results in Figure 40, in which clay gives maximum effect on IFT with Chatham oil. Therefore for very low NaOH concentra-

tions (0.001 wt.%), the small amount of clay in the aqueous phase can still influence the IFT. For higher NaOH concentrations (0.05%) the effect of NaOH becomes dominant.

It is observed from Figures 41 and 42 that for Cold Lake oil 0.05% clay increases IFT slightly as compared to pure alkaline solution against Cold Lake oil. This shows the reverse behaviour to Figure 40 in which 0.05% clay gives lower IFT than 0.01% clay in the aqueous phase.

The IFT responses of the Cold Lake and Lloydminster oils against alkaline solutions containing different clay concentrations are shown in Figures 41 and 42. It can be seen that with clay in the aqueous phase the minimum IFT is lower than the minimum IFT observed in the absence of clay. This is consistent with the results for Chatham oil. Table 23 lists the compositions of bentonite (clay) [42].

Table 23: The Compositions of Bentonite

Compositions	Weight, %
SiO_2	60%
Al_2O_3	15%
H_2O	8%
MgO	5%
Fe_2O_3	3%
CuO	2%
CaO	2%

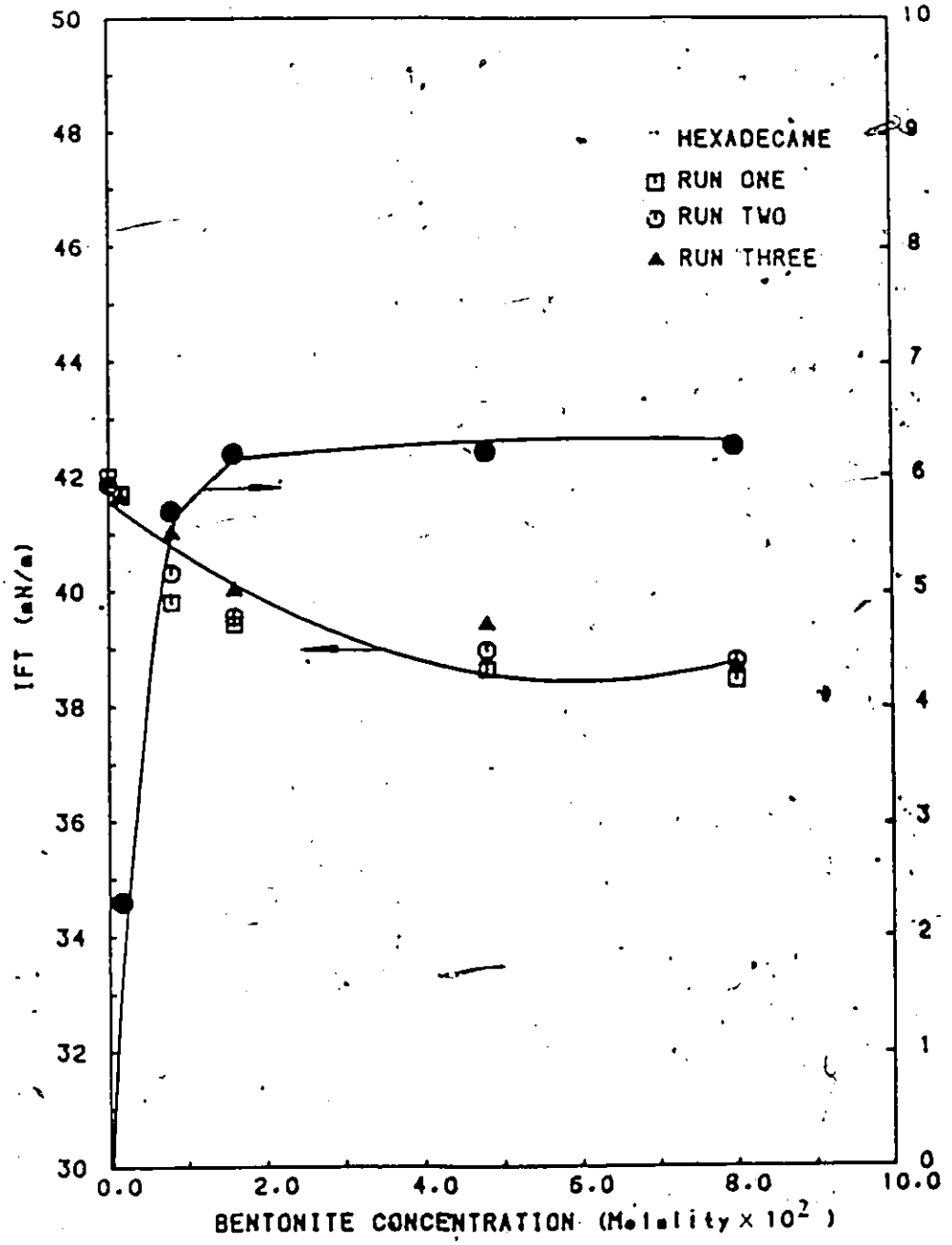

Figure 39: Effect of Bentonite Fines On IFT of Hexadecane at 25°C

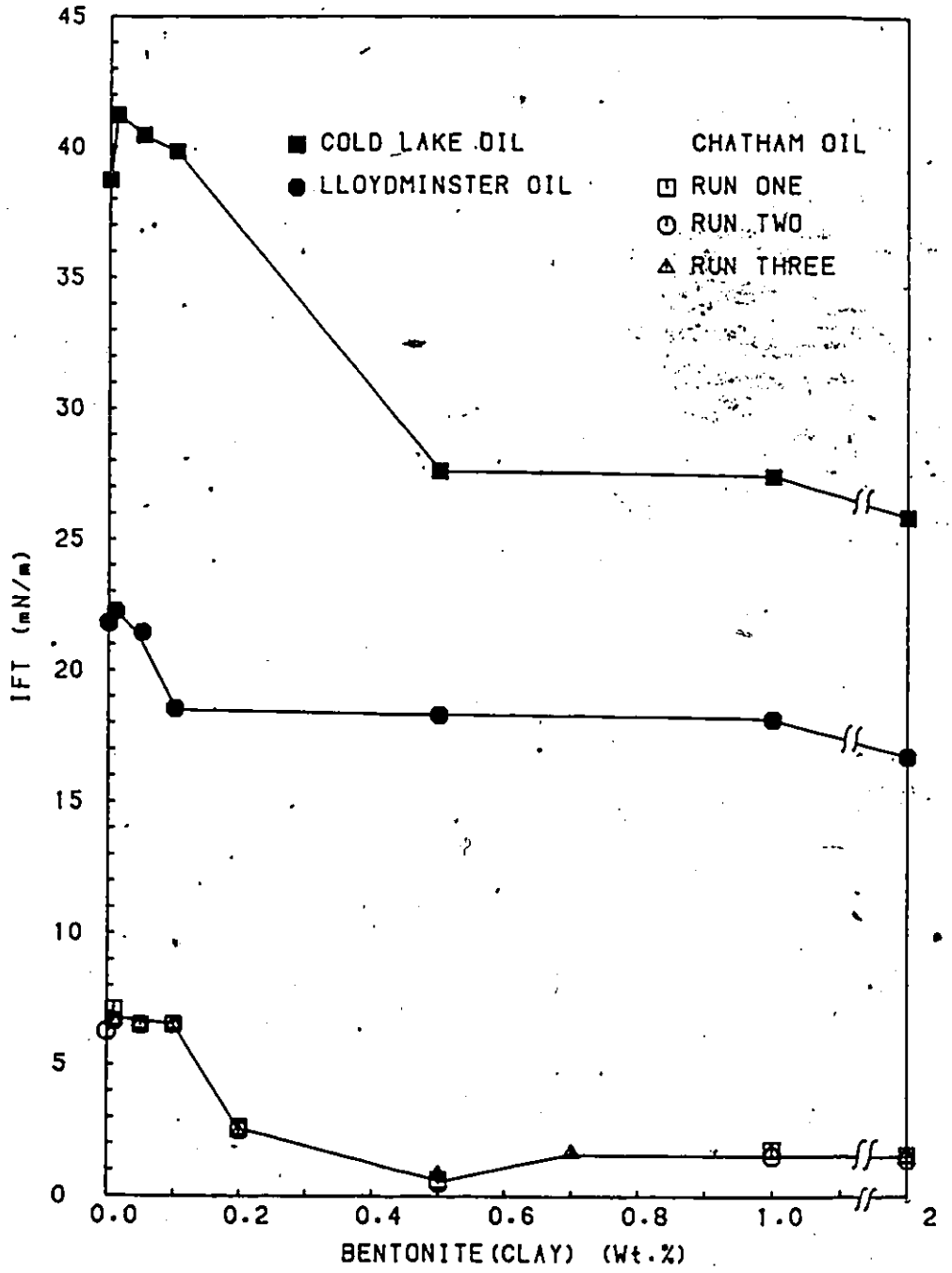

Figure 40: Effect of Bentonite Fines On IFT of Crude oils at 25°C

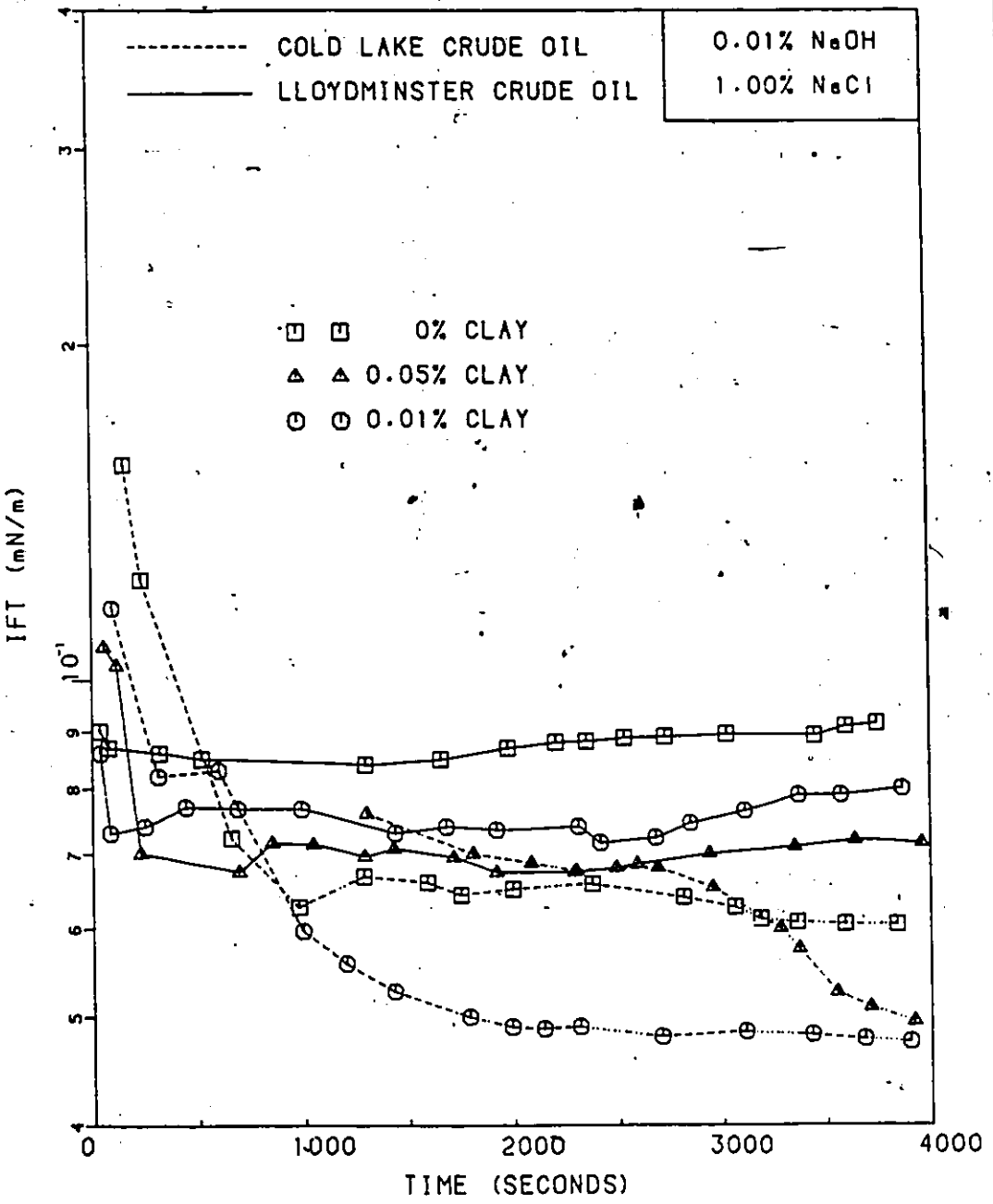

Figure 41: Effect of Bentonite (in alkaline solutions) On IFT of Crude oils at 6700 RPM and 29°C

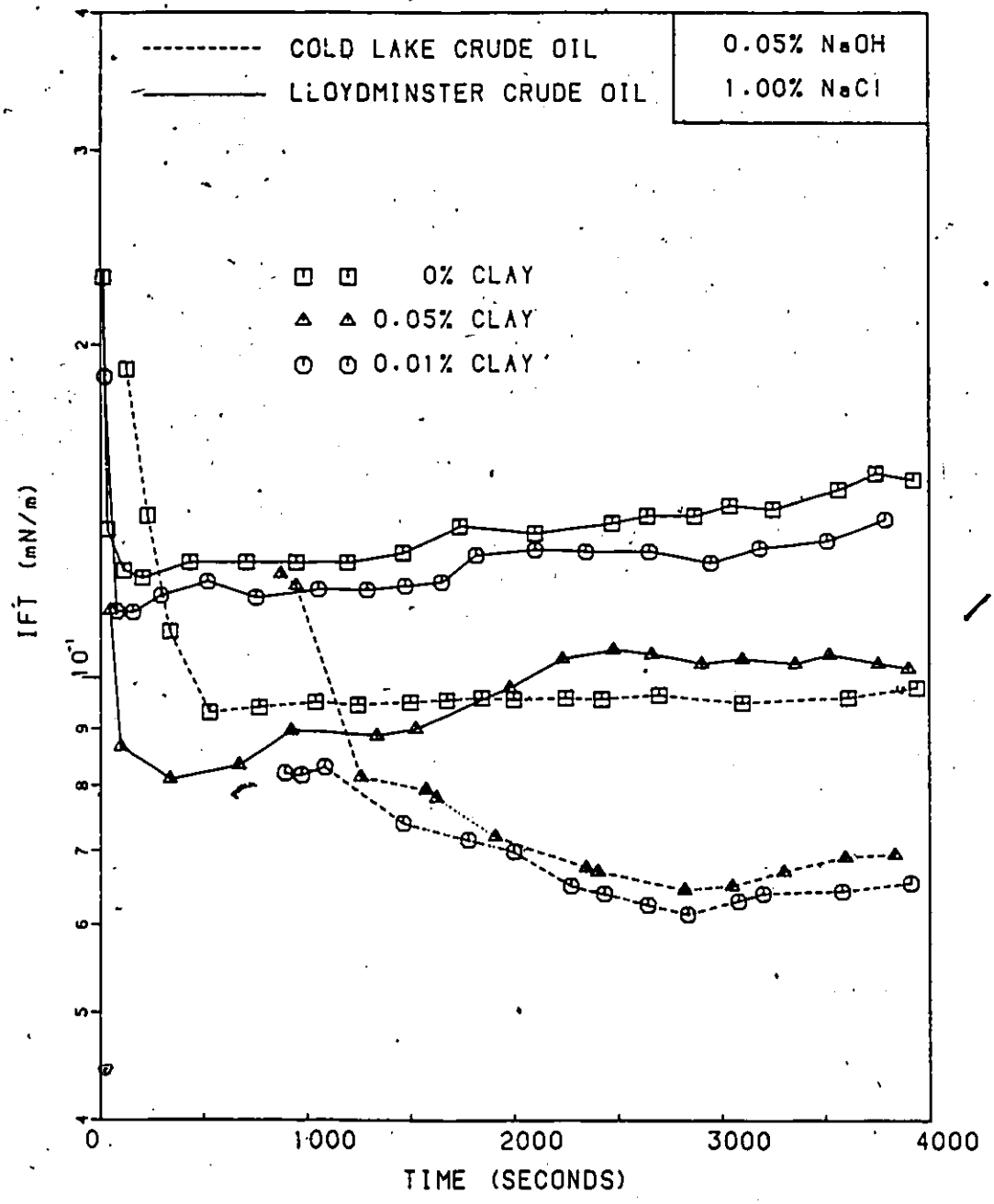

Figure 42: Effect of Bentonite (in alkaline solutions) On IFT of Crude oils at 6700 and 29°C

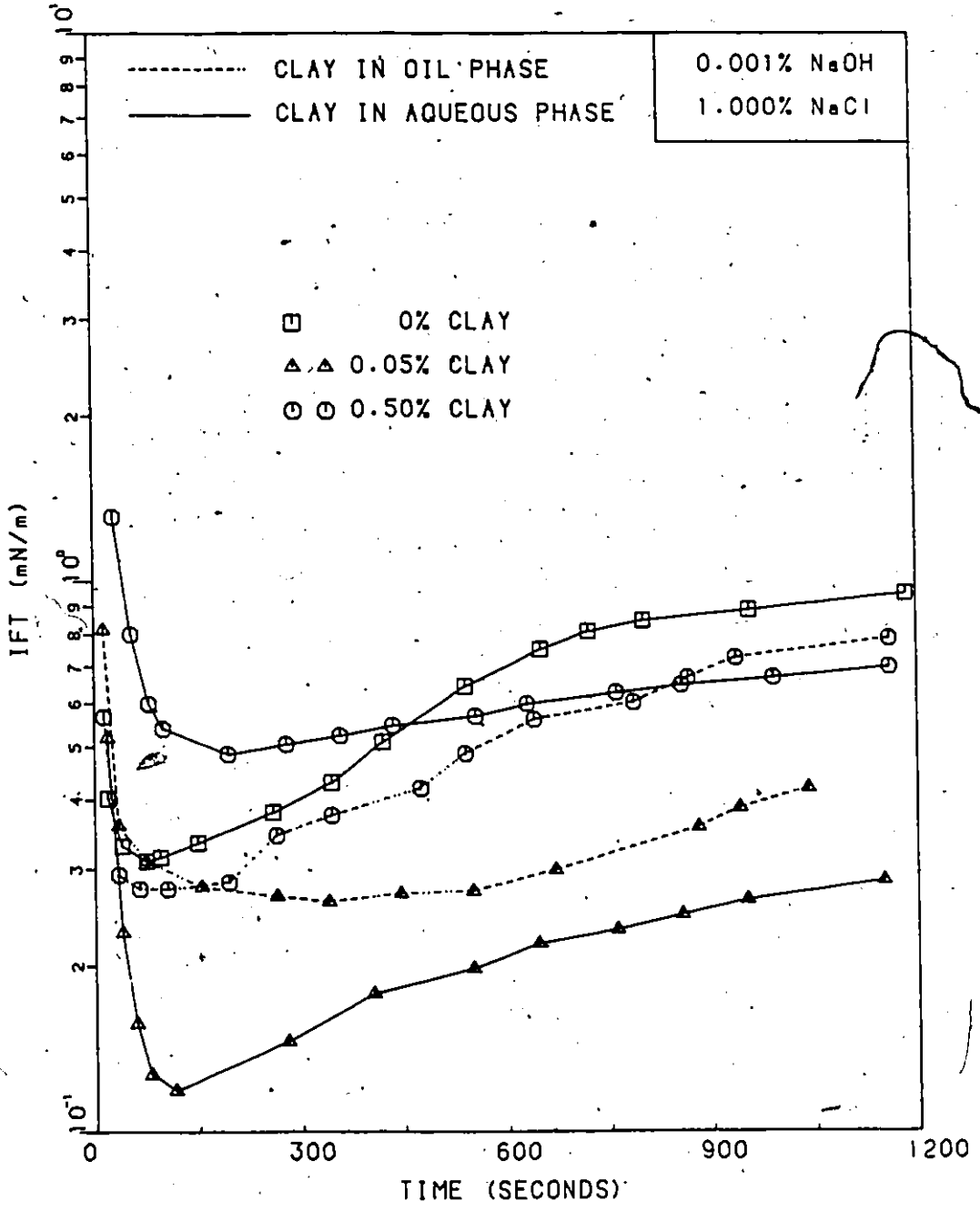

Figure 43: Effect of Bentonite (in alkaline solutions) On IFT of Chatham Crude Oil at 6700 RPM and 29°C

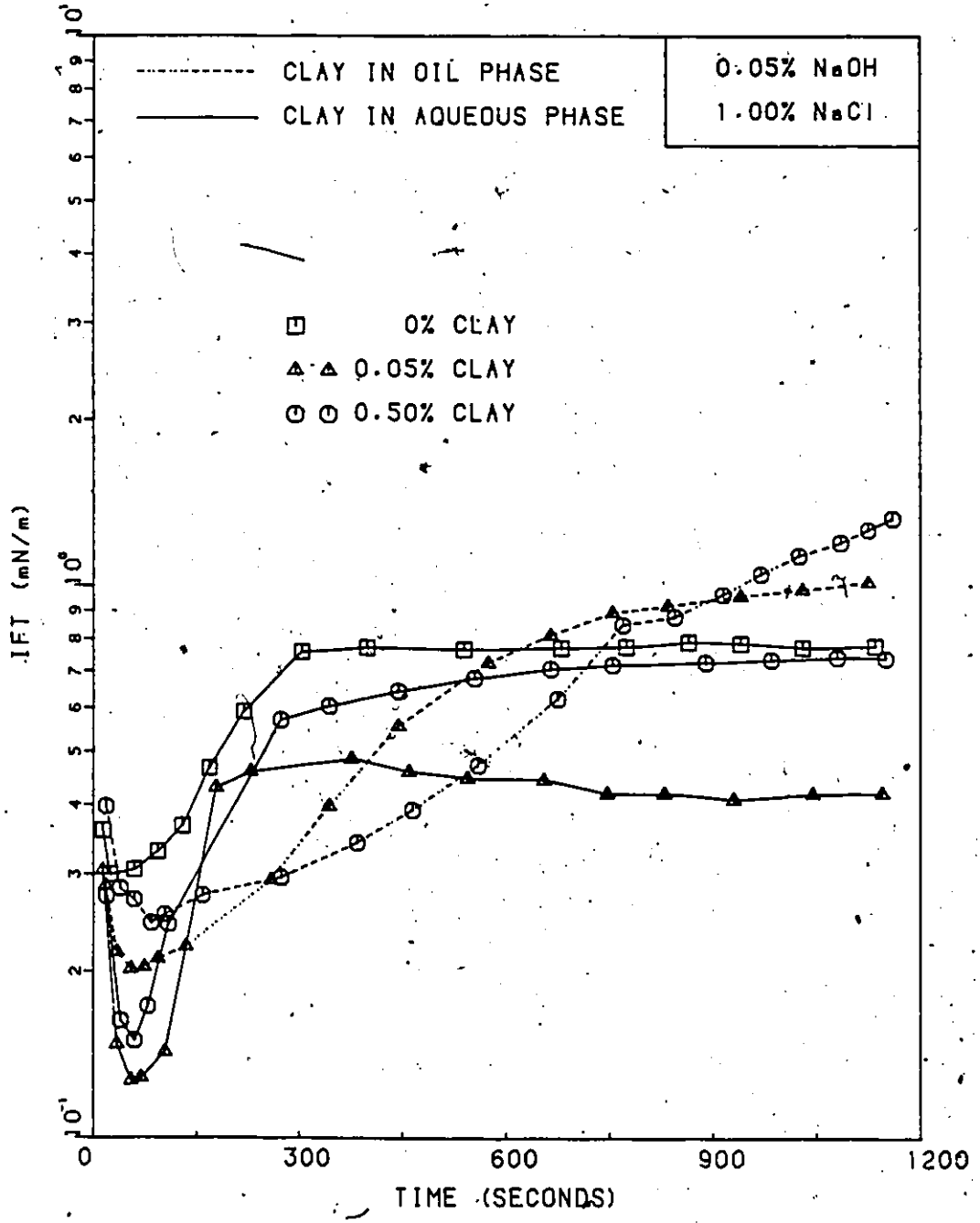

Figure 44: Effect of Bentonite (in alkaline solutions) On IFT of Chatham Crude Oil at 6700 and 29°C .

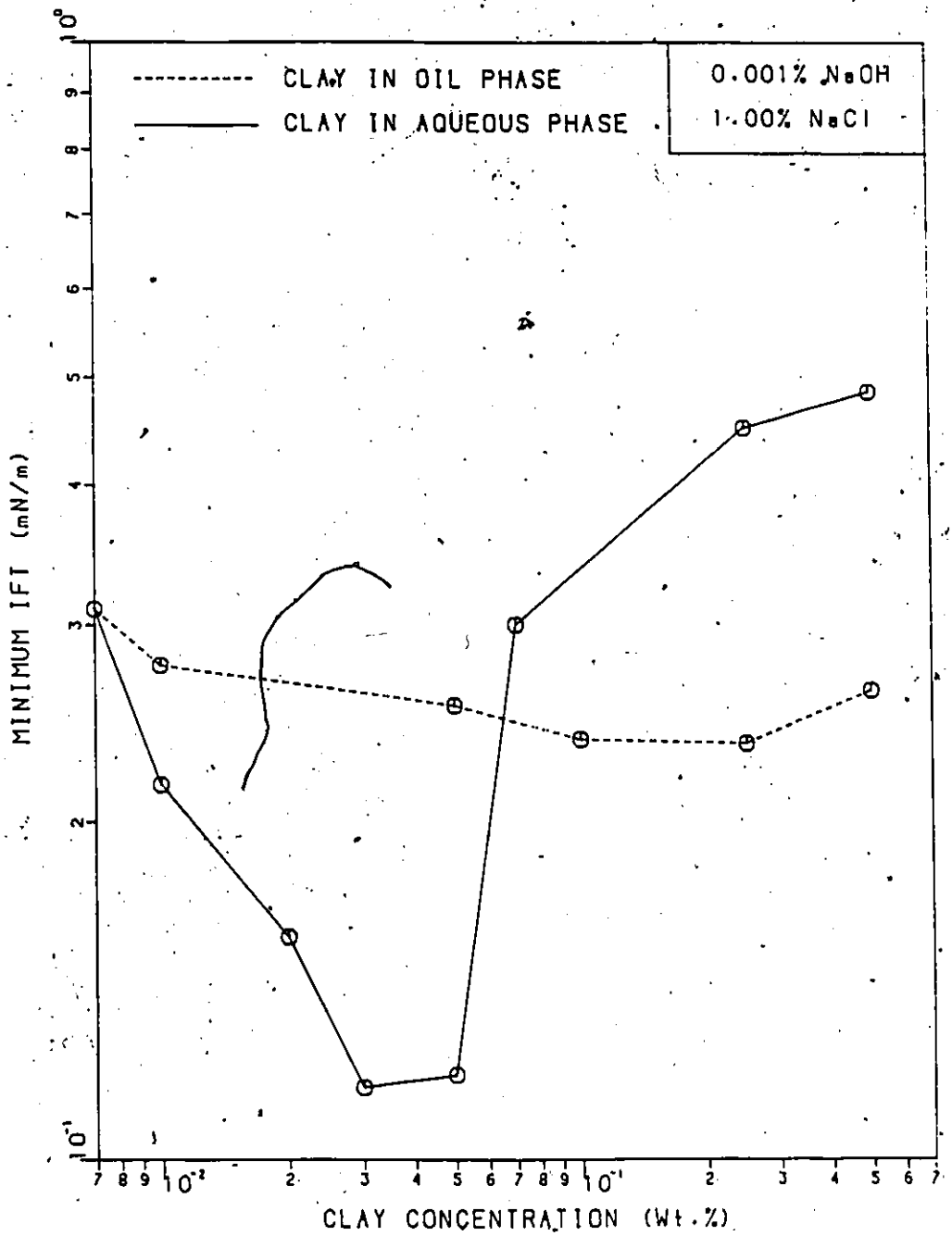

Figure 45: Effect of Bentonite Concentration On IFT of Chatham Crude Oil at 6700 and 29°C

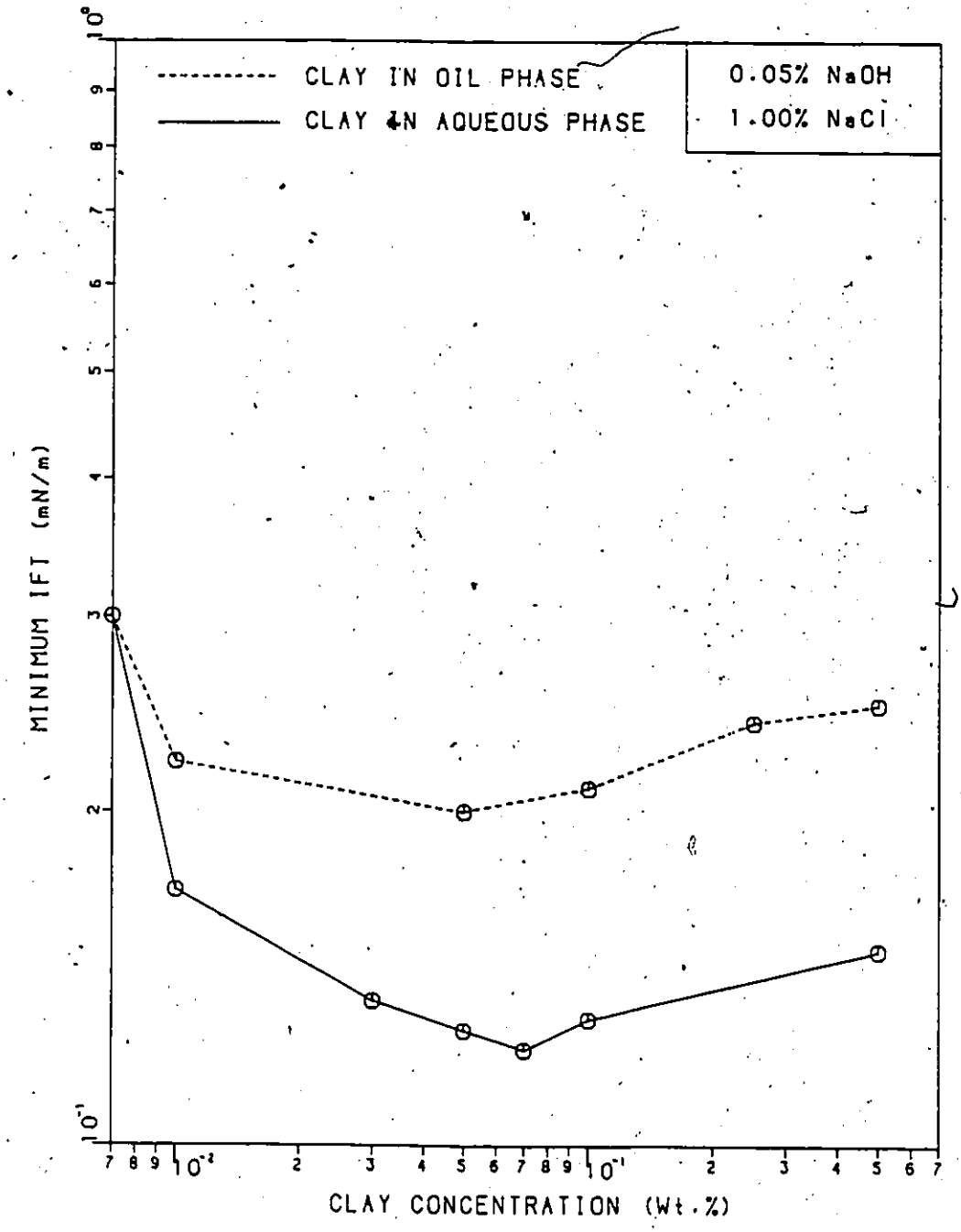

Figure 46: Effect of Bentonite Concentration On IFT of Chatham Crude Oil at 6700 RPM and 29°C

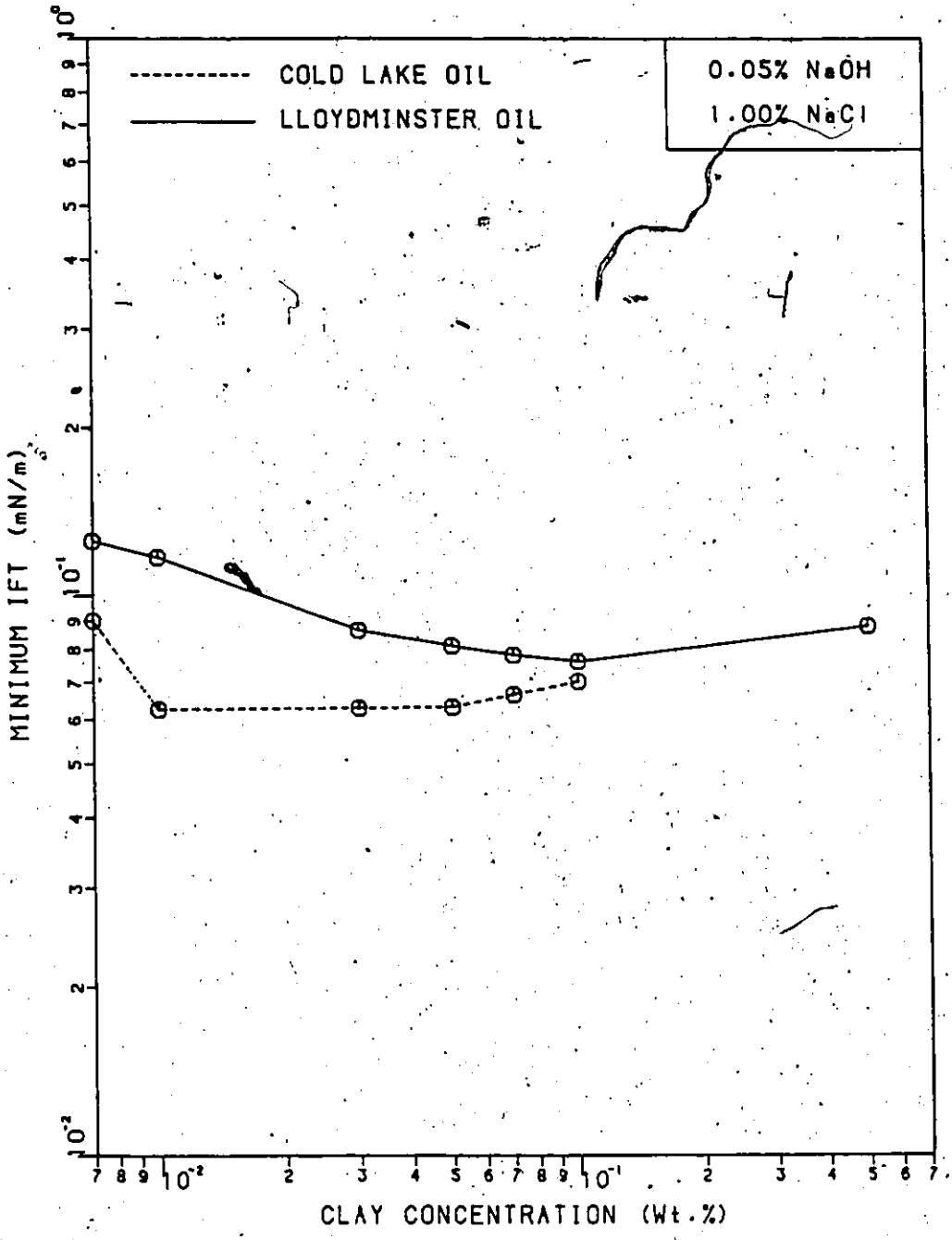

Figure 47: Effect of Bentonite Concentration On IFT of Crude oils at 6700 RPM and 29°C

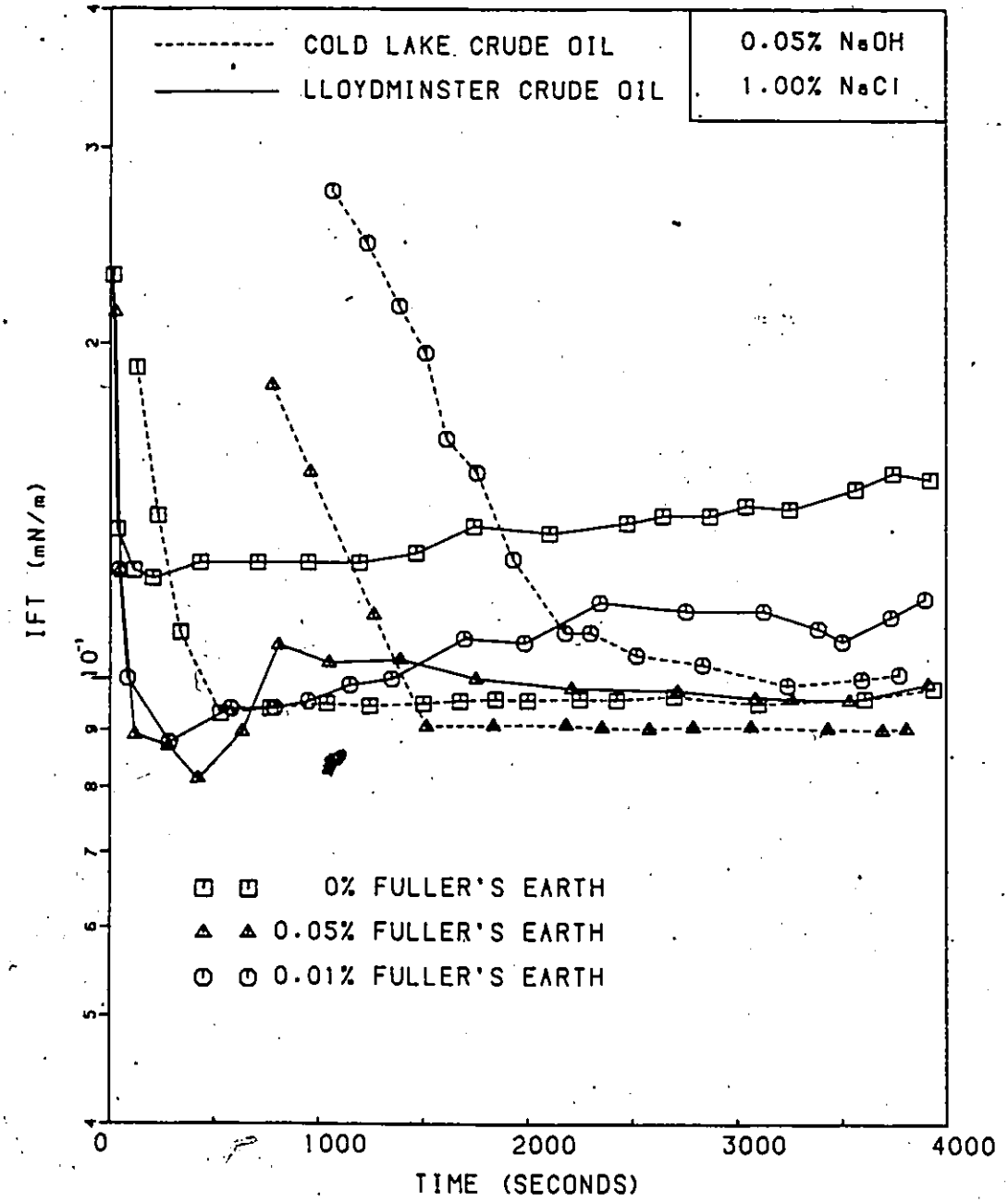

Figure 48: Effect of Fuller's Earth Fines On IFT of Crude oils at 6700 and 29°C

Chapter VIII

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. The 15 binary mixtures obtainable from benzene, toluene, o-xylene, octane, decane and hexadecane show a nearly quadratic dependence of all excess functions on composition. Negative excess interfacial tensions were observed for all binary mixtures. All the excess interfacial tensions were fitted with a polynomial Redlich-Kister equation which gave very good representations of the experimental data.

2. The excess volumes for hexadecane+benzene, toluene, o-xylene, octane and decane were calculated from density measurements and fitted by a smoothed Redlich-Kister equation. The systems hexadecane+benzene, toluene, benzene showed a positive deviation from ideal behaviour, but hexadecane+octane and +decane showed negative departure.

3. The minimum dynamic IFT for the three Canadian crude oils, Cold Lake, Lloydminster and Chatham were observed to be 10^{-3}, 10^{-3} and 10^{-2} (mN/m) with 0.04%, 0.03% and 0.1% NaOH solutions respectively. The IFT behaviour was highly dependent on interfacial

age. A pronounced minimum IFT was observed, especially for Chatham crude oil. The presence of NaCl in the aqueous phase at constant pH value raised the minimum IFT subsequently and reduced the amount of NaOH required.

4. The crude oils when diluted with hexadecane, toluene and 50 (Wt.%) hexadecane/toluene showed a continuous decrease in IFT for both heavy oils as the dilution was increased up to 90 (Wt.%), but the reverse phenomenon was observed for light Chatham oil.

5. For diluted crude oils against an alkaline solution, the minimum IFTs were higher than for the pure crudes. The higher the dilution, the higher the IFT and the greater the rate of subsequent IFT rise.

6. Bentonite (clay) had a significant effect on the IFT of hexadecane and Chatham light oil and less effect on IFT of Cold Lake and Lloydminster heavy oils.

7. When a low Bentonite concentration (0.01-0.05 Wt.%) was present in alkaline solutions, the dynamic minimum IFT of crude oils decreased slightly. However, when the Bentonite concentration was 0.1-0.5 Wt.%, the IFT of crude oils began to increase slightly. For the latter case, Bentonite had more effect on heavy oils than on light oil.

RECOMMENDATIONS

The results of this work suggest other avenues of investigation, namely:

1. Investigation of the contact angle for clay-oil-water systems since such data on contact angle are presently scarce and spotty. This would lead to an improved understanding of the effects which clays can have on IFT and related phenomena.

2. Development of an analytical equation for predicting excess interfacial tension. To accomplish this, the principle of Corresponding States and the Flory theory should be incorporated.

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