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An experimental study of the dependence of density, viscosity and excess molar volumes of several binary liquid non-electrolytes on composition at several temperature levels.

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AN EXPERIMENTAL STUDY OF THE DEPENDENCE OF DENSITY, VISCOSITY AND EXCESS MOLAR VOLUMES OF SEVERAL BINARY LIQUID NON-ELECTROLYTES ON COMPOSITION AT SEVERAL TEMPERATURE LEVELS

by

Mohammad H. Siddique

A thesis
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ABSTRACT

The densities and kinematic viscosities of eight-binary liquid non-electrolyte mixtures containing toluene, ethylbenzene and n-alkanes have been measured over the entire composition range at 20.00, 25.00, 35.00 and 40.00 °C.

The experimental data obtained in this study have been used in the calculation of absolute viscosities, excess molar volumes of mixing, excess activation energy of viscous flow, partial molal volumes and excess viscosities over the entire concentration range and at the aforementioned temperatures.

Several viscosity predictive models, e.g., McAllister, Heric's and Auslander's models, have been tested using the data collected during this investigation. The dependence of McAllister's model parameters on temperature, for systems investigated here, has been determined.

The activation energies of viscous flow for pure components as well as for mixtures have been determined.

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CHAPTER I

INTRODUCTION

1.1 General

The viscosity of liquid mixtures has attracted a great deal of attention both from a practical standpoint, where there is need for predicting the viscosity of a mixture from the properties of the pure components, and from a theoretical viewpoint where one can gain a clearer insight into the behavior of liquid mixtures [Frenkel, 1946; Partington, 1951; and Reid and Sherwood, 1977].

Viscosities of liquid mixtures provide information for the elucidation of the fundamental behavior of liquid mixtures. They also aid in testing the validity of correlations of mixture viscosities with those of the pure components. A survey of the literature on the subject of viscosities and densities of binary liquid mixtures reveals that viscosity of liquid mixtures are studied by various investigators. Reed and Taylor [1959] pointed out that a familiar approach is the hypothesis that there is a direct correlation between the viscosity and the thermodynamic behavior of a solution. They, however, could not obtain a simple relationship of that type as a result of their work.

Until now a general and global predictive equation for viscosity of liquids and liquid mixtures has not been obtained. In the kinetic theory of gases, the momentum transport which is observed in measuring the viscosity of a gas is considered to be due to the momentum which a moleclule carries with itself when moving through empty space between collisions. Every molecule is supposed to contribute the product of its momentum and its velocity in the case of viscous flow. Viscosity of gases at low density can thus be derived in terms of molecular properties assuming that the gas is composed of hard spheres. To predict temperature dependence of viscosity accurately one has to replace the rigid-sphere model by a more realistic molecular force field, e.g., Chapman-Enskog Theory [Bird et al. 1960]. Wilke [1950] extended the Chapman-Enskog Theory for multi-component systems which is in fairly good agreement with experimental results.

For liquids, however, present theoretical knowledge has not yet reached a stage of development where one can predict viscosity of liquids and liquid mixtures from molecular properties of the pure liquids. The biggest hindrance for this is the complexities in liquid state itself. Molecular volumes and other physical properties change with temperature. These changes are interpreted as changes in molecular packing in liquid due to the onset of specific molecular motions. Three distinct molecular arrangements are considered for liquid state; viz., (i) at low temperatures molecular motion being largely translational, molecular spacing is of crystalline form; (ii) at intermediate temperatures rocking or libration is an added factor; and (iii) at higher temperatures, free rotation of the molecules on their long axes is considered to take place.

Eyring's absolute reaction rate theory is the most popular viscosity model among researchers. This theory is based on partly developed kinetic theory where the motion of liquid molecules is assumed to be confined to vibration of each molecule within a cage formed by its nearest neighbors. This cage is pictured as the energy barrier, and for a molecule to escape from its cage into an adjoining site or "hole" the molecule has to overcome the potential-energy barrier related to the activation energy of viscous flow. Eyring's model is remarkably successful with simple molecules.

A reliable and generally valid theory for the quantitative prediction of viscosities of liquid mixtures from the properties of the pure components has not been established.

Arrhenius provided the simplest equation for calculating mixture viscosities for ideal binary mixtures. For non-ideal binary mixtures McAllister's cubic equation [1960] is regarded as the best correlating technique available [Reid and Sherwood, 1977]. McAllister's approach is based on Eyring's theory of absolute reaction rates thus satisfactory correlation of viscosity data is achieved whenever the viscosity of the pure components or the interaction viscosities agree with Eyring's viscosity model. Heric's model for calculating mixture viscostities is strictly empirical and can be applied to regular solutions. Auslander's approach of prediction of viscosity of binary mixtures is based on relatively elementary methods involving differential equations with partial derivatives. By integration he obtained a unitary system of equations which represents, with reasonable precision, the change with composition of the intensive properties of the mixtures (i.e., temperature, pressure, density, viscosity, surface tension... etc.).

1.2 Objectives

The objective of this work is to determine the densities and viscosities of some n-alkanes, toluene and ethylbenzene binary mixtures as accurately as possible. Such data are used in determining some of the thermodynamic properties of these systems, e.g., excess molar volume and partial molar volume over the complete composition range and at various temperature levels.

The viscosity-composition data are also used in critically testing some of the literature models which describe the dependence of viscosity on concentration.

The systems investigated in this study are: toluene (A) -n-octane (B); toluene (A)-n-decane (B); toluene (A)-n-dodecane (B); toluene (A)-n-tetradecane (B); toluene (A)-n-hexadecane(B); ethylbenzene (A)-n-octane (B); ethylbenzene (A)-n-tetradecane (B) and ethylbenzene (A)-n-hexadecane (B). Each of these systems has been investigated at the following temperatures: 20.00 °C, 25.00 °C, 35.00 °C, and 40.00 °C, respectively.

CHAPTER 2

LITERATURE SURVEY

2.1 General

The viscous properties of the liquid state, as contrasted with the gaseous state, and with the solid state in certain of its aspects, offers peculiar difficulties. The wide separation of molecules in space in gases leads to relatively little influence on each other. Consequently, the effect of the intermolecular forces can be considered negligible. Therefore, only encounters involving two, not more, molecules need be considered; since the relative orientation of two molecules involved in collision is random, the shape of the molecules is of little influence; when mechanical properties are in question it is generally possible to neglect the vibrations and rotations of the molecules. All these simplifying factors are absent when we come to consider liquids. With solids - that is crystalline solids - matters are simplified by the high degree of order in space of the atoms and molecules. The mechanical behavior is an example of a class of properties known as structure sensitive, for which local lattice irregularities have a supreme significance, involving the complication that the properties depend markedly upon the previous history of the specimen. Here liquids have an advantage, for with homogeneous liquids the constants concerned in flow are uniquely determined by the state-pressure and temperature - of the substance. A study of the viscosity of the liquids, then seems a possible source of significant information concerning the nature of the liquid state which does reveal certain striking general regularities.

This section reveals the study of viscosity of liquid and liquid mixture in a historical fashion. Starting from Newton's work on viscosity where viscosity is explicitly treated as a transport property that offers resistance to flow of liquid, with due consideration of the work of Stoke's and Poiseuille it covers the temperature dependence of viscosity where several hypotheses are presented by different researchers e.g., Duff [1897], Andrade [1930] and Hildebrand [1971]. The kinetic theory is briefly touched; giving detailed description of Eyring's absolute reaction rate theory, it moves to different literature models for predicting mixture viscosities. With a few words for excess activation energy of viscous flow the chapter ends.

2.2 Newton's Law

According to Newton, there is a physical property that characterizes the flow resistance of simple fluids which is termed viscosity. In his second book of the "Principia", he treated fluids maintained in circular motion either by an infinitely long rotating cylinder or by a rotating sphere. His objective was to investigate the properties of the Cartesian solar vortex of subtle fluid, which by its motion carried the planets round. For the purpose of calculation he had to assume a law according to which the motion or more specifically the momentum of one layer of liquid is transferred to an adjacent layer. Newton stated in his hypothesis: "the resistance arising from the want of slipperiness in the parts of the fluid is, other things being equal, proportional to the velocity with which the parts of the liquid are separated one from another". The fluid in Newton's treatment is divided into "innumerable" sheets of equal thickness, so that this assumption meant that the resistance to shearing motion is proportioned to the velocity, i.e.,

$$\tau_{yx} = -\eta \frac{dv_x}{dy} \qquad (2.1)$$

where $\frac{dv_x}{dy}$ is the velocity gradient and τ_{yx} is viscous momentum flux.

Newton did not apply to real liquids the consideration of liquid friction in motion of fluids.

2.3 Stoke's Equation

Stokes [1845] created the modern theory of the motion of viscous liquids. He attempted to relate the mobility to molecular properties. He calculated the frictional force F, acting on a hard sphere of radius, r, moving in a continuous medium of viscosity η_B with a terminal velocity V_t ... β_f is the coefficient of sliding friction. Thus Stoke's equation is given by:

$$F = 6 \pi r_A \eta_B \frac{\beta_f r_A + 2\eta_B}{\beta_f r_A + 3\eta_B} \tag{2.2}$$

Since is the friction coefficient between the surface of the sphere and the continuum, therefore if the continuum sticks to the sphere surface, then $\beta_f = \infty$, and this condition is called "non-slip condition" and Stoke's equation reduces to

$$F = 6 \pi r_A v_t \eta_B \tag{2.3}$$

Sutherland [1905] pointed out a limitation of Equation (2.3), which corresponds to $\beta_f = 0$. This is expected to apply when the diffusing molecules are considerably smaller than the solvent molecules, when the diffusing molecules can move more freely in the free spaces between the solvent molecules. Thus Equation (2.2) reduces to:

$$F = 4 \pi r_A v_t \eta_B \tag{2.4}$$

In 1845 when Stokes postulated his theory of viscous flow; Pouiseulle published his classical work on the flow of liquids through tubes. He was a doctor of medicine interested in the flow of blood through capillaries, a fact which has the furtunate consequence that, so as to compare with the anatomical vessels, he used much finer tubes. The diameters ranging from 0.14 to 0.03 mm. He worked with distilled water and obtained experimentally the well known formula for the volume V discharged in unit time

$$V = C \Delta p \frac{r^4}{l} \tag{2.5}$$

where C is a constant, Δp is the pressure difference at the two ends of the tube, r is the radius and l is the length of the capillary.

2.4 Variation of Viscosity with Temperature

The most striking feature of liquid viscosity is the very marked way in which it decreases with the rise of temperature, whereas the viscosity of gases increases with temperature. A generality seems to be that, roughly speaking, the more complicated the liquid the greater the

TABLE 2.1: Fractional Decrease in Kinematic Viscosity for a Temperature Rise From 20°C to 40°C.

Compounds	Molecular Weight	Fractional Decrease in Kinematic Viscosity
Toluene	92.14	0.813
n-Octane	114.23	0.813
Ethylbenzene	106.17	0.811
n-Decane	142.286	0.7695
n-Dodecane	170.34	0.733
n-Tetradecane	198.40	0.692
n-Hexadecane	226.45	0.657

influence of temperature. Thus with certain glasses, in the temperature range where they behave as normal, but very viscous liquids, a rise of 100 ° C diminishes the viscosity to 1000th or even much less; with a strong sucrose solution the viscosity falls to 1/70 when the temperature rises from 0 ° to 100° C; with a certain amyl alcohol to 1/18; with one of the octanes 1/3; with bromine to 5/7, for the same temperature interval. The liquid metals and monomolecular liquids in general show a comparatively small variation of viscosity with temperature: with liquid Gallium a change of temperature of over 1000°C, from 80° to 1100 ° C reduces the viscosity to 1/3 [Andrade, 1954].

In this work also it is found that this decrease in viscosity is more pronounced with heavy and complex components. Fractional decrease of kinematic viscosity associated with temperature change from 20° to 40 ° C are listed in Table 2.1.

2.4.1 Theories to account for temperature effect

To represent the variation of viscosity with temperature a variety of formulae are encountered. One class of formulae regards the change with temperature as entirely due to the change of volume. Typical of this class is Bachinski's formula [1913]:

$$\eta = C/(v - w) \tag{2.6}$$

where C and w are constants. Here v is the specific volume and w a limiting volume at which becomes infinite. The expression v − w is called the free volume: values for it can be derived from other formulae, but the results of different methods do not agree well. The essential objection to formulae of this type is that, as is clear from Bridgman's work [Bridgman, 1949] on the viscosities of liquid at high pressure, the viscosity is not a function of volume alone. Nevertheless volume-dependent formulae are still occasionally advocated Eisenschitz [1951]. Thorpe and Rodgers [1897] used Slotte's formula [Hatschek, 1928]

$$\eta = C/(1 + bT)^n \tag{2.7}$$

where T is the temperature in °C and there are three constants, but did not find it very satisfactory and obtained another three constant formula [Andrade, 1954]. Duff [1897] quoted seven formulae which had been proposed and suggested an eighth formula with four constants. After him Brillouin [Andrade, 1954] produced a formula with five constants, somewhat too many if a simple relationship is sought.

2.4.1.1 Andrade's formula

Andrade [1930] suggested the following equation to account for viscosity dependence on temperature:

$$\eta = Be^{b/T} \tag{2.8}$$

where B and b are constants. The above equation was later modified by the same author [1934] to the following form:

$$\eta v^{1/3} = C\,e^{c/vT} \tag{2.9}$$

where v is the specific volume, C and c are constants. Equation (2.9) accounts for the change in volume which accompanies change in temperature.

Andrade [1934] made a systematic comparison of Equation (2.9) with the experimental results of Thorpe and Rodger [1897] and others. Where the range of measurement, expressed as the ratio of the highest measured absolute viscosity to the lowest was 2 or less the agreement was in general within 0.3 percent; for ranges up to 3, within 1 percent; and even in more extended ranges the deviation seldom exceeded 2 percent. In the case of the normal propyl alcohol from -60° to 96°C where the viscosity changes from 0.319 to 0.0047 poise, a ratio of 67, the largest error was 2.2 percent. In general, it is to be remembered that viscosity is not a property that has been measured to a high degree of accuracy, for the liquids in question the measurements have practically all been made with some form of capillary viscometers, where the fourth power of the radius is involved, and a somewhat uncertain end-correction depending upon the volume passing through per second, is also necessary. It is not only in absolute measurements that these factors are concerned, for both the radius and the end correction change with temperature, especially the latter. Viscosities given to five significant figures are expression of genial optimism.

The general fit of the two constant formula, Equation (2.8), can then be claimed to be good for a variety of liquids, including metals, alkyl and alkenyl halides, thioethyl, primary and secondary alcohols, esters, aromatic hydrocarbons and fatty acids. Exceptional liquids are - of course - water and tertiary alcohols which are anomolous in other respects. It looks as if water behaves normally above 70 °C [Andrade, 1930].

Equation (2.8) is widely used to represent the variation of viscosity, since it is very simple to apply. Equation (2.9) gives, in general, a slightly better fit when the range of viscosity is large, but the best evidence for its validity is offered by the viscosity of the series of liquid alkali metals.

2.4.1.2 Hildebrand's theory

Hildebrand [1971] criticized the most commonly used assumption of quasi-lattice structure in case of liquids since it ignores clear evidence to the contrary. He also criticized the suggestion that there is an exponential dependence of viscosity on temperature. Moreover, he objected to the suggestion of the existence of an energy of activation, a notion that disregards the basic distinction between liquid and plastic flow. He valued Bachinski's [1913] volume dependent expression for viscosity, Equation (2.6), where the constant w is similar to the Van der Waal's b. Hildebrand modified Bachinski's formula since he failed to evaluate C as a function of molecular parameters. Hildebrand started with fluidity ($1/\eta$) depending on the ratio of free volume, V-Vo to intrinsic volume, Vo, the molar volume at which fluidity is zero. He plotted $1/\eta$ against molar volume V and obtained straight lines for all the simple liquids which yields values of Vo at the intercept, where $1/\eta = 0$; the slope of the line gives the value of C. He modified Equation (2.6) so as to recognize the fact that fluidity must depend upon relative expansion. (V - Vo)/Vo:

$$1/\eta = B \frac{V - V_o}{V_o} \qquad (2.10)$$

It is striking that the values of B for such different liquids as propane and n-heptane are the same within the precision of the data. He further reports that the values of Vo for the normal paraffins are accurately linear with molecular weight, a fact that can serve in interpolating missing values.

2.5 Kinetic Theory of Liquid State

The strict mathematical theory of liquid state aims at deducing the properties of liquids from a molecular mechanism, in particular from the potential $\phi_{(r)}$ of mutual interaction between the molecules and from their distribution. In transport phenomena, viscosity is essentially considered as the distortion of the equilibrium distribution, and the distortion is produced by the velocity gradient. The problem has been handled in particular by Kirkwood [1946], Eisenschitz [1951] and by Born and Green [Born and Green, 1949]. Kirkwood starting from fundamental considerations, simplified matters by the useful and ingenious assumption that the forces on a molecule at different instants are statistically independent, provided that the time interval between the instant is not too small, but he did not establish any relation between viscosity and temperature. Eisenschitz [1951] modified the theory of

Brownian motion so as to make it apply to a single molecule and is met, of course, with the difficulty as to what is the friction constant (or rather what are the friction constants, for he points out there are two), a matter with which Kirkwood has also dealt [Kirkwood, 1946].

Born and Green [1949] have developed an imposing theory based on distribution functions, which is not always easy to follow, especially in the matter of assumptions made in dealing with viscosity.

Eisenschitz and Born and Green [Eisenschitz, 1951] arrived at an exponential function for the variation of viscosity with temperature. None of these, however, approaching the matter from fundamental considerations of the type indicated has been able to produce results that can be checked quantitatively by experiment. In fact, Born and Green [Born and Green, 1949] say specifically "No attempt will be made to obtain exact numerical values for the physical constant, viscosity, as this will require extended and tedious calculations."

2.5.1 Eyring's absolute reaction rate theory

Eyring [1936] and Moore et al. [1953] adopted a more specialized theoretical viewpoint in developing a formula for viscosity. They considered viscous flow as a

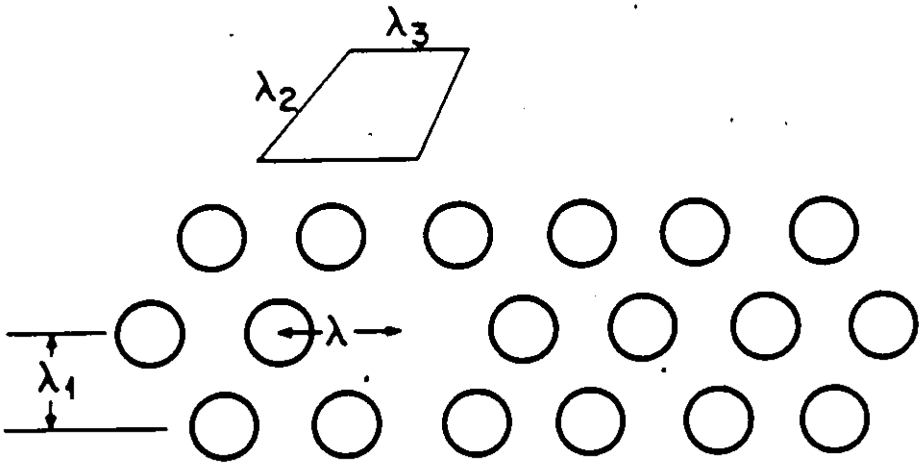


Fig. 2.1 Distance Between the Molecules in a Liquid

type of chemical reaction, such as that which takes place in a gaseous reaction or in a dilute solution.

The assumption of holes in the liquid plays an essential part in his work. Eyring's picture of shear between two layers of liquid involves the successive passage of individual molecules from one equilibrium position to another as indicated in Figure 2.1. Such a passage requires that either a hole or site becomes available. The production of such a site requires the expenditure of energy to push back other molecules. The movement of the molecule may be regarded as the passage of the system over a potential energy barrier, related to Δ^*G. In order to form a hole the size of a molecule in a liquid requires almost the same increase in free energy as to vaporize a molecule, the concentration of vapour above the liquid is a measure of such 'molecular' holes in the liquid. This provides an explanation for the law of rectilinear diameters of Cailletet and Mathias [Eyring, 1936].

The perpendicular distance between two neighboring layers of molecules sliding past each other is taken as λ_1. The motion is assumed to take place by an individual molecule in a plane (or layer) occasionally acquiring the activation energy necessary to slip over the potential barrier (arising from squeezing against its neighbors) to the next equilibrium position in this same plane. The average distance between these equilibrium positions in the direction of motion is taken as λ whereas the distance between neighboring molecules in this same direction is λ_2 which may or may not equal λ. The normal to the direction of motion is assumed to be λ_3. By definition then viscosity can be expressed as follows:

$$\eta = f\lambda_1 / \Delta v \tag{2.11}$$

where f is the force per unit area tending to displace one layer with respect to the other and Δv is the difference in velocity of these two layers which are at a distance λ_1 apart. The number of times that a molecule moves in the forward direction in a second may be written as the corresponding specific reaction rate

$$\begin{aligned} \kappa_f &= H \frac{F_a^*}{F_n} \frac{kT}{h} \left[1 + 24 \left(\frac{h\nu_i}{kT}\right)^2\right] \exp\left(- \frac{\Delta^* G - \frac{1}{2} f\lambda_2\lambda_3\lambda}{kT}\right) \\ &= \kappa_1 \exp\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right) \end{aligned} \tag{2.12}$$

where F_A^* is the partition function for the activated complex per unit of length calculated by using a zero of energy higher by $\Delta^* G$ than for F_n, the partition function for the normal state and H, the transmission coefficient, is the chance that a system having once crossed the potential barrier will react and not recross in the reverse direction. The rate constant κ, is the absolute rate for transition when no force is applied. Similarly for the backward direction:

$$\kappa_b = \kappa_1 \exp\left(\frac{-f\lambda_2\lambda_3\lambda}{2kT}\right) \quad . \tag{2.13}$$

Consequently, Δ v for each molecule in the fast layer and therefore the layer as a whole is simply

$$\Delta v = \lambda\kappa_1 \left[\exp\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right) - \exp\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right)\right] \tag{2.14}$$

or

$$\Delta v = \lambda\kappa_1 2 \text{ Sinh } (f\lambda_2\lambda_3 \lambda /2kT) \tag{2.15}$$

so that,

$$\eta = \lambda_1 f/[\lambda\kappa_1 2 \text{ Sinh } (f\lambda_2\lambda_3\lambda/2kT)] \tag{2.16}$$

For ordinary viscous flow, $f\lambda_2\lambda_3\lambda/2 << kT$ so that expanding the exponentials and keeping terms only up to the first power yields:

$$\eta = \lambda_1 kT/(\lambda^2\lambda 2\lambda 3\kappa_1) \tag{2.17}$$

when the explicit expression for this frequency κ_1, is substituted into Equation (2.17); then,

$$\eta = (\lambda_1 h F_n / \lambda^2 \lambda_2 \lambda_3 F_a^* H) \exp(\Delta^* G/kT) \tag{2.18}$$

The partition function F_n contains one more degree of freedom than F_a^*. The simplest assumption then is that all but this one degree of freedom cancels out in the ratio of partition functions and that

$$\frac{F_n}{F_a^*} = \left[1 - \exp(-h\nu_i/kT)\right]^{-1} \tag{2.19}$$

where ν_i is a vibration that can be estimated from the specific heat of liquid. In some cases ν_i may be fairly large in which case $F_n/F_a^* \simeq 1$. Taking the transmission coefficient, H, equal to 1, (which is in general a good approximateion), Equation (2.18) reduces to:

$$\eta = (\lambda_1 h/\lambda^2 \lambda_2 \lambda_3) \exp(\Delta^* G/kT) \tag{2.20}$$

For non-associated liquids instead of treating the partition function as a vibration, the liquid molecule may be treated as though it were moving in a box of length d and d^3 as the free space per molecule. So that

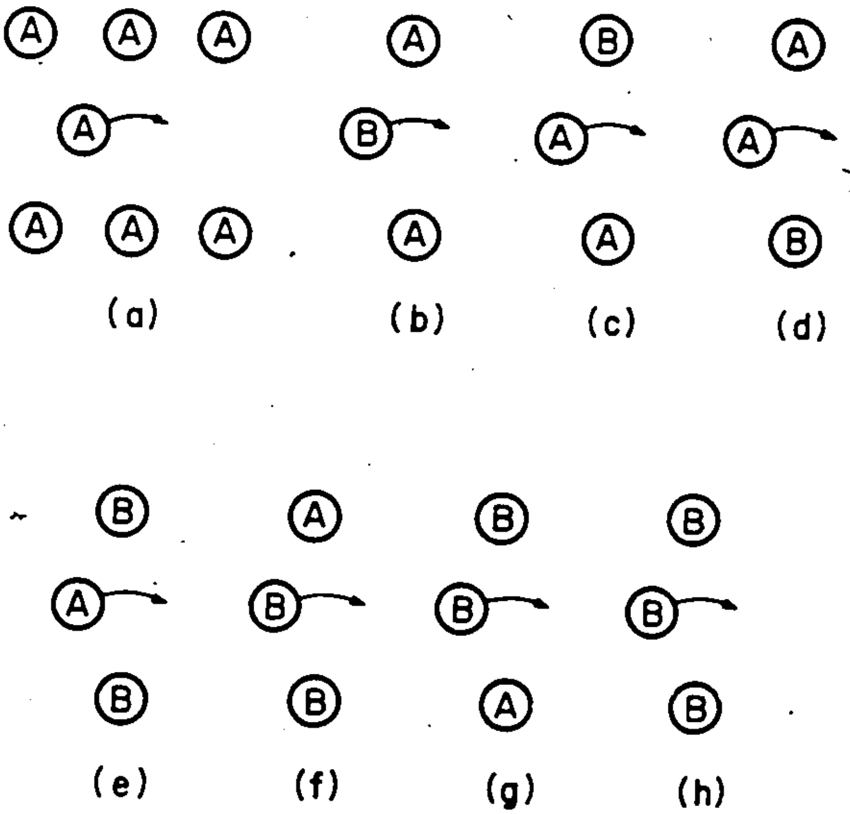


Fig. 2.2 Types of Viscosity Interactions in a Binary Mixture, Three-body Model

$$\frac{F_n}{F_a^{\star}} = (2\pi mkT)^{\frac{1}{2}}\, d/h \qquad (2.21)$$

$$\eta = \frac{\lambda_1 d}{\lambda^2 \lambda_2 \lambda_3} (2\pi mkT)^{\frac{1}{2}} \exp\,(\Delta^{\star}G/kT) \qquad (2.22)$$

Eyring [1936] pointed out that reasonable values for d gave agreement with experiment.

If the distance λ between minima for the moving molecule is taken equal to λ_1, one obtain from Equation (2.20)

$$\eta = \frac{Nh}{V} \exp\,(\Delta^{\star}G/kT) \qquad (2.23)$$

where N is Avogadro's number and V is the molar volume.

2.6 Predictive Equations for Viscosities of Liquid Mixtures

2.6.1 McAllister's model

McAllister [1960] proposed a model which is based on Eyring's theory of absolute reaction rates. In a study of the viscosity of a mixture of molecules of type A and B a number of different encounters must be considered, some of which are shown in Figure 2.2. The types of interaction considered in this case are only three bodied and are in effect all in one plane. If the two types of molecules are different in size (radius) by more than a factor of 1.5, it will probably become necessary to take into account other interactions involving more than three molecules, especially on a three dimensional basis (instead of simply in one plane). The ratios of 1.5 to 1 in size is chosen arbitrarily. The three-body model shown in Figure 2.2 seems to describe the situation well for the methanol-toluene system; the ratio of molar volumes for this sytem is about 2.6 resulting in a ratio of the radii of approximately 1.39.

The type of interaction shown in Figure 2.2.a would correspond to a free energy of activation $\Delta^* G_A$, that is for pure component A. The interaction shown in Figure 2.2.h, would be characteristic of $\Delta^* G_B$, or pure component B. Interactions of types b, c and d all correspond to two molecules of type A and one of type B. One would expect the activation energy for types c and d to be identical. They will be referred to as $\Delta^* G_{AAB}$. The free energy of activation for interaction b will be referred to as $\Delta^* G_{ABA}$. Similarly energies of activation for types f and g would be equal and designated by $\Delta^* G_{ABB}$, whereas type e may be designated by $\Delta^* G_{BAB}$.

In any binary mixture of mole fraction, x_A the fraction of the times interactions of type a would be x_A^3, as long as the number of molecules of types A and B is statistically large. Corresponding occurrences of the various types of interactions are listed below.

Type of interaction	A-A-A	A-B-A	B-A-A A-A-B	B-A-B	B-B-A A-B-B	B-B-B
Fraction of total occurrence	x_A^3	x_A^2	$2x_A^2 x_B$	$x_A x_B^2$	$2x_A x_B^2$	x_B^3

The assumption made here, of course, is that the probability of the interactions is dependent only on the concentration and not on the free energy of activation. This might well be a point to question. Perhaps the rate of each individual interaction is proportional to the energy of activation in much the same manner as the reaction rate of a chemical reaction. It may be assumed that for the mixture there is a free energy of activation $\Delta^{*}G$ and further that:

$$\Delta^{*}G = x_A^3\,\Delta^{*}G_A + x_A^2\,x_B\,\Delta^{*}G_{ABA} + 2x_A^2\,x_B\,\Delta^{*}G_{AAB} + x_A\,x_B^2\,\Delta^{*}G_{BAB}$$

$$+ 2\,x_A\,x_B^2\,\Delta^{*}G_{ABB} + x_B^3\,\Delta^{*}G_B \qquad (2.24)$$

Two additional assumptions are made at this point:

$$\Delta^{*}G_{ABA} = \Delta^{*}G_{AAB} \equiv \Delta^{*}G_{AB} \qquad (2.25)$$

$$\Delta^{*}G_{BAB} = \Delta^{*}G_{ABB} \equiv \Delta^{*}G_{BA} \qquad (2.26)$$

Incorporating Equation (2.25) and (2.26) into (2.24) results in the following expression:

$$\Delta^{*}G = x_A^3\,\Delta^{*}G_A + 3\,x_A^2\,x_B\,\Delta^{*}G_{AB} + 3\,x_A\,x_B^2\,\Delta^{*}G_{BA} + x_B^3\,\Delta^{*}G_B \qquad (2.27)$$

It was necessary to make assumptions (2.25) and (2.26) because with the cubic Equation (2.24) it is not possible to determine four arbitrary constants. Even though $\Delta^{*}G_{ABA}$ and $\Delta^{*}G_{AAB}$ are expected to be physically different, it is not possible to differentiate between them with viscosity composition data alone. Equation (2.24) may be written as follows:

$$\Delta^{*}G = x_A^3\,\Delta^{*}G_A + x_A^2\,x_B\,(\Delta^{*}G_{ABA} + 2\,\Delta^{*}G_{AAB}) + x_A\,x_B^3\,(\Delta^{*}G_{BAB} + 2\,\Delta^{*}G_{ABB}) + x_B^3\,\Delta^{*}G_B \qquad (2.28)$$

in which case

$$\Delta^{*}G_{AB} = (\Delta^{*}G_{ABA} + 2\,\Delta^{*}G_{AAB})/3 \qquad (2.29)$$

$$\Delta^{*}G_{BA} = (\Delta^{*}G_{BAB} + 2\,\Delta^{*}G_{ABB})/3 \qquad (2.30)$$

For system involving water, the three-body model, does not apply and a four-body three-dimensional interaction has to be employed.

For each type of energy of activation considered here a corresponding kinematic viscosity may be assigned.

For the mixture

$$\nu_m = \frac{hN}{M_{avg}} \exp\,(\Delta^{*}G/RT) \tag{2.31}$$

for pure component A

$$\nu_A = \frac{hN}{M_A} \exp\,(\Delta^{*}G_A/RT) \tag{2.32}$$

For interactions of the types b, c and d shown in Figure 2.2:

$$\nu_{AB} = \frac{hN}{M_{AB}} \exp\,(\Delta^{*}G_{AB}/RT) \tag{2.33}$$

For interactions of the types e, f, and g shown in Figure 2.2:

$$\nu_{BA} = \frac{hN}{M_{BA}} \exp\,(\Delta^{*}G_{BA}/RT) \tag{2.34}$$

and for pure component B

$$\nu_B = \frac{hN}{M_B} \exp\left(\Delta^{*}G_B / RT\right) \qquad (2.35)$$

substituting Equations (2.31) to (2.35) into Equation (2.27) and rearranging yields:

$$\begin{aligned} \ln \nu_m = {} & x_A^3 \ln \nu_A + 3\, x_A^2\, x_B \ln \nu_{AB} + 3\, x_B^2\, x_A \ln \nu_{BA} \\ & + x_B^3 \ln \nu_B + \ln \frac{hN}{M_{avg}} - x_A^3 \ln \frac{hN}{M_A} - 3\, x_A^2\, x_B \ln \frac{hN}{M_{AB}} \\ & - 3\, x_A\, x_B^2 \ln \frac{hN}{M_{BA}} - x_B^3 \ln \frac{hN}{M_B} \end{aligned} \qquad (2.36)$$

When one recalls that

$$x_A^3 + 3\, x_A^2\, x_B + 3\, x_A\, x_B^2 + x_B^3 = (x_A + x_B)^3 = 1$$

Equation (2.36) may be written as follows:

$$\begin{aligned} \ln \nu_m = {} & \theta(x) - \ln M_{avg} + x_A^3 \ln M_A + 3\, x_A^2\, x_B \ln M_{AB} \\ & + 3\, x_A\, x_B^2 \ln M_{BA} + x_B^3 \ln M_B \end{aligned} \qquad (2.37)$$

The various expressions for molecular weights can be written as follows:

$$M_{avg} = x_A M_A + x_B M_B$$

$$M_{AB} = (2 M_A + M_B)/3 , \quad \text{and}$$

$$M_{BA} = (M_A + 2 M_B)/3$$

Substituting these quantities into Equation (2.37) and condensing the equation results in:

$$\ln \nu_m = x_A^3 \ln \nu_A + 3 x_A^2 x_B \ln \nu_{AB} + 3 x_A x_B^2 \ln \nu_{BA}$$
$$+ x_B^3 \ln \nu_B - \ln [x_A + x_B M_B/M_A] + 3 x_A^2 x_B \ln [(2 + M_B/M_A)/3]$$
$$+ 3 x_A x_B^2 \ln [(1 + 2 M_B/M_A)/3] + x_B^3 \ln (M_B/M_A) \quad (2.38)$$

It is noted that the entire equation involves only two undetermined constants. ν_{AB} and ν_{BA} . Other features of the equation include the possibility of having a maximum, a minimum, neither or both for ν_m as a function of x_A.

If $M_B/M_A = 1$, the last four terms of the equation vanish.

2.6.2 Heric's empirical equation

Several empirical or semi-empirical relations have been used to describe the dependence of viscosity on concentration in binary liquid mixtures [Reid et al. 1977].

One of the most frequently used euations is that proposed by Arrhenius:

$$\ln \eta_m = x_A \ln \eta_A + x_B \ln \eta_B \tag{2.39}$$

where the parameters have their usual meaning. This represents well the data for nearly ideal binary mixtures but does not represent data for non-ideal solutions. The next order of approximation would appear to be a regular solution model. For this purpose Eyring's model for the viscosity of a pure liquid considering interaction between molecules is

$$\eta = \left(\frac{\lambda}{\alpha}\right)^2 \frac{hN}{V} \exp\,(f/RT) \tag{2.40}$$

where f is molar free energy of activation of flow which can be rewritten as:

$$\frac{f}{RT} = \ln \frac{\eta V}{hN} \left(\frac{\alpha}{\lambda}\right)^2 \tag{2.41}$$

for the mixture it is assumed that:

$$\frac{f_m}{RT} = x_A \frac{f_A}{RT} + x_B \frac{f_B}{RT} \quad , \quad \text{and} \tag{2.42}$$

$$\ln\left(\frac{\alpha_m}{\lambda_m}\right) = x_A \ln\frac{\alpha_m}{\lambda_A} + x_B \ln\frac{\alpha_m}{\lambda_B} \qquad (2.43)$$

so that:

$$\ln \eta_m V_m = x_A \ln \eta_A V_A + x_B \ln \eta_B V_B \qquad (2.44)$$

However, Katti and Chaudhri [1964] proposed that for regular solutions f_m would not be a linear function of f_A and f_B. Instead, there will be an additional term W given by the relation.

$$\frac{f_m}{RT} = x_A \ln\frac{f_A}{RT} + x_B \ln\frac{f_B}{RT} + x_A x_B \frac{W}{RT} \qquad (2.45)$$

W is defined as the interaction energy for the activation of flow. Equation (2.44) then takes the form

$$\begin{aligned}\ln \nu_m = {} & x_A \ln \nu_A + x_B \ln \nu_B + x_A \ln M_A \\ & + x_B \ln M_B - \ln (x_A M_A + x_B M_B) + x_A x_B \alpha_{12} \qquad (2.46)\end{aligned}$$

where α_{12} is a constant.

Heric and Brewer [1967] worked out their empirical formula along the above lines. They started from the following equation:

$$q = f_A q_A + f_B q_B + f_A f_B [A + B (f_A - f_B) + C (f_A - f_B)^2 + D (f_A - f_B)^3 + \ldots] \quad (2.47)$$

where f is a concentration variable (weight, volume or mole fraction) and q and q_A, q_B are, respectively, the physical property of mixture and pure components A and B. A power series expansion in mole fraction of the form in Equation (2.47) results in an equation extending Equation (2.46), replacing α_{12} by a power series so that

$$\ln \nu_m = x_A \ln \nu_A + x_B \ln \nu_B + x_A \ln M_A + x_B \ln M_B - \ln (x_A M_A + x_B M_B) + x_A x_B [A + B (x_A - x_B) + \ldots] \quad (2.48)$$

That order should be selected for a system beyond which additional terms did not significantly improve fitting of data. Thus the order of the fitting varies among systems.

2.6.3 Auslander's equation

Auslander [1964] approached the problem of predicting the viscosities of liquid mixtures by relatively elementary methods which are based on differential equations with partial derivatives involving intensive properties.

Generally, the change of an intensive property, L, at constant property L' is

$$\sum n_i \, (dL/dn_i)_j^{L'} = 0 \qquad (2.49)$$

where n_i is moles of the i component, subscript j refers to constant quantity of all molecules except i. The integral of Equation (2.49) considering Taylor series is given by:

$$\sum n_i \, K_i[f(L) - f(L_i)] = 0 \quad , \quad \text{or} \qquad (2.50)$$

$$f(L) = \frac{\sum n_i \, K_i f(L_i)}{\sum n_i \, K_i} \qquad (2.51)$$

where, $K_i = dE^{f(L_i)}/df(L_i)$ = constant.

E_i is the energy of component i. Now for mixtures with interaction between molecules a method of successive approximation is proposed. For a binary mixture in the first approximation one distinguishes between molecules A (noted AA) to which the closest molecule is another molecule A, and molecules A (noted AB) to which the nearest molecule is another molecule B. The same distinction is made of molecules BB and BA. For molecules randomly distributed, if their numbers are n_A, n_B and the mole fractions are x_A, x_B, , elementary statistical considerations show that the number of molecules AA, AB, BB and BA is $n_A x_A$, $n_A x_B$, $n_B x_B$, and $n_B x_A$, respectively. So that according to Equation (2.51):

$$f(L) = [K_{AA} n_A x_A f(L_{AA}) + K_{AB} n_A x_B f(L_{AB}) + K_{BB} n_B x_B f(L_{BB}) + K_{BA} n_B x_A f(L_{BA})] / \{K_{AA} n_A x_A + K_{AB} n_A x_B + K_{BB} n_B x_B + K_{BA} n_B x_A\} \qquad (2.52)$$

where L_{AA}, L_{AB}, L_{BB}, L_{BA} are the properties of pure components AA, AB, BB, BA and K_{AA}, K_{AB}, K_{BB}, K_{BA} are constants.

Substituting $K_{AA} = a_{AA}$, $K_{BB} = a_{BB}$ and

$$K_{AB} = (a_{AB} [f(L_A) - f(L_{BA})] + a_{BA} [f(L_B) - f(L_{BA})]) / [f(L_{AB}) - f(L_{BA})]$$

$$K_{BA} = (a_{AB} [f(L_A) - f(L_{AB})] + a_{BA} [f(L_B) - f(L_{AB})]) / [f(L_{BA}) - f(L_{AB})]$$

into Equation (2.52), Auslander obtained the following expression:

$$f(L) = [x_A\,(a_{AA}\,x_A + a_{AB}\,x_B)\,f(L_A) + x_B\,(a_{BA}\,x_A + a_{BB}\,x_B)\,f(L_B)]\;/\;\{x_A\,(a_{AA}\,x_A + a_{AB}\,x_B\,[a_{BA}\,x_A + a_{BB}\,x_B])\} \qquad (2.53)$$

The form of the function f(L) depends on the property considered, but the assumption may be made, justified by its success, that $f(L) = L$; so that Equation (2.53) assumes the form:

$$x_A\,(a_{AA}\,x_A + a_{AB}\,x_B)\,(L - L_A) + x_B\,(a_{BA}\,x_A + a_{BB}\,x_B)\,(L - L_B) = 0 \qquad (2.54)$$

or the following alternative form:

$$x_A\,(x_A + B_{12}\,x_B)\,(L - L_A) + A_{21}\,x_B\,(B_{21}\,x_A + x_B)\,(L - L_B) = 0 \qquad (2.55)$$

For kinematic viscosity Equation (2.55) becomes

$$x_A\,(x_A + B_{12}\,x_B)\,(\nu - \nu_A) + A_{21}\,x_B\,(B_{21}\,x_A + x_B)\,(\nu - \nu_B) = 0 \qquad (2.56)$$

The approximation may be continued and for a multi-component mixture and in the kth approximation one obtains:

$$f(L) = \frac{\sum n_i\, x_j\, x_k \,\ldots\ldots\, f(L_{ijk}\ldots.)\, K_{ijk}\ldots}{\sum n_i\, x_j\, x_k \ldots.\, k_{ijk}\ldots} \qquad (2.57)$$

Auslander [1964] pointed out that Equation (2.56) considers only the first approximation which is generally satisfactory for most of the regular mixtures with a few exceptions.

2.7 Excess Activation Energy of Viscous Flow

The liquid state is considered to be composed of molecules in box or cage. The molecular motion is considered to take place within the cage. This molecular motion may be translational (at low temperature) or rotational (at higher temperature) depending on the free volume in the 'cage'. For a molecule on the boundary of the cage to move to a new site or hole it has to attain an energy to cross the potential-energy barrier which is related to activation energy of viscous flow.

A common approach among researchers is to correlate the thermodynamic behavior with the viscosity behavior of solutions. Reed and Taylor [1959] pointed out that the free energy of mixing (activity coefficients) alone is insufficient thermodynamic information in attempting to correlate the thermodynamic behavior with the viscosity behavior of solutions. The excess volume of mixing and the entropy of mixing are also related to separate viscosity effects.

They obtained an expression for excess activation energy of viscous flow that incorporates both the viscosity and molal volume of the mixture and the pure components. They started from Eyring's absolute reaction rate theory of viscosity:

$$\eta = \left(\frac{\lambda}{a}\right)^2 \frac{hN}{V} \exp\left(\Delta^* G/RT\right) \tag{2.58}$$

For ideal solutions in the thermodynamic sense it has been suggested that the viscosity be given by

$$\ln \eta_m = x_A \ln \eta_A + x_B \ln \eta_B \tag{2.59}$$

since the volume of a solution varies with composition, a more reasonable relationship for ideal solution might better be:

$$\ln \eta_m V_m = x_A \ln \eta_A V_A + x_B \ln \eta_B V_B \tag{2.60}$$

and

$$\Delta^* G^i = x_A \Delta^* G_A + x_B \Delta^* G_B \tag{2.61}$$

For non-ideal solutions the free energy of activation differs from $\Delta^{\star}G^{i}$ by a term $\Delta^{\star}G^{E}$ which is a function of concentration

$$\Delta^{\star}G^{E} = \Delta^{\star}G_{m} - \Delta^{\star}G^{i} \tag{2.62}$$

Therefore

$$\Delta^{\star}G^{E} = \Delta^{\star}G_{m} - x_{A}\,\Delta^{\star}G_{A} - x_{B}\,\Delta^{\star}G_{B} \tag{2.63}$$

Introducing (2.58) in (2.63) one obtains

$$\frac{\Delta^{\star}G^{E}}{RT} = \ln\left(\frac{\eta_{m} V_{m}}{hN}\right) - 2\ln(\lambda/a)_{m} - \left[x_{A}\left\{\ln\frac{\eta_{A} V_{A}}{hN} - 2\ln(\lambda/a)_{A}\right\} + x_{B}\left\{\ln\frac{\eta_{B} V_{B}}{hN} - 2\ln(\lambda/a)_{B}\right\}\right] \tag{2.64}$$

and if it is assumed that for a mixture [Partington, 1951]:

$$\ln(\lambda/a)_{m} = x_{A}\ln(\lambda/a)_{A} + x_{B}\ln(\lambda/a)_{B} \tag{2.65}$$

then Equation (2.64) simplifies to

$$\frac{\Delta^{\star}G^{E}}{RT} = \ln \eta_{m} V_{m} - x_{A}\ln \eta_{A} V_{A} - x_{B}\ln \eta_{B} V_{B} \tag{2.66}$$

and if $\Delta^{\star}G^{E} > 0$, the viscosity is greater than that of an ideal mixture, [Heric and Brewer, 1967].

CHAPTER 3

EXPERIMENTAL EQUIPMENT AND PROCEDURES

3.1 Density and Viscosity Measurements

This section deals in detail with the experimental techniques and equipment used in the course of this work to measure density and viscosity.

3.1.1 Preparation of solutions

The solutions were prepared by weighing the individual components. For this purpose a Mettler HK 160 electronic balance was used which has a readability of 0.1 mg. and a reproducibility of ± 0.1 mg. The weighing range of the balance is 0 to 160 g. The balance has the special feature of taring which means that the display of the balance is reset to zero after a container has been placed on the pan. Thus the weight of the container is no longer taken into account when the weighing object is weighed in; the balance only indicates the weight of the object. This special feature was utilized while measuring the weight of each individual component. Another important feature of this electronic balance supplied by Mettler Instruments AG. Switzerland is that it offers the possibility of connecting the balance to a simple data receiver (e.g., printer) to a CL system, a calculator or a computer. Thus the balance becomes a very versatile system module. The balance takes power from an adjustable voltage line of 110/130/220/240 V permitting a voltage fluctuation of ± 10... - 15%, at a frequency of 50 / 60 Hz.

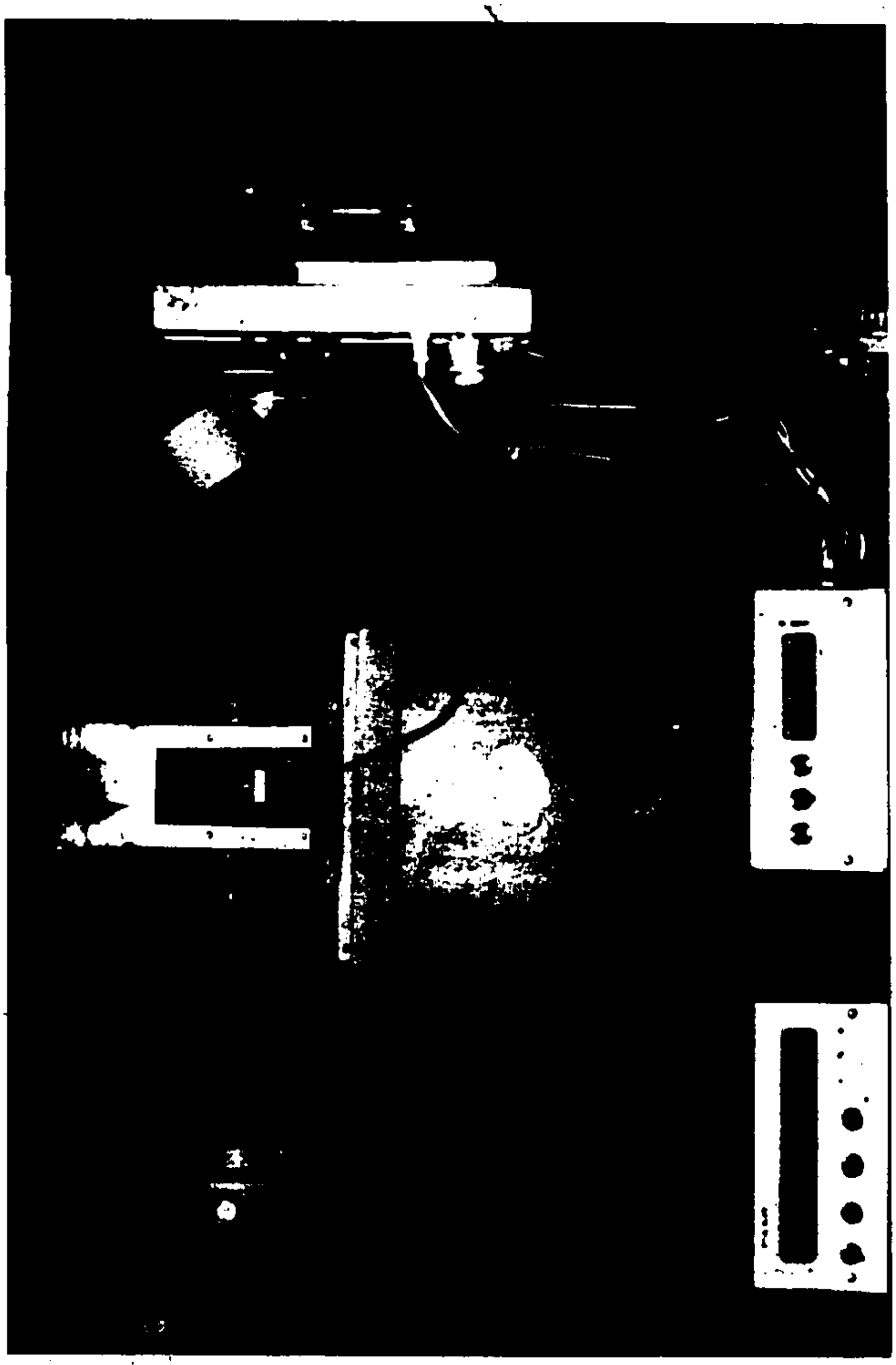
In order to eliminate evaporation losses, 0.03 liter glass vials supplied by Chromatographic Specialities Ltd. were used with teflon covering discs and aluminum seals also supplied by the same company. The pure components were injected to the vials during sample preparation using 0.01 liter hypodermic syringes fitted with a thin (size G23, 24) needle.

3.1.2 Density measurements using the density meter

A. Principle of operation and construction of the density meter:

The DMA 60 density meter in combination with DMA 602 remote measuring cells, provides a system for liquid or gas density measurement to the highest accuracy. Separating the remote cell and the electronic read-out unit permits a better thermostating of the sample cell. It also facilitates greater flexibility of the system configuration. The sample tube is electomagnetically excited to vibrate at its natural frequency. The electronic instrument (DMA 60 unit) utilizes the principle of variation of the natural frequency of vibration of the vibrating U-shaped sample tube

Figure 3.1 : Pictorial View of the Precision Density Meter



when filled with different liquids. The period of vibration of the U-shaped sample tube is displayed in an eighth decimal place period meter with selectable resolution. The oscillator is a hollow bent tube (U-shaped) made of glass. The frequency of the oscillator is influenced only by that part of the liquid which is between two fixed points on the oscillator. Overfilling of the oscillator is therefore, of no consequence. Since the volume taking part in the oscillations is exactly defined, the dependence of the oscillation frequency can be directly related to the density of the liquid.

The U-shaped sample tube in this model is made of glass (Duran 50) of which the temperature co-efficient of expansion is very small. This tube is fused into a double-walled, thermostated glass cylinder. To ensure quick temperature equilibration the cavity surrounding the sample tube is filled with a gas of high thermal conductivity.

Since the temperature in the remote measuring cell (DMA 602) is not affected by the heat generated in the electronic processing unit (DMA 60) maximum precision measurements are possible. The remote cells generate frequency analog square wave signals in synchronization with the zero amplitude positions of the oscillating sample tube. These signals are transmitted into the DMA 60 processing unit through an optical isolator for the purpose of electrical separation (between remote cell and DMA 60) and then through a noise filter. The processing unit can work only if the frequency of vibration of the sample tube is within 100 and 850 Hz.

The built-in time base gives clock pulses every 10^{-5} seconds. The period meter measures the time for the number of preselected oscillator periods by counting the number of clock pulses for the number of oscillations selected by the "period select switch". For example, if the period of the oscillator is 3.4×10^{-3} sec (DMA 602 filled with water) which corresponds to a frequency of 294 Hz (well within the range 100 - 850 Hz) and if the selector switch, "Period Select", is set at 2 k (i.e., 2000), the digital read out will show after a measurement time of 6.8 sec the value 680000; which is the number of clock pulses taken for 2000 oscillation of the sample tube $[\frac{2000}{10^{-5}} \times 3.4 \times 10^{-3} = 680{,}000]$. By means of the selector switch, higher precision read out can be obtained. By pressing the button marked "start" a new measurement cycle can be started (e.g., after filling of the sample tube). In case of operating the instrument under optimum time considerations, particularly when high values of periods is selected the two digits marked "K" gives percentage values for elapse time in the present counting cycle. The DMA 60 unit also has provisions for digital data output thus, it may be connected to a printer or a computer. The switch marked "Printer" allows the printing of either every value, every second, every fourth, every eighth or every sixteenth value. The positions 1 to 9 of the switch "Mode of Operation" are for use in phase locked loop (PLL). In this mode, remote cell 2 will be used as the time base, measurements are made on remote cell 1 and variations in the temperature or in the pressure will be automatically compensated. The window on the front panel in DMA 602 may be used to look at the measuring cell during the filling operation to ensure that no air bubbles or solids are present in the system and the liquid covers the two marks. The syringe is fitted with a plastic cap during the filling operation to ensure that there is no contact between syringe and measuring cell. As a further precaution a filling adapter with PTFE screws are attached to the measuring cell device.

The range of density that can be measured by this model is 0.5 to 2.0 g/cm^3. Assuming a thermostat accuracy of ± 0.01°C the instrument introduces a maximum error of ± 1.5 x 10^{-6} g/cm^3. The error in density of the sample itself due to its thermal expansion within the 0.02 °C range has to be added to the instruments error. This leads to a usable precision e.g., for water of + 3.5 x 10^{-6} g/cm^3. Measuring absolute densities in the range of 0 to 3 g/cm^3 the reproducible deviation from true density is not more than 1 x 10^{-4} g/cm^3.

The DMA 60 instrument is powered by alternating current allowing a frequency range in between 45 and 65 Hz. Standard operating voltages are 115 and 220 volts, depending on the position of the voltage selector switch. It allows a voltage fluctuation of ± 10%.

DMA 602 can work with a minimum sample size of 0.7 mL within a temperature range of -10°C to + 70° (controlled by ultrathermostat) and in a pressure range from vacuum to 10 bar. It takes power from standard 110 and 220 v alternating current permitting a fluctuation of ± 10%, within a frequency range of 40 - 60 Hz. It can operate under ambient condition of 0 to 45°C.

To maintain the liquid within the sample tube at a desired temperature DMA 602 has to be coupled to a circulating thermostatic bath with the two sockets provided at the back of the model.

The N4 electronic temperature controller is a high precision instrument supplied by Haake, West Germany. It has a precision of ± 0.01°C with the set-point ranging from 30 °C to 300°C. It takes power from a 220 V main at a frequency of 50 - 60 Hz. Deionized water is used as the circulating fluid for this instrument. Since the lowest set point permitted by the instrument is 30°C, this has to be coupled with another cooler in order to obtain temperature control at 20° and 25°C in the DMA 602 remote cells. The subsidiary cooler also takes power from 110V line.

The density meter is placed in a plywood box with a plexiglass front door. The box is provided with an exhaust fan, a 200 watt household bulb (two bulbs were used for temperatures at 40 and 35 C) and a precise temperature controller (thermonitor). The temperature inside the box was to be kept at the working temperature, i.e. 20, 25, 35 and 40 ± 0.1°C. The Sargent-Welch Thermonitor is supplied by Sargent-Welch Scientific Co., U.S.A.; it takes power from an 115 V A.C. line at a frequency of 30 - 60 Hz with 15 amp. current and its power rating is 1100 watt maximum. This thermonitor is connected to the electric household bulb. The box is cooled by a transmission cooler which is connected to a refrigeration machine. As the temperature in the box becomes lower than the set-point the bulb lights up to bring the temperature to the required level. As the temperature approaches the set-point the power supplied by the thermonitor decreases until it is completely cut-off as the temperature in the box reaches the set-point. An electric fan is placed inside the box to provide the required circulation. The temperature in the box is monitored by a mercury-in-glass thermometer graduated to 0.1 °C. Controlling the temperature in the box in this way has been proven to give extremely reliable results [Asfour, 1979].

With all these arrangements, after several hours of operation, almost constant readings on the density meter, were obtained with a possible error of ± 1 in the fifth decimal place.

B. Density meter equations [Asfour, 1979]

In order to obtain an equation for the calculation of density, one may consider the oscillating system in DMA 602 equivalent to a system represented by a hollow body of mass m which is suspended on a spring. Its volume V will be filled with a sample of density ρ.

The natural frequency, f of this system is given by

$$f = \frac{1}{2\pi}\left[S/(\rho V + m)\right]^{\frac{1}{2}} \tag{3.1}$$

where S is the spring constant. Therefore the period T is

$$T = 2\pi\,[(\rho V + m)/S]^{\frac{1}{2}} \qquad (3.2)$$

The simplified form of Equation (3.2) is

$$T^2 = A\rho + B \qquad (3.3)$$

or

$$\rho = \frac{1}{A}\,(T^2 - B) \qquad (3.4)$$

where

$$A = 4\pi^2\ V/S, \text{ and } B = 4\pi^2\ m/S \qquad (3.5)$$

The parameters A and B are the density meter constants which have to be obtained from a minimum of two calibration measurements on samples of known densities. Since both A and B are temperature dependent it is therefore necessary that the temperature be very well controlled. During this work seven liquids were used for the calibration of the machine constants which adequately covers the range of all the systems of binary mixtures used in this study.

For greater density differences, a deviation from the proportionality between the square of the period and the density results. The following model equation has been suggested by the supplier of the density meter

$$\rho = \frac{AT^2}{1 - BT^2} - C \tag{3.6}$$

The values of A, B and C are to be determined from known density values.

C. Procedure

Before injecting the sample into the remote cell it has to be cleaned, with ethanol. A sample is injected into the cell by means of a 0.002 liter teflon-tipped hypodermic syringe. This operation has to be done slowly and carefully in order not to entrap any air bubbles and also to prvent the syringe from any effect of lateral force which may destroy the measuring cell. At least 15 to 20 minutes period has to be allowed for temperature equilibration of the remote cell. The "start" button is pressed for a second or two. The period meter will display the reading according to the preselected resolution. Readings are taken until a stable reading is reached. Following that at least ten readings are taken and the average is used in Equation (3.6) in order to calculate the required density.

3.1.3 Viscosity measurement

The capillary tube method is still considered to be the most widely used technique for measuring liquid viscosities. This method was used throughout this work for viscosity measurement. Cannon-Ubbelohde viscometers designed by Ubbelohde in 1935 and improved recently by Cannon et al. [1960] were employed in this work. These viscometers have the following advantages:

(i) no significant variation of viscometer constants with temperature,

(ii) exact control of filling volume is not required, and

(iii) they are capable of high precision (approximately 0.2%) in routine use.

The range of viscosity of the hydrocarbon liquids used in this work varied from 0.55 to 4.5 cSt; as such two viscometers of size 25A (range 0.5 - 2.cSt), two viscometers of size 50B (range 0.8 - 4 cSt) and one visometer of size 75J) (range 1.6 - 8.cSt) were used. These were supplied by the Cannon Instrument Company. A Model M1-18M constant temperature bath also supplied by the Cannon Instrument Company was used. This b[illegible]as a range of control from approximately 10° above [illegible]t to 100°C. Temperature control is ± 0.01°C below [illegible]C using water as bath medium and ± 0.02°C above 60°C using oil as bath medium. Mercury-in-glass thermoregulator is set by turning magnetic cap until desired temperature is attained which has to be checked by another calibrated thermometer. The range was extended down below 10°C above ambient by means of 9726-C90 cooling coil also supplied by Cannon Instrument Company. All wetted parts of this instrument are made of stainless steel or glass.

The control panel has pilot light, on-off switches for preheater, stirrer motor and control circuit, and a switch used to set heater control for operation below or above 130 ° F. Below 130 °F, a relay operates a 200 watt heater to maintain control, above 130°F the same relay operates a 700-watt heater.

The method described in "Designation D445-53T", published by The American Society for Testing and Materials for Newtonian Liquids for the measurement of viscosity formed the basis of the procedures followed in this study.

A. Operation of Viscometers

After ensuring proper cleaning and drying liquid sample or liquid mixture is introduced through tube 1, Figure 3.2. to fill bulb A so that the level of the liquid was in between the upper and lower filling marks on bulb A, with the viscometer mounted in vertical position. While

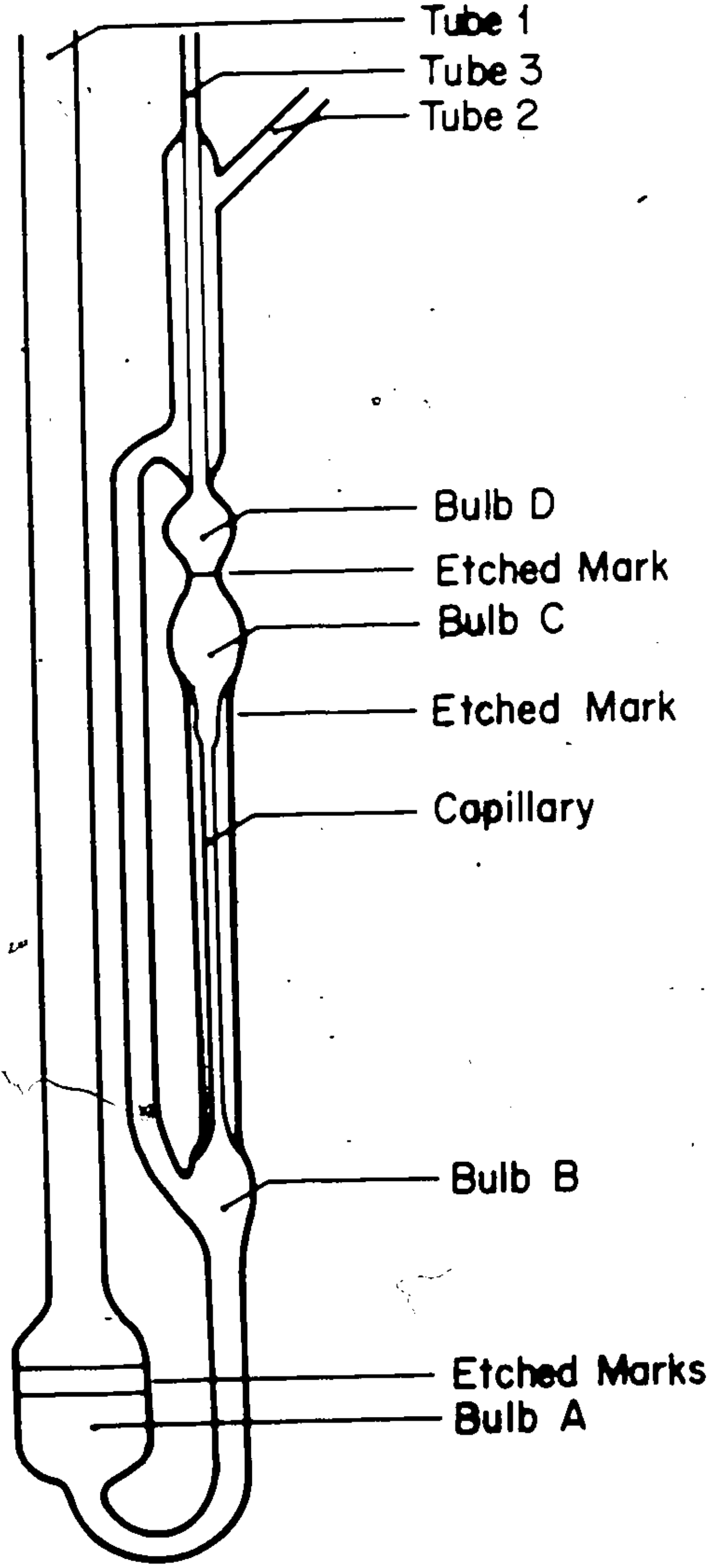


Figure 3.2 Cannon-Ubbelohde Viscometer

filling, the viscometer was [illegible]ted by an angle of 30° from the vertical in order not to entrap air bubble in bulb A. The viscometer is then placed in a constant temperature bath, and is supported by a plastic holder supplied by Cannon Instrument Company, so that the viscometer does not shake due to circulating bath water. The solution inside viscometer was allowed to reach thermal equilibrium with the bath; this takes roughly 30 minutes. Therefore, a minimum of 30 minutes was allowed for equilibration before taking any measurements.

Propipettes, a multivalve device for suction supplied by Fisher Scientific Co. was fitted to the opening of tube 3 for suction. Then a one end closed plastic tube was fitted to the opening of tube 2. Thus liquid rises through the capillary. Care was taken so that no air bubbles get entrapped within the capillary. It was reported by Howard and McAllister [1958] that sometimes air gets entrapped in the capillary during the process of suction. Once the liquid level crossed bulb D, propipette was removed from tube 3 and the plastic tube was also removed from tube 2. The efflux time was determined by measuring the time taken by the liquid meniscus to travel from the upper to the lower etched marks on bulb C. At least 3 such measurements were taken with each sample. These various runs always agreed within better than ± 0.1%.

B. Sources of error in viscometry .

Several sources of errors involved in viscometry have been discussed extensively in the literature e.g., [Cannon and Fenske, 1935, 1938, Raachou, 1938, Gennent, 1942 and Cannon, 1944].

C. Viscosity equations [Asfour, 1979]

The following equation has been used to calculate the viscosities (for the derivation see Appendix A).

$$\nu = Ct - B/t \qquad (3.7)$$

where C is a calibration constant and the term B/t is known as the "kinetic energy correction factor". B was found to be a function of time [Cannon, 1944, Cannon and Manning, 1959]. Cannon et al. [1960] introduced another parameter E, which is supposed to be time independent, resulting in the following equation:

$$\nu = Ct - E/t^n \qquad (3.8)$$

where the values of n depends on the shape of the capillary ends; for trumpet shaped ends, n has been estimated to be equal to 2, and this value was used throughout the course of this work.

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 General

The binary systems chosen for this work are all of the nonassociating type. Each of these sytems are new in a sense that the densities and viscosities of these binary mixtures are not available in the literature. All these mixtures contain an aromatic component and a saturated straight chain hydrocarbon. Present theoretical knowledge about mixtures and solutions has not yet reached a stage of development where solution properties can be expressed in terms which can be calculated completely from the properties of the pure components with any degree of generality. As such an extensive amount of data on the physical properties of solutions and mixtures are needed for their own value as well as for use in testing predictive models which are being proposed for calculating the properties of liquid mixtures from the molecular parameters of their pure components.

In this chapter some of the physical properties, viz.; densities and viscosities as well as some of the thermodynamic properties, e.g., the excess volume of mixing and the partial molar volumes of eight binary liquid mixtures over the entire composition range and at various

TABLE 4.1 : Calibration Data for the Density Meter

Temperature = 25.00°C

Substance	Density	Density Meter Reading
n-Hexane	0.65502 [Timmermans, 1950]	0.245653
n-Octane	0.69878 [Timmermans, 1950]	0.248598
n-Decane	0.72608 [Timmermans, 1950]	0.250467
Toluene	0.86220 [Timmermans, 1950]	0.259461
Benzene	0.87363 [Timmermans, 1965]	0.260212
Double Distilled Water	0.99707 [Perry, 1950]	0.268108
Carbon Tetrachloride	1.58445 [Timmermans, 1950]	0.302848

Parameters for the Density Meter, Equation

Parameters	Value
A	29.6793
B	- 0.0139029
C	1.13424

Standard Deviation of the Fit 2.15×10^{-4} (kg/L)

Temperature = 20.00°C

Substance	Density	Density Meter Reading
n-Hexane	0.65945 [Timmermans, 1950]	0.244856
n-Octane	0.70279 [Timmermans, 1950]	0.247712
n-Decane	0.72994 [Timmermans, 1950]	0.249548
Toluene	0.86683 [Timmermans, 1950]	0.258555
Benzene	0.87903 [Timmermans, 1950]	0.259343
Double Distilled Water	0.9982343 [Perry, 1950]	0.266855
Carbon Tetrachloride	1.594 [Timmermans, 1950]	0.301954

Parameters	Value
A	30.74147
B	- 0.1809495
C	1.1633883

Standard Deviation of the Fit 4.81×10^{-4} (kg/L)

TABLE 4.1, cont'd

Temperature = 35.00°C

Substance	Density	Density Meter Reading
n-Heptane	0.67104 [Garcia et al. 1986]	0.248618
n-Octane	0.69042 [Garcia et al. 1986]	0.249942
N1.0	0.7818 [Viscosity Standard]	0.256142
S3	0.8286 [Viscosity Standard]	0.259246
Benzene	0.86296 [Timmermans, 1965]	0.261512
Double Distilled Water	0.994061 [Perry, 1950]	0.269868

Parameter	Value
A	26.037965
B	0.85218661
C	1.0277652

Standard Deviation of the Fit 1.49 x 10^{-4} (kg/L)

Temperature = 40.00°C

Substance	Density	Density Meter Reading
n-Heptane	0.6668 [Timmermans, 1950]	0.249468
n-Octane	0.6862 [Timmermans, 1950]	0.250834
n-Decane	0.7150 [Marsh et al. 1986]	0.252811
Toluene	0.84836 [Timmermans, 1965]	0.261777
Benzene	0.85763 [Timmermans, 1965]	0.262414
Double Distilled Water	0.9922497 [Perry, 1950]	0.271143
Carbon Tetrachloride	1.55498 [Timmermans, 1965]	0.304983

Parameter	Value
A	28.798295
B	0.014068548
C	1.127189

Standard Deviation of the Fit 1.75 x 10^{-4} (kg/L) temperature levels are presented. These experimental data have also been utilized in testing some of the most commonly used literature viscosity models.

4.2 Calibration Data for the Density Meter

The density meter was calibrated at 20.00°C, 25.00°C, 35.00°C, and 40.00°C, using the density values of double-distilled water, n-hexane, n-octane, n-decane, carbon tetrachloride, toluene and benzene. However, at 35° C density values for n-hexane, n-decane, carbon tetrachloride and toluene were not available in the literature. Consequently, two viscosity standards and n-heptane were used instead. At 40°C n-hexane was forming bubbles in the density meter tube, so it was replaced by n-heptane. The density data used for the calibration along with their sources are reported in Table 4.1. Equation (3.6), discussed in Chapter 3, was fitted to these data. The values of the calculated parameters along with the standard deviation of the fit in kg/L are presented in Table 4.1.

It should be realized that the accuracy of the density meter is subject to the accuracy of the densities of the standard liquids used for calibration. Three highly accurate density values are required since there are three unknowns in the density meter equation, Equation (3.6). Extremely accurate density values were not available except

TABLE 4.2 : Viscometer Calibration Data

(i) Calibration Data for the Viscometer 7SJ29

Liquid	Efflux Time sec	Standard Viscosity cSt	Calculated Viscosity cSt	Percent Error	Parameters of the Viscometer	
					$C\times10^5$, cSt/sec	E, $cSt\cdot sec^2$
Temperature = 20.00°C						
N.8 N1.0 S3	90.15 152.03 489.41	0.7844 1.3280 4.2780	0.7845 1.3277 4.2781	0.01 0.02 0.001	8.741457	28.492583
Standard Deviation of the Fit = 2.85 x 10^{-5} (cSt)						
Temperature = 25.00°C						
N.4 N.8 N1.0 S3	54.51 85.447 141.153 431.663	0.4596 0.7416 1.235 3.781	0.45962 0.74152 1.23442 3.78299	0.01 0.01 0.05 0.05	8.76442	53.854
Standard Deviation of the Fit = 3.49 x 10^{-3} (cSt)						
Temperature = 35.00°C						
N1.0 S3	123.58 348.30	1.079 3.038	1.079 3.038	0.00 0.00	8.722029	-17.721295
Mean Absolute Error = 2.26 x 10^{-16} (cSt)						
Temperature = 40.00°C						
N1.0 S3	115.89 312.11	1.013 2.719	1.013 2.719	0.00 -0.00	8.7100872	-48.198533
Mean Absolute Error = 6.66 x 10^{-16} (cSt)						

TABLE 4.2 , cont'd

(ii) Calibration Data for the Viscometer SCB158

Liquid	Efflux Time	Standard Viscosity	Calculated Viscosity	Percent Error	Parameters of the Viscometer	
	sec	cSt	cSt		$T \times 10^3$, cSt/sec	E, cSt·sec^2
Temperature = 20.00°C						
N.8 N1.0 S3	183.06 311.16 1005.01	0.7844 1.3280 4.2780	0.7849 1.3265 4.2784	0.06 0.11 0.01	4.2568379	-189.06268
Standard Deviation of the Fit = 1.6 x 10^{-3} (cSt)						
Temperature = 25.00°C						
N.4 N.8 N1.0 S3	109.183 174.207 289.91 887.855	0.4596 0.7416 1.235 3.781	0.4598 0.7404 1.2351 3.7850	0.04 0.16 0.01 0.11	4.26329	67.960
Standard Deviation of the Fit = 2.96 x 10^{-3} (cSt)						
Temperature = 35.00°C						
N1.0 S3	253.263 715.74	1.079 3.038	1.079 3.038	0.00 0.00	4.2438242	-269.0818
Mean Absolute Error = 2.22 x 10^{-16} (cSt)						
Temperature = 40.00°C						
N.8 N1.0 S3	149.43 238.09 639.34	0.634 1.013 2.719	0.6343 1.0122 2.7192	0.05 0.08 0.01	4.2532982	28.073173
Mean Absolute Error = 4.58 x 10^{-4} (cSt)						

TABLE 4.2 , cont'd

iii) Calibration Data for the Viscometer 5CB159

Liquid	Efflux Time sec	Standard Viscosity cSt	Calculated Viscosity cSt	Percent Error	Parameters of the Viscometer: $C \times 10^{-3}$, cSt/sec	Parameters of the Viscometer: E, cSt-sec^2
Temperature = 20.00°C						
N.8	202.46	0.7844	0.7845	0.01	3.8820158	59.423611
N1.0	342.14	1.328	1.3277	0.02		
S3	1102.04	4.278	4.2781	0.002		
Standard Deviation of the Fit = 3.28×10^{-4} (cSt)						
Temperature = 25.00°C						
N.4	120.003	0.4596	0.4597	0.02	3.78611	78.385
N.8	191.743	0.7416	0.7411	0.07		
N1.0	318.493	1.2350	1.2337	0.10		
S3	976.940	3.7810	3.7866	0.15		
Standard Deviation of the Fit = 4.08×10^{-4} (cSt)						
Temperature = 35.00°C						
N1.0	278.59	1.079	1.079	0.00	3.8600963	-279.64623
S3	786.91	3.038	3.038	0.00		
Mean Absolute Error = 1.78×10^{-15} (cSt)						
Temperature = 40.00°C						
N.8	164.41	0.634	0.6345	0.08	3.8637558	19.529793
N1.0	261.90	1.013	1.0116	0.14		
S3	703.83	2.719	2.7194	0.01		
Mean Absolute Error = 7.57×10^{-4} (cSt)						

TABLE 4.2 , cont'd

(iv) Calibration Data for the Viscometer 25A483

Liquid	Efflux Time	Standard Viscosity	Calculated Viscosity	Percent Error	Parameters of the Viscometer	
	sec	cSt	cSt		$C\times10^3$, cSt/sec	E, $cSt\text{-}sec^2$
Temperature = 20.00°C						
N.4	266.253	0.4794	0.4796	0.03	1.7995855	-29.015616
N.8	435.50	0.7844	0.7839	0.07		
N1.0	738.057	1.3280	1.3283	0.02		
Standard Deviation of the Fit = 6.04×10^{-4} (cSt)						
Temperature = 25.00°C						
N.4	255.007	0.4596	0.45964	0.01	1.80158	-14.700
N.8	411.407	0.7416	0.74127	0.04		
N1.0	685.740	1.2350	1.23544	0.04		
Standard Deviation of the Fit = 5.51×10^{-4} (cSt)						
Temperature = 35.00°C						
N.4	234.917	0.4227	0.42285	0.03	1.797042	-38.317707
N.8	370.70	0.6669	0.66644	0.07		
N1.0	600.497	1.079	1.07922	0.02		
Mean Absolute Error = 2.78×10^{-4} (cSt)						
Temperature = 40.00°C						
N.4	225.68	0.4062	0.40637	0.04	1.7950546	-64.502209
N.8	352.61	0.634	0.63347	0.08		
N1.0	564.36	1.013	1.01326	0.03		
Mean Absolute Error = 3.20×10^{-4} (cSt)						

TABLE 4.2 , cont'd

(v) Calibration Data for the Viscometer 2SA498

Liquid,	Efflux Time	Standard Viscosity	Calculated Viscosity	Percent Error	Parameters of the Viscometer	
	sec	cSt	cSt		$C\times10^3$, cSt/sec	E, cSt-sec^2
Temperature = 20.00°C						
N.4	260.763	0.4794	0.47960	0.04	1.8402416	18.129912
N.8	425.953	0.7844	0.78376	0.08		
N1.0	721.830	1.3280	1.32831	0.02		
Standard Deviation of the Fit = 7.39 x 10^{-4} (cSt)						
Temperature = 25.00°C						
N.4	249.697	0.4596	0.45966	0.01	1.84088	0.209
N.8	402.563	0.7416	0.74107	0.07		
N1.0	671.260	1.2350	1.23571	0.06		
Standard Deviation of the Fit = 8.88 x 10^{-4} (cSt)						
Temperature = 35.00°C						
N.4	229.943	0.4227	0.42280	0.02	1.8365309	-26.743577
N.8	362.847	0.6669	0.66658	0.05		
N1.0	587.563	1.079	1.07916	0.01		
Mean Absolute Error = 1.92 x 10^{-4} (cSt)						
Temperature = 40.00°C						
N.4	220.710	0.4062	0.40629	0.02	1.8374763	-36.214221
N.8	344.720	0.6340	0.63372	0.04		
N1.0	551.310	1.0130	1.01314	0.01		
Mean Absolute Error = 1.70 x 10^{-4} (cSt)						

for water. In order to minimize errors due to uncertainty in the densities of the standard liquids, the substances listed in table 4.1 were chosen for calibration. The sources of the density data used for calibration are also reported in Table 4.1. The error in density measurement is discussed in Appendix E.

4.3 Calibration Data For the Viscometers

Cannon-Ubbelohde type viscometers have been used in this work. These viscometers were calibrated in this laboratory. Calibration was done using the standard liquids supplied by the Cannon Instrument Company. The viscosities of these standard liquids ranged from 0.4794 to 4.278 cSt at 20.00 ° C to 0.4062 to 2.719 cSt at 40.00°C. At least five readings were taken for each standard liquid for the purpose of calibration. Average values of the calibration constant "C" and the kinetic energy correction factor "E" were calculated at each temperature by the method of least squares. Details of the calibration data for each viscometers at different temperatures are listed in Table 4.2 along with the standard deviation of the fit. In total five viscometers were used in this work. Two were 25A type, two 50B type and one 75J type. The kinematic viscosities of the standard liquids used for the purpose of calibration

TABLE 4.3 : Physical Properties of Pure Components.

Compound	Density, kg/L			Kinematic Viscosity, cSt			Absolute Viscosity, cP		
	Experimental Value	Literature Values		Experimental Value	Literature Values		Experimental Value	Literature Values	
		Minimum	Maximum		Minimum	Maximum		Minimum	Maximum
Temperature = 20.00°C									
n-Octane	0.7022	0.7022 [23]	0.70267 [22]	0.7697		0.7758 [22]	0.5405		0.5479 [24]
n-Decane	0.7297	0.72672 [11]	0.73012 [2]	1.2543		1.268 [22]	0.9153	0.907 [4]	0.9256 [22]
n-Dodecane	0.7485	0.74869 [2]	0.7501 [4]	1.9743		2.008 [22]	1.4778		1.503 [22]
n-Tetradecane	0.7631	0.7596 [11]	0.7628 [2]	3.0189	2.851 [4]	3.061 [22]	2.3037	2.180 [4]	2.335 [22]
n-Hexadecane	0.7737	0.77344 [2]	0.7752 [4]	4.4614		4.492 [22]	3.4518	3.341 [4]	3.474 [22]
Toluene	0.8671	0.8666 [2]	0.8760 [12]	0.6777	0.6747 [22]	0.6786 [13]	0.5876	0.5848 [22]	
Ethylbenzene	0.8672	0.8670 [22]	0.8672 [23]	0.7701		0.780 [22]	0.6678		0.6763 [22]

TABLE 4.3, cont'd

Compound	Density, kg/L			Kinematic Viscosity, cSt			Absolute Viscosity, cP		
	Experimental Value	Literature Values		Experimental Value	Literature Values		Experimental Value	Literature Values	
		Minimum	Maximum		Minimum	Maximum		Minimum	Maximum
Temperature = 25.00°C									
n-Octane	0.6984	0.69849 [2]	0.69862 [22]	0.7298		0.7352 [22]	0.5097	0.5083 [4]	0.5136 [22]
n-Decane	0.7260	0.7260 [3]	0.72637 [1]	1.1722		1.182 [22]	0.8527	0.8527 [4]	0.8582 [3]
n-Dodecane	0.7443	0.7450 [3]	0.7465 [4]	1.8248		1.843 [22]	1.3582	1.353 [4]	1.374 [22]
n-Tetradecane	0.7598	0.75918 [1]	0.76032 [9]	2.7373	2.740 [9]	2.771 [22]	2.0799	2.035 [5]	2.104 [22]
n-Hexadecane	0.7703	0.76994 [22]	0.7709 [10]	3.9762	3.970 [10]	4.008 [22]	3.0630	3.060 [10]	3.086 [22]
Toluene	0.8619	0.8610 [19]	0.86232 [24]	0.6413	0.6378 [22]	0.6421 [7]	0.5528	0.550 [22]	0.556 [18]
Ethylbenzene	0.8620	0.8621 [8]	0.8630 [25]	0.72998		0.7367 [22]	0.6292		0.6354 [22]

TABLE 4.3, cont'd

Compound	Density, kg/L			Kinematic Viscosity, cSt			Absolute Viscosity, cP		
	Experimental Value	Literature Values		Experimental Value	Literature Values		Experimental Value	Literature Values	
		Minimum	Maximum		Minimum	Maximum		Minimum	Maximum
Temperature = 35.00°C									
n-Octane	0.6901	0.69445 [14]	0.69448 [6]	0.6580	-	0.6649 [22]	0.4541		0.4591 [22]
n-Decane	0.7178	0.71892 [1]	0.71915 [11]	1.0293	-	1.039 [22]	0.73898	-	0.7465 [22]
n-Dodecane	0.7376	-	0.73797 [1]	1.5556	-	1.575 [22]	1.1474		1.163 [22]
n-Tetradecane	0.7527	0.75212 [1]	0.75253 [11]	2.2732	-	2.305 [22]	1.71096	-	1.734 [22]
n-Hexadecane	0.7635	-	-	3.2199	-	3.252 [22]	2.4586		2.482 [22]
Toluene	0.8517	-	0.8527 [18]	0.5783	0.5741 [22]	-	0.4925	0.4898 [22]	0.4928 [8]
Ethylbenzene	0.8533	0.8497 [16]	0.8548 [15]	0.6565	-	0.6614 [22]	0.5602		0.5645 [22]

TABLE 4.3, cont'd

Compound	Density, kg/L			Kinematic Viscosity, cSt			Absolute Viscosity, cP		
	Experimental Value	Literature Values		Experimental Value	Literature Values		Experimental Value	Literature Values	
		Minimum	Maximum		Minimum	Maximum		Minimum	Maximum
Temperature = 40.00°C									
n-Octane	0.6863	0.68656 [21]	0.69042 [6]	0.6261	-	0.6343 [22]	0.4297	-	0.4355 [22]
n-Decane	0.7151	0.7150 [22]	-	0.9652	-	0.9770 [22]	0.6902	-	0.6989 [22]
n-Dodecane	0.7343	0.7344 [22]	0.73457 [21]	1.4462	-	1.4650 [22]	1.06195	-	1.0780 [22]
n-Tetradecane	0.7488	-	0.7491 [22]	2.0900	-	2.1180 [22]	1.5651	1.4650 [4]	1.5850 [22]
n-Hexadecane	0.7609	0.7595 [22]	-	2.9292	-	2.9530 [22]	2.2288	2.1500 [4]	2.2430 [22]
Toluene	0.8482	0.84725 [17]	0.85473 [20]	0.5508	0.5465 [22]	0.5675 [20]	0.4672	0.4636 [22]	0.4851 [20]
Ethylbenzene	0.8495	0.8494 [17]	0.8495 [22]	0.6242	-	0.6286 [22]	0.5303	-	0.5338 [22]

1. Aicart et al., [1981]
2. American Chemical Society, [1959]
3. Aucejo et al., [1986]
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22. Thermodynamic Research Center, [1986]
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24. Timmermans, [1965]
25. Vitali, G. and G.G. Lobbia, [1983]

cover the range of viscosities of the pure components used in this work as well as the binary mixtures.

4.4 Comparison Between the Literature Density and Viscosity Values of the Pure Components and Those Obtained in This Study

One of the objectives of this work is to measure the density and viscosity of the pure components as accurately as possible. Use of precision density meter provided a high degree of reproducibility of density measurements. While use of Cannon-Ubbelohde viscometers for measuring viscosity did produce highly reproducible results. This is in accordance with the advantages, that these viscometers have over other types of viscometers as mentioned in Chapter 3.

The experimental values for viscosity and density of the pure components obtained in this work are reported in Table 4.3 along with the corresponding literature values for comparison. In general the reproducibility of the viscosities were better than 0.1%. As can be seen from Table 4.3 the agreement between the obtained viscosities and the values reported in the literature where it is available is quite good in almost all cases. However, not many literature values are available at temperatures 35.00° and 40.00°C. Values reported by Evans [1937], were found to be

TABLE 4.4 : Density-Composition Data of the System: Toluene(A)-n-Octane(B)

Mass Fraction w_A	Mole Fraction x_A	Density kg/L	Mass Fraction w_A	Mole Fraction x_A	Density kg/L
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.0000	0.7022	0.0000	0.0000	0.6984
0.0477	0.0584	0.7082	0.0407	0.04995	0.7041
0.0840	0.1021	0.7128	0.0747	0.0910	0.7087
0.1735	0.2065	0.72497	0.1288	0.1548	0.7158
0.2609	0.3044	0.7374	0.2179	0.2566	0.7281
0.3438	0.3937	0.7496	0.3002	0.3472	0.7399
0.4492	0.5027	0.7659	0.3924	0.4447	0.7538
0.54197	0.5946	0.7809	0.4901	0.5437	0.76897
0.6507	0.6979	0.7995	0.58996	0.6408	0.7854
0.7665	0.8028	0.8203	0.7200	0.7612	0.8081
0.8778	0.8990	0.8416	0.8492	0.8747	0.8322
1.0000	1.0000	0.8671	1.0000	1.0000	0.8619
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.6901	0.0000	0.0000	0.6863
0.0358	0.0440	0.6944	0.0421	0.0517	0.6909
0.0849	0.1032	0.7008	0.0854	0.1038	0.6965
0.1685	0,2008	0.7115	0.1666	0.1986	0.7074
0.2515	0.2940	0.7226	0.2559	0.29896	0.7199
0.3481	0.3983	0.7362	0.3519	0.4023	0.7339
0.4421	0.4956	0.7504	0.4407	0.4942	0.7472
0.5478	0.6003	0.7673	0.5413	0.5939	0.7631
0.6502	0.6974	0.7852	0.6473	0.6947	0.7809
0.7655	0.8019	0.8060	0.7637	0.8003	0.8013
0.8764	0.8979	0.8269	0.8760	0.8976	0.8229
1.0000	1.0000	0.8517	1.0000	1.0000	0.8482

TABLE 4.5 : Density-Composition Data of the System Toluene(A)-n-Decane(B)

Mass Fraction w_A	Mole Fraction x_A	Density kg/L	Mass Fraction w_A	Mole Fraction x_A	Density kg/L
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.0000	0.7297	0.0000	0.0000	0.7260
0.0383	0.05798	0.7333	0.0342	0.0519	0.7299
0.0733	0.1088	0.7372	0.0675	0.1005	0.7335
0.1452	0.2078	0.7453	0.1408	0.20197	0.7414
0.22099	0.3046	0.7542	0.2202	0.3037	0.7505
0.3056	0.4047	0.7645	0.3068	0.4060	0.7609
0.38997	0.4968	0.7752	0.4039	0.5113	0.7729
0.4919	0.5992	0.7887	0.5038	0.6106	0.7860
0.6013	0.6996	0.8038	0.6075	0.7050	0.8004
0.7208	0.7994	0.8213	0.7241	0.8021	0.8173
0.8579	0.9031	0.8427	0.8476	0.8957	0.8363
1.0000	1.0000	0.8671	1.0000	1.0000	0.8619
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.7178	0.0000	0.0000	0.7151
0.0326	0.0495	0.7211	0.0284	0.0432	0.7189
0.0647	0.0966	0.7241	0.0677	0.1008	0.7230
0.1366	0.1964	0.7316	0.1409	0.2021	0.7312
0.2155	0.2979	0.7404	0.2167	0.2993	0.7396
0.2954	0.3929	0.7499	0.29596	0.3936	0.74899
0.3894	0.4962	0.7614	0.3880	0.4947	0.7603
0.4890	0.5965	0.7742	0.4856	0.5931	0.7726
0.5996	0.6981	0.7894	0.5971	0.6959	0.7876
0.71995	0.7988	0.8065	0.7226	0.8009	0.8055
0.8506	0.8979	0.8269	0.8483	0.8962	0.8242
1.0000	1.0000	0.8516	1.0000	1.0000	0.8482

TABLE 4.6 : Density-Composition Data of the System Toluene(A)-n-Dodecane(B)

Mass Fraction w_A	Mole Fraction x_A	Density kg/L	Mass Fraction w_A	Mole Fraction x_A	Density kg/L
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.0000	0.7485	0.0000	0.0000	0.7443
0.03597	0.0645	0.7517	0.0306	0.0551	0.7472
0.0600	0.1056	0.7540	0.0500	0.0887	0.7489
0.1245	0.2082	0.7604	0.1165	0.1959	0.7553
0.1885	0.3004	0.7669	0.1730	0.2789	0.7609
0.2681	0.4037	0.7753	0.2491	0.3802	0.7686
0.3512	0.5002	0.7841	0.3242	0.4701	0.7765
0.4484	0.6005	0.79497	0.4183	0.5707	0.7867
0.5597	0.7015	0.8079	0.5410	0.6854	0.8008
0.6870	0.8023	0.8236	0.6579	0.7805	0.8149
0.8311	0.90099	0.8427	0.8133	0.8895	0.8349
1.0000	1.0000	0.8671	1.0000	1.0000	0.8619
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.7376	0.0000	0.0000	0.7343
0.0292	0.0527	0.7403	0.0282	0.0508	0.7366
0.0564	0.0996	0.7429	0.0522	0.0924	0.7387
0.1224	0.2049	0.7494	0.1213	0.2033	0.7450
0.1819	0.2913	0.7550	0.1884	0.3003	0.7514
0.2667	0.4021	0.7634	0.2702	0.4063	0.7594
0.3497	0.4986	0.7720	0.3606	0.5104	0.7685
0.4422	0.5944	0.78199	0.4467	0.5988	0.7779
0.5544	0.69698	0.7947	0.5597	0.7015	0.7906
0.6811	0.7979	0.8101	0.6838	0.7999	0.8054
0.8266	0.8981	0.8285	0.82799	0.89898	0.8234
1.0000	1.0000	0.8517	1.0000	1.0000	0.8482

TABLE 4.7 : Density-Composition Data of the System Toluene(A)-n-Tetradecane(B)

Mass Fraction ω_A	Mole Fraction x_A	Density kg/L	Mass Fraction ω_A	Mole Fraction x_A	Density kg/L
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.0000	0.7631	0.0000	0.0000	0.7598
0.0318	0.0661	0.7653	0.0223	0.0469	0.7606
0.0537	0.1089	0.7671	0.0528	0.1073	0.7630
0.1082	0.2072	0.7717	0.1022	0.1969	0.7672
0.1678	0.3028	0.77699	0.1565	0.2754	0.7719
0.2360	0.3994	0.7830	0.2259	0.3858	0.7781
0.3201	0.5034	0.7909	0.3100	0.4918	0.7859
0.3927	0.5820	0.7979	0.4049	0.5944	0.79496
0.5232	0.7026	0.8113	0.4984	0.6815	0.8043
0.6569	0.8048	0.8256	0.6400	0.7929	0.8191
0.8100	0.9018	0.8430	0.7978	0.8947	0.8369
1.0000	1.0000	0.8671	1.0000	1.0000	0.8619
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.7527	0.0000	0.0000	0.7488
0.0245	0.0513	0.7545	0.0240	0.0503	0.7514
0.0486	0.0991	0.7564	0.0479	0.0977	0.7532
0.1027	0.1977	0.7608	0.0957	0.1856	0.7569
0.1638	0.29669	0.7660	0.1627	0.2950	0.7627
0.2266	0.3868	0.7715	0.2284	0.3892	0.7683
0.3150	0.4975	0.7794	0.3132	0.4954	0.7756
0.4079	0.5973	0.7880	0.4008	0.5902	0.7837
0.5180	0.6983	0.7986	0.5092	0.6908	0.7938
0.6448	0.7963	0.8118	0.6566	0.8046	0.8091
0.8052	0.89897	0.8291	0.8029	0.8977	0.8250
1.0000	1.0000	0.8517	1.0000	1.0000	0.8482

TABLE 4.8 : Density-Composition Data of the System Toluene(A)-n-Hexadecane(B)

Mass Fraction [illegible]	Mole Fraction x_A	Density kg/L	Mass Fraction ω_A	Mole Fraction x_A	Density kg/L
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.0000	0.7737	0.0000	0.0000	0.7703
0.0186	0.0444	0.7749	0.0284	0.06697	0.7724
0.0414	0.0959	0.7765	0.0578	0.13099	0.7745
0.0941	0.2033	0.7805	0.0886	0.1927	0.7767
0.1373	0.2811	0.7838	0.1313	0.2708	0.7801
0.2057	0.38898	0.7892	0.2373	0.4333	0.7885
0.2866	0.4969	0.7959	0.2914	0.5026	0.7929
0.3794	0.6004	0.8038	0.3763	0.5973	0.8001
0.4843	0.6977	0.8132	0.4890	0.7017	0.8099
0.6163	0.7978	0.8256	0.6170	0.7984	0.8218
0.7863	0.9004	0.8430	0.781[illegible]	0.89799	0.8383
1.0000	1.0000	0.8671	1.0[illegible]	1.0000	0.8619
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.7635	0.0000	0.0000	0.7609
0.0151	0.0363	0.7646	0.0224	0.0533	0.7624
0.0427	0.0987	0.7664	0.0415	0.0961	0.7637
0.0984	0.2114	0.7702	0.0986	0.2119	0.7679
0.1532	0.3078	0.7738	0.1455	0.2950	0.7712
0.2128	0.3992	0.7781	0.2103	0.3956	0.7762
0.2918	0.5031	0.7843	0.2879	0.4984	0.7823
0.3754	0.5953	0.7912	0.3786	0.5995	0.7896
0.4904	0.7028	0.8014	0.4865	0.6995	0.7987
0.6149	0.7969	0.8131	0.6118	0.7946	0.8099
0.7813	0.8978	0.82995	0.7856	0.9000	0.8266
1.0000	1.0000	0.8517	1.0000	1.0000	0.8482

TABLE 4.9 : Density-Composition Data of the System Ethylbenzene(A)-n-Octane(B)

Mass Fraction w_A	Mole Fraction x_A	Density kg/L	Mass Fraction w_A	Mole Fraction x_A	Density kg/L
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.0000	0.7022	0.0000	0.0000	0.6984
0.0508	0.0544	0.7086	0.0525	0.0562	0.7054
0.0962	0.1028	0.7146	0.0943	0.1008	0.7108
0.1936	0.2053	0.7280	0.18695	0.1983	0.7236
0.2899	0.3052	0.7419	0.2768	0.2917	0.7363
0.3924	0.40997	0.7574	0.3805	0.3979	0.7517
0.49298	0.5113	0.7734	0.5720	0.5898	0.7823
0.6019	0.6193	0.7916	0.6851	0.7007	0.8017
0.6961	0.7113	0.80795	0.7851	0.7972	0.8197
0.7955	0.8071	0.8261	0.8894	0.8964	0.8396
0.8945	0.9012	0.8452	1.0000	1.0000	0.8620
1.0000	1.0000	0.8672			
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.6901	0.0000	0.0000	0.6863
0.0480	0.0515	0.6963	0.04497	0.0482	0.6918
0.0908	0.0971	0.7018	0.0913	0.0976	0.6979
0.1757	0.1865	0.7131	0.1858	0.1971	0.7106
0.2819	0.2969	0.7281	0.27996	0.2949	0.7238
0.3809	0.3983	0.7428	0.3800	0.3974	0.7386
0.4718	0.4900	0.7568	0.4719	0.4902	0.7527
0.5742	0.5919	0.7734	0.5788	0.5966	0.7700
0.6861	0.7016	0.7926	0.6798	0.6955	0.7871
0.78596	0.7980	0.8108	0.7846	0.7967	0.8062
0.8918	0.8987	0.8311	0.8895	0.8965	0.8260
1.0000	1.0000	0.8533	1.0000	1.0000	0.8495

TABLE A4.11 Density-Composition Data of the System Ethylbenzene A – n-Tetradecane B

Mass Fraction w_A	Mole Fraction x_A	Density kg/L	Mass Fraction w_A	Mole Fraction x_A	Density kg/L
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.0000	0.7631	0.0000	0.0000	0.7598
0.0286	0.0522	0.7653	0.0347	0.0629	0.7622
0.0651	0.1152	0.7683	0.0593	0.1057	[illegible]
0.1246	0.2101	0.7734	0.1251	0.2109	0.7699
0.1817	0.2932	0.7784	0.1889	0.3033	0.7755
0.2664	0.4042	0.7860	0.2586	0.3946	0.7818
0.3452	0.4963	0.7935	0.3492	0.5007	0.7902
0.4426	0.5976	0.8031	0.4459	0.6007	0.7997
0.5526	0.6977	0.8145	0.5555	0.7002	0.8109
0.6798	0.7987	0.8281	0.6783	0.7976	0.8239
0.8279	0.8999	0.8452	0.8242	0.8976	0.8404
1.0000	1.0000	0.8672	1.0000	1.0000	0.8622
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.7522	0.0000	0.0000	0.7488
0.0290	0.0529	0.7547	0.0279	0.0509	0.7509
0.0567	0.1010	0.7565	0.0516	0.0925	0.7527
0.1178	0.1997	0.7613	0.1174	0.1991	0.7584
0.18295	0.2950	0.7665	0.1889	0.3032	0.7643
0.2573	0.3929	0.7734	0.2633	0.4005	0.7709
0.3463	0.4975	0.7816	0.3451	0.4961	0.7782
0.4264	0.5814	0.7892	0.4369	0.5918	0.7869
0.5527	0.6975	0.8020	0.5558	0.7004	0.7989
0.6827	0.8008	0.8158	0.6782	0.7975	0.8115
0.8240	0.8974	0.8316	0.8276	0.8997	0.82798
1.0000	1.0000	0.8533	1.0000	1.0000	0.8493

TABLE 4.11 Density-Composition Data of the System Ethylbenzene A - n-Hexadecane B

Mass Fraction w_A	Mole Fraction x_A	Density kg L^{-1}	Mass Fraction w_A	Mole Fraction x_A	Density kg L^{-1}
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.0000	0.7737	0.0000	0.0000	0.7703
0.0260	0.0539	0.7757	0.0337	0.0692	0.7725
0.0512	0.1029	0.7775	0.0570	0.1142	0.7742
0.1039	0.1983	0.7816	0.1283	0.2058	0.7779
0.1657	0.3022	0.7865	0.1729	0.3084	0.7829
0.2402	0.4028	0.7923	0.2421	0.4033	[illegible]
0.3129	0.4927	0.7984	0.3215	0.5027	[illegible]
0.4082	0.5953	0.8066	0.42296	0.6099	0.8037
0.5199	0.6978	0.8167	0.5202	0.69799	0.8127
0.6511	0.7992	0.8291	0.6564	0.8029	0.8257
0.8087	0.9002	0.8454	0.8098	0.9008	0.8408
1.0000	1.0000	0.8672	1.0000	1.0000	0.8622
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.7635	0.0000	0.0000	0.7609
0.0243	0.0505	0.7643	0.0242	0.0502	0.7623
0.0449	0.0912	0.7657	0.0488	0.0987	0.7637
0.0998	0.1912	0.7698	0.1039	0.1983	0.7678
0.1671	0.2997	0.7749	0.1695	0.3033	0.7727
0.2401	0.4026	0.7808	0.2333	0.3935	0.7776
0.3188	0.4995	0.7872	0.3176	0.4981	0.7845
0.4097	0.5968	0.7949	0.4115	0.5986	0.7921
0.5217	0.6994	0.8047	0.5215	0.6995	0.8016
0.6509	0.7991	0.8165	0.6558	0.8025	0.8137
0.8061	0.8987	0.8316	0.80599	0.8986	0.8286
1.0000	1.0000	0.8533	1.0000	1.0000	0.8495

somewhat lower than the corresponding experimental values obtained in this work whereas values reported by TRC [1986] were found to be higher than the corresponding experimental values in almost every case.

4.5 Density-Composition Data

The density of each system over the entire composition range at every temperature level was measured. The density values were obtained using the period reading of density meter and the density meter equation, Equation (3.6). These values are presented in Tables 4.4 to 4.11. The density values reported in these tables are the average of ten measurements. Each density meter reading is one hundred times greater than the actual period of the U-tube, therefore a density meter reading 0.260212 (Benzene at 20°C) correspond to a period of 2.60212×10^{-3} seconds. The reproducibility of the density meter readings was found to be better than 5×10^{-8} seconds in the case of double-distilled water at temperatures 20.00°C and 25.00°C and ± 1×10^{-7} seconds at temperatures 35.00°C and 40.00°C for n-octane. A change of 1×10^{-7} seconds in the density meter reading at 20.00°C correspond to a change of about 1.59×10^{-4} kg/L in density value.

TABLE 4.12: Least Squares Constants for the Equation $\rho = \sum_{i=0}^{n} A_i x_A^i$, kg/L

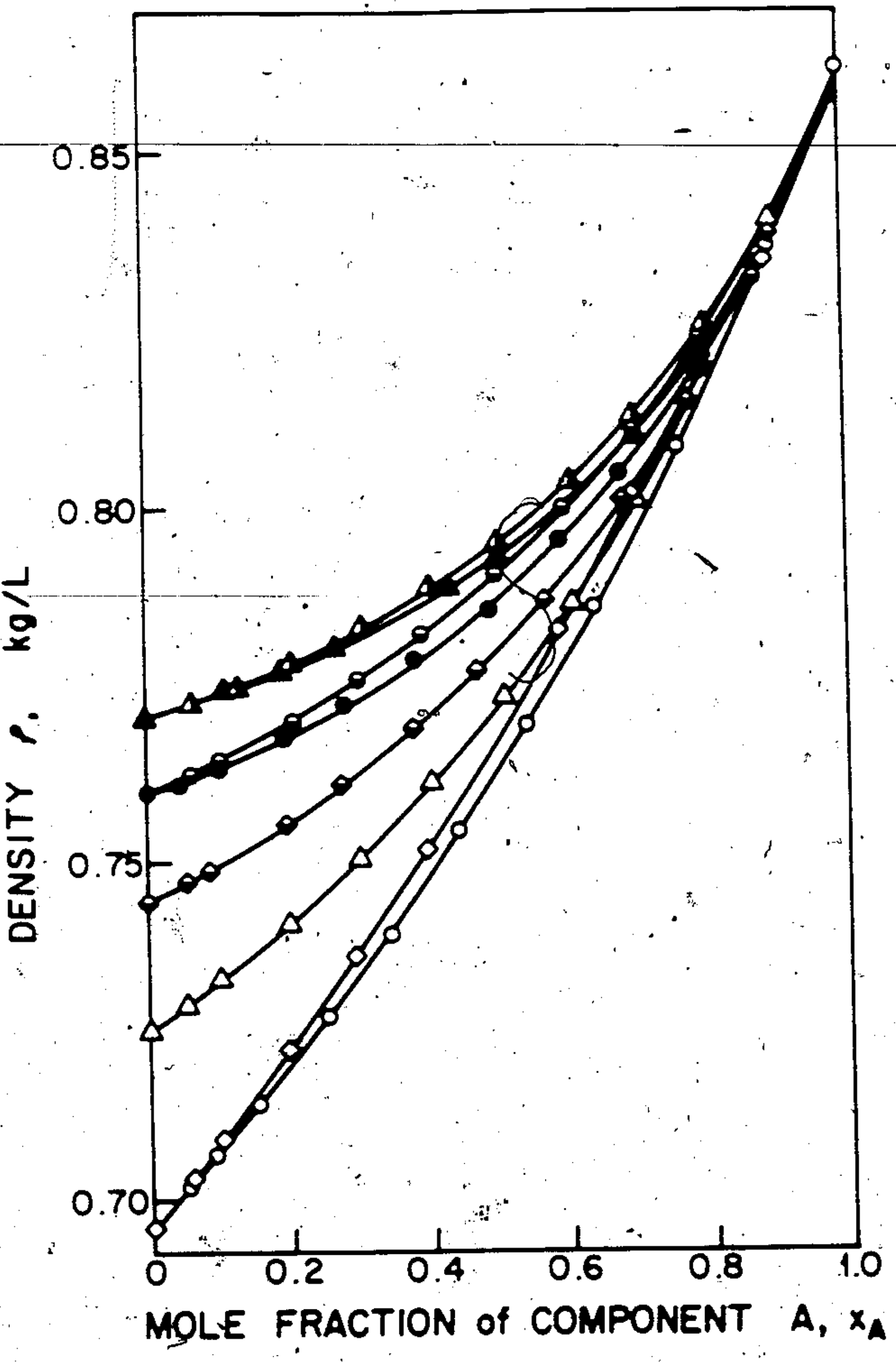
System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 20.00°C						
Toluene(A)-n-Octane(B)	0.7022	0.0974	0.0657	0.0320	0.0338	6.45×10^{5}
Toluene(A)-n-Decane(B)	0.7296	0.0609	0.0785	0.0628	0.0608	1.08×10^{4}
Toluene(A)-n-Dodecane(B)	0.7485	0.0442	0.0733	0.0783	0.0793	1.09×10^{4}
Toluene(A)-n-Tetradecane(B)	0.7652	0.0272	0.0847	0.1078	0.0997	2.42×10^{4}
Toluene(A)-n-Hexadecane(B)	0.7739	0.0178	0.0947	0.1447	0.1253	2.49×10^{4}
Ethylbenzene(A)-n-Octane(B)	0.7022	0.1145	0.0592	0.0335	0.0247	5.70×10^{5}
Ethylbenzene(A)-n-Tetradecane(B)	0.7632	0.0366	0.0681	0.0729	0.0721	1.91×10^{4}
Ethylbenzene(A)-n-Hexadecane(B)	0.7739	0.0282	0.0663	0.0878	0.0865	2.25×10^{4}
Temperature = 25.00°C						
Toluene(A)-n-Octane(B)	0.6986	0.1073	0.0227	0.0333		1.00×10^{4}
Toluene(A)-n-Decane(B)	0.7259	0.0761	0.0006	0.0602		5.08×10^{4}
Toluene(A)-n-Dodecane(B)	0.7438	0.0636	0.0278	0.0817		5.67×10^{4}
Toluene(A)-n-Tetradecane(B)	0.7588	0.0486	0.0318	0.0854		8.64×10^{4}
Toluene(A)-n-Hexadecane(B)	0.7696	0.0478	0.0555	0.0991		8.71×10^{4}
Ethylbenzene(A)-n-Octane(B)	0.6984	0.1215	0.0256	0.0167		7.91×10^{5}
Ethylbenzene(A)-n-Tetradecane(B)	0.7592	0.0526	0.0156	0.0652		5.10×10^{4}
Ethylbenzene(A)-n-Hexadecane(B)	0.7698	0.0442	0.0285	0.0758		6.02×10^{4}

TABLE 4.12 cont'd

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 35.00°C						
Toluene(A) n-Octane(B)	0.6900	0.1015	0.0136	0.0642	0.0177	1.299×10^{4}
Toluene(A) n-Decane(B)	0.71797	0.0568	0.0220	0.0448	0.0497	1.31×10^{4}
Toluene(A) n-Dodecane(B)	0.7376	0.0512	0.0283	0.0042	0.0389	7.83×10^{5}
Toluene(A) n-Tetradecane(B)	0.7528	0.0301	0.0659	0.0774	0.0803	9.35×10^{5}
Toluene(A) n-Hexadecane(B)	0.7636	0.0258	0.0258	0.01899	0.0556	1.05×10^{4}
Ethylbenzene(A) n-Octane(B)	0.6901	0.1166	0.0329	0.0004	0.0092	4.97×10^{5}
Ethylbenzene(A) n-Tetradecane(B)	0.7528	-0.0293	0.0703	0.0784	0.0702	1.41×10^{4}
Ethylbenzene(A) n-Hexadecane(B)	0.7635	0.0143	0.1175	0.15996	0.1178	2.43×10^{4}
Temperature = 40.00°C						
Toluene(A) n-Octane(B)	0.6861	0.0927	0.0790	0.0549	0.0453	1.698×10^{4}
Toluene(A) n-Decane(B)	0.7152	0.0775	0.0015	0.0569		1.90×10^{4}
Toluene(A) n-Dodecane(B)	0.7337	0.0602	0.0265	0.0803		6.38×10^{4}
Toluene(A) n-Tetradecane(B)	0.7491	0.0366	0.0419	0.0515	0.0719	2.41×10^{4}
Toluene(A) n-Hexadecane(B)	0.7610	0.0212	0.0666	0.0939	0.0932	1.49×10^{4}
Ethylbenzene(A) n-Octane(B)	0.6863	0.11296	0.0561	0.0346	0.0286	1.33×10^{4}
Ethylbenzene(A) n-Tetradecane(B)	0.7483	0.0542	0.0241	0.0704		5.56×10^{4}
Ethylbenzene(A) n-Hexadecane(B)	0.76097	0.0201	0.0892	0.1187	0.09795	1.29×10^{4}

Figure 4.1 : Density - Composition Plot at 25.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
⬙	Toluene(A)-n-Dodecane(B)
●	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
◒	Ethylbenzene(A)-n-Tetradecane(B)
◭	Ethylbenzene(A)-n-Hexadecane(B)


0.85
0.80
0.75
0.70
DENSITY ρ, kg/L
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

The density values for each system were fitted to a composition dependent equation of the following form:

$$\rho_m = \sum_{i=0}^{i=n} A_i x_A^i \qquad (4.1)$$

where x_A is the mole-fraction of component A in the mixture. The values of the parameters A_i were calculated by the method of least squares and the order of the polynomial was chosen for which standard deviation of the fit is minimum. These values of the parameters are listed in Table 4.12. The standard deviation of the fit is given for each system in the last column of this table.

The use of the precision density meter to measure the densities of the binary liquid systems in this study resulted in high reproducibility of the results. The density meter proved to be able to give density values reproducible with ± 1.0 x 10^{-5} kg/L on the average. Since the density of the sample is measured in a closed glass tube the evaporation problem is almost eliminated but at temperatures 35.00° and 40.00°C the samples had to be left in the glass tube for forty-five minutes which is relatively a long time interval. This may have caused some evaporation losses.

Figure 4.1 depicts density isotherms of all the binary systems of 25.00°C. Density isotherms are all monotonically increasing with the mole-fraction of component A; and the nature of these isotherms was found to be similar at all other temperatures.

The density-composition data were used to calculate the partial molar volume - composition data for each of the binary system at each temperature. The procedure followed in such calculations is given in Appendix B. The values of partial molar volumes obtained are reported in Appendix B.

4.5.1 Excess Volume of Mixing

Handa and Benson [1979] stated "that volume changes or excess volumes on mixing two liquids can arise from any one of the following factors: (i) difference in the size of the component molecules, (ii) difference in shape of the component molecules, (iii) structural changes such as changes in the correlation of molecular orientations, (iv) difference in the intermolecular interaction energy between like and unlike molecules, and (v) formation of new chemical species. Normally volume changes occur because of a combination of these various factors. Consequently the complexity associated with the

Figure 4.2 : Variation of Excess Volume of Mixing with Mole Fraction at 20.00°C.

Legend	System
●	Toluene(A)-n-Octane(B)
▲	Toluene(A)-n-Decane(B)
○	Toluene(A)-n-Dodecane(B)
◑	Toluene(A)-n-Tetradecane(B)
◮	Toluene(A)-n-Hexadecane(B)
◗	Ethylbenzene(A)-n-Octane(B)
○	Ethylbenzene(A)-n-Tetradecane(B)
△	Ethylbenzene(A)-n-Hexadecane(B)

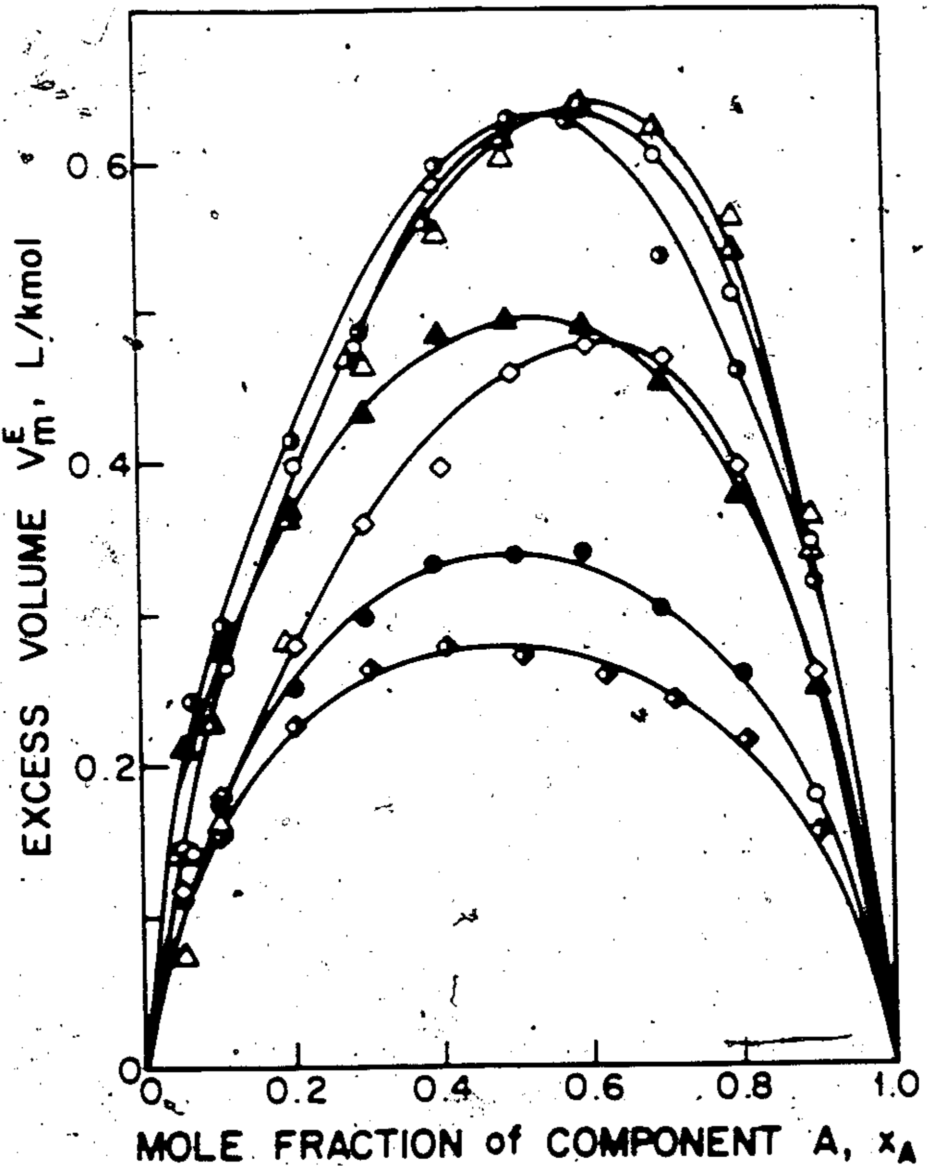

EXCESS VOLUME V_m^E, L/kmol
0
0.2
0.4
0.6
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.3 : Variation of Excess Volume of Mixing with Mole Fraction at 25.00°C.

Legend	System
●	Toluene(A)-n-Octane(B)
▲	Toluene(A)-n-Decane(B)
◇	Toluene(A)-n-Dodecane(B)
◑	Toluene(A)-n-Tetradecane(B)
◭	Toluene(A)-n-Hexadecane(B)
⬖	Ethylbenzene(A)-n-Octane(B)
○	Ethylbenzene(A)-n-Tetradecane(B)
△	Ethylbenzene(A)-n-Hexadecane(B)

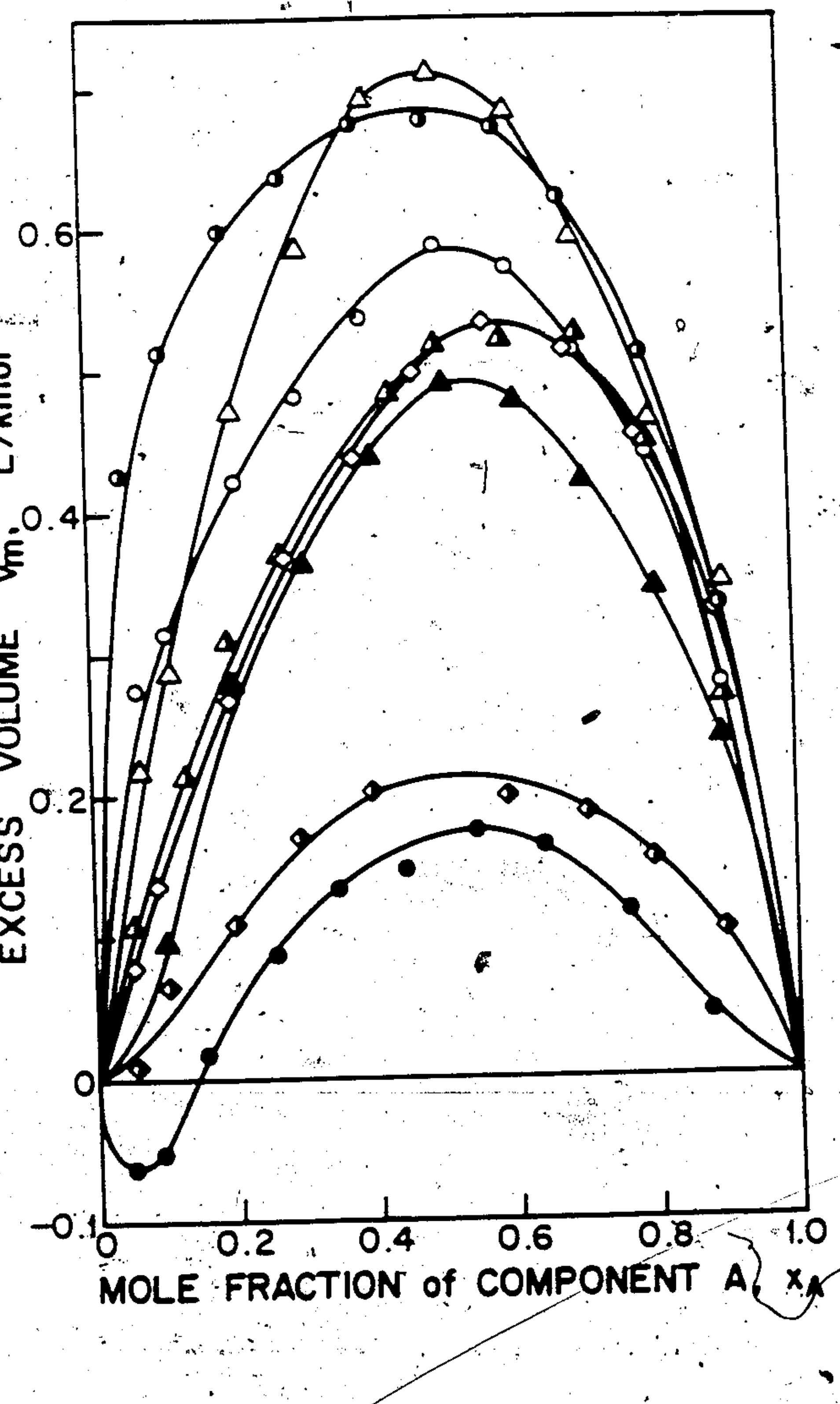
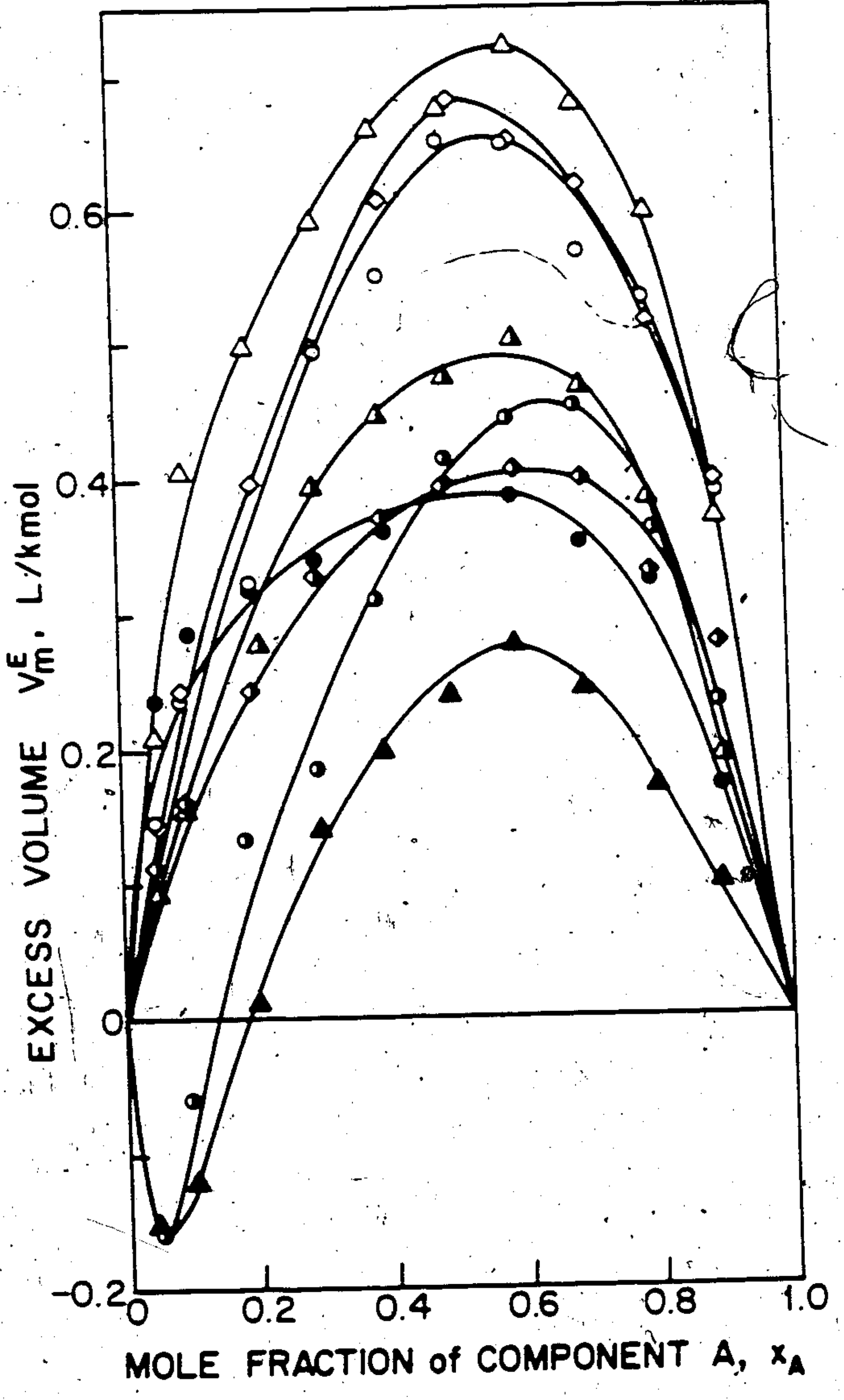

EXCESS VOLUME V_m^E, L/kmol
0.6
0.4
0.2
0
-0.1
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.4 : Variation of Excess Volume of Mixing with Mole Fraction at 35.00°C.

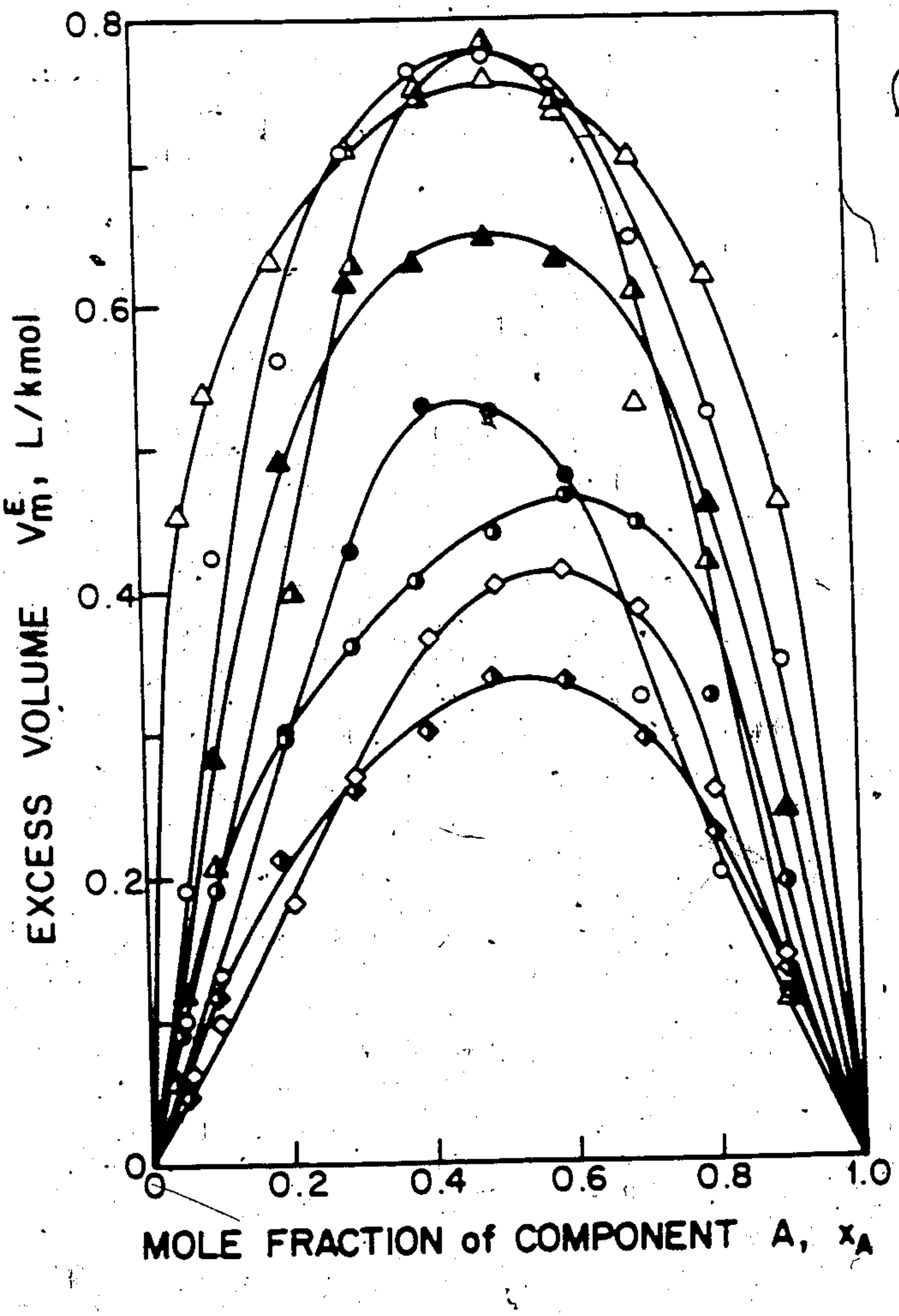
Legend	System
●	Toluene(A)-n-Octane(B)
▲	Toluene(A)-n-Decane(B)
◇	Toluene(A)-n-Dodecane(B)
◑	Toluene(A)-n-Tetradecane(B)
◭	Toluene(A)-n-Hexadecane(B)
⬗	Ethylbenzene(A)-n-Octane(B)
○	Ethylbenzene(A)-n-Tetradecane(B)
△	Ethylbenzene(A)-n-Hexadecane(B)



EXCESS VOLUME V_m^E, L/kmol
0.6
0.4
0.2
0
−0.2
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.5 : Variation of Excess Volume of Mixing with Mole Fraction at 40.00°C.

Legend	System
●	Toluene(A)-n-Octane(B)
▲	Toluene(A)-n-Decane(B)
◇	Toluene(A)-n-Dodecane(B)
◑	Toluene(A)-n-Tetradecane(B)
◭	Toluene(A)-n-Hexadecane(B)
⬖	Ethylbenzene(A)-n-Octane(B)
○	Ethylbenzene(A)-n-Tetradecane(B)
△	Ethylbenzene(A)-n-Hexadecane(B)


0.8
0.6
0.4
0.2
0
EXCESS VOLUME V_m^E, L/kmol
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

origin of excess volume of mixing, coupled with the ease with which the latter can be obtained experimentally with good precision, makes it a sensitive tool for testing the theories of liquid mixtures. Apart from this, excess volume of mixing data are useful in the conversion of excess thermodynamic functions determined at constant pressure to the condition of mixing at constant volume, in determining composition from density measurements on mixtures, and in industrial technology. Thus measurements of excess volumes of mixing continue to be an area of active interest and this is reflected by the enormous amount of data published over the last decade."

In this study excess volume of mixing of eight binary mixtures have been calculated from the density-composition data and are reported in Appendix C, over the entire composition range at four different temperature levels. The change of excess volume of mixing of all the binary mixtures with mole-fraction of component A are shown in Figures 4.2 to 4.5 at the following temperatures 20.00°, 25.00°, 35.00°, and 40.00°C, respectively.

These excess volumes of mixing-composition data were fitted to a composition dependent polynomial, called the smoothing equation which has the form:

TABLE 4.13 Least Squares Constants for the Equation $V_m^E = x_A(1-x_A)\sum_{i=0}^{n} A_i(2x_A-1)^i$

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 20.00°C						
Toluene(A) n Octane(B)	1.3697	0.0407	0.2525	0.0117	0.9698	0.0041
Toluene(A) n Decane(B)	2.0126	0.2285	0.0034	0.52596	2.2722	0.0097
Toluene(A) n Dodecane(B)	1.8091	0.7280	0.6764	0.59697	0.4914	0.0091
Toluene(A) n Tetradecane(B)	2.5222	0.3505	0.8816	0.1868	1.63999	0.00998
Toluene(A) n Hexadecane(B)	2.4866	0.8679	0.6299	0.1763	0.8909	0.0095
Ethylbenzene(A) n Octane(B)	1.0982	0.3075	0.4436	0.1208	0.9003	0.0060
Ethylbenzene(A) n Tetradecane(B)	2.5158	0.5855	0.2666	0.2247	1.3980	0.0084
Ethylbenzene(A) n Hexadecane(B)	2.4393	0.8958	0.6605	1.0285		0.0111
Temperature = 25.00°C						
Toluene(A) n Octane(B)	0.6413	0.1366	0.3687	0.4351	2.4596	0.0075
Toluene(A) n Decane(B)	1.9051	0.1433	0.2511	1.1481	0.7604	0.0143
Toluene(A) n Dodecane(B)	2.04695	0.6538	0.2860	0.6472	0.6663	0.0058
Toluene(A) n Tetradecane(B)	3.0496	0.8069				0.1102
Toluene(A) n Hexadecane(B)	2.0370	0.7216	1.2278	0.0476	1.0405	0.0066
Ethylbenzene(A) n Octane(B)	0.8345	0.0529	0.0203	0.6213		0.0071
Ethylbenzene(A) n Tetradecane(B)	2.3392	0.4513	0.2675	1.2052	2.9411	0.0115
Ethylbenzene(A) n Hexadecane(B)	2.8822	0.3344	1.0427	0.9182	2.9605	0.0110

TABLE 4.15, cont'd

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 35.00°C						
Toluene(A)-n-Octane(B)	2.1505	0.7432	2.4444	0.7497	2.1211	0.0156
Toluene(A)-n-Decane(B)	2.5520	0.3701	1.6996	0.1819	1.8425	0.0181
Toluene(A)-n-Dodecane(B)	1.6696	0.8008	1.47698	[illegible]7838	1.2534	0.0177
Toluene(A)-n-Tetradecane(B)	1.8025	0.5382	0.4547	0.8719		0.0105
Toluene(A)-n-Hexadecane(B)	3.1611	0.2629	1.5302	1.0842	1.0343	0.0216
Ethylbenzene(A)-n-Octane(B)	1.3309	0.3273	0.1317			0.0095
Ethylbenzene(A)-n-Tetradecane(B)	3.0775	0.40396	0.1380			0.0204
Ethylbenzene(A)-n-Hexadecane(B)	3.0751	0.2974	0.0985	1.7108	6.6053	0.0303
Temperature = 40.00°C						
Toluene(A)-n-Octane(B)	1.4693	0.2019	1.7072			0.0424
Toluene(A)-n-Decane(B)	0.9636	0.3548	0.3206	1.6021	3.4229	0.0338
Toluene(A)-n-Dodecane(B)	2.5711	0.7162	1.1099			0.0253
Toluene(A)-n-Tetradecane(B)	1.5664	1.3008	0.1776	0.9303	4.8699	0.0447
Toluene(A)-n-Hexadecane(B)	1.9467	0.6192	0.5764	0.53896	0.8714	0.0131
Ethylbenzene(A)-n-Octane(B)	1.6174	0.2930	0.0142	0.5653	1.91796	0.0133
Ethylbenzene(A)-n-Tetradecane(B)	2.5213	0.6075	1.0841	0.7865	3.9154	0.0206
Ethylbenzene(A)-n-Hexadecane(B)	2.7654	0.7766	1.5858	1.2293	0.9558	0.0215

TABLE 4.14 Parameters Obtained in Kato-Suzuki Model

System	$g_{BA}-g_{AA}$	$g_{AB}-g_{BB}$	BA	AB	Standard Deviation
Temperature = 25.00°C					
Toluene A - n-Octane B	1.2616	1.3724	0.8727	1.1585	0.0027
Toluene A - n-Decane B	0.7592	2.0024	-0.1513	1.1585	0.0345
Toluene A - n-Dodecane B	1.1802	1.4521	-0.2469	0.6015	0.0283
Toluene A - n-Tetradecane B	0.0066	2.6703	-0.1585	1.4773	0.0353
Toluene A - n-Hexadecane B	1.3858	5.2835	0.4535	0.2052	[illegible]
Ethylbenzene A - n-Octane B	1.2696	1.3954	[illegible]	2.1816	0.0311
Ethylbenzene A - n-Tetradecane B	0.7948	3.0980	-0.2377	0.6696	0.0330
Ethylbenzene A - n-Hexadecane B	1.2659	3.6236	0.0652	0.8247	0.0283
Temperature = 30.00°C					
Toluene A - n-Octane B	1.5465	0.9918	-1.0923	2.4606	0.0354
Toluene A - n-Decane B	1.5560	2.3670	1.2173	0.8215	0.028
Toluene A - n-Dodecane B	1.1568	2.8971	1.1312	0.6037	0.0225
Toluene A - n-Tetradecane B	1.7508	0.2002	1.0702	-0.2487	0.0303
Toluene A - n-Hexadecane B	1.4043	2.7437	-0.00088	0.6329	0.024
Ethylbenzene A - n-Octane B	1.6565	1.0040	-0.3801	0.7373	0.0224
Ethylbenzene A - n-Tetradecane B	4.8498	3.9090	0.1256	0.2521	0.0232
Ethylbenzene A - n-Hexadecane B	2.9441	2.8500	-0.2574	0.9823	0.0315
Temperature = 35.00°C					
Toluene(A)-n-Octane(B)	2.5901	2.5417	-0.27395	1.6921	0.0454
Toluene(A)-n-Decane(B)	1.9898	2.5007	0.5094	-0.27385	0.0271
Toluene(A)-n-Dodecane(B)	1.9810	2.2697	1.56035	3.65785	0.0338
Toluene(A)-n-Tetradecane(B)	1.4944	2.0963	-0.2405	1.7892	0.0202
Toluene(A)-n-Hexadecane(B)	3.2260	3.1742	5190.5	1.2039	0.0695
Ethylbenzene(A)-n-Octane(B)	1.2308	1.4464	0.9438	1.2595	0.0222
Ethylbenzene(A)-n-Tetradecane(B)	3.4955	2.6373	1.8309	-0.0861	0.0451
Ethylbenzene(A)-n-Hexadecane(B)	2.6893	2.6765	-0.0433	1.5153	0.0217
Temperature = 40.00°C					
Toluene(A)-n-Octane(B)	1.5015	1.5041	1.7025	2.0418	-0.0815
Toluene(A)-n-Decane(B)	0.5273	1.8262	2.6732	2.3697	0.0827
Toluene(A)-n-Dodecane(B)	1.8208	3.2250	0.0346	0.59745	0.0421
Toluene(A)-n-Tetradecane(B)	2.4168	3.2541	1.2095	0.8264	0.0726
Toluene(A)-n-Hexadecane(B)	1.4849	2.4703	2.7995	0.3572	0.0167
Ethylbenzene(A)-n-Octane(B)	1.0496	1.96296	-0.0397	0.7105	0.0401
Ethylbenzene(A)-n-Tetradecane(B)	1.5383	3.2400	-0.0353	0.63215	0.0463
Ethylbenzene(A)-n-Hexadecane(B)	2.2120	5.1781	-0.0405	0.8761	0.0666

$$V^E = x_A(1 - x_A)\sum_{i=0}^{i=n} A_i(2x_A - 1)^i \qquad (4.2)$$

The values of the constants, "A_i" of this Equation (4.2) along with the standard deviation of the fit are reported in Table 4.13.

The excess volumes of mixing-composition data were also fitted to an empirical correlation put forward by Kato and Suzuki [1978] which is given by:

$$V^E = x_A x_B \frac{\left(x_B \Lambda_{BA}(\bar{V}_A^{\infty} - V_A^*) + x_A \Lambda_{AB}(\bar{V}_B^{\infty} - V_B^*)\right)}{\left[(x_A + x_B \Lambda_{BA})(x_B + x_A \Lambda_{AB})\right]} \qquad (4.3)$$

where $\bar{V}_A^{\infty} - V_A^*$ and $\bar{V}_B^{\infty} - V_B^*$ are the two partial molar volumes at infinite dilution of components A and B, respectively and Λ_{BA} and Λ_{AB} are the two non-randomness factors or adjustable parameters of the equation. These values were calculated and reported in Table 4.14 along with the standard deviation of the fit. In general for every system at every temperature level, the fit is better with smoothing equation as can be seen in Tables 4.13 and 4.14.

All the systems showed positive excess volume of mixing at every temperature except toluene-n-octane at 25.00° C, toluene-n-decane and toluene-n-tetradecane at 35.00 ° C which showed negative excess volumes at low concentration of component A. At the lower temperature levels i.e. at 20.00°C and 25.00°C the excess volume of mixing gradually increased with the number of carbon atoms of the second component, i.e. n-alkanes. At 35.00°C and 40.00°C there were no such trends; but at every temperature level the excess volume of mixing was higher with systems containing n-hexadecane and n-tetradecane compared to systems containing n-octane or n-decane. The shape of the aromatic component, i.e., toluene and ethylbenzene are spheroidal while the shape of the second component, i.e., n-alkanes are all rod-like and it is this difference in molecular shape of the two components which is probably the primary factor for excess volume of mixing for these binary mixtures. Diaz Pena and Delgado [1974] have reported some values of excess volume of mixing for systems containing benzene and n-alkanes at 25.00°C. The excess volume of mixing for toluene-n-alkane show somewhat lower values at 25.00°C than the work of Diaz Pena and Delgado [1974]. Same trend is observed with systems containing ethylbenzene. Therefore it may be concluded that a methyl or ethyl group in the benzene ring helps the rodlike n-alkanes to accommodate in a more packed way in the binary mixture. As the temperature increases the free volume of a liquid is increased, as such one would expect a decrease in excess volume of mixing at

TABLE 4.13 Viscosity-Composition Data of the System Toluene 1 + n-Octane 2

Mole Fraction x_1	Kinematic Viscosity cSt	Absolute Viscosity cP	Mole Fraction x_1	Kinematic Viscosity cSt	Absolute Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.7697	0.5403	0.0000	0.7298	0.5097
0.0584	0.7577	0.5366	0.04995	0.7182	0.5057
0.1111	0.7443	0.53199	0.0912	0.7099	0.5031
0.2065	0.7246	0.5251	0.1548	0.6967	0.4987
0.3044	0.7074	0.5217	0.2566	0.6775	0.4933
0.3937	0.6924	0.5183	0.3472	0.6637	0.4911
0.5027	0.6771	0.5186	0.4447	0.6499	0.4892
0.5946	0.6686	0.5222	0.5437	0.6389	0.4913
0.6979	0.6615	0.5289	0.6408	0.6321	0.4964
0.8028	0.6603	0.5416	0.7612	0.6259	0.5058
0.8990	0.6647	0.5594	0.8745	0.6283	0.5229
1.0000	0.6777	0.5876	1.0000	0.6413	0.5528
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.6580	0.4541	0.0000	0.6261	0.4297
0.0440	0.6503	0.4516	0.0517	0.6178	0.4268
0.1032	0.63897	0.4479	0.1038	0.6093	0.4243
0.2008	0.6229	0.4432	0.1996	0.5949	0.4208
0.2940	0.6082	0.4395	0.29896	0.5805	0.4179
0.3983	0.5952	0.4382	0.4023	0.5681	0.4169
0.4956	0.5849	0.4389	0.4942	0.5581	0.4177
0.6003	0.5759	0.4419	0.5939	0.5495	0.4193
0.6974	[illegible]	0.4475	0.6947	0.5439	0.4247
0.8019	0.5673	0.4572	0.8003	0.5409	0.4334
0.8979	0.5697	0.4722	0.8976	0.5427	0.4466
1.0000	0.5783	0.4925	1.0000	0.5508	0.4672

TABLE 4.16 Viscosity-Composition Data of the System Toluene A - n-Decane B

Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP	Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	1.2543	0.9133	0.0000	1.1722	0.8522
0.05798	1.2189	0.8939	0.0519	1.1504	0.8351
0.1188	1.1649	0.8617	0.1005	1.0976	0.8051
0.2078	1.0955	0.8165	0.2019	1.0264	0.7609
0.3046	1.0264	0.7741	0.3037	0.9614	0.7226
0.4047	0.9618	0.7353	0.4060	0.9045	0.6882
0.4968	0.9074	0.7035	0.5113	0.8430	0.6516
0.5992	0.8488	0.6694	0.6106	0.7936	0.6238
0.6996	0.7992	0.6424	0.7150	0.7496	0.6000
0.7994	0.7489	0.6131	0.8021	0.7072	0.5780
0.9032	0.7072	0.59595	0.8957	0.6726	0.5616
1.0000	0.6777	0.5876	1.0000	0.6413	0.5528
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	1.0293	0.73898	0.0000	0.9652	0.6902
0.0495	1.00095	0.7217	0.0432	0.9434	0.6783
0.0966	0.9738	0.7065	0.1008	0.9127	0.6599
0.1964	0.91896	0.6723	0.2021	0.8609	0.6294
0.2979	0.8652	0.6406	0.2993	0.8150	0.6028
0.3929	0.8152	0.6135	0.3936	0.7726	0.5772
0.4962	0.7637	0.5815	0.4947	0.7258	0.5528
0.5965	0.7188	0.5565	0.5933	0.6834	0.5280
0.6981	0.6766	0.5340	0.6955	0.6434	0.5066
0.7988	0.6386	0.5151	0.8009	0.6065	0.4885
0.8979	0.6055	0.5007	0.8962	0.5750	0.4739
1.0000	0.5783	0.4925	1.0000	0.5508	0.4672

TABLE 4.1[illegible] Viscosity-Composition Data of the System Toluene (A) n-Dodecane (B)

Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP	Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	1.9743	1.4778	0.0000	1.8248	1.3582
0.0641	1.8637	1.4024	0.0551	1.7356	1.2967
0.1156	1.7937	1.3325	0.1087	1.6823	1.2603
0.2082	1.6264	1.2367	0.1959	1.5219	1.1496
0.3004	1.4802	1.1352	0.2789	1.4067	1.0703
0.4037	1.3409	1.0396	0.3802	1.2730	0.9785
0.5002	1.2221	0.9426	0.4701	1.1622	0.9024
0.6005	1.07896	0.8577	0.5707	1.0429	0.8205
0.7015	0.9629	0.77793	0.6654	0.9195	0.7563
0.8023	0.8532	0.7027	0.7805	0.8244	0.6719
0.90099	0.7597	0.6402	0.8895	0.7261	0.6063
1.0000	0.6777	0.5876	1.0000	0.6413	0.5528
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	1.5556	1.1474	0.0000	1.4462	1.06195
0.0527	1.48899	1.1023	0.0508	1.3892	1.0233
0.0996	1.4313	1.0633	0.0924	1.3435	0.9924
0.2049	1.3063	0.97896	0.2233	1.22396	0.9119
0.2913	1.2098	0.9134	0.3003	1.1242	0.8447
0.4021	1.0916	0.8333	0.4063	1.0227	0.7751
0.4986	0.9949	0.7680	0.5124	0.9239	0.7101
0.5944	0.9031	0.7062	0.5988	0.8489	0.6605
0.69698	0.8094	0.6432	0.7015	0.7633	0.6035
0.7979	0.7243	0.5864	0.7999	0.6876	0.5538
0.8981	0.6479	0.5367	0.89898	0.6151	0.5065
1.0000	0.5783	0.4925	1.0000	0.5508	0.4672

TABLE 4.18 Viscosity-Composition Data of the System Toluene(A)-n-Tetradecane(B)

Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP	Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	3.0189	2.3037	0.0000	2.7373	2.0799
0.0661	2.8050	2.1466	0.0469	2.6039	1.9805
0.1289	2.6683	2.0469	0.1072	2.4350	1.8798
0.2072	2.3681	1.8275	0.1969	2.1863	1.6773
0.3028	2.09099	1.6247	0.2854	1.9666	1.5181
0.3994	1.83899	1.43998	0.3858	1.7245	1.3419
0.5034	1.5879	1.2558	0.4918	1.4924	1.1729
0.5820	1.4090	1.1243	0.5944	1.2805	1.01795
0.7026	1.1624	0.9431	0.6815	1.12298	0.9032
0.8048	0.9765	0.8062	0.7929	0.9370	0.7675
0.9018	0.8177	0.6894	0.8947	0.7807	0.6533
1.0000	0.6777	0.5876	1.0000	0.6413	0.5528
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	2.2732	1.71096	0.0000	2.0900	1.5651
0.0513	2.1604	1.6301	0.0503	1.9874	1.4934
0.0991	2.0573	1.5561	0.0977	1.8893	1.4231
0.1977	1.8496	1.4072	0.1856	1.7329	1.3116
0.2967	1.6531	1.2663	0.29[illegible]0	1.5413	1.1756
0.3868	1.4842	1.1450	0.3892	1.3795	1.0600
0.4975	1.2890	1.0047	0.4984	1.2094	0.9381
0.5973	1.1241	0.8858	0.5902	1.0651	0.8348
0.6983	0.9703	0.7749	0.6908	0.9233	0.7329
0.7963	0.8387	0.6809	0.8046	0.7746	0.6267
0.89897	0.6967	0.5776	0.8977	0.6628	0.5468
1.0000	0.5783	0.4925	1.0000	0.5508	0.4672

TABLE 4.19 Viscosity-Composition Data of the System Toluene(A)-n-Hexadecane(B)

Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP	Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	4.4624	3.4528	0.0000	3.9762	3.0630
0.0444	4.2285	3.2611	0.06697	3.6575	2.82495
0.0959	3.9156	3.0406	0.13099	3.3766	2.6251
0.2033	3.3916	2.6471	0.1927	3.2863	2.39[illegible]
0.2811	2.9897	2.3433	0.2798	2.7794	2.1681
0.38898	2.5301	1.9968	0.4333	2.1675	1.7092
0.4969	2.1052	1.6756	0.5026	1.9329	1.5326
0.6004	1.7368	1.3961	0.5973	1.6303	1.3045
0.6977	1.4248	1.1586	0.7017	1.3218	[illegible]
0.7978	1.1435	0.9441	0.7984	1.0661	0.8762
0.9004	0.8881	0.7446	0.89799	0.8436	0.7073
1.0000	0.6777	0.5876	1.0000	0.6413	0.5525
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	3.2199	2.4586	0.0000	2.9292	2.2288
0.0363	3.0922	2.3641	0.0533	2.7556	2.1009
0.0987	2.8747	2.2031	0.0981	2.6168	1.9986
0.2114	2.4990	1.9248	0.2119	2.3072	1.7716
0.3079	2.1988	1.7014	0.2950	2.0638	1.5917
0.3992	1.9281	1.5003	0.3956	1.7957	1.3938
0.5031	1.6401	1.2863	0.4984	1.5362	1.2017
0.5965	1.4038	1.1107	0.5995	1.3125	1.0363
0.7073	1.1529	0.9240	0.6995	1.0903	0.8709
0.7969	0.9724	0.7744	0.7946	0.9037	0.7319
0.8978	0.7543	0.6261	0.9000	0.7117	0.5883
1.0000	0.5783	0.4925	1.0000	0.5508	0.4672

TABLE 4.22 Viscosity-Composition Data of the System Ethylbenzene A + n-Octane B

Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP	Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.7697	0.5405	0.0000	0.7298	0.5097
0.0544	0.7623	0.5402	0.0562	0.7221	0.5093
0.1128	0.7558	0.5401	0.1008	0.7158	0.5088
0.2253	0.7454	0.5427	0.1983	0.7042	0.5096
0.3052	0.7329	0.5438	0.2917	0.6971	0.5133
0.4097	0.7273	0.5509	0.3979	0.68999	0.5187
0.5113	0.7243	0.5602	0.5898	0.6871	0.5375
0.6193	0.7246	0.5735	0.7007	0.69099	0.55396
0.7123	0.7276	0.5879	0.7972	0.6976	0.5719
0.8071	0.7367	0.6056	0.8964	0.7091	0.5953
0.9012	0.7509	0.6347	1.0000	0.72998	0.6292
1.0000	0.7731	0.6675			
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.6580	0.4541	0.0000	0.6291	0.4297
0.0515	0.6529	0.4539	0.0482	0.6215	0.4299
0.0971	0.6471	0.4542	0.0976	0.6157	0.4298
0.1865	0.6384	0.4553	0.1971	0.6071	0.4315
0.2989	0.6304	0.4590	0.2949	0.6013	0.4352
0.3983	0.6252	0.4644	0.3974	0.5959	0.4401
0.4900	0.6229	0.4704	0.4902	0.5942	0.4473
0.5919	0.6219	0.4810	0.5966	0.5942	0.4575
0.7016	0.6248	0.4952	0.6955	0.5959	0.4690
0.7950	0.6308	0.5115	0.7967	0.6012	0.4847
0.8987	0.6412	0.5329	0.8965	0.6101	0.5039
1.0000	0.6565	0.5602	1.0000	0.6242	0.5303

TABLE 4.21 Viscosity-Composition Data of the System Ethylbenzene (A)-n-Tetradecane (B)

Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP	Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	3.0249	2.3037	0.0000	2.7373	2.0799
0.0521	2.8486	2.1797	0.0629	2.5554	1.9476
0.1152	2.6375	2.0263	0.1257	2.4305	1.8573
0.2101	2.3591	1.8245	0.2129	2.1575	1.6617
0.2932	2.1257	1.6547	0.3033	1.9316	1.4980
0.4042	1.8467	1.4515	0.3946	1.7277	1.3508
0.4963	1.6376	1.2995	0.5007	1.5153	1.1975
0.5976	1.4239	1.1435	0.6007	1.3254	1.0599
0.6977	1.2344	1.0052	0.7002	1.1538	0.9356
0.7987	1.0614	0.8789	0.7976	1.0014	0.8231
0.8999	0.9068	0.7664	0.8976	0.8581	0.7211
1.0000	0.7701	0.6678	1.0000	0.72995	0.6292
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	2.2732	1.7109	0.0000	2.0900	1.5652
0.0529	2.1682	1.6363	0.0509	1.9865	1.4916
0.1012	2.0534	1.5533	0.0923	1.9071	1.4355
0.1997	1.8477	1.4067	0.1991	1.7104	1.2971
0.2951	1.6667	1.2781	0.3032	1.5372	1.1747
0.3929	1.4884	1.1511	0.4005	1.3808	1.0645
0.4475	1.3163	1.0288	0.4961	1.2363	0.9621
0.5814	1.1882	0.9377	0.5918	1.1061	0.8724
0.6975	1.0225	0.8201	0.7004	0.9587	0.7659
0.8005	0.8887	0.72498	0.7975	0.8417	0.6830
0.8974	0.7695	0.6399	0.8997	0.7277	0.6026
1.0000	0.6565	0.5602	1.0000	0.6242	0.5303

TABLE 4.22 Viscosity-Composition Data of the System Ethylbenzene(A)-n-Hexadecane(B)

Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP	Mole Fraction x_A	Kinematic Viscosity cSt	Absolute Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	4.4614	3.4518	0.0000	3.9762	3.0630
0.0539	4.1464	3.2163	0.0692	3.6403	2.8122
0.1229	3.87695	3.0145	[illegible]	3.4305	2.6559
0.1983	3.3965	2.6548	0.2258	3.0287	2.3561
0.3022	2.8961	2.2779	0.3084	2.6157	2.0478
0.4028	2.4812	1.9658	0.4053	2.2621	1.7831
0.4927	2.1298	1.7005	0.5027	1.9396	1.5418
0.5953	1.7969	1.4494	0.6099	1.6225	1.3032
0.6978	1.5009	1.2258	0.69799	1.38399	1.1247
0.7992	1.2139	1.0065	0.8029	1.1272	0.9307
0.9002	0.9753	0.8245	0.9008	0.9154	0.7697
1.0000	0.7701	0.6678	1.0000	0.72998	0.6292
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	3.2199	2.4586	0.0000	2.9292	2.2259
0.0505	3.0354	2.3199	0.0502	2.7614	2.12499
0.0912	2.8926	2.2151	0.0987	2.6053	1.9896
0.1912	2.5562	[illegible]	0.1983	2.3217	1.7826
0.2997	2.2164	1.7177	0.3033	2.0145	1.5567
0.4026	1.9241	1.5022	0.3935	1.8077	1.4058
0.4995	1.6669	1.3122	0.4981	1.5558	1.2205
0.5968	1.4361	1.1416	0.5986	1.3356	1.0579
0.6994	1.2063	0.9706	0.6995	1.1322	0.9076
0.7991	1.00696	0.8222	0.8025	0.9433	0.7676
0.8987	0.8053	0.6697	0.8986	0.7807	0.6469
1.0000	0.6565	0.5602	1.0000	0.6242	0.5303

higher temperatures but the experimental results do not confirm this notion in all systems. Similar behavior was reported by Garcia et al. [1986], and Dieter and Heintz [1986]. The relatively small negative values of the excess molar volumes observed in Figures 4.3 and 4.5 at low concentrations of component A in the case of the systems toluene (A)-n-octane (B), toluene (A)-n-decane (B) and toluene (A)-n-tetradecane (B) are probably due to experimental error..

The excess volume of mixing curves fitted well to the "smoothing" equation, Equation (4.2) at lower temperatures but at 40.00°C there were some scattering of data points which may be due to the evaporation losses in the density meter tube since at higher temperatures samples were allowed to stay in the density meter tube for forty-five minutes to attain thermal equilibration.

4.6 Viscosity - Composition Data

The experimental viscosity data are presented in Tables 4.6 to 4.13. For each of these viscosity values, efflux times were measured at least three times and the average value was used in the determination of the viscosities. The kinematic viscosity isotherms at each

Figure 4.6 : Kinematic Viscosity-Composition Plot for Systems with Toluene at 20.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
⬙	Toluene(A)-n-Dodecane(B)
◒	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)

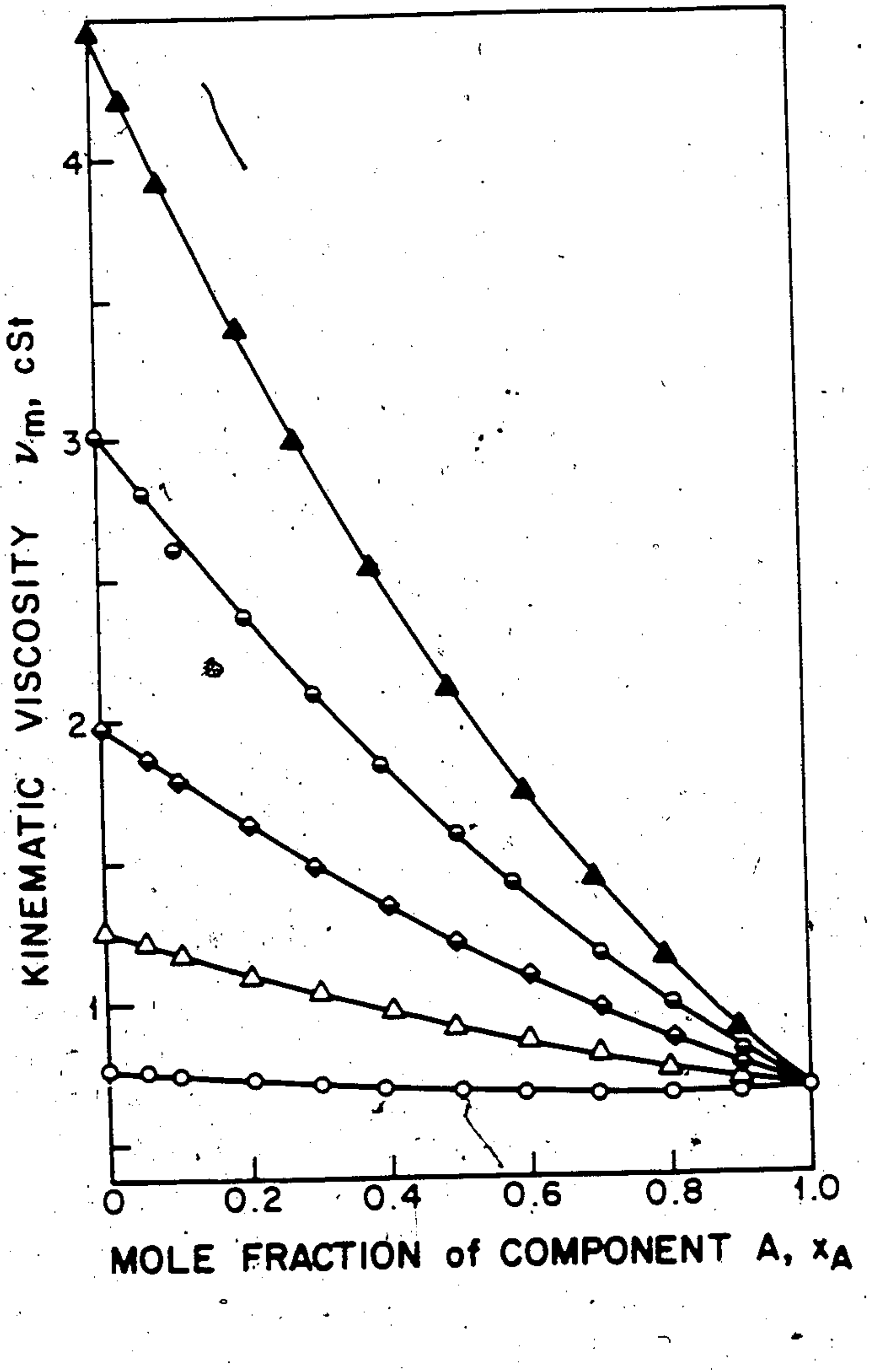

KINEMATIC VISCOSITY ν_m, cSt
4
3
2
1
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.7 : Kinematic Viscosity- Composition Plot for Systems with Ethylbenzene at 20.00°C.

Legend	System
◇	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
▲	Ethylbenzene(A)-n-Hexadecane(B)

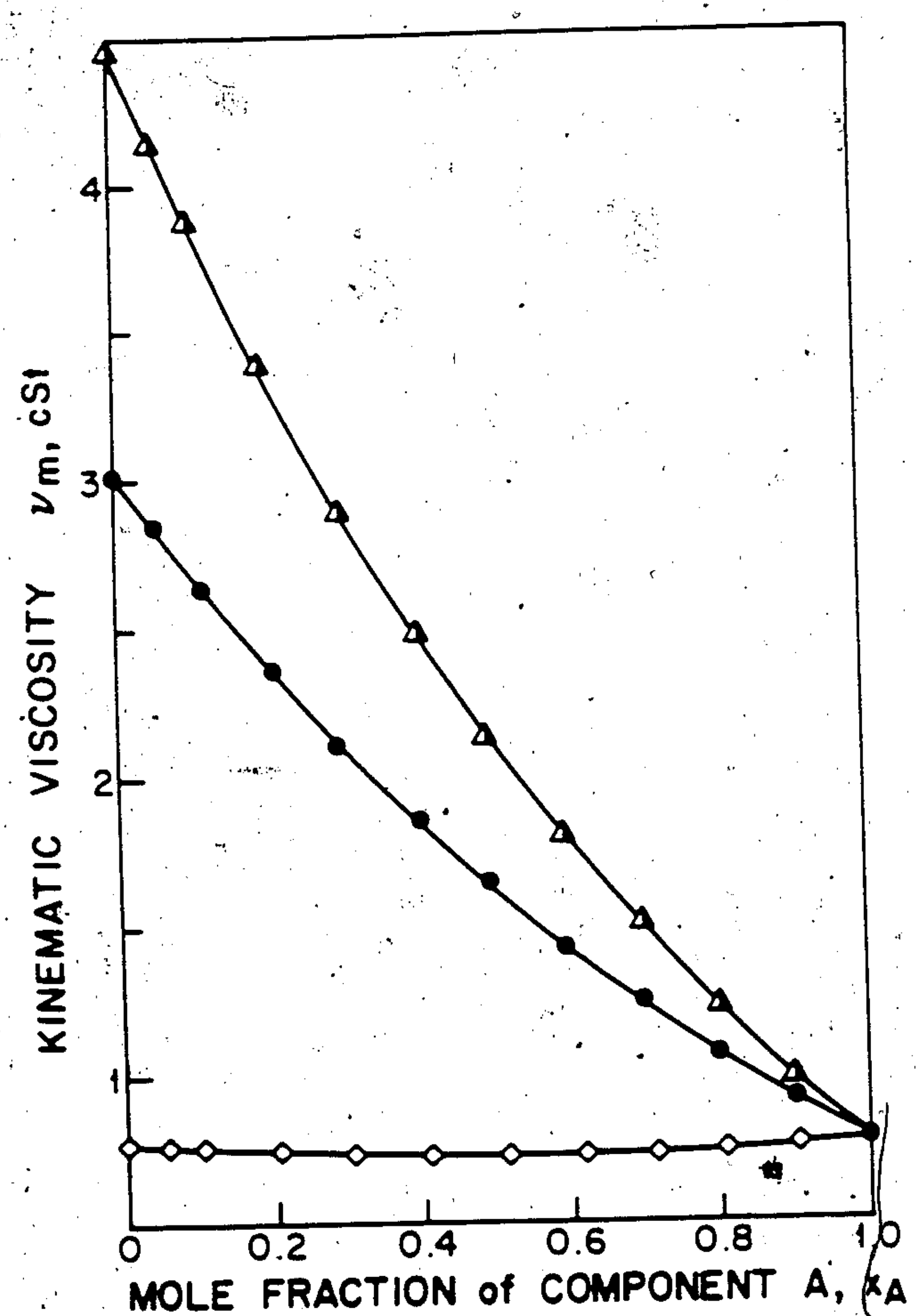

KINEMATIC VISCOSITY ν_m, cSt
4
3
2
1
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.8 : Kinematic Viscosity-Composition Plot for Systems with Toluene at 25.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
⬙	Toluene(A)-n-Dodecane(B)
◒	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)

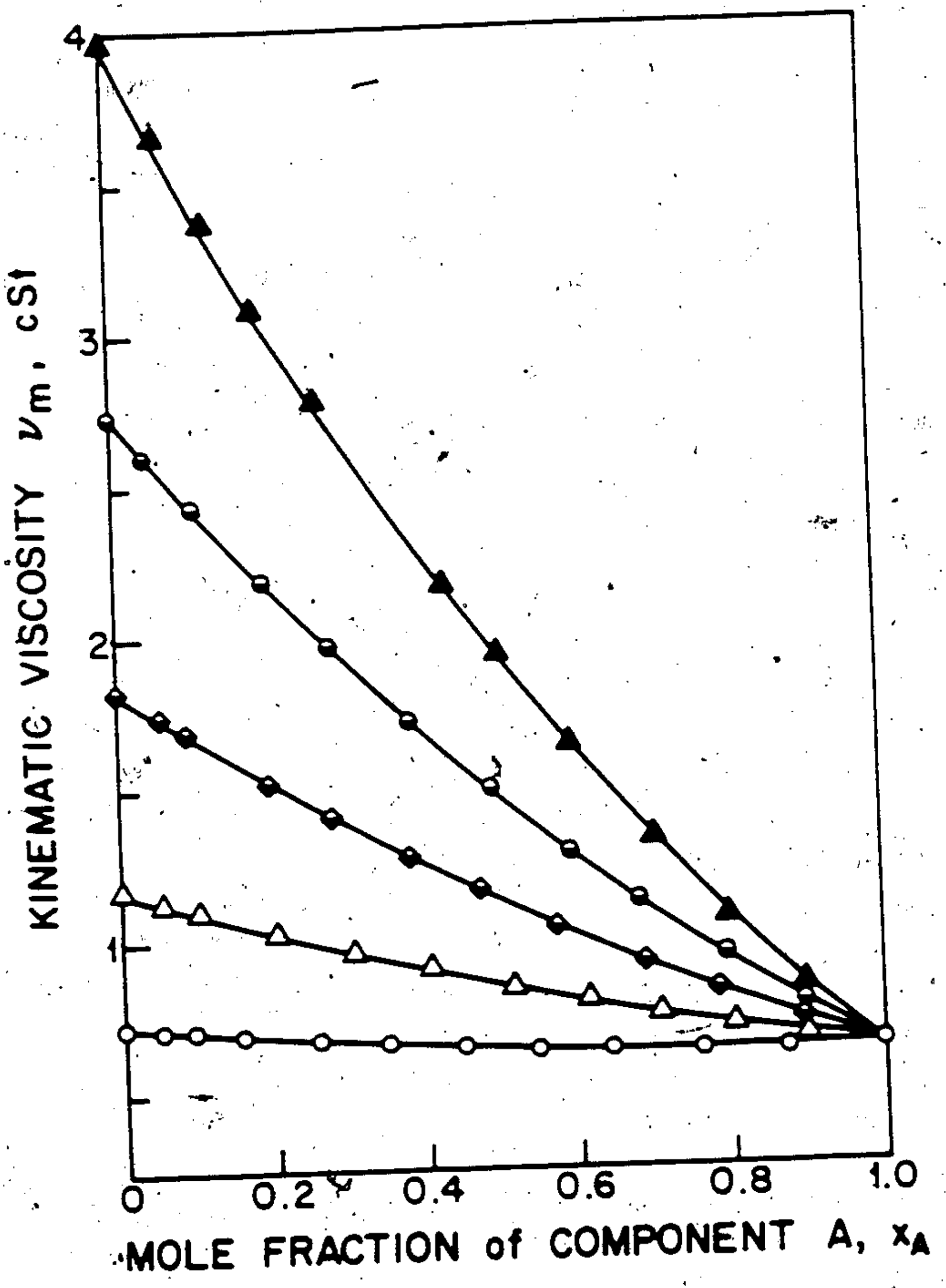

4
3
2
1
KINEMATIC VISCOSITY ν_m, cSt
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.9 : Kinematic Viscosity-Composition Plot for Systems with Ethylbenzene at 25.00°C.

Legend	System
◇	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
▲	Ethylbenzene(A)-n-Hexadecane(B)

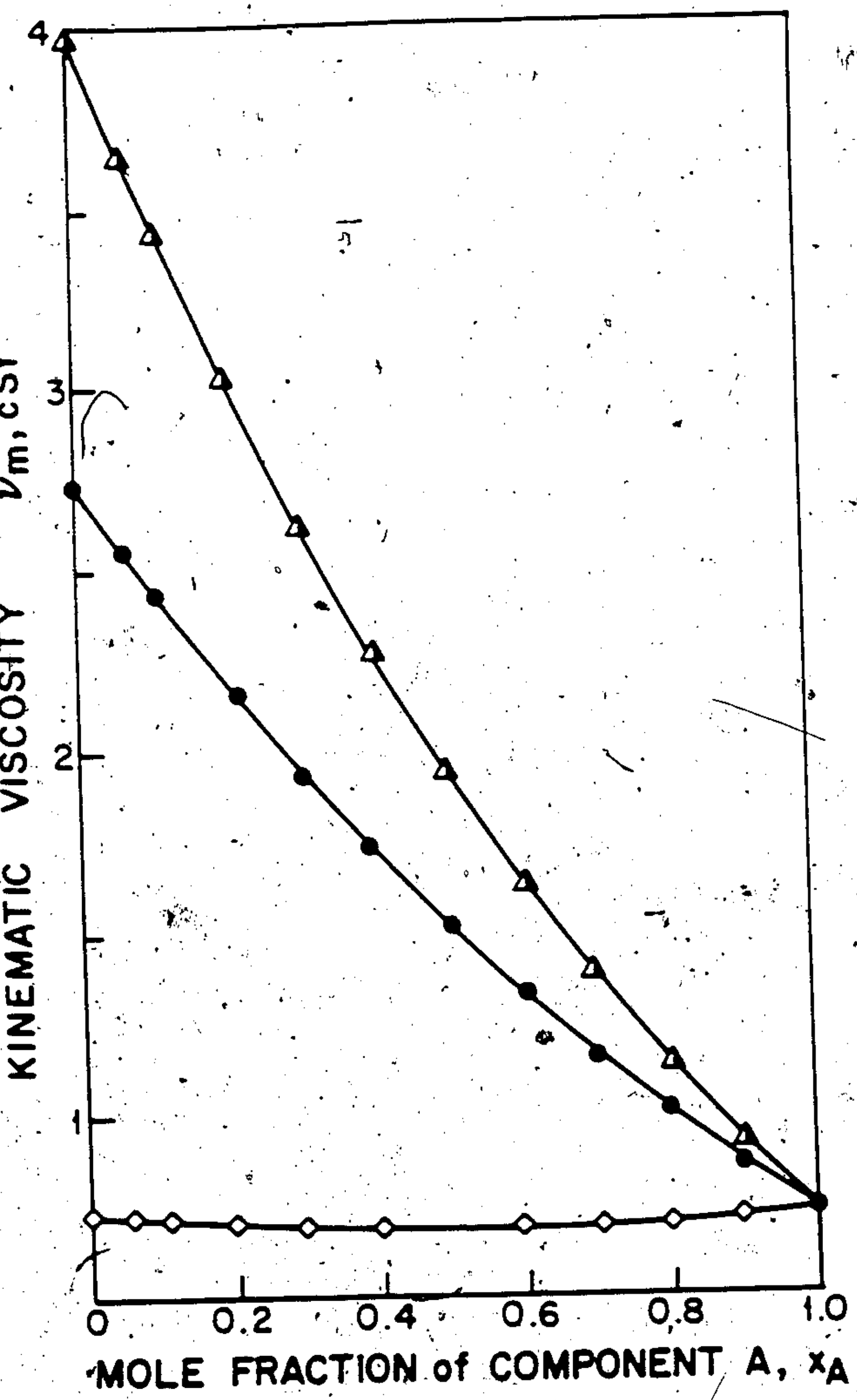

4
3
2
1
KINEMATIC VISCOSITY ν_m, cSt
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.10 : Kinematic Viscosity-Composition Plot for Systems with Toluene at 35.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
⬙	Toluene(A)-n-Dodecane(B)
◒	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)

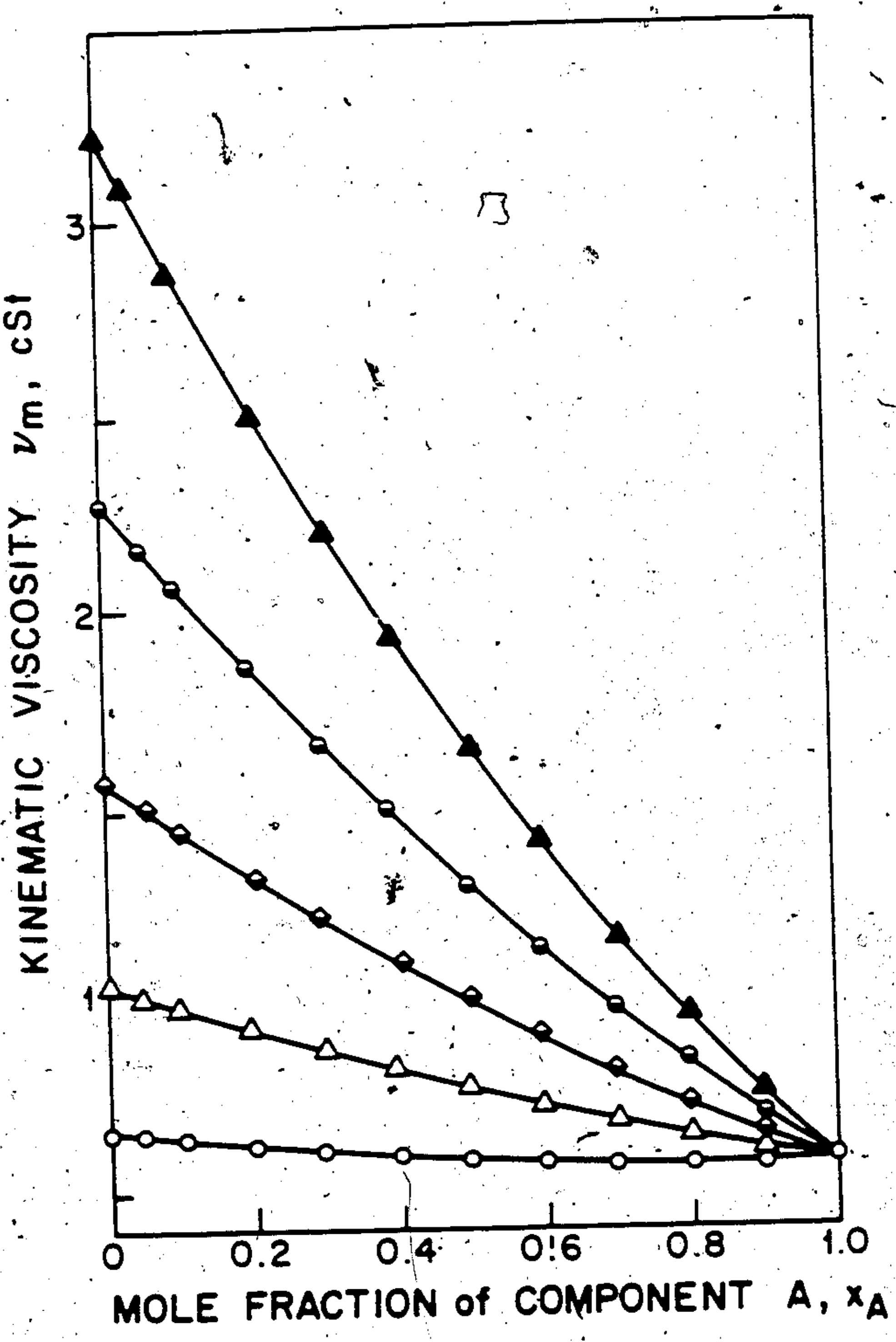

KINEMATIC VISCOSITY ν_m, cSt
3
2
1
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.11 : Kinematic Viscosity-Composition Plot for Systems with Ethylbenzene at 35.00°C.

Legend	System
◇	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
▲	Ethylbenzene(A)-n-Hexadecane(B)

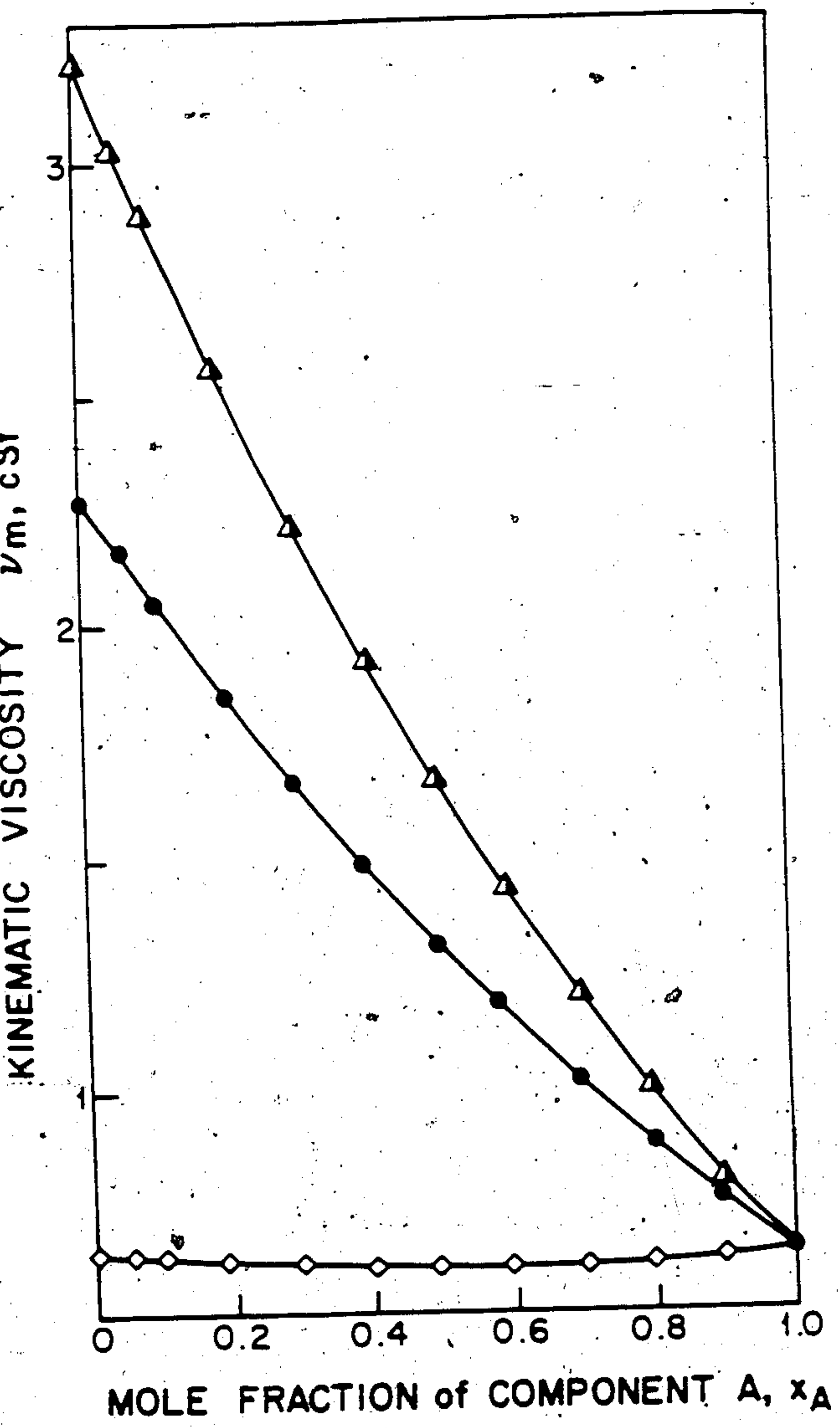

KINEMATIC VISCOSITY ν_m, cSt
3
2
1
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.12 : Kinematic Viscosity-Composition Plot for Systems with Toluene at 40.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
⬙	Toluene(A)-n-Dodecane(B)
◒	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)

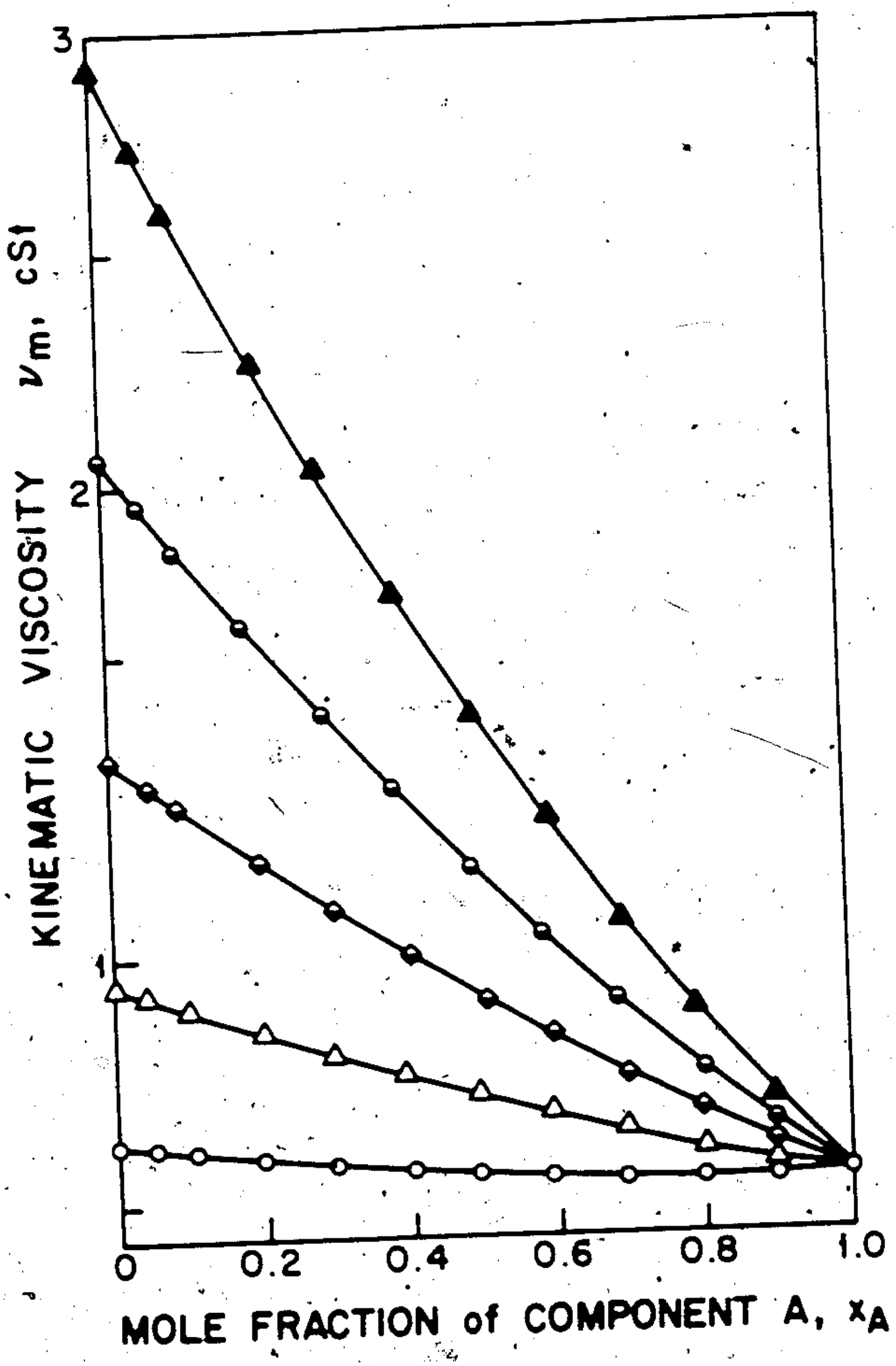

3
2
1
KINEMATIC VISCOSITY ν_m, cSt
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.13 : Kinematic Viscosity-Composition Plot for the Systems with Ethylbenzene at 40.00°C.

Legend	System
◇	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
▲	Ethylbenzene(A)-n-Hexadecane(B)

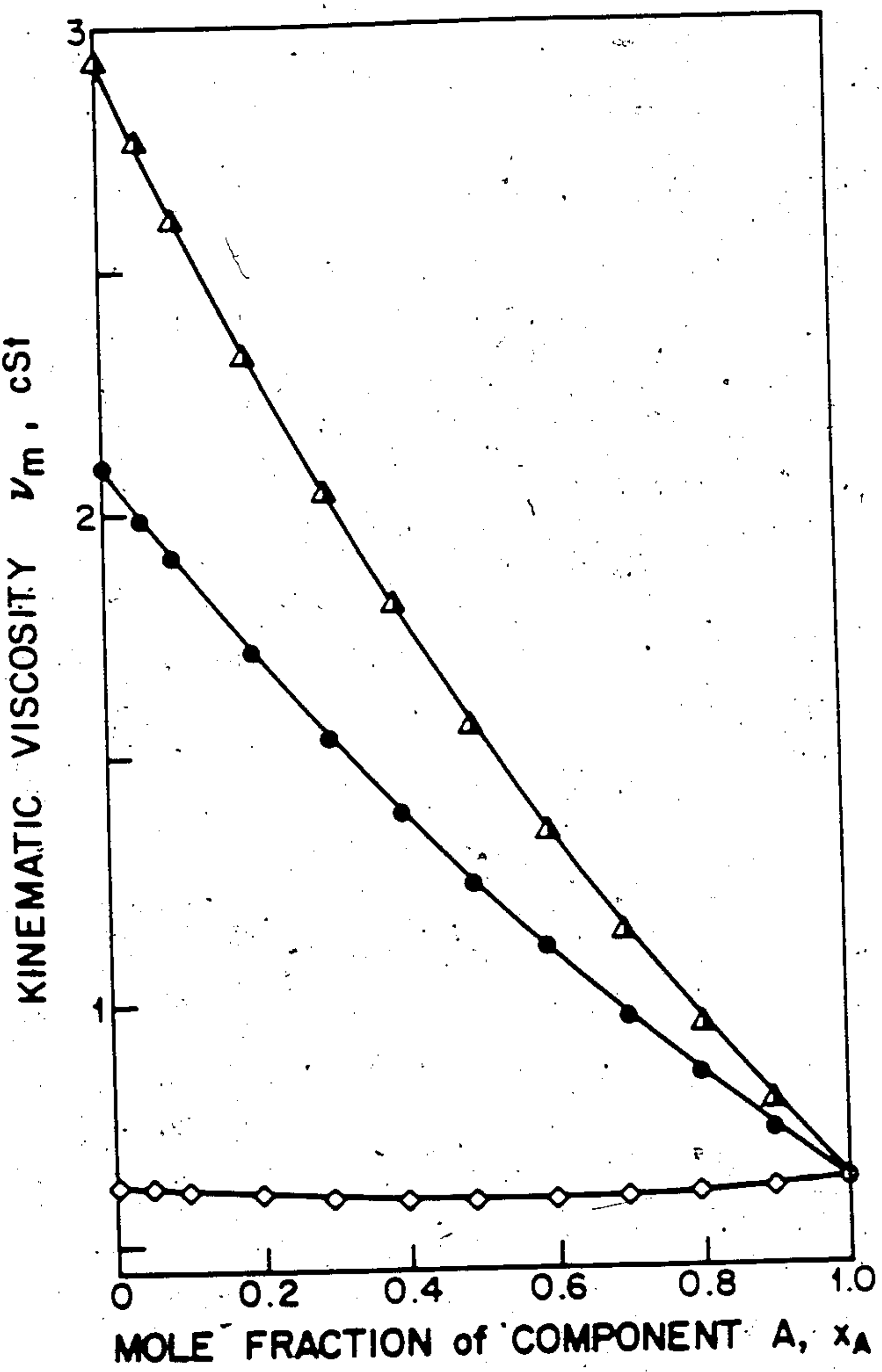

3
2
1
KINEMATIC VISCOSITY ν_m, cSt
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

TABLE 4.[illegible] Least Squares Constants for the Equation $\nu_m = \sum_{i=0}^{n} A_i x_A^i$, cSt

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 20.00°C						
Toluene(A)-n-Octane(B)	0.7705	0.2441	0.1232	0.0501	0.0781	2.64×10^{-4}
Toluene(A)-n-Decane(B)	1.25895	0.8565	0.2524			3.51×10^{-5}
Toluene(A)-n-Dodecane(B)	1.9754	1.7651	0.4295	0.0571		3.09×10^{-5}
Toluene(A)-n-Tetradecane(B)	3.0206	3.3640	1.0220			2.16×10^{-5}
Toluene(A)-n-Hexadecane(B)	4.4597	5.7796	2.1767	0.1797		8.88×10^{-5}
Ethylbenzene(A)-n-Octane(B)	0.7697	0.1383	0.0480	0.0908		8.59×10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	3.0199	3.4457	1.4462	0.2511		2.54×10^{-5}
Ethylbenzene(A)-n-Hexadecane(B)	4.4677	5.98096	2.8633	0.5760		8.08×10^{-5}
Temperature = 25.00°C						
Toluene(A)-n-Octane(B)	0.7291	0.2139	0.0391	0.0863		3.06×10^{-5}
Toluene(A)-n-Decane(B)	1.1703	0.7449	0.1971	0.0173		1.93×10^{-5}
Toluene(A)-n-Dodecane(B)	1.8232	1.6095	0.4194	0.0066		1.64×10^{-5}
Toluene(A)-n-Tetradecane(B)	2.7396	2.9624	0.8637	0.00098		2.65×10^{-5}
Toluene(A)-n-Hexadecane(B)	3.9744	4.8176	1.4848	0.0078		7.01×10^{-5}
Ethylbenzene(A)-n-Octane(B)	0.7295	0.1389	0.0725	0.0659		2.87×10^{-5}
Ethylbenzene(A)-n-Tetradecane(B)	2.7568	2.9806	1.1875	0.2054		2.46×10^{-5}
Ethylbenzene(A)-n-Hexadecane(B)	3.9772	5.0289	2.10496	0.3247		1.70×10^{-5}

TABLE 4.23, cont'd

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 35.00°C						
Toluene(A) n Octane(B)	0.6585	0.2040	0.1462	0.1178	0.0955	4.5×10^{4}
Toluene(A) n Decane(B)	1.0291	0.5619	0.0108	0.1001		1.06×10^{5}
Toluene(A) n Dodecane(B)	1.5559	1.29797	0.4464	0.2803	0.1542	4.10×10^{4}
Toluene(A) n Tetradecane(B)	2.2743	2.2601	0.5648			2.35×10^{5}
Toluene(A) n Hexadecane(B)	3.2204	3.5819	0.7685	0.2778	0.1069	9.98×10^{4}
Ethylbenzene(A) n Octane(B)	0.6581	0.1257	0.1199	0.04899	0.0533	1.29×10^{4}
Ethylbenzene(A) n Tetradecane(B)	2.2791	2.3081	0.8182	0.1327		4.01×10^{5}
Ethylbenzene(A) n Hexadecane(B)	3.2199	3.7145	1.2934	0.1485		5.83×10^{5}
Temperature = 40.00°C						
Toluene(A) n Octane(B)	0.6263	0.1731	0.0778	0.0458	0.0654	2.67×10^{4}
Toluene(A) n Decane(B)	0.9658	0.5436	0.1623	0.1458	0.1118	7.64×10^{4}
Toluene(A) n Dodecane(B)	1.4466	1.1412	0.2215	0.0[illegible]		8.79×10^{4}
Toluene(A) n Tetradecane(B)	2.0878	2.0325	0.6593	0.3688	0.2052	3.00×10^{5}
Toluene(A) n Hexadecane(B)	2.9244	3.1734	0.7965			5.30×10^{5}
Ethylbenzene(A) n Octane(B)	0.6265	0.1222	0.1415	0.0869	0.0652	3.97×10^{4}
Ethylbenzene(A) n Tetradecane(B)	2.0895	2.0553	0.8798	0.49899	0.2097	3.72×10^{5}
Ethylbenzene(A) n Hexadecane(B)	[illegible]232	3.2349	1.0401	0.1045		4.39×10^{5}

TABLE 4.24 Least Squares Constants for the Equation $\eta_m = \sum_{i=0}^{n} A_i x_1^i$, cP

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 20.00°C						
Toluene(A) n Octane(B)	0.5410	0.0986	0.1284	0.0970	0.1132	5.[illegible]0 x 10^{-4}
Toluene(A) n Decane(B)	0.9175	0.5072	0.1198	0.0559		2.77 x 10^{-3}
Toluene(A) n Dodecane(B)	1.4783	1.2144	0.2656	0.0573		2.48 x 10^{-3}
Toluene(A) n Tetradecane(B)	2.3049	2.4616	0.7442			1.41 x 10^{-3}
Toluene(A) n Hexadecane(B)	3.4501	4.3408	1.605	0.1273		3.00 x 10^{-3}
Ethylbenzene(A) n Octane(B)	0.5405	0.0109	0.0739	0.0161	0.0482	6.91 x 10^{-4}
Ethylbenzene(A) n Tetradecane(B)	2.3050	2.52397	1.1601	0.3278	0.1045	1.97 x 10^{-3}
Ethylbenzene(A) n Hexadecane(B)	3.45295	4.4751	2.1124	0.4234		6.56 x 10^{-3}
Temperature = 25.00°C						
Toluene(A) n Octane(B)	0.5091	0.0658	0.0014	0.1101		8.82 x 10^{-4}
Toluene(A) n Decane(B)	0.8496	0.4554	0.1086	0.0485		1.63 x 10^{-3}
Toluene(A) n Dodecane(B)	1.3568	1.1012	0.2624	0.0333		1.50 x 10^{-3}
Toluene(A) n Tetradecane(B)	2.0802	2.3552	0.6257	0.0019		1.85 x 10^{-3}
Toluene(A) n Hexadecane(B)	3.0614	3.5933	1.0785	0.00399		5.64 x 10^{-3}
Ethylbenzene(A) n Octane(B)	0.5092	0.0032	0.0299	0.0923		8.74 x 10^{-3}
Ethylbenzene(A) n Tetradecane(B)	2.0789	2.1555	0.8483	0.1442		2.02 x 10^{-3}
Ethylbenzene(A) n Hexadecane(B)	3.0636	3.7493	1.5617	0.2482		1.45 x 10^{-3}

TABLE 4.24, cont'd

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 35.00°C						
Toluene(A) n Octane(B)	0.4544	0.0766	0.1088	0.0775	0.0832	5.43×10^{4}
Toluene(A) n Decane(B)	0.7389	0.3449	0.0459	0.0075	0.0453	8.51×10^{4}
Toluene(A) n Dodecane(B)	1.1476	0.8773	0.3006	0.1974	0.1190	3.10×10^{4}
Toluene(A) n Tetradecane(B)	1.7117	1.61996	0.4033			1.82×10^{5}
Toluene(A) n Hexadecane(B)	2.4596	2.6441	0.5084	0.3033	0.1320	6.98×10^{4}
Ethylbenzene(A) n Octane(B)	0.4542	0.0112	0.1019	0.0477	0.0630	1.36×10^{4}
Ethylbenzene(A) n Tetradecane(B)	1.7152	1.6517	0.5998	0.1033		5.05×10^{5}
Ethylbenzene(A) n Hexadecane(B)	2.4594	2.8127	1.3277	0.17119	0.2943	4.88×10^{5}
Temperature = 40.00°C						
Toluene(A) n Octane(B)	0.4298	0.0625	0.07[illegible]	0.0973	0.0983	2.02×10^{4}
Toluene(A) n Decane(B)	0.6909	0.3185	0.1006	0.0980	0.0918	7.17×10^{4}
Toluene(A) n Dodecane(B)	1.0619	0.7667	0.1366	0.0346		8.49×10^{4}
Toluene(A) n Tetradecane(B)	1.5638	1.4367	0.4355	0.2575	0.1426	2.16×10^{5}
Toluene(A) n Hexadecane(B)	2.2237	2.2794	0.4347	0.0881		6.04×10^{5}
Ethylbenzene(A) n Octane(B)	0.42999	0.0146	0.1293	0.0965	0.0821	5.26×10^{4}
Ethylbenzene(A) n Tetradecane(B)	1.5646	1.4549	0.6492	0.4075	0.1793	1.28×10^{5}
Ethylbenzene(A) n Hexadecane(B)	2.2280	2.5039	1.2573	0.7286	0.2779	5.25×10^{5}

temperature are shown in Figures 4.6 to 4.13. All of these isotherms are also smoothly varying functions of mole fraction.

Kinematic and absolute viscosity values for each system were fitted to equations of the form:

$$ {}_{=} = \sum_{i=0}^{i=n} A_i x_A^i \qquad (4.4) $$

where ${}_{=}$ is the kinematic viscosity of the liquid mixture in cSt, and x_A is the mole-fraction of component A, and

$$ {}_{=} = \sum_{i=0}^{i=n} A_i x_A^i \qquad (4.5) $$

where ${}_{=}$ is the absolute viscosity of the liquid mixture in cP. The values of the constants A_i of Equation (4.4) and Equation (4.5) are calculated by the method of least squares and are reported in Tables 4.23 and 4.24, respectively. The last column in the previous two tables gives the standard deviation of the fit.

As one can see, the standard deviation of the fit is small. The higher values of standard deviation encountered in this work were with systems containing n-hexadecane and n-tetradecane where those viscometers had to be used which were calibrated with standard liquids having viscosity values reported up to third decimal place.

Figure 4.14 : Variation of Excess Activation Energy of Viscous Flow with Mole Fraction at 20.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
◑	Toluene(A)-n-Dodecane(B)
⬙	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
◬	Ethylbenzene(A)-n-Hexadecane(B)

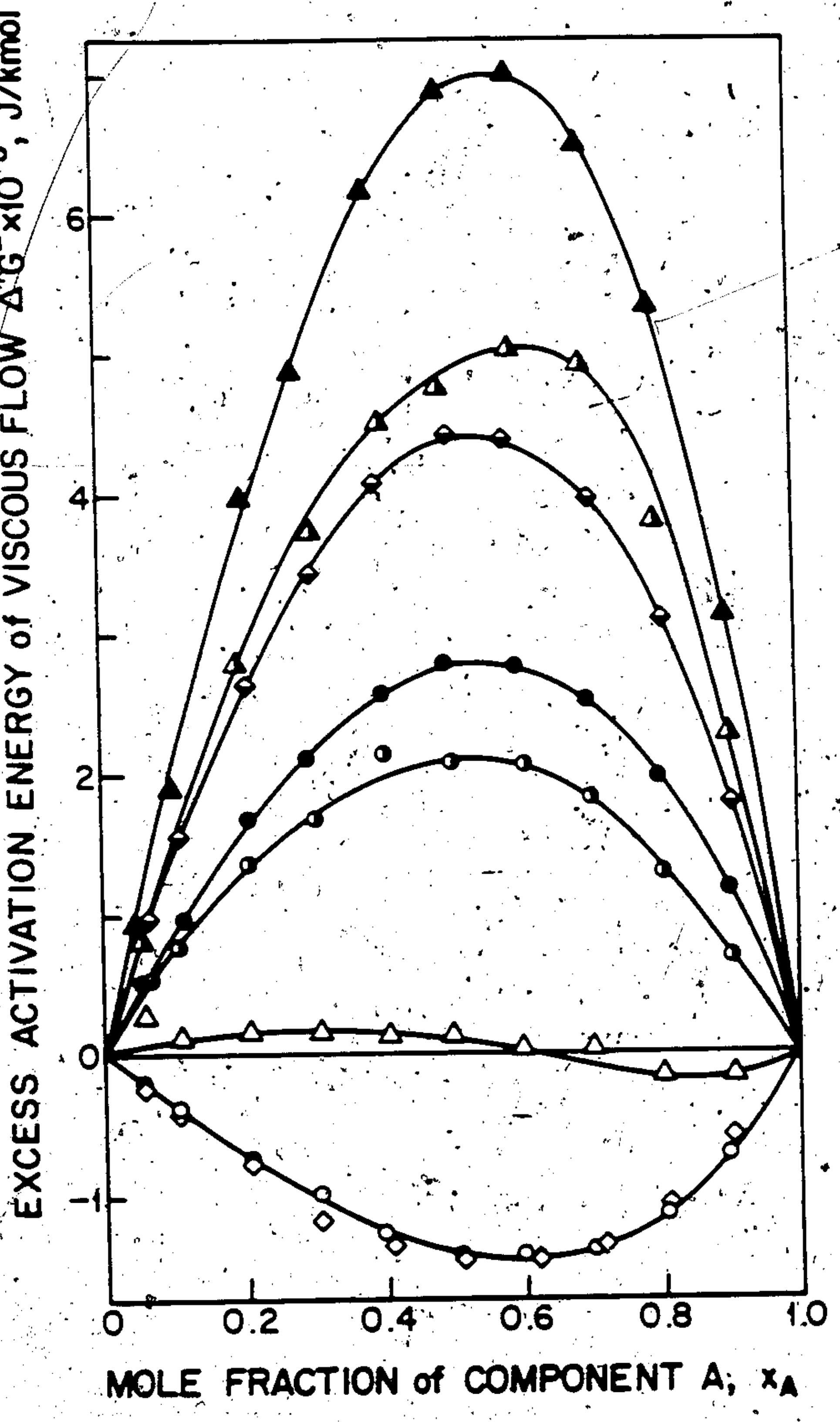

EXCESS ACTIVATION ENERGY of VISCOUS FLOW $\Delta^{*}G^{E} \times 10^{-6}$, J/kmol
6
4
2
0
-1
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.15 : Variation of Excess Activation Energy of Viscous Flow with Mole Fraction at 25.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
◐	Toluene(A)-n-Dodecane(B)
⬙	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
◬	Ethylbenzene(A)-n-Hexadecane(B)

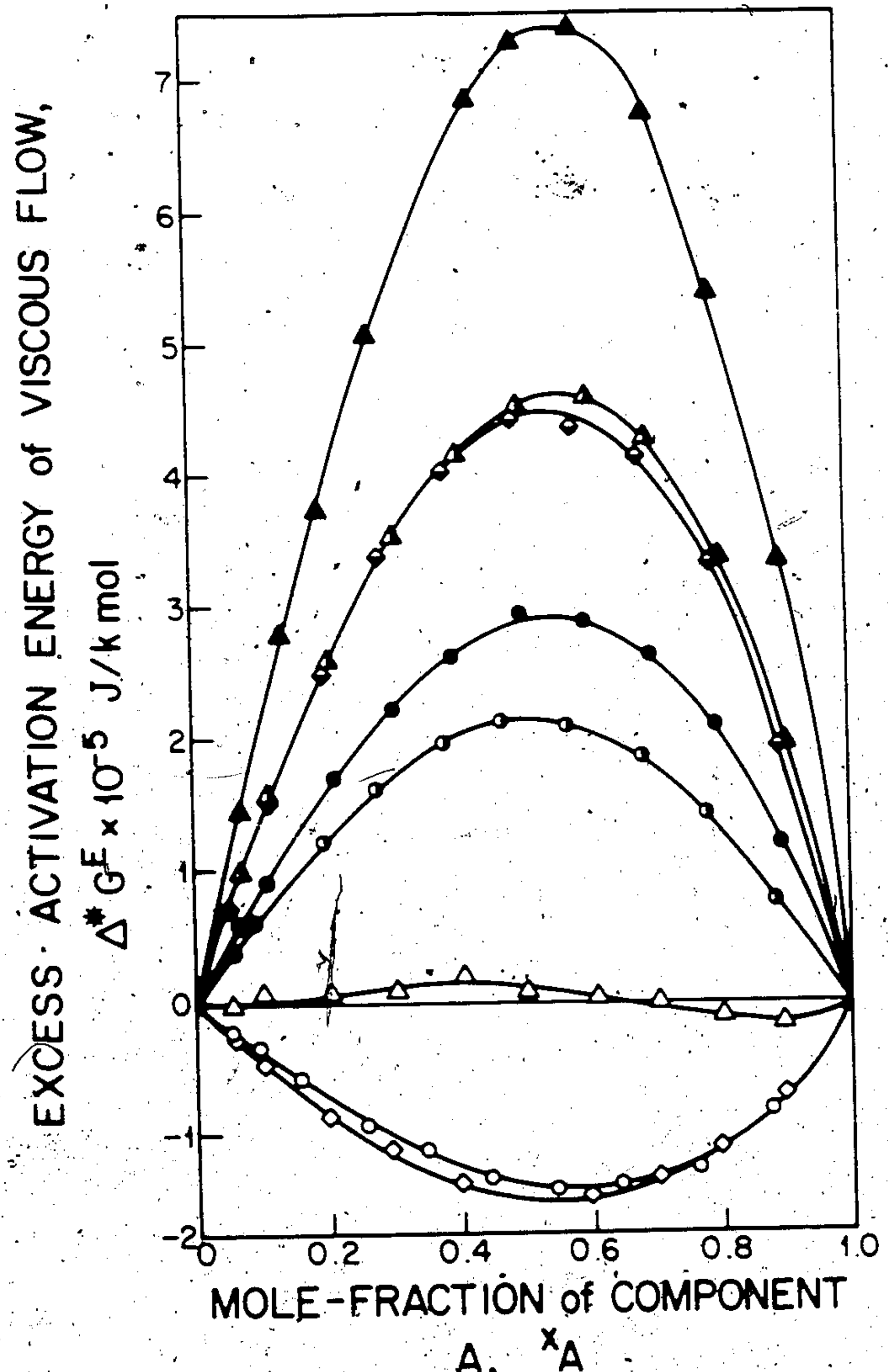

EXCESS ACTIVATION ENERGY of VISCOUS FLOW,
Δ* G^E × 10^-5 J/k mol
7
6
5
4
3
2
1
0
-1
-2
0
0.2
0.4
0.6
0.8
1.0
MOLE-FRACTION of COMPONENT
A, x_A

Figure 4.16 : Variation of Excess Activation Energy of Viscous Flow with Mole Fraction at 35.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
◑	Toluene(A)-n-Dodecane(B)
⬙	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
◭	Ethylbenzene(A)-n-Hexadecane(B)

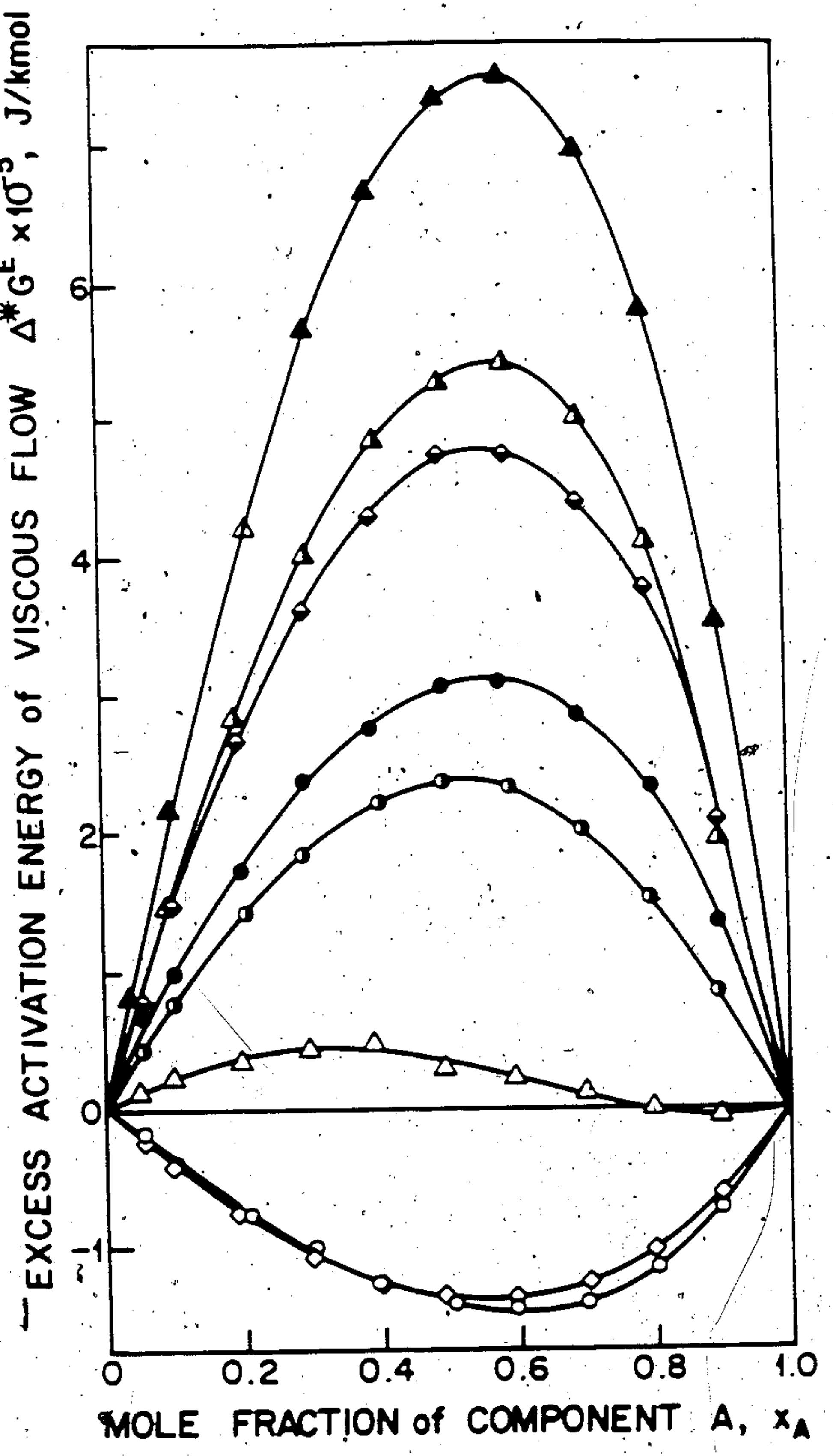
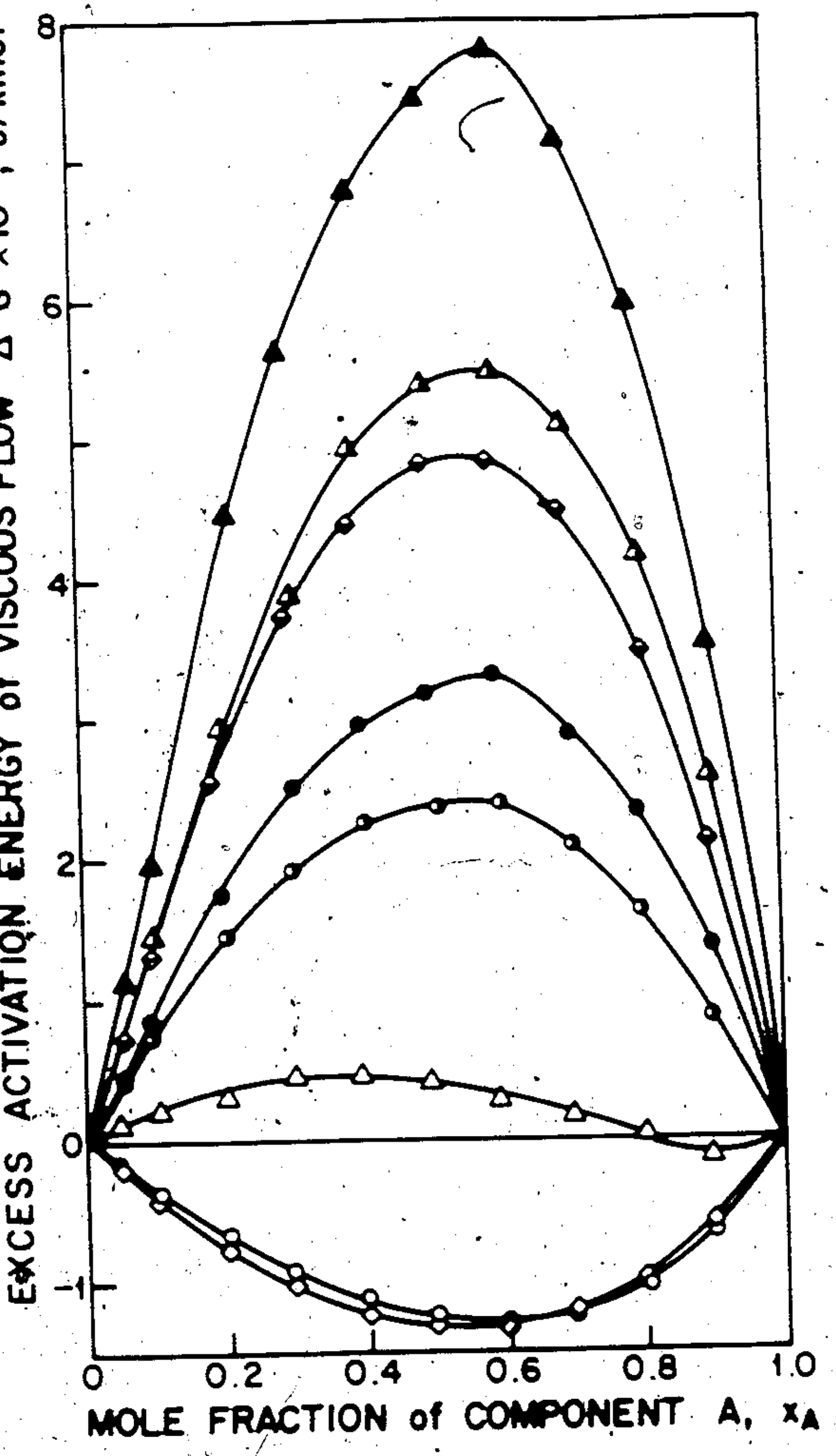

—EXCESS ACTIVATION ENERGY of VISCOUS FLOW Δ*G^E ×10^-5, J/kmol
6
4
2
0
-1
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.17 : Variation of Excess Activation Energy of Viscous Flow with Mole Fraction at 40.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
◑	Toluene(A)-n-Dodecane(B)
⬙	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
◭	Ethylbenzene(A)-n-Hexadecane(B)


EXCESS ACTIVATION ENERGY of VISCOUS FLOW $\Delta^{*}G^{E}\times10^{-6}$, J/kmol
8
6
4
2
0
-1
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

4.6.1 Excess activation energy of viscous flow

Grunberg, [1954] attempted to relate the excess activation energy of viscous flow to thermodynamic non-ideality. Reed and Taylor [1959] argued that there is no simple relationship between viscosity and the thermodynamic properties of a solution. These authors suggested the following equation discussed in Chapter 2.

$$\ln(\eta_m V_m) = x_A \ln(\eta_A V_A) + x_B \ln(\eta_B V_B) + \frac{\Delta^* G^E}{RT}$$

which relates viscosity of a mixture to $\Delta^* G^E$. The above equation along with the viscosity-composition data were used to calculate the excess activation energy of viscous flow. The change in excess activation energy with composition for each system at different temperatures is given in Appendix D as well as in Figures 4.14 to 4.17.

Two systems containing n-octane always exhibited negative $\Delta^* G^E$ over the entire composition range whereas the toluene-n-decane system showed positive $\Delta^* G^E$ up to x_A = 0.7 then at $x_A >$ 0.8 became negative. The remaining systems have positive values of $\Delta^* G^E$ over the entire composition range.

The values of $\Delta^* G^E$ were found to increase with the increase of temperature. The excess activation energy of viscous flow was fitted to a polynomial of the form

TABLE 4.15 Least Square Constants for the Equation $G^{E} \times 10^{-5} = x_A(1-x_A)\sum_{i=0}^{n} A_i(2x_A-1)^i$, J/kmol

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 20.00°C						
Toluene(A) n Octane(B)	0.0565	0.021	0.5966	0.686		0.022
Toluene(A) n Decane(B)	0.5266	0.016				0.083
Toluene(A) n Dodecane(B)	0.0856	0.4597	0.868	0.015		0.052
Toluene(A) n Tetradecane(B)	17.558	5.447	0.553	1.092		0.018
Toluene(A) n Hexadecane(B)	27.571	7.205	2.063			0.063
Ethylbenzene(A) n Octane(B)	5.917	1.485				0.026
Ethylbenzene(A) n Tetradecane(B)	11.073	1.984	0.246			0.023
Ethylbenzene(A) n Hexadecane(B)	19.509	6.761	6.435	2.850	2.6125	0.078
Temperature = 25.00°C						
Toluene(A) n Octane(B)	5.507	-1.7998	0.979	0.786		0.0205
Toluene(A) n Decane(B)	0.440	0.865	1.746	0.637		0.035
Toluene(A) n Dodecane(B)	8.563	0.599	1.469	0.834		0.0106
Toluene(A) n Tetradecane(B)	17.652	-3.275	1.053	0.121		0.040
Toluene(A) n Hexadecane(B)	28.989	[illegible]	0.828	0.1597		0.0641
Ethylbenzene(A) n Octane(B)	5.881	[illegible]	0.791	0.8596		0.013
Ethylbenzene(A) n Tetradecane(B)	11.606	2.656	0.368	1.209		0.023
Ethylbenzene(A) n Hexadecane(B)	18.132	4.916	0.925	1.274		0.017

TABLE 4.25, cont'd

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation
Temperature = 35.00°C						
Toluene(A) n Octane(B)	4.946	1.744	1.575	0.739	1.121	0.0097
Toluene(A) n Decane(B)	1.323	2.082	0.616			0.031
Toluene(A) n Dodecane(B)	9.510	0.9000	1.523	0.695	0.682	0.0073
Toluene(A) n Tetradecane(B)	18.999	4.656	1.871			0.065
Toluene(A) n Hexadecane(B)	5.503	11.067	21.622	30.509		0.013
Ethylbenzene(A) n Octane(B)	5.498	1.196	0.702	0.086	0.535	0.0058
Ethylbenzene(A) n Tetradecane(B)	12.275	3.328	1.372	1.967		0.041
Ethylbenzene(A) n Hexadecane(B)	21.099	7.600	6.259	2.566	12.729	0.092
Temperature = 40.00°C						
Toluene(A) n Octane(B)	4.797	2.147	0.769	0.553		0.0079
Toluene(A) n Decane(B)	1.613	1.507	1.558	1.369		0.025
Toluene(A) n Dodecane(B)	9.650	1.368	0.343	1.453		0.022
Toluene(A) n Tetradecane(B)	19.297	3.649	1.433	1.815	2.219	0.025
Toluene(A) n Hexadecane(B)	29.918	8.442	6.508	1.632	6.861	0.081
Ethylbenzene(A) n Octane(B)	5.263	0.828	0.527	0.537		0.014
Ethylbenzene(A) n Tetradecane(B)	12.88	2.798				0.033
Ethylbenzene(A) n Hexadecane(B)	21.554	6.849	1.325			0.079

Figure 4.18 : Variation of Excess Viscosity with Mole Fraction at 20.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
●	Toluene(A)-n-Dodecane(B)
◐	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
◆	Ethylbenzene(A)-n-Tetradecane(B)
⬙	Ethylbenzene(A)-n-Hexadecane(B)

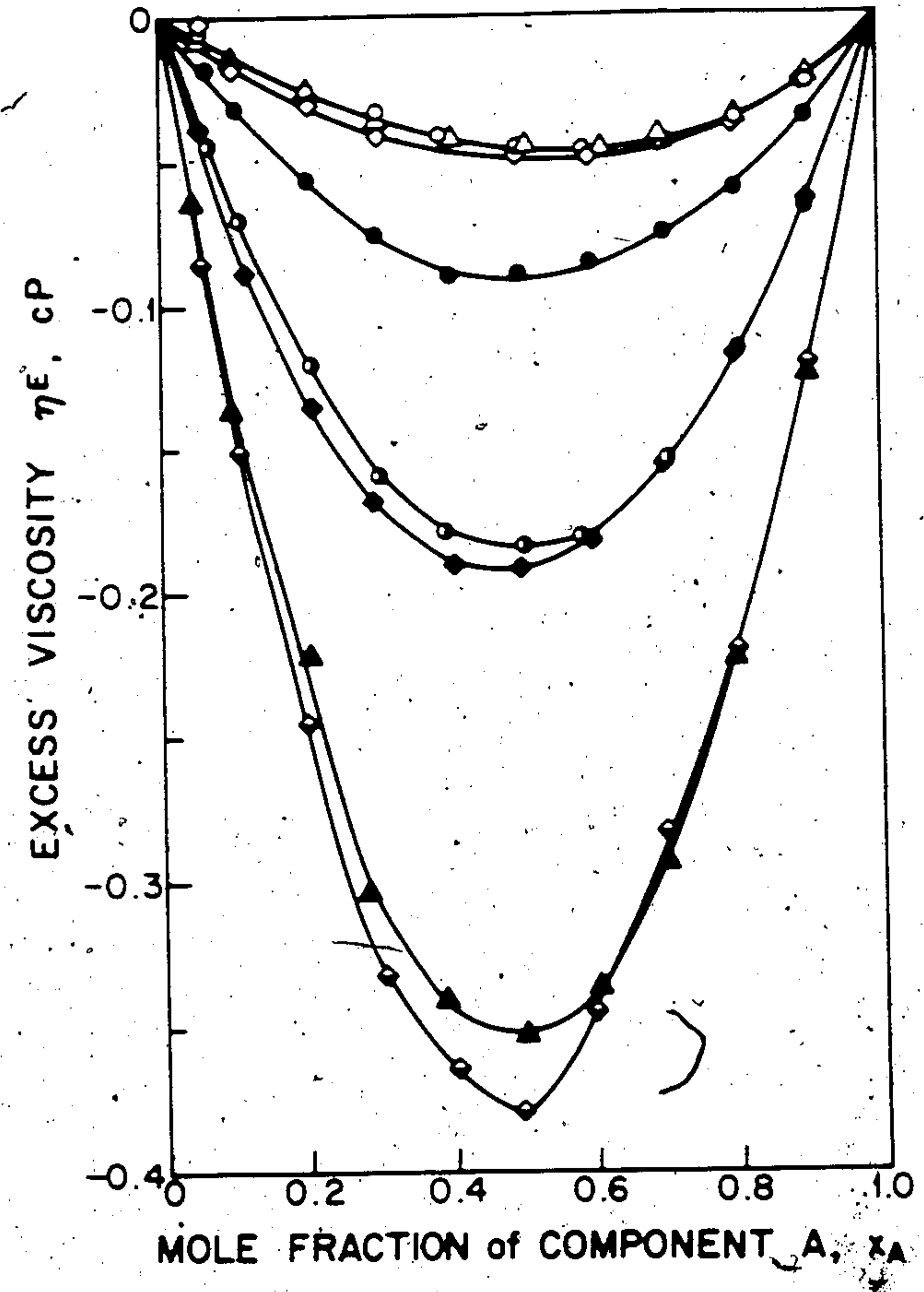

0
-0.1
-0.2
-0.3
-0.4
0
0.2
0.4
0.6
0.8
1.0
EXCESS VISCOSITY η^E, cP
MOLE FRACTION of COMPONENT A, x_A

Figure 4.19 : Variation of Excess Viscosity with Mole Fraction at 25.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
●	Toluene(A)-n-Dodecane(B)
◑	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
◆	Ethylbenzene(A)-n-Tetradecane(B)
⬙	Ethylbenzene(A)-n-Hexadecane(B)

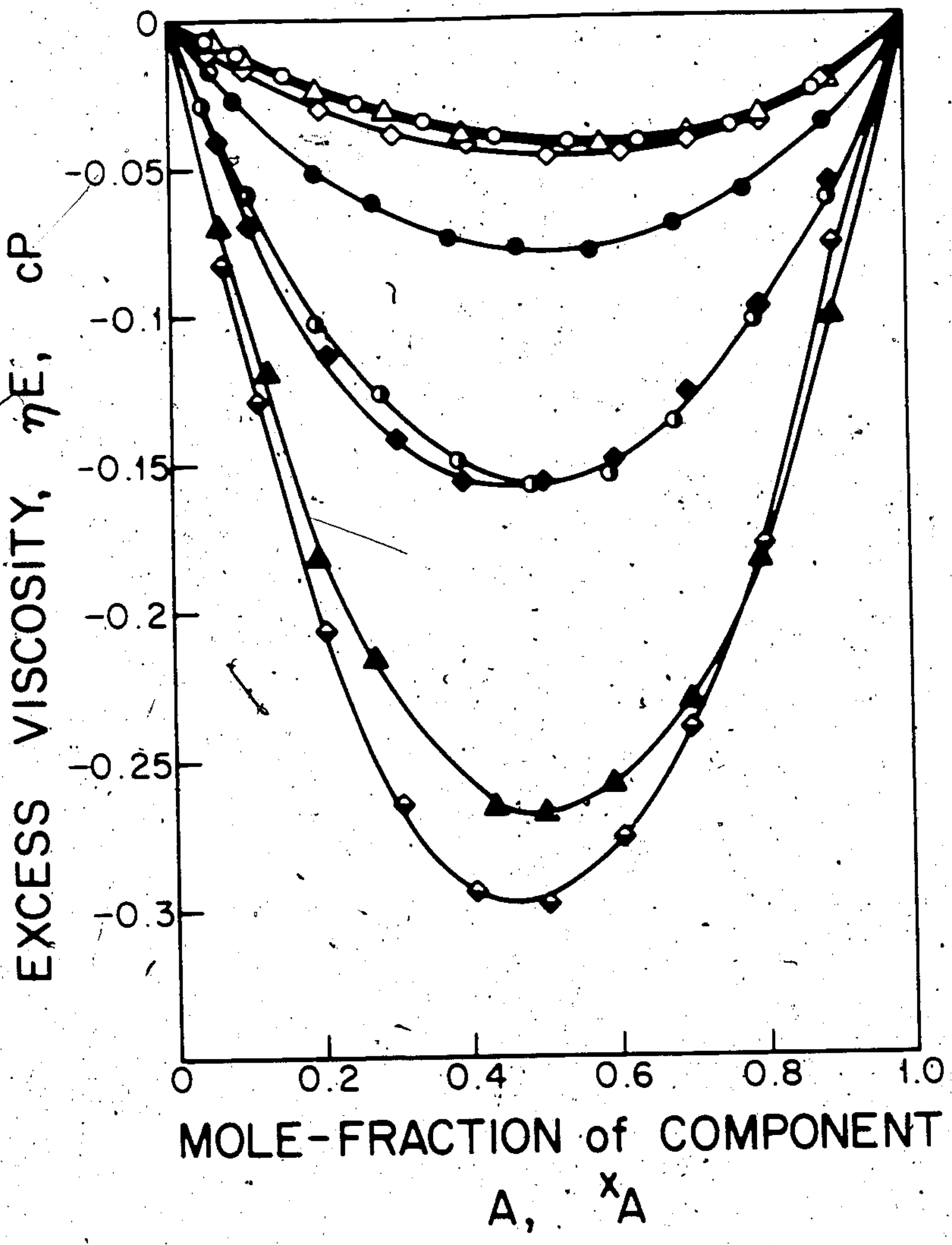

0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
EXCESS VISCOSITY, ηE, cP
0
0.2
0.4
0.6
0.8
1.0
MOLE-FRACTION of COMPONENT A, xA

Figure 4.20 : Variation of Excess Viscosity with Mole Fraction at 35.00° C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
●	Toluene(A)-n-Dodecane(B)
◑	Toluene(A)-n-Tetradecane(B)
▲	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
◆	Ethylbenzene(A)-n-Tetradecane(B)
⬙	Ethylbenzene(A)-n-Hexadecane(B)

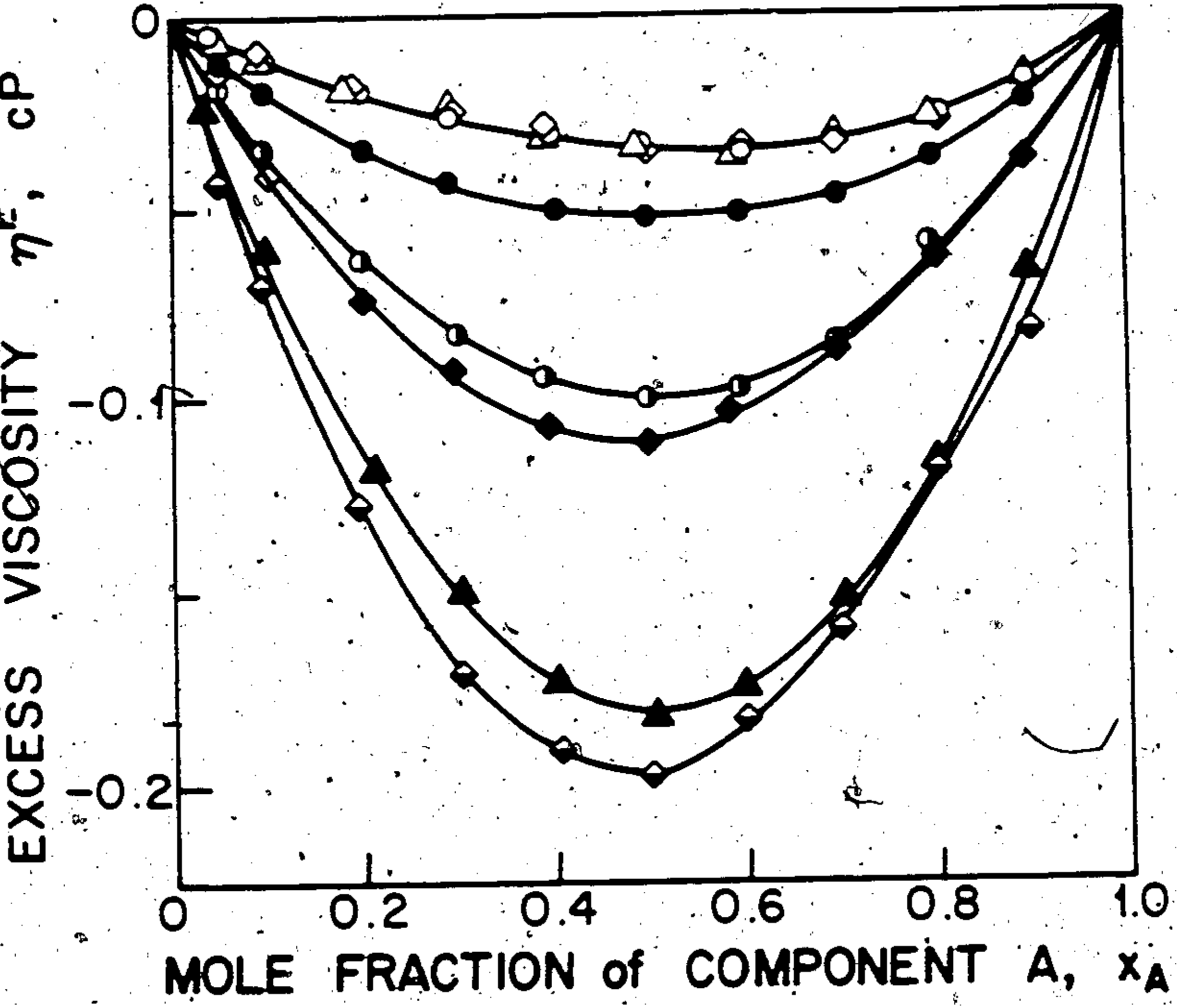
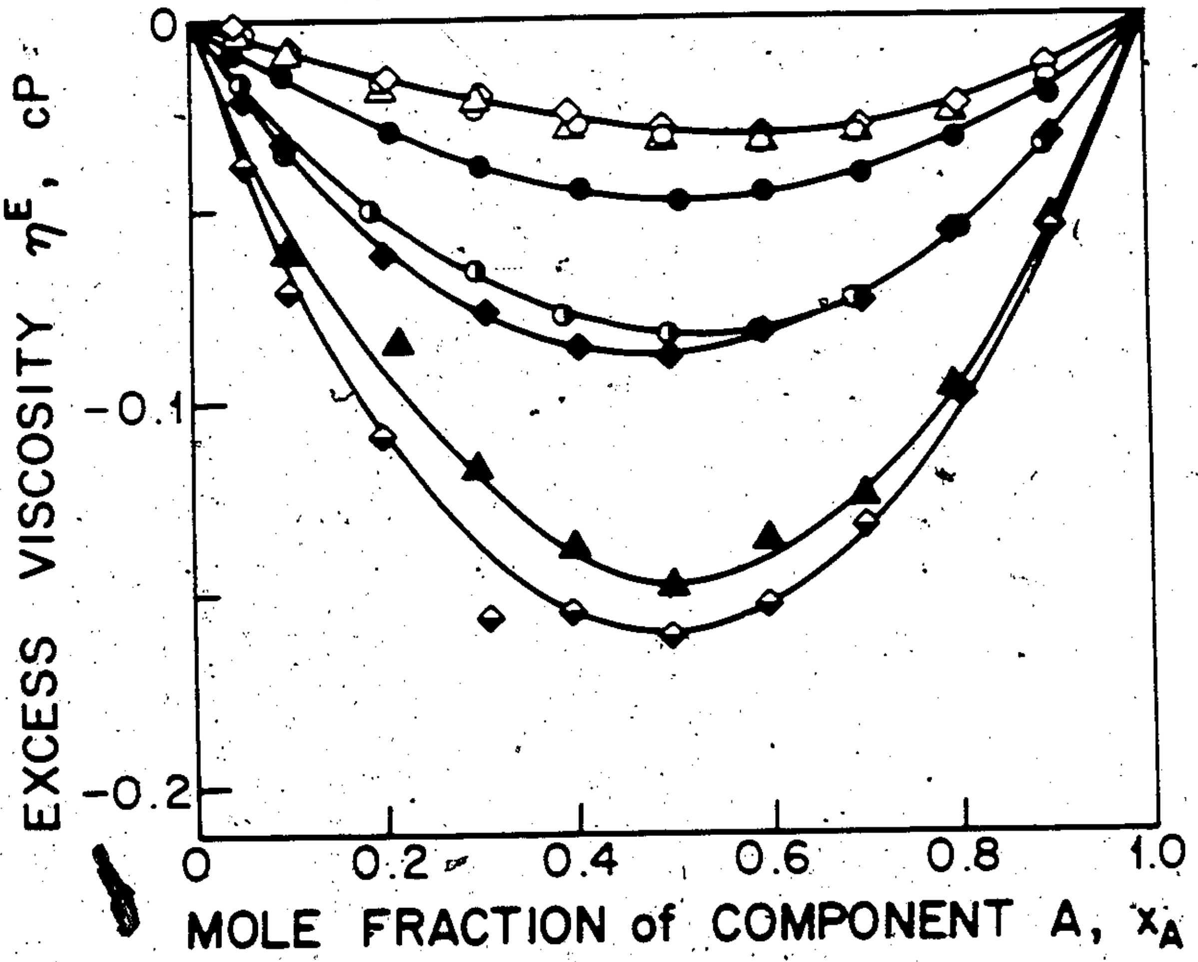

0
-0.1
-0.2
EXCESS VISCOSITY η^E, cP
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

Figure 4.21 : Variation of Excess Viscosity with Mole Fraction at 40.00°C.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
●	Toluene(A)-n-Dodecane(B)
◑	Toluene(A)-n-Tetradecane(B)
△	Toluene(A)-n-Hexadecane(B)
◇	Ethylbenzene(A)-n-Octane(B)
◆	Ethylbenzene(A)-n-Tetradecane(B)
⬙	Ethylbenzene(A)-n-Hexadecane(B)


EXCESS VISCOSITY η^E, cP
0
−0.1
−0.2
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

$$\Delta^{*}G^{E} \times 10^{-3} = x_A (1 - x_A) \sum_{i=0}^{i=n} A_i (2x_A - 1)^i \qquad (4.6)$$

Values of the parameters "A_i" were obtained by the method of least squares. These values are reported in Table 4.25. The standard deviation of the fit is listed in the last column of this table. This equation, Equation (4.6) fitted the data well as can be seen from small values of standard deviation listed in Table 4.25.

4.6.2 Excess viscosity

Viscosity-Composition data were also used to calculate the excess viscosity of the binary mixtures using the following equation:

$$\eta^{E} = \eta_m - x_A \eta_A - x_B \eta_B \qquad (4.7)$$

Excess viscosity-composition data for each system at different temperatures are given along with $\Delta^{*}G^{E}$ in Appendix D and depicted in Figures 4.18 to 4.21. As can be seen from these figures, the system including n-octane and n-decane exhibited almost the same value of excess viscosity in every instance. Another feature of these figures is that excess viscosity is found to increase with temperature. In every system excess viscosity was negative over the entire composition range.

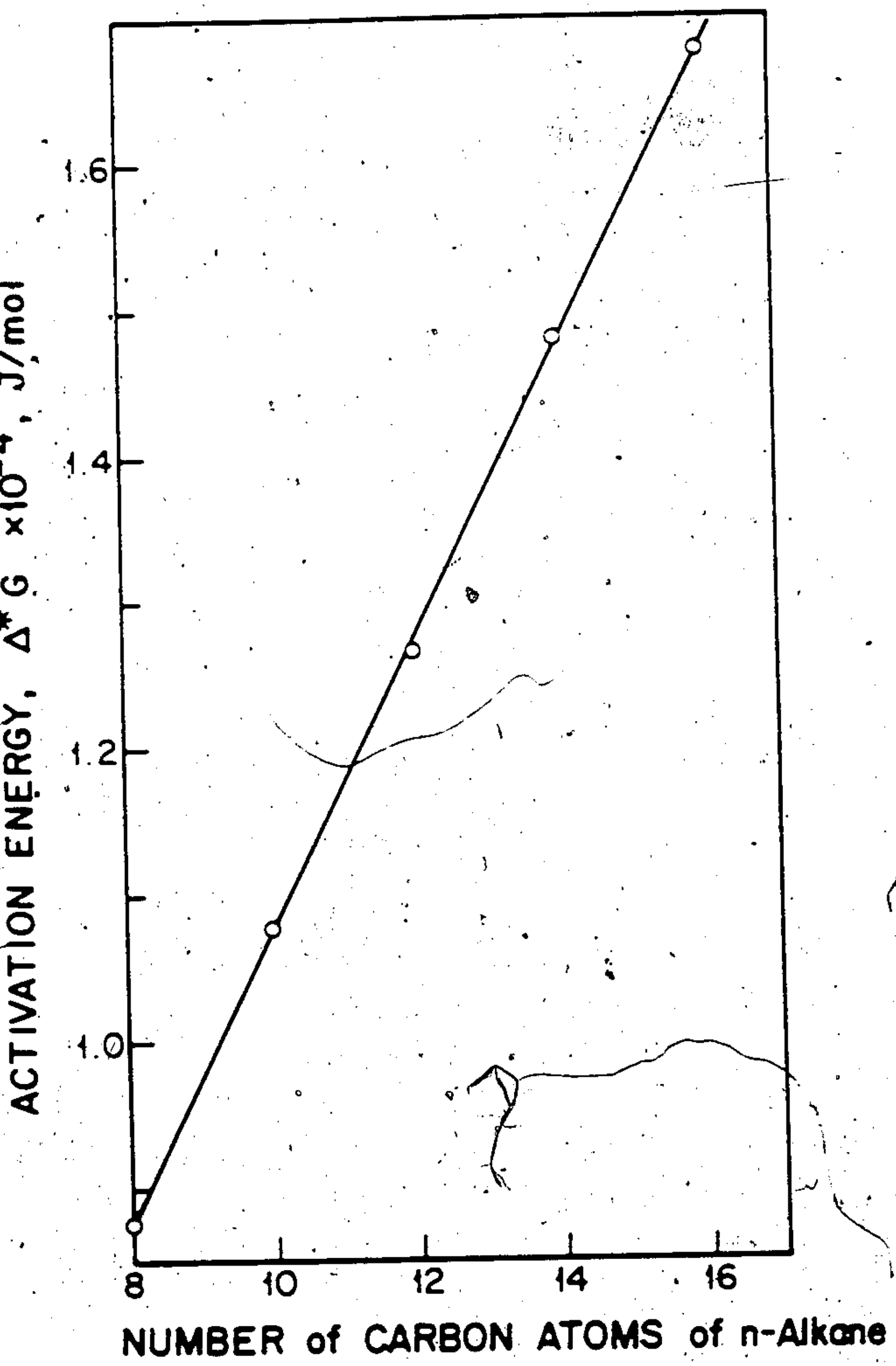
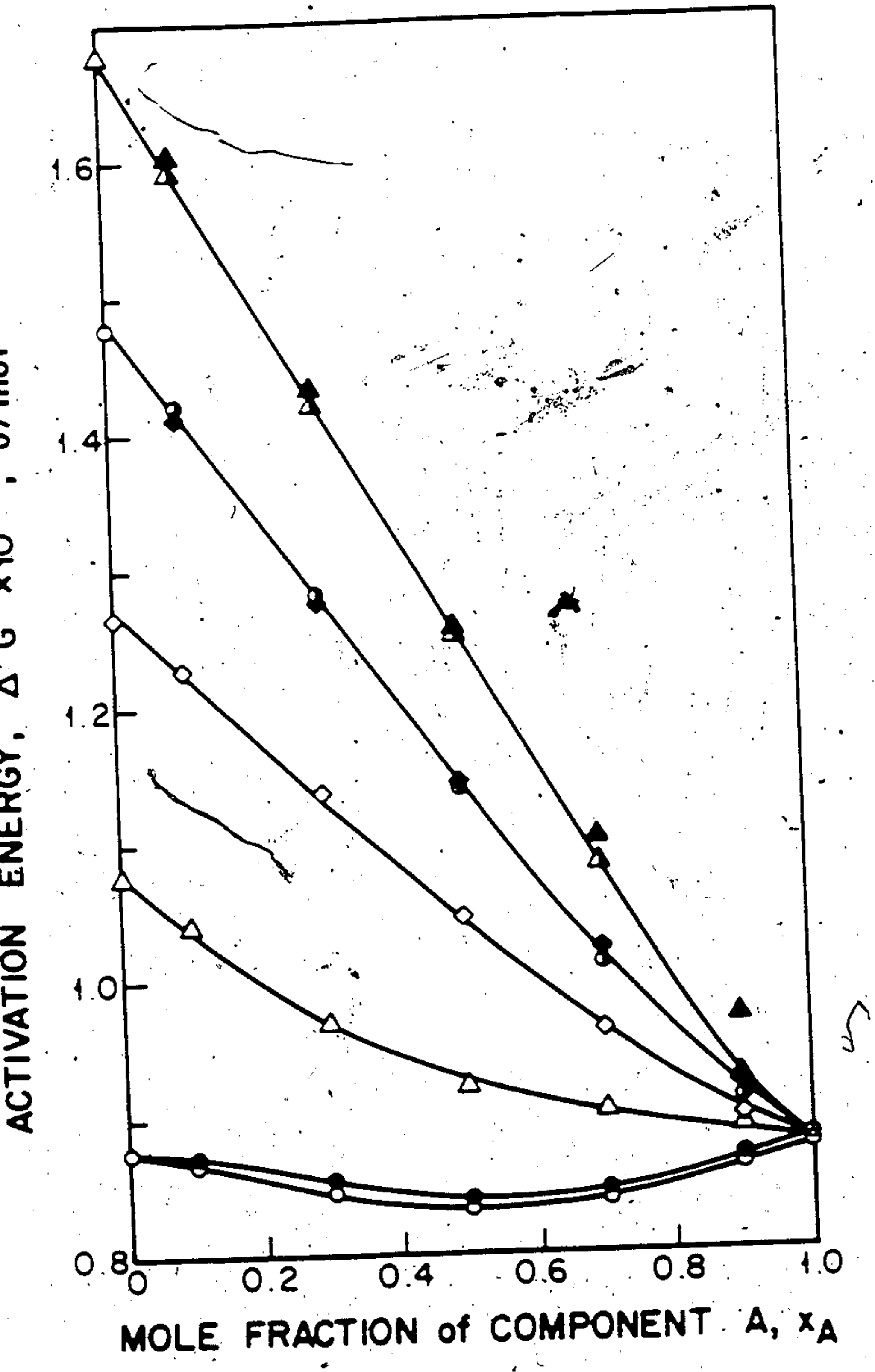


FIGURE 4.22: Variation of Activation Energy of Viscous Flow with Number of Atoms of Normal Alkanes.

Figure 4.23 : Variation of Activation Energy of Viscous Flow with Mole Fraction.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
◇	Toluene(A)-n-Dodecane(B)
◐	Toluene(A)-n-Tetradecane(B)
◭	Toluene(A)-n-Hexadecane(B)
○	Ethylbenzene(A)-n-Octane(B)
◆	Ethylbenzene(A)-n-Tetradecane(B)
▲	Ethylbenzene(A)-n-Hexadecane(B)


ACTIVATION ENERGY, $\Delta^{*}G \times 10^{-4}$, J/mol
1.6
1.4
1.2
1.0
0.8
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION of COMPONENT A, x_A

4.6.3 Activation energy of viscous flow

Viscosity-composition data were also used to calculate the activation energy of viscous flow for pure components as well as that of the mixture.

The activation energy of viscous flow was then plotted against number of carbon atoms of n-alkanes and a straight line relation was obtained as can be seen in Figure 4.22. However, the activation energy of viscous flow did not vary linearly with composition as can be seen in Figure 4.23.

4.7 Predictive Capability of the Various Viscosity Models

Viscosity as a possible and promising tool to reveal the mystery of the liquid structure has received a great deal of attention from researchers. Various models have been proposed for the prediction of viscosity of liquid mixtures. No satisfactory purely theoretical model has yet been proposed for the prediction of viscosity of liquid mixtures. The existing models are either empirical or semi-empirical and still need a lot of confirmation for their predictive capabilities.

The experimental data obtained in this study were used for testing the predictive capability of three existing literature models: The McAllister's three body model [1960], Heric's empirical equation [1967] with two

TABLE 4.1[illegible] Values of the Parameters Involved in McAllister's Model.

System	ν_{AB}	ν_{BA}	Standard Deviation
Temperature = 25.00°C			
Toluene(A)-n-Octane(B)	0.6099	0.7036	4.15×10^{-4}
Toluene(A)-n-Decane(B)	0.8000	1.1083	3.34×10^{-3}
Toluene(A)-n-Dodecane(B)	1.0411	1.4903	2.92×10^{-3}
Toluene(A)-n-Tetradecane(B)	1.3751	2.1176	2.67×10^{-3}
Toluene(A)-n-Hexadecane(B)	1.6549	2.5026	9.37×10^{-3}
Ethylbenzene(A)-n-Octane(B)	0.5954	0.7241	7.79×10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	1.2454	2.1862	2.40×10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	1.5155	2.6796	9.98×10^{-3}
Temperature = 30.00°C			
Toluene(A)-n-Octane(B)	0.6011	0.6621	9.17×10^{-4}
Toluene(A)-n-Decane(B)	0.7603	0.95297	1.17×10^{-3}
Toluene(A)-n-Dodecane(B)	0.9341	1.3754	1.83×10^{-3}
Toluene(A)-n-Tetradecane(B)	1.2412	1.9450	2.93×10^{-3}
Toluene(A)-n-Hexadecane(B)	1.7467	2.2765	5.19×10^{-3}
Ethylbenzene(A)-n-Octane(B)	0.6015	0.6840	7.59×10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	1.3048	1.9176	2.92×10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	1.6429	2.6349	4.13×10^{-3}
Temperature = 35.00°C			
Toluene(A)-n-Octane(B)	0.5477	0.6019	7.51×10^{-4}
Toluene(A)-n-Decane(B)	0.67896	0.8643	1.12×10^{-3}
Toluene(A)-n-Dodecane(B)	0.87899	1.2011	1.26×10^{-3}
Toluene(A)-n-Tetradecane(B)	1.15097	1.6471	3.12×10^{-3}
Toluene(A)-n-Hexadecane(B)	1.5138	2.1366	3.61×10^{-3}
Ethylbenzene(A)-n-Octane(B)	0.6016	0.6205	3.297×10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	1.1472	1.6497	4.82×10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	1.4699	2.21194	5.75×10^{-3}
Temperature = 40.00°C			
Toluene(A)-n-Octane(B)	0.52145	0.5773	5.48×10^{-4}
Toluene(A)-n-Decane(B)	0.64705	0.8164	1.39×10^{-3}
Toluene(A)-n-Dodecane(B)	0.83243	1.1272	8.44×10^{-4}
Toluene(A)-n-Tetradecane(B)	1.0860	1.5314	2.49×10^{-3}
Toluene(A)-n-Hexadecane(B)	1.4426	2.04199	4.91×10^{-3}
Ethylbenzene(A)-n-Octane(B)	0.5758	0.5913	4.99×10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	1.09154	1.5258	1.49×10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	1.39635	2.02474	3.61×10^{-3}

TABLE 4.17 McAllister's Parameters Fitted to the Equation: Parameter = $A_0 + A_1T$

System	Intercept	Slope x 10^2	Standard Deviation
McAllister's Parameter, ν_{AB}			
Toluene A - n-Octane B	2.215	0.5410	0.0010
Toluene A - n-Decane B	3.171	0.7749	0.0035
Toluene A - n-Dodecane B	4.113	1.1485	0.0033
Toluene A - n-Tetradecane B	3.655	1.4569	0.0175
Toluene A - n-Hexadecane B	4.041	[illegible]	0.0156
Ethylbenzene A - n-Octane B	2.447	0.3942	0.0029
Ethylbenzene A - n-Tetradecane B	3.752	-1.4910	0.0101
Ethylbenzene A - n-Hexadecane B	7.965	-2.1026	0.0229
McAllister's Parameter, ν_{BA}			
Toluene A - n-Octane B	11.495	-1.6132	0.0050
Toluene A - n-Decane B	3.995	1.6133	0.0128
Toluene A - n-Dodecane B	9.761	1.5018	0.0149
Toluene A - n-Tetradecane B	11.712	-2.9566	0.0156
Toluene A - n-Hexadecane B	15.815	-4.4022	0.0182
Ethylbenzene A - n-Octane B	2.650	1.6582	0.0041
Ethylbenzene A - n-Tetradecane B	20.215	-2.7774	0.0167
Ethylbenzene A - n-Hexadecane B	15.364	-4.2653	0.0204

Figure 4.24 : Variation of McAllister's Parameter $_{AB}$ with Temperature.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
◇	Toluene(A)-n-Dodecane(B)
◑	Toluene(A)-n-Tetradecane(B)
◭	Toluene(A)-n-Hexadecane(B)
⬘	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
▲	Ethylbenzene(A)-n-Hexadecane(B)

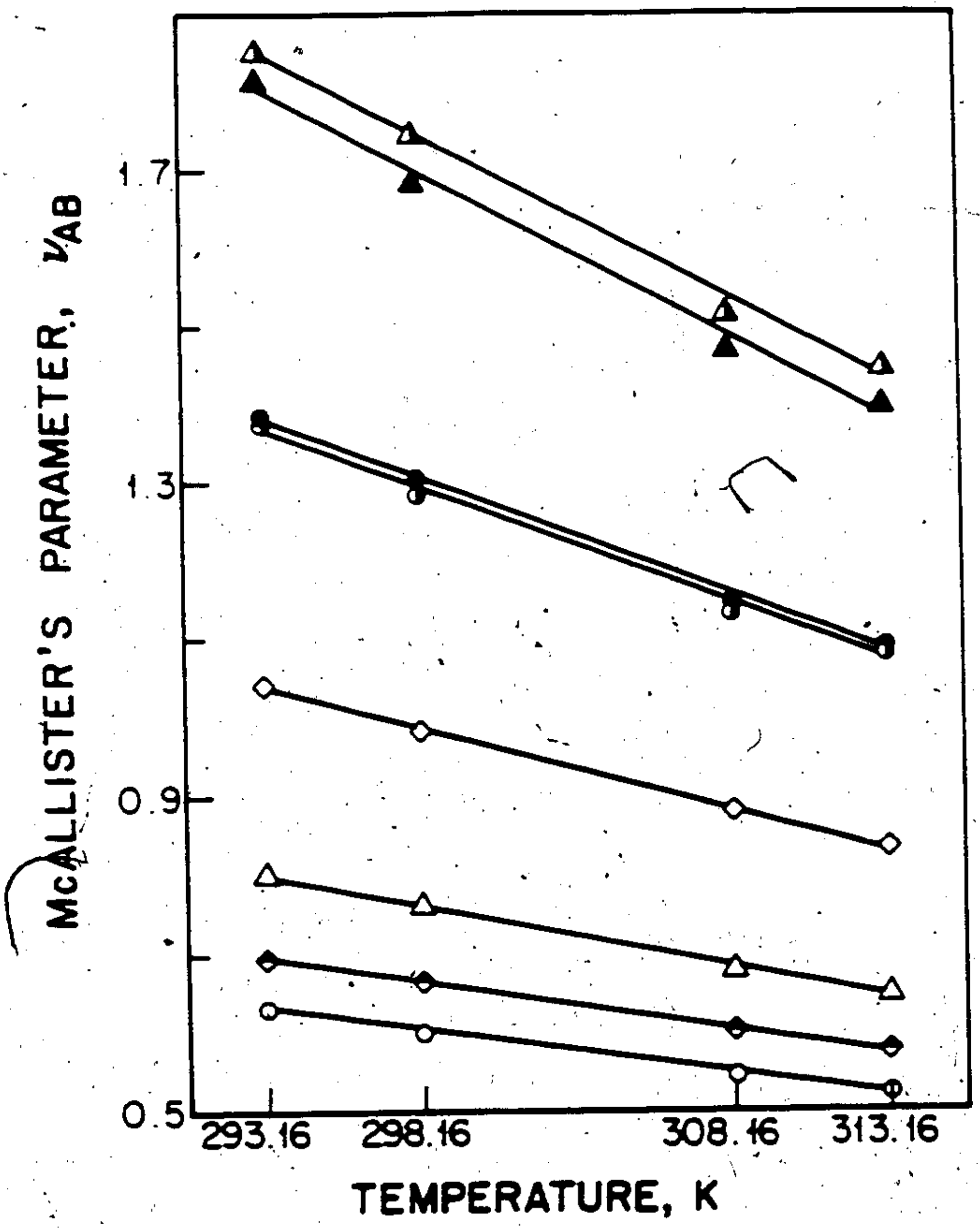

McALLISTER'S PARAMETER, ν_{AB}
1.7
1.3
0.9
0.5
293.16
298.16
308.16
313.16
TEMPERATURE, K

Figure 4.25 : Variation of McAllister's Parameter ν_{BA} with Temperature.

Legend	System
○	Toluene(A)-n-Octane(B)
△	Toluene(A)-n-Decane(B)
◇	Toluene(A)-n-Dodecane(B)
◐	Toluene(A)-n-Tetradecane(B)
◭	Toluene(A)-n-Hexadecane(B)
⬘	Ethylbenzene(A)-n-Octane(B)
●	Ethylbenzene(A)-n-Tetradecane(B)
▲	Ethylbenzene(A)-n-Hexadecane(B)

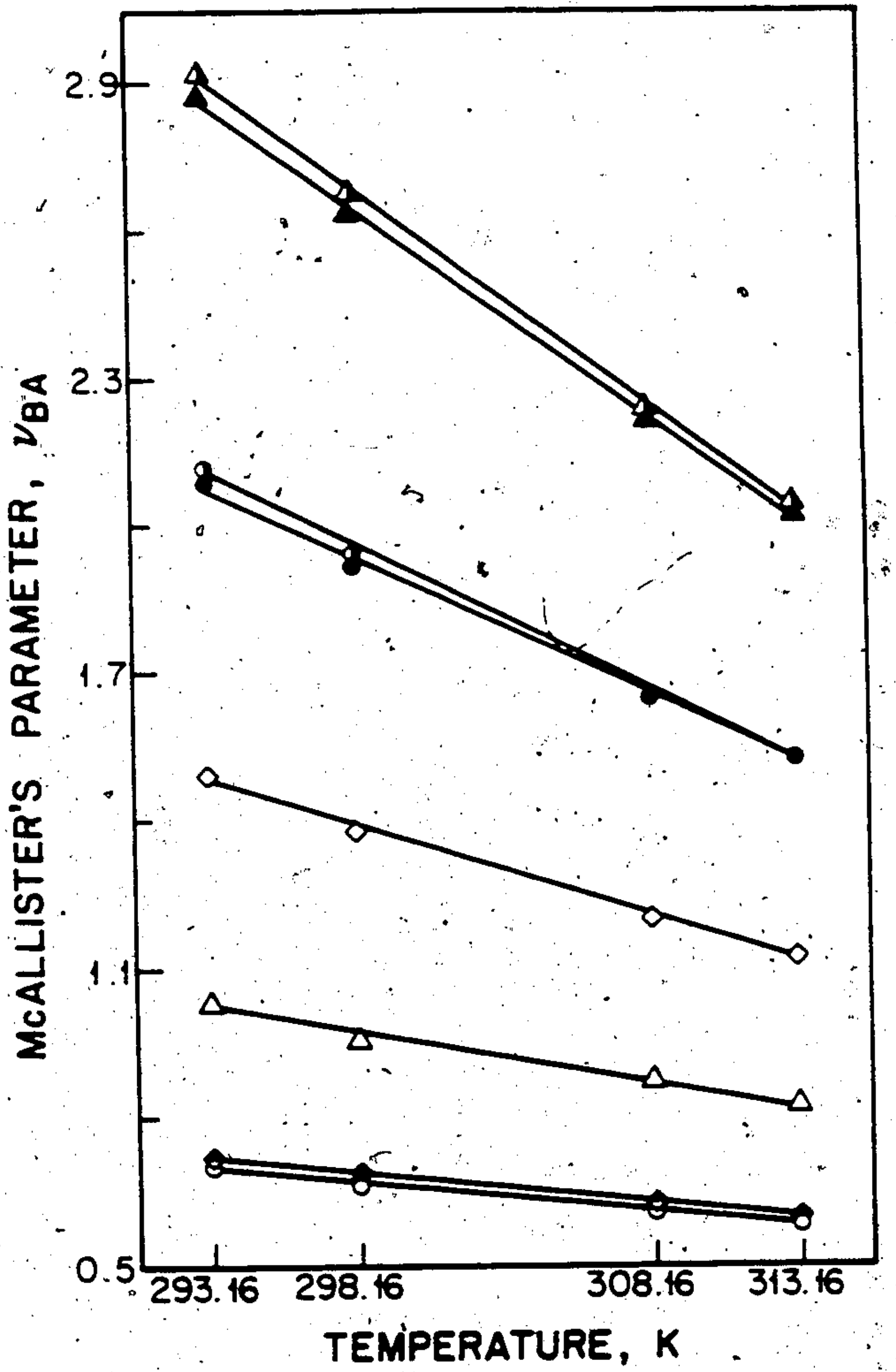

McALLISTER'S PARAMETER, ν_{BA}
2.9
2.3
1.7
1.1
0.5
293.16
298.16
308.16
313.16
TEMPERATURE, K

Figure 4.26 : Variation of Intercept of the Lines in Figures 4.24 and 4.25 with Number of Carbon Atoms of the n-Alkane Component for Systems with Toluene.

Legend

○ for the parameter ν_{AB}

△ for the parameter ν_{BA}

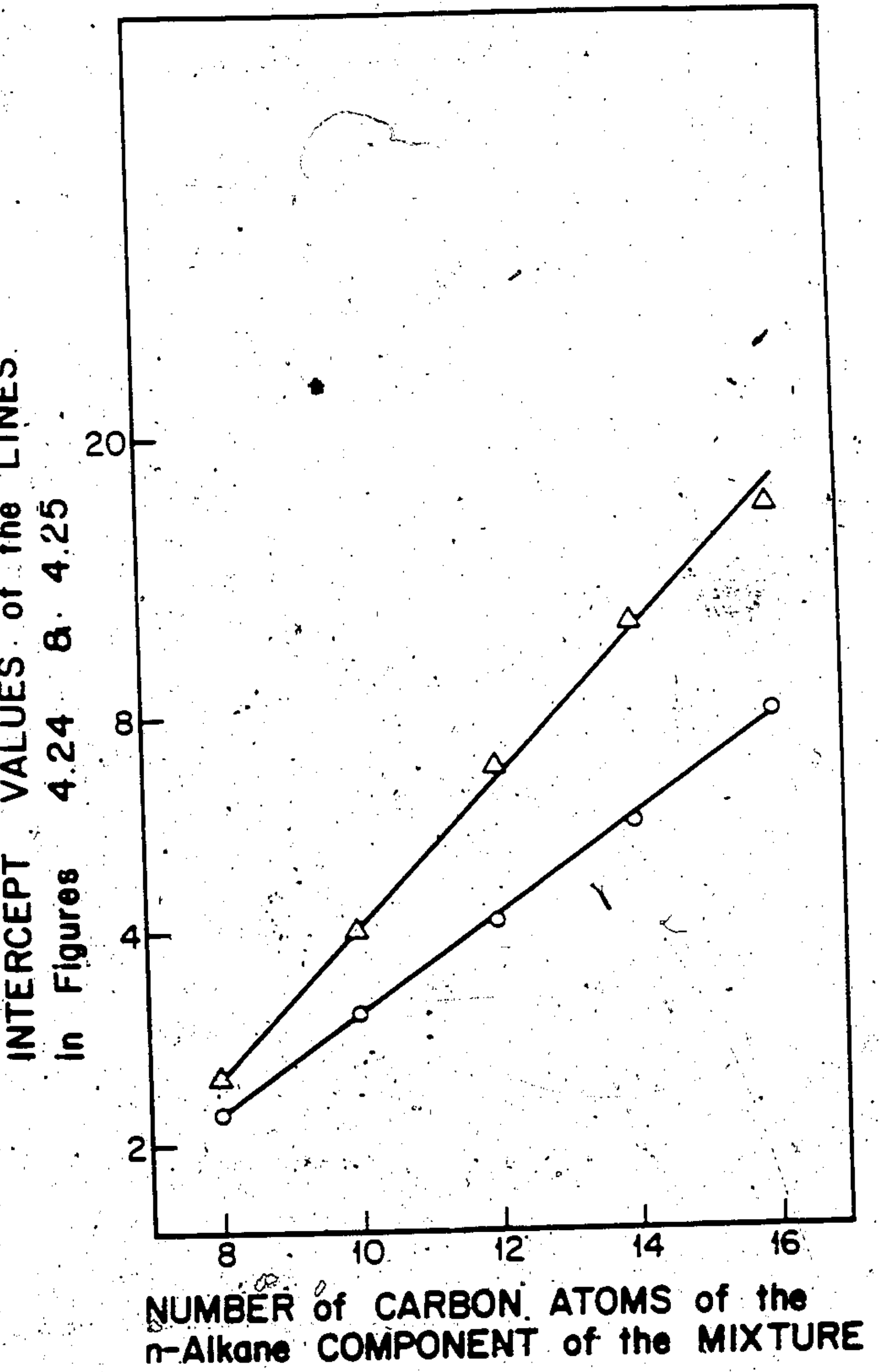
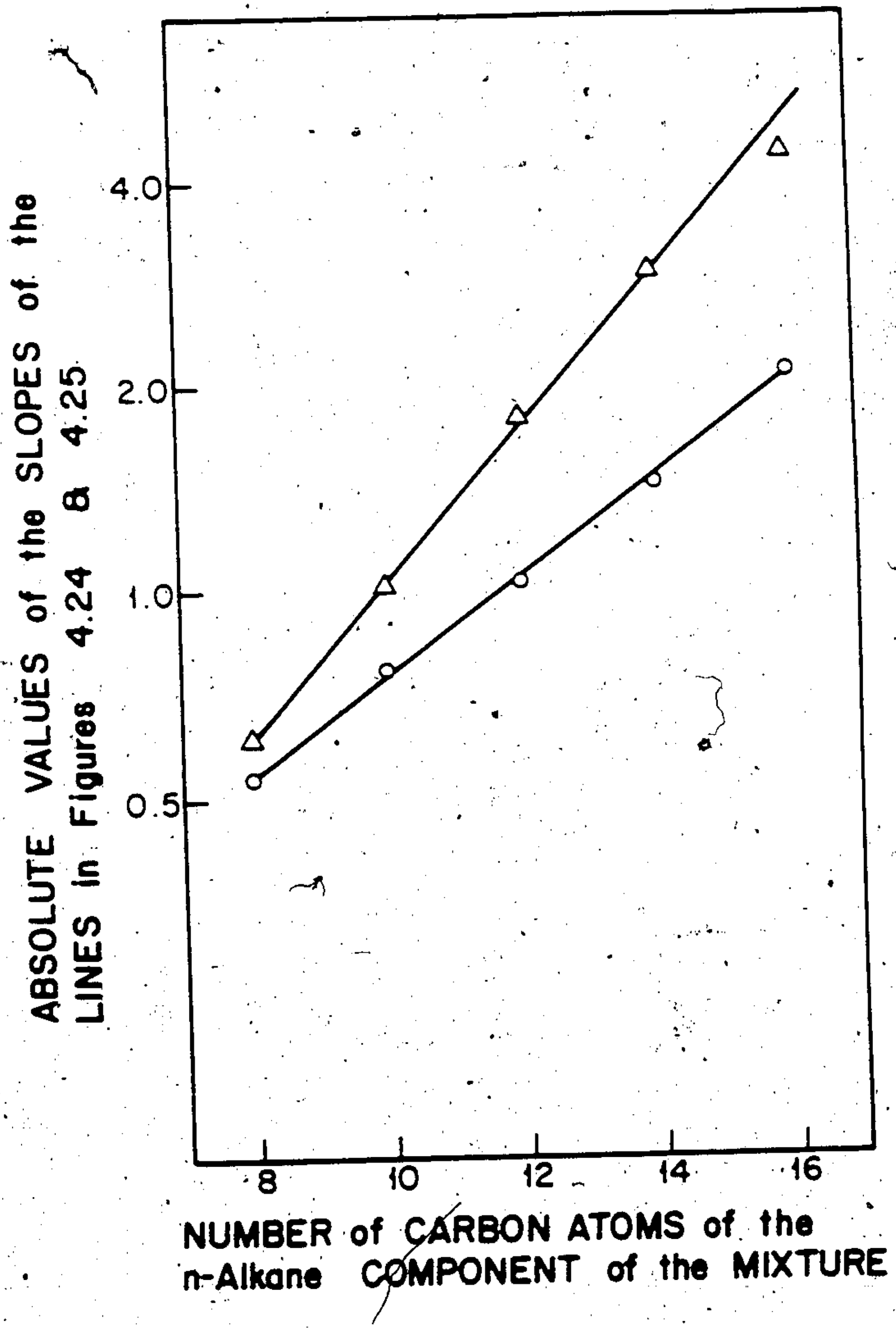

INTERCEPT VALUES of the LINES
In Figures 4.24 & 4.25
20
8
4
2
8
10
12
14
16
NUMBER of CARBON ATOMS of the
n-Alkane COMPONENT of the MIXTURE

Figure 4.27 : Variation of Slope of the Lines in Figures 4.24 and 4.25 with Number of Carbon Atoms of the Normal Alkane Component for Sytems with Toluene.

Legend

○ for the parameter ν_{AB}

△ for the parameter ν_{BA}


ABSOLUTE VALUES of the SLOPES of the LINES in Figures 4.24 & 4.25
4.0
2.0
1.0
0.5
8
10
12
14
16
NUMBER of CARBON ATOMS of the n-Alkane COMPONENT of the MIXTURE

parameters and Auslander's model with three parameters [1964].

These models are discussed in detail in Chapter 2. In general Auslander's three parameter model gave a better fit in more than fifty percent of the system investigated in this study. At 25.00°C this model did not adequately fit the data of systems with n-octane and n-decane.

The values of the parameters of McAllisters' model are listed in Table 4.26 along with the standard deviation of the fit. As one can see there is a trend in these parameters. Hence the parameters for each system were plotted against temperature and it can be seen from Figures 4.24 and 4.25, those parameters change linearly with temperature in the temperature range 'investigated ~~in this~~ study'. The slope and intercept of these straight lines are reported in Table 4.27. The last column of this table gives the standard deviation of the fit.

The natural logarithm of the absolute value of the slope for both the parameters was found to increase linearly with the number of carbon atoms of the n-alkane component of mixtures with toluene. Mixtures with ethylbenzene do not give perfect straight lines. This can be seen from Figure 4.27. The intercept of these two parameters was also found

TABLE 4.28 Values of the Parameters Involved in Heric's Model

System	α_{12}	α'_{12}	Standard Deviation
Temperature = 20.00°C			
Toluene(A)-n-Octane(B)	-0.2353	-0.0952	8.15 x 10^{-4}
Toluene(A)-n-Decane(B)	0.0134	-0.0657	3.38 x 10^{-3}
Toluene(A)-n-Dodecane(B)	0.3468	0.0046	2.92 x 10^{-3}
Toluene(A)-n-Tetradecane(B)	0.7224	0.1252	2.67 x 10^{-3}
Toluene(A)-n-Hexadecane(B)	1.1395	0.2855	9.37 x 10^{-3}
Ethylbenzene(A)-n-Octane(B)	-0.2428	-0.06096	7.79 x 10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	0.4554	0.0779	2.40 x 10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	0.81798	0.2018	9.98 x 10^{-3}
Temperature = 25.00°C			
Toluene(A)-n-Octane(B)	-0.2278	-0.0798	9.17 x 10^{-4}
Toluene(A)-n-Decane(B)	0.0076	-0.0340	2.17 x 10^{-3}
Toluene(A)-n-Dodecane(B)	0.33798	0.0259	1.87 x 10^{-3}
Toluene(A)-n-Tetradecane(B)	0.7169	0.1169	1.95 x 10^{-3}
Toluene(A)-n-Hexadecane(B)	1.1728	0.2974	6.19 x 10^{-3}
Ethylbenzene(A)-n-Octane(B)	-0.2431	-0.0503	7.69 x 10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	0.4663	0.0921	1.92 x 10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	0.8259	0.1904	4.13 x 10^{-3}
Temperature = 33.00°C			
Toluene(A)-n-Octane(B)	-0.1998	-0.0765	7.51 x 10^{-4}
Toluene(A)-n-Decane(B)	0.04824	-0.0777	1.12 x 10^{-3}
Toluene(A)-n-Dodecane(B)	0.36465	0.0348	1.26 x 10^{-3}
Toluene(A)-n-Tetradecane(B)	0.7501	0.1607	3.46 x 10^{-3}
Toluene(A)-n-Hexadecane(B)	1.1625	0.3002	5.61 x 10^{-3}
Ethylbenzene(A)-n-Octane(B)	-0.2175	-0.0453	3.297 x 10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	0.4851	0.08463	4.82 x 10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	0.83405	0.1974	5.75 x 10^{-3}
Temperature = 40.00°C			
Toluene(A)-n-Octane(B)	-0.18856	-0.0882	5.48 x 10^{-4}
Toluene(A)-n-Decane(B)	0.0537	-0.06599	1.39 x 10^{-3}
Toluene(A)-n-Dodecane(B)	0.3683	0.0345	8.44 x 10^{-4}
Toluene(A)-n-Tetradecane(B)	0.74475	0.1672	2.49 x 10^{-3}
Toluene(A)-n-Hexadecane(B)	1.1666	0.3305	4.91 x 10^{-3}
Ethylbenzene(A)-n-Octane(B)	-0.20515	-0.0384	4.99 x 10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	0.49515	0.1106	1.49 x 10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	0.84197	0.23096	3.62 x 10^{-3}

TABLE 4.29 Values of the Parameters Involved in Auslander's Model

System	B_{12}	B_{21}	A_{12}	Standard Deviation
Temperature = 20.00°C				
Toluene(A)-n-Octane(B)	4.8173	-0.9991	1.8806	6.79 x 10^{-4}
Toluene(A)-n-Decane(B)	-0.0173	423.27	1.0015	4.19 x 10^{-3}
Toluene(A)-n-Dodecane(B)	1.3724	1.4336	1.3770	1.93 x 10^{-3}
Toluene(A)-n-Tetradecane(B)	1.0091	1.8160	1.7123	2.02 x 10^{-3}
Toluene(A)-n-Hexadecane(B)	1.4795	1.5348	1.9643	5.39 x 10^{-3}
Ethylbenzene(A)-n-Octane(B)	-324.9	1460.2	1.2259	1.24 x 10^{-2}
Ethylbenzene(A)-n-Tetradecane(B)	1.1988	1.7333	0.7820	2.40 x 10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	0.5956	1.4438	0.3739	7.32 x 10^{-3}
Temperature = 25.00°C				
Toluene(A)-n-Octane(B)	-0.0158	4803.8	3.223 x 10^{-5}	1.28 x 10^{-2}
Toluene(A)-n-Decane(B)	0.0128	986.6	6.703 x 10^{-4}	6.54 x 10^{-3}
Toluene(A)-n-Dodecane(B)	0.0288	1836.3	3.987 x 10^{-4}	1.00 x 10^{-2}
Toluene(A)-n-Tetradecane(B)	0.8966	0.9316	0.6463	2.34 x 10^{-3}
Toluene(A)-n-Hexadecane(B)	2.6184	0.2906	0.7365	3.88 x 10^{-3}
Ethylbenzene(A)-n-Octane(B)	-1250.2	869.1	1.4425	7.77 x 10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	-2.9015	-0.3021	1.9211	1.86 x 10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	1.1384	0.7445	0.7365	1.69 x 10^{-3}
Temperature = 35.00°C				
Toluene(A)-n-Octane(B)	5.1215	-0.7655	2.0996	3.45 x 10^{-4}
Toluene(A)-n-Decane(B)	1.6276	0.4082	1.2998	9.95 x 10^{-4}
Toluene(A)-n-Dodecane(B)	4.6556	0.1745	3.5477	4.52 x 10^{-4}
Toluene(A)-n-Tetradecane(B)	0.6133	1.4572	0.4688	2.01 x 10^{-3}
Toluene(A)-n-Hexadecane(B)	1.1101	0.7547	0.8203	9.04 x 10^{-4}
Ethylbenzene(A)-n-Octane(B)	125.00	-80.126	1.5255	1.73 x 10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	0.2647	3.3342	0.1989	3.67 x 10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	14.8684	0.0376	10.0322	4.79 x 10^{-3}
Temperature = 40.00°C				
Toluene(A)-n-Octane(B)	4.6864	-0.7306	2.09298	1.86 x 10^{-4}
Toluene(A)-n-Decane(B)	4.0993	0.1385	3.1945	6.27 x 10^{-4}
Toluene(A)-n-Dodecane(B)	1.7836	0.4922	1.3981	8.57 x 10^{-4}
Toluene(A)-n-Tetradecane(B)	3.6164	0.2367	2.7400	3.10 x 10^{-3}
Toluene(A)-n-Hexadecane(B)	3.8031	0.2184	2.7981	5.24 x 10^{-3}
Ethylbenzene(A)-n-Octane(B)	90.777	-59.688	1.47315	3.51 x 10^{-4}
Ethylbenzene(A)-n-Tetradecane(B)	6.03365	0.1481	4.3371	1.78 x 10^{-3}
Ethylbenzene(A)-n-Hexadecane(B)	3.0434	0.2918	2.1149	4.36 x 10^{-3}

to behave in the same manner as can be seen from Figure 4.26.

Parameters for Heric's model are given in Table 4.28 along with the standard deviation of the fit. All the systems fitted well to this empirical correlation as can be seen from Table 4.28. The parameter ε'_{12} did show a trend to increase with the number of carbon atoms of the second component of a system and it also varies linearly with temperature but there was no such trend with the other parameter, ε''_{12}.

Parameters for Auslander's model are reported in Table 4.29 along with the standard deviation of the fit. All the systems fitted well to this model except for systems with n-octane and n-decane at 25.00°C. The parameters of this model did not show any particular trend of change with temperature as they did in case of the two previous models.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The precision density meter is the most vital instrument used in this work to measure accurate density values of the pure components as well as the binary mixtures. Controlling the temperature of the box where density meter was placed resulted in highly reproducible density measurements; particularly at temperatures 20.00°C and 25.00 ° C density values could be reproduced to better than ± 1.59 x 10^{-4} kg/L. Use of the Cannon-Ubbelohde viscometers also resulted in highly reproducible (better than 0.1%) viscosity measurements.

With proper precaution for evaporation losses, densities and viscosities of binary mixtures containing toluene, ethylbenzene, and n-alkanes were measured at temperature levels 20.00°C, 25.00°C, 35.00°C and 40.00 ° C, respectively over the entire composition range. From these values of the physical properties were determined some of the thermodynamic properties, viz, excess volumes of mixing, partial molar volumes and excess activation energies of viscous flow for each of the binary systems.

These physical and thermodynamic properties were critically tested to appropriate composition-dependent polynomials. The magnitude of standard deviation of fit indicate that the systems studied in this work may be well represented by these polynomials. Some of the existing literature models to predict mixture viscosities were also critically tested. These literature models were also found to represent kinematic viscosity of the binary mixtures studied in this work with reasonable precision. McAllister's parameters in particular showed some striking features for these systems. For example, both the parameters were found to vary linearly with temperature. This means that the viscosity-composition relationship may be interpolated or even extrapolated in a certain temperature range. The slope and intercept of these "parameter isotherms" showed an exponential relationship with the number of carbon atoms of the n-alkane components of the mixtures containing toluene. Utilizing this nature of McAllister's parameters, viscosity-composition relations may be predicted for some toluene-n-alkane systems at different temperature levels with a reasonable degree of precision.

Activation energies of viscous flow were also calculated for the pure components. They were found to vary linearly with the length of carbon chain of the n-alkanes. The activation energies of viscous flow in a binary mixture do not follow a linear relation with the mole-fraction of component A.

5.2 Recommendations

There are a few literature viscosity models and a model for predicting excess activation energy of viscous flow which were not investigated in this study. The experimental data obtained in this work can be utilized to test amd improve these predictive models. Examples of these literature models are given below:

(i) Extension of McAllister's model: McAllister's model [1960] discussed in Chapter 2 may further be extended to relate the viscosity of a liquid mixture to both composition and temperature. Kinematic viscosity can be related to enthalpy and entropy of activation for viscosity by the following expressions –

$$\nu_A = \frac{hN}{M_A} \exp\left(-\Delta^* S_A/R\right) \exp\left(\Delta^* H_A/RT\right) \tag{5.1}$$

$$\nu_{AB} = \frac{hN}{M_{AB}} \exp\left(-\Delta^* S_{AB}/R\right) \exp\left(\Delta^* H_{AB}/RT\right) \tag{5.2}$$

$$\nu_{BA} = \frac{hN}{M_{BA}} \exp\left(-\Delta^{*}S_{BA}/R\right) \exp\left(\Delta^{*}H_{BA}/RT\right) \tag{5.3}$$

$$\nu_{B} = \frac{hN}{M_{B}} \exp\left(-\Delta^{*}S_{B}/R\right) \exp\left(\Delta^{*}H_{B}/RT\right) . \tag{5.4}$$

If the adjustable parameters $\Delta^{*}S_{AB}$, $\Delta^{*}S_{BA}$, $\Delta^{*}H_{AB}$, and $\Delta^{*}H_{BA}$ in the above equations are assumed to be independent of temperature, a method can be provided for extrapolating viscosity-composition data at two temperatures to other temperatures.

(ii) Wei and Rowley [1985] provided a model for predicting mixture viscosity in multi-component systems. This model requires data on the excess enthalpies and the NRTL (non-random two liquid) model parameters for the excess free energy which can be obtained from vapor liquid equilibrium data. Wei and Rowley [1985] claimed that the local composition model can predict mixture viscosities more favorably to experimental results than some of the existing statistical mechanical methods, viz., Teja and Rice [1981], Ely and Hanley [1981].

(iii) Grunberg and Nissan [1949] provided an equation for calculating mixture viscosities involving one adjustable parameters, given by

$$\ln \eta_m = x_A \ln \eta_A + x_B \ln \eta_B + d x_A x_B \qquad (5.5)$$

The above equation may be rearranged to obtain

$$\frac{1}{x_A} \ln \frac{\eta_m}{\eta_B} = a - d x_A \qquad (5.6)$$

where [illegible] $= \ln \eta_A - \ln \eta_B + d = a$ constant. So that if Grunberg Nissan Equation is valid, a plot of $\ln \frac{\eta_m}{\eta_B}$ against x_B should be linear whose slope will be -d and the intercept given by "a" in Equation (5.6).

(iv) Tamura and Kurata [1952] provided a model for the calculation of mixture viscosity, assuming that the relaxation time of each collision is proportional to the probability of collision, and that the volume change on mixing is small. Their equation is given by

$$\eta_m = x_A \phi_A \eta_A + x_B \phi_B \eta_B + 2(x_A x_B \phi_A \phi_B)^{\frac{1}{2}} \eta_{AB} \qquad (5.7)$$

where η_{AB} is the only adjustable parameter, which depends on temperature.

(v) Reed and Taylor [1959] provided an equation for predicting excess activation energy of viscous flow at different temperatures. Their equation is given by

$$\frac{\Delta^* G_1^E}{RT_1} = \frac{\Delta^* G_2^E}{RT_2} - \ln \frac{v_2}{v_1} + \frac{\Delta^* H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad (5.8)$$

where subscript 1, and 2 refer to two different temperature levels. Thus values of $\Delta^{*}G^{E}$ can be predicted at temperature T_2K if value of $\Delta^{*}G^{E}$ is known at temperature T K provided ν_1 and ν_2 are available and $\Delta^{*}H$ is evaluated from that of pure components assuming it linear in mole-fraction.

NOMENCLATURE

A = constant
$\tilde{B}$ = constant
B = kinetic energy correction factor
b = constant
c = viscometer constant
C = constant
E = kinetic energy correction factor
F = frictional force
f = force per unit area
f = molar free energy of activation of viscous flow
f = natural frequency
F_n = partition function at normal state
F_a^* = partition function at activated state
$\Delta^* G$ = activation energy of viscous flow
$\Delta^* G^E$ = excess activation energy of viscous flow
H = transmission co-efficient
k = Boltzmann's constant
k = constant
L = intensive property
M = molecular weight
m = constant

n = constant

n = number of moles

N = Avogadro's number

Δp = pressure difference in a capillary

q = physical property of liquid

R = universal gas constant

r = radius of the capillary

r_A = radius of a sphere

S = spring constant

T = temperature

t = time of efflux

u = specific volume

V = molar volume, unless otherwise specified

V_i = molar volume of component i, i = A,B

V_o = molar volume at which viscosity is infinite

v_t = terminal velocity

v_x = x component of the velocity

w = limiting specific volume at which viscosity is infinite

x_i = mole fraction of component i, i = A, B

β = constant

β_f = coefficient of sliding friction

η = absolute viscosity

$\lambda_1\lambda_1,\lambda_2,\lambda_3$ = intermolecular distances involved in Eyring's equations

$\kappa_1, \kappa_f, \kappa_b$ = reaction rates involved in Eyring's equations

ν = kinematic viscosity

ρ = mass density

T_{yx} = shear stress

ϕ_i = volume fraction of component i, $i = A,B$

Subscripts

A,B,1,2,i,j = refer to various components in the mixture

m = refers to the mixture

Superscript

E = excess over the ideal solution property

o, ∞ = at infinite dilution

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APPENDICES

APPENDIX A

Derivation of the Viscosity Equation*

A force balance around a capillary viscometer of any type yield the following equation

$$X_1 - X_2 = F_f + F_c + F_e \qquad (A.1)$$

where $X_1 - X_2$ is the driving fluid head (vertical distance between the two menisci in the viscometer) and the terms on the right hand side of this equation represent various kinds of frictions encountered in viscometry; F_f is the friction in capillary, F_c is the friction at capillary entrance, and F_e is the friction at capillary exit.

The greatest friction is developed in the capillary. In a properly designed viscometer, flow will always be inertial. F_f can be calculated from Poiseuille's law.

$$F_f = \frac{32\ Lv\eta}{g\rho D^2} \qquad (A.2)$$

where v is the velocity of the fluid in capillary; g is acceleration due to gravity; L is the capillary length, ρ is the density of the fluid; η is the viscosity; D is the capillary diameter; and t is the efflux time.

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* Asfour [1979].

If [illegible] is replaced by the efflux volume V, we have

$$F_f = \frac{32\ L\eta}{4\ \rho g r^2} \cdot \frac{V}{\pi r^2 t} = \frac{8LV\eta}{\rho g \pi r^4 t} \qquad \text{(A.3)}$$

Both F_c and F_e can be correlated as functions of kinetic energy. That is,

$$F_c + F_e = \frac{mv^2}{g} \qquad \text{(A.4)}$$

Combining Equations (A.1), (A.3) and (A.4) one obtains

$$X_1 - X_2 = \frac{8LV\eta}{\pi r^4 \rho g t} + \frac{mv^2}{g} \qquad \text{(A.5)}$$

replacing v in the last term of this equation by V, one obtains

$$X_1 - X_2 = \frac{8LV\eta}{\pi r^4 \rho g t} + \frac{m}{g}\left\{\frac{V}{\pi r^2 t}\right\}^2 \qquad \text{(A.6)}$$

which after rearrangement, becomes

$$\frac{\eta}{\rho} = \frac{\pi r^4 g t}{8LV}\left[X_1 - X_2 - \frac{mV^2}{\pi^2 r^4 g t^2}\right] \qquad \text{(A.7)}$$

$$\frac{\eta}{\rho} = \frac{\pi r^4 g t}{8LV}\{X_1 - X_2\} - \frac{mV}{8\pi LT} \qquad \text{(A.8)}$$

Equation (A.8) is usually written as

$$\frac{\eta}{\rho} = Ct - B/t \qquad (A.9)$$

where C and B are given by

$$C = \frac{\pi r^4 g}{8LV} (X_1 - X_2) \quad , \quad \text{and} \qquad (A.10)$$

$$B = \frac{mV}{8\pi L} \qquad (A.11)$$

It has been experimentally established that, for a given viscometer, C is constant but B is not [Cannon et al. 1960]. B is constant only if m is constant. It has been observed experimentally that m is a function of Reynolds number. The value of m approaches zero as the Reynolds number reaches zero for all types of viscometers, and m increases as Reynolds number increases. It has been suggested by Cannon et al. [1960] that for Reynolds numbers in the range between 80 to 500, which are most usually encountered in capillary viscometry, m for trumpet shaped ends can be written as

$$m = 0.037\,(Re)^{\frac{1}{2}} \qquad (A.12)$$

or

$$m = 0.037 \left[\frac{4VD\rho}{\pi D^2 t\eta}\right]^{\frac{1}{2}}$$

$$= 0.037 \left[\frac{4VD\rho}{\pi D^2 tCt}\right]^{\frac{1}{2}} \qquad (A.13)$$

substituting this result into Equation (A.11), one obtains

$$B = \frac{1.66\ V^{3/2} \times 10^{-3}}{L\ (CD)^{\frac{1}{2}}\ t} \qquad (A.14)$$

This equation can be written as

$$B = E/t \qquad (A.15)$$

where $E = \dfrac{1.66 \times 10^{-3}\ V^{3/2}}{L\ (CD)^{\frac{1}{2}}}$ is independent of time.

Now substitution of Equation (A.15) in Equation (A.9) gives

$$\frac{\eta}{\rho} = Ct - E/t^2 \qquad (A.16)$$

which is known as the viscosity equation.

APPENDIX B

Partial Molar Volumes Calculated From Density-Composition Data

B.1 Partial Molar Volume Data

The density-composition data listed in Tables 4.4 to 4.11 have been used to obtain the molar volume of the mixture as a function of composition. Partial molar volume of component A in, say, a binary liquid mixture of components A and B is defined as

$$\bar{V}_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} \qquad (B.1)$$

where

$\bar{V}_A$ is the partial molar volume of component A

V is the molar volume of solution

n_A and n_B are the number of moles of components A and B in solution, respectively.

Molar volume of the mixture is fitted to a composition dependent polynomial of the form

$$V = \sum_{i=o}^{i=3} A_i\, x_A^i \qquad (B.2)$$

These constants were evaluated by the method of least squares and given in Table B.1

Realizing that x_A is the mole fraction of component A, one can utilize the fact that

$$x_A = n_A/n_T \tag{B.3}$$

where n_T is the total number of moles in solution.

Now substituting Equation (B.3) into Equation (B.2) gives

$$V = A_o\, n_T + A_1\, n_A + A_2\, \frac{nA^2}{n_T^2} + A_3\, \frac{n_A^3}{n_T^3} \tag{B.4}$$

Differentiation of Equation (B.4) with respect to n_A, keeping n_T constant and realizing that $n_T = n_A + n_B$, one obtains after rearrangement

$$\left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} = (A_o + A_1) + 2A_2\, x_A + (3A_3 - A_2)\, x_A^2 - 2A_3\, x_A^3 \tag{B.5}$$

setting

$B_o = A_o + A_1$

$B_1 = 2A_2$

$B_2 = 3A_3 - A_2$

$B_3 = -2A_3$

and using Equation (B.5), one obtains

$$\bar{V}_A = B_o + B_1\, x_A + B_2\, x_A^2 + B_3\, x_A^3 \tag{B.6}$$

TABLE B.1: Least Squares Constants for the Equation $V_m = \sum_{i=0}^{i=3} A_i x_A^i$

System	A_0	A_1	A_2	A_3		Standard Deviation
Temperature = 20.00°C						
Toluene(A)-n-Octane(B)	162.698	- 55.155	-1.152	-0.1098		0.024
Toluene(A)-n-Decane(B)	195.062	- 87.011	-1.516	-0.243		0.040
Toluene(A)-n-Dodecane(B)	232.967	-125.923	0.270	-1.034		0.028
Toluene(A)-n-Tetradecane(B)	260.053	-151.753	-1.343	-0.664		0.042
Toluene(A)-n-Hexadecane(B)	292.729	-184.856	0.112	-1.698		0.032
Ethylbenzene(A)-n-Octane(B)	162.703	- 39.149	-1.199	0.102		0.027
Ethylbenzene(A)-n-Tetradecane(B)	260.030	-135.773	-0.492	-1.303		0.031
Ethylbenzene(A)-n-Hexadecane(B)	292.691	-168.969	1.092	-2.358		0.027
Temperature = 25.00°C						
Toluene(A)n-Octane(B)	163.504	- 56.076	-0.101	-0.445		0.034
Toluene(A)-n-Decane(B)	195.946	- 87.479	-0.745	-0.811		0.024
Toluene(A)-n-Dodecane(B)	234.246	-126.429	0.415	-1.306		0.0196
Toluene(A)-n-Tetradecane(B)	261.278	-151.538	-3.390	0.609		0.096
Toluene(A)-n-Hexadecane(B)	293.979	-185.662	-0.039	-1.356		0.024
Ethylbenzene(A)-n-Octane(B)	163.551	- 39.655	-0.477	-0.247		0.012
Ethylbenzene(A)-n-Tetradecane(B)*	261.191	-136.018	-1.600	-0.378		0.049
Ethylbenzene(A)-n-Hexadecane(B)	293.980	-168.138	-2.438	-0.206		0.030

TABLE B.1: cont'd

System	A_0	A_1	A_2	A_3		Standard Deviation
Temperature = 35.00°C						
Toluene(A)-n-Octane(B)	164.495	- 54.766	-3.599	1.028		0.046
Toluene(A)-n-Decane(B)	198.218	- 87.024	-3.679	0.689		0.031
Toluene(A)-n-Dodecane(B)	230.936	-121.799	0.265	-1.246		0.033
Toluene(A)-n-Tetradecane(B)	263.617	-153.931	-0.892	-0.602		0.022
Toluene(A)-n-Hexadecane(B)	296.527	-185.188	-3.278	0.052		0.064
Ethylbenzene(A)-n-Octane(B)	165.530	- 39.870	-1.015	-0.216		0.011
Ethylbenzene(A)-n-Tetradecane(B)	263.633	-135.670	-4.354	0.858		0.046
Ethylbenzene(A)-n-Hexadecane(B)	296.775	-169.566	-2.702	0.013		0.118
Temperature = 40.00°C						
Toluene(A)-n-Octane(B)	166.535	- 56.575	-1.099	-0.203		0.061
Toluene(A)-n-Decane(B)	198.878	- 89.747	0.772	-1.299		0.059
Toluene(A)-n-Dodecane(B)	232.021	-121.524	-0.417	-1.404		0.039
Toluene(A)-n-Tetradecane(B)	264.856	-155.824	2.421	-2.837		0.058
Toluene(A)-n-Hexadecane(B)	297.616	-187.502	-0.499	-0.985		0.016
Ethylbenzene(A)-n-Octane(B)	166.472	- 40.405	-0.136	-0.913		0.0396
Ethylbenzene(A)-n-Tetradecane(B)	264.988	-138.431	0.163	-1.702		0.045
Ethylbenzene(A)-n-Hexadecane(B)	297.697	-170.461	-1.246	-0.966		0.068

TABLE B.2 : Partial Molar Volume of the System Toluene(A)-n-Octane(B)

Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol	Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	107.5435	162.6982	0.0000	107.4279	163.5038
0.0584	107.4117	162.7022	0.06697	107.4148	163.5041
0.1021	107.3171	162.7104	0.0910	107.3999	163.5053
0.2065	107.1049	162.7492	0.1548	107.3703	163.5095
0.3044	106.9247	162.8111	0.2566	107.3097	163.5255
0.3937	106.7774	162.8902	0.3472	107.2460	163.5533
0.5027	106.6212	163.0172	0.4447	107.1721	163.6021
0.5946	106.5106	163.1517	0.5437	107.0960	163.6769
0.6979	106.4110	163.3338	0.6408	107.0256	163.7796
0.8028	106.3378	163.5540	0.7612	106.9512	163.9553
0.8990	106.2968	163.7887	0.8747	106.9022	164.1773
1.0000	106.2819	164.0696	1.0000	106.8814	164.4956
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	110.7283	165.4946	0.0000	109.9606	166.5354
0.0440	110.4243	165.5014	0.0517	109.8484	166.5384
0.1032	110.0546	165.5306	0.1038	109.7384	166.5477
0.2008	109.5359	165.6230	0.1986	109.5467	166.5819
0.2940	109.1377	165.7534	0.29896	109.3583	166.6444
0.3983	108.7921	165.9355	0.4023	109.1822	166.7397
0.4956	108.5527	166.1281	0.4942	109.0434	166.8526
0.6003	108.3715	166.3464	0.5939	108.9134	167.00797
0.6974	108.2621	166.5472	0.6947	108.8067	167.2015
0.8019	108.1943	166.74796	0.8003	108.72396	167.4469
0.8979	108.1657	166.9069	0.8976	108.6766	167.7137
1.0000	108.1581	167.0363	1.0000	108.6591	168.0395

TABLE B.3 : Partial Molar Volume of the System Toluene(A)-n-Decane(B)

Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol	Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	108.0509	195.0621	0.0000	108.4671	195.9457
0.05798	107.8778	195.0672	0.0519	108.3855	195.9479
0.1088	107.73096	195.0806	0.1005	108.3019	195.9548
0.2078	107.4591	195.1319	0.20197	108.1107	195.9894
0.3046	107.21398	195.2165	0.3037	107.9045	196.0598
0.4047	106.9849	195.3425	0.4060	107.6925	196.1770
0.4968	106.7983	195.4958	0.5113	107.4808	196.3573
0.5992	106.6211	195.7109	0.6106	107.2973	196.5926
0.6996	106.4811	195.9705	0.7050	107.1460	196.8844
0.7994	106.3781	196.2794	0.8021	107.0231	197.2618
0.9031	106.3123	196.6568	0.8957	106.9439	197.7090
1.0000	106.2917	197.0644	1.0000	106.9111	198.3126
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	111.1945	198.2183	0.0000	109.1311	198.8783
0.0495	110.8444	198.2272	0.0432	109.1893	198.8771
0.0966	110.5365	198.2514	0.1008	109.2418	198.8731
0.1964	109.9608	198.3498	0.2021	109.2737	198.8683
0.2979	109.4762	198.5084	0.2993	109.2444	198.8789
0.3929	109.10698	198.7028	0.3936	109.1736	198.9172
0.4962	108.78998	198.9558	0.4947	109.0665	199.0041
0.5965	108.5578	199.2347	0.5931	108.9462	199.1489
0.6981	108.3896	199.5424	0.6959	108.8197	199.3801
0.7988	108.2812	199.8633	0.8009	108.7071	199.7180
0.8979	108.2230	200.1866	0.8962	108.6345	200.1286
1.0000	108.2048	200.5190	1.0000	108.6038	200.7045

TABLE B.4 : Partial Molar Volume of the System Toluene(A)-n-Dodecane(B)

Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol	Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	107.3623	227.6241	0.0000	108.0811	228.8759
0.0645	107.3824	227.6236	0.0551	108.1283	228.8747
0.1056	107.3781	227.6241	0.0887	108.1413	228.8737
0.2082	107.3176	227.6362	0.1959	108.1130	228.8796
0.3004	107.2143	227.6722	0.2789	108.0305	228.9060
0.4037	107.0601	227.7571	0.3802	107.8771	228.9827
0.5002	106.8948	227.8946	0.4701	107.7086	229.1084
0.6005	106.7176	228.1130	0.5707	107.5036	229.3327
0.7015	106.54998	228.4277	0.6854	107.2748	229.7226
0.8023	106.4104	228.8534	0.7805	107.1110	230.1750
0.90099	106.3170	229.3941	0.8895	106.9762	230.8640
1.0000	106.2822	230.0762	1.0000	106.9243	231.7729
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	109.1370	230.9363	0.0000	110.4968	232.0210
0.0527	109.1542	230.9359	0.0508	110.4450	232.0225
0.0996	109.1525	230.9361	0.0924	110.3897	232.0268
0.2049	109.0989	230.9466	0.2033	110.1940	232.0619
0.2913	109.0133	230.9754	0.3003	109.9804	232.1346
0.4021	108.8649	231.0554	0.4063	109.7200	232.2781
0.4986	108.7150	231.1793	0.5104	109.4560	232.5030
0.5944	108.5610	231.3660	0.5988	109.2397	232.7735
0.69698	108.4055	231.6513	0.7015	109.0137	233.1957
0.7979	108.2772	232.0334	0.7999	108.8389	233.7249
0.8981	108.1894	232.5276	0.89898	108.7203	234.3981
1.0000	108.1559	233.1632	1.0000	108.6760	235.2461

TABLE B.5 : Partial Molar Volume of the System Toluene(A)-n-Tetradecane(B)

Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol	Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	108.3004	260.0532	0.0000	109.7077	261.2797
0.0661	108.1205	260.0594	0.0469	109.4089	261.2866
0.1089	108.0021	260.0708	0.1072	109.0554	261.3161
0.2072	107.7279	260.01226	0.1969	108.5912	261.3991
0.3028	107.4647	260.2131	0.2854	108.2011	261.5229
0.3994	107.2087	260.3521	0.3858	107.8343	261.7080
0.5034	106.9534	260.5628	0.4918	107.5276	261.9470
0.5820	106.7794	260.7697	0.5944	107.3019	262.2148
0.7026	106.5537	261.1765	0.6815	107.1598	262.4643
0.8048	106.4110	261.6148	0.7929	107.0375	262.8061
0.9018	106.3247	262.1186	0.8947	106.9765	263.1335
1.0000	106.2938	262.7234	1.0000	106.9569	263.4799
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	109.6857	263.6171	0.0000	109.0321	264.8559
0.0513	109.5919	263.6196	0.0503	109.2487	264.8505
0.0991	109.5011	263.6270	0.0977	109.4062	264.8381
0.1977	109.3065	263.6612	0.1856	109.5903	264.8088
0.2967	109.1072	263.7271	0.2950	109.6545	264.7909
0.3868	108.9283	263.8203	0.3892	109.5948	264.8238
0.4975	108.7198	263.9863	0.4954	109.4372	264.9518
0.5973	108.5503	264.1921	0.5902	109.2477	265.1795
0.6983	108.4039	264.4621	0.6908	109.0300	265.5714
0.7963	108.2932	264.7907	0.8046	108.8056	266.2446
0.89897	108.2176	265.2129	0.8977	108.6731	267.0101
1.0000	108.1913	265.7134	1.0000	108.6153	268.1100

TABLE B.6 : Partial Molar Volume of the System Toluene(A)-n-Hexadecane(B)

Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol	Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	107.8734	292.7292	0.0000	108.3262	293.9777
0.0444	107.8734	292.7293	0.06697	108.3005	293.9787
0.0959	107.8500	292.7312	0.13099	108.2474	293.9846
0.2033	107.7323	292.7531	0.1927	108.1735	293.9990
0.2811	107.6004	292.7958	0.2708	108.0543	294.0354
0.38898	107.3728	292.9121	0.4333	107.7457	294.2075
0.4969	107.1161	293.1181	0.5026	107.6024	294.3339
0.6004	106.8663	293.4238	0.5973	107.4092	294.5712
0.6977	106.6491	293.8279	0.7017	107.2141	294.9350
0.7978	106.4631	294.3824	0.7984	107.0659	295.3820
0.9004	106.3337	295.1171	0.89799	106.9615	295.9697
1.0000	106.2876	296.0127	1.0000	106.9219	296.7214
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	111.3384	296.5268	0.0000	110.1148	297.6164
0.0363	111.1050	296.5311	0.0533	110.0548	297.6182
0.0987	110.7245	296.5587	0.0961	109.9978	297.6228
0.2114	110.1049	296.6724	0.2119	109.8114	297.6576
0.3078	109.6429	296.8343	0.2950	109.6568	297.7105
0.3992	109.2620	297.0425	0.3956	109.4571	297.8166
0.5031	108.8961	297.3433	0.4984	109.2506	297.9845
0.5963	108.6281	297.6703	0.5995	109.0575	298.2207
0.7028	108.3908	298.10996	0.6995	108.8884	298.5355
0.7969	108.2420	298.5561	0.7946	108.7585	298.9207
0.8978	108.1451	299.0[illegible]37	0.9000	108.6624	299.4580
1.0000	108.1124	299.7011	1.0000	108.6299	300.0868

TABLE B.7 : Partial Molar Volume of the System Ethylbenzene(A)-n-Octane(B)

Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol	Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	123.5546	162.7033	0.0000	123.8560	163.5532
0.0544	123.4286	162.7068	0.0562	123.8128	163.5544
0.1028	123.3239	162.7157	0.1008	123.7763	163.5575
0.2053	123.1241	162.7520	0.1983	123.6915	163.5726
0.3052	122.9573	162.8091	0.2917	123.6068	163.6003
0.40997	122.8105	162.8907	0.3979	123.5100	163.6516
0.5113	122.6948	162.9894	0.5898	123.3480	163.8118
0.6193	122.5984	163.1147	0.7007	123.2708	163.9528
0.7113	122.5370	163.2366	0.7972	123.2185	164.1094
0.8071	122.4923	163.3773	0.8964	123.1830	164.3070
0.9012	122.4666	163.5280	1.0000	123.1695	164.5572
1.0000	122.4576	163.6986			
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	125.6598	165.5301	0.0000	126.0669	166.4722
0.0515	125.5563	165.5329	0.0482	126.0479	166.4727
0.0971	125.4665	165.5401	0.0976	126.0172	166.4752
0.1865	125.2967	165.5682	0.1971	125.9260	166.4915
0.2969	125.1006	165.6309	0.2949	125.8069	166.5309
0.3983	124.9367	165.7184	0.3974	125.6620	166.6084
0.4900	124.8040	165.8246	0.4902	125.5229	166.7201
0.5919	124.6764	165.9753	0.5966	125.3655	166.9085
0.7016	124.5655	166.1788	0.6955	125.2325	167.1526
0.7980	124.4932	166.3958	0.7967	125.1208	167.4825
0.8987	124.4456	166.6630	0.8965	125.0461	167.8980
1.0000	124.4290	166.9765	1.0000	125.0173	168.4352

TABLE B.8 : Partial Molar Volume of the System Ethylbenzene(A)-n-Tetradecane(B)

Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol	Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	124.2574	260.0299	0.0000	127.9133	261.0129
0.0521	124.1973	260.10316	0.0629	127.2180	261.0354
0.1152	124.1028	260.0404	0.1057	126.7830	261.0754
0.2101	123.9241	260.0758	0.2109	125.8367	261.2527
0.2932	123.7409	260.1379	0.3033	125.1406	261.4931
0.4042	123.4736	260.2824	0.3946	124.0647	262.2017
0.4963	123.2462	260.4696	0.5007	124.0377	262.2284
0.5976	123.0054	260.7618	0.6007	123.6568	262.6943
0.6977	122.7928	261.1545	0.7002	123.3810	263.2060
0.7987	122.6197	261.6715	0.7976	123.2008	263.7419
0.8999	122.5041	262.3274	0.8976	123.0967	264.3175
1.0000	122.4626	263.1280	1.0000	123.0635	264.9219
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	127.9635	263.6332	0.0000	126.5562	264.9877
0.0529	127.5222	263.6451	0.0509	126.5597	264.9877
0.1010	127.1527	263.6758	0.0923	126.5442	264.9890
0.1997	126.4873	263.7931	0.1991	126.4393	265.0081
0.2950	125.9535	263.9681	0.3032	126.2658	265.0675
0.39297	125.5075	264.2013	0.4005	126.0608	265.1801
0.4975	125.1350	264.4994	0.4961	125.8373	265.3630
0.5814	124.9056	264.7676	0.5918	125.6100	265.6358
0.6978	124.6779	265.1699	0.7004	125.3700	266.0769
0.8008	124.5522	265.5438	0.7975	125.1924	266.6098
0.8974	124.4886	265.8990	0.8997	125.0642	267.3341
1.0000	124.4680	266.2704	1.0000	125.0180	268.2277

TABLE B.9 : Partial Molar Volume of the System Ethylbenzene(A)-n-Hexadecane(B)

Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol	Mole Fraction x_A	$V_{m,A}$ L/kmol	$V_{m,B}$ L/kmol
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	123.7218	292.6912	0.0000	125.8423	293.2799
0.0539	123.8165	292.6887	0.0692	125.5138	293.9917
0.1029	123.8652	292.6847	0.1142	125.3096	294.0123
0.1983	123.8706	292.6850	0.2058	124.9195	294.0867
0.3022	123.7663	292.7216	0.3084	124.5238	294.2238
0.4028	123.5849	292.8222	0.4053	124.1925	294.4078
0.4927	123.3797	292.9901	0.5027	123.9034	294.6482
0.5953	123.1230	293.2990	0.6099	123.6388	294.9802
0.6978	122.8720	293.7618	0.69799	123.4656	295.3078
0.7992	122.6590	294.4008	0.8029	123.3138	295.7649
0.9002	122.5102	295.2459	0.9008	123.2279	296.2594
1.0000	122.4560	296.3147	1.0000	123.1982	296.8299
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	127.2092	296.7751	0.0000	127.2365	297.6974
0.0505	126.9432	296.7820	0.0502	127.1074	297.7007
0.0912	126.7390	296.7976	0.0987	126.9764	297.7113
0.1912	126.2760	296.8737	0.1983	126.6925	297.7614
0.2997	125.8350	297.0172	0.3033	126.3826	297.8659
0.4026	125.4762	297.2113	0.3935	126.1178	298.0080
0.4995	125.1903	297.4462	0.4981	125.8241	298.2453
0.5968	124.9547	297.7321	0.5986	125.5672	298.5583
0.6994	124.7614	298.0880	0.6995	125.3463	298.9682
0.7991	124.6277	298.4873	0.8025	125.1712	299.4983
0.8987	124.5473	298.9387	0.8986	125.0651	300.1053
1.0000	124.5199	299.4516	1.0000	125.0245	300.8754

and similarly

$$\bar{V}_B = C_o + C_1 x_A^2 + C_2 x_A^3 \tag{B.7}$$

where $C_o = A_o$

$C_1 = -A_2$

$C_2 = -2A_3$

Calculating the values of the constants B_0 to B_3 and C_0 to C_2 from the known values of A_0 to A_3 (given in Table B.1), partial molar volumes V_m^A and V_m^B were obtained for each system at different temperatures over the entire composition range. These values are given in Tables B.2 to B.9.

APPENDIX C

Excess Volume of Mixing

The density-composition data obtained in this study have been used to calculate the excess volume of mixing for each of the binary mixtures at different temperatures studied in this work. Tables C.1 to C.8 gives the numerical values of the excess volumes of mixing over the complete composition range for each system. These data are illustrated in figures 4.2 to 4.5.

The excess volume of mixing has been calculated from the equation

$$V_m^E = \frac{M_A x_A + M_B x_B}{\rho_m} - \frac{M_A x_A}{\rho_A} - \frac{M_B x_B}{\rho_B} \qquad (C.1)$$

where, M_A and M_B are the molecular weights of the two components, ρ_A, ρ_B and ρ_m are the densities of component A, B and of mixture respectively and V_m^E is the excess volume of mixing of the mixture.

TABLE C.1 : Excess Volume of Mixing of the System Toluene(A)-n-Octane(B)

Mole Fraction x_A	Excess Volume L/kmol	Mole Fraction x_A	Excess Volume L/kmol
Temperature = 20.00°C		Temperature = 25.00°C	
0.0000	0.0000	0.0000	0.0000
0.0584	0.1139	0.04995	-0.0623
0.1021	0.1749	0.0910	-0.0503
0.2065	0.2529	0.1548	0.0164
0.3044	0.2972	0.2566	0.0875
0.3937	0.3323	0.3472	0.1336
0.5027	0.3370	0.4446	0.1469
0.5946	0.3401	0.5437	0.1746
0.6979	0.3016	0.6408	0.1632
0.8028	0.2587	0.7612	0.1168
0.8990	0.1774	0.8747	0.0444
1.0000	0.0000	1.0000	0.0000
Temperature = 35.00°C		Temperature = 40.00°C	
0.0000	0.0000	0.0000	0.0000
0.0440	0.0915	0.0517	0.2357
0.1032	0.1322	0.1038	0.2855
0.2008	0.3035	0.1986	0.3197
0.2940	0.4274	0.29896	0.3396
0.3983	0.5275	0.4023	0.3597
0.4956	0.5245	0.4942	0.3960
0.6003	0.4786	0.5939	0.3874
0.6974	0.3218	0.6947	0.3514
0.8019	0.2004	0.8003	0.3247
0.8979	0.1149	0.8976	0.1704
1.0000	0.0000	1.0000	0.0000

TABLE C.2 : Excess Volume of Mixing of the System Toluene(A)-n-Decane(B)

Mole Fraction x_A	Excess Volume L/kmol	Mole Fraction x_A	Excess Volume L/kmol
Temperature = 20.00°C		Temperature = 25.00°C	
0.0000	0.0000	0.0000	0.0000
0.05798	0.2106	0.0519	0.0125
0.1088	0.2752	0.1005	0.0970
0.2078	0.3621	0.20197	0.2798
0.3046	0.4327	0.3037	0.3637
0.4047	0.4841	0.4060	0.4381
0.4968	0.4942	0.5113	0.4911
0.5992	0.4901	0.6106	0.4772
0.6996	0.4519	0.7050	0.4200
0.7994	0.3762	0.8021	0.3451
0.9031	0.2487	0.8957	0.2389
1.0000	0.0000	1.0000	0.0000
Temperature = 35.00°C		Temperature = 40.00°C	
0.0000	0.0000	0.0000	0.0000
0.0495	0.1187	0.0432	-0.1765
0.0966	0.2834	0.1008	-0.07099
0.1964	0.4901	0.2021	0.0121
0.2979	0.6156	0.2993	0.1402
0.3929	0.6286	0.3936	0.1980
0.4962	0.6464	0.4947	0.2370
0.5965	0.6294	0.5931	0.2761
0.6981	0.5282	0.6959	0.2423
0.7988	0.4576	0.8009	0.1701
0.8979	0.2416	0.8962	0.0994
1.0000	0.0000	1.0000	0.0000

TABLE C.3 : Excess Volume of Mixing of the System Toluene(A)-n-Dodecane(B)

Mole Fraction x_A	Excess Volume L/kmol	Mole Fraction x_A	Excess Volume L/kmol
Temperature = 20.00°C		Temperature = 25.00°C	
0.0000	0.0000	0.0000	0.0000
0.0645	0.1433	0.0551	0.0795
0.1056	0.1795	0.0887	0.1373
0.2082	0.2785	0.1959	0.2660
0.3004	0.3590	0.2789	0.3673
0.4037	0.3952	0.3802	0.4386
0.5002	0.4568	0.4701	0.4975
0.6005	0.4755	0.5707	0.5344
0.7015	0.4674	0.6854	0.5131
0.8023	0.3954	0.7805	0.4524
0.90099	0.2563	0.8895	0.3269
1.0000	0.0000	1.0000	0.0000
Temperature = 35.00°C		Temperature = 40.00°C	
0.0000	0.0000	0.0000	0.0000
0.0527	0.0637	0.0508	0.1439
0.0996	0.0984	0.0924	0.2417
0.2049	0.1326	0.2033	0.3962
0.2913	0.2606	0.3003	0.4987
0.4021	0.3659	0.4063	0.6085
0.4986	0.4040	0.5104	0.6822
0.5944	0.4124	0.5988	0.6510
0.69698	0.3844	0.7015	0.6184
0.7979	0.2569	0.7999	0.5151
0.8981	0.1327	0.89898	0.3969
1.0000	0.0000	1.0000	0.0000

TABLE C.4 : Excess Volume of Mixing of the System Toluene(A)-n-Tetradecane(B)

Mole Fraction x_A	Excess Volume L/kmol	Mole Fraction x_A	Excess Volume L/kmol
Temperature = 20.00°C		Temperature = 25.00°C	
0.0000	0.0000	0.0000	0.0000
0.0661	0.2429	0.0469	0.4275
0.1089	0.2919	0.1072	0.5147
0.2072	0.4156	0.1969	0.59999
0.3028	0.4895	0.2854	0.6385
0.3994	0.5849	0.3858	0.6766
0.5034	0.6287	0.4918	0.6772
0.5820	0.6268	0.5944	0.6727
0.7026	0.5354	0.6815	0.6229
0.8048	0.4602	0.7929	0.5106
0.9018	0.3191	0.8947	0.3304
1.0000	0.0000	1.0000	0.0000
Temperature = 35.00°C		Temperature = 40.00°C	
0.0000	0.0000	0.0000	0.0000
0.0513	0.1006	0.0503	-0.1592
0.0991	0.1907	0.0977	-0.0595
0.1977	0.2973	0.1856	0.1291
0.2967	0.3606	0.2950	0.1839
0.3868	0.4050	0.3892	0.3109
0.4975	0.4393	0.4954	0.4144
0.5973	0.4646	0.5902	0.4435
0.6983	0.4444	0.6908	0.5038
0.7963	0.3242	0.8046	0.3607
0.89897	0.1942	0.8977	0.2347
1.0000	0.0000	1.0000	0.0000

TABLE C.5 : Excess Volume of Mixing of the System Toluene(A)-n-Hexadecane(B)

Mole Fraction x_A	Excess Volume L/kmol	Mole Fraction x_A	Excess Volume L/kmol
Temperature = 20.00°C		Temperature = 25.00°C	
0.0000	0.0000	0.0000	0.0000
0.0444	0.1402	0.06697	0.1099
0.0959	0.2268	0.13099	0.2128
0.2033	0.3661	0.1927	0.3082
0.2811	0.4693	0.2708	0.3690
0.38898	0.5597	0.4333	0.4850
0.4969	0.6154	0.5026	0.5189
0.6004	0.6396	0.5973	0.5218
0.6977	0.6221	0.7017	0.5262
0.7978	0.5383	0.7984	0.4480
0.9004	0.3413	0.89799	0.2673
1.0000	0.0000	1.0000	0.0000
Temperature = 35.00°C		Temperature = 40.00°C	
0.0000	0.0000	0.0000	0.0000
0.0363	0.0577	0.05333	0.0946
0.0987	0.2080	0.0961	0.1554
0.2114	0.3979	0.2119	0.2764
0.3078	0.6266	0.2950	0.3941
0.3992	0.7504	0.3956	0.4470
0.5031	0.7852	0.4984	0.4749
0.5963	0.7411	0.5995	0.5024
0.7028	0.60696	0.6995	0.4676
0.7969	0.4156	0.7946	0.3824
0.8978	0.1170	0.9000	0.1924
1.0000	0.0000	1.0000	0.0000

TABLE C.6 : Excess Volume of Mixing of the System Ethylbenzene(A)-n-Octane(B)

Mole Fraction x_A	Excess Volume L/kmol	Mole Fraction x_A	Excess Volume L/kmol
Temperature = 20.00°C		Temperature = 25.00°C	
0.0000	0.0000	0.0000	0.0000
0.0544	0.1156	0.0562	0.0084
0.1028	0.1542	0.1008	0.0658
0.2053	0.2261	0.1983	0.1087
0.3052	0.2618	0.2917	0.1700
0.40997	0.2770	0.3979	0.2018
0.5113	0.2705	0.5898	0.1988
0.6193	0.2579	0.7007	0.1858
0.7113	0.2416	0.7972	0.1539
0.8071	0.2139	0.8964	0.1030
0.9012	0.1515	1.0000	0.0000
1.0000	0.0000		
Temperature = 35.00°C		Temperature = 40.00°C	
0.0000	0.0000	0.0000	0.0000
0.0515	0.0486	0.0482	0.1131
0.0971	0.1164	0.0976	0.1561
0.1865	0.2129	0.1971	0.2431
0.2969	0.2687	0.2949	0.3269
0.3983	0.3001	0.3974	0.3694
0.4900	0.3374	0.4902	0.3931
0.5919	0.3347	0.5966	0.4058
0.7016	0.2945	0.6955	0.3994
0.7980	0.2278	0.7967	0.3281
0.8987	0.1412	0.8965	0.2759
1.0000	1.0000	1.0000	1.0000

TABLE C.7: Exess Volume of Mixing of the System Ethylbenzene(A)-n-Tetradecane(B)

Mole Fraction x_A	Excess Volume L/kmol	Mole Fraction x_A	Excess Volume L/kmol
Temperature = 20.00°C		Temperature = 25.00°C	
0.0000	0.0000	0.0000	0.0000
0.0521	0.1472	0.0629	0.2751
0.1152	0.2648	0.1057	0.2530
0.2101	0.3979	0.2109	0.4230
0.2932	0.4763	0.3033	0.4826
0.4042	0.5970	0.3946	0.5381
0.4963	0.6172	0.5007	0.5887
0.5976	0.6345	0.6007	0.5729
0.6977	0.6030	0.7002	0.5126
0.7987	0.5108	0.7976	0.4400
0.8999	0.3458	0.8976	0.2754
1.0000	0.0000	1.0000	0.0000
Temperature = 35.00°C		Temperature = 40.00°C	
0.0000	0.0000	0.0000	0.0000
0.0529	0.1924	0.0509	0.14596
0.1010	0.4243	0.0923	0.2356
0.1997	0.6121	0.1991	0.3231
0.2950	0.7071	0.3032	0.4961
0.39297	0.7639	0.4005	0.5518
0.4975	0.7759	0.4961	0.6520
0.5814	0.7620	0.5918	0.6494
0.6978	0.6459	0.7004	0.5673
0.8008	0.5214	0.7975	0.5338
0.8974	0.3478	0.8997	0.3673
1.0000	0.0000	1.0000	0.0000

TABLE C.8 : Excess Volume of Mixing of the System Ethylbenzene(A)-n-Hexadecane(B)

Mole Fraction x_A	Excess Volume L/kmol	Mole Fraction x_A	Excess Volume L/kmol
Temperature = 20.00°C		Temperature = 25.00°C	
0.0000	0.0000	0.0000	0.0000
0.0539	0.0743	0.0692	0.2158
0.1029	0.1606	0.1142	0.2869
0.1983	0.2829	0.2058	0.4713
0.3022	0.46399	0.3084	0.5854
0.4028	0.5502	0.4053	0.6941
0.4927	0.6008	0.5027	0.7107
0.5953	0.6363	0.6099	0.6824
0.6978	0.6208	0.69799	0.5934
0.7992	0.5599	0.8029	0.4625
0.9002	0.3629	0.9008	0.3493
1.0000	0.0000	1.0000	0.0000
Temperature = 35.00°C		Temperature = 40.00°C	
0.0000	0.0000	0.0000	0.0000
0.0505	0.4578	0.0502	0.2093
0.0912	0.5387	0.0987	0.4053
0.1912	0.6308	0.1983	0.4976
0.2997	0.7091	0.3033	0.5916
0.4026	0.7454	0.3935	0.6607
0.4995	0.7571	0.4981	0.6750
0.5968	0.7330	0.5986	0.7218
0.6994	0.7007	0.6995	0.6758
0.7991	0.6176	0.8025	0.5973
0.8987	0.4578	0.8986	0.3691
1.0000	0.0000	1.0000	0.0000

APPENDIX D

The Excess Activation Energy for Viscous Flow and the Excess Viscosity

The variation of excess activation energy for viscous flow and the excess viscosity with composition for each binary mixture at different temperature levels studied in this work are reported in Tables D.1 to D.8. The variation of these two excess properties are also shown in Figures 4.19 to 4.26.

TABLE D.1: Excess Energy of Viscous Flow and Excess Viscosity of the System Toluene(A)-n-Octane(B)

Mole Fraction x_A	$\Delta^*G^E \times 10^{-5}$ J/kmol	Excess Viscosity cP	Mole Fraction x_A	$\Delta^*G^E \times 10^{-5}$ J/kmol	Excess Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0584	-0.174	-0.0067	0.04995	-0.212	-0.0061
0.1021	-0.387	-0.0133	0.0910	-0.347	-0.0105
0.2065	-0.755	-0.0252	0.1548	-0.582	-0.0176
0.3044	-0.996	-0.0332	0.2566	-0.914	-0.0274
0.3937	-1.2595	-0.0408	0.3472	-1.114	-0.0336
0.5027	-1.424	-0.0456	0.4447	-1.346	-0.0397
0.5946	-1.4498	-0.0465	0.5437	-1.412	-0.0418
0.6979	-1.404	-0.0445	0.6408	-1.376	-0.0408
0.8028	-1.152	-0.0367	0.7612	-1.260	-0.0367
0.8990	-0.732	-0.0235	0.8747	-0.843	-0.0245
1.0000	0.000	0.0000	1.0000	0.000	0.0000
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0440	-0.133	-0.0042	0.0517	-0.148	-0.0048
0.1032	-0.359	-0.0103	0.1038	-0.311	-0.0093
0.2008	-0.651	-0.0186	0.1986	-0.579	-0.0164
0.2940	-0.925	-0.0259	0.29896	-0.851	-0.0230
0.3983	-1.112	-0.0312	0.4023	-1.048	-0.0279
0.4956	-1.231	-0.0342	0.4942	-1.194	-0.0312
0.6003	-1.283	-0.0352	0.5939	-1.272	-0.0327
0.6974	-1.244	-0.0333	0.6947	-1.219	-0.0311
0.8019	-1.049	-0.0277	0.8003	-1.036	-0.0263
0.8979	-0.662	-0.0175	0.8976	-0.671	-0.0168
1.0000	0.000	0.0000	1.0000	0.000	0.0000

TABLE D.2 : Excess Energy of Viscous Flow and Excess Viscosity of the System Toluene(A)-n-Decane(B)

Mole Fraction x_A	$\Delta^*G^E x10^{-5}$ J/kmol	Excess Viscosity cP	Mole Fraction x_A	$\Delta^*G^E x10^{-5}$ J/kmol	Excess Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.05798	0.282	-0.0024	0.0519	-0.024	-0.0105
0.1088	0.113	-0.0179	0.1005	0.063	-0.01598
0.2078	0.166	-0.0307	0.20197	0.071	-0.0299
0.3046	0.140	-0.0414	0.3037	0.092	-0.0389
0.4047	0.135	-0.0474	0.4060	0.190	-0.0417
0.4968	0.134	-0.0491	0.5113	0.056	-0.04695
0.5992	0.036	-0.0496	0.6106	0.031	-0.0451
0.6996	0.020	-0.0437	0.7050	-0.028	-0.0407
0.7994	-0.174	-0.0383	0.8021	-0.130	-0.0338
0.9031	-0.189	-0.0234	0.8957	-0.171	-0.0222
1.0000	0.000	0.0000	1.0000	0.000	0.0000
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0495	0.117	-0.0051	0.0432	0.125	-0.0023
0.0966	0.247	-0.0086	0.1008	0.213	-0.0078
0.1964	0.345	-0.0182	0.2021	0.335	-0.0157
0.2979	0.425	-0.0249	0.2993	0.451	-0.0206
0.3929	0.4799	-0.0286	0.3936	0.452	-0.0252
0.4962	0.283	-0.0352	0.4947	0.410	-0.0281
0.5965	0.206	-0.0354	0.5931	0.279	-0.0299
0.6981	0.100	-0.0329	0.6959	0.151	-0.0283
0.7988	-0.008	-0.02697	0.8009	0.026	-0.0231
0.8979	-0.082	-0.0170	0.8962	-0.1396	-0.0164
1.0000	0.000	0.0000	1.0000	0.000	0.0000

TABLE D.3 : Excess Energy of Viscous Flow and Excess Viscosity of the System Toluene(A)-n-Dodecane(B)

Mole Fraction x_A	$\Delta^* G^E x10^{-5}$ J/kmol	Excess Viscosity cP	Mole Fraction x_A	$\Delta^* G^E x10^{-5}$ J/kmol	Excess Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0645	0.536	-0.0179	0.0551	0.389	-0.0171
0.1056	0.783	-0.0313	0.0887	0.611	-0.0265
0.2082	1.370	-0.0557	0.1959	1.228	-0.0508
0.3004	1.6897	-0.0753	0.2789	1.631	-0.0633
0.4037	2.143	-0.0788	0.3802	1.965	-0.0735
0.5002	2.077	-0.0899	0.4701	2.135	-0.0771
0.6005	2.056	-0.0855	0.5707	2.089	-0.0780
0.7015	1.815	-0.0754	0.6854	1.852	-0.0698
0.8023	1.280	-0.0609	0.7805	1.425	-0.0578
0.90099	0.688	-0.0356	0.8895	0.755	-0.0354
1.0000	0.000	0.0000	1.0000	0.000	0.0000
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0527	0.415	-0.0107	0.0508	0.429	-0.0084
0.0996	0.759	-0.01895	0.0924	0.752	-0.0146
0.2049	1.415	-0.0343	0.2033	1.468	-0.0291
0.2913	1.851	-0.0433	0.3003	1.930	-0.0386
0.4021	2.220	-0.0508	0.4063	2.264	-0.0452
0.4986	2.377	-0.0529	0.5104	2.376	-0.0483
0.5944	2.331	-0.0519	0.5988	2.392	-0.0453
0.69698	2.023	-0.0478	0.7015	2.097	-0.0412
0.7979	1.519	-0.0381	0.7999	1.629	-0.0324
0.8981	0.845	-0.0225	0.89898	0.859	-0.0208
1.0000	0.000	0.0000	1.0000	0.000	0.0000

TABLE D.4 : Excess Energy of Viscous Flow and Excess Viscosity of the System Toluene(A)-n-Tetradecane(B)

Mole Fraction x_A	$\Delta^*G^E \times 10^{-5}$ J/kmol	Excess Viscosity cP	Mole Fraction x_A	$\Delta^*G^E \times 10^{-5}$ J/kmol	Excess Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0661	0.972	-0.0437	0.0469	0.709	-0.0278
0.1089	1.526	-0.06999	0.1072	1.528	-0.0582
0.2072	2.632	-0.1207	0.1969	2.494	-0.1019
0.3028	3.420	-0.1595	0.2854	3.384	-0.12599
0.3994	4.064	-0.1782	0.3858	4.024	-0.1488
0.5034	4.423	-0.1841	0.4918	4.426	-0.15597
0.5820	4.395	-0.1807	0.5944	4.3499	-0.1543
0.7026	3.9499	-0.1549	0.6815	4.129	-0.1359
0.8048	3.094	-0.1165	0.7929	3.319	-0.1015
0.9018	1.781	-0.0668	0.8947	1.925	-0.0603
1.0000	0.000	0.0000	1.0000	0.000	0.0000
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.0000	0.0000	0.0000	0.000	0.0000
0.0513	0.791	-0.0183	0.0503	0.729	-0.0165
0.0991	1.468	-0.0342	0.0977	1.316	-0.0347
0.1977	2.666	-0.0629	0.1856	2.546	-0.0497
0.2967	3.642	-0.0831	0.2950	3.727	-0.0656
0.3868	4.297	-0.0946	0.3892	4.388	-0.0778
0.4975	4.752	-0.1000	0.4954	4.824	-0.0831
0.5973	4.767	-0.0973	0.5902	4.837	-0.0823
0.6983	4.398	-0.0853	0.6908	4.479	-0.0738
0.7963	3.785	-0.0599	0.8046	3.481	-0.0550
0.89897	2.068	-0.03797	0.8977	2.126	-0.0327
1.0000	0.000	0.0000	1.0000	0.000	0.0000

TABLE D.5 : Excess Energy of Viscous Flow and Excess Viscosity of the System Toluene(A)-n-Hexadecane(B)

Mole Fraction x_A	$\Delta^* G^E x10^{-5}$ J/kmol	Excess Viscosity cP	Mole Fraction x_A	$\Delta^* G^E x10^{-5}$ J/kmol	Excess Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0444	0.940	-0.0635	0.06697	1.446	-0.06998
0.0959	1.897	-0.1366	0.13099	2.787	-0.1191
0.2033	3.981	-0.2223	0.1927	3.723	-0.1820
0.2811	4.872	-0.3033	0.2708	5.068	-0.2151
0.38898	6.174	-0.3409	0.4333	6.855	-0.2661
0.4969	6.897	-0.3531	0.5026	7.281	-0.2687
0.6004	7.013	-0.3360	0.5973	7.384	-0.2593
0.6977	6.498	-0.2949	0.7017	6.735	-0.2311
0.7978	5.329	-0.2225	0.7984	5.372	-0.1827
0.9004	3.136	-0.1243	0.89799	3.346	-0.1016
1.0000	0.000	0.0000	1.0000	0.000	0.0000
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0363	0.836	-0.0231	0.0533	1.140	-0.0340
0.0987	2.167	-0.0614	0.0961	1.969	-0.0609
0.2114	4.245	-0.1181	0.2119	4.471	-0.0838
0.3078	5.693	-0.1520	0.2950	5.618	-0.1174
0.3992	6.695	-0.1735	0.3956	6.771	-0.1382
0.5031	7.359	-0.1832	0.4984	7.424	-0.1491
0.5963	7.518	-0.1755	0.5995	7.778	-0.1363
0.7028	6.979	-0.15279	0.6995	7.128	-0.1256
0.7969	5.812	-0.1174	0.7946	5.965	-0.0971
0.8978	3.515	-0.0675	0.9000	3.525	-0.05498
1.0000	0.000	0.0000	1.0000	0.000	0.0000

TABLE D.6 : Excess Energy of Viscous Flow and Excess Viscosity of the System Ethylbenzene(A)-n-Octane(B)

Mole Fraction x_A	$\Delta^*G^E \times 10^{-5}$ J/kmol	Excess Viscosity cP	Mole Fraction x_A	$\Delta^*G^E \times 10^{-5}$ J/kmol	Excess Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0544	-0.234	-0.0073	0.0562	-0.261	-0.0071
0.1028	-0.441	-0.0135	0.1008	-0.473	-0.0129
0.2053	-0.774	-0.02398	0.1983	-0.874	-0.0238
0.3052	-1.183	-0.0356	0.2917	-1.123	-0.0313
0.40997	-1.369	-0.0418	0.3979	-1.377	-0.0386
0.5113	-1.471	-0.0454	0.5898	-1.483	-0.0427
0.6193	-1.465	-0.0458	0.7007	-1.344	-0.0395
0.7113	-1.367	-0.0432	0.7972	-1.111	-0.0331
0.8071	-1.068	-0.0347	0.8964	-0.713	-0.0216
0.9012	-0.608	-0.0206	1.0000	0.000	0.0000
1.0000	0.000	0.0000			
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0515	-0.232	-0.0056	0.0482	-0.187	-0.0047
0.0971	-0.415	-0.0102	0.0976	-0.422	-0.0098
0.1865	-0.753	-0.0186	0.1971	-0.775	-0.0181
0.2969	-1.067	-0.0266	0.2949	-1.016	-0.0242
0.3983	-1.272	-0.03197	0.3974	-1.241	-0.0296
0.4900	-1.558	-0.0347	0.4902	-1.308	-0.0318
0.5919	-1.393	-0.0359	0.5966	-1.298	-0.0322
0.7016	-1.273	-0.0333	0.6955	-1.218	-0.0306
0.7980	-1.023	-0.0273	0.7967	-0.982	-0.0251
0.8987	-0.604	-0.0166	0.8965	-0.5996	-0.0160
1.0000	0.000	0.0000	1.0000	0.000	0.0000

TABLE D.7 : Excess Energy of Viscous Flow and Excess Viscosity of the System Ethylbenzene(A)-n-Tetradecane(B)

Mole Fraction x_A	$\Delta^{*}G^{E}x10^{-5}$ J/kmol	Excess Viscosity cP	Mole Fraction x_A	$\Delta^{*}G^{E}x10^{-5}$ J/kmol	Excess Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0521	0.515	-0.0386	0.0629	0.596	-0.0411
0.1152	0.956	-0.08899	0.1057	0.906	-0.0690
0.2101	1.683	-0.1355	0.2109	1.719	-0.1130
0.2932	2.111	-0.1693	0.3033	2.228	-0.1419
0.4042	2.568	-0.1909	0.3946	2.612	-0.1568
0.4963	2.786	-0.1924	0.5007	2.938	-0.1561
0.5976	2.756	-0.1826	0.6007	2.894	-0.1487
0.6977	2.511	-0.1572	0.7002	2.616	-0.1286
0.7987	1.977	-0.1182	0.7976	2.084	-0.0978
0.8999	1.157	-0.0652	0.8976	1.177	-0.0567
1.0000	0.000	0.0000	1.0000	0.000	0.0000
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0529	0.681	-0.0138	0.0509	0.485	-0.0208
0.1010	0.996	-0.0414	0.0923	0.878	-0.0341
0.1997	1.748	-0.0745	0.1991	1.759	-0.0619
0.2950	2.385	-0.0933	0.3032	2.518	-0.0766
0.39297	2.780	-0.1077	0.4005	2.963	-0.0862
0.4975	3.064	-0.1096	0.4961	3.188	-0.0897
0.5814	3.1198	-0.1042	0.5918	3.308	-0.0823
0.6978	2.867	-0.0879	0.7004	2.889	-0.0744
0.8008	2.318	-0.0644	0.7975	2.332	-0.0569
0.8974	1.347	-0.0383	0.8997	1.381	-0.0315
1.0000	0.000	0.0000	1.0000	0.000	0.0000

TABLE D.8 : Excess Energy of Viscous Flow and Excess Viscosity of the System Ethylbenzene(A)-n-Hexadecane(B)

Mole Fraction x_A	$\Delta^* G^E x10^{-5}$ J/kmol	Excess Viscosity cP	Mole Fraction x_A	$\Delta^* G^E x10^{-5}$ J/kmol	Excess Viscosity cP
Temperature = 20.00°C			Temperature = 25.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0539	0.810	-0.0854	0.0692	0.981	-0.0824
0.1029	1.511	-0.15097	0.1142	1.558	-0.1290
0.1983	2.791	-0.2450	0.2058	2.597	-0.2061
0.3022	3.720	-0.3327	0.3084	3.5195	-0.2648
0.4028	4.513	-0.3646	0.4053	4.154	-0.2936
0.4927	4.774	-0.3797	0.5027	4.519	-0.2979
0.5953	5.0498	-0.3451	0.6099	4.5795	-0.2755
0.6978	4.923	-0.2832	0.69799	4.262	-0.2395
0.7992	3.782	-0.2204	0.8029	3.352	-0.1781
0.9002	2.251	-0.1212	0.9008	1.954	-0.10096
1.0000	0.000	0.0000	1.0000	0.000	0.0000
Temperature = 35.00°C			Temperature = 40.00°C		
0.0000	0.000	0.0000	0.0000	0.000	0.0000
0.0505	0.829	-0.0428	0.0502	0.774	-0.0385
0.0912	1.470	-0.0703	0.0987	1.465	-0.0716
0.1912	2.842	-0.1279	0.1983	2.943	-0.1094
0.2997	4.016	-0.1719	0.3033	3.869	-0.15699
0.4026	4.857	-0.1921	0.3935	4.929	-0.1547
0.4995	5.276	-0.1981	0.4981	5.399	-0.1622
0.5968	5.440	-0.1841	0.5986	5.490	-0.1541
0.6994	5.013	-0.1602	0.6995	5.107	-0.1331
0.7991	4.127	-0.1195	0.8025	4.161	-0.0982
0.8987	1.922	-0.0829	0.8986	2.573	-0.0556
1.0000	0.000	0.0000	1.0000	0.000	0.0000

APPENDIX E

Predicted Experimental Error

E.1 Density Measurement

The reproducibility of density meter readings at 20.00 °C for organic liquids was 1 x 10^{-7} seconds which correspond to a change in density of 1.59 x 10^{-4} kg/L. The average standard deviation of fit of composition-dependent density polynomial Equation (4.1) was 1.5 x 10^{-4} kg/L at 20.00°C.

E.2 Error with Excess Volume of Mixing

The equation used to calculate excess volume of mixing is given in Appendix C as

$$V_m^E = \frac{M_A x_A + M_B x_B}{\rho_m} - \frac{M_A x_A}{\rho_A} - \frac{M_B x_B}{\rho_B} \qquad (E.1)$$

where

$$x_A = \left(1 + \frac{W_B M_A}{W_A M_B}\right)^{-1}$$

and

$$x_B = 1 - x_A \qquad (E.2)$$

where W_A and W_B are mass of component A and B respectively; M_A and M_B are molecular weight of component A and B respectively.

Let us consider a particular case, say error expected for V_m^E at $x_A = 0.4$ for toluene (A)-n-octane (B) system at 20.00°C

$W_A = 7.8358 \pm 1 \times 10^{-4}$; $W_B = 14.9576 \quad 1 \times 10^{-4}$

$M_A = 92.14$ $M_B = 114.23$

$x_A = 0.39374$

expecting maximum error in weighing one obtains

$\partial \rho_m = 1 \times 10^{-5}$

maximum deviation in density measurement

$\partial \rho_m = 1.59 \times 10^{-4} = \partial \rho_A = \partial \rho_B$

Now V_m^E is a function of

$$V = f\,(x_A,\ x_B,\ \rho_m,\ \rho_A,\ \rho_B) \tag{E.3}$$

so that to calculate predicted error in V_m^E due to an error in x_A, x_B, ρ_m, ρ_B, ρ_A one should differentiate Equation (E.1) to obtain

$$\partial V_m^E = M_A\left[\frac{1}{\rho_m} - \frac{1}{\rho_A}\right]\partial x_A + M_B\left[\frac{1}{\rho_m} - \frac{1}{\rho_B}\right]\partial x_B + \left[\frac{x_A\ M_A + x_B\ M_B}{\rho_m^2}\right]\partial\rho_A + \left[\frac{M_A\ x_A}{\rho_A^2}\right]\partial\rho_A + \left[\frac{M_B\ x_B}{\rho_B^2}\right]\partial\rho \tag{E.4}$$

$= 0.06$ L/kmol

This is the maximum error that can be expected for the toluene-n-octane system at 20.00°C, which will be the worst case. The standard deviation of fit of V_m^E to the smoothing Equation (4.2) for this sytem was 0.0041. Maximum standard deviation found at 20.00°C was 0.011 for ethylbenzene-n-hexadecane system.

E.3 Viscosity Measurements

The equation used for calculating the viscosities is given by

$$\nu = Ct - E/t^2$$

To calculate the predicted error in the kinematic viscosity value due to an error in t, the efflux time one should differentiate Equation (3.9) to obtain

$$\frac{d\nu}{dt} = C + \frac{2E}{t^3}$$

or

$$d\nu = Cdt + 2(E/t^2)dt \qquad (E.5)$$

Every viscosity value reported in this work was measured at least three times. The time of efflux's scatter was about 0.15 seconds on the average. This scatter when substituted into Equation (E.5) would change the measured viscosity by

$$d\nu = 1.8168 \times 10^{-3} \ (\pm 0.15) + \frac{2x\ (-32.5306)\ (\pm 0.15)}{(330.9)^3}$$

$$= \pm 2.73 \times 10^{-4} \text{ cSt}$$

In the above calculation the values of the viscometer constants C and E were taken as the average values of C and E for the two 25A type viscometers used in this study at 35.00 C and reported in Table 4.12. The value of t, time of efflux was taken as the average value of all efflux time for toluene-n-octane system at 35.00 C where these two viscometers were only used. The standard deviation for the composition dependent kinematic viscosity for this system as can be seen from Table 4.23 was 2.67 x 10 cSt. This is in good agreement with the predicted error.

E.4 Excess Activation Energy of Viscous Flow

The equation used for calculation of excess activation energy for viscous flow is given in Chapter 3 by

$$\frac{\Delta^* G^E}{RT} = \ln \eta_m V_m - x_A \ln \eta_A V_A - x_B \ln \eta_B V_B$$

This equation ~~after~~ substitution of by x and rearranging becomes

$$\Delta^* G^E = RT\ [\ln \nu_m + \ln (M_A x_A + M_B x_B) - x_A \ln \nu_A M_A - x_B \ln \nu_B M_B \qquad \text{(E.6)}$$

$$= F\ (\nu_m, \nu_A, \nu_B, x_A, x_B, T)$$

Thus $\Delta^{*}G^{E} = F(\nu_m, \nu_A, \nu_B, x_A, x_B, T)$

Predicted error can now be obtained by differentiation of Equation (E.6) which is given by

$$\partial(\Delta^{*}G^{E}) = RT\left[\frac{\partial\nu_m}{\nu} + \{\frac{M_A}{M_A\, x_A + M_B\, x_B} - \ln \nu_A M_A\}\ \partial x_A + \{\frac{M_B}{M_A\, x_A + M_B\, x_B}\right.$$

$$\left. \ln \nu_B M_B\}\ \partial x_B - \frac{x_A}{\nu_A}\,\partial\nu_A - \frac{x_B}{\nu_B}\,\partial\nu_B\right] + R\,\{\ln \nu_m +$$

$$\ln (M_A\, x_A + M_B\, x_B) - x_A \ln \nu_A M_A - x_B \ln \nu_B M_B\}\ \partial T$$

Taking absolute value where necessary and after rearrangement the above equation reduces to

$$\partial(\Delta^{*}G^{E}) = RT\left[(\frac{1}{\nu_m} + \frac{1}{\nu_A} + \frac{1}{\nu_B})\ \partial\nu + \{\frac{M_A + M_B}{x_A\, M_A + x_B\, M_B} - \ln \nu_A M_A\right.$$

$$\left. - \ln \nu_B M_B\}\ \partial x_A\right] + R\left[\ln \nu_m + \ln (x_A M_A +\right.$$

$$\left. x_B M_B) - x_A \ln \nu_A M_A - x_B \ln \nu_B M_B\right]\ \partial T \qquad \text{(E.7)}$$

Now taking a particular data, say values

at $x_A \simeq 0.4$ for toluene-n-octane system at 35.00°C

$x_A = 0.3983$; $\nu_m = 0.5952$; $\nu_B = 0.658$; $\nu_A = 0.5783$

$\partial x_A = 1 \times 10$; $\partial\nu = 2.73 \times 10^{-4}$; $\partial T = 0.02$K

$R = 8.3136$ J/mol ; $T = 308.16$ K

we get

$$\partial\, (\Delta^{*}G^{E}) \times 10^{-5} = 0.0246, \quad \text{J/kmol}$$

Standard deviation for this particular system when excess activation energy of viscous flow was fitted to the polynomial

$$\Delta^{*}G^{E} \times 10^{-5} = x_A\,(1 - x_A) \sum_{i=o}^{i=n} A_i\,(2x_A - 1)^{i}$$

was found to be 0.009 which proves that the experimental data fitted the polynomial Equation (4.6) well.

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