Thermodynamic Properties of Liquid Mixtures

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***Abstract*— Density (ρ), Viscosity (Δn), and Refractive Index (r) values of; Anisole with Hexane, Heptane, Octane, Nonane, Decane, Dodecane mixtures; over the range of different mole fractions at temperatures (293.15,298.15 and 303.15K) have been investigated at atmospheric temperature. The excess molar volume (Ve) has been calculated from experimental density data. The experimental refractive indices data were used to calculate change in specific refractivity (ΔR) and also correlated with Lorentz – Lorentz equation. The effect of n –alkanes chain length as well as temperature on the excess molar volume has been studied. The calculated values have been qualitatively used to explain the intermolecular interactions between the mixing components. The results indicated good agreement between activity of solvent calculated by the proposed model and experimental data. The proposed model has advantage that using only simple density measurements, the activity values that are necessary in the calculation of thermodynamic properties can be evaluated.**

***Keywords*—refractive index; excess volume; alkanes; inter molecular interactions; thermodynamic properties.**

I. Introduction

Thermodynamic interactions in binary liquid mixtures and a study of these physical properties continue to be pursed with great interest by physical chemists and chemical engineers, such a study has great importance in many areas of applied and theoretical research in addition to engineering and design processes. Several note worthy theoretical contributions have been made in literature from schools of Flory, Prigogine, Patteron and Kehiaian[11].

Empirical equation have been routinely used to calculated excess thermodynamic properties of liquid mixtures using experimental data of density, viscosity, and refractive index while some of their equations are not completely satisfactory, others require further investigations. A unified understanding of the mixing behavior of liquids with varying structure polarity, etc, is not an easy task. Such a study would definitely be useful to physical chemists in order to gain a sight in to the thermodynamic behavior of mixing process. This would also help to understand the nature of intermolecular interactions between mixing components.

Physical properties like density, viscosity and refractive index are determined experimentally at 3 temperatures and over the whole range of mixture compositions. From these properties excess quantities can be calculated.

From basic physical properties of binary mixtures, excess molar volume, deviations in molar refractivity and viscosity have been calculated, such a approach would provide a considerable amount of knowledge about mixing behavior. These properties are also useful in arriving at some of the important decision about suitability of binary mixture in practical application such as liquid – liquid distillation, separation, miscibility, solubility, etc. Additionally from fundamental viewpoint the parameters will add a wealth to the existing knowledge about the intermolecular interactions between components of mixtures and thereby help in predicting mixing behavior in liquids.

II. Experimental Selections

A. Materials

Chemicals used are listed below. Chemicals used were all of analytical grade samples.

Chemicals: Anisole, Hexane, Heptane, Octane, Nonane Decane, Dodecane.

III. Methods

The experimental techniques used in preparation methods employed are given here.

A. Binary Mixtures

The binary mixtures were prepared by mass in specially designed ground glass stopper bottles.

Numbers of compositions were made in increment of 0.1 mole fraction. The possible error in mole fractions is estimated to be around +-0.0001.

Compositions of the mixtures are expressed as mole fractions, Xi and also, volume fractions Si and these are given by equations:

$$Xi = (gi/Mi)/\sum (gi/Mi)$$
$$Si = (Xi \times vi)/\sum (Xi \times vi)$$

In above equations, gi, Mi and vi refer to mass, molecular weight and molar volume of the component of the mixtures. Where vi is molar volume of the liquid component.

In this Anisole with Hexane, Heptane, Octane, binary mixtures were used to calculate properties.

B. Viscosity Measurement

Solutions of known concentration of anisole-alkanes, water-polyethylene glycol, hydro ethyl cellulose-water etc

was prepared. Kinematic viscosities of these solutions were measured at 293.15K, 298.15K, 303.15K using schott gerate viscometer.

Approximately 5cm³ volume of the liquid was injected into the viscometer and equilibriated to a constant temperature maintained for about 20 minutes. Then, the flow times of pure solvent as well as of the polymer solutions were measured. The kinematic viscosity n, the of the solution was calculated using equation,

$$nk=t\times k$$

where k: viscometric constant 0.03174 mm²/sec²

Which was determined by comparing with a reference viscometer of which the constants were determined.

C. *Density Measurements*

Density measurements of polymer solutions were made using density meter DMA 4500 (Anton Paar). The DMA 4500 is the oscillating u-tube density meter, which measures highest accuracy in wide viscosity and temperature ranges.

To perform measurements, sample is filled in a measuring cell. An acoustic signal will inform when the measurements is finished. Results are automatically converted in to concentration, specific gravity or other density related units using the built in conversion tables and functions.

D. *Refractive Index Measurements*

The refractive indices for pure components and their mixtures were measured with an Abbe refractometer (Atago 3T, Japan).

The refractive indices measured were accurate up to (+ or –0.0002 units). The refractometer is fitted with hollow prism casing through which water can be circulated.

The temperature of the prism casing is observed with a display (+ or –k). The instrument is provided with two prisms placed one above the other in front of the telescope, which smoothly moves with the scale. The instrument directly gives the values of refractive indices of the mixtures. The RI measurements were carried out at 298.15K, and 303.15 K by circulating water from thermostat.

IV. Computations Of Mixing Functions

Excess functions represent the properties of mixtures, which are in excess of those of ideal mixtures under the same conditions of temperature, pressure and compositions. For instance, excess volume is calculated from the density values of liquids and there mixtures. Extremely accurate density measurements needed to get the true values of Ve.

Experimental densities of the binary mixtures and of liquids are used to calculate Ve (m³.mol-1) using Lorentz – Lorentz equation:

$$Ve = (1/\rho)-((M1/\rho1)+(M2/\rho2))$$

Where ρ1 is density and M1 is product of mole fraction and molecular weight of the first component in the mixture. The same symbols with subscript 2 refer to the second component.

The term ρis is density of the mixture at given composition. Deviation in viscosity, molar refractivity have been calculated respectively from viscosity, refractive index data using general equation of the type:

$$\Delta Y=Ym-(Y1\times C1)-(Y2\times C2)$$

Where, ΔY refers to Δn (pa.s.mol-l), ΔR (m³mol) respectively.

Parameter Ym, is the measured mixture property under consideration, i.e., viscosity, molar refractivity; C1 and C2 are the mixture compositions containing components 1 and 2 to calculate Δn mole fraction xi is used for Ci.

For calculating ΔR, McAllister relation for molar refractivity ri, is used:

$$ri= [(nD2-1)/((nD2+2)]\times(Mi/\rho i))$$

Where nd is viscosity of anisole + n-alkanes.

ΔR has been calculated using volume fraction ϕ in equation. The calculated results of Ve, Δn, ΔR have been fitted to the Redlich-Kister polynomial[10].

V. Results And Discussions

Data estimated from the mixtures are used to calculate excess volume (Ve), deviation in viscosity (Δn) and deviation in refractive index (ΔR). These results are fitted in Redlich-Kister polynomial [10] to estimate the binary interaction parameters. Experimental values of density, viscosity and refractive indices are used to calculate excess volumes, deviation in viscosity and refractive indices. The calculations are made through c-programming method.

The fig 1 to 3 shows dependency of excess volume on mole fractions (x1), at 293.15K, 298.15K, 303.15K respectively for binary mixtures of anisole and n-alkanes.

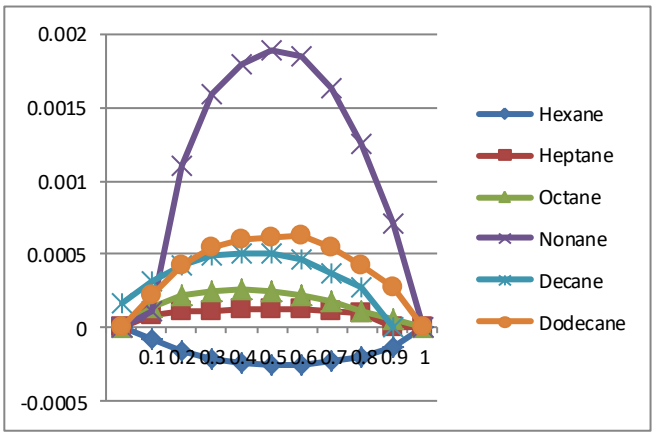

Fig.1 Excess volumes vs. mole fractions for anisole + n-alkanes at 293.15K.

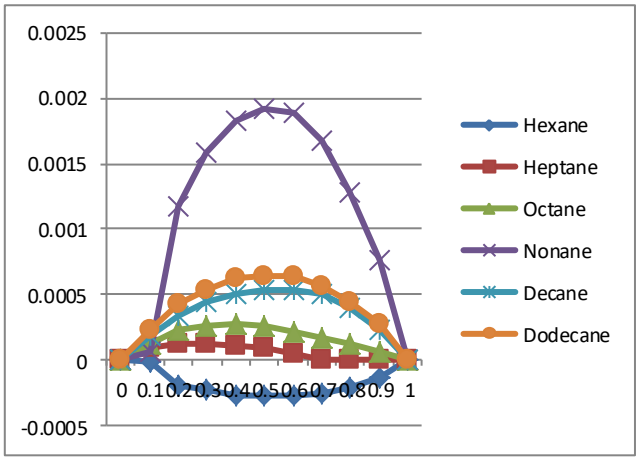

Fig. 2 Excess volumes vs. mole fractions for anisole + n-alkanes at 298.15K.

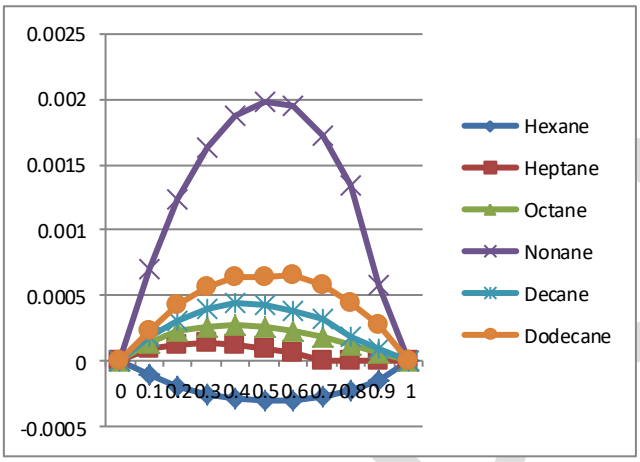

Fig. 3 Excess volumes vs. mole fractions for anisole + n-alkanes at 303.15K.

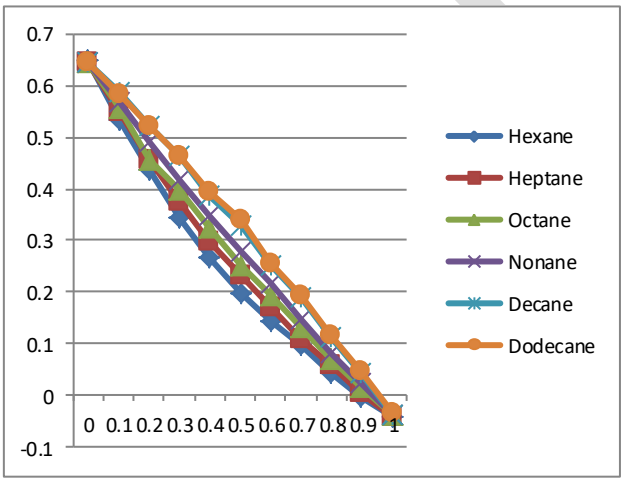

Fig. 4 Deviations in refractive index (ΔR) vs. mole fractions Anisole + n-alkanes at 293.15K.

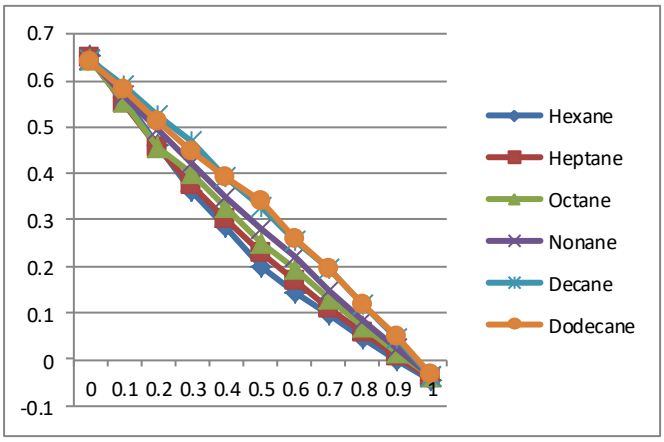

Fig. 5 Deviations in refractive index (ΔR) vs. mole fractions Anisole + n-alkane at 298.15K.

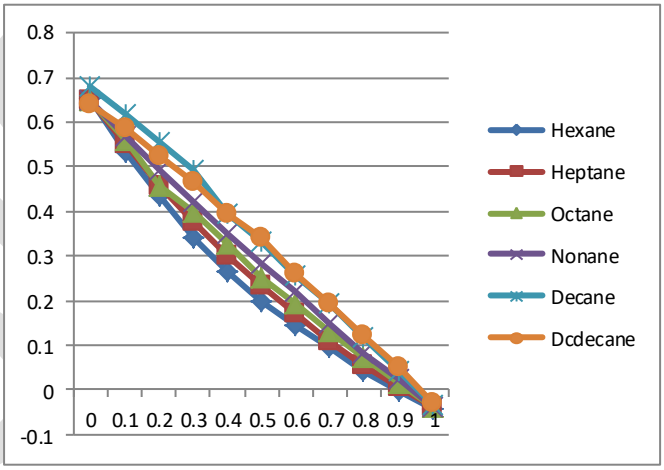

Fig. 6 Deviations in refractive index (ΔR) vs. mole fractions Anisole + n-alkane at 303.15K.

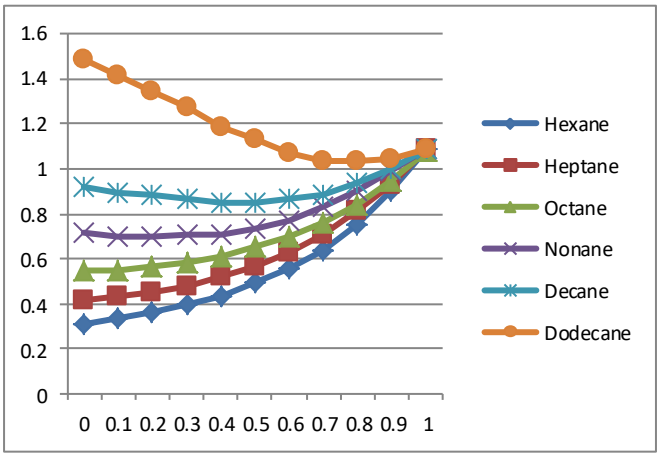

Fig. 7 Deviations in refractive index (ΔR) vs. mole fractions Anisole + n-alkane at 293.15K.

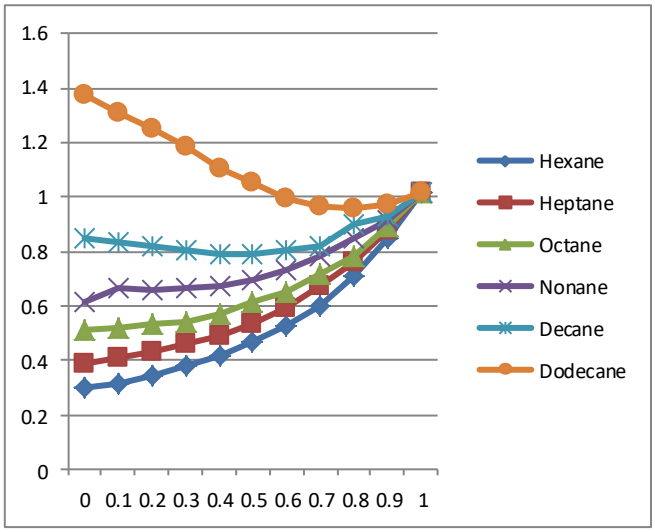

Fig. 8 Deviations in refractive index (ΔR) vs. mole fractions Anisole + n-alkane at 298.15K.

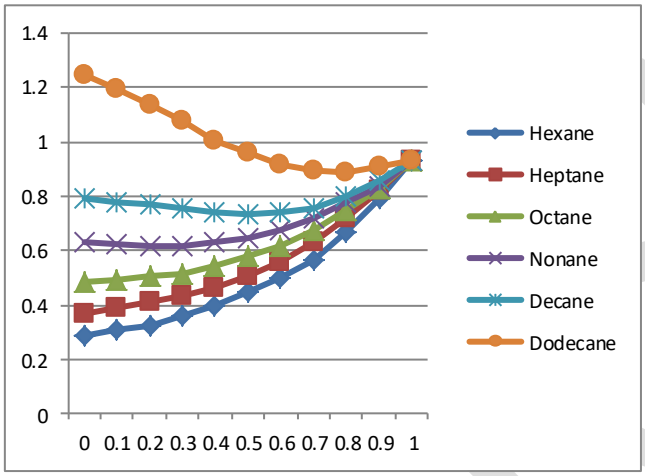

Fig. 9 Deviations in refractive index (ΔR) vs. mole fractions Anisole + Heptane at 303.15K.

VI. Conclusion

This report presents useful physical property data such as density, viscosity, and refractive index on organic liquids and their binary mixtures over the different mixture compositions at 293.15K, 298.15K & 303K. From the measured physical properties, excess molar volume (Ve), deviations in viscosity (Δn) and deviation in molar refractivity (ΔR) have been calculated. Information on these quantities provides a considerable amount of knowledge about the nature and type of intermolecular interactions in liquid mixtures. Thus, the present results are useful in practical applications such as liquid liquid distillation, separation, miscibility, solubility etc. Also, from fundamental viewpoint, derived parameters will add fruitfully to the bulk of the literature in the understanding of the mixing behaviour of the liquids.

In this report, the binary liquid mixture have been selected depending upon the type of intermolecular interactions such as dispersion forces, dipole-dipole interactions, and hydrogen –bonding effects etc.

Dispersion type interactions have been interpreted in terms of negative values of excess volume, whereas specific interactions are interpreted in terms of negative values of excess volume. Ideality of the proposed system has been observed by the results obtained i.e., negative values of Ve shows that the system is non ideal .The solvent activities for solvent solutions have been calculated from the experimental data. This will help to calculate vapor pressure of solvent in solution.

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