GLOBAL JOURNAL OF ENGINEERING RESEARCH VOL.1, NO. 2, 2002: 97 - 105
COPYRIGHT(C) BACHUDO SCIENCE CO. LTD. PRINTED IN NIGERIA. ISSN 1596-292X

ON THE MOLAR POLARIZABILITIES OF BINARY MIXTURES FROM TERTIARY BUTYL ALCOHOL ISO-PROPYL ALCOHOL AND TOLUENE AT 298K

L. UYIGUE

(Received 24 September 2001; Revision accepted 1 February 2002).

ABSTRACT

Three pairs of binary mixtures from pure grade liquids of Tertiary-Butyl Alcohol (TBA), Iso-Propyl alcohol (IPA) and Toluene (TOL) were prepared at 298K and 1 atm. Subsequently, the densities, mole fractions and refractive indices of the mixtures and their pure components were obtained at 298K. The average molar polarizabilities (α_{AV}) and excess molar polarizabilities ($\Delta\alpha$) for the binary mixtures were obtained.

The results showed linear trends for average molar polarizabilities over the entire composition range for the three binary mixtures. Positive excess molar polarizabilities dominated the composition range of the three binary mixtures, but it is however absolutely dominant in the Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) mixture.

The magnitude of the induced molar polarizability for the three binary mixtures at 298K are in the order of Tertiary-Butyl Alcohol (IPA) and Toluene (TOL) > Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) > Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixtures.

Keywords: Binary Mixture, Molar Polarizability, Temperature, Molar Refractivity, Mole Fraction.

INTRODUCTION

Two liquids when mixed can interact in several ways depending on their molecular size, polarity and closeness. Hence, factors affecting the stability of mixtures are Van der Waals forces, dipole-dipole interaction and hydrogen bonding (Morrison and Boyd, 1973).

Molar polarizability of liquids and their mixtures could be described as a dielectric property which amounts to the distortion on the electron cloud found in the liquids molecules. However, the ease with which different liquids and their mixtures become polarized differs greatly, hence the variations in their polarizabilities (Daniels and Alberty, 1975).

Molar polarizability of liquids may be said to be of three contributions namely: orientational, electronic and vibrational polarizabilities. Thus, in the visible and ultra violet regions of radiation, electronic polarizability contributes more to total polarizability (α) due to the following reasons: one is the insufficient time for molecular orientation before the field is reversed and the other is the required high frequency electric field (Linneth, 1966).

Molar polarizability measurement is based on the Lorentz-Lorentz equations, composed of experimental and additive rules, and requires adequate information on densities and refractive indices of liquids at pure component or mixture state (Akhadov, 1980). The arithmetic difference between the experimental and additive values of molar polarizability is referred to as excess molar polarizability ($\Delta\alpha$).

This excess value is simply a deviation which indicates the extent of the effect of dipole-dipole interaction on the liquid mixtures. Hence forms one of the basis for classifying liquid mixtures as either ideal or non-ideal. (Bettelheim, 1971).

L. UYIGUE, Department of Chemical Engineering, University of Port Harcourt, Port Harcourt, Nigeria

Therefore, the focus of this work is to estimate the average molar polarizabilities and the excess molar polarizabilities for three pairs of binary liquid mixtures of Tertiary-Butyl Alcohol (TBA) and Iso-Propyl Alcohol (IPA), Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) and Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixtures at a temperature of 298K and 1 atm.

This work is however significant for predicting the dielectric values of binary liquid mixtures. Consequently, these values may be vital in the design of vessels and mixers often used in large scale production of these mixtures. Common products that are often obtained by mere mixing includes: oil extracts, wine blends, methylated spirits, syrups, octane boosting oxygenates, coolants, etc (Chemical and Engineering News, 1983).

REVIEW OF LITERATURE

Reported works on molar polarizabilities are rare, but notable ones are reported as follows: Jain (1984) reported the use of refractivity and density measurements to determine the dielectric properties of calcium nitrate solution.

Apelblat et al (1980) and Apelblat (1973) reported the use of Anton Paar DMA 60 densitometer equipped with DMA 601 cell for density measurements of associated mixtures from organic acids, ketones and alcohols. The results were found to be accurate within the precision of ± 0.001

Akhadov (1980) studied the dielectric properties of binary mixtures of Methanol and Iso-Propyl Alcohol. Methanol and Tertiary-Butyl Alcohol and Iso-Propyl Alcohol and Tertiary-Butyl Alcohol at 303K. The composition dependence of the dielectric properties of these mixtures were observed to be linear.

Aminabhavi et al (1983) studied the excess molar polarizabilities of four different binary mixtures with Bromo-Benzene as a common liquid component amongst the mixtures at 298K. The Lorentz-Lorentz mixing rule was adopted and the composition dependence on excess molar polarizability was linear.

Aniemeka (1989) investigated the excess molar polarizabilties of binary mixtures of Methanol, 2-Methyl-2-Propanol and Propan-2-ol at 303K. The results showed that maximum interaction existed between Propan-2-ol and 2-Methyl-2-Propanol, while minimum interaction existed between Methanol and Propan-2-ol. Also the polarizability versus composition relationship was equally linear.

PROCEDURES

The procedures required for these measurements are both experimental and empirical.

EXPERIMENTAL

The materials required for these experiments are basically three solvents (liquids) of analar grades namely: Iso-Propyl Alcohol (IPA), Tertiary-Butyl Alcohol (TBA) and Toluene (TOL). Their percentage purity were specified as 99.7, 97.6 and 99.5% respectively.

The experiments conducted were for the measurement of densities and refractive indices for the three pairs of binary mixtures at 298K.

(a) DENSITY

Two separate densities were measured at 298K and 1atm for each mixture, one for the binary liquid mixture and the other for its pure components. The sample bottles from the water bath were weighed empty (m_1) and then filled with liquid(s) in various volume ratios amounting to 10ml and reweighed (m_2). Each mixture with specified volume ratio where coded sample A to H.

The weights of liquid(s) in the sample bottles were therefore divided by the volume of samples according to the relationship.

$$\rho = \frac{m_2 - m_1}{V} \qquad (1)$$

This procedure was repeated for the three pairs of binary mixtures and their pure components.

(b) REFRACTIVE INDEX

Each mixture were prepared to 10ml volume and coded sample A to H. Also prepared were pure sample liquids of 10ml volume each. The Abbe 60 /ED refractometer was placed towards a sodium-D line source while the prism box was opened by releasing the toggle switch on the right hand side of the prism box. The hinged box was swung over to the left revealing the polished surfaces of the prisms and was calibrated with de-ionized water.

Drops of each of the samples in thin layers were placed between the surfaces of the two prisms (i.e upper and lower prism) while the prism box was subsequently closed. The divergent critical angle rays emanating from the samples were measured using the eyepiece of the telescope equipped with cross hairs. The mode of operation is by turning the control knob to a position where the light-dark interface just coincide with the cross hairs shown in the field view. The refractive indices were measured from the fixed telescope scale normally graduated in convertible degrees.

This procedure was repeated for the three pairs of binary mixtures and their pure components.

EMPIRICAL

The following parameters were measured empirically namely: mole fraction (X), molar refraction (R) and molar polarizability (α).

(a) MOLE FRACTION

The mole fractions (X) were estimated from the density measurements, hence the masses of sample components were obtained by multiply the density of pure component by the volume of mixtures according to the relationship

$$m_i = V_i \times \rho \qquad (i = 1, 2). \ldots\ldots \qquad (2)$$

Moles of components were equally obtained by the dividing the masses by its molecular weights (M) based on the equation below.

$$N_i = \frac{m_i}{M} \qquad (i = 1,2) \ldots\ldots \qquad (3)$$

Thus, the mole fractions of components were obtained by dividing the number of moles of components by its total moles of sample, based on the equation.

$$X_i = \frac{N_i}{\sum N_i} \qquad (i = 1,2) \ldots\ldots \qquad (4)$$

(b) EXCESS AND AVERAGE MOLAR POLARIZABILITY

The procedures for measuring the excess molar polarizability was based on the Lorentz-Lorentz equation (Daniels and Alberty, 1975 and Akahdov, 1980). First, the experimental molar refraction (R_{exp}) for binary mixtures obtained using the correlation below

$$R_{exp} = \left(\frac{n_R^2 - 1}{n_R^2 + 2}\right)\left(\frac{X_1 M_1 + X_2 M_2}{\rho}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where n_R is the refractive index of mixtures and M_1, M_2 are molecular weights of the liquids respectively, ρ is the density of the mixtures and X_1, X_2 are the mole fractions of components 1 and 2 respectively.

The additive molar refraction (R_{add}) for the binary mixtures were obtained from the correlation below.

$$R_{add} = \left(\frac{X_1 M_1}{\rho_1}\right)\left(\frac{n_1^2 - 1}{n_1^2 + 2}\right) + \left(\frac{X_2 M_2}{\rho_2}\right)\left(\frac{n_2^2 - 1}{n_2^2 + 2}\right) \qquad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

where n_1, n_2 are the refractive indices of pure liquid components 1 and 2, ρ_1, ρ_2 are the densities of pure components 1 and 2; while M_1, M_2 are the molecular weights of components 1 and 2.

The experimental and additive molar polarizabilities were obtained from their respective molar refraction using the Lorentz-Lorentz equation as shown below.

$$\alpha_{exp} = \frac{3R_{exp}}{4\pi N_A} \qquad \ldots\ldots\ldots(7)$$

$$\alpha_{add} = \frac{3R_{add}}{4\pi N_A} \qquad \ldots\ldots\ldots\ (8)$$

where N_A is the Avogadro constant.

Thus, the excess molar polarizabilities ($\Delta\alpha$) were obtained from the difference between the experimental molar polarizability and additive molar polarizability as shown below.

$$\Delta\alpha = \alpha_{exp} - \alpha_{add} \qquad \ldots\ldots\ldots\ (9)$$

Also, the average molar polarizabilities (α_{av}) were equally obtained as the arithmetic mean of both experimental and additive molar polarizabilities.

$$\alpha_{av} = \frac{\alpha_{exp} + \alpha_{add}}{2} \qquad \ldots\ldots\ldots\ldots\ (10)$$

TABLE 1: DENSITIES, REFRACTIVE INDICES AND MOLECULAR WEIGHTS OF THE PURE LIQUIDS AT 298K

MPLE	MASS OF SAMPLE $m_2 - m_1$ (g)	SAMPLE DENSITY, ρ_i (g/ml)		SAMPLE REFRACTIVE INDEX, n_i		MOLECULAR WEIGHT (M) (g/mol)
		EXPERIMENTAL VALUE AT 298K	LITERATURE VALUE AT 293K	EXPERIMENTAL VALUE AT 298K	LITERATURE VALUE AT 293K	
ERTIARY- JTYL COHOL	7.729	0.7729	0.7887	1.3805	1.3878	74
O- ROPYL COHOL	7.697	0.7697	0.7855	1.3755	1.3776	60
OLUENE	8.481	0.8481	0.8669	1.4935	1.4961	92

TABLE 2: COMPOSITION DEPENDENCE OF MOLAR POLARIZABILITIES FOR IPA + TBA BINARY MIXTURE AT 298K

Samples	Mole Fractions		$\rho^{298}_{(g/ml)}$	n^{298}_R	R_{exp} (cm³ mol⁻¹)	R_{add} (cm³ mol⁻¹)	α_{exp} x 10^{23} (cm³)	α_{add} x 10^{23} (cm³)	$\Delta\alpha$ x 10^{23} (cm³)	α_{av} x 10^{23} (cm³)
	X_1 (IPA)	X_2 (TBA)								
A	0.1199	0.8801	0.7671	1.3800	21.8384	21.2920	0.8657	0.8440	0.0217	0.8548
B	0.2351	0.7649	0.7639	1.3780	21.3402	21.1837	0.8460	0.8398	0.0062	0.8429
C	0.3450	0.6550	0.7601	1.3775	20.9555	20.7070	0.8307	0.8209	0.0098	0.8258
D	0.4500	0.5500	0.7579	1.3765	20.5265	20.2516	0.8137	0.8028	0.0109	0.8082
E	0.5512	0.4488	0.7570	1.3710	19.8528	19.8126	0.7870	0.7854	0.0016	0.7862
F	0.6481	0.3519	0.7571	1.3700	19.3970	19.3922	0.7689	0.7687	0.0002	0.7688
G	0.7415	0.2585	0.7584	1.3690	18.9279	18.9871	0.7503	0.7527	-0.0024	0.7515
H	0.8308	0.1692	0.7606	1.3685	18.4798	18.5997	0.7326	0.7373	0.0047	0.7350

DISCUSSION OF RESULTS

The results of this work are presented in the Tables and Figures. Table 1 shows the pure liquids densities and refractive indices at 298K in comparison to their literature values at 293K. The molecular weights of the liquids were equally presented. Similarly Tables 2 to 4 show the polarizabilities of mixtures with respect to their mole fractions for binary mixtures of Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA), Iso-Propyl Alcohol (IPA) and Toluene (TOL) and Tertiary-Butyl Alcohol (TBA) and Toluene (TOL).

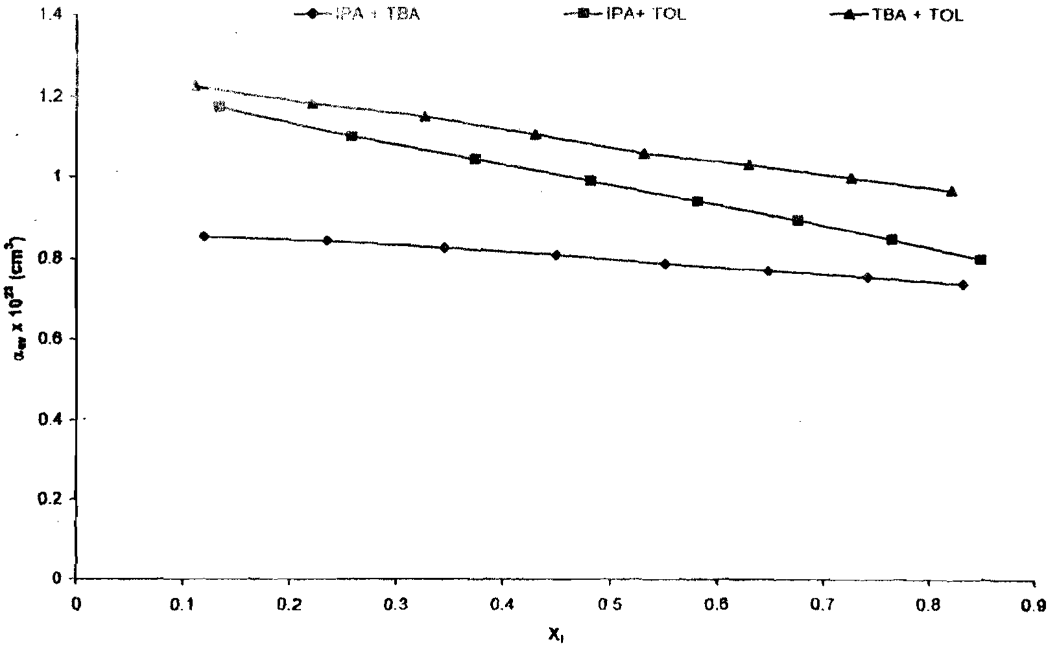

Figure 1: Plots of Average Molar Polarizability Versus Mole Fraction For IPA + TBA, IPA + TOL and TBA + TOL Binary Mixtures at 298K

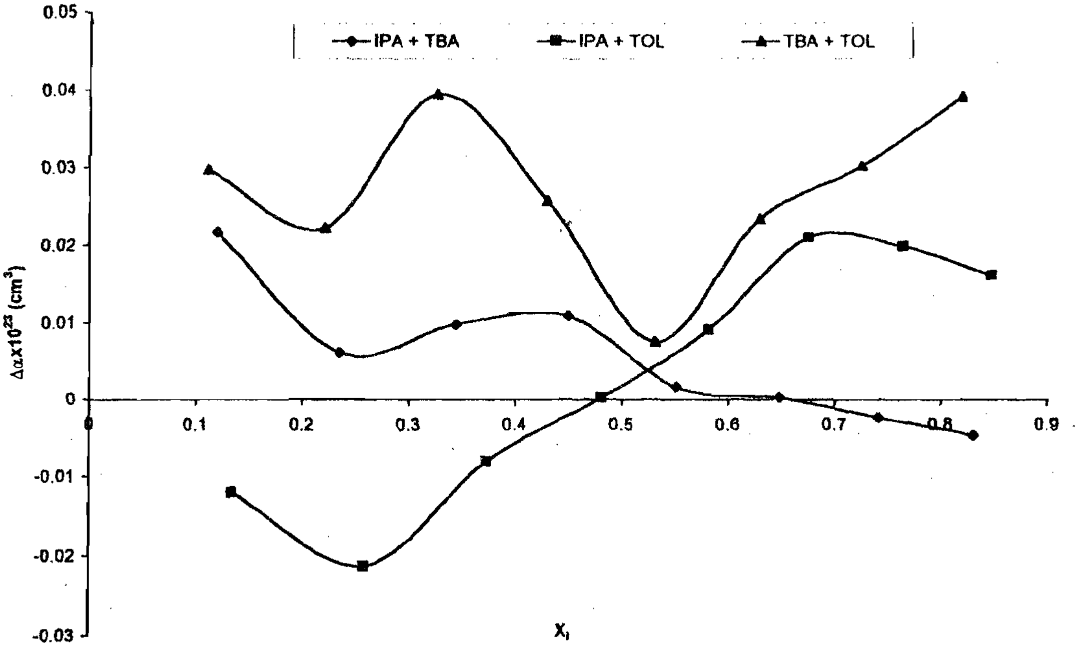

Figure 2: Plots of Excess Molar Polarizability Versus Mole Fraction for TBA + TOL, IPA + TOL and IPA + TBA Mixtures at 298K

TABLE 3: COMPOSITION DEPENDENCE OF MOLAR POLARIZABILITIES FOR IPA + TOL BINARY MIXTURE AT 298K

Samples	Mole Fractions		$\rho^{298}_{(g/ml)}$	n^{298}_{R}	R_{exp} (cm^3 mol^{-1})	R_{add} (cm^3 mol^{-1})	α_{exp} x 10^{23} (cm^3)	α_{add} x 10^{23} (cm^3)	$\Delta\alpha$ x 10^{23} (cm^3)	α_{av} x 10^{23} (cm^3)
	X_1 (IPA)	X_2 (TOL)								
A	0.1336	0.8664	0.8439	1.4780	29.4251	29.7244	1.1665	1.1784	-0.0119	1.1724
B	0.2586	0.7414	0.8416	1.4645	27.4766	28.0135	1.0893	1.1105	-0.0212	1.0999
C	0.3738	0.6262	0.8278	1.4550	26.2333	26.4367	1.0399	1.0480	-0.0081	1.0439
D	0.4812	0.5188	0.8100	1.4410	24.9732	24.9667	0.9900	0.9898	0.0002	0.9899
E	0.5815	0.4183	0.7958	1.4300	23.8179	23.5876	0.9442	0.9351	0.0091	0.9396
F	0.6760	0.3240	0.7800	1.4200	22.8301	22.3004	0.9051	0.8840	0.0211	0.8945
G	0.7643	0.2357	0.7750	1.4100	21.5928	21.0919	0.8560	0.8361	0.0199	0.8460
H	0.8479	0.1521	0.7700	1.3985	20.3548	19.9476	0.8069	0.7908	0.0161	0.7988

TABLE 4: COMPOSITION DEPENDENCE OF MOLAR POLARIZABILITIES FOR TBA + TOL BINARY MIXTURE AT 298K

Samples	Mole Fractions		$\rho^{298}_{(g/ml)}$	n^{298}_{R}	R_{exp} (cm^3 mol^{-1})	R_{add} (cm^3 mol^{-1})	α_{exp} x 10^{23} (cm^3)	α_{add} x 10^{23} (cm^3)	$\Delta\alpha$ x 10^{23} (cm^3)	α_{av} x 10^{23} (cm^3)
	X_1 (TBA)	X_2 (TOL)								
A	0.1113	0.8887	0.8250	1.4850	31.2644	30.5124	1.2394	1.2096	0.0298	1.2245
B	0.2209	0.7791	0.8100	1.4651	30.0478	29.4877	1.1912	1.1689	0.0223	1.1800
C	0.3267	0.6733	0.8000	1.4602	29.4950	28.4986	1.1689	1.1298	0.0395	1.1496
D	0.4305	0.5695	0.7879	1.4400	28.1817	27.5281	1.1172	1.0913	0.0259	1.1042
E	0.5310	0.4695	0.7790	1.4200	26.7967	26.6042	1.0623	1.0547	0.0076	1.0585
F	0.6295	0.3705	0.7742	1.4180	26.2581	25.6676	1.0410	1.0175	0.0235	1.0292
G	0.7252	0.2748	0.7700	1.4125	25.5387	24.7728	1.0124	0.9821	0.0303	0.9972
H	0.8196	0.1804	0.7701	1.4105	24.8792	23.8902	0.9863	0.9471	0.0392	0.9667

AVERAGE MOLAR POLARIZABILITY

The binary mixture of Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) present higher positive values of average molar polarizabilities (α_{av}) than the other mixtures of Iso-Propyl Alcohol (IPA) and Toluene (TOL) and Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) (Figure 1).

The trends of the plots of average molar polarizabilities (α_{av}) against mole fractions for all the three binary mixtures is linear (Figure 1) indicating decrease in average molar polarizabilities with increasing mole fraction. This trend validates the Lorentz-Lorentz rule and corroborates the findings of Akhadov (1980), Aminabhavi et al (1983) and Aniemeka (1989).

EXCESS MOLAR POLARIZABILITY

Positive excess molar polarizabilities ($\Delta\alpha$) dominates over the composition range for the binary mixtures from Tertiary-Butyl Alcohol (TBA), Iso-Propyl Alcohol (IPA) and Toluene (TOL). But excess molar polarizabilities of Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) mixtures are entirely positive while Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) and Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixtures presents some regions of negative excess molar polarizabilities, such as –0.0119, –0.0212 and –0.0081 for Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixtures and –0.0024, –0.0047 for Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) mixtures (Figure 2).

INDUCED MOLAR POLARIZABILITY

The dominant positive excess molar polarizabilities for the binary mixtures indicates expansion and greater freedom of motion for the methyl groups. Hence Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) binary mixture has the highest induced polarizability due to repulsive Van der Waals strains.

However, some regions of negative excess molar polarizabilities associated with the Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) mixtures and Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixtures indicates contraction with less freedom of motion for the methyl groups. Hence possesses lower induced polarizabiity due to attractive Van der Waals strains.

Consequently, the magnitude of the induced molar polarizability for the three binary mixtures at 298K are in the order of Tertiary-Butyl Alcohol (IPA) and Toluene (TOL) > Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) > Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixtures.

CONCLUSION

The dominant positive excess molar polarizabilities for the composition range of binary mixtures from Tertiary-Butyl Alcohol (TBA), Iso-Propyl Alcohol (IPA) and Toluene (TOL) (Figure 2) indicates non-ideal behaviour of mixtures.

However, there are likely indications that the non-ideal behaviour of these binary mixtures may also be due to structural problems arising from "hydrogen bonds" or self-interaction of the liquids in the mixtures resulting in molecular complexes like dimers or higher interactants. This is however beyond the scope of this work.

NOMENCLATURE

ρ, ρ_i = Density of mixture and density of pure component respectively.

m_1, m_2 = Masses of components of 1 and 2.

M_1, M_2 = Molecular weights of components 1 and 2.

N_1, N_2 = Moles of components of 1 and 2.

V, V_i = Volume of mixtures and Volume of pure components respectively.

X_1,X_2 = Mole fractions of components 1 and 2.

n_R = Refractive index of mixture.

n_1, n_2 = Refractive indices of pure components.

R_{exp}, R_{add} = Experimental and additive refraction.

α_{exp}, α_{add} = Experimental and additive polarizability.

N_A = Avogadro constant

$\Delta\alpha$ = Excess molar polarizability.

α_{av} = Average molar polarizability.

TBA = Tertiary-Butyl Alcohol

TPA = Iso-Propyl Alcohol

TOL = Toluene

atm = Atmosphere

REFERENCES

Akhadov, Y. Y. 1980. Dielectric Properties of Binary Solutions: A Data Handbook. Pergamon Press, Oxford. 75-115.

Aminabhavi, T.M., Jayadevappa, E.S and Prasad, B.R. 1983. Excess Properties of Binary Solvent mixtures containing Bromo-Benzene. Indian Journal of Chemistry. 22A(3): 227-228.

Aniemeka, M. K. 1989. Solution Thermodynamic Study of Binary Mixtures of Alcohols from Methanol, Propan-2-ol and 2-methyl-2-Propanol. M. Phill Thesis (U.S.T) Unpublished. 7 – 36.

Apelblat, A. 1973. Thermodynamic Properties of Associated Solutions. Israeli Journal of Chemistry, 11(6): 765-780

Apelblat, A., Tamir, A. and Wagner, T. 1980. Thermodynamics of Acetone-Chloroform mixtures. Journal of Fluid Phase Equilibria 4: 229-255.

Bettelheim, F. A. 1971. Experimental Physical Chemistry. W. B. Saunders Company, Philadelphia. 103-113, 148-153.

Chemical and Engineering News. 1983. New Raw Material Source Looms for Fast Rising Octane Booster's. McGraw Hill. 9-10.

Daniels, F. and Alberty, R. A. 1975. Physical Chemistry, Fourth Edition. John Wiley and Sons, Incorporated. 434-482.

Jain, S. K. 1984. Solution Properties of Concentrated Solutions: Densities and Refractive Indices of calcium nitrate solutions. Indian Journal of Chemistry, 23A(10): 808-811.

Linneth, J. W. 1966. The Electronic Structure of Molecules. Barnes and Noble, New York. 76.

Morrison, R. T. and Boyd, R. N. 1973. Organic Chemistry. Third Edition. Allyn and Bacon, Incorporated. 72.