EXCESS MOLAR VOLUME OF BINARY MIXTURES FROM ISO-PROPYL ALCOHOL, TERTIARY - BUTYL ALCOHOL AND TOLUENE LIQUIDS AT 298K.

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ABSTRACT

In this work, binary mixtures from Tertiary-Butyl alcohol (TBA), Toluene (TOL) and Iso-Propyl alcohol (IPA) were prepared at 298K. The mixtures physical properties which includes densities of mixtures (ρ) and pure components (ρ_i) and mole fractions of components (x) were equally measured at 298K. Excess molar volumes (V^E) were subsequently determined for each mixtures using the Ideal Association Model of the type $A + B + A_2$.

The results from the Tables and Figure showed positive excess molar volumes for the binary mixtures of Iso-Propyl Alcohol (IPA) and Tertiary- Butyl Alcohol (TBA), and Tertiary-Butyl Alcohol (TBA) and Toluene (TOL), while negative excess molar volumes were observed at some points in the Iso-Propyl Alcohol (IPA) and Toluene (TOL) binary mixtures at 298K. Consequently, strong self association and weak dipole-induced-dipole interaction were probably evident in the Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) Binary Mixture, and Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) mixture, while weak self association and strong dipole-induced-dipole interaction was characteristic of the Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixture. However, the Ideal Association Model of the type $A + B + A_2$ were observed to be adequate for interpreting the behaviours of the Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) mixture, and Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) mixture.

KEYWORDS: Binary Mixture, Excess Molar Volume, Mole Fraction, Non-Ideal Behaviour, Temperature

INTRODUCTION

Excess molar volume (V^E) is a thermodynamic property applied primarily to liquids and its mixtures for which we rarely know an adequate equation of state. It simply means volume measured above ideal value and which actually represents the difference between actual volume and that measured at the same conditions of temperature, pressure and mole fraction (Smith and Van Ness, 1985).

Mixing of liquids is a common phenomenon in chemical process industries and common products are often obtained, such products includes oil extracts, wine blends, methylated spirits, syrups, octane boosting oxygenates, coolants, solution polymer blends,etc. (Aminabhavi et al., 1983, Chemical and Engineering News, 1983). Thus, two liquids when mixed can interact in several ways depending on their molecular size, polarity and closeness. These interactions may be repulsive or attractive, resulting in stability or instability of the mixtures (Morrison and Boyd, 1973). Hence, factors affecting the stability of liquid-liquid interaction are Van der waals strains, dipole-dipole interaction and hydrogen bonding (Morrison and Boyd, 1973). Others are molecular interaction attractive forces such as dispersion, induction and electrostatic forces (Smith et al., 1996).

The significance of excess molar volume as a thermodynamic property of liquid mixtures are that it enable engineers to predict the behaviours of liquid mixtures, as well as design appropriate process and equipment for large scale production of liquid mixtures. Fundamentally, excess molar volume is not measurable in the laboratory via any equipment unless by empirical correlations.

Notable empirical correlations applicable to excess molar volume measurement are the Ideal Association Model of the type $A + B + A_2$ and the Mecke-Kempter Model. The former is the simplest and more realistic molecular model for describing the behaviours of liquid mixtures and it is presented as follows:

$$V^E = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2} \right) \qquad (1)$$

Where ρ is the density of mixture, x_1 and x_2 are the mole fractions of components 1 and 2 respectively. ρ_1, ρ_2, M_1 and M_2 are densities of pure components and their molecular weights, respectively (Apelblat and Manzurola, 1987)

The Mecke-Kempter Model is a continuous association model of the type $A + B + A_2 + A_3 + A_4 + \ldots + A_n$, n being infinite, while it is often used in the interpretation of binary liquid mixtures of polar and non polar nature. Frequent structural problems arising from the mixtures is due mainly to dimerization and oligomerization of the more polar component. The model is presented as follows:

$$V^E = \Delta V^o \left(\frac{\varepsilon}{1+\varepsilon} - \frac{x \, \varepsilon^o}{1+\varepsilon^o} \right) \qquad (2)$$

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Where ΔV^{o} is the standard molar volume of dimerization reaction and ε, ε^{o} are the mole fraction of the dimer in the mixture and pure state respectively.

In the literature, there are reported experimental data on the physical and thermodynamic properties for some binary mixtures and multi component mixtures at different temperatures and pressures. Rarely available are those for excess thermodynamic properties such as excess molar volumes (V^{E}), excess molar Gibbs free energies (G^{E}), excess molar enthalpies (H^{E}) and excess molar entropy (TS^{E}). Notable reported works on excess properties especially for organic liquid mixtures are presented below.

Apelblat and Manzurola (1987), first determined the excess molar volumes (V^{E}) for Formic Acid and Water systems at the entire temperature ranges of 288.15K, 298.15K and 308.15K. While at another time, determined the excess molar volumes (V^{E}) of carboxylic acids binary mixtures from Acetic, Propionic and Iso-Pentanioc acids with water at same temperature above. The results showed positive excess molar volumes for all the mixtures.

Marsh (1980), investigated the excess molar volume (V^{E}), excess molar Gibbs free energy (G^{E}) and excess molar enthalpy (H^{E}) over the entire composition range for Methyl Cyclohexane and n-Hexane mixtures at temperatures of 298.15K and 309.15K. He discovered that G^{E} and V^{E} curves were approximately symmetrical while the H^{E} curve was badly skewed.

Takayoshi (1979), studied the excess molar volumes (V^{E}) and excess partial molar volumes $(\overline{V}^{E})$ of Benzene and O–terphenyl mixtures at 288.15, 298.02 and 302.78K and discovered that the excess molar volumes were all negatives.

Subash et al. (1983), investigated the excess molar volumes (V^{E}) and other thermodynamic functions for the dilution of Polytetramethylene Oxide in Benzene systems. The results showed negative excess molar volume for the binary mixture.

Aniemeka (1989) estimated the excess molar volumes for three pairs of binary mixtures from Methanol, Propan-2-ol and 2-Methyl-2-Propanol. The results showed positive excess molar volumes for Propan-2-ol and 2-Methyl-2-Propanol mixture, negative excess molar volumes for Methanol and Propan-2-ol mixture while both positive and negative excess molar volume were evident in the Methanol and 2-Methyl-2-Propanol mixture.

Therefore, the objective of this work is to measure experimentally and empirically some physical properties of binary mixtures from Iso-Propyl Alcohol (IPA), Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) at 298K such as densities and mole fractions. Empirically, the excess molar volumes (V^{E}) for these binary mixtures would be subsequently determined.

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

Major equipment
Equipment used for this work are basically sample bottles, measuring cylinder, weighing balance, constant temperature water bath and thermometer.

MATERIALS
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.

Experimental
The experiments conducted were purely for the measurement of densities for the three pairs of binary mixtures at 298K.

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

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

$$\rho = \frac{m_2 - m_1}{V} \qquad (3)$$

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) and excess molar volume (V^{E}).

a)   Mole Fractions
The mole fractions (x) were estimated from the density measurements, however the masses of sample components were obtained by multiplying the density of pure component by the volume of mixtures according to the relationship

$$m_i \quad = V \ X \ \rho_i \qquad (i = 1, 2) \qquad (4)$$

The moles of components were equally obtained by dividing the masses by its molecular weight (M) based on the equation below.

$$n_i = \frac{m_i}{M} \qquad (i = 1, 2) \qquad (5)$$

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

$$x_i = \frac{n_i}{\sum n_i} \qquad (i = 1, 2) \qquad (6)$$

b)   Excess Molar Volume (V^{E}) of Binary Mixtures
The procedure for measuring the excess molar volume was based on the substitution for physical

properties (mole fractions and densities) in the Ideal Association Model of the type A + B + A_2 as presented in equation (1).

$$V^E = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2} \right)$$

However equation (1) has been used by contemporary authors like Subash et al (1983), Apelblat and Manzurola (1987), Takayoshi (1979) and Aniemeka (1989), and their results were found to be relatively accurate while their excess molar volumes were symmetrical with respect to composition.

RESULTS

The results of this work are presented in the tables and figure. Table 1 shows the densities and molecular weights of pure components of Tertiary-Butyl Alcohol (TBA), Iso-Propyl Alcohol (IPA) and Toluene (TOL) compared with standard literature values at 293K. Tables 2 and 3 shows the densities, mole fractions and excess molar volumes of 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).

DISCUSSION

Excess molar volume

Positive excess molar volumes dominates the entire composition range for the three pairs of binary mixtures except for Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixtures where negative excess molar volumes are observed at some given points of −0.4479, -0.3805 and −1.1011 at 298K (Figure 1).

Table 1: Densities and Molar Masses of the Pure Liquids At 298K.

SAMPLE	MASS OF SAMPLE (M_f-M_i) (g)	DENSITY (ρ_i^{298}) (g/ml) EXPERIMENTAL VALUES	DENSITY (ρ_i^{298}) (g/ml) LITERATURE VALUES	MOLAR MASS (M)
TERTIARY-BUTYL ALCOHOL	7.729	0.7729	0.7887	74
ISO-PROPYL ALCOHOL	7.697	0.7697	0.7855	60
TOLUENE	8.481	0.8481	0.8669	92

Table 2: Densities of Binary Mixture of IPA + TBA, IPA + TOL, and TBA + TOL at 298K

Samples	IPA + TBA		IPA + TOL		TBA + TOL	
	Mass of Samples (m_f-m_i) (g)	Density (ρ^{298}) (g/ml)	Mass of samples (m_f-m_i) (g)	Density (ρ^{298}) (g/ml)	Mass of samples (m_f-m_i) (g)	Density (ρ^{298}) (g/ml)
A	7.671	0.7671	8.439	0.8439	8.250	0.8250
B	7.639	0.7639	8.416	0.8416	8.100	0.8100
C	7.601	0.7601	8.278	0.8278	8.000	0.8000
D	7.577	0.7577	8.100	0.8100	7.879	0.7879
E	7.570	0.7570	7.958	0.7958	7.790	0.7790
F	7.571	0.7571	7.800	0.7800	7.742	0.7742
G	7.584	0.7584	7.750	0.7750	7.700	0.7700
H	7.606	0.7606	7.700	0.7700	7.701	0.7701

These results, however, are at variance to the findings of Takayoshi (1979), Apelblat and Manzurola (1987) in which their mixtures excess molar volumes were all negative. But corroborates the findings of Aniemeka (1989) where positive excess molar volumes
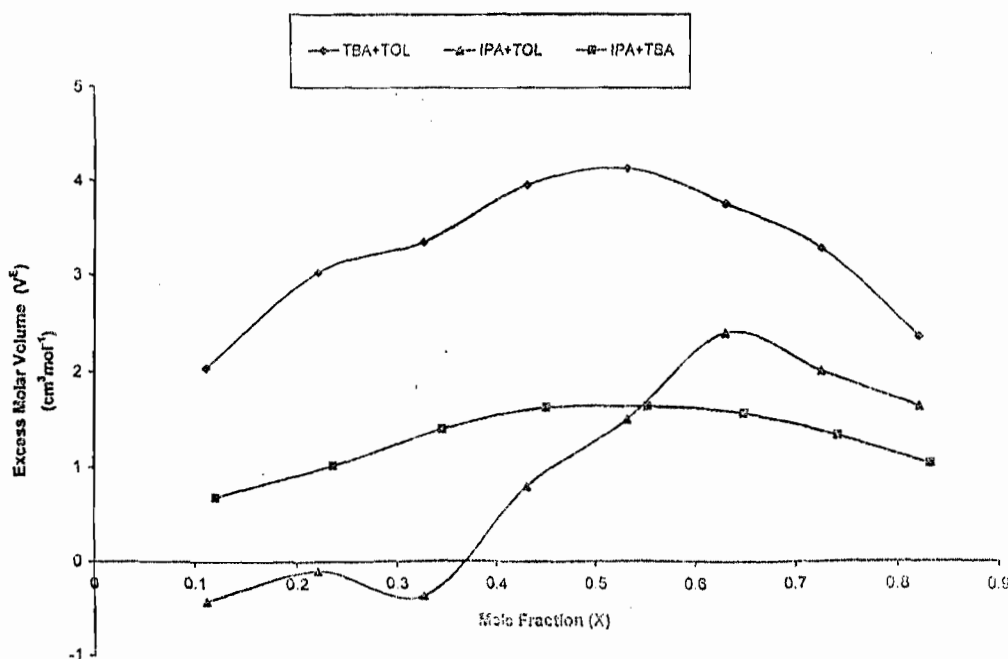

FIGURE 1: Plots of Excess Molar Volumes Against Mole Fractions

TABLE 3: Composition Dependence of Excess Molar Volumes for Binary Mixture of IPA + TBA, IPA + TOL and TBA + TOL at 298K

Samples	IPA + TBA			IPA + TOL			TBA + TOL		
	X_1	X_2	V^E (cm³/mol)	X_1	X_2	V^E (cm³/mol)	X_1	X_2	V^E (cm³/mol)
A	0.1199	0.8801	0.6699	0.1336	0.8664	-0.4479	0.1113	0.8887	2.0252
B	0.2357	0.7849	1.0056	0.2585	0.7414	-0.1011	0.2209	0.7791	3.0104
C	0.3450	0.6550	1.3961	0.3738	0.6262	-0.3805	0.3267	0.6733	3.3329
D	0.4580	0.5580	1.6144	0.4812	0.5188	0.7839	0.4305	0.5695	3.9370
E	0.5512	0.4488	1.6243	0.5815	0.4185	1.4957	0.5310	0.4695	4.1164
F	0.6481	0.3519	1.5430	0.6760	0.3240	2.3766	0.6295	0.3705	3.7404
G	0.7415	0.2585	1.3375	0.7643	0.2357	2.0032	0.7252	0.2748	3.2367
H	0.8308	0.1692	1.0405	0.8479	0.1521	1.6482	0.8196	0.1804	2.2668

of mixing were observed for the binary system of Propan-2-ol and 2-Methyl-2-propanol, along side positive and negative excess molar volumes for the Methanol and 2-Methyl-2-propanol mixture.

Liquid mixture behaviour

The large positive excess molar volumes evident in the Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) mixture, and Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) mixture are positive deviations from ideal behaviour, indicating strong self association resulting in volume expansion due to Van der Waals repulsive interaction, weak hydrogen bonding and weak dipole-induced-dipole interaction for the above liquid mixtures.

However, negative excess molar volumes evident at some points for Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixture are negative deviations from Ideal behaviour, hence indicates weak self association resulting in volume contraction due to Van der Waals attractive interaction, strong hydrogen bonding and strong dipole-induced-dipole interaction as shown in Figure 1. An ideal mixture behaviour is however observed for the Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixture at 0.42 mole fraction composition of Iso-Propyl Alcohol (IPA), which shown an excess molar volume of 0cm³/mol.

Applicability of ideal association model

The excess molar volumes (V^E) for the Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) mixture and that of Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) mixture are observed to be almost symmetrical with respect to composition (Figure 1). Consequently, the Ideal Association Model of the type $A + B + A_2$ is adequate and applicable to both Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) mixture, and Iso-Propyl Alcohol (IPA) and Tertiary-Butyl Alcohol (TBA) mixture.

But the Iso-Propyl Alcohol (IPA) and Toluene (TOL) mixture showed excess molar volumes (V^E) that are asymmetrical and badly skewed with respect to composition (Figure 1), indicating that the Ideal Association Model of the type $A + B + A_2$ is not adequate and not applicable to this mixture.

CONCLUSION

Evidently, all three pairs of binary mixtures from Iso-Propyl Alcohol (IPA), Tertiary-Butyl Alcohol (TBA) and Toluene (TOL) had shown non-ideal behaviours, apparently due to self association of the alcohols or complexes formation with Toluene. Such self association may results in dimers or oligomers (higher Associates).

Therefore, a continuous association model of the type $A + B + A_2 + A_3 + ... + A_n$ may be more suitable for predicting the excess molar volumes (V^E) for all three pairs of binary mixtures from Iso-Propyl Alcohol (IPA), Tertiary-Butyl Alcohol (TBA) and Toluene (TOL), since the model can effectively account for any possible dimerization.

NOMENCLATURE

V^E	=	Excess molar volume
x	=	Mole fraction
x_1, x_2	=	Mole fractions of components 1 and 2
ρ	=	Density of mixtures
ρ_1, ρ_2	=	Densities of components 1 and 2
n_1, n_2	=	Moles of components 1 and 2
M	=	Molecular weight
m_1, m_2	=	Masses of components 1 and 2
TBA	=	Tertiary-Butyl Alcohol
IPA	=	Iso-Propyl Alcohol
TOL	=	Toluene
M_1, M_2	=	Molecular weights of components 1 and 2
V	=	Volume
Σ	=	Summation
atm	=	Atmosphere
A	=	Component 1
B	=	Component 2
A_2	=	Dimer of component 1
A_n	=	Oligomer of component 1
ΔV^o	=	Standard molar volume of reaction
ε	=	Mole fraction of dimer in the mixture
ε^o	=	Mole fraction of dimer in the pure state

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