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Viscosity modelling of tri-n-butyl phosphate + benzene mixtures at 308.15K

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ABSTRACT

Dynamic viscosities (η) of a binary liquid system: Tri-n-butyl phosphate (TBP) + benzene have been experimentally measured over the entire range (X_1) of TBP at temperature 308.15K and pressure 0.1MPa. The dynamic viscosity of liquid mixtures hasbeen calculated using five mathematical relations of zero adjustable parameters such as Croenaurer-Rothfus- Kermore relation, Gambrill relation, Bingham relation, Kendall-Munroe relation and Arrhenius – Eyring relation. The validity of these relations has been verified separately by taking the average percentage deviations (APD) and root mean square deviation relative (RMSDs) between experimental and computed values and displayed graphically. Furthermore, the mixture viscosities have been correlated with those predicted one by using another six models of single and double adjustable / interaction parameters such as Grunberg-Nissan, Katti and Chaudhri, Hind, Tamura -Kurata, Heric and Eyring-Margules. A comparison between theoretical and experimental values of viscosity divulges that Gambrill's relation predicts the data reasonably well in case of zero adjustable parameters whereas Eyring-Margules shows the best fit in case of single and double interaction parameters.

Keywords:*Dynamic viscosity; TBP; benzene; binary liquid system; mathematical models.*

1. INTRODUCTION

Dynamic viscosity (η) and density (ρ) of binary or ternary liquid systems have been reported by a number of workers [1-3] over the past several decades. Such studies have great relevance in many areas of applied and theoretical research of several industrial applications in processing and product formulations [4, 5]. Various theoretical contributions have been routinely used to calculate the excess/ deviation in acoustic and thermodynamic properties of liquid mixtures using the experimental data of viscosity and density. These excess/deviation in the above said properties are of considerable interest in understanding the inter- and intra-molecular interactions among components of liquid mixtures. Tri-n-butyl phosphate (TBP) is an efficient extracting and separating agent and widely used as an exractant for the extraction of actinides, lanthanides and rare earth metal ions [6-8]. The addition of various diluents such as kerosene, benzene, octane, dodecaneetc with the extractant facilitates the extraction rate for greater dispersal and more rapid phase disengagement [8-10].

Viscosity property of a binary and ternary system plays an important transport property [2] in solvent extraction, fluid transportation, mixing, agitation, heat exchange, filtration etc. This property at different compositions of liquid mixtures depends on the nature of each component liquids. Hence, it becomes of considerable interest to compute viscosity in liquid mixtures by applying various mathematical models and to identify the suitable relation for the studied liquid mixtures. As a continuation of our effort [11, 12], dynamic viscosities of binary system: Tri-n-butyl phosphate (TBP) + benzene are estimated by using different mathematical relations of zero, one and two adjustable parameters [13-21] at 308.15K and then comparing the computed values of viscosities with that of the experimentally measured values. Our survey of the literature shows that there have not been any theoretical viscosity data reported for the binary system of TBP with benzene.

2. MATERIALS AND METHODS

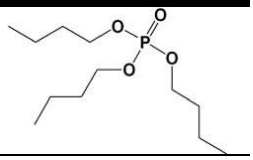
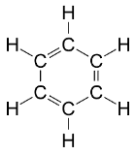
2.1. Materials.

The chemicals used were of analytical reagent (AR) grade and the specification of samples used is reported in Table 1. The purities of the chemicals used were checked by comparing the experimental viscosity (η) and density (ρ) values of the pure chemicals with the literature values [22, 23] and show fairly well with literature data.

2.2. Properties measurements.

The binary liquid mixtures over different mole fraction range of TBP were prepared in air-tight bottles by mass measurement. Required measures were taken to avoid evaporation and environmental damages. The mass measurements were performed by using single pan digital balance (Mettler Toledo, AB54-S, Switzerland) with an accuracy of ±0.0001g. The probable error in mole fraction was estimated to be less than ± 2.10^{-4}. The detailed procedure for measurements of density and viscosity of liquid mixtures are the same as described elsewhere [11, 12] and the values reported in Table 2. The temperature was controlled at 308.15K within ± 0.1K using thermostatic bath in measurements of all sample properties.

Table 1. Provenance, purity, CAS number, molecular mass and structure of the used chemicals.

Chemical used	Provenance	Mass fraction purity	CAS Number	Molecular Mass (g mol^{-1})	Structure
Tri-n-butyl phosphate ($C_{12}H_{27}O_4P$)	E Merck Chemicals, India	0.99	126-73-8	266.318	
Benzene (C_6H_6)	SD Fine Chem, India	0.995	71-43-2	78.114	

3. RESULTS

From the experimental values of viscosity (η) and density (ρ) of binary mixture: TBP + benzene, the theoretical values of viscosity were estimated by using the following five different mathematical relations of zero adjustable parameters [13-16].

Bingham relation: $\eta = \Sigma X_i\eta_i$ (1)

Kendall-Munroe relation: $\log \eta = \Sigma X_i \log \eta_i$ (2)

Arrhenius-Eyring relation: $\log (\eta V) = \Sigma X_i \log (V_i\eta_i)$ (3)

Croenauer-Rothfus-Kermore relation: $\log v = \Sigma X_i \log (v_i)$ (4)

Gambrill relation: $v^{1/3} = \Sigma X_i v_i^{1/3}$ (5)

Where, η, V and v are dynamic viscosity, molar volume and kinematic viscosity of mixture respectively. Whereas X_i, η_i ,V_i and v_i are mole fraction, viscosity, molar volume and kinematic viscosity respectively of individual pure liquids.

The values of computed dynamic viscosities along with experimental values for all the three binary liquid mixtures are presented in Table 2 and the consequent nature of variations in all the studied relations are displayed in Fig. 1.

The root mean square deviation relative ($RMSD_r$)between the experimental and theoretical values of viscosity was calculated and is presented in Table 3. The value of $RMSD_r$is used to estimate the relative merits of the theoretical relations.

$$RMSD_r = \left[(1/p)\sum\left((\eta_{th} - \eta_{exp})/\eta_{exp}\right)^2\right]^{1/2} \quad (6)$$

where p is the number of experimental data points.

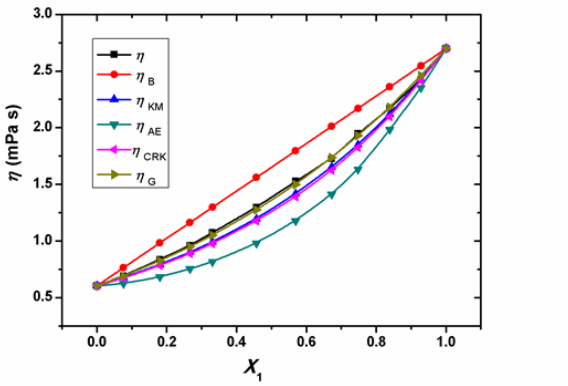


Figure 1. Experimental and computed viscosity (η) vs. mole fraction (X_1) of TBP at 308.15K.

The observed deviations of the theoretical viscosity from the experimental values are attributed to the presence of intermolecular interactions [16, 17] between the component molecules of the mixture. The average percentage deviations (APD) and root mean square deviation relative (RMSDs) between experimental and computed values have been calculated and are presented in Table 3. It is found that the computed values from all the theoretical relations are reasonably closer to the experimental values, thus showing approximate validity of all these theories for the studied binary mixture.

The observed deviations of the theoretical dynamic viscosity from the experimental values (Fig. 1 and Table 3) may be due to the presence of intermolecular interactions between the component molecules of the mixture [13-15]. The suitability of these theories based on APD and RMSDr values is as follows

$$\eta_G > \eta_{KM} > \eta_{CRK} > \eta_B > \eta_{AE}$$

In the studied binary mixture, least values of both APD and RMSDs of estimated viscosities have been found in Gambrill's relation.

Again, the experimental viscosity of liquid mixtures has been correlated with the following six different theoretical models of single and double adjustable parameters [16-21],

Grunberg-Nissan,

$$\eta = \exp\left(X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1X_2d_{12}\right) \quad (7)$$

where X_1 and X_2 are the mole fraction of pure components (TBP and benzene) respectively and d_{12} is a parameter proportional to the interchange energy and has been regarded as an indicator for the non-ideal behaviour of binary mixtures.

Katti-Chaudhri,

$$\ln \eta V = X_1 \ln \eta_1V_1 + X_2 \ln \eta_2V_2 + X_1X_2\left(W_{vis}/RT\right) \quad (8)$$

whereW_{vis} / RT is an interaction term.

Hind, $$\eta = X_1^2\eta_1 + X_2^2\eta_2 + 2X_1X_2\eta_{12} \quad (9)$$

where η_{12} is an attributed to unlike pair interaction.

Tamura-Kurata, $$\eta = X_1\phi_1\eta_1 + X_2\phi_2\eta_2 + 2(X_1X_2\phi_1\phi_2)^{1/2}C \quad (10)$$

where (ϕ_1 and ϕ_2) and (η_1 and η_2) are the volume fraction and viscosities of pure components respectively and C is an adjustable parameter.

Heric

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 \ln M_1 + X_2 \ln M_2 - \ln(X_1M_1 + X_2M_2) + X_1X_2\left[\upsilon_{12} + \upsilon_{21}(X_1 - X_2)\right] \quad (11)$$

where (v_{12} and v_{21})are the adjustable parameters and (M_1 and M_2) are molecular mass of pure components.

Eyring-Margules two-parameter equation

$$\ln (\eta V) = X_1 \ln (\eta_1V_1) + X_2 \ln (\eta_2V_2) + X_1X_2(A_{21}X_1 + A_{12}X_2) \quad (12)$$

where V_1, V_2 and V are the molar volumes of pure components and mixture respectively and A_{21} and A_{12} are adjustable parameters.

Eyring-Margules > Grunberg-Nissan > Heric > Hind > Tamura-Kurata > Katti-Choudhri

The plausible cause may be approximations and limitations incorporated in the above relations [24 - 27].

Table 2. Experimental density (ρ), viscosity (η) and computed values of viscosities of all the binary liquid system {TBP (X_1) + benzene (X_2)} at T = 308.15 K.

X_1	ρ Kgm^{-3}	H mPa s	Computed viscosities (mPa s)				
			η_B	η_{KM}	η_{AE}	η_{CRK}	η_G
0	862.8	0.604	0.604	0.604	0.604	0.604	0.604
0.0762	864.1	0.692	0.764	0.677	0.624	0.672	0.690
0.1804	870.7	0.837	0.982	0.791	0.681	0.783	0.824
0.2666	877.2	0.959	1.162	0.900	0.754	0.888	0.950
0.3311	881.6	1.075	1.297	0.991	0.815	0.976	1.051
0.4566	893.5	1.296	1.560	1.196	0.978	1.177	1.275
0.5691	901.7	1.528	1.796	1.416	1.177	1.389	1.499
0.6723	914.1	1.723	2.012	1.652	1.411	1.624	1.736
0.7482	924.4	1.948	2.171	1.851	1.630	1.825	1.929
0.8387	937.6	2.172	2.360	2.119	1.984	2.098	2.181
0.9285	953.4	2.422	2.548	2.424	2.350	2.416	2.461
1	964.3	2.698	2.698	2.698	2.698	2.698	2.698

Table 3.APD and RMSDs values of computed viscosities using Bingham relation (η_B), Kendall-Munroe relation (η_{KM}), Arrhenius – Eyring relation (η_{AE}), Croenaurer-Rothfus- Kermore relation (η_{CRK}) and Gambrill relation (η_G) relations in the mixture at T = 308.15 K

Deviation	η	η_B	η_{KM}	η_{AE}	η_{CRK}	η_G
Average percentage deviation (APD)	0	0.1666	0.0528	0.1874	0.0669	0.0046
Root mean square deviation relative (RMSDs)	0	0.1448	0.0495	0.1657	0.0605	0.0125

Table 4.Adjustable parameters and standard deviations in correlating viscosities of the binary mixture: TBP + benzene at 308.15 K.

Grunberg-Nissan		Katti-Chaudhri		Hind		Tamura-Kurata		Heric			Eyring-Margules		
d_{12}	Σ	W_{vis}/RT	Σ	η_{12}	σ	C	σ	v_{12}	v_{21}	σ	A_{21}	A_{12}	σ
0.3275	**0.0003**	**0.9457**	**0.0073**	**1.1166**	**0.0018**	**0.761**	**0.004**	**1.052**	**0.395**	**0.0006**	**1.2499**	**0.6087**	**0.0002**

The values of standard deviations, σ (Table 4)in binary mixture of TBP + benzene show the decreasing trend of viscosity models fitting to experimental values:

4. CONCLUSIONS

From the experimental values of viscosity and density of binary system: TBP + benzene, theoretical values of viscosity such as η_B, η_{KM},η_{AE} ,η_{CRK}andη_G have been calculated and the legitimacy of different relations has been verified. It is found that there are deviations between theoretical values and experimental values, obtained by five relations, which show molecular interaction between components of liquid mixtures. Among the five relations, Gambrill's relation is more suitable in favour of experimental values of viscosity. Furthermore, viscosity data were analyzed based on the different mathematical models of one and two adjustable parameters of the studied binary system. The adjustable parameters of the models confer qualitative information about molecular interactions among components of liquid system and here Eyring-Margules is the best fit to experimental value of viscosity.

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