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Excess Volumes and Viscosities for the Binary Systems of 2-Propanol with alkyl acetates at 303.15 K

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ABSTACT

Measurements of excess volumes and viscosities of binary mixtures of 2-propanol with methyl acetate (MA), ethyl acetate (EA), butyl acetate (BA), and iso-amyl acetate (IAA) are reported at 303.15 K over the entire range of composition. Excess volumes are measured using batch dilometer technique. The viscosity data are analysed on the basis of corresponding states approach and Grunburg-Nissan treatment. Excess volumes are positive and deviations in viscosities are negative over the entire range of composition. The experimental results are discussed in terms of possible interactions between like and unlike molecules.

Keywords: Excess volumes; Viscosities; 2-Propanol; Acetates.

INTRODUCTION

The thermodynamic functions of mixtures containing 2-propanol as one of the binary mixtures have been investigated.[1-3] The thermodynamic properties of binary mixtures of 2-propanol with acetates are very scarce. So we report in this paper the excess volumes and deviation in viscosities for the binary systems of 2-propanol with MA, EA, BA, IAA. Further viscosity data are analysed on the basis of corresponding states approach and Grunberg-Nisan treatment. The objective of this study is to study the interactions between 2-propanol and acetates.

The study and understanding of thermodynamic and transport properties properties of pure liquids, liquid mixtures and solutions have found many applications chemical, textile, leather, pharmaceutical, nuclear industries and in understanding solute solvent interactions as well[4-6].The thermodynamic properties are found to be sensitive to molecular interactions. The study on thermophysical properties were going on in our lab. We reported thermophysical properties for the system diisopropyl ether with acetates in our earlier paper [7].

EXPERIMENTAL SECTION

The component chemicals were purified by the methods described in literature[8]. Finally the purity of the samples was checked by comparing the measured densities and boiling points of the components with those reported in the literature[9-12] (Table-1).

Table-1: Boiling points and densities of pure components at 303.15 K.

Component	Boiling point (Tbp)/k		Density p/gcm^{-3}	
	Present work	Literature	Present work	Literature
2-propanol	354.9	355.4	0.78100	0.78120*
Methyl acetate	329.0	329.4	0.92721	0.92790*
Ethyl acetate	350.9	350.2	0.89149	0.89455*
Butyl acetate	399.1	399.2	0.87138	0.87632
Iso amyl acetate	415.7	415.1	0.86842	0.86640*

** 298.15 k.*

Excess volumes were measured with the dilatometer technique described by Reddy et al.[13] with an accuracy of ±0.003 cm^3 mol^{-1}. Four dilatometers which differ in the capacities of compartment 1 and 2 are used to cover the entire range of composition of the mixtures. The densities were measured with bicapillary pycnometer described by Rao and Naidu[14]. The viscosity of pure liquids and liquid mixtures were determined with an accuracy of ± 0.001 using suspended ubbelohde type viscometer[15].

RESULTS

Experimental excess volume data at 303.15 K for the binary systems of 2-propanol with MA, EA, BA, IAA are included in Table 2. The dependence of V^E on mole fraction of 2-propanol is graphically represented in Fig.1.

The excess volume V^E was calculated using the relation

$$V^E = \pi r^2 \Delta h (n_1 + n_2)^{-1} \quad (1)$$

The viscosity of the mixture was calculated using the equation

$$\eta = K_V . \rho . t \quad (2)$$

where Kv is viscometer constant, ρ and t are the density and flow time respectively. The densities of mixtures are calculated from excess volume data. Deviations in viscosity (Δ ln η) of the mixtures were calculated using the equation

$$\Delta \ln \eta = \ln \eta_{mix} - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad (3)$$

where η_{mix} is the viscosities of the mixture, η_1 and η_2 are the viscosities of 2-propanol and acetate respectively. The viscosity data were analyzed in terms of corresponding states approach and Grunberg and Nissan treatment Teja and Rice[16, 17] proposed the following expression for the liquid mixtures viscosity,

$$\ln (\eta_{mix} \ \varepsilon_{mix}) = x_1 \ln (\eta_1 \varepsilon_1) + x_2 \ln (\eta_2 \varepsilon_2) \quad (4)$$

where $\varepsilon = (Vc)^{2/3} / (TcM)^{½}$, Tc, Vc and M are critical temperature, critical volume and molecular mass respectively. The values of these parameters were evaluated by the procedure described by Krishnaiah and Viswanath[18]. The values of interaction parameter (ε_{12}) used in this theory are given in Table 4 along with absolute average deviation (AAD). ADD was calculated using the equation.

$$AAD\,(Cp) = \frac{1}{n} \Sigma [n_{\exp} - n_{cal}] \quad (5)$$

where η_{exp} and η_{cal} are the experimental and calculated viscosities respectively.

Grumberg and Nissan[19] proposed the following equation for the viscosity of liquid mixtures at low temperatures.

$$\ln \eta_{mix} = x \ln \eta_1 + (1\text{-}x) \ln \eta_2 + x\,(1\text{-}x)\, d_{12} \quad (6)$$

where η_1 η_2 and η_{mix} are viscosity of 2 propanol, acetate and mixture respectively, d_{12} is the interaction parameter which is the function of chemical nature of components and temperature. The value d_{12}, obtained from equation 6 using experimental viscosity data at equi-mole fraction was used to compute the viscosities over the entire range of composition. The value of d_{12} are given in Table 4 along with AAD. The computed values of viscosity on the basis of the two theories are included in Table 2.

Excess molar volumes (V^E), and deviations in viscosity (Δ ln η) were correlated by Red lich-Kister polynomial equation

$$A = x_1 x_2 \, [a_0 + a_1 \, (x_1 - x_2) + a_2 \, (x_1 - x_2)^2 \quad (7)$$

where x_1 and x_2 represent the mole fraction and A is corresponding thermodynamic property. The value of the parameters a_0, a_1, a_2, obtained following the least square analysis, are included in Table 3 along with standard deviation.

$$\sigma(A) = \left[\frac{\Sigma \left(A_{\exp} - A_{cal} \right)^2}{n - p} \right]^{1/2} \quad (8)$$

where n is the number of experimental data, p is the number of parameter in eq. (7) and A is the corresponding thermodynamic property (VE, $\Delta \ln \eta$).

CONCLUSION

The values of V^E are positive in all the systems. These results indicate that the interaction between like molecules are stronger compared to that between unlike molecules. The V^E follows the algebric order.

2 propanol + MA > 2 propanol + EA > 2 propanol + BA > 2 propanol + 1AA

The dilution of strong hydrogen bonded liquid 2-propanol by a non common component acetate leads to the cleavage of hydrogen bonds. This would be accompanied by adsorption heat and expansion in volume. The magnitude of volume change will be determined by the breaking and stretching of dipole-dipole interactions in acetates and also the structure breaking of alcohols by acetates. Ranjith[20] et al. reported sigmoid shape of V^E for the binary mixtures of phenyl acetonitrile +2 propanol.

The data presented in Table 2 indicate that deviations in viscosity ($\Delta \ln \eta$) are negative over the whole composition range for all the systems. In general, for system where dispersion and dipolar interactions are operating $\Delta \ln \eta$ values are found to be negative whereas charge transfer and hydrogen bonding interactions lead to positive $\Delta \ln \eta$ values[21]. The $\Delta \ln \eta$ values support the contention that the interaction between like molecules is stronger. The negative deviations in viscosity for the binary systems of 2-propanol with acetate follow the order, which is exactly opposite to the order observed with respect to V^E.

2 propanol + MA > 2 propanol + EA > 2 propanol + BA > 2 propanol + 1AA

Viscosity data derived from corresponding states approach, and Grunberg-Nissan model are reported in Table 2. The values of interaction parameters ε_{12} and d_{12} derived from above two models are included in Table 3. The average absolute deviations (AAD) between the experimental and calculated values of viscosities are also given in Table 3.

A comparison of experimental viscosity data with those predicted on the basis of corresponding state theory and Grunbeig-Nisson models indicate that both the theories are capable of predicting the viscosity data for all the systems with a maximum average absolute deviation of less than 1%. The d values in Table 4 show that they are high and negative indicating no specific interactions between unlike components.

Table-2: Data on mole fraction of 2-propanol (x_1) density (f) excess volume (V^E) and viscosity (η) for the binary systems of 2-propanol with MA, EA, BA, IAA.

Mole fraction (x_1)	V^E ($cm^3\ mol^{-1}$)	Density (ρ) ($g\ cm^{-3}$)	η_{Exp}	$\eta_{(c.s.t)}$	$\eta_{(G.N)}$	$\Delta \ln\eta$
2-propanol with methyl acetate						
0.0000	0.000	0.9201	0.343	-	-	-
0.1654	0.184	0.8951	0.411	0.408	0.420	-0.089
0.3123	0.244	0.8836	0.460	0.437	0.467	-0.104
0.3889	0.286	0.8734	0.508	0.469	0.515	-0.116
0.4215	0.334	0.8575	0.601	0.535	0.608	-0.127
0.5079	0.362	0.8449	0.692	0.607	0.698	-0.126
0.6479	0.351	0.8249	0.879	0.781	0.887	-0.116
0.7988	0.284	0.8037	1.176	1.085	1.174	-0.071
0.8892	0.199	0.7913	1.408	1.344	1.403	-0.039
1.0000	0.000	0.7769	1.755	-	-	-
2-propanol with ethyl acetate						
0.0000	0.000	0.8883	0.424	-	-	-
0.1467	0.129	0.8739	0.480	0.493	0.477	-0.043
0.2138	0.186	0.8671	0.515	0.541	0.518	-0.079
0.3245	0.277	0.8553	0.592	0.633	0.598	-0.093
0.4198	0.322	0.8450	0.679	0.725	0.681	-0.097
0.5026	0.344	0.8359	0.771	0.818	0.768	-0.096
0.6213	0.326	0.8226	0.927	0.975	0.920	-0.089
0.7569	0.255	0.8069	1.161	1.199	1.147	-0.059
0.8767	0.131	0.7926	1.429	1.447	1.410	-0.023
1.0000	0.000	0.7769	1.755	-	-	-
2-propanol with butyl acetate						
0.0000	0.000	0.8712	0.621	-	-	-
0.1378	0.095	0.8625	0.693	0.739	0.693	-0.033
0.2158	0.163	0.8570	0.730	0.797	0.730	-0.061
0.3494	0.252	0.8469	0.822	0.906	0.822	-0.081
0.4987	0.314	0.8342	0.961	1.048	0.961	-0.081
0.5786	0.306	0.8268	1.047	1.134	1.047	-0.078
0.6924	0.266	0.8154	1.200	1.272	1.200	-0.060
0.7865	0.193	0.8052	1.356	1.402	1.356	-0.035
0.8905	0.093	0.7924	1.540	1.565	1.540	-0.017
1.0000	0.000	0.7769	1.755	-	-	-
2-propanol with iso-amyl acetate						
0.0000	0.000	0.8640	0.712	-	-	-
0.1726	0.094	0.8549	0.809	0.836	0.809	-0.027
0.2784	0.158	0.8485	0.866	0.920	0.866	-0.055
0.3996	0.197	0.8404	0.954	1.026	0.954	-0.067
0.5012	0.216	0.8327	1.044	1.125	1.044	-0.068
0.6562	0.195	0.8193	1.212	1.296	1.212	-0.059
0.7432	0.167	0.8105	1.332	1.403	1.332	-0.043
0.8056	0.132	0.8035	1.429	1.485	1.429	-0.029
0.8978	0.076	0.7919	1.581	1.613	1.581	-0.012
1.0000	0.000	0.7769	1.755	-	-	-

Table-3: Values of Parameters eq. (7) and standard deviation at 303.15 k.

System	a_0	a_1	a_2	σA
2 Propanol + MA				
V^E (cm^3 mol^{-1})	1.413	0.392	0.440	0.005
Δ ln η (Cp)	-0.511	0.137	-0.027	0.005
2 Propanol+EA				
V^E (cm^3 mol^{-1})	1.380	0.174	0.482	0.004
Δ ln η (Cp)	-0.404	0.093	-0.200	0.003
2 Propanol+BA				
V^E (cm^3 mol^{-1})	1.250	0.178	-0.612	0.004
Δ ln η (Cp)	-0.340	0.090	0.179	0.003
2 Propanol+1AA				
V^E (cm^3 mol^{-1})	0.086	0.130	-0.228	0.003
Δ ln η (Cp)	-0.288	0.018	0.229	0.002

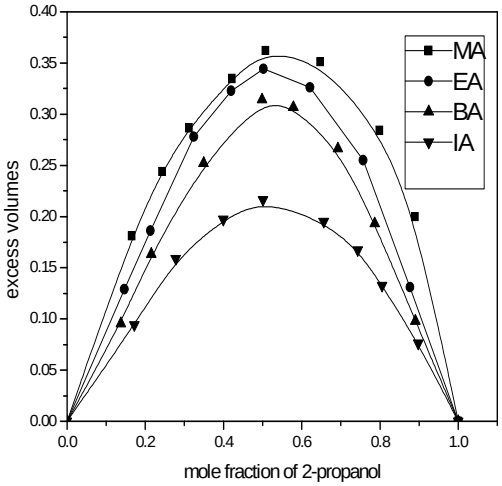

Fig. 1: Excess volume (v^E) vs. mole fraction of 2-propanol (x_1) for 2-propanol with MA (■) EA (●), BA (▲) and IA (▼)

Table-4: Values of interaction parameters (ε_{12}, d_{12}) and average absolute deviation (AAD) for the binary system of 2-propanol with acetates at 303.15 k.

System	Teja-Rice		Grumberg-Nissan	
	ε_{12}	AAD	d_{12}	AAD
2-propanol+methyl acetate	0.1340	0.058	-0.4846	-0.004
2-propanol+ethyl acetate	0.8540	-0.034	-0.3944	0.003
2-propanol+butyl acetate	0.8864	-0.064	-0.2898	-0.004
2-propanol+isoamyl acetate	0.8559	-0.059	-0.2377	-0.003

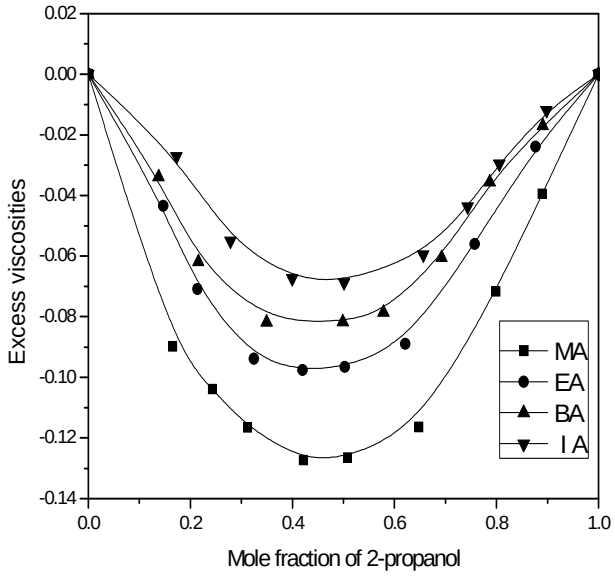

Fig. 2. Deviation in viscosity ($\Delta \ln\eta$) vs. mole fraction of 2-propanol, for 2-propanol with MA (■), EA (●), BA (▲) and IA (▼)

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