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Research Article

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Excess volumes and viscosities of binary liquid mixtures of 2-ethoxyethanol and chlorobenzene at 303.15K

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ABSTRACT

The density and viscosity (T=303.15K) in the binary mixtures of 2-ethoxyethanol and chlorobenzene has been measured as a function of composition. Excess volumes were measured by using relative density method and the viscosity of pure liquids and liquid mixtures were determined using an Oswald's viscometer. Theseresults have been fitted to the Redlich and Kister type polynomial equation to estimate the interaction parameter and standard deviation. Excess volumes exhibited both positive and negative trends in binary mixtures, depending upon the nature of the second component of the mixture. For the binary mixture calculated thermodynamic quantities have been discussed in terms of intermolecular interaction between mixing components.

Keywords: Density, Viscosity, Excess volume, Free energy, Excess viscosity.

INTRODUCTION

A deeper knowledge of thermodynamic and transport properties of binary solvent system is of great help in many industrial applications, such as design calculation, heat transfer, fluid flow, etc[1]. Thethermodynamic properties of the solvents such as density(ρ) and viscosity (η) which are two important physical properties of solvent systems are often used to explain the medium effect of solvent on transport phenomena[1]. The nature of interaction in liquid mixtures involving alcohols and chloro compounds have been reported for binary liquid mixtures of 2-ethoxyethanol. We report here the nature of interactions in the binary liquid mixtures of 2-ethoxyethanol and chlorobenzene from density and viscosity measurements at 303.15K[2]. From these values excess volume, excess viscosity and Gibb's free energyhave been calculated and correlated with the Redlich-Kister type polynomial equation to derive thebinary coefficients and standard deviations[1,2].

EXPERIMENTAL SECTION

Liquid mixtures of various concentrations were prepared by taking AR grade chemicals. Binary liquid mixtures of various compositions were prepared by mixing fixed amount of pure liquids in air tight stoppered bottles of 50ml capacity. The density of pure liquids and liquid mixtures were determined using a 10ml relative density bottle with an accuracy of ±0.0001kgm^{-3}.

An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with an accuracy of ±0.001cP. The viscometer was calibrated using standard liquids before the experiments. All the measurements were made at 303.15K with help of a digital thermostat with a temperature accuracy of ±0.01K.

RESULTS AND DISCUSSION

The experimental densities (ρ/kg m^{-3}) and viscosity(η/kg m^{-1} s^{-1}) for the pure liquids and binary system are presented in Table1and Table2

Table 1: Comparison of experimental densities (ρ) and viscosities(η) of pure liquids at T=303.15K with literature data.

Component	**Temp. (K)**	**Density (10^{-3}kg m^{-3})**		**Viscosity (cP)**	
		Expt.	Lit.	Expt.	Lit.
2-ethoxyethanol	303.15	0.8936	0.8954[3]	2.42	2.349[3]
Chlorobenzene	303.15	1.0931	1.0952[4]	0.7529	0.7553[5]

The excess volume (V^E) have been evaluated from density using following equation[2,6].

$$V^E = \left(\frac{(x_1M_1+x_2M_2)}{\rho}\right)-\left(\left(\frac{x_1M_1}{\rho_1}\right)+\left(\frac{x_2M_2}{\rho_2}\right)\right) \qquad (1)$$

x_1, M_1 & x_2, M_2 are the molefration & molecular weight of pure component 1 and 2 respectively.

The viscosity of pure liquids and mixtures were calculated using the relation[2,6].

$$\eta = \left(At - \frac{B}{t}\right)\rho \qquad (2)$$

Where A and B represent the characteristic constants of the viscometer, ρ is density and t is time flow.

The deviation in viscosity is calculated using the relation[7].

$$\Delta \ln\eta = \ln\eta_m - (x_1 \ln\eta_1 + x_2 \ln\eta_2) \qquad (3)$$

Where η_m, η_1 & η_2 are viscosities of the liquid mixtures and of the pure component 1 and 2

The Gibb's free energy G^{*E} of activation of flow in the mixtures were calculated from the relation[8].

$$G^{*E} = RT[\ln\eta_m x V_m - (x_1 \ln\eta_1 V_1 + x_2 \ln\eta_2 V_2)] \qquad (4)$$

Where R is gas constant, T temperature of study, η_m the viscosity of mixture ,V_m molar volume of the mixture and x_1, η_1, V_1 and x_2, η_2, V_2 are mole fraction, viscosity and molar volume of components present in the liquid mixture.

All the calculated excess values were fitted to Redlich-Kister type polynomial equation[2].

$$\Delta A = x_1 x_2 [a + b(x_1 - x_2) + c(x_1 - x_2)] \qquad (5)$$

By the method of least squares to derive the adjustable parameters a, b &c.

The standard deviation values were calculated using the relation[2].

$$\sigma = [(\Delta A_{exp} - \Delta A_{cal})^2/(n-m)]^{1/2} \qquad (6)$$

Where n is the number of measurements and m is the number of adjustable parameters.

From the Table 2 it is noted that the density of binary mixture decreases with increasing mole fractions of 2-ethoxyethanol. And the viscosity of the binary liquid mixtures increases with increasing mole fraction of 2-ethoxyethanol[9,10,11].

Table-2: Density (ρ), Excess volume(V^E) and Viscosity (η) for the binary systems of 2-ethoxyethanol and Chlorobenzene, at 303.15K.

X_1	ρ (10^{-3}kg m^{-3})	V^E (10^{-3} m^{-3} mol^{-1})	η (cP)	Δη (cP)	Δlnη (cP)	ΔG*^{E} (KJ mol^{-1})
0.0000	1.0931	0.0000	0.7529	0.0000	0.0000	0.0000
0.1062	1.0718	0.0668	0.7333	-0.1964	-0.1498	-21392
0.2047	1.0520	0.0910	0.8225	-0.2715	-0.1503	-11907
0.2866	1.0336	0.1236	0.9348	-0.2959	-0.1200	1041
0.3918	1.0158	0.0111	1.0489	-0.3572	-0.1259	4518
0.4913	0.9981	-0.2019	1.2056	-0.3662	-0.1028	11431
0.5960	0.9757	-0.2691	1.3586	-0.3880	-0.1078	8947
0.7918	0.9580	-0.2245	1.5017	-0.5712	-0.2128	-25631
0.8241	0.9377	-0.1431	2.0761	-0.0507	-0.0596	33744
0.8994	0.9158	-0.0470	2.3915	0.1391	-0.1056	36398
1.0000	0.8936	0.0000	2.4200	0.0000	0.0000	0.0000

Table-3: Values of Parameters of equation (5) and standard deviation at 303.15K.

Parameters	A	b	c	σ
V^E (10^{-6} m^3 mol^{-1})	-0.6497	-1.6170	1.2760	0.002596
Δη (cP)	-1.6347	0.1345	0.5312	0.002683
Δlnη (cP)	-0.4790	0.5523	-0.1787	0.001049

Excess volume values are positive at lower molefraction of 2-ethoxyethanol and negative at higher mole fraction of 2-ethoxyethanol. This may be due to (i) positive contributions arepredominantly attributed to hydrogen bond rupture and stretching of self-associatedmolecules of 2-ethoxyethanol (ii) negative contributions are consideredto be a consequence of dipolar complexes involving 2-ethoxyethanol and chlorobenzene (due tounlike intermolecular dipolar interactions)[12-14].

In the mixture of chlorobenzene with 2-ethoxyethanol, as2-ethoxyethanol molecules were added to Chlorobenzene it would induce depolymerization of 2-ethoxyethanol resulting in positive values of V^E. The positive V^Evalues forthese mixtures show thatthe effects due to the factor (i) are dominating over corresponding negative contributions.

Negative factors (ii) are dominant over the higher composition ranges ofthese mixtures.

Namely, there is a formation of -OH---Cl- atom hydrogen bonded complexes between OH group of alcohols and a chlorine atom of chlorobenzene[12,15,16,17]. The attraction between the unshielded proton of ahydrogen and an electronegative chlorine atom is relatively strong.In addition, the π-electronic cloud of the aromatic ring and OH group interactions takes placeinfluencing in relatively weak extent on contraction in volume.

The data presented in Table 2 indicate that deviations in viscosity (Δ□ln η) are low negative over the whole composition range for all the systems. In general, for system where dispersion and dipolar interactions are operating Δ□ln η□values are found to be negative whereas charge transfer and hydrogen bonding interactions lead to positive Δ□ ln η□ values[8,18]. The Δ□ln η□ values support the contention that the interaction between like molecules is stronger. The average absolute deviations (AAD) between the experimental and calculated values of viscosities are also given in Table 3.

CONCLUSION

Density, viscosity and excess volumes for the binary mixtures of 2-ethoxyethanol and chlorobenzene at various mole fractions at 303.15K has been studied. It is found that there predominates dipole-dipole type of interactions.

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