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Molecular interactions in the mixtures of 2-chloroaniline with equimolar mixture of methanol and isopropanol/isobutanol

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Abstract

Densities and viscosities of mixtures of 2-chloroaniline(CA) with equimolar mixture of methanol and isopropanol/isobutanol (mixtureI/mixtureII) are measured at 308.15 K. Excess viscosity, excess molar volume and excess Gibb's free energy of activation of viscous flow are calculated from the experimental values of densities and viscosities. Molecular interactions in the liquid mixtures are investigated in the light of variation of excess properties evaluated. Excess properties are fitted to a Redlich–Kister type polynomial equation. The experimental data are used to test the applicability of empirical relations of Grunberg–Nissan, Hind–McLaughlin, Katty–Chaudhary and Heric–Brewer for the systems studied.

Keywords: liquid mixtures; molecular interactions; density and viscosity

1. Introduction

The study of excess properties of liquid mixtures provides useful information regarding the nature and strength of molecular interactions [1,2]. Volumetric and viscometric investigations of liquid mixtures enable determination of some useful thermodynamic and other parameters that are highly sensitive to molecular interactions [3,4]. The properties of liquid mixtures can be altered continuously within a reasonable range by varying composition of the mixture/solution till an optimum value of some desired parameter is attained. Pure liquids lack such flexibility. The study of properties of liquid mixtures finds direct applications in the fields of chemistry and biology [5].

CA is used as dye intermediate, as rubber chemicals intermediate, in the manufacture of petroleum solvents and in fungicides. Isopropanol is a solvent of gums, oils, alkaloids, resins and is used in the making of antiseptic solutions. Isobutanol is a solvent for castor-oil-base break fluids and used as a substitute for 1-butanol in making urea resins. CA, isopropanol and isobutanol are associated and polar. There is ample scope for specific interactions between amino($-NH_2$) and chloro($-Cl$) groups of CA and $-OH$ group of alcohols. The volumetric and viscometric studies of molecular interactions in the mixtures of CA with mixtureI/mixtureII are reported in this paper.

2. Experimental details

The density of liquid mixtures is measured using a two-stem pycnometer of Parker and Parker [6]. In this method the mass of a given volume of liquid sample is determined accurately. The volume of the pycnometer cell is calibrated using triply distilled deionized water, as it is not practicable to determine this volume exactly from the geometry of the pycnometer cell. The capillary of the pycnometer stems is calibrated using mercury. The estimated accuracy of this method is 1 in 10^5 parts.

Viscosity is determined using an Ostwald viscometer, which is calibrated using triply distilled deionized water. In this method time of flow of a given volume of liquid sample through a capillary is compared with that of a reference liquid of known density and viscosity. The dynamic viscosity of sample liquid can be determined if the density of liquid sample is known. The estimated accuracy in the measurement of viscosity is ±0.1%.

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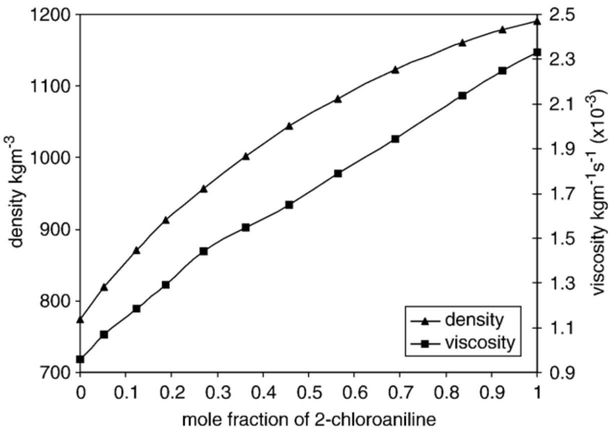

Fig. 1. Variation of density and viscosity in the mixtures of CA and mixtureI.

Table 1
Coefficients A_i of Eq. (4) and the corresponding standard deviations for the ternary mixtures of CA and mixtureI/mixtureII at 308.15 K

Function	A_1	A_2	A_3	A_4	A_5	σ
CA + mixtureI						
η^E kg^{-1} s^{-1} ($\times 10^{-3}$)	0.2642	0.4267	0.4416	−0.3711	−0.2319	0.0095
V^E m^3 mol^{-1} ($\times 10^{-6}$)	−5.4845	0.1282	−2.6842	−3.1353	−1.1200	0.0507
ΔG^{*E} kJ	1.6583	1.1363	0.9341	−0.3601	−0.3547	0.0187
CA + mixtureII						
η^E kg^{-1} s^{-1} ($\times 10^{-3}$)	0.8173	−0.3894	−0.3372	1.0559	−0.1316	0.0098
V^E m^3 mol^{-1} ($\times 10^{-6}$)	−5.1474	1.0928	−5.1929	−2.9522	1.8777	0.0271
ΔG^{*E} kJ	1.7688	−0.0363	−0.6572	1.2233	0.4133	0.0159

Equimolar mixtures of methanol with isopropanol and isobutanol (mixtureI and mixtureII) are prepared. These solutions are in turn used to prepare liquid mixtures with CA so that the entire range of composition is covered (i.e., 0–100% of 2-chloroaniline). All the mixtures are prepared by weight and kept in airtight bottles.

3. Results and discussion

The variation of density (ρ) and viscosity (η) at 308.15 K of the liquid mixtures investigated is shown in Figs. 1 and 2. The density and viscosity increased monotonically but non-linearly with increasing concentration of CA. This non-linear variation, which is a deviation from ideal behavior, suggests interactions between molecules of the component liquids of the mixtures.

The excess molar volume of the liquid mixtures is calculated using the relation

$$V^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2, \tag{1}$$

where x and M are mole fraction and molecular weight; subscripts 1 and 2 stand for CA and mixtureI/mixtureII, respectively. In the calculation of excess parameters, mixtureI/mixtureII is considered as one component of the binary liquid mixture.

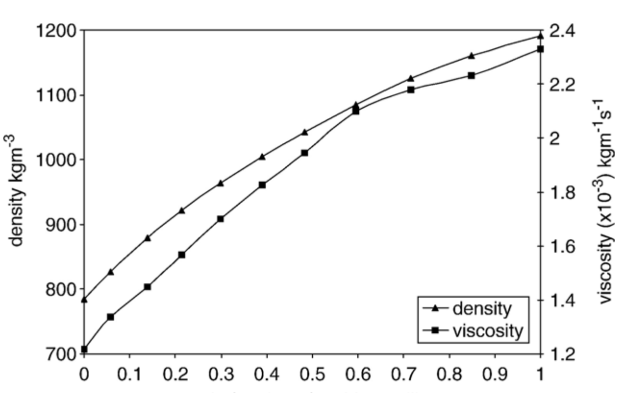

Fig. 2. Variation of density and viscosity in the mixtures of CA and mixtureII.

The excess viscosity is calculated using the relation

$$\eta^E = \eta - x_1\eta_1 - x_2\eta_2. \tag{2}$$

Eyring's relation is used for the evaluation of excess Gibb's free energy of activation ΔG^{*E} of viscous flow

$$\Delta G^{*E} = \mathrm{RT}[\ln(\eta V) - x_1\ln(\eta_1V_1) - x_2\ln(\eta_2V_2)], \tag{3}$$

where $V(=M/\rho)$ is the molar volume of the mixture.

The excess molar volume, excess viscosity and excess Gibb's free energy of activation of viscous flow are fitted to a Redlich–Kister [7] type polynomial equation

$$Y^E = x_1x_2\sum A_i(x_2 - x_1)^{i-1}, \tag{4}$$

where Y^E is V^E or η^E or ΔG^{*E}. The subscript i in the summation of Eq. (4) takes values from 1 to 5. The values of coefficients A_i in the above equation are determined using the least squares method and are compiled in Table 1 along with the standard deviations $\sigma(Y^E)$ calculated using the expression

$$\sigma(Y^E) = \left[\sum\left(Y^E_{\exp} - Y^E_{cal}\right)^2/(m-n)\right]^{\frac{1}{2}} \tag{5}$$

where m is the total number of experimental points and n is the number of coefficients in Eq. (4). The value of n in the present study is 5.

The variation of excess viscosity is shown in Fig. 3. The excess viscosity is positive over the entire range of composition of liquid mixtures. Generally negative values of excess viscosity indicate presence of dispersion forces operating in the system arising due to weak intermolecular interactions and positive values of excess viscosity indicate strong specific interactions [3,4,8–12]. The chlorine atom of CA has three lone pairs of electrons. Due to resonance the carbon–chlorine bond develops partial double bond character with positive charge on the chlorine atom. The nitrogen atom of the amino group becomes negative. The addition of CA to the mixtureI/mixtureII leads to (1) hydrogen bonding (–N⋯HO–); (2) interactions between the oxygen atom of the −OH group of alcohol and the chlorine atom of CA (–Cl⋯OH–); and (3) dipole–dipole interactions