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Ultrasonic and viscometric study of molecular interactions in binary mixtures of aniline with 1-propanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol at different temperatures

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Abstract

Ultrasonic speeds, u and viscosities, η of pure aniline, 1-propanol, 2-propanol, 2-methyl-1-propanol, 2-methyl-2-propanol, and their binary mixtures with aniline as common component, over the entire composition range were measured at the temperatures 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15 K. From the experimental data, the deviations in isentropic compressibility, Δk_s, and in viscosity, $\Delta\eta$ were calculated. The partial molar compressibilities, $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ of aniline and alkanols in the mixtures over the whole composition range and $\bar{K}^{\circ}_{m,1}$ and $\bar{K}^{\circ}_{m,2}$ at infinite dilution and excess partial molar compressibilities, $\bar{K}^{E}_{m,1}$ and $\bar{K}^{E}_{m,2}$, over the whole composition range and $\bar{K}^{\circ E}_{m,1}$ and $\bar{K}^{\circ E}_{m,2}$ at infinite dilution were calculated by using two different approaches. The variation of these parameters with composition and temperature of the mixtures has been discussed in terms of molecular interaction in these mixtures. It is observed that aniline–alkanol interaction in these mixtures follows the order: 1-propanol < 2-propanol < 2-methyl-1-propanol < 2-methyl-2-propanol, and Δk_s values depend upon the number and position of hydroxyl and alkyl groups in these alkanol molecules. Furthermore, the free energies, ΔG^*, enthalpies, ΔH^* and entropies, ΔS^* of activation of viscous flow have also been obtained by using Eyring viscosity equation and their dependence on composition of the mixtures have been discussed.

Keywords: Ultrasonic speed; Aniline–alkanol mixtures; Viscosity; Excess functions; Partial molar compressibility

1. Introduction

The knowledge of physicochemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research and such results are frequently used in design process (flow, mass transfer or heat transfer calculations) in many chemical and industrial processes [1–3]. In previous papers [4–11] we have reported the studies on volumetric, transport, and acoustic properties of binary mixtures containing alkanols. Here we report the results of our study on acoustic and transport properties of binary mixtures of aniline with 1-propanol, 2-propanol, 2-methyl-1-propanol and 2-methyl-2-propanol, over the entire composition range at different temperatures. Aniline molecules are polar ($\mu = 1.51$ D at 298.15 K) [12] and self-associated through hydrogen bonding of their amino groups [13], and alkanol molecules are polar and self-associated through hydrogen bonding of their hydroxyl groups [14]. Aniline is used in manufacture of synthetic dyes, drugs, and as an accelerator in vulcanization of rubber; and the alkanols are of interest in their own right and serve as simple examples of biologically and industrially important amphiphilic materials [15]. Therefore, the study of intermolecular interactions in aniline + alkanol mixtures would be interesting owing to their industrial applications. Literature survey indicates that there has been no temperature-dependent study of these systems from the point of view of their ultrasonic and viscometric behaviour.

In the present paper, we report densities, ρ of binary mixtures of aniline + 1-propanol, 2-propanol, 2-methyl-1-propanol and 2-methyl-2-propanol, including those of pure liquids at the temperatures $T = 293.15$, 298.15, 303.15, 308.15, 313.15, and 318.15 K, covering the entire composition range, expressed by

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the mole fraction x_1 of aniline. The density, ρ data for the calculations was taken from our previous work [16]. The experimental values of ρ, u and η were used to calculate the deviations in isentropic compressibility, Δk_s, deviations in viscosity, $\Delta\eta$ and excess molar compressibility, K_s^E. The partial molar compressibilities, $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ of aniline and alkanol in the mixture over the whole composition range and $\bar{K}^\circ_{m,1}$ and $\bar{K}^\circ_{m,2}$ at infinite dilution, and excess partial molar compressibilities, $\bar{K}^E_{m,1}$ and $\bar{K}^E_{m,2}$, over the whole composition range and $\bar{K}^{\circ E}_{m,1}$ and $\bar{K}^{\circ E}_{m,2}$ at infinite dilution were also calculated. The variation of these parameters with composition and temperature of the mixtures were discussed in terms of molecular interaction in these mixtures. Furthermore, the free energies, ΔG^*, enthalpies, ΔH^*, and entropies, ΔS^* of activation of viscous flow have also been obtained by using Eyring viscosity equation [17,18]. The dependence of ΔH^* and ΔS^* on composition of the mixtures have been discussed.

2. Experimental details

Aniline, 1-propanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol used in the study were the products from s.d. fine chemicals, India and these chemicals were purified by using the methods described in the literature [19,20]; the mass fraction purities as determined by gas chromatography are: aniline > 0.996, 1-propanol > 0.996, 2-propanol > 0.995, 2-methyl-1-propanol > 0.995, and 2-methyl-2-propanol > 0.993. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water content, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done an electronic balance (Model: GR-202, AND, Japan) with a precision of ±0.01 mg. The uncertainty in the mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$.

The ultrasonic speeds in pure liquids and in their binary mixtures were measured using a single-crystal variable-path multifrequency ultrasonic interferometer operating at 3 MHz by the method described elsewhere [4–11]. The ultrasonic speed data were reproducible within ±0.03%. The viscosities of pure liquids and their binary mixtures were measured by using Ubbelohde type suspended level viscometer. The viscometer was calibrated with triply distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostatic water bath so that the thermal fluctuations in viscometer were minimized. The time of flow was recorded in triplicate with a digital stopwatch with an accuracy of ±0.01 s. The viscosity data were reproducible within $\pm 5 \times 10^{-7}$ N s m^{-2}. The temperature of the test liquids during the measurements was maintained to an accuracy of ±0.01 K in an electronically controlled thermostatic water bath (Model: ME-31A, JULABO, Germany). The reliability of experimental measurements of u and η was ascertained by comparing the experimental data of pure liquids with the corresponding values, which were available in the literature [21–35] at the studied temperatures. This comparison is given in Table 1 and a good agreement between the experimental and the literature values is observed.

3. Theory

The excess function such as Δk_s, $\Delta\eta$ and K_s have been calculated by using the following standard relations:

$$\Delta k_s = k_s - (x_1 k_{s,1} + x_2 k_{s,2}) \tag{1}$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

$$K_s^E = K_s - (x_1 K_{s,1} + x_2 K_{s,2}) \tag{3}$$

where x is the mole fraction; subscripts 1 and 2 stand for the pure components, aniline and alkanol, respectively; k_s and K_s are the isentropic compressibility and molar isentropic compressibility, calculated by using the relations:

$$k_s = \frac{1}{u^2\rho} \tag{4}$$

$$K_s = k_s V \tag{5}$$

where V is the molar volume. The excess functions Δk_s, $\Delta\eta$ and K_s^E were fitted to a Redlich–Kister type [36] polynomial equation:

$$Y^E = x_1(1-x_1)\sum_{i=0}^{n} A_i(1-2x_1)^i \tag{6}$$

where Y^E is Δk_s or $\Delta\eta$ or K_s^E. The values of coefficients, A_i were evaluated by using least-squares method with all points weighted equally, and the corresponding standard deviations, $\sigma(Y^E)$ were calculated by using the relation:

$$\sigma(Y^E) = \left[\sum \frac{(Y^E_{\text{calc.}} - Y^E_{\text{expt.}})^2}{(n-j)}\right]^{1/2} \tag{7}$$

where n is the number of experimental data points and j is the number of A_i coefficients considered. The values of $Y^E_{\text{calc.}}$ were obtained from Eq. (6) by using the best-fit values of A_i coefficients.

The partial molar compressibilities, $\bar{K}_{m,1}$ of component 1 (aniline) and $\bar{K}_{m,2}$ of component 2 (alkanol) in these mixtures at 298.15 K were calculated adopting the approach (that has been used earlier [7,37] for the calculation of partial molar volumes), in which $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ are given by the following relations:

$$\bar{K}_{m,1} = K_s^E + K^*_{s,1} + x_2\left(\frac{\partial K_s^E}{\partial x_1}\right)_{T,p} \tag{8}$$

$$\bar{K}_{m,2} = K_s^E + K^*_{s,2} - x_1\left(\frac{\partial K_s^E}{\partial x_1}\right)_{T,p} \tag{9}$$

where $K^*_{s,1}$ and $K^*_{s,2}$ are the molar isentropic compressibilities of pure components, aniline and alkanol, respectively. The derivative, $(\partial K_s^E/\partial x_1)_{T,p}$ in Eqs. (8) and (9) was obtained by differentiation of Eq. (6) on substituting K_s^E for Y^E, which leads to the following equations for $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$:

$$\bar{K}_{m,1} = K^*_{s,1} + x_2^2\sum_{i=0}^{n} A_i(1-2x_1)^i - 2x_1x_2^2\sum_{i=1}^{n} A_i(1-2x_1)^{i-1} \tag{10}$$