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Ultrasonic and viscometric studies of molecular interactions in binary mixtures of formamide with ethanol, 1-propanol, 1,2-ethanediol and 1,2-propanediol at different temperatures

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Abstract

The ultrasonic speeds, u and viscosities, η of binary mixtures of formamide (FA) with ethanol, 1-propanol, 1,2-ethanediol, and 1,2-propanediol, including those of pure liquids, over the entire composition range were measured at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K. From the experimental values of u and η, the deviations in isentropic compressibility, Δk_s, in ultrasonic speed, Δu, and in viscosity, $\Delta\eta$ were calculated. The variation of these parameters with composition and temperature of the mixtures are discussed in terms of molecular interaction in these mixtures. The observed trends in Δk_s values indicate the presence of specific interactions between FA and alkanol molecules. The Δk_s values follow the order: ethanol <1-propanol <1,2-propanediol <1,2-ethanediol. It is observed that the Δk_s values depend upon the number of hydroxyl groups and alkyl chain length 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; Viscosity; Formamide; Alkanols; Deviations in isentropic compressibility; Molecular interactions

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 [1,2]. Moreover, amides are convenient model systems for the investigation of peptide and protein interactions in biological systems [3]. In continuation to our previous works [4–11], here we report the results of our studies on acoustic and transport properties of binary mixtures of formamide (FA) with ethanol, 1-propanol, 1,2-ethanediol, and 1,2-propanediol, over the entire composition range at various temperatures. FA molecules are highly polar (μ=3.37 D at 298.15 K) [12] and are strongly self-associated through extensive three-dimensional network of hydrogen bonds, through its three hydrogen bond donors (3 H-atoms) and three acceptors (two lone pairs of electrons at oxygen and one at nitrogen atom) [13,14]. Alkanol molecules are polar and self-associated through hydrogen bonding of their hydroxyl groups [14], whereas alkanediol molecules are self-associated through inter- and intra-hydrogen bonding. Since the components of these binary mixtures (FA and alkanols) have both proton-donating as well as proton-accepting abilities, significant interaction through hydrogen bonding between unlike molecules in these binary systems is expected. A survey of literature indicates that there has been no temperature-dependent study on these systems from the point of view of their ultrasonic and viscometric behaviour. However, Garcia et al. [15] have studied the viscometric behaviour of FA+ethanol/1-propanol mixtures at 298.15 K.

In the present paper, we report ultrasonic speeds, u and viscosities, η of binary mixtures of FA with ethanol, 1-propanol, 1,2-ethanediol, and 1,2-propanediol, including those of pure liquids at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K, covering the entire composition range, expressed by the mole

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fraction, x_1, of FA ($0 \le x_1 \le 1$). The density, ρ data for the calculations was taken from our previous study [16]. The experimental values of ρ, u and η were used to calculate Δk_s, Δu, and $\Delta \eta$. The variation of these parameters with composition and temperature of the mixtures are discussed in terms of molecular interaction in these mixtures. Furthermore, values of ΔG^*, ΔH^*, and ΔS^* have also been obtained by using Eyring viscosity equation [17,18] and their dependence on composition of the mixtures have been discussed.

2. Experimental section

Formamide, ethanol, 1-propanol, 1,2-ethanediol, and 1,2-propanediol, used in the study were the products from S.D. Fine-Chem Ltd., India and were purified by using the methods described in the literature [19,20]; the mass fraction purities as determined by gas chromatography are: FA > 0.996, ethanol > 0.995, 1-propanol > 0.995, 1,2-ethanediol > 0.994, and 1,2-propanediol > 0.993. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water content, as far as possible, 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 on an electronic balance with a precision of ±0.1 mg. The average uncertainty in the mole fraction was estimated to be less than ±0.0001.

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 [2,4,16,18,21–33] at the studied temperatures. This comparison is given in Table 1 and the agreement between the experimental and the literature values is found good in general.

3. Results and discussion

3.1. Excess functions

The experimental values of ultrasonic speed, u and viscosity, η of binary mixtures of FA with ethanol, 1-propanol, 1,2-ethanediol, and 1,2-propanediol, with FA as a common component, over the whole composition range, expressed in mole fraction, x_1, of FA at different temperatures are listed in Tables 2 and 3. The values of Δk_s, Δu, and $\Delta \eta$ have been calculated by using the following standard relations [34,35]

$$\Delta k_s = k_s - k_s^{id} \tag{1}$$

$$\Delta u = u - \left(\rho^{id} k_s^{id}\right)^{-1/2} \tag{2}$$

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{3}$$

where the subscripts 1 and 2 represent the pure components, FA and alkanol, respectively; the superscript 'id' represents ideal mixture; and the values of k_s, ρ^{id}, and k_s^{id} are calculated by using the following relations [35]

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

$$\rho^{id} = \phi_1 \rho_1 + \phi_2 \rho_2 \tag{5}$$

$$k_s^{id} = \phi_1 k_{s,1} + \phi_2 k_{s,2} + T\left[\frac{\phi_1 V_{m,1}\left(\alpha_{p,1}\right)^2}{C_{p,1}} + \frac{\phi_2 V_{m,2}\left(\alpha_{p,2}\right)^2}{C_{p,2}} - \frac{V_m^{id}\left(\alpha_p^{id}\right)^2}{C_p^{id}}\right] \tag{6}$$

where

$$V^{id} = x_1 V_{m,1} + x_2 V_{m,2} \tag{7}$$

$$\alpha_p^{id} = \phi_1 \alpha_{p,1} + \phi_2 \alpha_{p,2} \tag{8}$$

$$C_p^{id} = x_1 C_{p,1} + x_2 C_{p,2} \tag{9}$$

where ϕ is the volume fraction; V_m is the molar volume, α_p is the isobaric expansivity; and C_p is the molar isobaric heat capacity. The values of α_p (calculated from the temperature dependence of the density data [16] of pure liquids by using the relation, $(-1/\rho)(\partial\rho/\partial T)_p$) and C_p (taken from the literature [20,21,36–38], at 298.15 K and 318.15 K, are listed in Table 4. The values of Δk_s, Δu, and $\Delta \eta$ were fitted to a Redlich–Kister [39] type polynomial equation

$$Y^E = x_1(1 - x_1) \sum_{i=0}^{n} A_i (1 - 2x_1)^i \tag{10}$$

where Y^E is Δk_s or Δu or $\Delta \eta$. The variations of Δk_s, Δu, and $\Delta \eta$ with composition of the mixtures, along with smoothed values using Eq. (10), at 298.15 and 318.15 K are presented graphically in Figs. 1–3.

The results shown in Fig. 1 indicate that Δk_s values are negative for FA + ethanol/1-propanol mixtures, whereas positive for FA + 1,2-ethanediol/1,2-propanediol mixtures over the entire composition range and at each temperature. The observed negative/positive values of Δk_s for FA + alkanol mixtures indicate the presence of specific interactions between FA and alkanol molecules in these mixtures. The magnitude of Δk_s values at equimolar composition follows the sequence: ethanol < 1-propanol < 1,2-propanediol < 1,2-ethanediol (Fig. 1). This suggests that there is an expansion in volume resulting in an increase in the compressibility of the mixtures in the same order.