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Molecular interactions in binary mixtures of formamide with 1-butanol, 2-butanol, 1,3-butanediol and 1,4-butanediol at different temperatures: An ultrasonic and viscometric study

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Abstract

The ultrasonic speeds, u and viscosities, η of binary mixtures of formamide (FA) with 1-butanol, 2-butanol, 1,3-butanediol and 1,4-butanediol, including those of pure liquids, over the entire composition range were measured at temperatures 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15 K. From the experimental u and η data, the deviations in isentropic compressibility, Δk_s, in ultrasonic speed, Δu, and in viscosity, $\Delta\eta$ were calculated. The partial molar compressibilities, $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ of FA and alkanol 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 variations of these parameters with composition and temperature of the mixtures are discussed in terms of molecular interaction in these mixtures. It is observed that the FA-alkanol interactions in these mixtures follows the order: 1-butanol < 2-butanol < 1,3-butanediol < 1,4-butanediol. The effect of the number and position of the hydroxyl groups in these alkanol molecules on the molecular interactions in these mixtures is discussed. Furthermore, the free energies, ΔG^*, enthalpies, ΔH^*, and entropies, ΔS^* of activation of viscous flow have also been obtained by using Eyring viscosity equation. The dependence of ΔG^*, ΔH^* and ΔS^* on composition of the mixtures have been discussed.

Keywords: Ultrasonic speed; Viscosity; Formamide; Alkanols; Alkanediols; Deviations in isentropic compressibility; Partial molar compressibility; Molecular interactions

1. Introduction

Mixed solvents are frequently used as media for many chemical, industrial and biological processes, because they provide a wide range of desired properties [1]. The study of physicochemical properties of amide + alkanol mixed solvents is interesting because amides are convenient model systems for investigating peptide and protein–solvent interactions. Formamide (FA) is chosen for the study, as it is the simplest amide that contains a peptide linkage, the fundamental building block of proteins [2]. Alkanols are of interest in their own right and serve as simple examples of biologically and industrially important amphiphilic materials [3]. In previous papers [4–11] we have studied the volumetric, acoustic and transport properties of non-aqueous binary mixtures containing alkanols. Here we report the results of our studies on acoustic and transport properties of binary mixtures of FA with 1-butanol, 2-butanol, 1,3-butanediol, and 1,4-butanediol, over the entire composition range at various temperatures. FA molecules are highly polar ($\mu = 3.37$ D at 298.15 K) [13] 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 on 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 have both proton-donating/accepting abilities, significant interaction through hydrogen bonding between unlike molecules is expected. To the best of our knowledge, there has been no temperature-dependent study on these systems from the point of view of their acoustic and viscometric behaviour, except the

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work of Garcia et al. [15], who studied the viscometric behaviour of FA + 1-butanol mixtures at 298.15 K and Ali et al. [11], who studied ultrasonic and viscometric behaviour of FA + 1-butanol mixtures at 308.15 K.

The present paper reports the ultrasonic speeds, u and viscosities, η of binary mixtures of FA with 1-butanol, 2-butanol, 1,3-butanediol, 1,4-butanediol and 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 fraction x_1 of FA. 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 the deviations in isentropic compressibility, Δk_s, deviations in ultrasonic speed, Δu, 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 FA and alkanols 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 has been 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. The dependence of ΔG^*, ΔH^* and ΔS^* on composition of the mixtures have been discussed.

2. Experimental details

Formamide, 1-butanol and 2-butanol (all AR grade products from s.d. fine chemicals, India), 1,3-butanediol and 1,4-butanediol (both products from E. Merck, Germany) used in the study were purified by using the methods described in the literature [17,18]; the mass fraction purities as determined by gas chromatography are: FA > 0.995, 1-butanol > 0.995, 2-butanol > 0.994, 1,3-butanediol > 0.992 and 1,4-butanediol > 0.992. 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 on electronic balance with a precision of ±0.1 mg. The probable error 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 [6,15,18–32] 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

The experimental values of ultrasonic speeds and viscosities of binary mixtures of FA with 1-butanol, 2-butanol, 1,3-butanediol, and 1,4-butanediol, with FA as a common component, over the whole composition range expressed in mole fraction x_1 of FA ($0 \le x_1 \le 1$), at different temperatures are listed in Tables 2 and 3, respectively. The excess function such as Δk_s, Δu, $\Delta\eta$ and K_s^E have been calculated by using the following standard relations:

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

$$\Delta u = u - (x_1 u_1 + x_2 u_2) \quad (2)$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

$$K_s^E = K_s - (x_1 K_{s,1} + x_2 K_{s,2}) \quad (4)$$

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

$$k_s = \frac{1}{u^2\rho} \quad (5)$$

$$K_s = k_s V \quad (6)$$

where V is the molar volume, calculated using the relation:

$$V = \frac{x_1 M_1 + x_2 M_2}{\rho} \quad (7)$$

The excess functions Δk_s, Δu, $\Delta\eta$ and K_s^E were fitted to a Redlich–Kister type polynomial equation:

$$Y^E = x_1(1-x_1)\sum_{i=0}^{n} A_i(1-2x_1)^i \quad (8)$$

where Y^E is Δk_s or Δu or $\Delta\eta$ or K_s^E. The values of coefficients, A_i evaluated by using least-squares method with all points weighted equally, and the corresponding standard deviations, σ (Y^E) are listed in Table 4. The variations Δk_s, Δu and $\Delta\eta$ with composition of the mixtures, along with smoothed values using Eq. (8), at 298.15 and 318.15 K are presented graphically in Figs. 1–3.

The results shown in Fig. 1 indicate that the Δk_s values are negative for FA + 1-butanol/2-butanol and are positive for FA + 1,3-butanediol/1,4-butanediol mixtures over entire mole fraction range and at all temperatures investigated. The magnitude of Δk_s values follows the sequence: 1-butanol < 2-butanol < 1,3-butanediol < 1,4-butanediol. This suggests that