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Study of intermolecular interactions in binary mixtures of 2-(dimethylamino)ethanol with methanol and ethanol at various temperatures

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ABSTRACT

The densities, ρ and ultrasonic speeds, u of the binary mixtures of 2-(dimethylamino)ethanol (DMAE) with methanol/ethanol, including those of pure liquids, over the entire composition range were measured at 298.15, 308.15 and 318.15 K. From the experimental data, the excess molar volumes, V_m^E and excess isentropic compressibilities, κ_s^E have been calculated. The excess partial molar volumes, $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$ and excess partial molar isentropic compressions, $\bar{K}_{s,m,1}^E$ and $\bar{K}_{s,m,2}^E$ over the whole composition range; and partial molar volumes, $\bar{V}_{m,1}^\circ$ and $\bar{V}_{m,2}^\circ$, partial molar isentropic compressions, $\bar{K}_{s,m,1}^\circ$ and $\bar{K}_{s,m,2}^\circ$, excess partial molar volumes, $\bar{V}_{m,1}^{\circ E}$ and $\bar{V}_{m,2}^{\circ E}$, and excess partial molar isentropic compressions, $\bar{K}_{s,m,1}^{\circ E}$ and $\bar{K}_{s,m,2}^{\circ E}$ at infinite dilution have also been calculated. The variations of these parameters with composition and temperature are discussed in terms of intermolecular interactions. The IR spectra of these mixtures have also been recorded at 298.15 K.

1. Introduction

The knowledge of the volumetric and ultrasonic properties of non-aqueous binary liquid mixtures has significance in theoretical and applied areas of research [1–3]. The ultrasonic speed may be considered as a thermodynamic property, provided that a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and of low amplitude is observed; in which case, the ultrasonic absorption of the acoustic waves is negligible [4]. Hydrogen bonding is ubiquitous in nature and plays a pivotal role in simple acid–base chemistry to convoluted pathways in biology [5,6]. Hydrogen bonding in simple (hydrogen bond) donor and (hydrogen bond) accepter complexes is well understood. But, one of the major challenges that need to be addressed in hydrogen bonding is to know, *a priori*, how the individual functional groups in multifunctional molecules will behave when they are made to interact with suitable hydrogen-bonding partners. In multifunctional molecules the exact hydrogen bonding patterns will be a result of subtle competition between various possibilities. In continuation to our earlier work [7–16], here we report the results of our studies on acoustic, volumetric and spectroscopic properties of binary mixtures of 2-(dimethylamino)ethanol (DMAE) with methanol and ethanol.

DMAE is a bifunctional organic compound having polar hydroxyl and amino groups, leading to complex intermolecular interactions with other molecules having polar groups. DMAE molecules are self-associated through intra-molecular and intermolecular hydrogen-bonding. It is used as chemical intermediate in many applications in pharmaceutical industry [17]. Alkanols molecules are polar and self-associated through hydrogen bonding of their hydroxyl groups and are expected to interact strongly with others fluids by hydrogen-bonding [18] forming polymeric chains with different lengths. Alkanols are having large number of industrial applications [19]. Thus, volumetric and acoustic properties of mixtures of DMAE with alkanols are expected to show a complex behaviour, wherein they have been used to obtain more information about the intermolecular interactions [20]. Therefore, the binary systems of DMAE with methanol/ethanol are of great interest for investigating the intra- and intermolecular behaviour of present solvent systems. A detailed survey of literature shows that

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Table 1
Details of chemical source, purification method, purity and analysis method.

Chemical name (CAS number)	Source	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
2-(Dimethylamino)ethanol (108-01-0)	HiMedia Laboratories Pvt. Ltd., India	0.98	Distillation	0.992	GC[a]
Methanol (67-56-1)	Merck, India	0.998	Distillation	0.998	GC
Ethanol (64-17-5)	Merck, India	0.998	Distillation	0.999	GC

[a] GC = gas chromatography.

there has been no study on these systems from the point of view of their volumetric, ultrasonic and spectroscopic behaviour.

In the present article, we report the densities, ρ and ultrasonic speeds, u of binary mixtures of DMAE with methanol and ethanol at the temperatures (298.15, 308.15 and 318.15 K) and at atmospheric pressure, covering the entire composition range expressed by the mole fraction, x_1 of DMAE. Using the experimental data, excess molar volumes, V_m^E and excess isentropic compressibilities, κ_s^E have been calculated. The excess partial molar volumes, $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$ and excess partial molar isentropic compressions, $\bar{K}_{s,m,1}^E$ and $\bar{K}_{s,m,2}^E$ over the whole composition range; and partial molar volumes, $\bar{V}_{m,1}^\circ$ and $\bar{V}_{m,2}^\circ$, partial molar isentropic compressions, $\bar{K}_{s,m,1}^\circ$ and $\bar{K}_{s,m,2}^\circ$, excess partial molar volumes, $\bar{V}_{m,1}^{\circ E}$ and $\bar{V}_{m,2}^{\circ E}$, and excess partial molar isentropic compressions, $\bar{K}_{s,m,1}^{\circ E}$ and $\bar{K}_{s,m,2}^{\circ E}$ at infinite dilution have also been calculated. The IR spectra of these mixtures have also been recorded at 298.15 K. The variations of these parameters with composition and temperature are discussed in terms of intermolecular interactions in these binary mixtures.

2. Experimental

The chemicals DMAE (HiMedia Laboratories Pvt. Ltd., India, mass fraction purity >0.98), methanol (Merck, India, mass fraction purity >0.998), Ethanol (Merck, India, mass fraction purity >0.998) used in the study were purified by the methods described in literature [21,22]; the mass fraction purities of the purified liquids as determined by gas chromatography are: DMAE > 0.992, methanol > 0.998 and ethanol > 0.999 (Table 1). The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done by using an electronic balance (Sartorius electronic balance, model CPA225D) 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 densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of ~13.5 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The uncertainty in density measurements was within $\pm 2 \times 10^{-2}$ kg m^{-3}. The ultrasonic speeds in pure liquids and in their binary mixtures were measured using a single-crystal variable-path multifrequency ultrasonic interferometer (Mittal Enterprises, India, model M-81X) operating at 2 MHz. The ultrasonic speed data were reproducible within ±0.2 m s^{-1}. The infrared spectra for the DMAE–methanol/ethanol mixtures have been recorded using FT-IR spectrophotometer (Perkin-Elmer, model: 8201). The temperature of the test liquids during the measurements was maintained within an uncertainty of ±0.01 K in an electronically controlled thermostatic water bath (Orbit, India).

The reliability of experimental measurements of u and ρ were ascertained by comparing the experimental data of pure liquids at different temperatures with the corresponding literature values [23–29]. This comparison is given in Table 2 and the agreement between the experimental and the literature values is found good.

3. Results and discussion

The experimental values of densities, ρ and ultrasonic speeds, u of the binary mixtures of DMAE with methanol and ethanol, over the entire composition range, expressed in mole fraction, x_1 of DMAE at different temperatures are listed in Tables 3 and 4, respectively.

3.1. Excess properties

The values of excess molar volume, V_m^E, excess isentropic compressibility, κ_s^E and excess molar isentropic compression, $K_{s,m}^E$ have been calculated by using the following standard relations [7,30,31]

$$V_m^E = V_m - (x_1 V_{m,1} + x_2 V_{m,2}) \quad (1)$$

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (2)$$

$$K_{s,m}^E = K_{s,m} - K_{s,m}^{id} \quad (3)$$

where the subscripts 1 and 2 refer to pure component, DMAE and methanol/ethanol respectively, the superscript 'id' represents ideal mixture; and the values of molar volume, V_m, isentropic

Table 2
Experimental values of density, ρ and ultrasonic speed, u of pure liquids along with the corresponding values available in the literature at different temperatures and atmospheric pressure.[a]

Liquid	T/K	ρ/kg m^{-3}		u/m s^{-1}	
		Expt.	Lit.	Expt.	Lit.
2-(Dimethylamino)ethanol	298.15	883.34	883.6 [23]	1344.4	–
	308.15	874.99	875.0 [23]	1309.1	–
	318.15	866.37	866.3 [23]	1274.1	–
Methanol	298.15	786.74	786.6 [24]	1100.7	1101.6 [27]
	308.15	777.45	777.1 [24]	1068.2	1068.9 [28]
	318.15	768.01	767.5 [24]	1037.0	1037.3 [28]
Ethanol	298.15	785.48	785.6 [25]	1143.2	1143.1 [29]
	308.15	776.82	776.5 [26]	1109.6	1109.4 [29]
	318.15	768.08	768.3 [24]	1075.5	1075.9 [29]

[a] Standard uncertainties s are $s(T) = \pm 0.01$ K, $s(\rho) = \pm 2.0 \times 10^{-2}$ kg m^{-3} and $s(u) = \pm 0.2$ m s^{-1}.