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Densities, ultrasonic speeds and excess properties of binary mixtures of methyl acrylate with 1-butanol, or 2-butanol, or 2-methyl-1-propanol, or 2-methyl-2-propanol at temperatures from 288.15 to 318.15 K

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ABSTRACT

The densities, ρ and ultrasonic speeds, u of binary mixtures of methyl acrylate with 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, including those of pure liquids, over the entire composition range were measured at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K and atmospheric pressure. Using the experimental data, the excess molar volume, V_m^E and deviations in isentropic compressibility, Δk_s, partial molar volumes, $V_{m,1}^{\circ\infty}$ and $V_{m,2}^{\circ\infty}$, and excess partial molar volumes, $V_{m,1}^{\circ E,\infty}$ and $V_{m,2}^{\circ E,\infty}$ of the components at infinite dilution were calculated. The variation of these parameters with composition and temperature of the mixtures have been discussed in terms of molecular interaction in these mixtures. The values of V_m^E and Δk_s were found to be negative for all the mixtures at each temperature studied, indicating the presence of specific interactions between methyl acrylate and alkanol molecules. The negative V_m^E and Δk_s values follow the order: 1-butanol<2-butanol<2-methyl-1-propanol<2-methyl-2-propanol. It is observed that the values of V_m^E, Δk_s, $V_{m,1}^{\circ E,\infty}$ and $V_{m,2}^{\circ E,\infty}$ depend upon the positions of hydroxyl and methyl groups in these alkanol molecules.

1. Introduction

The knowledge of composition and temperature dependence of excess properties of binary liquid mixtures provides substantial information regarding the intermolecular interactions between the component molecules [1–5]. In previous papers [6–11] we reported the studies on volumetric, transport, and acoustic properties of non-aqueous binary liquid mixtures. The present work deals with the study of volumetric and ultrasonic behaviour of binary mixtures of methyl acrylate with 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, over the entire composition range at different temperatures. Methyl acrylate molecules are polar ($\mu = 1.77$ D at 298.15 K) [12] and alkanol molecules are also polar and self-associated through hydrogen bonding of their hydroxyl groups [13]. Methyl acrylate is a very important industrial chemical and is widely used commercially for the production of technically important high polymeric and latex compounds; and the alkanols are of interest in their own right and serve as simple examples of biologically and industrially important amphiphilic materials [14]. Therefore, the study of intermolecular interactions in methyl acrylate + 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 volumetric and ultrasonic behaviour, except for the study by Sastry et al. [15], who reported densities and ultrasonic speeds for methyl acrylate + 1-butanol mixtures at 308.15 and 318.15 K.

In the present paper, we report densities, ρ and ultrasonic speeds, u of binary mixtures of methyl acrylate with 1-butanol, or 2-butanol, or 2-methyl-1-propanol, or 2-methyl-2-propanol, including those of pure liquids at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K and atmospheric pressure, covering the entire composition range expressed by the mole fraction x_1 of methyl acrylate. The experimental values of ρ and u were used to calculate the excess molar volumes, V_m^E and deviation in isentropic compressibilities, Δk_s of the mixtures. The variations of V_m^E and Δk_s with composition and temperature of the mixtures have been discussed in terms of molecular interaction in these mixtures. The effect of the positions of hydroxyl and methyl groups in these alkanol molecules on V_m^E and Δk_s has also been discussed.

2. Experimental

Methyl acrylate, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol used in the study were the AR grade products from S. D. Fine Chemicals, India and were purified by using the methods described in the literature [16,17]; the mass fraction purities

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as determined by gas chromatography are: methyl acrylate>0.995, 1-butanol>0.996, 2-butanol>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 by using 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 $\pm 1 \cdot 10^{-4}$.

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 ≈ 10 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 $\pm 2 \cdot 10^{-5}\,g \cdot cm^{-3}$. 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 [6–11]. The uncertainty in the ultrasonic speed measurements was within $\pm 0.03\%$. 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 (Model: ME-31A, JULABO, Germany). The reliability of experimental measurements of ρ and u were ascertained by comparing the experimental data of pure liquids with the corresponding values, which were available in the literature [15,17–32] at 298.15 K. This comparison is given in Table 1 and the agreement between the experimental and the literature values is found good in general. Also, the comparison between our density values for methyl acrylate + 1-butanol mixtures over the whole composition ranges from 308.15 to 318.15 K with those reported for this system by George et al. [16] has been shown graphically in Fig. 1, these values are found in agreement with each other.

Table 1
Comparison of experimental values of density, ρ and ultrasonic speed, u of pure liquids with the corresponding literature values different temperatures.

Liquid	T/(K)	$\rho/(kg \cdot m^{-3})$		$u/(m \cdot s^{-1})$	
		Experimental	Literature	Experimental	Literature
Methyl acrylate	293.15	953.51	953.5 [17]		
	298.15	947.56	947.5 [18]	1183.5	–
	303.15	941.61	935.62 [15]	1139.2	–
	308.15	935.66			1140.0 [15]
	313.15	929.71	925.18 [15]	1095.8	–
	318.15	923.76			1095.0 [15]
1-Butanol	293.15	809.17	809.56[17]	1262.4	–
	298.15	805.54	809.8 [19]	1242.6	1241.0 [20]
			805.56 [20]		
	303.15	801.90	805.67 [21]	1224.6	1224.0 [22]
			801.95 [21]		
	308.15	798.25	801.91 [23]	1207.6	1208.8[24]
			798.12 [21]		
	313.15	794.60	798.2 [20]	1189.2	1189.5 [20]
			794.2 [20]		
	318.15	790.97	–	1170.0	1172.13 [24]
2-Butanol	293.15	806.57	806.52 [17]	1232.6	–
			806.3 [19]		
	298.15	802.28	802.41 [17]	1212.6	1211.5 [24]
			802.25 [20]		1212.4 [20]
	303.15	797.99	–	1194.6	1205.0 [26]
	308.15	793.72	793.9 [25]	1174.5	1174.8 [24]
	313.15	789.43	789.41 [21]	1155.9	1155.3 [20]
	318.15	785.17	785.15 [25]	1138.6	1138.1 [24]
2-Methyl-	293.15	801.48	801.6 [17]	1230.9	–
1-propanol	298.15	797.54	797.37 [25]	1211.4	–
			797.72 [20]		
	303.15	793.60	793.8 [27]	1192.5	1188.9 [20]
	308.15	789.66	789.7 [28]	1175.2	–
	313.15	785.72	785.8 [29]	1156.8	–
	318.15	781.78	781.8 [28]	1137.2	–
2-Methyl-	293.15	785.75	–	1141.5	–
2-propanol	298.15	780.63	780.59 [30]	1123.5	1122.9 [20]
			780.68 [20]		
	303.15	775.51	775.45 [17]	1104.3	–
			775.51 [31]		
	308.15	770.39	770.19 [25]	1084.3	–
	313.15	765.26	765.01 [32]	1065.3	1057.8 [20]
			765.32 [20]		
	318.15	760.13	–	1046.3	–

3. Results and discussion

The experimental values of densities, ρ and ultrasonic speeds, u of binary mixtures of methyl acrylate with 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, with methyl acrylate as a common component, over the entire composition range, expressed in mole fraction x_1 of methyl acrylate at seven different temperatures are listed in Tables 2, 3, 4 and 5. The variations of ρ and u with mole fraction, x_1 at different temperatures have been shown in Figs. S1–S8 (Appendix A). The values of V_m^E and Δk_s for the mixtures at each temperature were calculated by using the following relation

$$V_m^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \quad (1)$$

$$\Delta k_s = k_s - (\phi_1 k_{s,1} + \phi_2 k_{s,2}) \quad (2)$$

where M is the molar Mass; ϕ is the volume fraction (calculated using the molar volumes of the pure components obtained from the density data); and the subscripts 1 and 2 stand for pure components, methyl acrylate and alkanol, respectively. The values of V_m^E and Δk_s are listed in Tables 2, 3, 4 and 5. The values of V_m^E and Δk_s were fitted to a Redlich-Kister type [33] polynomial equation

$$V_m^E = x_1 x_2 \sum_{i=0}^{j} A_i (1-2x_1)^i. \quad (3)$$

In case of Δk_s, volume fraction ϕ has been used in place of x in Eq. (3). The values of coefficients, A_i were evaluated by using the method of least squares, with all points weighted equally. The coefficients A_0, A_1, A_2, A_3 and A_4 along with standard deviations σ of fit for all the mixtures are listed in Tables 6 and 7. The variations of V_m^E and Δk_s with x_1 of methyl acrylate at 298.15 and 318.15 K, along with

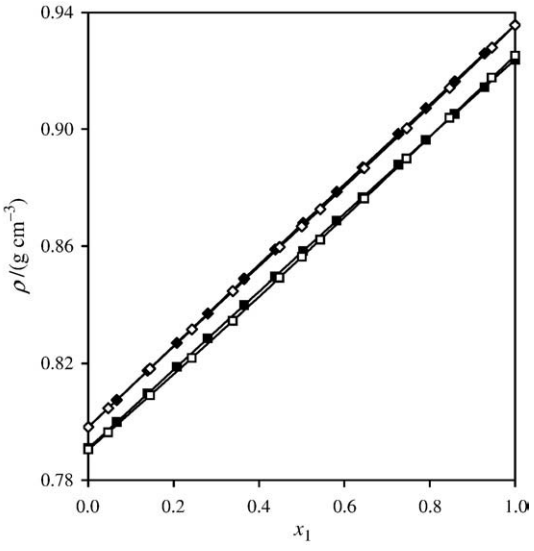

Fig. 1. Plots of density, ρ against mole fraction, x_1 of methyl acrylate for methyl acrylate + 1-butanol mixtures at $T = 308.15$ K: this work, ♦, Ref. [15], ◇; and at $T = 318.15$ K: this work, ■; Ref. [15], □.