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Studies on liquid–liquid interactions of some ternary mixtures by density, viscosity, ultrasonic speed and refractive index measurements

Lovely Sarkar, Mahendra Nath Roy*

Department of Chemistry, North Bengal University, Darjeeling 734013, India

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ABSTRACT

The excess molar volumes, V^E, and viscosity deviations, $\Delta\eta$, were calculated from the measured density and viscosity data over the whole composition range for the ternary systems of 1,3-dioxolane (DO), dichloromethane (DM) + methyl acetate (MA), ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and isoamyl acetate (IA) at 298.15 K. From the experimental observations the speed of sounds and refractive indices of these ternary mixtures have been measured over the entire range of composition at the same temperature. Also the isentropic compressibility, deviation in isentropic compressibility and deviation in molar refraction have been evaluated. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures.

1. Introduction

Densities and viscosities of liquids and liquid mixtures are essential for many engineering and industrial applications. The mixture functions such as the excess molar volume (V^E), the viscosity deviation ($\Delta\eta$), deviation in isentropic compressibility (ΔK_S), and deviation in molar refraction (ΔR), are often used to describe the intermolecular forces in mixtures to help us understand their real behavior and to develop models for their description as well as simulation processes. Therefore, over the years, studies on multicomponent liquid systems have attracted the attention of many researchers [1–6].

To the best of our knowledge, the properties of mixtures of these liquids have not been reported earlier. In the present paper, we report density (ρ), viscosity (η), speed of sound (u) and refractive index (n_D) for the ternary systems consisting of 1,3-dioxolane (DO), dichloromethane (DM) + methyl acetate (MA), ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and isoamyl acetate (IA) at 298.15 K and atmospheric pressure over the entire composition range. The experimental data are used to calculate excess molar volumes (V^E), deviations in viscosity ($\Delta\eta$), deviations in isentropic compressibility (ΔK_S) and deviation in the molar refraction ΔR of the mixtures at 298.15 K under atmospheric pressure.

2. Experimental

2.1. Chemicals

High-purity spectroscopic and analytical grade samples of DO, MA, EA, PA, BA and IA were procured from S.D. Fine Chemicals Ltd., Mumbai, India. DM was purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. All the samples were used without further purification because their purities exceeded 99% as tested by gas chromatography (HP 6890 series) using a flame ionization detector with a packed column. DM (A.R.) was fractionally distilled over calcium oxide, and the middle colorless fractions were collected. Experimental values of η and n_D of the pure liquids are compared in Table 1 [7–12] at 298.15 K and these values agree well with the published results. Mixtures were prepared by mass in specially designed glass stoppered bottles and were used on the same day. The weights were taken on a Mettler electronic analytical balance (AG285).

2.2. Measurements

Densities were measured with an Ostwald-Sprengel-type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at ±0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried, and weighed in an electronic balance with

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* Corresponding author. Tel.: +91 353 2776381; fax: +91 353 2699001.
E-mail address: mahendraroy2002@yahoo.co.in (M.N. Roy).

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Table 1
Physical properties of pure solvents at 298.15 K.

Components	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)		u (m s^{-1})		n_D	
	Exp	llt	Exp	Lit	Exp	Lit	Exp	Lit
1,3-Dioxolane	1.0570	1.0577 [7]	0.588	0.5878 [7]	1339	1338.8 [7]	1.398	1.3983 [11]
Dichloromethane	1.3180	1.3163 [8]	0.380	0.380 [8]	1035	1035 [8]	1.422	1.4228 [8]
Methyl acetate	0.9282	0.92680 [10]	0.374	0.384 [10]	1155	1150 [10]	1.446	1.3606 [9]
Ethyl acetate	0.8928	0.89455 [10]	0.428	0.428 [10]	1142	1138 [10]	1.371	1.3710 [11]
Propyl acetate	0.8823	0.8831 [11]	0.550	0.551 [11]	1179	1172 [11]	1.384	1.3835 [11]
Butyl acetate	0.8756	0.87619 [10]	0.660	0.674 [10]	1201	1190 [10]	1.393	1.3931 [11]
Isoamyl acetate	0.8671	0.86621 [10]	0.780	0.781 [10]	1194	1195 [10]	1.398	1.39836 [12]

a precision of ±0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The estimated uncertainty for V^E is within 0.001–0.014 cm^3 mol^{-1}. The details of the methods and measurement techniques had been described earlier [13].

The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature [14,15]. The flow times were accurate to ±0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, is ±0.003 mPa s. The details of the methods and techniques have been described earlier [13].

Speeds of sound were determined by a multi-frequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 1 MHz, which was calibrated with water, methanol and benzene at 298.15 K. The precision of the speed measurements was ±0.2 m s^{-1}. The details of the methods and techniques have been described earlier [16].

The refractive indices of pure liquids and their binary mixture were measured by using a thermostated Abbe refractometer. The refractometer was calibrated by measuring the refractive indices of triply distilled water and toluene at desired temperatures. The values of refractive indices were obtained using sodium D light. The uncertainty of refractive index measurements was within 0.0002. All measurements described above were performed at least three times at atmospheric pressure and an average of at least three measurements was calculated for each temperature.

3. Results

The experimentally determined density values along with the excess molar volumes, V^E are listed in Table 2. The excess molar volumes, V^E, are calculated from density data according to the following equation [17]:

$$V^E = \sum_{i=1}^{3} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \qquad (1)$$

where ρ is the density of the mixture and M_i, x_i, and ρ_i, are the molecular weight, mole fraction, and density of the ith component in the mixture, respectively.

In Table 2, the experimentally determined viscosities, speeds of sound, isentropic compressibilities, refractive indices and molar refractivities of the ternary mixtures are presented along with the mole fraction of DO, x_A, and DM, x_B, at the experimental temperature. Quantitatively, as per the absolute reaction rates theory [18], the deviations of viscosities can be calculated as

$$\Delta\eta = \eta - \sum_{i=1}^{3} (x_i \eta_i) \qquad (3)$$

where η is the dynamic viscosity of the mixture and x_i and η_i are the mole fraction and viscosity of the ith component in the mixture, respectively.

Isentropic compressibilities (K_S), and the deviations in isentropic compressibilities (ΔK_S), are calculated from the experimental densities (ρ), and speeds of sound (u), using the following equations [19]

$$K_S = \frac{1}{(u^2 \rho)} \qquad (5)$$

$$\Delta K_S = K_S = \sum_{i=1}^{3} (x_i K_{S,i}) \qquad (6)$$

where u is the speed of sound of the mixture and x_i and $K_{S,\,i}$ are the mole fraction and isentropic compressibility of the ith component in the mixture, respectively.

The molar refractivity (R) is calculated using the Lorentz–Lorenz equation [20]

$$R = \left[\frac{(n_D{}^2 - 1)}{(n_D{}^2 + 2)} \right] V \qquad (7)$$

where n_D and V being the refractive indices and the molar volume, respectively.

The deviation in the molar refraction ΔR was calculated on a mole fraction basis as suggested by Brocos et al. [21]

$$\Delta R = R - \sum_{i=1}^{3} (x_i R_i) \qquad (8)$$

where R is the molar refraction of the mixture and x_i and R_i are the mole fraction and molar refraction of the ith component in the mixture, respectively.

4. Discussion

A perusal of Table 2 shows that for the studied ternary systems of DO + DM + alkyl acetates, the V^E values are shifted from positive to negative as the alkyl chain length of the alkyl acetates increases. The negative V^E values may be attributed to specific interactions [22,23] among the mixing components in the mixtures, the positive values often suggest dominance of dispersion forces [22,23] among them. Therefore, specific interactions for the alkyl acetates in the studied ternary systems with DO and DM follow the order

IA > BA > PA > EA > MA

Fig. 1 represents the excess molar volume, V^E, for the five ternary mixtures under taken as a function of mole fraction of DO, x_A. The investigated ternary mixtures show the minima at the mole fraction range, x_A = 0.6–0.7. The V^E values shift from positive to negative as the amount of DO increases in the mixture, which indicates unlike molecular interactions in this system for all the ternary mixtures.