Journal of Molecular Liquids 194 (2014) 100–109

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Ultrasonic studies of molecular interactions in binary mixtures of formamide with some isomers of butanol at 298.15 K and 308.15 K

Manju Rani [a], Suman Gahlyan [b], Hari Om [c], Naveen Verma [c], Sanjeev Maken [b,*]

[a] Department of Chemical Engineering, Deenbandhu Chhotu Ram University of Science and Technology, Murthal 131 039, India
[b] Department of Chemistry, Deenbandhu Chhotu Ram University of Science and Technology, Murthal 131 039, India
[c] Department of Chemistry, Maharshi Dayanand University, Rohtak 124 001, India

ARTICLE INFO

Article history:
Received 10 November 2013
Received in revised form 25 December 2013
Accepted 7 January 2014
Available online 24 January 2014

Keywords:
Ultrasonic velocity
Isentropic compressibility
Graph theory
Formamide
Butanol
Intermolecular interaction

ABSTRACT

Ultrasonic speeds have been measured at 298.15 K and 308.15 K for formamide + 1-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol mixtures and correlated by various correlations like Nomoto's relation, Van Dael's mixing relation and impedance dependence relation. The ultrasonic speed data were further analyzed in terms of Jacobson's free length theory and Schaaff's collision factor theory. Excess isentropic compressibility was calculated from experimental ultrasonic velocity and excess volume data. For an equimolar mixture, excess molar compressibility follows the sequence: 2-methyl-2-propanol < 2-methyl-1-propanol < 1-butanol. The excess molar ultrasonic speed and isentropic compressibility values were also fitted to Redlich–Kister polynomial equation and other properties like molecular association, available volume, free volume, and intermolecular free length were also reported.

1. Introduction

Ultrasonic study of binary mixture helps in understanding their nonideal behavior, as various thermodynamic properties derived from ultrasonic speed and density give significant information about the structure and molecular interactions. Thermodynamic behavior of binary mixture of amide and alcohol is to be investigated, as these are of biological interest. Both formamide and butanol are self associated through H-bonding. The mixing behavior of a binary mixture depends on the size and structure of both components as well as on the strength of inter- and intra-molecular interactions [1–13]. In continuation of our previous work [14–17] on associated binaries, ultrasonic speeds in formamide + 1-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol mixtures have been measured at 298.15 K and 308.15 K. The measured ultrasonic speed data were correlated by correlations like Nomoto's relation, Van Dael's mixing relation and impedance dependence relation. The ultrasonic speed data were further analyzed in terms of Jacobson's free length theory (FLT) and Schaaff's collision factor theory (CFT). Excess isentropic compressibility was calculated from experimental ultrasonic velocity and excess volume data. Excess isentropic compressibility data were also interpreted in terms of graph theoretical approach. The excess molar ultrasonic speed and isentropic compressibility values were fitted to Redlich–Kister polynomial equation and other properties like molecular association, available volume, free volume, and intermolecular free length were also calculated.

2. Experimental

Formamide, 1-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol (Merck or Sigma) was purified by standard procedures [18,19]. The purities of the purified samples were checked by measuring their densities and refractive indices at 298.15 K. The densities were measured with a precision of $\pm 5 \times 10^{-5}$ g cm^{-3} by a specially designed densimeter, consisting of a bulb with an approximate volume of 35 cm^3 attached to a calibrated capillary through a B-10 standard joint in the manner described by Wiesenberger [20]. Air buoyancy correction was also applied to achieve greater accuracy. Refractive indices were measured with a thermostatically controlled Abbe refractometer (OSAW, India) using sodium D-line with an accuracy of ±0.0001. Our experimental values for the density, and refractive index of the pure compounds compared well with the literature values [21–30] as shown in Table 1. Ultrasonic velocities were measured using an ultrasonic interferometer (Model M-81) operating at 2 MHz and the data were reproducible within ±3%. The temperature of the water thermostat was controlled at ±0.01 K by a mercury-in-toluene regulator.

* Corresponding author. Tel.: +91 94663 02603; fax: +91 130 2484119.
E-mail address: sanjeevmakin@gmail.com (S. Maken).

0167-7322/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2014.01.016

Table 1
Comparison of experimental values of ultrasonic speed (m/s) of pure liquids with the corresponding literature values, critical temperature (K) of pure liquids [21,22], isobaric expansivity, α (K^{-1}), and specific heat ($J\ mol^{-1}\ K^{-1}$) at constant pressure [21,22] of pure liquids.

Compound	T/K	u		T_c	$\alpha \times 10^3$	C_p
		Exptl.	Literature			
Formamide	298.15	1599	1601 [23], 1591.3 [24]	650	7.49 [28]	107.8
	308.15	1576.57	1577.2 [23]		7.58 [28]	105.2
1-Butanol	298.15	1251.78	1242.6 [23], 1268 [25]	562.9	0.948 [19]	177.2
	308.15	1220.4	1207.6 [23]		1.041 [29]	181.6
2-Methyl-1-propanol	298.15	1209.60	1189.6 [26], 1170 [25]	547.7	0.978 [30]	181.05
	308.15	1161	1156.2 [26]		1.066 [29]	185.6
2-Methyl-2-propanol	298.15	1121.40	1121.2 [27]	506.2	1.387 [30]	215.37
	308.15	1084	1082.8 [27]		1.482 [29]	219.2

3. Results

Ultrasonic velocity of binary mixtures of formamide (1) + alkanol (2) was measured at 298.15 K and 308.15 K and recorded in Table 2. Following empirical, semi-empirical or statistical relations have been used for theoretical estimation of speed of sound in the present binary mixture:

Nomoto's relation [31] which is based on assumption of additivity of molar sound velocity and no volume change on mixing is given as

$$u = \left(\frac{R_m}{V_{\text{mix}}}\right)^3 = \left[\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right]^3 \tag{1}$$

where x_1, x_2, V_1, V_2, R_1, and R_2 are the mole fractions, molar volumes and molar sound velocity of the first and second components respectively.

$$R_m = \left[\frac{\left(M_i u_i^{1/3}\right)}{\rho_i^*}\right]^3. \tag{2}$$

Van Dael's ideal mixing relation [32]

$$\frac{1}{x_1M_1 + x_2M_2}\cdot\frac{1}{u_{\text{id.mix}}^2} = \frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2} \tag{3}$$

where x_1 and x_2 are mole fractions and M_1 and M_2 are molar mass of formamide and alkanol respectively and $u_{\text{id.mix}}$ is the ultrasonic velocity of the ideal mixture.

Impedance dependence relation [33]

$$\text{u} = \frac{\sum(\text{x}_i Z_i)}{\sum(\text{x}_i\rho_i^*)} \tag{4}$$

where $Z_i = \mu_i\rho_i^*$ is the specific acoustic impedance of component i.

Schaaff's collision factor theory (CFT) [34–36] was also applied to calculate the ultrasonic molecular free lengths (L_f) using following equations

$$Y = \left(36\Pi N_A V_0^2\right)^{1/3} \tag{5}$$

$$V_a = V_T\left(1 - \frac{u}{u_\infty}\right) \tag{6}$$

where u is the ultrasonic velocity at temperature T and u_∞ is 1600 m/s.

According to Schaaff's collision factor theory (CFT) [34–36],

$$u_{\text{mix}} = \frac{u_\infty(x_1S_1 + x_2S_2)(x_1b_1 + x_2b_2)}{V_{\text{mix}}} \tag{7}$$

where b and S are the geometric volume and collision factor respectively. The actual volume of the molecule per mole of the liquid has been computed using the relations.

$$b = \frac{4\Pi \text{r}^3 N_A}{3} \tag{8}$$

where r is the molecular radius which has been computed using Schaaff's [36] relation

$$\text{r} = \left(\frac{M}{\rho N_A}\right)^{1/3}\left[\frac{3}{16\Pi}\left[1 - \frac{\Upsilon RT}{Mu^2}\left(\sqrt{1 + \frac{Mu^2}{3\Upsilon RT}} - 1\right)\right]\right]^{1/3} \tag{9}$$

$$b' = \frac{M}{\rho} - \frac{\Upsilon RT}{Mu^2}\left(\sqrt{1 + \frac{Mu^2}{3\Upsilon RT}} - 1\right) \tag{10}$$

$$\text{r} = \left(\frac{3b'}{16\Pi N_A}\right)^{1/3} \tag{11}$$

where b' is the van der Waals constant and is equal to four times the actual volume of the molecules per mole of the liquid i.e. $b' = 4b$. The value of the collision factor S has been calculated using the relation

$$S = \frac{uV_T}{bu_\infty}. \tag{12}$$

In order to carry out numerical comparison of the estimation capability of the various relations, percentage standard deviations were calculated using following relation and given in Table 3.

$$\sigma(\%) = \left[\frac{\sum\left\{100\left(X_{\text{exptl.}} - X_{\text{theo.}}\right)/X_{\text{exptl.}}\right\}^2}{(n-1)}\right]^{1/2} \tag{13}$$

where n represents the number of experimental data points. Various basic parameters of the pure components were used in theoretical estimation of ultrasonic velocity by using various correlations.

Molecular association (M_A) has been calculated [37] using the relation

$$M_A = \left(\frac{u_{\text{mix}}}{x_1u_1 + x_2u_2}\right) - 1. \tag{16}$$

The molar free volume (V_f) was obtained according to Eyring [38], from the following equation.

$$V_f = Vu^{-3}\left(\frac{\gamma RT}{M}\right)^{3/2}. \tag{17}$$

Jacobson [39,40] derived the intermolecular free length from molar volume and surface area for a large number of liquids. It was suggested that compressibility can be well understood in terms of the intermolecular free length which is the distance between the