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Ultrasonic study on molecular interactions in binary mixtures of formamide with 1-propanol or 2-propanol

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ABSTRACT

Ultrasonic speeds have been measured at 298.15 K and 308.15 K for mixtures of formamide + 1-propanol or 2-propanol. For an equimolar mixture, excess molar compressibility follows the sequence of 1-propanol > 2-propanol. The ultrasonic speed data are correlated by various correlations such as Nomoto's relation, van Dael's mixing relation and impedance dependence relation, and analyzed in terms of Jacobson's free length theory and Schaaff's collision factor theory. Excess isentropic compressibility is calculated from experimental ultrasonic speed data and previously reported excess volume data. The excess molar ultrasonic speed and isentropic compressibility values are fitted to Redlich–Kister polynomial equation. Other properties such as molecular association, available volume, free volume, and intermolecular free length are also calculated. The excess isentropic compressibility data are also interpreted in terms of graph theoretical approach. The calculated isentropic compressibility values are well consistent with the experimental data. It is found that the interaction between formamide and propanol increases when hydroxyl group attached to a carbon atom has more $-CH_3$ groups.

1. Introduction

Amides are important bio-organic solvents and convenient model systems for investigating peptide and protein–solvent interactions [1,2]. Alkanol and amide molecules are associated through hydrogen bonding and their mixtures with other solvents show a pronounced thermodynamic non-ideal behavior [3–5]. The thermo-physical properties of binary mixtures are of great significance for chemical engineers in process designs and also important to chemists to understand the nature of molecular interactions [6,7]. Ultrasonic study of binary mixtures helps in understanding their non ideal behavior, as various thermodynamic properties derived from ultrasonic speed and density reveal significant information about the structure and molecular interactions [8–10]. Formamide is selected for this study, as it is the simplest amide that contains a peptide linkage, the fundamental building block of proteins. Formamide molecules are highly polar [11] 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) [2]. Since the components of these binary mixtures have both proton-donating/accepting abilities, significant interaction through hydrogen bonding between unlike molecules is expected. In our previous work, excess molar volumes and excess molar enthalpies of formamide with propanol and butanol were studied in terms of graph theoretical approach, Mecke–Kempter type association model of Treszczanowicz–Benson association model and Prigogine–Flory–Patterson theory [12–15]. In this paper, ultrasonic speeds are measured at 298.15 K and 308.15 K for mixtures of formamide + 1-propanol or 2-propanol over the entire range of composition. The ultrasonic speed data are correlated by various correlations such as Nomoto's relation, Van Dael's mixing relation and impedance dependence relation, and further analyzed in terms of Jacobson's free length theory and Schaaff's collision factor theory (CFT). Excess isentropic compressibility is calculated from experimental ultrasonic speed data and previously reported excess volume data. The excess molar ultrasonic speeds and isentropic compressibility values are fitted to Redlich–Kister polynomial equation. Other properties such as molecular association, available volume, free volume, and intermolecular free length are also calculated.

2. Experimental

Formamide, 1-propanol, and 2-propanol (Sigma) were purified by standard procedures [16,17]. The purities of the purified samples were

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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 of an approximate volume of 35 cm^3 attached to a calibrated capillary through a B-10 standard joint in the manner described by Wiesenberger [18]. Air buoyancy correction was also applied to achieve a 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 are in good agreement with the literature values [19–25] as shown in Table 1. Ultrasonic speeds were measured using ultrasonic interferometer (Model M-81) operating at 2 MHz and the data were reproducible within ±3%. The temperature of water thermostat was controlled to ±0.01 K by a mercury-in-toluene regulator.

Table 1
Experimental ultrasonic speeds, critical temperature [19,20], isobaric expansivity, and specific heat at constant pressure [19,20] of pure liquids

Compound	T/K	u/m·s^{-1}		T_c/K	$10^3\alpha$/K^{-1}	C_p/J·mol^{-1} K^{-1}
		Exptl.	Literature			
Formamide	298.15	1599	1601 [21] 1591.3 [22]	650	0.749	107.8
	308.15	1576.57	1577.2 [21]		0.758	105.2
1-Propanol	298.15	1212.57	1209.9 [23] 1206 [24]	536.7	1.004	143.87
	308.15	1174.04	1175.2 [23]		1.070	151.38
2-Propanol	298.15	1134	1144 [24]	508.3	1.064	155.78
	308.15	1102.01	1102.3 [25]		1.175	164.04

3. Results

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

Nomoto's relation based on the assumption of additivity of molar sound speed and no volume change in mixing is given as [26]

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

where x_1, x_2, V_1, V_2, R_1, and R_2 are the mole fractions, molar volumes and molar sound speed of components 1 and 2, respectively, and

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

van Dael's ideal mixing relation is [27]

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

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

Table 2
Speed and excess speed of sound for binary mixtures

x_1	u/m·s^{-1}	u^E/m·s^{-1}	x_1	u/m·s^{-1}	u^E/m·s^{-1}
Formamide (1) + 1-propanol (2), T = 298.15 K					
0.0551	1223.0	9.1	0.6065	1388.8	103.0
0.0902	1231.1	16.0	0.6532	1410.8	109.3
0.1731	1245.8	26.7	0.6886	1429.3	114.1
0.2495	1263.6	39.2	0.7386	1452.3	114.0
0.2925	1276.1	47.8	0.7777	1471.1	111.2
0.3202	1284.5	53.4	0.8147	1491.8	107.9
0.3730	1300.9	63.5	0.8496	1511.2	100.8
0.4467	1324.6	76.0	0.8828	1530.4	90.2
0.5036	1345.5	86.0	0.9143	1546.7	73.4
0.5567	1369.2	97.3	0.9443	1565.3	55.1
Formamide (1) + 1-propanol (2), T = 308.15 K					
0.0551	1188.2	12.8	0.6065	1364.3	115.2
0.0902	1197.1	20.4	0.6532	1388.9	123.7
0.1731	1216.4	35.7	0.6886	1405.6	126.2
0.2495	1234.2	48.0	0.7386	1429.8	126.5
0.2925	1246.4	56.3	0.7777	1449.5	123.9
0.3202	1253.7	60.7	0.8147	1472.6	122.3
0.3730	1270.9	71.4	0.8496	1487.8	109.7
0.4467	1296.4	85.4	0.8828	1508.0	99.1
0.5036	1320.1	98.0	0.9143	1525.2	81.6
0.5567	1342.1	107.3	0.9443	1544.3	61.8
Formamide (1) + 2-propanol (2), T = 298.15 K					
0.0699	1156.0	32.8	0.6121	1362.6	153.9
0.1139	1169.2	44.0	0.6585	1388.5	161.3
0.1765	1190.4	61.2	0.6936	1407.0	163.5
0.2539	1215.5	79.7	0.7431	1436.6	165.6
0.2974	1231.5	91.0	0.7817	1460.5	163.7
0.3253	1241.2	97.4	0.8182	1486.3	160.5
0.3785	1260.2	108.8	0.8526	1508.4	150.2
0.4525	1289.0	124.3	0.8852	1527.2	132.5
0.5094	1314.6	137.0	0.9162	1546.6	110.7
0.5625	1339.1	146.9	0.9455	1565.6	82.7
Formamide (1) + 2-propanol (2), T = 308.15 K					
0.0699	1119.6	28.5	0.6121	1340.2	162.7
0.1139	1132.5	39.2	0.6585	1363.5	167.4
0.1765	1151.2	53.9	0.6936	1384.2	171.5
0.2539	1179.8	75.8	0.7431	1412.1	171.7
0.2974	1197.8	89.1	0.7817	1433.6	167.1
0.3253	1210.0	97.9	0.8182	1457.6	161.7
0.3785	1231.4	111.6	0.8526	1477.3	148.5
0.4525	1263.6	130.4	0.8852	1496.0	130.0
0.5094	1291.1	144.9	0.9162	1517.6	109.3
0.5625	1315.2	154.3	0.9455	1540.5	84.0

The impedance dependence relation is [28]

$$u = \frac{\sum(x_i Z_i)}{\sum(x_i \rho_i^*)} \quad (4)$$

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

Schaaff's collision factor theory (CFT) [29–31] is applied to calculate the ultrasonic molecular free lengths (L_f) using following equations

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

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

where u is the ultrasonic speed at temperature T and u_∞ is 1600 m·s^{-1}.

According to Schaaff's collision factor theory (CFT) [29–31],

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

where b and S are the geometric volume and collision factor, respectively.