Study of a Binary Liquid Mixture of Diethylamine and 1-Decanol and Validation of Theoretical Approaches of Sound Speed at Different Temperatures

Rita Mehra* and Avneesh K. Gaur

Acoustic & Environmental Laboratory, Department of Pure & Applied Chemistry, M. D. S. University, Ajmer-305009

Excess parameters like excess acoustic impedance (Z^E), excess internal pressure (π_i^E) and excess enthalpy (H^E) have been calculated from measured densities (ρ), sound speed (u), and viscosities (η) of a binary mixture of diethylamine and 1-decanol at (293, 303, and 313) K over the entire range of compositions. Further, these excess parameters are fitted into the Redlich–Kister polynomial equation to find smoothing coefficients and standard error. Different theoretical models of sound speed are also applied to experimental sound speed to find the best fit theory for the system under investigation.

Introduction

Sound speed measurements have significance in science and technology since they provides valuable information about acoustic and thermodynamic parameters, the sign and magnitude of their excess functions being used to evaluate structure-making and/or structure-breaking effects arising due to mixing of two or more unlike liquids in varying proportions.[1,2] The interaction parameter (α) is significant as it is a measure of departure of experimental sound speed from theoretically predicted sound speed and is a quantitative measure of molecular interactions. In continuation of our ongoing research works,[3–8] the present paper deals with the study of interactions in binary mixtures of diethylamine and 1-decanol at three different temperatures through acoustic and thermodynamic parameters. We have also applied different theoretical approaches of sound speed like the Nomoto Relation (NOM), the Impedance Dependence Relation (IDR), the Vandeal Vangeel Ideal Mixing Relation (VAN), the Junjie Relation (JR), and Schaaff's Collision Factor Theory (CFT) to the experimental sound speed to find the best suited theory for the system under investigation.

Experimental

All chemicals used were of analytical grade. Diethylamine is supplied by Qualigene and 1-decanol by Himedia, India (both > 99 % pure). The purity of the liquids was ascertained by comparing the boiling point, density, and viscosity of pure components with those reported in the literature[9,10] and tabulated in Table 1. The weighings were done on an electronic balance with a precision of ± 0.1 mg. The density measurements have been done using a bicapillary pyknometer having 13 cm^3 volume of bulb and capillary tubes of uniform bore size of 1 mm. It was calibrated with standard liquids prior to measurements. The volume (V) was calculated with the help of the following relation

$$V = mX + c \tag{1}$$

where m and c are the calibration constants of the pyknometer and X is the number of divisions of the liquid on the two capillaries.

The calibration constants m and c are derived from the equation

$$m = \frac{\sum X \sum V - N \sum XV}{\left(\sum X\right)^2 - N\left(\sum X^2\right)}$$
$$c = \frac{\sum X \sum XV - \sum X^2 \sum V}{\left(\sum X\right)^2 - N\left(\sum X^2\right)} \tag{2}$$

where N is the number of observations.

The density was then calculated using the relation

$$\rho = \frac{M}{V} \tag{3}$$

where M is the mass of liquid.

Viscosity measurements were made by a precalibrated Ostwald's viscometer, using the method based on the measurement of flow time of the liquid as follows

$$\eta = at - \frac{b}{t} \tag{4}$$

where t is flow time of liquid and a and b are the calibration constants of the viscometer.

Sound speeds have been measured using a single frequency ultrasonic interferometer (model F-81) at 2 MHz. The ultrasonic waves of known frequency produced by a quartz crystal are reflected by a movable metallic plate kept parallel to the quartz plate. When the state of acoustic resonance is reached due to the formation of standing waves, an electrical reaction occurs on the generator driving the quartz plate, and its anode current becomes maximum. The micrometer is slowly moved until the anode currentmeter on a high frequency generator shows a maximum. A number of maximum readings of anode current (n) are passed and counted. The total distance (d) thus moved by the micrometer gives the values of wavelength (λ) with the following relation

$$d = n \cdot \frac{\lambda}{2} \tag{5}$$

where $n = 10$ in the present investigation.

* Corresponding author. E-mail: mehra_rita@rediffmail.com.

10.1021/je700619q CCC: $40.75
Published on Web 02/16/2008

Table 1. Comparison of Boiling Point, Density ρ, and Viscosity η Values of Pure Liquids with the Literature

	bp/°C		ρ/kg·m^{-3}		10^{-3} η/Pa·s	
pure liquid	exptl	lit.	exptl	lit.	exptl	lit.
diethylamine	55.3	55.5	707.6[20]	707.4[20]	0.3192[25]	0.3190[25]
1-decanol	229.8	230.2	830.1[20]	829.7[20]	10.9069[25]	10.9000[25]

Table 2. Variation of Viscosity η, Density ρ, Sound Speed u, and Derived Parameters for Diethylamine (1) + 1-Decanol (2)

	10^{-3} η	ρ	u	10^5 Z	10^5 π_i	
x_1	Pa·s	kg·m^{-3}	m·s^{-1}	kg·m^{-2}·s^{-1}	Pa	α
			T/K = 293			
0.0000	13.4141	830.1	1408.0	11.6878	2.3604	0.0000
0.0989	11.0431	828.2	1383.2	11.4557	2.2995	0.1213
0.1963	8.9738	824.8	1352.0	11.1513	2.2346	0.1965
0.3062	7.1047	818.1	1347.2	11.0214	2.1455	0.3025
0.4062	5.4232	814.4	1333.6	10.8608	2.0301	0.3551
0.4898	3.9483	799.0	1321.8	10.5612	1.8409	0.3793
0.5973	2.6089	795.6	1310.4	10.4255	1.6486	0.3943
0.6708	1.9246	785.4	1302.4	10.2290	1.5103	0.3894
0.7388	1.4305	779.4	1293.6	10.0823	1.3924	0.3717
0.8012	1.0665	770.2	1288.8	9.9263	1.2776	0.3540
0.8562	0.7924	759.5	1247.2	9.4725	1.1804	0.2555
0.9031	0.6052	741.4	1211.2	8.9798	1.0893	0.1697
0.9601	0.4396	720.7	1173.2	8.4553	0.9945	0.0760
1.0000	0.3212	707.6	1140.8	8.0723	0.8980	0.0000
			T/K = 303			
0.0000	9.2620	822.1	1375.2	11.3055	2.0391	0.0000
0.0989	7.8250	820.7	1372.4	11.2633	1.9975	0.1712
0.1963	6.3523	814.6	1350.0	10.9971	1.9296	0.2760
0.3062	4.9773	810.0	1340.0	10.8540	1.8498	0.3874
0.4062	3.5235	808.4	1326.0	10.7194	1.6887	0.4489
0.4898	2.8574	794.2	1314.0	10.4358	1.6178	0.4785
0.5973	2.0154	790.7	1302.4	10.2981	1.4969	0.4986
0.6708	1.6516	779.9	1295.6	10.1044	1.4439	0.4987
0.7388	1.2533	773.3	1278.8	9.8890	1.3485	0.4632
0.8012	0.9298	763.6	1266.4	9.6702	1.2374	0.4287
0.8562	0.6890	753.7	1216.8	9.1710	1.1465	0.3073
0.9031	0.5352	737.6	1176.0	8.6742	1.0714	0.2071
0.9601	0.3609	709.2	1130.4	8.0168	0.9391	0.0944
1.0000	0.2750	693.6	1089.6	7.5575	0.8675	0.0000
			T/K = 313			
0.0000	6.5149	815.7	1344.8	10.9695	1.7772	0.0000
0.0989	5.5316	811.5	1332.8	10.8157	1.7473	0.1676
0.1963	4.5221	806.3	1326.0	10.6915	1.6854	0.3107
0.3062	3.5576	803.7	1316.0	10.5767	1.6217	0.4328
0.4062	2.7931	802.1	1297.2	10.4048	1.5621	0.4904
0.4898	2.2444	788.9	1290.8	10.1831	1.4877	0.5374
0.5973	1.6307	782.9	1274.8	9.9804	1.3966	0.5512
0.6708	1.2575	773.7	1258.4	9.7362	1.3135	0.5298
0.7388	0.9795	769.7	1238.4	9.5320	1.2475	0.4866
0.8012	0.7247	755.5	1212.0	9.1567	1.1454	0.4191
0.8562	0.5424	745.6	1164.8	8.6847	1.0663	0.3000
0.9031	0.4368	728.2	1123.2	8.1791	1.0144	0.1958
0.9601	0.3265	694.8	1082.0	7.5177	0.9304	0.0896
1.0000	0.2577	678.4	1045.0	7.0893	0.8728	0.0000

From the knowledge of the wavelength, the sound speed can be obtained by the relation

$$u = \lambda \cdot \nu \tag{6}$$

where ν = 2 MHz.

Uncertainties in density, viscosity, and sound speed measurements were up to ± 0.4 kg·m^{-3}, ± 0.007·10^{-3} Pa·s, and ± 0.4 m·s^{-1}, respectively. All the measurements have been carried out in a thermostatically controlled water bath with circulating medium with an accuracy up to ± 0.1 °C and at atmospheric pressure without varying the pressure.

Results and Discussion

Derived parameters like acoustic impedance (Z), internal pressure (π_i), and molecular interaction parameter (α) are

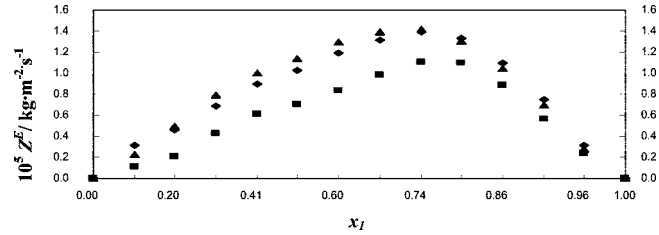

Figure 1. Variation of excess acoustic impedance Z^E with mole fraction of diethylamine x_1 at T =: ♦, 293 K; ■, 303 K; ▲, 313 K.

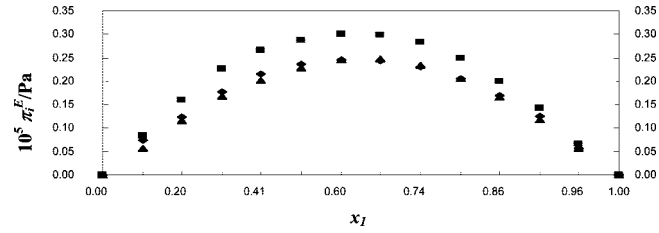

Figure 2. Variation of excess internal pressure π_i^E with mole fraction of diethylamine x_1 at T =: ♦, 293 K; ■, 303 K; ▲, 313 K.

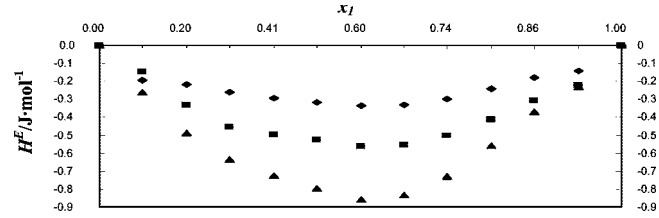

Figure 3. Variation of excess enthalpy H^E with mole fraction of diethylamine x_1 at T =: ♦, 293 K; ■, 303 K; ▲, 313 K.

Table 3. Smoothening Coefficients A_i of the Redlich–Kister Polynomial Equation and Standard Deviations σ

	A_1	A_2	A_3	σ
		T/K = 293		
10^5 Z^E/kg·m^{-2}·s^{-1}	3.7405	−5.8502	−3.4756	0.0394
10^5 π_i^E/Pa	1.2052	−0.5386	0.0202	0.0059
H^E/J·mol^{-1}	−2.0544	0.2803	−1.8478	0.0216
		T/K = 303		
10^5 Z^E/kg·m^{-2}·s^{-1}	4.9544	−6.1040	−2.9107	0.0361
π_i^E/Pa	0.9531	−0.3764	0.2509	0.0037
H^E/J·mol^{-1}	−0.9630	−0.6487	−3.8896	0.0161
		T/K = 313		
10^5 Z^E/kg·m^{-2}·s^{-1}	5.4660	−6.1451	−4.6571	0.0174
10^5 π_i^E/Pa	0.9486	−0.5373	0.0306	0.0050
H^E/J·mol^{-1}	−2.9772	0.3644	−2.7855	0.0411

Table 4. Average % Deviations for Various Theoretical Sound Speed Models

	u^{NOM}	u^{IDR}	u^{VAN}	u^{JR}	u^{CFT}
T/K = 293	4.09	2.69	11.19	2.96	1.75
T/K = 303	3.34	4.63	13.93	5.17	2.58
T/K = 313	3.49	4.75	14.67	5.64	3.31

calculated using the following well-established relations[11]

$$Z = u\rho \tag{7}$$

$$\pi_i = bRT\left[\frac{k\eta}{u}\right]^{\frac{1}{2}} \frac{\rho^{\frac{2}{3}}}{M^{\frac{7}{6}}} \tag{8}$$

$$\alpha = \left[\frac{u_{exptl}^2}{u_{VAN}^2}\right] - 1 \tag{9}$$

where b stands for cubic packing which is assumed to be 2 for liquids; k is a dimensionless constant which is independent of

temperature and the nature of liquids and its value is $4.28 \cdot 10^9$; R is the gas constant; T is the absolute temperature; and M is effective molecular weight.

Excess parameters (Y^E) are calculated using the relation

$$Y^E = Y_{mix} - (x_1 Y_1 + x_2 Y_2) \tag{10}$$

where Y^E is excess acoustic impedance (Z^E), excess internal pressure (π_i^E), and x_1 and x_2 are mole fraction of diethylamine and 1-decanol, respectively.

Excess enthalpy is obtained by the following expression

$$H^E = x_1 \pi_{i1} V_1 + x_2 \pi_{i2} V_2 - \pi_{im} V_m \tag{11}$$

All the excess functions are fitted to the following Redlich–Kister polynomial equation to find smoothening coefficients

$$Y^E = x_1 x_2 \sum_{i=0}^{2} A_i (1 - 2x)^i \tag{12}$$

A_i is the smoothing coefficient, and Y^E represents the excess functions. The standard deviation was calculated using following relation

$$\sigma(Y^E) = \left[\frac{\sum (Y^E_{obsd} - Y^E_{calcd})^2}{(n-p)} \right]^{\frac{1}{2}} \tag{13}$$

where n is the number of data points and p is the number of smoothing coefficients considered ($p = 3$ in the present case).

The theoretical values of sound speed have been calculated using the following empirical and semiempirical relations:

Nomoto relation:

$$u^{NOM} = \left[\frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right]^3 \tag{14}$$

where R is the molar sound speed and V is molar volume.

Impedance Dependence Relation:

$$u^{IDR} = \sum \frac{x_i Z_i}{x_i \rho_i} \tag{15}$$

Vandeal Vangeel Ideal Mixing Relation:

$$\left[\frac{1}{x_1 M_1 + x_2 M_2} \right] \left[\frac{1}{u^{(VAN)2}} \right] = \frac{x_1}{M_1 {u_1}^2} + \frac{x_2}{M_2 {u_2}^2} \tag{16}$$

Junjie Relation:

$$u^{JR} = \left[\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right] [x_1 M_1 + x_2 M_2]^{-\frac{1}{2}} \left[\frac{x_1 M_1}{{\rho_1}^2 {u_1}^2} + \frac{x_2 M_2}{{\rho_2}^2 {u_2}^2} \right]^{-\frac{1}{2}} \tag{17}$$

Schaaff's Collision Factor Theory:

$$u^{CFT} = \left[\frac{(x_1 S_1 + x_2 S_2)(x_1 B_1 + x_2 B_2)}{x_1 V_1 + x_2 V_2} \cdot u_\infty \right] \tag{18}$$

where S is the collision factor and B is the actual volume of the molecule per mole. Subscripts 1 and 2 stand for diethylamine and 1-decanol, respectively. The details of derivations used in the above-mentioned relations may be obtained from the literature.[11–13]

Table 2 represents measured sound speed, density, viscosity, and derived parameters like acoustic impedance, internal pressure, and molecular interaction parameter (α) over the entire mole fraction range of diethylamine at all three temperatures investigated. The observed negative values of H^E are due to predominance of formation of NH—OH and/or OH—NH_2 bonds over the rupture of OH—OH and NH—NH_2 bonds present in pure alcohol and amine and in agreement with the positive contribution of Z^E and π_i^E (Figures 1 to 3).[14–21] The qualitative interpretation of these excess parameters is supported by positive values of α.[22,23] Smoothing coefficients of the Redlich–Kister polynomial equation and standard error for the computed excess functions are given in Table 3. Further, the temperature dependence of different thermoacoustic parameters suggest that the extent of deviation from ideality is temperature sensitive.

The average percentage deviations from theoretically computed sound speed values are listed in Table 4. A perusal of this table shows that the collision factor theory best suits the experimental sound speed for the present system.[24,25]

Literature Cited

(1) George, J.; Sastry, N. V. Densities, Viscosities, Speeds of Sound, and Relative Permittivities for Water + Cyclic Amides (2-Pyrrolidinone, 1-Methyl-2-pyrrolidinone and 1-Vinyl-2-pyrrolidinone) at Different Temperatures. *J. Chem. Eng. Data* **2004**, *49*, 235–242.

(2) Palaiologou, M. M.; Arianas, G. K.; Tsierkezos, N. G. Thermodynamic Investigation of Dimethyl Sulfoxide Binary Mixtures at 293.15 and 313.15 K. *J. Solution Chem.* **2006**, *35*, 1551–1565.

(3) Mehra, R. Ultrasonic, volumetric and viscometric studies of molecular interactions in binary liquid mixture of hexadecane with 1-pentanol, 1-hexanol and 1-heptanol at 298, 308 and 318K. *Z. Phys. Chem.* **2005**, *219*, 425–437.

(4) Mehra, R.; Israni, R. Ultrasonic and viscometric behaviour of hexadecane-butanol mixtures at different temperatures. *Indian J. Chem. Technol.* **2002**, *9*, 341–345.

(5) Mehra, R.; Sajnani, H. Acoustical parameters of CuCl-KCl system in acetonitrile-water solvent mixture. *Phys. Chem. Liq.* **2001**, *39*, 581–588.

(6) Mehra, R.; Pancholi, M. Acoustic, thermodynamic, viscometric and volumetric studies in multicomponent system of hexane + 1-dodecanol + cyclohexane with respect to temperature. *Z. Phys. Chem.* **2007**, *221*, 847–866.

(7) Mehra, R.; Gupta, A.; Israni, R. Excess volume, excess isentropic compressibility, partial molar volume and specific heat ratio of ternary mixture of cyclohexane + decane + alkanols at 298.15 and 308.15K. *Indian J. Chem.* **2001**, *40A*, 505–508.

(8) Mehra, R.; Gaur, A. K. Interaction studies in binary mixture of ethanolamine and 1-decanol at 313K from sound speed measurements. *Proc. XVth Natl. Sym. Ultrason.* **2006**, *96*, 97.

(9) Dean, J. A. *Lange's Hand Book of Chemistry*; McGraw Hill: New York, 1987.

(10) David, R. L. *CRC Hand Book of Chemistry and Physics*; CRC Press: FL, 2000.

(11) Mehra, R.; Pancholi, M. Temperature-dependent studies of thermoacoustic parameters in hexane + 1-dodecanol and application of various theories of sound speed. *Indian J. Phys.* **2006**, *80*, 253–263.

(12) Prabakar, S.; Rajagopal, K. Study of molecular interactions in aprotic-protic binary mixtures through ultrasonic measurements. *J. Pure Appl. Ultrason.* **2005**, *27*, 41–48.

(13) Mehra, R.; Israni, R. A new approach to collision factor theory applied to binary and ternary liquid mixtures at different temperatures. *Indian J. Chem.* **2004**, *43A*, 743–747.

(14) Angela, F. S. S. M.; Florbela, A. D.; Isabel, M. S. L. Ultrasound speeds and molar compressions of aqueous binary mixtures of diethylamine from 278.15 to 308.15 K. *J. Solution Chem.* **2007**, *36*, 13–26.

(15) Mehta, S. K.; Ram, G.; Mani, C.; Bhasin, K. K. A comparative study of thermophysical and spectroscopic properties in mixtures of isomeric butanediol and N, N-dimethylformamide. *J. Chem. Thermodyn.* **2006**, *38*, 836–848.

(16) Nikam, P. S.; Jadhav, M. C.; Hasan, M. Molecualr interactions in mixtures of dimethylsulfoxide with some alkanols- an ultrasonic study. *Acust. Acta Acust.* **1997**, *83*, 86–89.

(17) Tiwari, K.; Patra, C.; Padhy, S.; Chakravortty, V. Molecualr interaction study on binary mixtures of dimethyl sulfoxide + isobutyl methyl ketone (IBMK), + acetylacetone and + tri-N-butylphosphate (TBP) from excess properties of ultrasonic velocity, viscosity and density. *Phys. Chem. Liq.* **1996**, *32*, 149–157.

(18) Rao, T. S.; Veeraiah, N.; Rao, G. S.; Ramachandran, D.; Rambabu, C. Temperature dependence of excess thermodynamic properties of binary mixtures consisting of o-chloro phenol, o-cresol amd m-cresol

with N,N-diethyl acetamide at different temperatures. *J. Pure Appl. Ultrason.* **2003**, *25*, 38–54.
(19) Ali, A.; Abida Hyder, S.; Nain, A. K. Ultrasonic, volumetric and viscometric study of molecular interactions in binary mixtures of 2,2,4-trimethyl pentane with n-hexane and cyclohexane at 308 K. *Indian J. Phys.* **2002**, *76B*, 661–667.
(20) Rajendran, V.; Benny, J. C. N. Ultrasonic studies of isentropic compressibility in polar liquid mixtures at 303K. *Acoust. Lett.* **1993**, *17*, 33–36.
(21) Oswal, S. L.; Desai, H. S. Studies of viscosity and excess molar volume of binary mixtures of 2 butylamine + 1-alkanol mixtures at 303.15 and 313.15 K. *Fluid Phase Equilib.* **1999**, *161*, 191–204.
(22) Rath, D. C.; Kar, P. K. Intermolecular free length and molecular interaction studies in binary mixtures of ketones with aromatic hydrocarbons. *J. Pure Appl. Ultrason.* **2003**, *25*, 58–63.
(23) Gupta, A. K.; Yadav, C. K.; Kumar, K. Ultrasonic studies of binary liquid mixtures of hexane with some chloroalkanes. *J. Ind. Coun. Chem.* **2004**, *21*, 28–32.
(24) Nikam, P. S.; Mahale, T. R.; Hasan, M. Ultrasonic study of alkanols (C_1-C_4) in binary mixtures containing ethyl acetate as common component. *Acust. Acta Acust.* **1998**, *84*, 579–584.
(25) Rao, G. V. R.; Samantha, K.; Sarma, A. V.; Rambabu, C. A comparative study of ultrasonic velocity and allied parameters of binary mixtures at different temperatures. *J. Acoust. Soc. Ind.* **2004**, *32*, 213–223.

Received for review October 24, 2007. Accepted January 21, 2008.

JE700619Q