Research Paper

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Excess Thermo Acoustic Parameters in 1,4-Dioxane With 1-Pentanol Binary System

Physics

KEYWORDS : Ultrasonic velocity, density, deviations in isentropic compressibility, excess molar volumes

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ABSTRACT

Excess thermo acoustic parameters are calculated from the measured values of ultrasonic velocity and density in binary liquid mixtures of 1,4-dioxane with 1-pentanol at 298.15 to 308.15 K over the entire range of composition using Anton Paar. The calculated deviations in excess thermodynamic parameters viz., deviations in isentropic compressibility, excess molar volume, excess free length, excess acoustic impedance and excess ultrasonic velocity are calculated from the experimental measurements, and also the results were fitted to Redlich–Kister equation.

INTRODUCTION

The different types of intermolecular interaction and their relative strength in varied liquid systems are often understood in an elaborate way with the measurement of ultrasonic velocity and density[1]. The ultrasonic study is an incredibly powerful tool in characterizing the assorted aspects of physic-chemical molecular interactions in liquid mixtures[2]. The assorted acoustical parameters derived from ultrasonic velocity and density throw much light upon the structural and molecular interactional aspects of the liquid mixtures [3]. Also, the study of excess thermodynamic functions is of considerable interest in understanding the nature of intermolecular interactions in liquid mixtures[4]. Thermodynamic and acoustic studies of binary mixtures are pursued by number of authors for a number of years as a means in knowing the intermolecular interactions between molecules[5-10].

The present work deals with the ultrasonic velocity, density and computation of related parameters in binary system at above three temperatures.

Experimental Details

Materials

The measurements were performed using the sound analyzer incorporated in the Anton Paar device, model DSA 5000M, equipped with the machine sampler SP-1m. All controls and adjustments were done using manufacturer's software system put in within the device. A computer connected to the U tube densimeter enabled us to read the raw data from the device memory and to perform the ensuing analysis. Mole fractions of these samples were determined by measuring the mass of each component with a precision balance (Sartorius, model CP 225D, +/-0.01mg).

Measurements

Measurements of 1,4-dioxane and 1-pentanol with mass fraction purities >0.998 were purchased from Aldrich Chemical Co. the chemicals were kept in airtight stopped glass bottles were performed in an isothermal mode; that is, the measurements of all prepared solution were done at the similar explicit temperature, then the temperature was changed and the measurements were perennial. The instrument in calibrated with the double distilled water for sound velocity and density at room temperature. The accuracy of density measurements was $5*10^{-6}$ g·cm^{-3}, and also the temperature of the equipment was maintained constant to within ± 0.01 K.

Table 1- Comparison of experimental data of pure liquids with literature values

compound	T (K)	u (ms^{-1})		ρ (kgm^{-3})	
		Observed	Literature	Observed	Literature
	298.15	1344.3	1344.8 [11,12]	1026.8	1027.9 [11,13]
	303.15	1322.3		1021.2	1022.5 [14,15]
1,4-dioxane	308.15	1300.5	1325 [16,17]	1015.5	1016.8 [18]
	298.15	1275.8	1275.2 [21]	811.3	810.8 [21,22]
	303.15	1258.9	1258.0 [23]	807.6	807.9 [24]
1-pentanol	308.15	1242.2	1243.6 [23]	803.9	803.4 [23]

RESULTS AND DISCUSSIONS

From the experimentally measured data, the various thermo

$$\sigma(Y) = \left[\frac{\sum (Y_{expt} - Y_{calc})^2}{N - n} \right]^{1/2}$$

acoustical parameters such as deviations in isentropic compressibility (ΔK_s), molar volume (V_m), intermolecular free length (L_f), acoustic impedance (Z) and excess ultrasonic velocity (u^E) are calculated. The comparison of experimental data to the literature values and they are good agreement with each other as given in the table-1. The values of ultrasonic velocity, densities for the binary liquid mixture at different temperatures are given in tables-2, 3. The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality. They have been calculated using the following equation

$$Y^E = Y_{mix} - (x_1 y_1 + x_2 y_2) \quad \textbf{(1)}$$

where x1 and x2 are mole fractions of 1,4-dioxane and 1-pentanol respectively.

Further, the excess parameters were fitted to Redlich – Kister polynomial equation to estimate the adjustable parameters.

$$Y^E = x_1 x_2 \sum_{i=0}^{n} a_i (1 - 2x)^i \quad \textbf{(2)}$$

using least-squares regression method, the ai coefficients are obtained by fitting above equation to the experimental values. The optimum number of coefficients is ascertained from an examination of the variation in standard deviation (σ)

$$\sigma(Y) = \left[\frac{\sum (Y_{expt} - Y_{calc})^2}{N - n} \right]^{1/2} \quad \textbf{(3)}$$

Where N is the number of data points and n is the degree of fitting (number of coefficients)

Table 2 - Experimental data (u, ρ) and Excess thermo acoustic parameters ΔK_s, Vm^E, L_f^E, Z^E, u^E for binary system at 298.15, 303.15 & 308.15 K

x_1	u ms^{-1}	ρ kgm^{-3}	$\Delta K_s * 10^{-10}$ m^2N^{-1}	$V_m^E * 10^{-4}$ m^3 mol^{-1}	$L_f^E * 10^{-11}$ m	$Z^E * 10^6$ $kgm^{-2}s^{-1}$	u^E ms^{-1}
298.15 K							
0.0000	1275.8	811.3	0.0000	0.0000	0.0000	0.0000	0.0000
0.1235	1277.0	831.8	0.0679	0.0012	0.0334	-0.0153	-7.2322
0.2500	1280.0	854.5	0.1213	0.0026	0.0604	-0.0283	-13.1245
0.3476	1283.3	872.0	0.1437	0.0032	0.0729	-0.0353	-16.0415
0.4549	1289.7	893.8	0.1497	0.0035	0.0781	-0.0396	-17.4985
0.5645	1297.3	917.3	0.1386	0.0033	0.0749	-0.0402	-17.1703
0.6542	1304.9	937.5	0.1191	0.0029	0.0666	-0.0376	-15.6164
0.7446	1313.9	959.2	0.0921	0.0022	0.0536	-0.0319	-12.9389
0.8342	1323.7	981.9	0.0602	0.0013	0.0367	-0.0232	-9.2354
0.9228	1334.3	1005.9	0.0267	0.0004	0.0173	-0.0117	-4.6288
1.0000	1344.3	1026.8	0.0000	0.0000	0.0000	0.0000	0.0000
303.15 K							
0.0000	1258.9	807.6	0.0000	0.0000	0.0000	0.0000	0.0000
0.1235	1259.6	827.9	0.0709	0.0013	0.0341	-0.0148	-7.0014
0.2500	1262.3	850.4	0.1276	0.0027	0.0623	-0.0276	-12.8373
0.3476	1265.3	867.6	0.1481	0.0033	0.0739	-0.0341	-15.3538
0.4549	1271.3	889.3	0.1522	0.0036	0.0783	-0.0379	-16.5146
0.5645	1278.4	912.6	0.1428	0.0035	0.0758	-0.0386	-16.3881
0.6542	1285.5	932.7	0.1260	0.0030	0.0687	-0.0364	-15.2282
0.7446	1293.0	954.1	0.0994	0.0023	0.0560	-0.0310	-12.7633
0.8342	1303.2	976.7	0.0627	0.0014	0.0373	-0.0222	-8.8167
0.9228	1313.6	1000.4	0.0226	0.0005	0.0154	-0.0106	-3.8508
1.0000	1322.3	1021.2	0.0000	0.0000	0.0000	0.0000	0.0000
308.15 K							
0.0000	1242.2	803.9	0.0000	0.0000	0.0000	0.0000	0.0000
0.1235	1242.7	823.9	0.0727	0.0013	0.0346	-0.0142	-6.7115
0.2500	1244.8	846.2	0.1269	0.0027	0.0614	-0.0262	-11.9003
0.3476	1248.0	863.3	0.1497	0.0035	0.0738	-0.0326	-14.4451
0.4549	1252.9	884.8	0.1569	0.0038	0.0793	-0.0366	-15.7968
0.5645	1259.4	907.9	0.1472	0.0036	0.0767	-0.0371	-15.6265
0.6542	1266.1	927.8	0.1275	0.0031	0.0686	-0.0347	-14.2603
0.7446	1274.0	949.0	0.0981	0.0023	0.0549	-0.0293	-11.7061
0.8342	1282.6	971.4	0.0617	0.0014	0.0365	-0.0210	-8.0678
0.9228	1292.4	995.0	0.0243	0.0005	0.0159	-0.0103	-3.7274
1.0000	1300.5	1015.5	0.0000	0.0000	0.0000	0.0000	0.0000

The excess thermo acoustic parameters of the mixtures are influenced by three main types of contributions, viz., (i) due to non specific Van der Waals type forces; (ii) due to hydrogen bonding dipole-dipole, and donor-acceptor interaction between unlike molecules; (iii) due to the fitting of smaller molecules into the voids created by the bigger molecules. The first effect leads to contraction in volume hence leads to negative contribution towards u^E and positive contribution towards ΔK_s, where as the second effect leads to negative contribution towards ΔK_s and positive contribution towards u^E. For the present liquid mixture, the results of the deviations in isentropic compressibility ΔK_s plotted in fig-1 are positive at all temperatures studied. The positive values of ΔK_s suggest that the mixture is more compressible than the corresponding ideal mixture. The strength of the interactions between component molecules decreases when excess values tend to become increasingly positive. The same is well supported by excess intermolecular free length L_f^E presented in fig-2. It is observed that L_f^E values are positive for the entire mole fraction range, for all the three temperatures studied. The positive values of L_f^E shows week interactions are present among the molecules of the mixture. This result is just alike to the studies reported by srinivasu et al. [26-27].

In general the positive excess values of Z^E suggest that there exist strong molecular interactions between the molecules of the mixture[28]. In the present study the excess values of Z^E which are plotted in fig -3 are all negative in the liquid systems over the entire composition. This conforms weak molecular interactions exists between the components of the mixture

Further the results of uE plotted in fig -4 shows negative values at all the temperatures studied. This is due to non specific Van der Waals type forces, exits among 1,4dioxane and 1-pentanol. It is contrary to the reports made by srinivasu et al.[27] in their binary studies on quinoline with m-cresol.

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Table 3 - Parameters (a_i) and standard deviations σ (Y) for the Redlich–Kister equations

Property	T (K)	a_0	a_1	a_2	a_3	a_4	σ (10^2)
	298.15	0.5881	0.1803	-0.0724	-0.0611	-0.0910	0.3778
ΔK_s (10^{-10} m^2N^{-1})	303.15	0.5990	0.1542	0.1079	0.0274	-0.4140	0.5014
	308.15	0.6194	0.1524	-0.0615	0.0476	-0.1486	0.2430
	298.15	0.0139	0.0020	-0.0031	0.0005	-0.0075	0.0300
V_m^E (m^3 mol^{-1})	303.15	0.0144	0.0020	-0.0034	0.0010	-0.0068	0.0303
	308.15	0.0150	0.0024	-0.0050	0.0000	-0.0059	0.0343
	298.15	0.3112	0.0455	-0.0294	-0.0181	-0.0375	0.1474
L_f^E (10^{-11} m)	303.15	0.3122	0.0347	0.0464	0.0165	-0.1747	0.1994
	308.15	0.3169	0.0338	-0.0203	0.0258	-0.0692	0.0967
	298.15	-0.1613	0.0168	0.0035	-0.0001	0.0178	0.0465
Z^E (10^6 $kgm^{-2}s^{-1}$)	303.15	-0.1545	0.0181	-0.0156	-0.0086	0.0525	0.0587
	308.15	-0.1490	0.0171	0.0025	-0.0094	0.0234	0.0371
	298.15	-70.3169	-3.1928	4.1178	4.6591	4.8571	18.0110
U^E (ms^{-1})	303.15	-66.4616	-0.1839	-14.8127	-5.0176	38.6842	30.5100
	308.15	-63.6781	-0.4551	2.2635	-6.3786	10.6947	9.6991

CONCLUSION

From the experimental values of ultrasonic velocity and density we have calculated the excess parameters in the binary liquid mixture of 1,4-dioxane with 1-pentanol at three temperatures each 5K over the entire range of composition it is observed that there exists a weak molecular interaction between the unlike molecules in the binary liquid mixture.

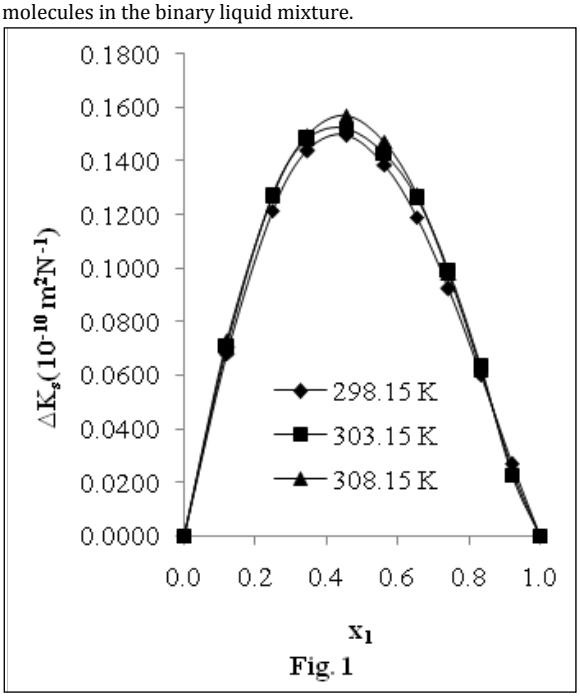

Fig. 1

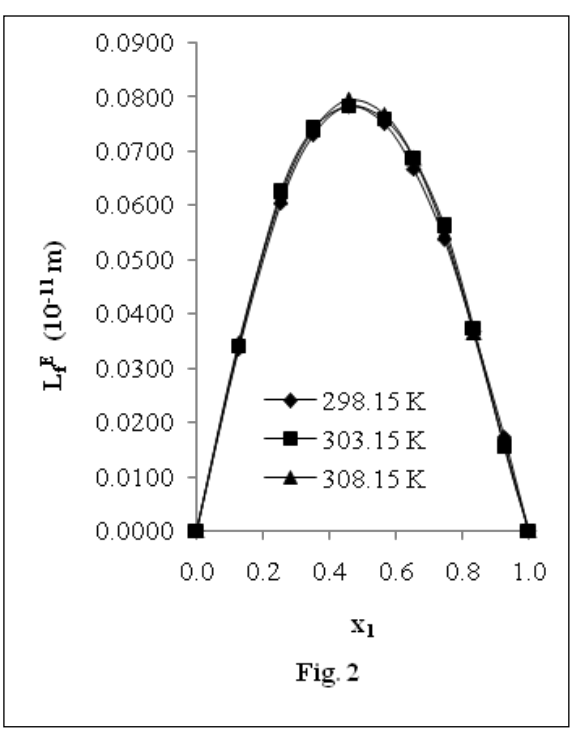

Fig. 2

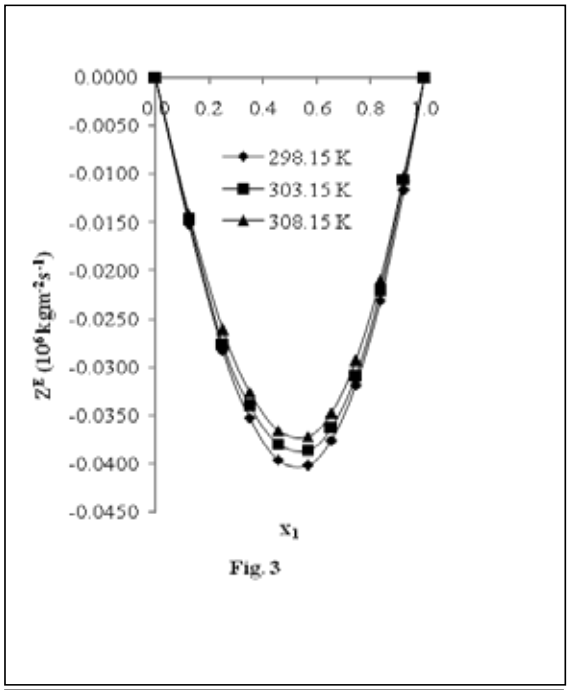

Fig. 3

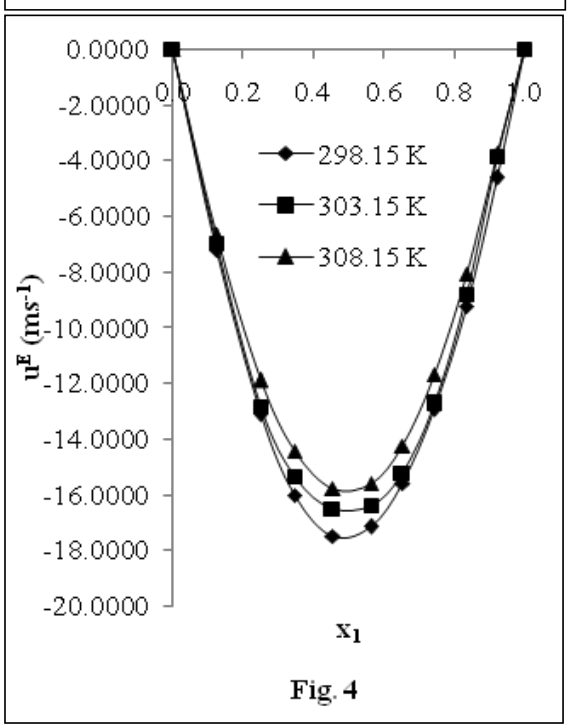

Fig. 4

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