

Ultrasonic study of molecular interaction in binary liquid mixtures at 30°C

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Abstract. Densities ρ and ultrasonic speeds u of the binary mixtures of tetrahydrofuran (THF) with 1-butanol and tert-butanol, at 30°C, over the entire composition range were measured. From these data isentropic compressibility, K_s , intermolecular free length L_f , relative association R_A , acoustic impedance Z , molar sound speed R_m , deviations in isentropic compressibility ΔK_s , and excess volume V^E were calculated. The variation of these parameters with composition of the mixture helps us in understanding the nature and extent of interaction between unlike molecules in the mixtures. Further, theoretical values of ultrasonic speed were evaluated using theories and empirical relations. The relative merits of these theories and relations were discussed.

Keywords. Ultrasonic speed; intermolecular interactions; binary mixtures; theoretical evaluation.

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1. Introduction

Mixed solvents, rather than pure solvents, find practical applications in most chemical processes, their properties are less known [1,2]. Derived parameters from ultrasonic speed measurement and the corresponding excess functions provide qualitative information regarding the nature and strength of interactions in liquid mixtures [3,4]. In continuation of our earlier studies on mixed solvents [5,6], we report the results of our study on the binary mixtures of tetrahydrofuran (THF) with 1-butanol and tert-butanol, covering the entire composition range, at 30°C. THF is commonly used for preparation of the Grignard reagents, the most useful and versatile reagents known to the organic chemists. The use of alcohols in preparing a number of compounds like aldehydes, ketones, acids, alkenes, alkanes, alkynes, halides, etc. are well-known. Thus, THF+1-butanol/tert-butanol mixed solvents would enable us to have a large number of solvents, with appropriate physico-chemical properties, which can be used for a particular chemical process. Moreover, literature survey indicates that no ultrasonic study on these binary systems has been reported. Therefore, the present study was undertaken in order to have a deeper understanding of the intermolecular interaction between the components of the above binary mixtures.

From the experimental values of ρ and u , the values of $K_s, L_f, R_A, Z, R_m, \Delta K_s$ and V^E were calculated. The changes in these parameters with composition of the mixtures are

helpful in understanding the nature and extent of the interaction between unlike molecules in the mixture. Further, the ultrasonic speeds for all the mixtures were theoretically calculated by using free length theory (FLT) [7], collision factor theory (CFT) [8], Nomoto's relation [9] and Van Dael and Vangeel's ideal mixing relation [10]. The relative merits of these theories and relations were examined by comparing the theoretical values of ultrasonic speed with the experimental values.

2. Experimental

THF (Qualigens fine chemicals, HPLC grade, 99.8%) was used without further purification, except drying over molecular sieves. 1-Butanol and tert-butanol (s.d. fine chemicals, AR grade, 99.5 and 99.0%, respectively) were purified by standard procedure [11]. The mixtures were prepared by weight and were kept in special airtight bottles. The weighings were done on an Afcoset-ER-120A electronic balance with a precision of ± 0.1 mg.

The densities of pure liquids and binary mixtures were measured using a single-capillary pycnometer (made of Borosil glass) of bulb capacity $8 \times 10^{-3} \text{ dm}^3$. The marks on the stem were calibrated with triple distilled water. The ultrasonic speeds in pure liquids and in their binary mixtures were measured using single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, Model: M-82) operating at 2 MHz by the method described elsewhere [5,6]. The measured densities and ultrasonic speeds of pure liquids compared well with the literature values. The experimental values of densities of pure THF, 1-butanol and tert-butanol obtained were 876.4, 801.7 and 776.2 kg m^{-3} , respectively, at 30°C (corresponding literature values are: 876.3 [12], 802.1 [13] and 776.23 [13]/776.16 [14] kg m^{-3} , respectively). The observed values of ultrasonic speeds in THF, 1-butanol and tert-butanol were 1256.3, 1228.0 and 1104.8 m s^{-1} , respectively, at 30°C (literature values are: 1254.0 [12], 1232.0 [13] and 1104.0 [13] m s^{-1} , respectively). The temperature of the samples was maintained at $30 \pm 0.05^\circ\text{C}$ in an electronically controlled thermostatic water bath.

3. Results and discussion

The experimental values of ρ and u were used to calculate K_s, L_f, R_A, Z and R_m using the standard relations given in refs [5,6]. The values of $\rho, u, K_s, L_f, R_A, Z$ and R_m as functions of mole fraction x of THF at 30°C are listed in table 1. It is observed (table 1) that the values of u, R_A , and Z increase, while those of K_s, L_f , and R_m decrease with mole fraction of THF for both the systems under study. The variation of u through the mixture depends on the increase or decrease of L_f . In general, u and L_f have been reported to vary inverse of each other with composition of the mixture [5,6,15], as in the present systems. The non-linear decrease of K_s and L_f , and also an increase in R_A and Z (table 1) with the mole fraction of THF in both the systems indicates the presence of molecular interaction [16] between unlike molecules.

The strength of interaction between the component molecules is well-reflected in the deviations in isentropic compressibilities ΔK_s and excess volumes V^E . These parameters were calculated using the relation

$$Y^E = Y - [(1-x)Y_1 + xY_2] \quad (1)$$

Table 1. Densities ρ , ultrasonic speeds u , isentropic compressibilities K_s , intermolecular free lengths L_f , relative associations R_A , acoustic impedances Z and molar sound speeds R_m of binary mixtures of THF with 1-butanol and tert-butanol at 30°C.

x (THF)	ρ (kg m ⁻³)	u (m s ⁻¹)	K_s (10 ⁻¹⁰ m ² N ⁻¹)	L_f (10 ⁻¹¹ m)	R_A	Z (10 ⁶ kg m ⁻² s ⁻¹)	R_m [10 ⁻⁴ m ³ mol ⁻¹ (m s ⁻¹)]
THF+1-Butanol							
0.0000	801.7	1228.0	8.2716	5.9694	1.0000	0.9845	9.9005
0.0996	806.9	1230.3	8.1876	5.9390	1.0059	0.9927	9.8162
0.1993	812.9	1232.3	8.1008	5.9075	1.0128	1.0017	9.7226
0.2990	819.5	1234.0	8.0135	5.8755	1.0205	1.0113	9.6225
0.3989	826.1	1236.3	7.9199	5.8411	1.0281	1.0213	9.5255
0.4989	833.2	1238.3	7.8271	5.8068	1.0364	1.0318	9.4235
0.5989	840.8	1240.6	7.7276	5.7698	1.0452	1.0431	9.3184
0.6990	848.5	1244.0	7.6157	5.7278	1.0538	1.0555	9.2168
0.7993	856.8	1248.2	7.4912	5.6808	1.0629	1.0695	9.1124
0.8996	866.1	1252.6	7.3588	5.6304	1.0732	1.0849	9.0001
1.0000	876.4	1256.3	7.2295	5.5807	1.0849	1.1010	8.8782
THF+tert-Butanol							
0.0000	776.2	1104.8	10.5550	6.7432	1.0000	0.8575	9.8716
0.1150	781.5	1120.8	10.1863	6.6243	1.0020	0.8759	9.8211
0.2262	787.3	1135.4	9.8526	6.5150	1.0051	0.8939	9.7610
0.3338	795.1	1149.8	9.5134	6.4018	1.0108	0.9142	9.6777
0.4380	804.5	1164.0	9.1742	6.2867	1.0186	0.9364	9.5764
0.5390	814.1	1178.0	8.8522	6.1754	1.0266	0.9590	9.4754
0.6368	824.6	1192.6	8.5264	6.0607	1.0356	0.9834	9.3675
0.7317	837.2	1207.4	8.1935	5.9411	1.0471	1.0108	9.2403
0.8238	849.5	1222.9	7.8718	5.8234	1.0580	1.0388	9.1224
0.9132	861.6	1238.6	7.5654	5.7089	1.0685	1.0672	9.0098
1.0000	876.4	1256.3	7.2295	5.5807	1.0817	1.1010	8.8782

where Y^E is ΔK_s or V^E , x the mole fraction of THF (volume fraction ϕ is used in case of ΔK_s) and subscripts 1 and 2 denote 1-butanol/tert-butanol and THF, respectively. The values of ΔK_s and V^E for each mixture have been least-squares fitted to Redlich–Kister [17] type polynomial equation

$$Y^E = x(1-x) \sum_{i=0}^4 A_i (1-2x)^i \quad (2)$$

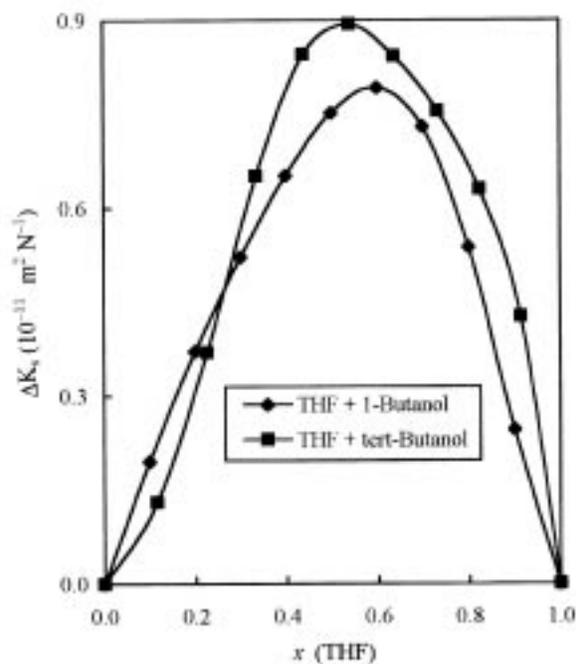
The values of coefficients A_i and corresponding standard deviations $\sigma(Y^E)$ are calculated using the relation

$$\sigma(Y^E) = \left[\sum (Y_{\text{expt}}^E - Y_{\text{cal}}^E)^2 / (m-n) \right]^{1/2}, \quad (3)$$

where m is the number of experimental data points and n the number of coefficients considered ($n = 5$ in the present calculation) in eq. (2), are listed in table 2. Y_{cal}^E has been obtained from eq. (2) using the best-fit values of A_i . The variations in ΔK_s and V^E with mole fraction x of THF are shown graphically in figures 1 and 2.

Table 2. Coefficients A_i of eq. (2) along with standard deviations $\sigma(Y^E)$ of binary mixtures.

Properties	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
THF+1-Butanol						
ΔK_s ($10^{-11} \text{ m}^2 \text{ N}^{-1}$)	3.0118	-1.5146	0.0165	1.8429	-1.3820	0.0091
V^E ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)	1.4890	-0.2621	0.4628	0.2144	0.5306	0.0097
THF+tert-Butanol						
ΔK_s ($10^{-11} \text{ m}^2 \text{ N}^{-1}$)	3.5660	-0.6269	-3.3230	3.3451	4.8431	0.0234
V^E ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)	5.5728	1.1369	-2.1546	-1.8618	3.6803	0.0058

**Figure 1.** Variation of deviations in isentropic compressibility ΔK_s with mole fraction of tetrahydrofuran for the binary mixtures at 30°C .

Figures 1 and 2 show that ΔK_s and V^E are positive for both the systems (THF+1-butanol/tert-butanol) under study over the whole composition range of THF. In general, ΔK_s and V^E can be considered as arising from two types of interactions between the component molecules: (i) physical interaction consisting mainly of dispersion forces or weak dipole-dipole interaction and making a positive contribution towards ΔK_s and V^E and (ii) chemical or specific interaction which include charge-transfer forces, forming of H-bonds

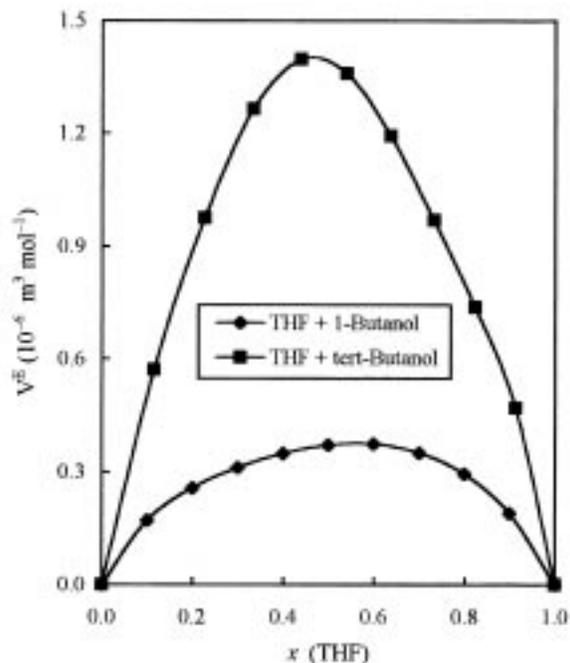


Figure 2. Variation of excess volume V^E with mole fraction of tetrahydrofuran for the binary mixtures at 30°C.

and other complex forming interactions, resulting in negative values of ΔK_s and V^E . It is well-known that alkanols are protic and associated through hydrogen bond in pure state. The mixing of THF, an aprotic liquid, with alkanols (1-butanol and tert-butanol) tends to break the associates present in the alkanol molecules with subsequent increase in ΔK_s and V^E . On the other hand, there is the possibility of H-bonding between oxygen atom of THF (with its lone pair of electrons) and the hydrogen atom of $-OH$ group of alkanols. The observed positive values of ΔK_s and V^E over the whole composition range (figures 1 and 2) suggest that the effect due to the rupture of hydrogen bonded chains of alkanols dominates over that of hydrogen bond between the unlike molecules, making ΔK_s and V^E values positive. Moreover, since the molecular sizes of THF (molar volume = $8.228 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$), 1-butanol (molar volume = $9.245 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) and tert-butanol (molar volume = $9.549 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) are not much different, it seems that the component molecules do not pack well into each other's structure. This results in expansion in volume and hence positive ΔK_s and V^E values. Fort and Moore [16] suggested that the liquids of almost equal molecular size usually mix with positive excess compressibilities and volumes. Similar trends in ΔK_s and V^E were also reported by others for methanol + 1-butanol [18] and toluene + 1-butanol/tert-butanol [19] binary mixtures.

The presence of three methyl groups at 3°-carbon atom in tert-butanol, as compared to one butyl group in 1-butanol, create more crowding, hence, more steric hindrance for the formation of H-bonds between $-OH$ group of tert-butanol and THF. As a result, relatively weaker H-bonding is expected between tert-butanol and THF molecules, than that between

Table 3. Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's and Van Dael and Vangeel's ideal mixing relation and percentage error in calculated values for the binary mixtures.

<i>x</i> (THF)	<i>u</i> (m s ⁻¹)				% error			
	FLT	CFT	NOM	VD	FLT	CFT	NOM	VD
THF+ 1-Butanol								
0.0000	1228.0	1228.0	1228.0	1228.0	0.00	0.00	0.00	0.00
0.0996	1221.4	1228.5	1230.5	1230.8	0.73	0.14	0.02	0.04
0.1993	1218.6	1230.1	1233.1	1233.5	1.11	0.18	0.06	0.10
0.2990	1218.6	1232.3	1235.7	1236.3	1.25	0.14	0.14	0.19
0.3989	1217.7	1234.3	1238.5	1239.1	1.50	0.16	0.17	0.23
0.4989	1218.9	1236.8	1241.2	1242.0	1.57	0.12	0.24	0.30
0.5989	1222.1	1239.8	1244.1	1244.8	1.49	0.07	0.28	0.34
0.6990	1225.0	1242.6	1247.0	1247.6	1.53	0.11	0.24	0.29
0.7993	1230.5	1246.0	1250.0	1250.5	1.42	0.17	0.15	0.19
0.8996	1240.9	1250.6	1253.1	1253.4	0.94	0.16	0.04	0.06
1.0000	1256.3	1256.3	1256.3	1256.3	0.00	0.00	0.00	0.00
THF+ tert-Butanol								
0.0000	1104.8	1104.8	1104.8	1104.8	0.00	0.00	0.00	0.00
0.1150	1095.2	1115.4	1119.5	1119.8	2.28	0.48	0.12	0.09
0.2262	1088.0	1126.1	1134.2	1134.8	4.18	0.82	0.10	0.05
0.3338	1088.9	1139.2	1149.1	1149.9	5.30	0.93	0.06	0.00
0.4380	1097.0	1154.0	1164.1	1165.0	5.76	0.86	0.00	0.08
0.5390	1106.8	1168.6	1179.2	1180.1	6.04	0.80	0.10	0.18
0.6368	1122.1	1184.2	1194.4	1195.2	5.91	0.71	0.15	0.22
0.7317	1148.7	1202.3	1209.7	1210.4	4.86	0.42	0.19	0.25
0.8238	1176.5	1219.5	1225.1	1225.7	3.79	0.28	0.18	0.23
0.9132	1206.8	1236.2	1240.7	1241.0	2.57	0.19	0.17	0.19
1.0000	1256.3	1256.3	1256.3	1256.3	0.00	0.00	0.00	0.00

1-butanol and THF molecules, yielding more positive ΔK_s and V^E values in the former system.

The theoretical values of ultrasonic speeds in all the three binary mixtures were calculated using the theoretical and empirical relations [7–10]. The details of derivations and terms used may be obtained from refs [7–10,20]. The theoretical values of ultrasonic speeds and percentage error in the calculated values, are presented in table 3 for comparison. It is observed that out of the four theories and relations discussed above, the Nomoto's relation provides best results for ultrasonic speeds of the systems under study. Thus, the linearity of molar sound speed and additivity of molar volumes, as suggested by Nomoto [9] have been truly observed in the present systems. The applicability of Nomoto's relation in predicting experimental ultrasonic speeds for polar-polar mixtures has also been emphasized by others [20,21]. Also, the values predicted by FLT show maximum deviations for both the systems. This is in good agreement with the conclusions drawn by others [7,20] that large deviations from FLT are observed for mixtures containing self-associated liquid(s), as alkanols in the present systems.

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