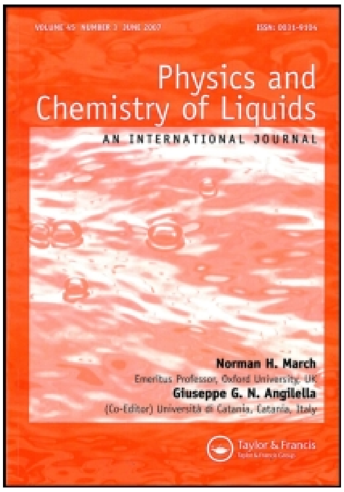

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EXCESS VOLUMES AND ULTRASONIC STUDIES OF TRIETHYLAMINE WITH SUBSTITUTED BENZENES AT 308.15 K

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Molar excess volumes, (V^E) and the ultrasonic sound velocity (U) of binary mixtures of triethylamine with ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene have been measured at 308.15 K. The speed of sound data were used to compute isentropic compressibilities (K_s) and deviation in isentropic compressibilities (ΔK_s). V^E values and ΔK_s values are negative in all the systems, over the entire range of composition. The results are interpreted on the basis of intermolecular interactions between unlike molecules.

Keywords: Binary mixtures; isentropic compressibilities; triethylamine; substituted benzenes; dipolar interactions

1. INTRODUCTION

In recent years there has been considerable progress in the experimental investigation of the excess thermodynamic properties of liquid mixtures. Excess thermodynamic functions have been used as a qualitative guide to predict the extent of complex formation in binary liquid mixtures. As part of our continuing study on thermodynamic properties of non-electrolyte solutions [1–3], in this work we report molar excess volumes and speed of sound and related properties of triethylamine with ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene at 308.15 K. We have undertaken this work to investigate the effect of aromatization and the influence of different substituents in the aromatic ring on V^E and ΔK_s values.

2. EXPERIMENTAL

All the chemicals used were of analytical grade. Triethylamine and ehtylbenzene were purified by the methods described by Venkatesu and Rao [4]. Chlorobenzene, bromobenzene and nitrobenzene were further purified by the methods described by Ramadevi and Rao [5]. The purities of the samples were checked by comparing the measured densities of the compounds with those reported in the literature [6,7]. The purities of the samples were further confirmed by GLC single sharp peaks. The measured densities and ultrasonic sound velocities which reported in the literature are listed in Table I.

Molar excess volumes were measured directly using the dilatometer technique described by Rao and Naidu [8]. The molar excess volumes are accurate to ± 0.003 $cm^3. mol^{-1}$. The sound velocities were measured by a single crystal ultrasonic interferometer at 4 MHz frequency at 308.15 K. These were accurate to 0.02%. Densities of pure components were measured with a bicapillary type pycnometer, which offers an accuracy of 2 parts in 10^5. In the case of mixtures, the density data were obtained from measured excess volumes. A thermostatically controlled, well-stirred water bath with temperature controlled to 308.15 ± 0.01 K was used for all the measurements.

3. RESULTS AND DISCUSSION

The V^E data at 308.15 K for all the mixtures are reported in Table II and are graphically represented in Figure 1. The isentropic compres-

TABLE I Ultrasonic sound velocities and (U) and Densities (ρ) of Pure Components at 303.15 K

Component	*U/m.s−1*		*$\rho/(g.cm^{-3})$*	
	Exptl.	*Lit.(9,10)*	*Exptl.*	*Lit.(6,7)*
triethylamine	1118*	1120*	0.718 96	0.718 99
ethylbenzene	1299	1297	0.858 08	0.858 10
chlorobenzene	1249	1248	1.095 47	1.095 50
bromobenzene	1137	1136	1.481 48	1.481 50
nitrobenzene	1438	1440	1.193 38	1.193 41

*298.15K

TABLE II Molar excess volumes (V^E) for the binary mixtures of triethylamine (1) with substituted benzenes (2) at 308.15 K

x_1	V^E $cm^3.mol^{-1}$	x_1	V^E $cm^3.mol^{-1}$
	Triethylamine (1) + Ethylbenzene (2)		
0.1366	−0.161	0.6297	−0.300
0.2214	−0.235	0.7515	−0.254
0.2775	−0.269	0.8390	−0.183
0.4664	−0.321	0.9010	−0.127
0.5313	−0.319		
	Triethylamine (1) + Chlorobenzene (2)		
0.1358	−0.415	0.5551	−0.891
0.2522	−0.666	0.6836	−0.793
0.3491	−0.806	0.7663	−0.667
0.4311	−0.872	0.8437	−0.499
0.4981	−0.896		
	Triethylamine (1) + Bromobenzene (2)		
0.0810	−0.340	0.5132	−0.992
0.1512	−0.570	0.6098	−0.949
0.2441	−0.786	0.7213	−0.815
0.3128	−0.887	0.8224	−0.609
0.4338	−0.984	0.8936	−0.404
	Triethylamine (1) + Nitrobenzene (2)		
0.0729	−0.389	0.5138	−0.978
0.1543	−0.667	0.6170	−0.942
0.2241	−0.819	0.7183	−0.860
0.3186	−0.926	0.8063	−0.723
0.4281	−0.971	0.8965	−0.476

sibility (K_s) was calculated using the relation:

$$K_s = U^{-2}\rho^{-1} \tag{1}$$

where U and ρ denote the speed of sound and density respectively. The density of the binary mixtures was computed using the relation:

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V + V^E} \tag{2}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molar masses of pure components. V is the ideal molar volume and V^E the molar excess volume of the mixture.

Deviation in isentropic compressibility (ΔK_s) was calculated using the expression

$$\Delta K_s = K_s - \phi_1 K_{s1} - \phi_2 K_{s2} \tag{3}$$

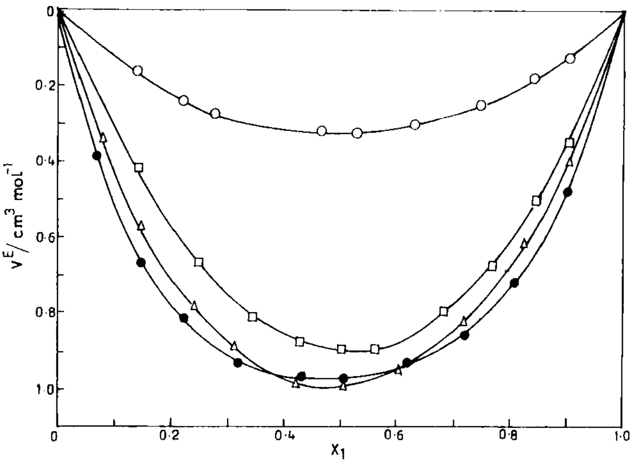

FIGURE 1 Excess volumes (V^E) for triethylamine + ethylbenzene (○), + chlorobenzene (□), + bromobenzene (△) and + nitrobenzene (●) at 308.15 K.

where ϕ_1, ϕ_2 and K_{s1}, K_{s2} are volume fractions and isentropic compressibilities of pure components respectively. The values of ρ, U, K_s, and ΔK_s are included in Table III. The variation of ΔK_s with volume fraction is graphically presented in Figure 2.

The composition dependence of the V^E and ΔK_S values were fitted by the method of least squares using the polynomial form,

$$Z = x_1 x_2 \sum_{i=0}^{2} a_i (x_1 - x_2)^i \tag{4}$$

where if Z is the excess volume, the composition is mole fraction, and if Z is the deviation in isentropic compressibility, the volume fraction is the composition variable. a_i's are the adjustable parameters obtained by the least squares method and are listed in Tables IV and V along with the standard deviation.

The data included in Table II show that V^E values are negative in mixtures of triethylamine with ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene at 308.15 K. The excess volumes are possibly influenced by two effects: (1) expansion in volume because of the loss of dipolar association, and the difference in size and shape of

TABLE III Volume fraction (ϕ_1) of triethylamine, ρ, U, K_s and ΔK_s for triethylamine (1) + Substituted benzenes (2) at 308.15 K

ϕ_1	ρ $g.cm^{-3}$	U_{exp} $m.s^{-1}$	K_s TPa^{-1}	ΔK_s TPa^{-1}
Triethylamine (1) + Ethylbenzene (2)				
0.0000	0.85388	1278	717	–
0.1527	0.83364	1248	770	−24
0.2447	0.82126	1225	811	−30
0.3044	0.81312	1212	837	−34
0.4989	0.78619	1172	926	−43
0.5636	0.77712	1159	958	−44
0.6596	0.76357	1140	1008	−43
0.7750	0.74715	1119	1069	−40
0.8558	0.73547	1103	1118	−32
0.9120	0.72732	1093	1151	−27
1.0000	0.71439	1070	1223	–
Triethylamine (1) + Chlorobenzene (2)				
0.0000	1.09006	1235	601	–
0.1773	1.02738	1212	663	−48
0.3163	0.97700	1189	724	−74
0.4239	0.93731	1171	778	−87
0.5097	0.90518	1157	825	−93
0.5765	0.87993	1144	868	−92
0.6312	0.85908	1135	904	−90
0.7477	0.81416	1117	984	−82
0.8181	0.78668	1105	1041	−69
0.8810	0.76189	1095	1095	−54
1.0000	0.71439	1070	1223	–
Triethylamine (1) + Bromobenzene (2)				
0.0000	1.47481	1121	540	–
0.1050	1.39935	1120	569	−43
0.1916	1.33594	1116	601	−70
0.3005	1.25487	1108	643	−96
0.3772	1.19704	1102	688	−110
0.5048	1.09986	1095	758	−127
0.5838	1.03918	1091	808	−131
0.6752	0.96854	1086	875	−126
0.7749	0.89104	1081	960	−109
0.8603	0.82429	1078	1044	−84
0.9179	0.77914	1075	1111	−56
1.0000	0.71439	1070	1223	–
Triethylamine (1) + Nitrobenzene (2)				
0.0000	1.18847	1423	416	–
0.0971	1.14664	1388	453	−41
0.1997	1.10052	1350	499	−78
0.2831	1.06200	1320	540	−104
0.3900	1.01167	1279	604	−127
0.5058	0.95642	1235	686	−138
0.5910	0.91556	1206	751	−142
0.6878	0.86885	1174	835	−136
0.7771	0.82548	1144	926	−117
0.8506	0.78949	1120	1010	−92
0.9221	0.75391	1097	1102	−58
1.0000	0.71439	1070	1223	–

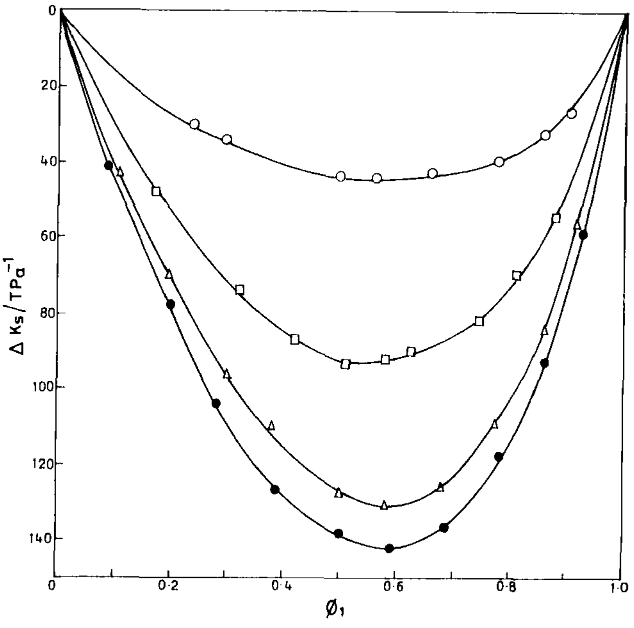

FIGURE 2 Deviation in isentropic compressibilities (ΔK_s) for triethylamine + ethylbenzene (○), + chlorobenzene (□), + bromobenzene (△) and + nitrobenzene (●) at 308.15 K.

TABLE IV Parameters of Eq.4 and standard deviation $\sigma(V^E)$ at 308.15 K

System	a_0	a_1 $cm^3.mol^{-1}$	a_2	$\sigma(V^E)$
triethylamine (1) + ethylbenzene (2)	− 1.2894	− 0.0024	− 0.1864	0.003
triethylamine (1) + chlorobenzene (2)	− 3.5832	− 0.1751	− 0.1575	0.001
triethylamine (1) + bromobenzene (2)	− 3.9856	0.1627	− 0.6586	0.003
triethylamine (1) + nitrobenzene (2)	3.9046	0.2163	− 2.2521	0.003

the component molecules. (2) contraction in volume because of dipole–dipole and dipole-induced dipole interactions. The actual value of V^E would depend upon the relative strength of the two opposing effects. The experimental results suggest that the latter effect is dominant in the mixtures. The V^E values for equimolar mixtures are found to vary in the following order.

TABLE V Parameters of Eq.4 and standard deviation $\sigma(\Delta K_s)$ at 308.15 K

System	b_0	b_1 TPa^{-1}	b_2	$\sigma(\Delta K_s)$
triethylamine (1) + ethylbenzene (2)	−161.4	−63.9	−143.1	2
triethylamine (1) + chlorobenzene (2)	−361.9	−106.5	−102.8	2
triethylamine (1) + bromobenzene (2)	−501.8	−167.1	−140.9	1
triethylamine (1) + nitrobenzene (2)	−554.7	−180.6	−110.7	2

ethylbenzene > chlorobenzene > bromobenzene ≃ nitrobenzene

Figure 2 indicates that deviations in isentropic compressibilities are negative in all systems. The negative deviations is attributed to dipolar interactions between unlike molecules which lead to increase in free length and decrease in sound velocity. The algebraic values of ΔK_s at equimolar mixtures are found to vary in the following order:

ethylbenzene > chlorobenzene > bromobenzene > nitrobenzene

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