Speeds of Sound, Isentropic Compressibilities, and Excess Volumes of Binary Mixtures. 1. Tri-*n*-alkylamines with Cyclohexane and Benzene

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Isentropic compressibilities K_S, excess isentropic compressibilities K_S^E, and excess volumes V^E have been determined from the densities and speeds of sound for eight binary mixtures of (tri-*n*-butylamine, tri-*n*-hexylamine, tri-*n*-octylamine, or tri-*n*-dodecylamine + cyclohexane or benzene) at 303.15 K. The values of V^E and K_S^E are more positive for mixtures with benzene than for the mixtures with cyclohexane. The experimental results have been analyzed by the Prigogine–Flory–Patterson theory.

Introduction

The effect of molecular size and shape or molecular association of alkylamines on thermodynamic properties of their mixtures with nonpolar solvents has been investigated by several researchers (*1–14*). We are engaged in a systematic study of the thermodynamic, transport, and acoustic properties of binary liquid mixtures containing alkylamines (*15–20*). In earlier papers (*15–17*), we reported viscosities of binary mixtures of alkylamines in cyclohexane and benzene and discussed the deviations of viscosities from linear dependence on mole fraction as a function of the association and size of the alkylamines. To achieve more information about molecular interactions and to examine the Prigogine–Flory–Patterson theory (*21–24*), isentropic compressibilities K_S, excess isentropic compressibilities K_S^E, and excess volumes V^E were determined from the measurements of densities ρ and speeds of sound U for eight binary mixtures of tri-*n*-butylamine ($(C_4H_9)_3N$), tri-*n*-hexylamine ($(C_6H_{13})_3N$, tri-*n*-octylamine ($(C_8H_{17})_3N$), and tri-*n*-dodecylamine ($(C_{12}H_{25})_3N$) with cyclohexane (C_6H_{12}) and benzene (C_6H_6) at 303.15 K.

Experimental Section

Samples of cyclohexane and all tri-*n*-alkylamines were obtained from Fluka AG with purities of 99 mol % or greater, and AR benzene was from BDH. C_6H_{12} was dried over molecular sieves (type 4A) and fractionally distilled twice over sodium. C_6H_6 was shaken with H_2SO_4 to remove traces of thiophene (*25*) and washed with $NaHCO_3$ and distilled water. It was dried over sodium prior to distillation. $(C_4H_9)_3N$ was kept over sodium and fractionally distilled three times. $(C_6H_{13})_3N$, $(C_8H_{17})_3N$, and $(C_{12}H_{25})_3N$ were dried over molecular sieves (type 4A) and used. The purities of the samples were checked with gas–liquid chromatography, and from the measurements of densities and refractive indices. Table 1 shows the densities and refractive indices at 298.15 K of all the liquids used in this work as well as accepted literature values (*2–5, 25–28*). The estimated purities of C_6H_{12}, C_6H_6, $(C_4H_9)_3N$, $(C_6H_{13})_3N$, $(C_8H_{17})_3N$, and $(C_{12}H_{25})_3$ are 99.8, 99.8, 99.5, 99.2, 99.5 and 99.2 mol %, respectively.

Table 1. Densities and Refractive Indices at 298.15 K and Thermal Expansion Coefficients and Isobaric Molar Heat Capacities of Pure Liquids at 303.15 K

	$\rho/(kg\cdot m^{-3})$		n_D		$\alpha/$	$C_P/$
liquid	exptl	lit.	exptl	lit.	kK^{-1}	$(J\cdot K^{-1}\cdot mol^{-1})$
C_6H_6	873.6	873.6[a]	1.4979	1.497 92[a]	1.233[b]	136.8[a]
C_6H_{12}	773.9	773.89[a]	1.4236	1.423 54[a]	1.233[b]	158.1[a]
$(C_4H_9)_3N$	774.2	773.78[c] 774.0[d] 774.3[a]	1.4267	1.426 5[e] 1.426 8[d]	0.990[f]	374.0[a]
$(C_6H_{13})_3N$	796.4	796.4[g]	1.4399	1.439 8[e] 1.440 4[g]	0.879[f]	560[h]
$(C_8H_{17})_3N$	808.3	807.4[i] 808.6[j] 809.8[d]	1.4474	1.447 6[e] 1.447 8[d]	0.838[f]	692[h]
$(C_{12}H_{25})_3N$	821.4	820.7[e] 821.15[k]	1.4567	1.456 8[g]	0.790[f]	1071[h]

[a] Reference 25. [b] Reference 35. [c] Reference 2. [d] Reference 4. [e] Reference 27. [f] Derived from densities in ref 36. [g] Reference 26. [h] Estimated by Missenard's group contribution method, ref 37. [i] Reference 28. [j] Reference 3. [k] Reference 5.

Table 2. Properties of Cyclohexane (1) + Tri-*n*-Alkylamine (2) at 303.15 K

x_1	$U/(m\cdot s^{-1})$	K_S/TPa^{-1}	K_S^E/TPa^{-1}	$V^E/(cm^3\cdot mol^{-1})$
	Cyclohexane (1) + Tri-*n*-butylamine (2)			
0.0000	1229	859		
0.1133	1228	861	3	0.092
0.2987	1225	866	4	0.173
0.4020	1225	866	4	0.231
0.4990	1223	869	6	0.274
0.5952	1221	872	8	0.303
0.7042	1221	871	8	0.306
0.8018	1222	870	6	0.268
0.9005	1225	867	5	0.173
1.0000	1230	859		
	Cyclohexane (1) + Tri-*n*-hexylamine (2)			
0.0000	1296	751		
0.0994	1292	756	0	0.104
0.2988	1283	770	1	0.244
0.5012	1271	788	2	0.360
0.5994	1265	797	1	0.404
0.6983	1257	810	1	0.419
0.8013	1250	822	−2	0.379
0.9005	1240	839	−1	0.253
1.0000	1230	859		
	Cyclohexane (1) + Tri-*n*-octylamine (2)			
0.0000	1353	678		
0.1179	1347	685	1	0.099
0.1582	1344	689	1	0.141
0.3086	1334	701	2	0.274
0.4099	1326	712	2	0.334
0.6074	1304	741	3	0.412
0.7022	1291	759	3	0.435
0.8023	1275	783	2	0.422
0.9020	1255	815	1	0.319
1.0000	1230	859		
	Cyclohexane (1) + Tri-*n*-dodecylamine (2)			
0.0000	1401	623		
0.2026	1388	635	−1	0.295
0.3989	1374	652	−1	0.522
0.5152	1362	666	−2	0.563
0.6218	1348	683	−3	0.661
0.8043	1307	735	−2	0.546
1.0000	1230	859		

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Table 3. Properties of Benzene (1) + Tri-*n*-Alkylamine (2) at 303.15 K

x_1	$U/(\mathrm{m \cdot s^{-1}})$	$K_S/\mathrm{TPa^{-1}}$	$K_S^E/\mathrm{TPa^{-1}}$	$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$
Benzene (1) + Tri-*n*-butylamine (2)				
0.0000	1229	859		
0.0987	1227	858	5	0.158
0.2044	1225	856	9	0.285
0.2999	1224	853	13	0.394
0.3993	1224	847	16	0.466
0.5014	1226	837	17	0.514
0.5987	1227	828	20	0.573
0.6972	1231	812	20	0.611
0.7984	1239	789	18	0.491
0.8916	1250	761	15	0.348
1.0000	1279	704		
Benzene (1) + Tri-*n*-hexylamine (2)				
0.0000	1296	751		
0.2976	1284	758	10	0.462
0.5002	1277	759	14	0.663
0.6958	1270	758	17	0.725
0.8987	1274	753	9	0.430
1.0000	1279	704		
Benzene (1) + Tri-*n*-octylamine (2)				
0.0000	1353	678		
0.3056	1332	696	13	0.546
0.5049	1320	705	17	0.782
0.7005	1305	714	20	0.922
0.8961	1291	713	10	0.616
1.0000	1279	704		
Benzene (1) + Tri-*n*-dodecylamine (2)				
0.0000	1401	623		
0.2217	1394	631	3	0.461
0.4154	1380	642	7	0.876
0.5191	1369	650	10	1.034
0.6278	1354	662	15	1.179
0.8091	1328	680	13	1.100
1.0000	1279	704		

The speeds of sound U in the pure liquids and the binary mixtures were measured with a single-crystal multifrequency ultrasonic interferometer (supplied by Mittal Enterprise, New Delhi). In the present work, a steel cell fitted with a quartz crystal of 2-MHz frequency was employed. Densities ρ were measured using a fine capillary single-stem calibrated pycnometer. The temperature was controlled to ±0.02 K, by water thermostats. The details of the apparatus and procedure have been described previously (*29–31*). The values of the speeds of sound U and densities ρ were reproducible to within ± 1.0 m $\mathrm{s^{-1}}$ and ± 0.1 kg $\mathrm{m^{-3}}$, respectively. The isentropic compressibilities K_S determined from the relation $K_S = 1/(U^2\rho)$ are believed to be reliable to within 1.0 $\mathrm{TPa^{-1}}$.

Results and Discussion

The speed of sound U, isentropic compressibility K_S, excess isentropic compressibility K_S^E, and excess volume V^E for the eight binary mixtures are given in Tables 2 and 3. K_S^E and V^E in each mixture were calculated from

$$Y^E = Y - Y^{id} \tag{1}$$

where Y is either K_S or V.

The V^{id} for an ideal mixture was calculated from the usual relation

$$V^{id} = \sum x_i V_i^\circ = \sum x_i M_i/\rho_i \tag{2}$$

while K_S^{id} for an ideal mixture was calculated from the relation recommended by Benson and Kiyohara (*32*), Tamura, Ohomuro, and Murakami (*33*), and Douheret, Moreau, and Viallard (*34*):

$$K_S^{id} = K_T^{id} - TV^{id}(\alpha^{id})^2/C_P^{id} \tag{3}$$

Here,

Table 4. Coefficients A_i and Standard Deviations S for Eqs 8 and 9 for the Binary Mixtures at 303.15 K

property	A_0	A_1	A_2	A_3	A_4	S
Cyclohexane (1) + Tri-*n*-Butylamine (2)						
$U/(\mathrm{m \cdot s^{-1}})$	1228.7	4.6	−64.9	61.5		0.7
$K_S/\mathrm{TPa^{-1}}$	859.7	−0.2	84.7	−81.4		1.0
$K_S^E/\mathrm{TPa^{-1}}$	23.4	−16.4	28.4			1.0
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	1.099	−0.774	0.332			0.007
Cyclohexane (1) + Tri-*n*-Hexylamine (2)						
$U/(\mathrm{m \cdot s^{-1}})$	295.7	−31.4	−33.7			0.6
$K_S/\mathrm{TPa^{-1}}$	750.4	64.7	−9.2	52.5		1.0
$K_S^E/\mathrm{TPa^{-1}}$	6.9	8.7	−21.0			0.8
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	1.486	−0.742	0.862			0.001
Cyclohexane (1) + Tri-*n*-octylamine (2)						
$U/(\mathrm{m \cdot s^{-1}})$	1353.3	−58.4	8.9	−73.2		0.7
$K_S/\mathrm{TPa^{-1}}$	676.8	89.7	−86.7	177.4		1.8
$K_S^E/\mathrm{TPa^{-1}}$	10.6	−1.5	−2.4			0.5
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	1.486	−0.742	1.169	−1.460		0.003
Cyclohexane (1) + Tri-*n*-dodecylamine (2)						
$U/(\mathrm{m \cdot s^{-1}})$	1401.4	−94.3	161.4	−238.1		1.1
$K_S/\mathrm{TPa^{-1}}$	623.1	16.5	305.5	−615.6	529.3	0.6
$K_S^E/\mathrm{TPa^{-1}}$	−11.0	16.2				1.0
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	2.346	−1.356	0.836			0.030
Benzene (1) + Tri-*n*-butylamine (2)						
$U/(\mathrm{m \cdot s^{-1}})$	1229.5	−54.7	224.3	−404.1	283.4	1.1
$K_S/\mathrm{TPa^{-1}}$	858.3	35.0	−299.1	482.1	−371.1	1.5
$K_S^E/\mathrm{TPa^{-1}}$	68.9	−54.6	55.3			1.2
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	2.189	−1.733	0.979	2.124		0.002
Benzene (1) + Tri-*n*-hexylamine (2)						
$U/(\mathrm{m \cdot s^{-1}})$	1296.0	−22.8	−75.4	81.4		1.2
$K_S/\mathrm{TPa^{-1}}$	751.3	−10.9	154.0	−189.4		2.0
$K_S^E/\mathrm{TPa^{-1}}$	63.1	−46.1				1.5
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	2.631	−1.500	1.323			0.007
Benzene (1) + Tri-*n*-octylamine (2)						
$U/(\mathrm{m \cdot s^{-1}})$	1352.5	−58.2	−13.8			1.2
$K_S/\mathrm{TPa^{-1}}$	678.3	28.1	115.1	−116.0		2.8
$K_S^E/\mathrm{TPa^{-1}}$	74.4	−42.1				1.4
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	3.069	−2.304	2.723			0.010
Benzene (1) + Tri-*n*-dodecylamine (2)						
$U/(\mathrm{m \cdot s^{-1}})$	1401.4	−29.6	−27.1	−64.9		2.2
$K_S/\mathrm{TPa^{-1}}$	623.0	5.0	106.1	−30.4		1.3
$K_S^E/\mathrm{TPa^{-1}}$	44.7	−59.8				1.5
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	4.063	−3.137	2.000	−1.578		0.001

$$K_T^{id} = \sum \phi_i [K_{S,i}^\circ + TV_i^\circ(\alpha_i^\circ)^2/C_{P,i}^\circ] \tag{4}$$

$$\alpha^{id} = \sum \phi_i \alpha_i^\circ \tag{5}$$

and

$$C_P^{id} = \sum x_i C_{P,i}^\circ \tag{6}$$

in which V_i°, α_i°, and $C_{P,i}^\circ$ are, respectively, the molar volume, isobaric thermal expansion coefficient, and molar isobaric heat capacity for pure component i and $\phi_i = x_i V_i^\circ / \sum x_j V_j^\circ$ is the volume fraction of i in the mixture, stated in terms of the unmixed components. The values of α_i° and $C_{P,i}^\circ$ used for these calculations are listed in Table 1 along with their sources (*25*, *35–37*).

The values of U and K_S are expressed by

$$U \text{ or } K_S = \sum_{i=0}^{m} A_i x_1^{\,i} \tag{7}$$

and the excess functions K_S^E or V^E by

$$K_S^E \text{ or } V^E = x_1 x_2 \sum_{i=0}^{m} A_i (1 - 2x_1)^i \tag{8}$$

The coefficients A_i of eqs 7 and 8 obtained by the least-squares method together with the standard deviations are

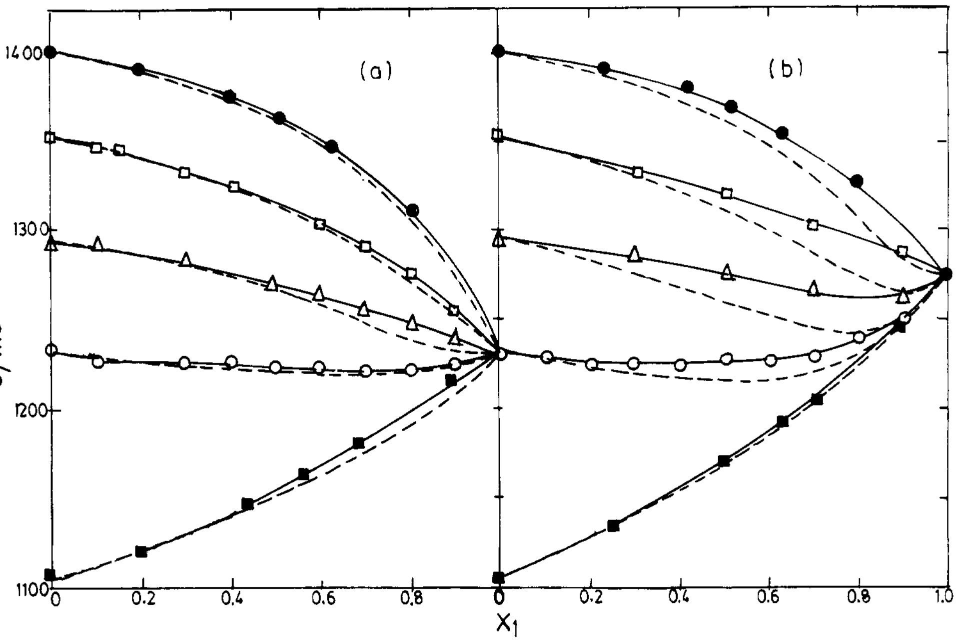

Figure 1. Dependence of the speed of sound on mole fraction at 303.15 K for mixtures of (a) cyclohexane and (b) benzene with trialkylamines. Experimental points: ○, $(C_4H_9)_3Ni$; △, $(C_6H_{13})_3N$; □, $(C_8H_{17})_3Ni$; ●, $(C_{12}H_{25})_3N$; ■, $(C_2H_5)_3N$ from ref 40; —, calculated with eq 7; - - -, estimated from the Prigogine–Flory–Patterson theory.

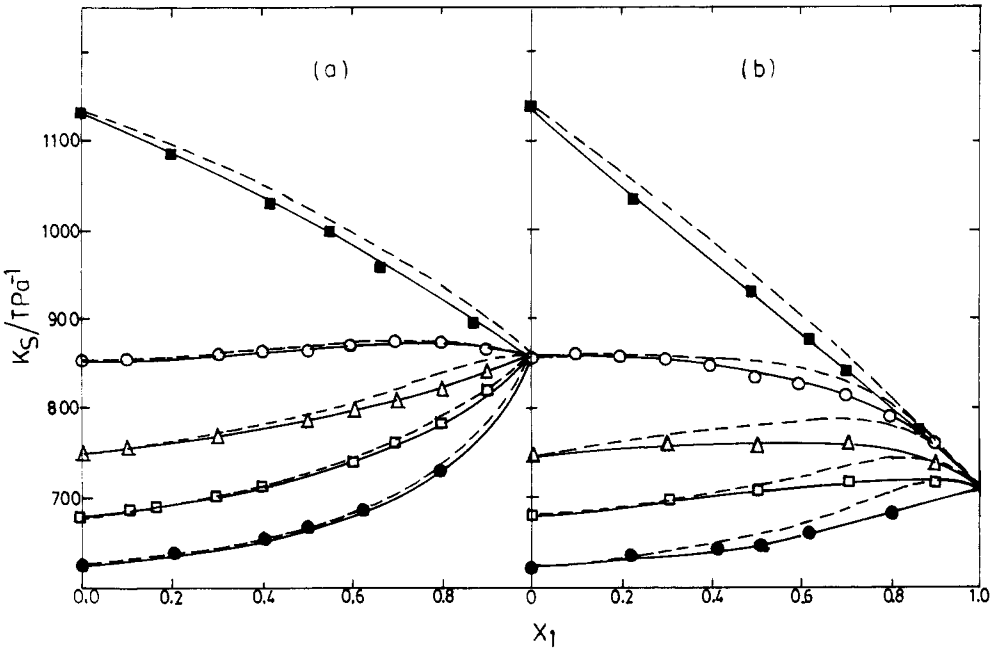

Figure 2. Dependence of isentropic compressibility on mole fraction at 303.15 K for mixtures of (a) cyclohexane and (b) benzene with trialkylamines. Key as in legend to Figure 1.

given in Table 4. The results of U, K_S, V^E, and K_S^E are plotted in Figures 1–4.

The speed of sound deviates negatively from linear additivity on the mole fraction for C_6H_{12} + $(C_4H_9)_3N$, C_6H_6 + $(C_4H_9)_3N$, and C_6H_6 + $(C_6H_{13})_3N$ mixtures and deviates positively for C_6H_{12} + $(C_6H_{13})_3N$, C_6H_{12} + $(C_8H_{17})_3N$, C_6H_{12} + $(C_{12}H_{25})_3N$, C_6H_6 + $(C_8H_{17})_3N$, and C_6H_6 + $(C_{12}H_{25})_3N$ mixtures. The trend of deviations in the case of K_S plots (Figure 2) is opposite that observed for U.

The V^E values are positive for all the eight binary mixtures at 303.15 K (Figure 3). Letcher (*2*) has studied C_6H_{12} + $(C_4H_9)_3N$ and C_6H_6 + $(C_4H_9)_3N$, while Riedl et al. (*4*, *7*) investigated C_6H_{12} + $(C_4H_9)_3N$, + $(C_6H_{12})_3N$, + $(C_8H_{17})_3N$, and + $(C_{12}H_{25})_3N$ at 298.15 K. Our results of V^E at 303.15 K for C_6H_{12} + $(C_4H_9)_3N$ and C_6H_6 + $(C_4H_9)_3N$ are within 0.004–0.006 cm^3 mol^{-1} of those reported by Letcher (*2*). However, V^E for C_6H_{12} + $(C_4H_9)_3N$, reported by Riedl et al. (*7*), is higher by 0.055 cm^3 mol^{-1} at $x_1 = 0.5$. The equimolar V^E values at 303.15 K for C_6H_{12} + $(C_6H_{13})_3N$ and C_6H_{12} + $(C_8H_{17})_3N$ agree with the literature (*4*) to within 0.008 cm^3 mol^{-1}, and for C_6H_{12} + $(C_{12}H_{25})_3N$ literature values (*4*) are lower by 0.060 cm^3 mol^{-1} for the corresponding mixtures at 298.15 K. The sequence of V^E for the cyclohexane and benzene mixture series containing tri-*n*-alkylamine is $(C_4H_9)_3N$ < $(C_6H_{13})_3N$ < $(C_8H_{17})_3N$ < $(C_{12}H_{25})_3N$.

The values of K_S^E (Tables 2 and 3 and Figure 4) are positive for C_6H_{12} + $(C_4H_9)_3N$, C_6H_6 + $(C_4H_9)_3N$, C_6H_6 + $(C_6H_{12})_3N$, C_6H_6 + $(C_8H_{17})_3N$, and C_6H_6 + $(C_{12}H_{25})_3N$, while they are negative for C_6H_{12} + $(C_{12}H_{25})_3N$. For the mixtures C_6H_{12} + $(C_6H_{12})_3N$ and C_6H_{12} + $(C_8H_{17})_3N$, the values of K_S^E approach zero. Further, it is observed that the values of V^E and K_S^E are

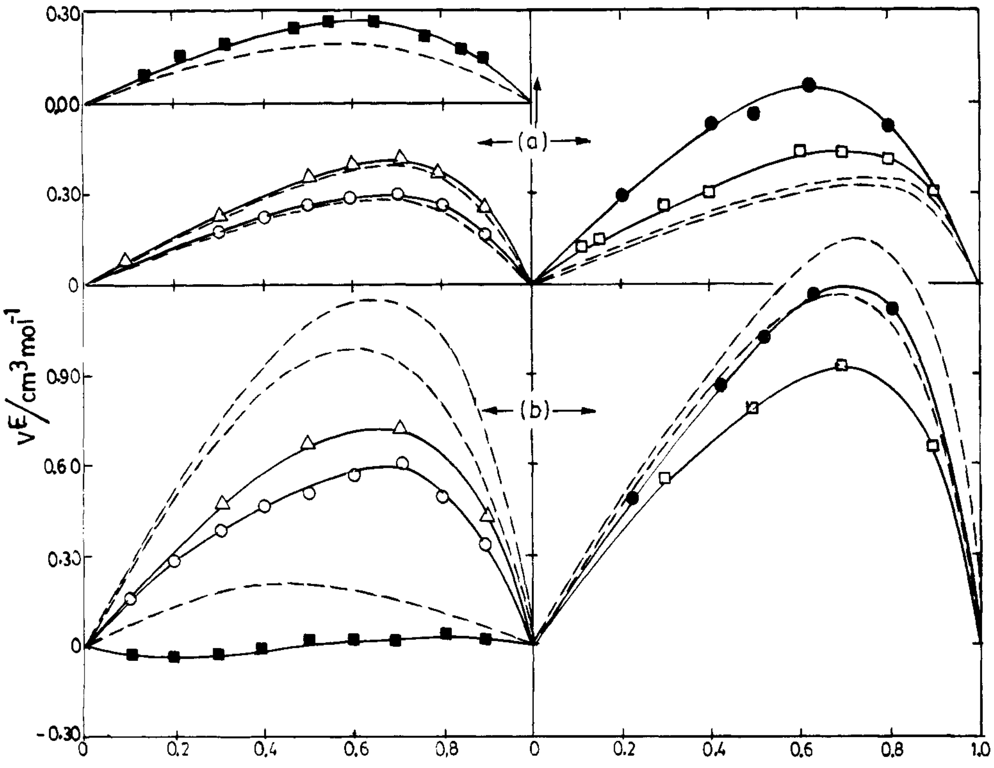

Figure 3. Dependence of excess volume on mole fraction at 303.15 K for mixtures of (a) cyclohexane and (b) benzene with trialkylamines. Symbols same as in Figure 1; V^E for $(C_2H_5)_3N$ mixtures from ref 2; —, calculated with eq 8; - - -, estimated from the Prigogine–Flory–Patterson theory.

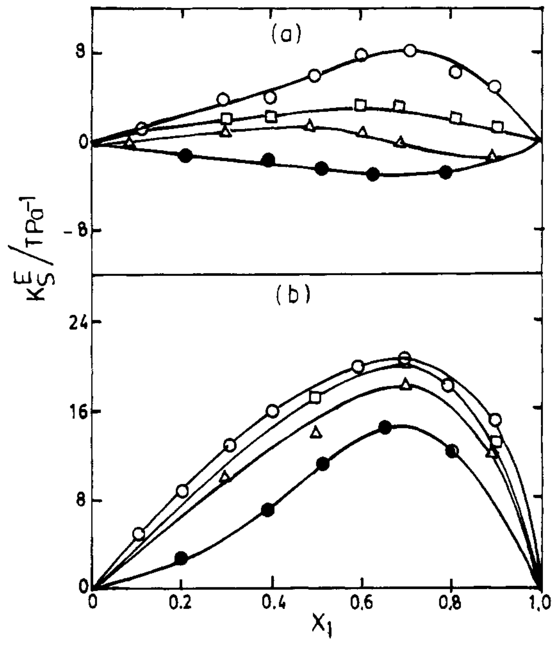

Figure 4. Dependence of excess isentropic compressibility on mole fraction at 303.15 K for mixtures of (a) cyclohexane and (b) benzene with trialkylamines. Symbols same as in Figure 1.

more positive for mixtures of trialkylamines with benzene than for the mixtures with cyclohexane.

The positive values of V^E and K_S^E are attributable to the reduction of dipole–dipole interaction in tri-*n*-alkylamine (*2*). The larger values of V^E and K_S^E in the case of the benzene mixture series may be due to stronger dispersive forces (disruption) of so-called π–π interactions in aromatic hydrocarbons (*38*).

The increasing size difference between the two components may be responsible for the increasing trend in the values of V^E from the butyl to dodecyl alkyl chain in trialkylamine.

Theoretical Analysis

The Prigogine–Flory–Patterson theory of solutions (*21–24, 39*) has been used to analyze U, K_S, U^E, K_S^E, and V^E for the present binary mixtures along with two more mixtures of triethylamine with cyclohexane and benzene. The results for the latter mixtures have been collected from the literature (*2, 40*).

Excess Volume. The excess volume V^E of a mixture as per the Prigogine–Flory–Patterson theory (*23, 39*) can be separated into three terms, namely, (i) the interaction contribution $V^E(H^E)$ which has the sign of H^E, (ii) the free volume contribution $V^E(\text{fv})$ which is negative, and (iii) the internal pressure contribution $V^E(P^*)$ which can have either sign, since it is proportional to $(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)$. In the notation of Van and Patterson (*39*) the terms $V^E(H^E)$, $V^E(\text{fv})$, and $V^E(P^*)$ are

$$V^E(H^E) = V^*\tilde{T}_v(\partial\tilde{V}/\partial\tilde{T}_v)(X_{12}\theta_2\psi_1/P_1^*) \qquad (9)$$

$$V^E(\text{fv}) = -\frac{V^*}{2}\left\{\frac{\tilde{V}_1 - \tilde{V}_2}{\partial\tilde{V}/\partial\tilde{T}_v}\right\}^2\frac{\partial^2\tilde{V}}{\partial\tilde{T}_v^{\,2}}\{\psi_1\psi_2 + (\psi_1 - \phi_1)^2\} \qquad (10)$$

$$V^E(P^*) = V^*(\tilde{V}_1 - \tilde{V}_2)(\psi_1 - \phi_1) \qquad (11)$$

$$V^E(\text{theor}) = V^E(H^E) + V^E(\text{fv}) + V^E(P^*) \qquad (12)$$

where $V^* = x_1V_1^* + x_2V_2^*$, $\tilde{V}_v = \phi_1\tilde{V}_1 + \phi_2\tilde{V}_2$, $\tilde{T}_v$ corresponds to $\tilde{V}_v$ so defined.

Table 5 lists the values of Flory's parameters, used in the theoretical calculations. The compatible values of the contact

Table 5. Flory's Parameters for the Pure Components at 303.15 K

liquid	$\tilde{V}$	V^*/ (cm^3·mol^{-1})	P^*/ (J·cm^{-3})	T^*/K	S^a/Å^{-1}
cyclohexane	1.2975	84.33	533	4730	0.93
benzene	1.2975	69.33	623	4730	1.00
triethylamine	1.3126	107.24	469	4591	0.95
tributylamine	1.2491	192.35	448	5299	0.88
trihexylamine	1.2255	277.44	448	5669	0.85
trioctylamine	1.2165	361.20	462	5830	0.84
tridodecylamine	1.2059	529.00	474	6042	0.83

[a] Taken from ref 4.

interaction parameter X_{12} estimated using the equimolar excess enthalpy H^E (*3, 4, 7*) are given in the last column of Table 6.

The excess volume V^E estimated from the Prigogine–Flory–Patterson theory and the experimental V^E at all the mole fractions are compared in Figure 3. Different contributions to V^E for the two series cyclohexane + trialkylamine and benzene + trialkylamine at the equimolar composition are given in Table 6. The difference $\delta = V^E(\text{exptl}) - V^E(\text{theor})$ is given in the second to last column of Table 6.

As can be seen from Table 6 the term V^E(fv) is negative for all 10 binary mixtures and gradually increases as the alkyl chain length of the amine is increased. The terms $V^E(H^E)$ and $V^E(P^*)$ are positive for all the binary mixtures, except the $V^E(P^*)$ term, being negative for two mixtures involving triethylamine. Like the V^E(fv) term, the magnitudes of the $V^E(H^E)$ and $V^E(P^*)$ terms also increase with the chain length of the alkylamine.

In the cyclohexane + trialkylamine series, agreement between the experimental and theoretical V^E is quite good for the mixtures cyclohexane + triethylamine, + tributylamine, and + trihexylamine. The V^E(theor) are smaller for cyclohexane + trioctylamine and + tridodecylamine mixtures by 0.082 and 0.326 cm^3 mol^{-1}, respectively, than the V^E(exptl). On the other hand, for the benzene + trialkylamine series, the V^E(theor) are higher by 0.122–0.414 cm^3 mol^{-1} than the V^E(exptl). Thus, the Prigogine–Flory–Patterson theory estimates larger values of V^E for trialkylamine mixtures containing benzene, while the opposite is the case with most mixtures involving cyclohexane. The overestimation of V^E by the Prigogine–Flory–Patterson theory for benzene + trialkylamine mixtures may be due to the presence of n–π interactions between the unlike molecules (*1–3*). The positive values of $\delta = V^E(\text{exptl}) - V^E(\text{theor})$ for cyclohexane + trioctylamine and + tridodecylamine mixtures, as explained by Riedl and Delmas (*4*), may be due to the presence of short-range orientation order in trioctyl- and tridodecylamines, because of large alkyl chains, which in turn is disrupted by the order-breaking cyclohexane molecules.

Excess Isentropic Compressibility and Apparent Excess Speed of Sound. The isentropic compressibility K_S is defined by

$$K_S = V^{-1}(\mathrm{d}V/\mathrm{d}P)_S \tag{13}$$

and the speed of sound U is related to K_S by

$$U = (V/MK_S)^{1/2} \tag{14}$$

The thermodynamic equation

$$(\mathrm{d}V/\mathrm{d}P)_S = (\mathrm{d}V/\mathrm{d}P)_T + TC_P^{-1}(\mathrm{d}V/\mathrm{d}T)_P^{\,2} \tag{15}$$

interconnects the term $(\mathrm{d}V/\mathrm{d}P)_S$ with the terms $(\mathrm{d}V/\mathrm{d}P)_T$ and $(\mathrm{d}V/\mathrm{d}T)_P$ which can easily be derived from the Flory theory of liquid mixtures (*22*). In the notation of Flory, the terms $(\mathrm{d}V/\mathrm{d}P)_T$ and $(\mathrm{d}V/\mathrm{d}T)_P$ are

$$(\mathrm{d}V/\mathrm{d}P)_T = \frac{-\tilde{V}^{7/3} + 2\tilde{V}^2 - 2\tilde{V}^{5/3}}{4/3 - \tilde{V}^{1/3}} \frac{V^*T^*}{P^*T} \tag{16}$$

$$(\mathrm{d}V/\mathrm{d}T)_P = \frac{\tilde{V}(\tilde{V}^{1/3} - 1)}{4/3 - \tilde{V}^{1/3}} \frac{V^*}{T} \tag{17}$$

The theoretical values of K_S and U and, hence, K_S^E and ΔU (apparent excess speed of sound as defined by Douheret et al. (*41*)) for the present binary mixtures were estimated form the knowledge of Flory's parameters $\tilde{V}$, V^*, P^*, and T^* and the molar isobaric heat capacities C_P of pure liquids and mixtures, using eqs 13–17, as described elsewhere (*24*).

The theoretically estimated values of U and K_S are shown in Figures 1 and 2 as dashed lines, and the values of K_S^E and ΔU at equimolar composition have been compared with the experimental values in Table 7.

Agreement between the theoretical and experimental values of U and K_S is quite satisfactory for cyclohexane + trialkylamine mixtures over the whole composition range. However, in the case of benzene + trialkylamine mixtures, agreement is reasonable only in the lower mole fraction region of benzene. Considerable discrepancies for both U and K_S are observed in the benzene-rich region. Values of percentage standard deviations σ (%) between the theoretical and smoothed experimental values for U and K_S are 0.19 ± 0.07 and 0.61 ± 0.32, respectively, for cyclohexane + trialkylamine mixtures, while the respective values of σ (%) for benzene + trialkylamine mixtures are up to 0.98 ± 0.20 and 2.30 ± 0.49.

It is interesting to note that the Prigogine–Flory–Patterson theory has always predicted the correct sign of both K_S^E and ΔU (Table 7) for the presently investigated mixtures. However, the agreement between theoretical and experimental K_S^E and ΔU is good only for the mixtures involving cyclohexane, while considerable differences are observed for the benzene mixtures.

From the foregoing discussion, it may be concluded that though the Prigogine–Flory–Patterson theory is quite successful in giving good theoretical accounts of K_S, U, V^E,

Table 6. Values of the Three Contributions $V^E(H^E)$, V^E(fv), and $V^E(P^*)$ in Eq 12, V^E(theor), V^E(exptl), Their Difference δ, and the Flory Interaction Parameter X_{12} for Equimolar Mixture at 303.15 K

mixture	$V^E(H^E)^a$	$V^E(\text{fv})^a$	$V^E(P^*)^a$	$V^E(\text{theor})^a$	$V^E(\text{exptl})^a$	δ^a	$X_{12}{}^b$
C_6H_{12} + Et_3N	0.236	−0.008	−0.046	0.182	0.264^c	0.082	9.8
C_6H_{12} + But_3N	0.136	−0.109	0.253	0.280	0.275	−0.005	5.5
C_6H_{12} + Hex_3N	0.205	−0.275	0.425	0.354	0.302	−0.052	8.2
C_6H_{12} + Oct_3N	0.270	−0.365	0.386	0.290	0.372	0.082	11.4
C_6H_{12} + Dod_3N	0.351	−0.502	0.415	0.260	0.586	0.326	15.1
C_6H_6 + Et_3N	0.227	−0.008	−0.093	0.127	0.005^c	−0.122	16.3
C_6H_6 + But_3N	0.614	−0.104	0.436	0.946	0.547	−0.399	30.7
C_6H_6 + Hex_3N	0.610	−0.262	0.725	1.072	0.658	−0.414	30.9
C_6H_6 + Oct_3N	0.610	−0.348	0.751	1.013	0.767	−0.246	31.8
C_6H_6 + Dod_3N	0.723	−0.479	0.657	1.150	1.016	−0.134	38.4

[a] In cm^3·mol^{-1}. [b] In J·cm^{-3}. [c] From ref 2. [d] $\delta \equiv V^E(\text{exptl}) - V^E(\text{theor})$.

Table 7. Comparison of Theoretical and Experimental K_S^E and ΔU for an Equimolar Composition at 303.15 K

	K_S^E/TPa^{-1}		$\Delta U/(m \cdot s^{-1})$	
mixture	theor	exptl	theor	exptl
$C_6H_{12} + (C_2H_5)_3N$	6	2	−2	−1
$C_6H_{12} + (C_4H_9)_3N$	11	6	−7	−4
$C_6H_{12} + (C_6H_{13})_3N$	9	2	−6	−1
$C_6H_{12} + (C_8H_{17})_3N$	4	3	−3	−1
$C_6H_{12} + (C_{12}H_{25})_3N$	−1	−3	1	3
$C_6H_6 + (C_2H_5)_3N$	−15	−34	10	21
$C_6H_6 + (C_4H_9)_3N$	37	17	−24	−12
$C_6H_6 + (C_6H_{13})_3N$	34	16	−25	−10
$C_6H_6 + (C_8H_{17})_3N$	26	18	−21	−15
$C_6H_6 + (C_{12}H_{25})_3N$	19	11	−18	−7

K_S^E, and ΔU for the binary mixtures of cyclohexane with trialkylamines, it fails to estimate correct values for the benzene + trialkylamines mixtures, which may be on account of π–n interaction between unlike components or due to the disruption of π–π interaction in benzene molecules.

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