Speeds of Sound, Isentropic Compressibilities, and Excess Volumes of Binary Mixtures. 3. Di-*n*-alkylamines with Cyclohexane and Benzene

Shantilal Oswal,* Prem Oswal,† and Ashok T. Patel

Department of Chemistry, South Gujarat University, Surat 395 007, India

Isentropic compressibilities K_S, excess isentropic compressibilities K_S^E, and excess volumes V^E have been determined from speeds of sound U and densities ϱ for six binary mixtures of butylamine, dihexylamine, and dioctylamine with cyclohexane or benzene as a function of the mole fraction at 303.15 K. Variable-degree polynomials have been fitted to the results. V^E and K_S^E values are positive over the entire range of composition for all mixtures except cyclohexane + dioctylamine which have negative K_S^E.

Introduction

In previous work (Oswal and Rao, 1985; Oswal and Patel, 1991, 1992, 1994, 1995) we have reported studies of the speed of sound U, isentropic compressibilities K_S, viscosities η, excess isentropic compressibilities K_S^E, and excess volumes V^E for binary mixtures of tri-*n*-alkylamines and mono-*n*-alkylamines with cyclohexane and benzene. As an extension in this paper we present the speed of sound, density, isentropic compressibilities, excess isentropic compressibilities, and excess volumes for six binary mixtures of dibutylamine ($(C_4H_9)_2NH$), dihexylamine ($(C_6H_{13})_2NH$), and dioctylamine ($(C_8H_{17})_2NH$) with cyclohexane (C_6H_{12}) and benzene (C_6H_6) as a function of the mole fraction at 303.15 K. The present results will assist in the in-depth understanding of molecular interactions in di-*n*-alkylamine + cyclohexane and di-*n*-alkylamine + benzene and the effect of increasing the amine chain length on the excess properties.

Experimental Section

Cyclohexane (Fluka, AG) and benzene (BDH, AR) were purified as described in part 2 (Oswal and Patel, 1995). Dibutylamine (Fluka, AG), dihexylamine (Fluka, AG), and dioctylamine (Fluka, AG) were kept over sodium and fractionally distilled twice. The estimated purities by gas–liquid chromatography were better than 99.8% for C_6H_{12} and C_6H_6 and 99.5% for dialkylamines. The densities ϱ and refractive indices n_D of purified liquids are compared with the reliable literature data (Letcher, 1972; Riddick et al., 1986; Weast, 1979) in Table 1.

Mixtures were prepared by mixing known masses of pure liquids in air-tight, narrow-mouth ground-glass-stoppered bottles, taking due precaution to minimize the evaporation losses. A Mettler (AE 163, Switzerland) balance with a precision of 0.01 mg was used to measure the masses of the liquids. Hence, the possible error in the mole fraction is estimated to be less than $\pm 2 \times 10^{-4}$.

The speeds of sound U were measured with a single crystal ultrasonic interferometer using a steel cell fitted with a quartz crystal of 2 MHz frequency. Densities ϱ were measured using a fine capillary single-stem calibrated pycnometer. The temperature was controlled to ±0.02 K by water thermostats. Details of these appratus and operational procedure for the measurements have been described previuosly (Oswal and Palsanawala, 1989; Patel, 1991). The values of the speeds of sound U and densities ϱ were reproducible to within ±1.0 m·s^{-1} and ±0.1 kg·m^{-3}, respectively. The isentropic compressibilities K_S determined from the relation $K_S = 1/(U^2\varrho)$ are believed to be reliable to within 2.0 TPa^{-1}.

* To whom correspondence should be addressed.
† Present address: Department of Chemistry, Government College, Pratapgarh, Rajasthan 312 605, India.

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

liquid	ϱ/(kg·m^{-3}) exptl	ϱ/(kg·m^{-3}) lit.	n_D exptl	n_D lit.	$10^3\alpha$/K^{-1}	C_P/(J·K^{-1}·mol^{-1})
C_6H_{12}	773.90	773.89[a]	1.4236	1.42354[a]	1.233[e]	158.1[a]
C_6H_6	873.62	873.60[a]	1.4979	1.49792[a]	1.233[e]	136.8[a]
$(C_4H_9)_2NH$	755.95	755.72[b] 757.7[a]	1.4159	1.4152[a]	1.066[f]	305.2[a]
$(C_6H_{13})_2NH$	782.93		1.4336	1.4319[c,d]	0.921[g]	418.8[h]
$(C_8H_{17})_2NH$	797.3	796.8[c,d]	1.4420	1.4415[c,d]	0.831[g]	532.3[h]

[a] Riddick et al. (1986). [b] Letcher (1972). [c] Weast (1979). [d] At 303.15 K. [e] Tamura and Murakami (1984). [f] Sindhe (1986). [g] Patel 1991. [h] Estimated by the Missenard group contribution method (Reid et al., 1987).

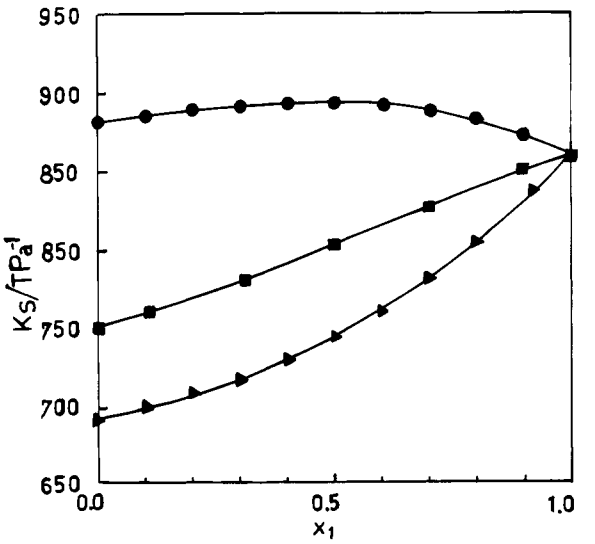

Figure 1. Isentropic compressibility for cyclohexane (1) + dialkylamines (2) at 303.15 K. Experimental points: ●, $(C_4H_9)_2NH$; ■, $(C_6H_{13})_2NH$; ▲, $(C_8H_{17})_2NH$; (—) calculated with eq 1.

Results and Discussion

The speed of sound, density, isentropic compressibility, excess volume, and excess isentropic compressibility for the binary mixtures are given in Table 2. The relations used

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Table 2. Properties of Cyclohexane (1) or Benzene (1) + Dialkylamines (2) at 303.15 K

x_1	U/(m·s^{-1})	ϱ/(kg·m^{-3})	K_S/TPa^{-1}	V^E/(cm^3·mol^{-1})	K_S^E/TPa^{-1}
Cyclohexane (1) + Dibutylamine (2)					
0.0000	1227	751.94	883		
0.1011	1224	752.42	887	0.147	3
0.2001	1221	753.02	891	0.273	6
0.3025	1219	753.82	893	0.375	7
0.4034	1217	754.74	895	0.464	9
0.4997	1216	755.86	895	0.517	10
0.6050	1216	757.42	893	0.536	10
0.7025	1217	759.19	889	0.523	9
0.7989	1219	761.59	884	0.433	8
0.8971	1224	764.75	873	0.273	4
1.0000	1230	769.18	859		
Cyclohexane (1) + Dihexylamine (2)					
0.0000	1305	782.93	750		
0.1070	1297	781.91	760	0.086	2
0.3102	1283	779.36	780	0.304	2
0.4992	1267	776.57	802	0.452	5
0.6981	1251	773.35	826	0.473	4
0.8959	1236	770.35	850	0.254	2
1.0000	1230	769.18	859		
Cyclohexane (1) + Dioctylamine (2)					
0.000	1348	795.88	691		
0.1052	1342	794.49	699	0.109	−2
0.2021	1335	793.06	708	0.196	−4
0.3020	1328	791.42	717	0.266	−6
0.4044	1318	789.47	729	0.329	−7
0.5039	1307	787.29	744	0.373	−8
0.6016	1295	784.86	760	0.382	−9
0.7009	1280	781.92	781	0.371	−7
0.8006	1264	778.41	804	0.319	−6
0.9216	1243	773.26	837	0.164	−3
1.0000	1230	769.18	859		
Benzene (1) + Dibutylamine (2)					
0.0000	1227	751.94	883		
0.1013	1228	758.02	875	0.087	0
0.1827	1228	763.49	869	0.131	1
0.3015	1229	772.31	857	0.204	3
0.4024	1231	780.93	845	0.237	3
0.5013	1233	790.36	832	0.280	4
0.5989	1236	801.11	817	0.287	5
0.7013	1243	814.09	795	0.281	3
0.7983	1251	828.50	771	0.245	2
0.8983	1262	846.23	742	0.155	1
1.0000	1279	868.29	704		
Benzene (1) + Dihexylamine (2)					
0.000	1305	782.93	750		
0.2083	1295	790.23	755	0.120	5
0.2986	1290	793.92	757	0.217	8
0.4986	1281	804.32	758	0.411	12
0.7009	1271	820.31	755	0.461	16
0.8978	1269	846.50	734	0.262	11
1.0000	1279	868.29	704		
Benzene (1) + Dioctylamine (2)					
0.0000	1348	795.88	691		
0.3085	1325	802.88	709	0.433	11
0.5015	1308	810.18	721	0.566	17
0.7039	1290	822.99	730	0.527	20
1.0000	1279	868.29	704		

to calculate K_S^E and V^E for each mixture have already been described in parts 1 and 2 of the series (Oswal and Patel, 1994, 1995). The values of α_i° and $C^\circ_{P,i}$ used for these calculations are included in Table 1. The values of U and K_S are expressed by

$$U \text{ or } K_S = \sum_{i=0}^{m} A_i x_1^{\,i} \qquad (1)$$

and the excess functions Y^E (K_S^E or V^E) by

$$Y^E = x_1 x_2 \sum_{i=0}^{m} A_i (1 - 2x_1)^i \qquad (2)$$

Table 3. Coefficients A_i and Standard Deviations S for Eqs 1 and 2 for the Binary Mixtures at 303.15 K

property	A_0	A_1	A_2	A_3	S
Cyclohexane (1) + Dibutylamine (2)					
U/(m·s^{-1})	1226.9	−28.1	−6.8	38.0	0.3
K_S/TPa^{-1}	993.2	36.4	10.4	−70.8	0.6
V^E/(cm^3·mol^{-1})	2.0712	−0.844	0.350		0.004
K_S^E/TPa^{-1}	39.9	−8.6			0.5
Cyclohexane (1) + Dihexylamine (2)					
U/(m·s^{-1})	1305.3	76.4			1.0
K_S/TPa^{-1}	750.4	74.9	81.7	−47.4	0.9
V^E/(cm^3·mol^{-1})	1.828	−0.883	0.310		0.005
K_E^E/TPa^{-1}	18.1				1.0
Cyclohexane (1) + Dioctylamine (2)					
U/(m·s^{-1})	1347.7	−43.6	−74.9		0.7
K_S/TPa^{-1}	691.5	62.0	61.7	44.6	0.8
V^E/(cm^3·mol^{-1})	1.470	−0.653	0.345		0.003
K_S^E/TPa^{-1}	−31.6	11.4			0.4
Benzene (1) + Dibutylamine (2)					
U/(m·s^{-1})	1226.8	159.5	−52.8	88.6	0.5
K_S/TPa^{-1}	883.3	−83.8	24.3	−119.4	0.7
V^E/(cm^3·mol^{-1})	1.090	−4.900	0.356		0.005
K_S^E/TPa^{-1}	13.5				0.8
Benzene (1) + Dihexylamine (2)					
U/(m·s^{-1})	1304.9	−30.9	−92.8	97.7	0.4
K_S/TPa^{-1}	750.3	−4.5	146.7	−188.0	1.1
V^E/(cm^3·mol^{-1})	1.741	−1.063	0.204		0.005
K_S^E/TPa^{-1}	48.9	34.3	−35.4		0.6
Benzene (1) + Dioctylamine (2)					
U/(m·s^{-1})	1348.6	−87.7	17.8		1.6
K_S/TPa^{-1}	691.1	13.5	195.8	−196.3	1.8
V^E/(cm^3·mol^{-1})	2.268	−0.631			0.002
K_S^E/TPa^{-1}	62.1	−19.6			1.7

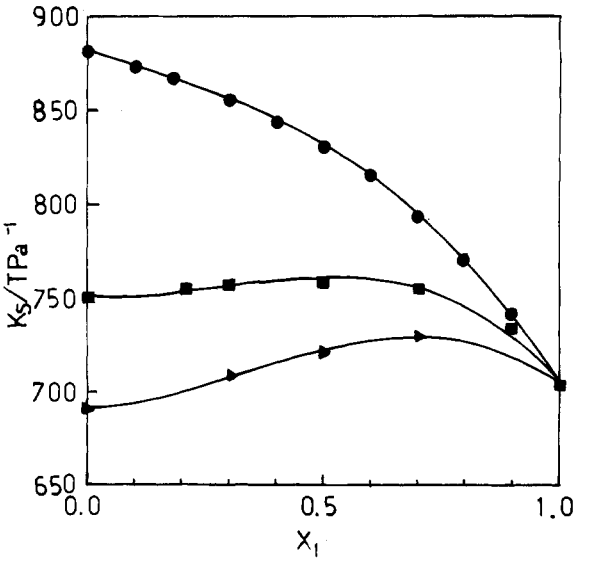

Figure 2. Isentropic compressibility for benzene (1) + dialkylamines (2) at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 1.

The coefficients A_i of eqs 1 and 2 obtained by the least squares method together with the standard deviations are given in Table 3. The dependence of K_S on the mole fraction x_1 is shown in Figures 1 and 2 while the results of V^E and K_S^E are plotted in Figures 3–6.

It can be seen from Figures 1 and 2 that there is a striking difference in the behavior of K_S for the mixtures of dialkylamine with cyclohexane and those of dialkylamine with benzene. In the case of mixtures involving cyclohexane, the deviations in K_S from a linear dependence on mole fraction change the sign from positive for dibutylamine to negative for dioctylamine. The K_S is almost linear for

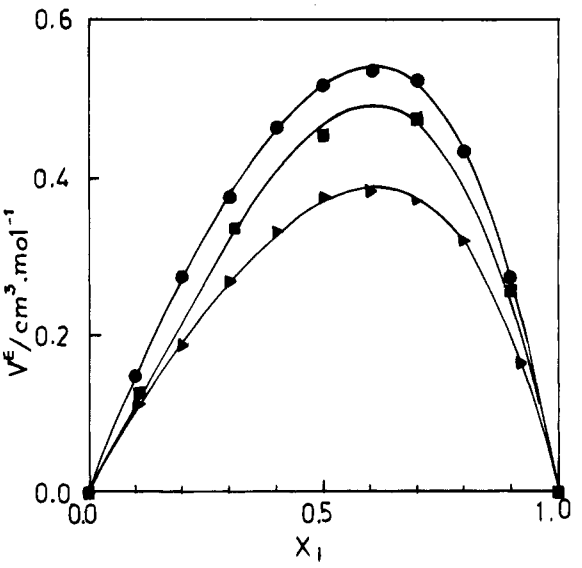

Figure 3. Excess volume for cyclohexane (1) + dialkylamines (2) at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 2.

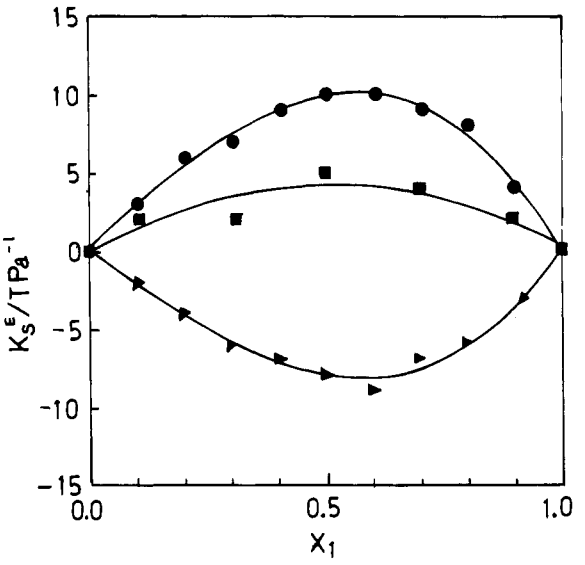

Figure 5. Excess isentropic compressibility for cyclohexane (1) + dialkylamines (2) at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 2.

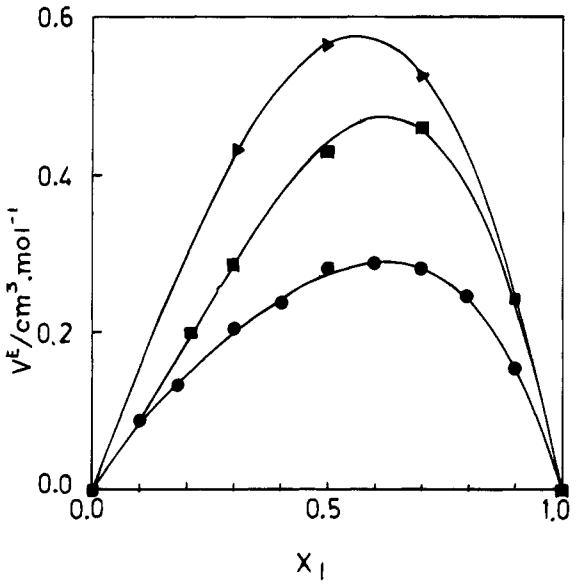

Figure 4. Excess volume for benzene (1) + dialkylamines (2) at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 2.

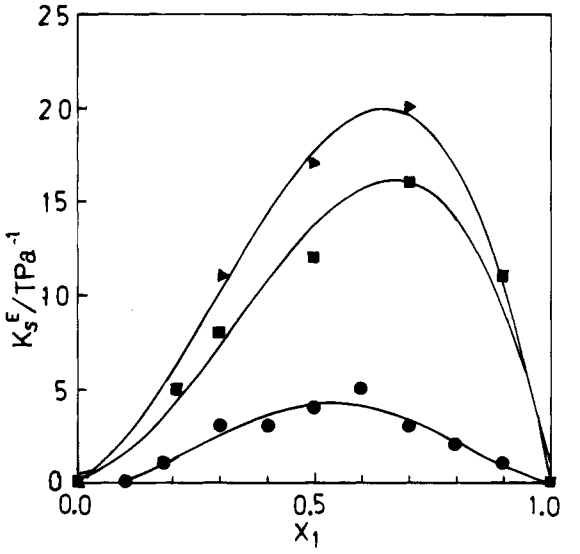

Figure 6. Excess isentropic compressibility for benzene (1) + dialkylamines (2) at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 2.

cyclohexane + dihexylamine. On the other hand, all three corresponding mixtures with benzene show considerable positive deviations, with a maximum in two mixtures.

The V^E values are positive for all six binary mixtures at 303.15 K (Figures 3 and 4). Present equimolar V^E values for C_6H_{12} + $(C_4H_9)_2NH$ and C_6H_6 + $(C_4H_9)_2NH$ at 303.15 K are within 0.02–0.04 $cm^3 \cdot mol^{-1}$ to those reported by Letcher (1972) at 298.15 K. It is observed that V^E for benzene + dibutylamine and benzene + dihexylamine is smaller than that for the corresponding cyclohexane mixtures while for the benzene + dioctylamine mixture V^E is larger than that for the cyclohexane + dioctylamine mixture. The mixing of the dialkylamines (A) with benzene (B) is complicated because intermolecular interaction in A–B is masked by the self-associations in A–A and B–B (Letcher, 1972).

The values of K_S^E (Figures 5 and 6) are positive over the entire range of composition for all mixtures except for C_6H_{12} + $(C_8H_{17})_2NH$. For the C_6H_{12} + $(C_8H_{17})_2NH$ mixtures K_S^E is negative over the entire range of composition. The maximum or minimum in K_S^E is in the range 0.55–0.65 mole fraction of the first component for most mixtures. The maximum or minimum shifts toward higher mole fraction x_1 of the first component as the alkyl chain length in the amine is increased. In the case of mixtures with benzene, the magnitudes of K_S^E increase with the chain length of the secondary amines, while the reverse occurs with the mixtures involving cyclohexane. The value of K_S^E for C_6H_{12} + $(C_4H_9)_2NH$ is large and positive. It is a small positive value for C_6H_{12} + $(C_6H_{13})_2NH$ and changes sign for C_6H_{12} + $(C_8H_{17})_2NH$. For the benzene series, the value of K_S^E is small and positive for C_6H_6 + $(C_4H_9)_2NH$ and then increases as the alkyl chain of the amine is increased.

It is observed that the order of magnitude of K_S^E at x_1 = 0.5 for the present mixtures is roughly the same as that of V^E though the values of K_S^E are not strictly proportional to the values of V^E.

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