

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231533979>

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

ARTICLE *in* JOURNAL OF CHEMICAL & ENGINEERING DATA · MAY 1995

Impact Factor: 2.04 · DOI: 10.1021/je00019a015

---

CITATIONS

17

---

READS

21

3 AUTHORS, INCLUDING:



**Shantilal Oswal**

Veer Narmad South Gujarat University

102 PUBLICATIONS 1,620 CITATIONS

SEE PROFILE



**Ashok D. Patel**

Anand Agricultural University

13 PUBLICATIONS 94 CITATIONS

SEE PROFILE

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

Shantilal Oswal,\* Prem Oswal,<sup>†</sup> 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  $\rho$  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  $\eta$ , 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<sub>4</sub>H<sub>9</sub>)<sub>2</sub>NH), dihexylamine ((C<sub>6</sub>H<sub>13</sub>)<sub>2</sub>NH), and dioctylamine ((C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>NH) with cyclohexane (C<sub>6</sub>H<sub>12</sub>) and benzene (C<sub>6</sub>H<sub>6</sub>) 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<sub>6</sub>H<sub>12</sub> and C<sub>6</sub>H<sub>6</sub> and 99.5% for dialkylamines. The densities  $\rho$  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.

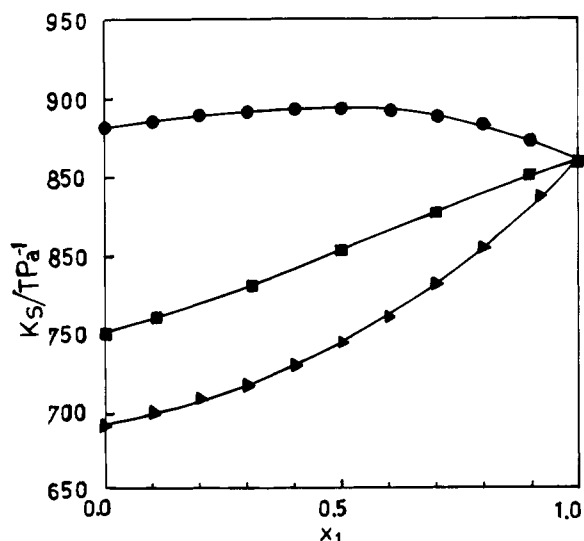
Mixtures were prepared by mixing known masses of pure liquids in air-tight, narrow-mouth ground-glass-stoppered bottles, taking due precaution to minimize the evaporation losses. A Mettler (AE 163, Switzerland) balance with a precision of 0.01 mg was used to measure the masses of the liquids. Hence, 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  $\rho$  were measured using a fine capillary single-stem calibrated pycnometer. The temperature was controlled to  $\pm 0.02$  K by water thermostats. Details of these apparatus and operational procedure for the measurements have been described previously (Oswal and Palsanawala, 1989; Patel,

**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	$\rho/(\text{kg m}^{-3})$		$n_D$		$10^3\alpha/\text{K}^{-1}$	$C_p/(\text{J K}^{-1}\text{mol}^{-1})$
	exptl	lit.	exptl	lit.		
C <sub>6</sub> H <sub>12</sub>	773.90	773.89 <sup>a</sup>	1.4236	1.42354 <sup>a</sup>	1.233 <sup>e</sup>	158.1 <sup>a</sup>
C <sub>6</sub> H <sub>6</sub>	873.62	873.60 <sup>a</sup>	1.4979	1.49792 <sup>a</sup>	1.233 <sup>e</sup>	136.8 <sup>a</sup>
(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NH	755.95	755.72 <sup>b</sup>	1.4159	1.4152 <sup>a</sup>	1.066 <sup>f</sup>	305.2 <sup>a</sup>
		757.7 <sup>a</sup>				
(C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub> NH	782.93		1.4336	1.4319 <sup>c,d</sup>	0.921 <sup>g</sup>	418.8 <sup>h</sup>
(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> NH	797.3	796.8 <sup>c,d</sup>	1.4420	1.4415 <sup>c,d</sup>	0.831 <sup>g</sup>	532.3 <sup>h</sup>

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



**Figure 1.** Isentropic compressibility for cyclohexane (1) + di-alkylamines (2) at 303.15 K. Experimental points: ●, (C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>NH; ■, (C<sub>6</sub>H<sub>13</sub>)<sub>2</sub>NH; ▲, (C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>NH; (—) calculated with eq 1.

1991). The values of the speeds of sound  $U$  and densities  $\rho$  were reproducible to within  $\pm 1.0 \text{ m s}^{-1}$  and  $\pm 0.1 \text{ kg m}^{-3}$ , respectively. The isentropic compressibilities  $K_S$  determined from the relation  $K_S = 1/(U^2\rho)$  are believed to be reliable to within  $2.0 \text{ TPa}^{-1}$ .

## 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

\* To whom correspondence should be addressed.

<sup>†</sup> Present address: Department of Chemistry, Government College, Pratapgarh, Rajasthan 312 605, India.

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

$x_1$	$U/$ (m·s <sup>-1</sup> )	$\rho/$ (kg·m <sup>-3</sup> )	$K_S/TPa^{-1}$	$V^E/$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$K_S^E/TPa^{-1}$
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  $\alpha_i^\circ$  and  $C^\circ_{p,i}$  used for these calculations are included in Table 1. The values of  $U$  and  $K_S$  are expressed by

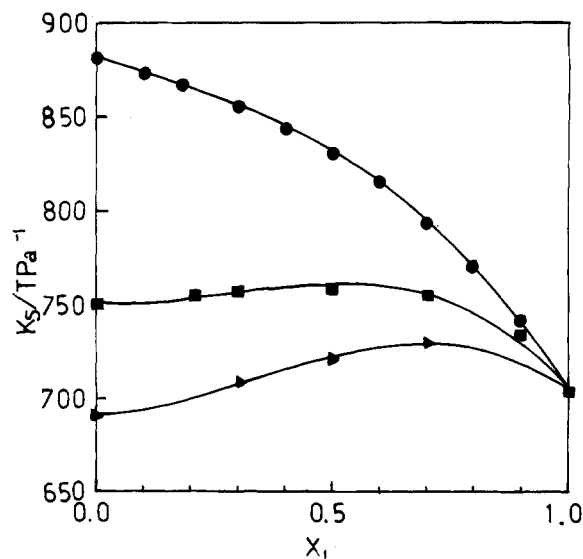
$$U \text{ or } K_S = \sum_{i=0}^m A_i x_1^i \quad (1)$$

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

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

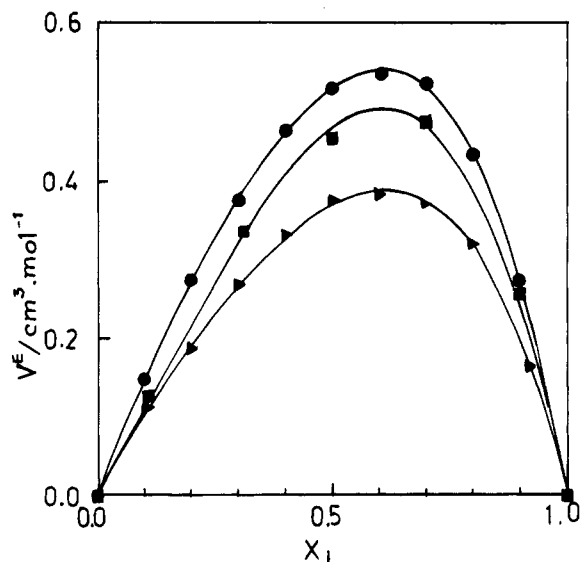
**Table 3. Coefficients  $A_i$  and Standard Deviations  $S$  for Eqs 1 and 2 for the Binary Mixtures at 303.15 K**

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

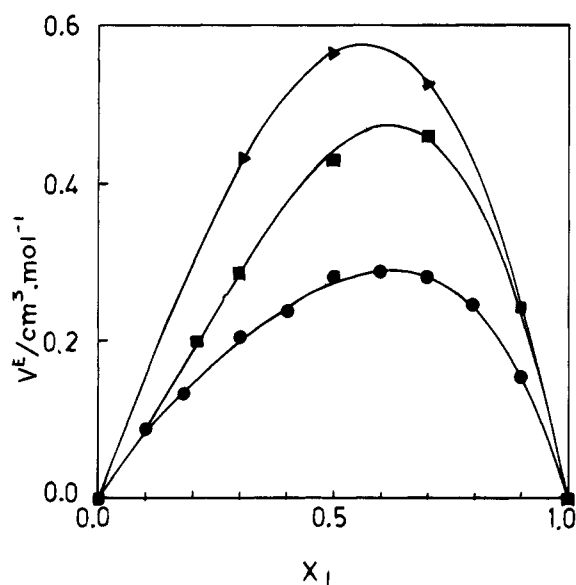
**Figure 2.** Isentropic compressibility for benzene (1) + dialkylamines (2) at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 1.

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.

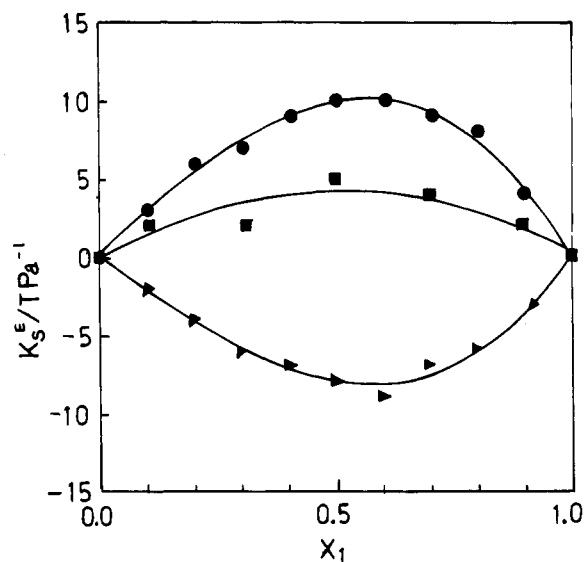


**Figure 4.** Excess volume for benzene (1) + dialkylamines (2) at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 2.

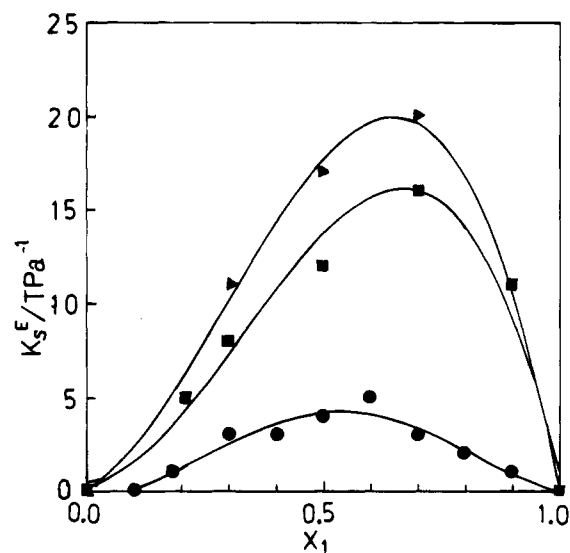
cyclohexane + dihexylamine. On the other hand, all three corresponding mixtures with benzene show considerable positive deviations, with a maximum in two mixtures.

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



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

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  $V^E$ .

## Literature Cited

- Letcher, T. M. Thermodynamics of Mixtures Containing Aliphatic Amines. II. Excess Volumes of Primary, or Secondary or Tertiary Aliphatic Amines + Substituted Cyclohexanes. *J. Chem. Thermodyn.* 1972, 4, 551–564.

- Oswal, S. L.; Palsanawala, P. P. Ultrasonic Velocity, Refractive Index and Isentropic Compressibility of Cyclohexane + Benzene, Ethyl Acetate + Cyclohexane and Ethyl Acetate + Benzene from 303.15 to 323.15 K *Acoust. Lett.* **1989**, *13*, 66–73.
- Oswal, S. L.; Patel, A. T. Viscosity of Binary Mixtures. I. Mono-, Di-, and Tri-*n*-Butyl and -*n*-Octylamine with Cyclohexane. *Int. J. Thermophys.* **1991**, *12*, 821–835.
- Oswal, S. L.; Patel, A. T. Viscosity of Binary Mixtures. II. *n*-Butyl, *n*-Hexyl, *n*-octyl, *n*-Decyl, *n*-Dodecylamine with Benzene and *n*-Hexyl, *n*-Octyl, *n*-Decyl, *n*-Dodecylamine with Cyclohexane. *Int. J. Thermophys.* **1992**, *13*, 629–641.
- Oswal, S. L.; Patel, A. T. Speeds of Sound, Isentropic Compressibilities, and Excess Volumes of Binary Mixtures. 1. Tri-*n*-Alkylamines with Cyclohexane and Benzene. *J. Chem. Eng. Data* **1994**, *39*, 366–371.
- Oswal, S. L.; Patel, A. T. Speeds of Sound, Isentropic Compressibilities, and Excess Volumes of Binary Mixtures. 2. Mono-*n*-alkylamines with Cyclohexane and Benzene. *J. Chem. Eng. Data* **1995**, *40*, 194–198.
- Oswal, S. L.; Rao, A. V. Studies on Viscosity & Volume of Mixing of Binary Liquid Mixtures of Tertiary Amines with Cyclohexane and Benzene. *Indian J. Chem.* **1985**, *24A*, 1026–1030.
- Patel, A. T. Studies of Acoustic, Transport and Thermodynamic Properties of Binary Liquid Mixtures of Alkylamines with Cyclohexane and Benzene. Ph.D. Thesis, South Gujarat University, Surat, 1991.
- Patel, S. G. Molecular Interactions in Liquid and Liquid Mixtures Containing Alkylamines. Ph.D. Thesis, South Gujarat University, Surat, 1991.
- Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill International: New York, 1987.
- Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents Physical Properties and Methods of Purifications*, 4th ed.; Wiley-Interscience: New York, 1986.
- Sindhe, R. G. Studies on Density, Ultrasonic Velocity, Refractive Index and Viscosity of Mono-, Di-, and Tri-Alkylamines. M. Phil. Dissertation, South Gujarat University, Surat, 1986.
- Tamura, K.; Murakami, S. Speeds of Sound, Isentropic and Isothermal Compressibilities, and Isochoric Heat Capacities of {*xc*-C<sub>6</sub>H<sub>12</sub> + (1-*x*)C<sub>6</sub>H<sub>6</sub>} from 293.15 to 303.15 K. *J. Chem. Thermodyn.* **1984**, *16*, 33–38.
- Weast, R. C. *Handbook of Chemistry and Physics*, 59th ed.; Chemical Rubber Co.: Cleveland, OH, 1979.

Received for review September 22, 1994. Accepted January 25, 1995.\*

JE9401981

\* Abstract published in *Advance ACS Abstracts*, March 1, 1995.