# Speeds of Sound, Isentropic Compressibilities, and Excess Volumes of Binary Mixtures. 2. Mono-*n*-alkylamines with Cyclohexane and Benzene

**Shantilal 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 the densities $\varrho$ and speeds of sound $U$ for 10 binary mixtures of (butylamine, hexylamine, octylamine, decylamine, or dodecylamine + cyclohexane or + benzene) at 303.15 K. The relative magnitude and sign of $V^E$ and $K_S^E$ have been interpreted in terms of molecular interactions.

## Introduction

As a part of our systematic study of the thermodynamic, transport, and acoustic properties of binary liquid mixtures containing alkylamines (*1*–*7*), in the previous paper (*8*) we reported isentropic compressibilities $K_S$, excess isentropic compressibilities $K_S^E$, and excess volumes $V^E$ for eight binary mixtures of tri-*n*-alkylamines with cyclohexane ($C_6H_{12}$) and benzene. In this paper, we report isentropic compressibilities $K_S$, excess isentropic compressibilities $K_S^E$, deviations in the speed of sound $\Delta U$, and excess

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

| liquid | $\varrho$/(kg·m$^{-3}$) exptl | $\varrho$/(kg·m$^{-3}$) lit. | $n_D$ exptl | $n_D$ lit. | $\alpha$/kK$^{-1}$ | $C_P$/(J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|---|---|
| cyclohexane | 773.90 | 773.89[a] | 1.4236 | 1.423 54[a] | 1.233[b] | 136.8[a] |
| benzene | 873.62 | 873.60[a] | 1.4979 | 1.497 92[a] | 1.233[b] | 158.1[a] |
| butylamine | 733.23 | 733.08[c]<br>734.52[d] | 1.3997 | 1.398 75[e] | 1.319[f] | 190.7[a] |
| hexylamine | 761.20 | 760.70[g] | 1.4160 | 1.416 11[e] | 1.068[f] | 247.5[h] |
| octylamine | 779.35 | 778.90[i] | 1.4271 | 1.427 03[e] | 0.967[f] | 304.3[h] |
| decylamine | | | 1.4345 | 1.434 80[e] | 0.909[f] | 361.0[h] |
| dodecylamine | 794.7 | 791.2[g] | 1.4377 | 1.437 36[e] | 0.872[f] | 417.8[h] |

[a] Reference 9. [b] Reference 23. [c] Reference 11. [d] Reference 12. [e] Reference 13. [f] Derived from densities in refs 24 and 25. [g] Reference 14. [h] Estimated by the Missenard group contribution method, ref 26. [i] Reference 15.

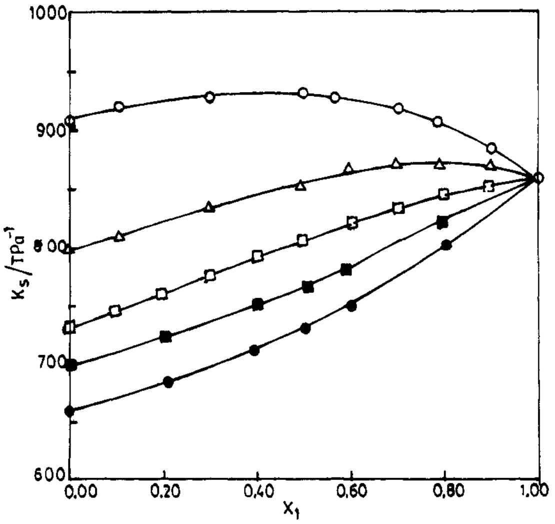

**Figure 1.** Dependence of isentropic compressibility on mole fraction for cyclohexane + alkylamines at 303.15 K. Experimental points: ○, $C_4H_9NH_2$; △, $C_6H_{13}NH_2$; □, $C_8H_{17}NH_2$; ■, $C_{10}H_{21}NH_2$; ●, $C_{12}H_{25}NH_2$; solid lines, calculated with eq 9.

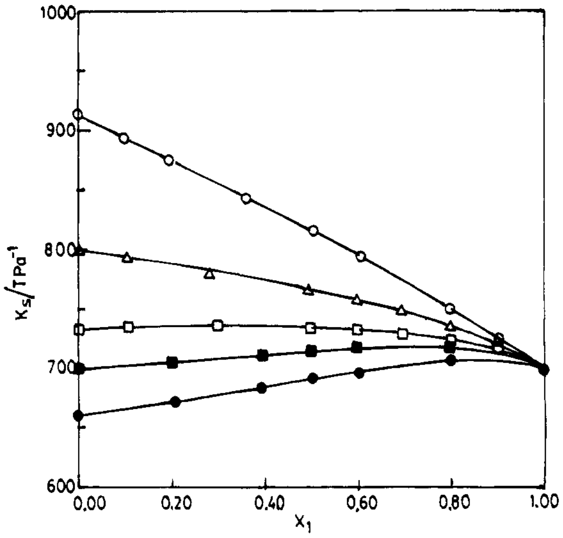

**Figure 2.** Dependence of isentropic compressibility on mole fraction for benzene + alkylamines at 303.15 K. Symbols as in legend to Figure 1.

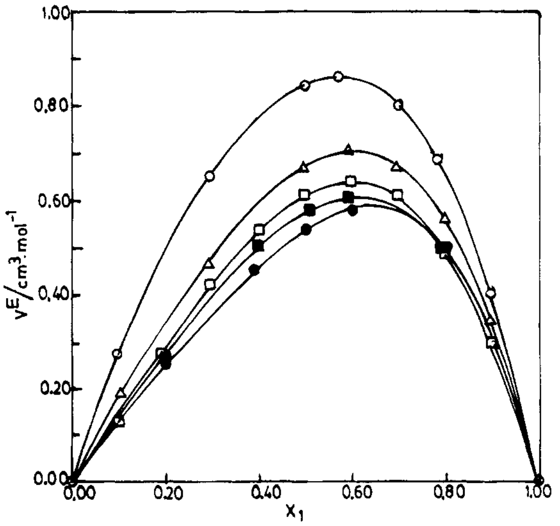

**Figure 3.** Dependence of excess volume on mole fraction at 303.15 K for mixtures of cyclohexane with alkylamines. Experimental points: ○, $C_4H_9NH_2$; △, $C_6H_{13}NH_2$; □, $C_8H_{17}NH_2$; ■, $C_{10}H_{21}NH_2$; ●, $C_{12}H_{25}NH_2$; solid lines, calculated with eq 10.

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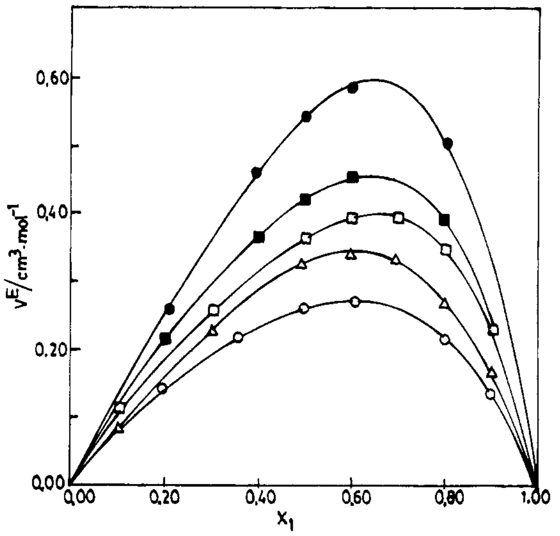

**Figure 4.** Dependence of excess volume on mole fraction at 303.15 K for mixtures of benzene with alkylamines. Symbols as in legend to Figure 3.

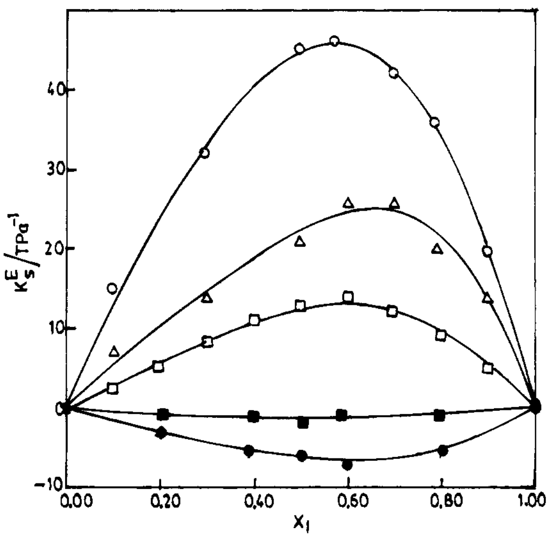

**Figure 5.** Dependence of excess isentropic compressibility on mole fraction at 303.15 K for mixtures of cyclohexane with alkylamines. Symbols as in legend to Figure 3.

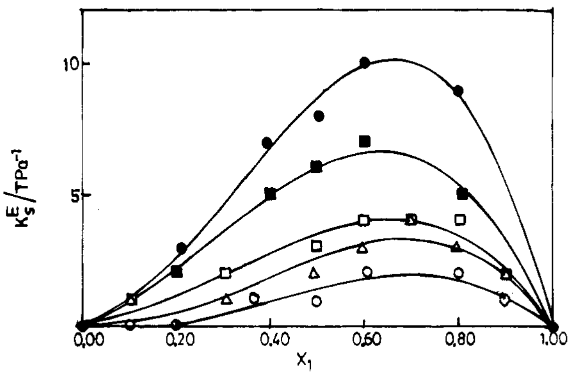

**Figure 6.** Dependence of excess isentropic compressibility on mole fraction at 303.15 K for mixtures of benzene with alkylamines. Symbols as in legend to Figure 3.

volumes $V^E$ determined from the measurements of densities $\varrho$ and speeds of sound $U$ for 10 binary mixtures of butylamine ($C_4H_9NH_2$), hexylamine ($C_6H_{13}NH_2$), octylamine ($C_8H_{17}NH_2$), decylamine ($C_{10}H_{21}NH_2$), and dodecylamine ($C_{12}H_{25}NH_2$) with cyclohexane ($C_6H_{12}$) and benzene ($C_6H_6$) at 303.15 K.

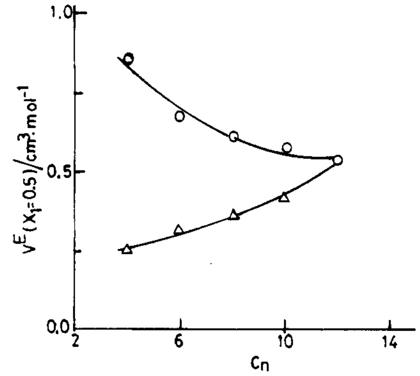

**Figure 7.** Variation of equimolar $V^E$ at 303.15 K with the number of carbon atoms $C_n$ in the alkylamine: (a) ○, cyclohexane + alkylamine; (b) △, benzene + alkylamine.

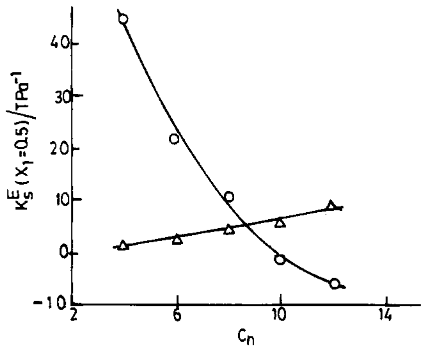

**Figure 8.** Variation of equimolar $K_S^E$ at 303.15 K with the number of carbon atoms $C_n$ in the alkylamine; (a) ○, cyclohexane + alkylamines; (b) △, benzene + alkylamine.

## Experimental Section

Cyclohexane (Fluka, AG) and benzene (BDH, AR), of purity better than 99.8%, butylamine (Fluka, AG), hexylamine (Fluka, AG), and octylamine (Fluka, AG), of purity better than 99%, were used. Decylamine and dodecylamine were of research grade form Sisco Research Laboratory Ltd., Bombay. $C_6H_{12}$ was dried over type 4A molecular sieves and fractionally distilled twice over sodium metal pieces. $C_6H_6$ was shaken with $H_2SO_4$ to remove traces of thiophene (*9*) and washed with $NaHCO_3$ and distilled water. It was dried over sodium prior to distillation. All the amines were kept over sodium and fractionally distilled three times (*10*). The purities of all the liquid samples were ascertained by the constancy of their boiling points, and also from their density and refractive index values which agreed as shown in Table 1 with the literature values (*9–15*). The estimated purities (as tested by gas–liquid chromatographic analysis) of $C_6H_{12}$ and $C_6H_6$ were better than 99.9 mol % while those of amines were better than 99.5 mol %.

Mixtures were prepared by weighing the liquids in ground stoppered weighing bottles taking due precaution to minimize the evaporation losses. All the weighings were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

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 $\varrho$ were measured using a fine capillary single-stem calibrated pycnometer. The temperature was controlled to ±0.02 K by water thermostats. The details of

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

| $x_1$ | $U/(\mathrm{m \cdot s^{-1}})$ | $K_S/\mathrm{TPa^{-1}}$ | $V^E/(\mathrm{cm^3 \cdot mol^{-1}})$ | $K_S^E/\mathrm{TPa^{-1}}$ | $\Delta U/(\mathrm{m \cdot s^{-1}})$ | $x_1$ | $U/(\mathrm{m \cdot s^{-1}})$ | $K_S/\mathrm{TPa^{-1}}$ | $V^E/(\mathrm{cm^3 \cdot mol^{-1}})$ | $K_S^E/\mathrm{TPa^{-1}}$ | $\Delta U/(\mathrm{m \cdot s^{-1}})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cyclohexane (1) + Butylamine (2) | | | | | | | | | | | |
| 0.0000 | 1227 | 912 | | | | 0.7003 | 1203 | 919 | 0.810 | 42 | −24 |
| 0.1009 | 1218 | 922 | 0.280 | 15 | −8 | 0.7863 | 1207 | 908 | 0.693 | 36 | −21 |
| 0.3012 | 1208 | 930 | 0.660 | 32 | −18 | 0.8993 | 1217 | 885 | 0.409 | 20 | −12 |
| 0.4982 | 1201 | 932 | 0.848 | 45 | −25 | 1.0000 | 1230 | 859 | | | |
| 0.5729 | 1200 | 930 | 0.867 | 46 | −26 | | | | | | |
| Cyclohexane (1) + Hexylamine (2) | | | | | | | | | | | |
| 0.0000 | 1286 | 799 | | | | 0.6964 | 1227 | 873 | 0.678 | 26 | −15 |
| 0.1064 | 1274 | 814 | 0.196 | 7 | −5 | 0.7966 | 1226 | 873 | 0.575 | 20 | −11 |
| 0.2992 | 1257 | 836 | 0.480 | 14 | −9 | 0.8980 | 1225 | 871 | 0.356 | 14 | −8 |
| 0.4953 | 1241 | 856 | 0.678 | 21 | −12 | 1.0000 | 1230 | 859 | | | |
| 0.5974 | 1232 | 868 | 0.716 | 26 | −15 | | | | | | |
| Cyclohexane (1) + Octylamine (2) | | | | | | | | | | | |
| 0.0000 | 1327 | 733 | | | | 0.5993 | 1258 | 823 | 0.642 | 14 | −8 |
| 0.0971 | 1316 | 746 | 0.131 | 2 | −1 | 0.6975 | 1250 | 834 | 0.616 | 12 | −6 |
| 0.1959 | 1304 | 761 | 0.278 | 5 | −3 | 0.7993 | 1242 | 844 | 0.496 | 9 | −4 |
| 0.2997 | 1292 | 777 | 0.421 | 8 | −5 | 0.8960 | 1236 | 852 | 0.307 | 5 | −2 |
| 0.4010 | 1280 | 793 | 0.540 | 11 | −6 | 1.0000 | 1230 | 859 | | | |
| 0.4970 | 1269 | 808 | 0.611 | 13 | −7 | | | | | | |
| Cyclohexane (1) + Decylamine (2) | | | | | | | | | | | |
| 0.0000 | 1350 | 698 | | | | 0.5875 | 1284 | 782 | 0.606 | −1 | 4 |
| 0.2056 | 1328 | 724 | 0.279 | −1 | 1 | 0.7947 | 1256 | 822 | 0.502 | −1 | 2 |
| 0.3987 | 1306 | 752 | 0.506 | −1 | 2 | 1.0000 | 1230 | 859 | | | |
| 0.5065 | 1295 | 767 | 0.580 | −2 | 4 | | | | | | |
| Cyclohexane (1) + Dodecylamine (2) | | | | | | | | | | | |
| 0.0000 | 1380 | 661 | | | | 0.6032 | 1305 | 752 | 0.578 | −7 | 9 |
| 0.2093 | 1358 | 686 | 0.258 | −3 | 4 | 0.8037 | 1269 | 802 | 0.506 | −5 | 6 |
| 0.3927 | 1335 | 713 | 0.438 | −5 | 6 | 1.0000 | 1230 | 859 | | | |
| 0.5029 | 1320 | 732 | 0.544 | −6 | 8 | | | | | | |
| Benzene (1) + Butylamine (2) | | | | | | | | | | | |
| 0.0000 | 1227 | 912 | | | | 0.6051 | 1248 | 796 | 0.270 | 2 | 0 |
| 0.0974 | 1229 | 894 | 0.078 | 0 | 0 | 0.7995 | 1261 | 752 | 0.219 | 2 | 0 |
| 0.1974 | 1232 | 875 | 0.141 | 0 | 1 | 0.9004 | 1269 | 729 | 0.137 | 1 | 0 |
| 0.3596 | 1237 | 845 | 0.219 | 1 | 1 | 1.0000 | 1279 | 704 | | | |
| 0.5007 | 1243 | 817 | 0.262 | 1 | 1 | | | | | | |
| Benzene (1) + Hexylamine (2) | | | | | | | | | | | |
| 0.0000 | 1286 | 799 | | | | 0.6955 | 1272 | 752 | 0.339 | 4 | −1 |
| 0.1050 | 1283 | 794 | 0.083 | 1 | 0 | 0.7954 | 1273 | 739 | 0.269 | 3 | 0 |
| 0.2983 | 1279 | 783 | 0.230 | 1 | 0 | 0.8997 | 1275 | 723 | 0.167 | 2 | 0 |
| 0.4910 | 1275 | 770 | 0.325 | 2 | 0 | 1.0000 | 1279 | 704 | | | |
| 0.5946 | 1273 | 762 | 0.342 | 3 | −1 | | | | | | |
| Benzene (1) + Octylamine (2) | | | | | | | | | | | |
| 0.0000 | 1327 | 733 | | | | 0.6967 | 1288 | 732 | 0.390 | 5 | −2 |
| 0.1044 | 1321 | 735 | 0.108 | 2 | −1 | 0.7998 | 1284 | 726 | 0.348 | 3 | −1 |
| 0.3007 | 1311 | 736 | 0.244 | 2 | −1 | 0.8990 | 1280 | 718 | 0.228 | 3 | −1 |
| 0.4980 | 1300 | 735 | 0.365 | 3 | −1 | 1.0000 | 1279 | 704 | | | |
| 0.5970 | 1294 | 734 | 0.390 | 4 | −1 | | | | | | |
| Benzene (1) + Decylamine (2) | | | | | | | | | | | |
| 0.0000 | 1350 | 698 | | | | 0.5993 | 1305 | 719 | 0.452 | 7 | −4 |
| 0.2011 | 1337 | 705 | 0.215 | 2 | −1 | 0.7973 | 1290 | 719 | 0.391 | 5 | −3 |
| 0.3988 | 1322 | 712 | 0.366 | 5 | −3 | 1.0000 | 1279 | 704 | | | |
| 0.4963 | 1314 | 716 | 0.420 | 6 | −3 | | | | | | |
| Benzene (1) + Dodecylamine (2) | | | | | | | | | | | |
| 0.0000 | 1380 | 661 | | | | 0.6046 | 1322 | 699 | 0.574 | 10 | −7 |
| 0.2072 | 1364 | 672 | 0.290 | 3 | −2 | 0.7998 | 1299 | 709 | 0.502 | 9 | −6 |
| 0.4348 | 1342 | 686 | 0.495 | 7 | −5 | 1.0000 | 1279 | 704 | | | |
| 0.5228 | 1332 | 693 | 0.557 | 8 | −6 | | | | | | |

the apparatus and procedure have been described previously (*16−18*). The values of the speeds of sound $U$ and densities $\varrho$ were reproducible to within $\pm 1.0\ \mathrm{m \cdot s^{-1}}$ and $\pm 0.1\ \mathrm{kg \cdot m^{-3}}$, respectively. The isentropic compressibilities $K_S$ determined from the relation $K_s = 1/(U^2 \varrho)$ are believed to be reliable to within 1.0 $\mathrm{TPa^{-1}}$.

## Results and Discussion

The speed of sound $U$, isentropic compressibility $K_S$, excess volume $V^E$, excess isentropic compressibility $K_S^E$, and deviation in the speed of sound $\Delta U$ for the present binary mixtures are given in Table 2. $V^E$ and $K_S^E$ in each mixture were calculated from

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

where $Y$ is either $V$ or $K_S$.

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

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

while $K_S^{id}$ for an ideal mixture was calculated from the relations recommended by Benson and Kiyohara (*19*), Tamura, Ohomuro, and Murakami (*20*), and Douheret, Moreau, and Viallard (*21*):

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

Here

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

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

and

$$C_P^{id} = \sum x_i C^\circ_{P,i} \tag{6}$$

The deviations in the speeds of sound from their values in an ideal mixture $\Delta U$ were calculated following Douheret et al. (*22*):

$$\Delta U = U - U^{id} \tag{7}$$

where

$$U^{id} = V^{id}/(K_S^{id}\sum_i x_i M_i)^{1/2} \tag{8}$$

In eqs 2–6, $V_i^\circ$, $\alpha_i^\circ$, and $C^\circ_{P,i}$ are, respectively, the molar volume, isobaric thermal expansion coefficient, and molar isobaric heat capacity for pure component $i$ and $\phi_i = x_iV_i^\circ/\sum x_jV_j^\circ$ is the volume fraction of $i$ in the mixture, stated in terms of the unmixed components. The values of $\alpha_i^\circ$ and $C^\circ_{P,i}$ used for these calculations are listed in Table 1.

The values of $U$ and $K_S$ are expressed by

$$U \text{ or } K_S = \sum_{i=0}^{m} A_i x_1^i \tag{9}$$

and of the functions $V^E$, $K_S^E$, or $\Delta U$ by

$$V^E, K_S^E, \text{ or } \Delta U = x_1x_2\sum_{i=0}^{m} A_i(1 - 2x_1)^i \tag{10}$$

The coefficients $A_i$ of eqs 9 and 10 obtained by the least-squares method together with the standard deviations $S$ are given in Table 3. The dependence of $K_S$, $V^E$, and $K_S^E$ on composition is shown in Figures 1–6, while the variation of $V^E$ and $K_S^E$ at equimolar composition with number of carbon atoms in the alkylamine is depicted in Figures 7 and 8.

The $V^E$ values are positive for all 10 binary mixtures at 303.15 K. Present equimolar $V^E$ values for $C_6H_{12}$ + $C_4H_9NH_2$ and $C_6H_6$ + $C_4H_9NH_2$ at 303.15 K are within 0.018–0.027 $cm^3 \cdot mol^{-1}$, respectively, of those at 298.15 K reported by Letcher (*11*). The slight difference in the two values may be due the effect of temperature on $V^E$. The $V^E$ versus $x_1$ curves (Figures 3 and 4) are asymmetrical about $x_1$ = 0.5, and maxima are inclined toward the cyclohexane or benzene rich region. The maximum shifts from 0.57$x_1$ to 0.65$x_1$ as the number of carbons in the *n*-alkyl chain of the amine is increased from 4 to 12. The asymmetry of the curves may originate from the self-association in the primary alkylamine.

Figure 7 reveals that $V^E$ increases as the chain length of the alkylamine is increased in benzene + alkylamine mixtures while the reverse is the case of cyclohexane + alkylamine. The excess volumes $V^E$ for all five binary mixtures of the primary amines (butyl to dodecyl) with benzene are smaller than the corresponding cyclohexane series. Thus, by replacing benzene for cyclohexane in the binary mixture, the values of $V^E$ are reduced, and this reduction clearly supports π–n interaction between benzene and the primary amine (*3*, *11*).

**Table 3. Coefficients $A_i$ and Standard Deviations $S$ for Eqs 9 and 10 for the Binary Mixtures at 303.15 K**

| property | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $S$ |
|---|---|---|---|---|---|
| Cyclohexane (1) + Butylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1126.3 | −70.8 | 4.1 | 70.3 | 0.8 |
| $K_S/TPa^{-1}$ | 912.9 | 74.3 | −12.9 | −115.3 | 1.1 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 3.397 | −0.899 | 0.636 | | 0.001 |
| $K_S^E/TPa^{-1}$ | 177.7 | −41.8 | 24.0 | | 1.6 |
| $\Delta U/(m \cdot s^{-1})$ | −104.3 | 30.4 | | | 0.9 |
| Cyclohexane (1) + Hexylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1285.2 | −88.0 | 48.0 | 80.4 | 1.2 |
| $K_S/TPa^{-1}$ | 800.2 | 100.8 | 107.2 | −148.5 | 1.8 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 2.713 | −1.157 | 0.403 | | 0.005 |
| $K_S^E/TPa^{-1}$ | 89.0 | −51.8 | 35.0 | | 1.7 |
| $\Delta U/(m \cdot s^{-1})$ | −51.8 | 22.6 | 26.5 | | 1.2 |
| Cyclohexane (1) + Octylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1328.7 | −139.0 | 39.4 | | 1.2 |
| $K_S/TPa^{-1}$ | 732.6 | 137.0 | 61.0 | 72.1 | 0.5 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 2.473 | −1.097 | −0.144 | | 0.004 |
| $K_S^E/TPa^{-1}$ | 52.0 | −20.3 | −21.8 | | 0.4 |
| $\Delta U/(m \cdot s^{-1})$ | −23.1 | 30 | 19.4 | | 0.5 |
| Cyclohexane (1) + Decylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1350.0 | −101.4 | −19.0 | | 1.0 |
| $K_S/TPa^{-1}$ | 697.8 | 117.3 | 45.0 | | 1.7 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 2.310 | −1.150 | 0.237 | | 0.005 |
| $\Delta U/(m \cdot s^{-1})$ | 11.8 | | | | 1.0 |
| Cyclohexane (1) + Dodecylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1379.6 | −88.1 | −61.4 | | 0.6 |
| $K_S/TPa^{-1}$ | 661.2 | 101.1 | 64.3 | 32.8 | 0.9 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 2.170 | −1.356 | 0.555 | | 0.006 |
| $K_S^E/TPa^{-1}$ | −24.7 | 12.3 | | | 0.3 |
| $\Delta U/(m \cdot s^{-1})$ | 31.3 | −13.6 | | | 0.7 |
| Benzene (1) + Butylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1227.6 | 10.3 | 40.3 | | 0.7 |
| $K_S/TPa^{-1}$ | 910.0 | −169.5 | −36.5 | | 1.1 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 1.040 | −0.398 | 0.257 | | 0.001 |
| Benzene (1) + Hexylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1285.6 | −16.0 | −35.5 | 44.7 | 0.4 |
| $K_S/TPa^{-1}$ | 799.3 | −59.7 | 39.0 | −74.5 | 0.4 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 1.318 | −0.595 | 0.065 | | 0.006 |
| $K_S^E/TPa^{-1}$ | 12.6 | −9.3 | | | 1.1 |
| Benzene (1) + Octylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1326.5 | −39.6 | −51.3 | 43.1 | 0.7 |
| $K_S/TPa^{-1}$ | 733.8 | −5.4 | 63.8 | −87.4 | 1.1 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 1.443 | −0.842 | 0.617 | | 0.004 |
| $K_S^E/TPa^{-1}$ | 18.4 | 7.5 | | | 1.1 |
| Benzene (1) + Decylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1349.9 | −49.8 | −71.8 | 50.6 | 0.3 |
| $K_S/TPa^{-1}$ | 698.3 | 11.5 | 105.2 | −110.7 | 0.9 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 1.685 | −0.906 | 0.549 | | 0.001 |
| $K_S^E/TPa^{-1}$ | 23.5 | −16.0 | | | 0.4 |
| $\Delta U/(m \cdot s^{-1})$ | −13.2 | 10.4 | | | 0.3 |
| Benzene (1) + Dodecylamine (2) | | | | | |
| $U/(m \cdot s^{-1})$ | 1379.8 | −54.3 | −100.8 | 54.1 | 0.6 |
| $K_S/TPa^{-1}$ | 661.5 | 17.4 | 148.9 | −123.3 | 1.5 |
| $V^E/(cm^3 \cdot mol^{-1})$ | 2.153 | −1.139 | 0.820 | 0.006 | 0.006 |
| $K_S^E/TPa^{-1}$ | 34.5 | −32.3 | | | 0.7 |
| $\Delta U/(m \cdot s^{-1})$ | −24.1 | 21.7 | | | 0.2 |

The values of $K_S^E$ (Figures 5 and 6) are positive for all the mixtures except for $C_6H_{12}$ + $C_{10}H_{21}NH_2$ and $C_6H_{12}$ + $C_{12}H_{25}NH_2$. For the latter mixture $K_S^E$ is slightly negative. The maximum/minimum in the $K_S^E$ curves is in the range 0.55–0.70 mole fraction of the first component for most mixtures. The maximum/minimum generally shifts toward higher $x_1$ as the alkyl chain length in the amine is increased. Thus, the sign and magnitude of $K_S^E$ are dependent on the size of the alkylamine molecules and the type of solvent used. In the case of mixtures with benzene, the values of $K_S^E$ marginally increase with the chain length of the alkylamines (Figure 8) while there is a substantial decrease in $K_S^E$ from large positive to negative values in the case of mixtures involving cyclohexane. Further, it is noticed that the order of magnitudes of $K_S^E$ for the present mixtures is roughly the same as that of $V^E$ though values of $K_S^E$ are not strictly proportional to the values of $V^E$. This behavior qualitatively reflects the differences in the molecular interactions of the component molecules.

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Received for review May 16, 1994. Accepted August 28, 1994.[⊗] A.T.P. thanks the Government of Gujarat for the award of a research fellowship during the course of this work.

JE940093Y

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.