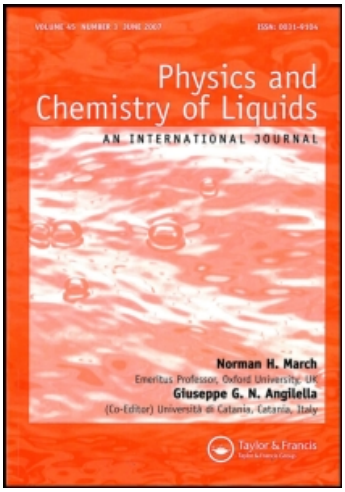


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# Ultrasonic Behaviour of Amine and Alcohol Mixtures

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# Ultrasonic Behaviour of Amine and Alcohol Mixtures

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Sound velocities for binary liquid mixtures of diethylamine (DEA) and triethylamine (TEA) with isomeric butanols have been measured at 303.15 K. The sound velocity data along with densities have been used to compute isentropic compressibilities ($K_s$) and the deviation in isentropic compressibilities ($\Delta K_s$). The values of $\Delta K_s$ were found to be negative over the entire range of composition in all the systems. The negative values suggest that strong hydrogen bonding interaction exists between unlike molecules. The results also indicate that the interaction decreases with increase in branching of the alcohol.

Key Words: Sound velocities, amine and alcohol mixtures, isentropic compressibilities ($K_s$).

## 1 INTRODUCTION

Isentropic compressibilities of binary mixtures containing associated liquids like water, alcohols, acids and amines as one component have been studied. However, very few attempts have been made to study isentropic compressibilities of mixtures containing two associated components. Properties of these mixtures depend on (a) the degree of association of each component in pure state, (b) the structure breaking effect of the components and (c) the possible interaction between unlike molecules. We report here new experimental data of sound velocity ($u$), density ($\rho$), isentropic compressibilities ($K_s$) and deviation in isentropic compressibilities ($\Delta K_s$) for the mixtures of DEA and TEA with *n*-butanol, *i*-butanol, *s*-butanol and *t*-butanol at 303.15 K. This study has been undertaken to understand the possible interaction between unlike molecules.

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**Table 1** Densities of pure component liquids at 303.15 K

| Component | Density ($\rho$)/(g cm$^{-3}$) | |
|---|---|---|
| | Experimental | Literature |
| diethylamine | 0.69612 | 0.69620 |
| triethylamine | 0.71891 | 0.71899 |
| *n*-butanol | 0.80195 | 0.80200 |
| *i*-butanol | 0.79434 | 0.79437 |
| *s*-butanol | 0.79901 | 0.79895 |
| *t*-butanol | 0.77560 | 0.77570 |

## 2 EXPERIMENTAL SECTION

### (a) Materials

The component liquids have been purified as described by Reddick and Bunger.[1] The amines have been dried over potassium hydroxide pellets for 3 days, then kept over sodium wire followed by 2 h refluxion and finally fractionally distilled. Butanols are refluxed over freshly ignited calcium oxide for 4 h and fractionally distilled. The purity of the samples has been checked by measuring the densities and comparing with literature values.[2] The data have been given in Table 1. The densities of pure components have been measured using bicapillary pycnometer.[3]

### (b) Sound velocities

Sound velocities have been measured with the ultrasonic interferometer at a frequency of 3 MHz and are accurate to $\pm 0.02\%$. The measurements have been made at 303.15 K by circulating water around the cell from U-10 thermostat maintained at 303.15 $\pm$ 0.01 K.

### (c) Isentropic compressibility

The isentropic compressibilities have been calculated from the relation[4]

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

where $u$ and $\rho$ denote sound velocity and density respectively. Density values have been computed from experimental excess volume data using the equation

$$\rho = \frac{xM_1 + (1-x)M_2}{V^0 + V^E} \tag{2}$$

**Table 2** Volume fractions ($\phi$), densities ($\rho$), sound velocities ($u$), isentropic compressibilities ($K_s$) and deviation in isentropic compressibilities ($\Delta K_s$) of binary liquid mixtures at 303.15 K

| $\phi$ | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $K_s$ (T Pa$^{-1}$) | $\Delta K_s$ (T Pa$^{-1}$) | $\phi$ | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $K_s$ (T Pa$^{-1}$) | $\Delta K_s$ (T Pa$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| diethylamine + *n*-butanol | | | | | diethylamine + *i*-butanol | | | | |
| 0.0000 | 0.80195 | 1225.4 | 830.6 | — | 0.0000 | 0.79434 | 1172.5 | 915.7 | — |
| 0.1492 | 0.79323 | 1220.5 | 846.3 | −39.6 | 0.1398 | 0.78617 | 1180.2 | 913.6 | −42.1 |
| 0.2199 | 0.78867 | 1216.5 | 856.8 | −55.4 | 0.2310 | 0.78084 | 1179.0 | 921.4 | −60.3 |
| 0.3198 | 0.78129 | 1209.6 | 874.8 | −74.4 | 0.3476 | 0.77313 | 1173.7 | 938.5 | −76.7 |
| 0.4209 | 0.77255 | 1200.9 | 897.5 | −89.2 | 0.4179 | 0.76774 | 1169.4 | 952.8 | −82.4 |
| 0.5140 | 0.76320 | 1191.8 | 922.5 | −98.8 | 0.5043 | 0.76013 | 1163.3 | 972.6 | −87.3 |
| 0.5826 | 0.75535 | 1183.8 | 944.7 | −102.0 | 0.6214 | 0.74981 | 1153.6 | 1000.4 | −88.9 |
| 0.6797 | 0.74313 | 1170.5 | 982.2 | −100.6 | 0.6905 | 0.73952 | 1146.8 | 1028.1 | −85.0 |
| 0.7556 | 0.73317 | 1157.3 | 1018.3 | −92.6 | 0.7584 | 0.73043 | 1139.1 | 1055.0 | −77.6 |
| 0.8454 | 0.71948 | 1138.3 | 1072.7 | −71.5 | 0.8663 | 0.71557 | 1122.7 | 1108.5 | −54.9 |
| 0.9230 | 0.70769 | 1118.0 | 1130.5 | −42.5 | 0.9352 | 0.70553 | 1109.1 | 1152.4 | −30.7 |
| 1.0000 | 0.69612 | 1093.4 | 1201.6 | — | 1.0000 | 0.69612 | 1093.4 | 1201.6 | — |
| diethylamine + *s*-butanol | | | | | diethylamine + *t*-butanol | | | | |
| 0.0000 | 0.79901 | 1199.8 | 869.4 | — | 0.0000 | 0.77560 | 1133.4 | 1003.7 | — |
| 0.1495 | 0.78954 | 1195.7 | 885.9 | −33.2 | 0.1277 | 0.77045 | 1127.8 | 1020.5 | −8.5 |
| 0.2670 | 0.78102 | 1191.5 | 901.8 | −56.3 | 0.2589 | 0.76286 | 1122.8 | 1039.7 | −15.2 |
| 0.3328 | 0.77538 | 1188.5 | 912.9 | −67.0 | 0.3506 | 0.75653 | 1120.0 | 1053.7 | −19.4 |
| 0.4876 | 0.76125 | 1176.7 | 948.8 | −82.6 | 0.4532 | 0.74861 | 1115.9 | 1072.7 | −20.7 |
| 0.5307 | 0.75680 | 1171.8 | 962.3 | −83.4 | 0.5469 | 0.74069 | 1112.7 | 1090.5 | −21.4 |
| 0.6665 | 0.74114 | 1154.1 | 1013.0 | −77.8 | 0.6463 | 0.73171 | 1108.6 | 1112.0 | −19.6 |
| 0.7226 | 0.73413 | 1144.7 | 1039.5 | −69.9 | 0.6954 | 0.72704 | 1106.2 | 1123.9 | −17.4 |
| 0.7792 | 0.72677 | 1135.3 | 1067.5 | −60.7 | 0.7598 | 0.72085 | 1103.7 | 1138.8 | −15.3 |
| 0.8368 | 0.71892 | 1125.1 | 1098.8 | −48.6 | 0.8579 | 0.71101 | 1099.4 | 1163.7 | −9.8 |
| 0.9295 | 0.70605 | 1107.5 | 1154.8 | −23.4 | 0.9373 | 0.70303 | 1095.3 | 1185.7 | −3.5 |
| 1.0000 | 0.69612 | 1093.4 | 1201.6 | — | 1.0000 | 0.69612 | 1093.4 | 1201.6 | — |

**Table 3** Volume fractions ($\phi$), densities ($\rho$), sound velocities ($u$), isentropic compressibilities ($K_s$) and deviations in isentropic compressibility ($\Delta K_s$) of binary liquid mixtures at 303.15 K

| $\phi$ | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $K_s$ (T Pa$^{-1}$) | $\Delta K_s$ (T Pa$^{-1}$) | $\phi$ | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $K_s$ (T Pa$^{-1}$) | $\Delta K_s$ (T Pa$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| triethylamine + *n*-butanol | | | | | triethylamine + *i*-butanol | | | | |
| 0.0000 | 0.80195 | 1225.4 | 830.6 | — | 0.0000 | 0.79434 | 1172.5 | 915.7 | — |
| 0.1584 | 0.79559 | 1219.4 | 845.3 | −38.2 | 0.1417 | 0.78933 | 1181.6 | 907.5 | −43.5 |
| 0.3472 | 0.78574 | 1212.9 | 865.1 | −81.5 | 0.1599 | 0.78862 | 1182.2 | 907.4 | −48.1 |
| 0.4858 | 0.77608 | 1202.4 | 891.2 | −101.6 | 0.3351 | 0.78030 | 1181.8 | 917.7 | −81.4 |
| 0.5543 | 0.77060 | 1194.5 | 909.4 | −106.3 | 0.4448 | 0.77371 | 1176.8 | 933.4 | −93.0 |
| 0.6816 | 0.75858 | 1172.8 | 958.4 | −99.8 | 0.5428 | 0.76687 | 1169.2 | 954.1 | −96.7 |
| 0.7871 | 0.74691 | 1150.8 | 1011.7 | −81.8 | 0.6517 | 0.75765 | 1157.3 | 985.5 | −92.4 |
| 0.8355 | 0.74100 | 1138.5 | 1042.1 | −67.6 | 0.7232 | 0.75117 | 1147.3 | 1011.6 | −84.2 |
| 0.8551 | 0.73853 | 1133.4 | 1054.4 | −61.8 | 0.7960 | 0.74375 | 1135.9 | 1042.3 | −71.5 |
| 0.9055 | 0.73198 | 1122.4 | 1084.4 | −48.6 | 0.8397 | 0.73890 | 1127.8 | 1064.3 | −60.4 |
| 0.9488 | 0.72609 | 1107.5 | 1122.7 | −24.8 | 0.9225 | 0.72898 | 1114.8 | 1104.2 | −41.1 |
| 1.0000 | 0.71891 | 1092.9 | 1164.6 | — | 1.0000 | 0.71891 | 1092.9 | 1164.6 | — |
| triethylamine + *s*-butanol | | | | | triethylamine + *t*-butanol | | | | |
| 0.0000 | 0.79901 | 1199.8 | 869.4 | — | 0.0000 | 0.77560 | 1133.4 | 1003.7 | — |
| 0.2053 | 0.78838 | 1202.1 | 878.0 | −52.0 | 0.1487 | 0.77047 | 1131.9 | 1013.7 | −14.5 |
| 0.2653 | 0.78499 | 1199.3 | 885.7 | −61.7 | 0.2080 | 0.76811 | 1131.0 | 1017.7 | −19.5 |
| 0.3310 | 0.78095 | 1195.1 | 896.5 | −70.6 | 0.3576 | 0.76182 | 1126.7 | 1034.0 | −27.2 |
| 0.4477 | 0.77309 | 1185.6 | 920.4 | −81.2 | 0.4662 | 0.75673 | 1122.2 | 1049.9 | −29.1 |
| 0.5314 | 0.76677 | 1177.2 | 941.3 | −85.0 | 0.5494 | 0.75224 | 1118.8 | 1062.3 | −29.8 |
| 0.6435 | 0.75730 | 1164.0 | 974.8 | −84.6 | 0.6396 | 0.74646 | 1113.9 | 1079.6 | −27.4 |
| 0.7333 | 0.74887 | 1151.0 | 1008.0 | −77.9 | 0.7136 | 0.74176 | 1110.2 | 1094.1 | −24.4 |
| 0.8018 | 0.74186 | 1139.4 | 1038.7 | −67.4 | 0.7892 | 0.73624 | 1106.1 | 1110.5 | −20.2 |
| 0.8445 | 0.73723 | 1131.1 | 1060.5 | −58.2 | 0.8482 | 0.73134 | 1102.9 | 1124.2 | −16.0 |
| 0.9367 | 0.72660 | 1110.2 | 1117.1 | −28.8 | 0.9058 | 0.72662 | 1099.1 | 1139.2 | −10.2 |
| 1.0000 | 0.71891 | 1092.9 | 1164.6 | — | 1.0000 | 0.71891 | 1092.9 | 1164.6 | — |

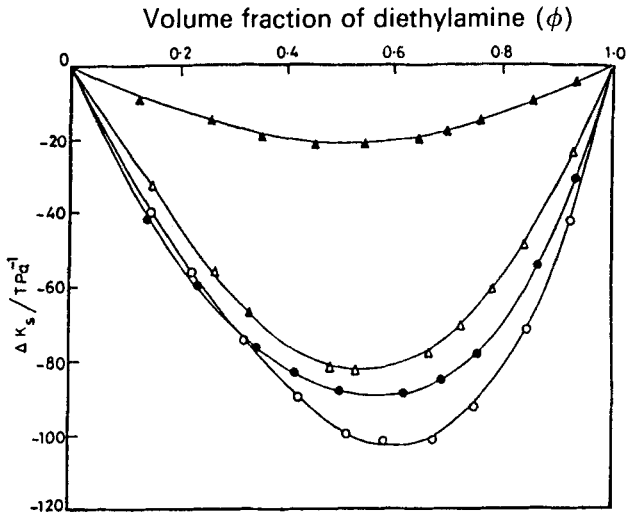


**Figure 1** The values of $\Delta K_s$ against volume fraction of diethylamine $(\phi)_0^0$ diethylamine + *n*-Butanol (○), + *i*-Butanol (●), + *s*-Butanol (△), + *t*-Butanol (▲).

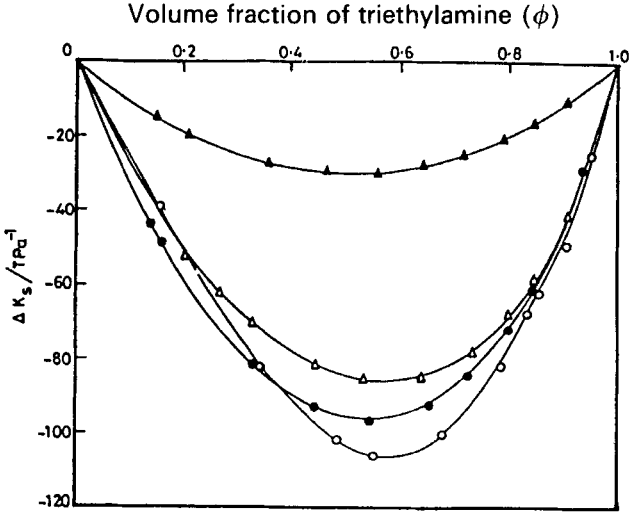


**Figure 2** The values of $\Delta K_s$ against volume fraction of triethylamine $(\phi)_0^0$ triethylamine + *n*-Butanol (○), + *i*-Butanol (●), + *s*-Butanol (△), + *t*-Butanol (▲).

where $x$, $M_1$ and $M_2$ stand for the mole fraction of amine, molecular weights of amine and alcohol respectively. $V^0$ and $V^E$ denote the ideal molar volume and excess molar volume respectively. The deviation in isentropic compressibility ($\Delta K_s$) have been obtained from the relation

$$\Delta K_s = K_s - \phi K_{s,1} - (1 - \phi)K_{s,2} \tag{3}$$

where $K_s$, $K_{s,1}$ and $K_{s,2}$ are the isentropic compressibilities of the mixture and pure components respectively. $\phi$ is the volume fraction of the amine.

## 3 RESULTS AND DISCUSSION

Experimental data for density ($\rho$), sound velocity ($u$), isentropic compressibility ($K_s$) and deviation in isentropic compressibility ($\Delta K_s$) at 303.15 K as a function of volume fraction for the mixtures of DEA and TEA with isomeric butanols are included in Tables 2 and 3 respectively. The dependence of $\Delta K_s$ on volume fraction have been graphically illustrated in Figures 1 and 2 for mixture containing DEA and TEA respectively. The values of $\Delta K_s$ are fitted to an empirical equation of the form

$$\Delta K_s = \phi(1 - \phi)[b_0 + b_1(2\phi - 1) + b_2(2\phi - 1)^2] \tag{4}$$

The values of the empirical parameters, $b_0$, $b_1$, and $b_2$ calculated by the method of least squares, are given in Table 4 along with the standard deviation, $\sigma(\Delta K_s)$. The values of $\Delta K_s$ are negative over the whole range of composition in all the systems. The negative values may be ascribed to the hydrogen bond formation between amine and alcohol. There is



**Table 4** Values of parameters in Eq. (4) and the standard deviation $\sigma$ ($\Delta K_s$) at 303.15 K

| System | $b_0$ | $b_1$ | $b_2$ | $\sigma$ ($\Delta K_s$) |
|---|---|---|---|---|
| diethylamine + *n*-butanol | −390.06 | −169.53 | −89.16 | 0.3 |
| diethylamine + *i*-butanol | −349.97 | −80.96 | −117.68 | 0.3 |
| diethylamine + *s*-butanol | −331.21 | −67.94 | 50.31 | 0.3 |
| diethylamine + *t*-butanol | −85.23 | −0.88 | 11.98 | 0.3 |
| triethylamine + *n*-butanol | −412.78 | −153.15 | 45.17 | 0.4 |
| triethylamine + *i*-butanol | −382.80 | −66.27 | −46.68 | 0.2 |
| triethylamine + *s*-butanol | −335.75 | −85.72 | −99.86 | 0.2 |
| triethylamine + *t*-butanol | −118.43 | −4.57 | −3.12 | 0.3 |

spectroscopic evidence for hydrogen bonding between amines and alcohols.[5] Hydrogen bond association between amine and alcohol have been reported in terms of heats of mixing and physical properties, dielectric constant and viscosity by Ratkovics and Coworkers.[6–8] The algebraic values of $\Delta K_s$ for the system of DEA and TEA with butanols fall in the order

$$n\text{-butanol} > i\text{-butanol} > s.\ \text{butanol} > t.\ \text{butanol}.$$

This shows that the hydrogen bonding interaction between amine and alcohol decreases with increase in branching of alcohols. The negative deviation in isentropic compressibilities for amine with butanols are increasing from DEA to TEA. This may be attributed to the more $N$-electron density on nitrogen in TEA than in DEA.

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## References

1. J. A. Reddick and W. B. Bunger, *Organic Solvents*, Wiley-Interscience, New York (1970).
2. J. Timmermans, *Physico-chemical Constants of Pure Organic Compounds*, Elsevier, New York (1950).
3. M. V. P. Rao and P. R. Naidu, *Can. J. Chem.*, **52**, 788 (1974).
4. M. V. P. Rao and P. R. Naidu, *J. Chem. Thermodyn.*, **6**, 1195 (1974).
5. L. S. Springer, Jr. and D. W. Meek, *J. Phys. Chem.*, **70**, 481 (1966).
6. F. Ratkovics, M. Laszlo, *Acta Chim.* (Budapest), **79**, 395 (1973).
7. J. Liszi, T. Salaman, F. Ratkovics, *Acta Chim.* (Budapest), **81**, 467 (1974).
8. F. Ratkovics, T. Salaman, L. Domonkos, *Acta Chim.* (Budapest), **83**, 53 (1974).