# Ultrasonic Studies of Binary Mixtures of Some Aromatic Ketones with *N*-Methyl-acetamide at 308.15 K

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The speed of sound and density of 1-phenyl-ethanone, 1-phenyl-propan-1-one, 1-*p*-tolyl-ethanone, and 1-(4-chloro-phenyl)-ethanone with *N*-methyl-acetamide, over the entire range of composition, have been measured at a temperature of 308.15 K. From the above experimental data, values of deviations in the speed of sound and isentropic compressibility have been calculated. The results are fitted to the Redlich−Kister polynomial equation of the third degree to derive the binary coefficients and standard deviations. Furthermore, the experimental results are used to study the nature of the binary interactions in these mixtures.

## Introduction

Solvent structure determines the nature of interactions between the like and unlike molecules of a liquid binary mixture. It also provides basic information to use in evaluating the solute−solvent interactions. *N*-Methyl-acetamide is an important solvent possessing strong hydrogen bonds and protic and basic character. Acetophenone and other aromatic ketones have industrial importance because they are used in perfumery. A survey of the literature indicates that no acoustical data on these mixtures has been produced. This prompted us to undertake a study on the speed of sound at a temperature of 308.15 K.

## Experimental Section

*N*-Methyl-acetamide (Merck Schuchrdt-Germany, G. R.) is a solid at room temperature. Its melting point is 301.15 K. It is purified by distillation under reduced pressure over an inert atmosphere.[1] The middle fraction of the distillate is collected and stored over 0.3-nm molecular sieves.

All four phenones (1-phenyl-ethanone, 1-phenyl-propan-1-one, 1-*p*-tolyl-ethanone and 1-(4-chloro-phenyl)-ethanone) purchased from SISCO (India) company are dried over anhydrous potassium carbonate for 3 days. After 3 days, they are filtered and distilled.[2] The middle fractions of distillates are retained and stored over 0.4-nm molecular sieves. Experimentally determined values of the density and speed of sound for the pure liquids are compared with the literature in Table 1.

Binary mixtures are prepared by mixing appropriate volumes of the liquid components in specially designed glass bottles with airtight Teflon-coated caps, and mass measurements are performed on a Dhona 100 DS (India) single-pan analytical balance, with a precision of ±0.01 mg. The required properties are measured on the same day immediately after preparing each composition. The uncertainty in the mole fraction is ±0.0001.

A double-arm pycnometer with a bulb volume of 10 $cm^3$ and a capillary of an internal diameter of about 1 mm is used to measure the density of pure liquids and binary liquid mixtures.[3,4] The pycnometer is calibrated by using the conductivity of water (conductivity less than $1 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$) with 0.9970 and 0.9940 g·$cm^{-3}$ as its density at 298.15 and 308.15 K, respectively.[3,4] The pycnometer filled with air-bubble-free liquids is kept in a thermostat (INSREF model IRI-017 C, India) with a thermal stability of ±0.01 K for 30 min to attain thermal equilibrium. The capillary end limbs of the pycnometer are covered with Teflon caps with small orifices to avoid evaporation and maintain atmospheric pressure. The reproducibility of the densities for *N*-methyl-acetamide, freshly distilled pure ketone liquids, and prepared binary mixtures has been

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**Table 1. Comparison of Experimental Densities ρ and Speed of Sound *u* of Pure Liquids with Literature Values**

| | 298.15 K | | 308.15 K | |
|---|---|---|---|---|
| | ρ/g·$cm^{-3}$ | | *u*/m·$s^{-1}$ | |
| liquid | exptl | lit | exptl | lit |
| 1-phenyl-ethanone | 1.0231 | 1.0225[10] | 1444.96 | 1440[12] |
| 1-phenyl-propan-1-one | 1.0092 | 1.0087[11] | 1432.06 | |
| 1-*p*-tolyl-ethanone | 0.9963[a] | | 1437.94 | |
| 1-(4-chloro-phenyl)-ethanone | 1.1889 | 1.1880[11] | 1389.98 | 1395[12] |
| *N*-methyl-acetamide | 0.9497[a] | 0.9462[1 a] | 1360.04 | 1354[1] |

[a] Values at 308.15 K.

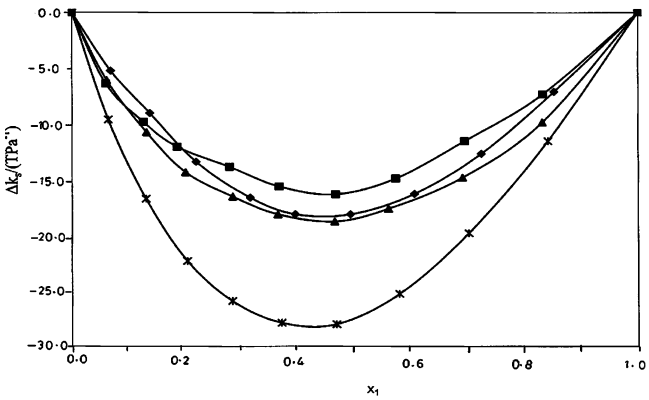


**Figure 1.** Deviations in the isentropic compressibility $\Delta k_s$ as a function of mole fraction $x_1$ for the binary mixtures of *N*-methyl-acetamide (2) with *, 1-(4-chloro-phenyl)-ethanone (1); ▲, 1-*p*-tolyl-ethanone (1); ■, 1-phenyl-propan-1-one (1); and ◆, 1-phenyl-ethanone (1) at 308.15 K.

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**Table 2. Speed of Sound $u$, Excess Molar Volume $V^E$, Deviations in the Speed of Sound $\Delta u$, and Isentropic Compressibility $\Delta k_s$ of Binary Mixtures at 308.15 K**

| $x_1$ | $u$/m·s$^{-1}$ | $V^E$/cm$^3$·mol$^{-1}$ | $\Delta u$/m·s$^{-1}$ | $\Delta_{ks}$/TPa$^{-1}$ | $x_1$ | $u$/m·s$^{-1}$ | $V^E$/cm$^3$·mol$^{-1}$ | $\Delta u$/m·s$^{-1}$ | $\Delta_{ks}$/TPa$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1-Phenyl-ethanone (1) + *N*-Methyl-acetamide (2) | | | | | | | | | |
| 0.0000 | 1360.04 | 0.0000 | 0.0000 | 0.000 | 0.4912 | 1415.35 | −0.2365 | 13.5973 | −18.125 |
| 0.0686 | 1368.65 | −0.1018 | 2.7845 | −5.228 | 0.6042 | 1424.15 | −0.1695 | 12.8013 | −16.268 |
| 0.1380 | 1376.60 | −0.1732 | 4.8410 | −9.004 | 0.7223 | 1431.42 | −0.1212 | 10.0423 | −12.633 |
| 0.2189 | 1386.81 | −0.2437 | 8.1810 | −13.380 | 0.8517 | 1437.99 | −0.0509 | 5.6236 | −7.088 |
| 0.3143 | 1398.00 | −0.2579 | 11.2696 | −16.614 | 1.0000 | 1444.96 | 0.0000 | 0.0000 | 0.000 |
| 0.3938 | 1406.07 | −0.2476 | 12.5885 | −18.096 | | | | | |
| 1-Phenyl-propan-1-one (1) + *N*-Methyl-acetamide (2) | | | | | | | | | |
| 0.0000 | 1360.04 | 0.0000 | 0.0000 | 0.000 | 0.4649 | 1406.62 | −0.1397 | 13.0979 | −16.333 |
| 0.0600 | 1368.34 | −0.2003 | 3.9788 | −6.375 | 0.5709 | 1413.51 | −0.0814 | 12.3538 | −14.878 |
| 0.1269 | 1374.74 | −0.3185 | 5.5607 | −9.805 | 0.6929 | 1419.59 | −0.0192 | 9.6473 | −11.507 |
| 0.1862 | 1380.63 | −0.3356 | 7.1799 | −12.039 | 0.8315 | 1426.58 | 0.0382 | 6.6554 | −7.291 |
| 0.2778 | 1388.9 | −0.2912 | 8.8528 | −13.830 | 1.0000 | 1432.06 | 0.0000 | 0.0000 | 0.000 |
| 0.3654 | 1397.77 | −0.2106 | 11.4139 | −15.598 | | | | | |
| 1-*p*-Tolyl-ethanone (1) + *N*-Methyl-acetamide (2) | | | | | | | | | |
| 0.0000 | 1360.04 | 0.0000 | 0.0000 | 0.000 | 0.4632 | 1411.53 | −0.3458 | 15.4067 | −18.807 |
| 0.0617 | 1368.93 | −0.1519 | 4.0836 | −6.076 | 0.5582 | 1418.44 | −0.3114 | 14.9162 | −17.668 |
| 0.1321 | 1377.69 | −0.2517 | 7.3594 | −10.740 | 0.6890 | 1426.93 | −0.2508 | 13.2169 | −14.862 |
| 0.2004 | 1385.84 | −0.3355 | 10.1888 | −14.342 | 0.8305 | 1434.00 | −0.1920 | 9.2641 | −9.915 |
| 0.2836 | 1394.44 | −0.3410 | 12.3076 | −16.554 | 1.0000 | 1437.94 | 0.0000 | 0.0000 | 0.000 |
| 0.3629 | 1402.42 | −0.3520 | 14.1101 | −18.158 | | | | | |
| 1-(4-Chloro-phenyl)-ethanone (1) + *N*-Methyl-acetamide (2) | | | | | | | | | |
| 0.0000 | 1360.04 | 0.0000 | 0.0000 | 0.000 | 0.4664 | 1379.54 | −0.5934 | 5.5360 | −28.028 |
| 0.0644 | 1363.00 | −0.2110 | 1.0319 | −9.582 | 0.5774 | 1382.61 | −0.5393 | 5.2826 | −25.315 |
| 0.1311 | 1366.05 | −0.3300 | 2.0849 | −16.727 | 0.7003 | 1385.12 | −0.4298 | 4.1130 | −19.827 |
| 0.2036 | 1369.32 | −0.4530 | 3.1842 | −22.352 | 0.8405 | 1387.61 | −0.2520 | 2.4054 | −11.495 |
| 0.2825 | 1372.41 | −0.5363 | 3.9120 | −25.952 | 1.0000 | 1389.98 | 0.0000 | 0.0000 | 0.000 |
| 0.3696 | 1375.83 | −0.5889 | 4.7242 | −27.904 | | | | | |

**Table 3. Estimated Coefficients $a$ from Equation 5 and Standard Deviations $\sigma$ from Equation 6 at 308.15 K**

| system | function | $a_o$ | $a_1$ | $a_2$ | $\sigma$ |
|---|---|---|---|---|---|
| 1-phenyl-ethanone (1) + *N*-methyl-acetamide (2) | $\Delta k_s$/TPa$^{-1}$ | −69.3031 | 15.2938 | 0.7864 | 0.7927 |
| | $V^E$/cm$^3$·mol$^{-1}$ | −0.9055 | 0.8028 | 0.0054 | 0.0072 |
| 1-phenyl-propan-1-one (1) + *N*-methyl-acetamide (2) | $\Delta k_s$/TPa$^{-1}$ | −65.2287 | 33.0702 | −0.3378 | 1.1659 |
| | $V^E$/cm$^3$·mol$^{-1}$ | −0.8691 | 2.3714 | −0.2625 | 0.1459 |
| 1-*p*-tolyl-ethanone (1) + *N*-methyl-acetamide (2) | $\Delta k_s$/TPa$^{-1}$ | −77.1348 | 21.9513 | −0.3570 | 0.8578 |
| | $V^E$/cm$^3$·mol$^{-1}$ | −1.6292 | 0.7709 | −0.3404 | 0.1483 |
| 1-(4-chloro-phenyl)-ethanone (1) + *N*-methyl-acetamide (2) | $\Delta k_s$/TPa$^{-1}$ | −111.3732 | 47.3390 | −0.1431 | 0.3305 |
| | $V^E$/cm$^3$·mol$^{-1}$ | −2.4145 | 0.8703 | −0.1733 | 0.0684 |

found to be better than $2 \times 10^{-5}$ g·cm$^{-3}$. We have estimated the uncertainty in our measured densities of the ketone liquids by comparing our data at the required temperature with the literature values as given in Table 1. This comparison gave a mean deviation of $5 \times 10^{-5}$ g·cm$^{-3}$. Therefore, the densities reported in the present work have an uncertainty of 0.0005 g·cm$^{-3}$.

The speed of sound is measured using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, model F-81, New Delhi, India) operating at a fixed frequency of 2 MHz, which is calibrated with water and benzene.[5,6] The temperature stability is maintained within ±0.01 K by circulating thermostated water around the cell with a circulating pump.

To minimize the uncertainty of the measurement, several maxima are allowed to pass, and their number $n$ (20) is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance, $d$ (cm), moved by the reflector is given by

$$d = \frac{n\lambda}{2} \tag{1}$$

where $\lambda$ is the wavelength.

With the frequency of the crystal $\nu$ being accurately known (2 MHz), the speed of sound, $u$ in m·s$^{-1}$, is calculated by using the relation

$$u = \lambda\nu \tag{2}$$

Among the 20 readings, the value of the 1st reading is subtracted from the value of the 20th reading, and the speed of sound is calculated by using eqs 1 and 2. Similarly, the value of the 1st reading is subtracted from that of 19th, and finally the speed of sound is calculated. In the same manner, the value of the 1st reading is subtracted from 18th one, and the corresponding speed of sound is calculated. An analogous procedure is adopted in the case of the second and third readings, and nine speeds of sound are calculated for each sample. The average of nine speeds of sound gives the speed of sound for that particular sample. The results compiled in Table 2 represent the average of three independent measurements for each composition of the mixture and pure compound. The repeatability of the speed of sound values thus calculated is better than ±1 in 1000 m·s$^{-1}$, and an uncertainty in the reported speed of sound values is ±3 in 1000 m·s$^{-1}$.

## Results

From the experimental data of the density and speed of sound, the isentropic compressibility is calculated from the relation

$$k_s = \frac{1}{u^2\rho} \tag{3}$$

where $u$ is the speed of sound and $\rho$ is the density of the experimental liquid.

The deviation in isentropic compressibility is computed using the equation

$$\Delta k_s = k_s - x_1 k_{s1} - x_2 k_{s2} \tag{4}$$

where $k_s$, $k_{s1}$, and $k_{s2}$ are the isentropic compressibility of the mixtures and the pure components and $x_1$ and $x_2$ are the mole fractions.

The experimentally determined speed of sound and other computed properties are included in Table 2 for the four binary mixtures. Values of $\Delta k_s$ are also graphically presented in Figure 1. The dependence of $\Delta k_s$ on the mole fraction of phenone is fitted to the Redlich−Kister equation[7]

$$\Delta k_s = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \tag{5}$$

where $a_0$, $a_1$, and $a_2$ are the polynomial coefficients. The values of the coefficients determined by the method of least squares are given in Table 3 along with the standard deviation $\sigma(\Delta k_s)$. The standard deviations are calculated by using the equation

$$\sigma(\Delta k_s) = \left[\sum \frac{(\Delta k_{s\ \mathrm{obsd}} - \Delta k_{s\ \mathrm{calcd}})^2}{n - m}\right]^{1/2} \tag{6}$$

where $n$ is the total number of experimental points and $m$ is the number of coefficients.

## Discussion

The data included in Table 2 shows negative deviations in $\Delta k_s$ values and positive deviation in $\Delta u$ values over the entire range of composition in the four systems. Figure 1 reveals that all of the systems show clear minima in the mole fraction range of $x = 0.4$ to 0.5, indicating that the mixtures are less compressible than their corresponding ideal mixtures. The negative deviations in $\Delta k_s$ and positive deviations in $\Delta u$ may be interpreted in terms of two opposing effects.

(i) Components exert a mutual structure-breaking effect on mixing (i.e., the *N*-methyl-acetamide liquid being highly structured with polymeric chains linked by hydrogen bonding[1] and dipole−dipole interaction association between aromatic ketones[8]).

(ii) Hydrogen bond interactions between unlike molecules (i.e., the hydrogen atom of the amido group and the oxygen atom of the ketoxy group).

The former effect contributes to an increase in the free length, leading to a negative deviation in the speed of sound and a positive deviation in the isentropic compressibility.[9] However, the latter effect contributes to a positive deviation in the speed of sound and a negative deviation in the isentropic compressibility. The sign and magnitude of the actual deviation depend on the relative strengths of the two effects. The experimental values of $\Delta k_s$ and $\Delta u$ point out that the latter effect dominates in the four mixtures. From the above consideration, it is clear that there is a strong association between unlike molecules in the *N*-methyl-acetamide and phenone mixtures, and this interaction may be accompanied by the disruption of the *N*-methyl-acetamide and/or ketone structure.

Generally, the deviation parameters are considered to be reflecting agents of the magnitude of polarity at the site of interactions in the molecules. The negative $\Delta k_s$ values decrease in the following order: 1-(4-chloro-phenyl)-ethanone > 1-*p*-tolyl-ethanone > 1-phenyl-ethanone > 1-phenyl-propan-1-one.

1-(4-Chloro-phenyl)-ethanone, 1-*p*-tolyl-ethanone, and 1-phenyl-ethanone are perfectly in the order of their polarity based on the austerity of conjugation. 1-phenyl-propan-1-one is expected to precede 1-phenyl-ethanone because of its slightly higher +I inductive effect. This desultoriness may be due to the size and shape of the molecule.

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