Ultrasound speeds and excess isentropic compressibilities of mixtures containing nitrobenzene

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Received 28 April, 1998; revised 24 August 1998

Measurements of ultrasonic speeds, \( u \), of nitrobenzene (i) + benzene, or + toluene, or + o-, or + p-xylene binary mixtures have been carried out at 298.15 K over the entire composition range. The observed data have been utilized to calculate the isentropic compressibilities, \( K_s \) and excess isentropic compressibilities, \( K_s^E \). The \( K_s \) values for these mixtures have also been evaluated from Flory theory. It has been observed that \( K_s^E \) values predicted by Flory theory make a reasonably good agreement with their corresponding experimental values.

In an earlier publication, we reported molar excess volumes, \( V^E \), and molar excess enthalpies, \( H^E \), of nitrobenzene (i) + benzene, or + toluene, or + o-, or + p-xylene binary mixtures. In the present investigation, ultrasonic speeds have been measured for these mixtures at 298.15 K to gain insight into molecular interactions operating between the various components in these mixtures.

Experimental

Nitrobenzene, benzene, toluene, o-xylene and p-xylene (E. Merck) were purified by standard methods. The purities of the final samples were checked by measuring their densities at 298.15 ± 0.01 K and these agreed to within ±5 x 10⁻³ g cm⁻³ with their corresponding literature values. Ultrasonic speeds of sound, at a frequency of 2 MHz, were determined using a quartz-crystal interferometer (Mittal Enterprises, India). The measuring cell was specially designed one in which water was circulated to maintain a constant temperature.

Results and discussion

We are unaware of any existing ultrasonic speed data for nitrobenzene (i) + benzene, or + toluene, or + o-, or + p-xylene mixtures with which to compare our results. However, good agreement is observed between the experimental and literature values of speed of sound in pure components [Nitrobenzene: 1473.2 m s⁻¹ (1475.0)⁴, benzene: 1300.0 m s⁻¹ (1298.9)⁴, toluene: 1305.0 m s⁻¹ (1304.0)⁵, o-xylene: 1344.0 m s⁻¹ (1345.0)⁷, p-xylene: 1310.0 m s⁻¹ (1309.6)⁸].

The isentropic compressibilities, \( K_s ^E \), of the mixtures were obtained from ultrasonic speed \( u \), using the relation:

\[
K_s^E = (\rho_i u^2)^{-1} \quad \ldots (1)
\]

The density \( \rho_i \) of the mixture was evaluated from the molar excess volume data using the expression

\[
V^E = 2 \Sigma x_i M_i / \rho_i - \Sigma x_i M_i / \rho_i \quad \ldots (2)
\]

where \( x_i, M_i \) and \( \rho_i \) are the mole fraction, molecular mass, and density of the component i of (i+j) mixture. The excess isentropic compressibilities, \( K_s^E \), values were calculated using Eq. 3

\[
K_s^E = K_s - K_{si}^{id} \quad \ldots (3)
\]

\( K_{si}^{id} \) values were evaluated from the Eq. 4

\[
K_{si}^{id} = \Sigma \phi_i \left[ K_s^* + TV_i^* (\alpha_i^* C_{pj}^*) - TV_i^* \left( \Sigma \phi_j \alpha_j^2 \right) / \Sigma \phi_i x_i (\Sigma \phi_j C_{pj}^*)^2 \right] \quad \ldots (4)
\]

where \( \phi_i \) is the volume fraction of component in (i+j) mixture referred to unmixed state, \( x_i \) is the corresponding mole fraction \( K_s^* \), \( V_i^* \), \( \alpha_i^* \) and \( C_{pj}^* \) are the isentropic compressibility, molar volume, isobaric thermal expansivity and molar isobaric heat capacity of pure component. The values of \( \alpha_i^* \) and \( C_{pj}^* \) were taken from literature.

The calculated \( K_s \) and \( K_s^E \) values for the various (i+j) mixtures are recorded in Table 1 and presented in Fig. 1. The \( K_s^E \) values were then fitted to Redlick-Kister equation.
Fig.1 - Molar excess isentropic compressibilities, $K_S^E$, for (i) nitrobenzene(i) + benzene(j) (ii) nitrobenzene(i) + toluene(j) (iii) nitrobenzene(i) + o-xylene (j) and (iv) nitrobenzene(i) + p-xylene(j) at 298.15K

$$K_S^E = x_i \frac{A + B (2x_i -1) + C(2x_i^2)}{x_j}$$  \hspace{1cm} (5)

were A, B and C are constants, and have been determined by least squares method. The standard deviation, $\sigma(K_S^E)$, of $K_S^E$, have been calculated using Eq. 6

$$\sigma(K_S^E) = \left[ \sum (K_{s\text{exp}}^E - K_{s\text{cal}}^E)^2 / (m-n) \right]^{0.5}$$  \hspace{1cm} (6)

where $m$ is the number of observations and $n$ is the number of adjustable parameters. The standard deviations, $K_S^E$, along with A, B, C parameters are recorded in Table I.

The excess isentropic compressibilities, $K_S^E$, values for these binary mixtures are negative over the entire range of composition and for an equimolar composition vary in the order: benzene > toluene > o-xylene > p-xylene. The negative values of $K_S^E$ for nitrobenzene(i) + benzene, + toluene, +o-xylene, +p-xylene mixtures indicate the existence of molecular interactions between delocalised $\pi$-electron cloud over nitrogen and oxygen atom of nitrogroup of nitrobenzene and $\pi$-electron cloud of aromatic hydrocarbons. Further more negative values of $K_S^E$ for nitrobenzene + benzene mixture than nitrobenzene + toluene, or + xylene mixtures suggest that benzene gives relatively more packed structure than toluene or xylenes with nitrobenzene. The molar excess volumes, $V_E$, values for these mixtures also vary in the same order.

The negative values of $K_S^E$ and $V_E$ in nitrobenzene(i) + aromatic hydrocarbons(j) mixtures indicate the combination of several contributions like those from, (i) specific interaction between delocalised $\pi$-electron cloud of aromatic hydrocarbons, (ii) closer molecular arrangement, (iii) depolymerisation of associated entities of pure nitrobenzene. The negative $K_S^E$ and $V_E$ data for these mixtures suggest that contribution from first two factors outweigh the contribution from third factor. Thus the
Table 2 — Comparison of the measured excess isentropic compressibilities $K_s^E$ (TPa$^{-1}$) with the corresponding values evaluated from Flory theory along with interaction energy parameter, $\chi_a$ values for the various (i+j) mixtures at 298.15 K.

<table>
<thead>
<tr>
<th>Property</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
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<tbody>
<tr>
<td>Nitrobenzene (i) + benzene</td>
<td></td>
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<tr>
<td>$K_s^E$ (Exp.)</td>
<td>-10.0</td>
<td>-19.4</td>
<td>-26.8</td>
<td>-31.5</td>
<td>-30.7</td>
<td>-25.5</td>
<td>-17.8</td>
<td>-8.8</td>
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<tr>
<td>$K_s^E$ (Flory)</td>
<td>-12.3</td>
<td>-28.8</td>
<td>-39.2</td>
<td>-44.5</td>
<td>-41.8</td>
<td>-34.8</td>
<td>-24.7</td>
<td>-11.6</td>
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<tr>
<td>$\chi_a = 14.373$ J.mol$^{-1}$</td>
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<tr>
<td>Nitrobenzene (i) + toluene</td>
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<tr>
<td>$K_s^E$ (Exp.)</td>
<td>-11.7</td>
<td>-21.5</td>
<td>-28.4</td>
<td>-32.2</td>
<td>-29.4</td>
<td>-23.4</td>
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<td>$K_s^E$ (Flory)</td>
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<td>-23.7</td>
<td>-19.7</td>
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<tr>
<td>$\chi_a = 13.300$ J.mol$^{-1}$</td>
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<tr>
<td>Nitrobenzene (i) + o-xylene</td>
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<tr>
<td>$K_s^E$ (Exp.)</td>
<td>-12.7</td>
<td>-22.5</td>
<td>-29.1</td>
<td>-32.3</td>
<td>-28.9</td>
<td>-23.2</td>
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<tr>
<td>$K_s^E$ (Flory)</td>
<td>-2.4</td>
<td>-6.6</td>
<td>-9.6</td>
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<td>-9.4</td>
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<tr>
<td>$\chi_a = 12.248$ J.mol$^{-1}$</td>
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<tr>
<td>Nitrobenzene (i) + p-xylene</td>
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<tr>
<td>$K_s^E$ (Exp.)</td>
<td>-14.4</td>
<td>-24.3</td>
<td>-30.5</td>
<td>-33.4</td>
<td>-30.9</td>
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<td>-19.3</td>
<td>-10.5</td>
</tr>
<tr>
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<td>-12.8</td>
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<td>-6.8</td>
<td>-1.3</td>
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</table>

addition of aromatic hydrocarbons to nitrobenzene (i) results in the net enhancing of structure in (i+j) mixtures. $K_s^E$ values for the studied mixture were next evaluated in terms of Flory theory $^{11,12}$. The isothermal compressibility, $K_T$, of a mixture according to this theory, at effectively zero pressure is expressed by Eq. 7.

$$K_T = 3V^2 \left(4 - 3V^{1/3}\right)/p^*\left(V^{1/3} - 1\right)$$ ...(7)

where all the terms have same significance as described by Flory $^{11,12}$. The isentropic compressibility, $K_s$, were determined using the relation

$$K_s = (K_T - TV^* \alpha_p^2)/C_{pm}$$ ...(8)

where

$$V^* = \sum \phi_i V_{i}^*$$ ...(9)

$$\alpha_p = 3(V^{1/3} - 1)/T(4-3V^{1/3})$$ ...(10)

$$C_{pm} = (pH_e/\partial T) + \chi_p C_p^* + (1-\chi) C_j^*$$ ...(11)

$$p^* = \sum \phi_i p_i^* - \phi_i \phi_j x_{ij}$$ ...(12)

where $C_p^*$ etc. are the molar heat capacities of i and j in the (i+j) binary mixture. The values of $(\delta H_e/\partial T)$ were calculated from the experimental $H_e$ data $^{1}$ ($x_i = 0.5$) at 298.15 and 308.15K. The interchange energy parameter, $x_{ij}$ was determined using $H_e$ experimental values $^{1}$ for (i + j) mixture at $x_i = 0.5$ using expression.

$$H_m^e = x_i p^*_i v_i^* (v_i^* - v_j^* + x_j p^*_j v_j^* [v_j^* - v_i^*] + x_i v_i^* \chi_j v_j^*$$ ...(13)

and are reported in Table 2. The parameters of the pure components were determined by using the isothermal compressibility ($K_T$) values reported in the literature $^9$. The excess isentropic compressibility, $K_s^E$, were determined using the expression

$$K_s^E = K_s - K_s^id$$
Values of $K_s^{id}$ for the corresponding ideal mixtures were obtained via Eq 8, where $K_s^{id}$ and $a_{ij}^{id}$ are volume fraction averages and $C_{ij}^{id}$ is the mole fraction averages for the pure components. The $K_s^{E}$ values thus calculated for the studied (i+j) mixtures are recorded in Table 2 and are also compared with the corresponding experimental values.

Examination of Table 2 reveals that $K_s^{E}$ values predicted from Flory theory make a reasonably good agreement with the corresponding experimental values for these binary mixtures.

Acknowledgement

One of the authors (A K) is thankful to the University authorities for the award of fellowship.

References


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