Title: Ultrasonic velocity in binary mixtures under high pressures and their thermodynamic properties II: binary mixtures for benzene-toluene and benzene-o-xylene

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Kyoto University
ULTRASONIC VELOCITY IN BINARY MIXTURES UNDER HIGH PRESSURES AND THEIR THERMODYNAMIC PROPERTIES II

—Binary Mixtures for Benzene-Toluene and Benzene-o-Xylene—

BY TOSHIHARU TARAGI

The ultrasonic velocities in the binary mixtures of benzene-toluene and benzene-o-xylene were measured at 20, 30 and 40°C under pressures up to 2000 bar (106 Pa), by a pulse technique of fixed-path type at a frequency of 1 MHz with an estimated error of less than 0.3 percent.

At atmospheric pressure, the isotherms for the ultrasonic velocity in benzene-o-xylene mixture changed smoothly with the composition, while that in benzene-toluene mixture showed some irregularity in the benzene-rich region. As to pressure effects, the ultrasonic velocity in the pure components and their mixtures of a certain composition increased parabolically with increasing pressure.

The densities have been calculated from the experimental results by using the pressure dependency of ultrasonic velocity under the experimental condition. The densities thus obtained for pure liquids coincided with the experimental values reported in the literature within 0.3 percent in the range of pressures from 1 to 2000 bar.

Then, from the measured values of ultrasonic velocity and the calculated densities, some thermodynamic properties, i.e. the isothermal and adiabatic compressibilities and the expansion coefficient were also derived with a good accuracy. For benzene-toluene mixtures, the composition dependencies of these values showed unusual behaviors at the benzene-rich region.

Introduction

The value of ultrasonic velocity accompanied by the isothermal compressibility data, \( \kappa_T \), is an important source for obtaining thermodynamic properties of the system under high pressure. However, the systematic study in this field has a restriction, that is, the precise data on the \( P-V-T \) relations, especially for binary liquid solutions have scarcely been reported.

Gibson et al.\(^1\) measured the \( P-V-T \) relation of the mixture of nitrobenzene and aniline. Therefore, the author measured the ultrasonic velocity in this mixture at a temperature of 30°C and pressures up to 2100 bar, and some thermodynamic properties were derived using the \( P-V-T \) data of Gibson et al. The results were reported in the previous paper (Part I).\(^2\)

For the system where the \( P-V-T \) data are not given, we must determine the density in order to

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(Received April 7, 1978)

2) T. Takagi, Tōsō Journal, 48, 10 (1978)
T. Takagi
calculate some thermodynamic properties using ultrasonic velocities, and the author has already
determined the densities of liquid n-alkanes using the ultrasonic velocities under high pressure. The
result was in good agreement with that of the $P-V-T$ data.

In this paper, the author tried to determine the densities of binary solutions (benzene-toluene
or benzene-$o$-xylene) as an extension of the previous work, and the isothermal and
adiabatic compressibilities and the expansion coefficient were calculated.

**Experimental**

The ultrasonic velocity was measured at a frequency of $1$ MHz by using a pulse technique of
fixed-path type, which was described in detail in Part I. The measurements were carried out at
temperatures $20, 30$ and $40^\circ C$ under pressures up to $2000$ bar.

The pure liquid materials were obtained from Wako Pure Chemical Ltd. (G. R. Grade). The
binary solutions were prepared by the weighing method, and their compositions in mole fraction of
toluene and $o$-xylene, were determined within the accuracy of $0.03$ percent. The densities for
samples at atmospheric pressure were measured by the pycnometer of Ostwald type (about $20 cm^3$) with
the reproducibility of $\pm 0.0003 g \cdot cm^{-3}$, at every $5$ degrees from $10$ to $50^\circ C$.

**Results and Discussions**

**Ultrasonic velocity**

The experimental values of the ultrasonic velocity in benzene-toluene and benzene-$o$-xylene
mixtures at $20, 30$ and $40^\circ C$, and atmospheric pressure are plotted against the mole fraction in
Fig. 1. The values of velocity in the pure liquids are approximately linear functions of temperature,
and the values of $(\partial c/\partial T)_{P=1}$ at $30^\circ C$ are evaluated as $-4.65$ for benzene, $-4.38$ for toluene and
$-4.03 \text{ m} \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$ for $o$-xylene, which are found to agree with respective literature values
within the experimental error. The velocity in benzene-$o$-xylene mixture increases smoothly with
increasing composition of $o$-xylene. The velocity in pure toluene differs from that in pure benzene
only by $11 \text{ m} \cdot \text{sec}^{-1}$ at $30^\circ C$, and, when both the liquids are mixed, the velocity of the system is
almost constant in the benzene-rich region. As the composition becomes toluene-rich, the velocity
increases gradually. However, when the temperature becomes higher, the velocity constant region is
pushed to benzene-rich side. The values at $20^\circ C$ as shown in Fig. 1 are also found to agree with the
results obtained by Vilcu et al. Figures 2 and 3 show the relationships between the ultrasonic
velocity and the pressure for benzene-toluene and benzene-$o$-xylene mixtures at $30^\circ C$. The velocity

3) T. Takagi, Kagaku Kogaku Ronbunshu, 4, 1 (1978)
7) R. Vilcu and A. Simon, Revue Roumaine de Chimie, 20, 1359 (1975)
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Fig. 1 Composition dependency of the ultrasonic velocity in binary mixtures at atmospheric pressure

- $\square$, $\triangle$: Benzene (A)-Toluene (B)
- $\bullet$: Benzene (A)-o-Xylene (B)

Fig. 2 Pressure dependency of the ultrasonic velocity in binary mixtures at 30°C
Benzene (A)-Toluene (B)

Fig. 3 Pressure dependency of the ultrasonic velocity in binary mixtures at 30°C
Benzene (A)-o-Xylene (B)

†: Freezing pressure
increases parabolically with increasing pressure throughout the experimental conditions.

For each temperature and composition, the experimental results are used to determine the coefficients in the following quadratic equation by means of the least square method:

\[ c = A_1 + A_2 P + A_3 P^2. \]  

(1)

where \( P \) is the pressure. The values of the coefficients \( A_1, A_2 \) and \( A_3 \) of the equation are listed in Table 1 together with the maximum deviations of the experimental data from equation (1). The larger deviations for pure liquids and their mixtures are observed frequently under lower pressure ranges.

**Derived \( P-V-T \) relations**

According to Wilhelm et al., the pressure dependency of the isothermal compressibility, \( \kappa_T \), can be calculated as follows:

\[ -\frac{1}{\kappa_T} \left( \frac{\partial \kappa_T}{\partial P} \right)_T = \frac{\partial}{\partial P} \left( \frac{1}{\kappa_T} \right)_T = C, \]

(2)

and the value of constant \( C \) is given as approximately 10.0. Integration of this equation gives

\[ \frac{1}{\kappa_T^{(n)}} = \frac{1}{\kappa_T^{(i)}} + CP, \]

(3)

where \( \kappa_T^{(i)} \) and \( \kappa_T^{(n)} \) are the isothermal compressibilities under the pressure, \( P \) and atmospheric pressure, respectively, and equation (3) is expressed as follows:

\[ C = \frac{\partial}{\partial P} \left( \frac{1}{\kappa_T} \right)_T = \left( \frac{\partial \ln \kappa_T}{\partial \ln \nu} \right)_T, \]

(4)

where \( \nu \) is the specific volume.

From Mie's theory, equation (5) can be derived at the vicinity of the minimum potential energy:

\[ \frac{\partial}{\partial P} \left( \frac{1}{\kappa_T} \right)_T = \frac{1}{3} (m + n + 6), \]

(5)

where \( n \) and \( m \) are the exponential terms of Mie's potential equation. Then, the constant, \( C \) of equation (4) can be expressible by equation (6):

\[ C = \frac{1}{3} (n + m + 6). \]

(6)

The values of \( C \) and \( "n + m" \) can be calculated from \( P-V-T \) relations by equations (2) and (5).

On the other hand, Nomura et al. have derived a relation between the ultrasonic velocity, \( c \) and the isothermal compressibility, \( \kappa_T \), standing on Mie's potential equation as follows:

\[ C = \frac{\partial}{\partial P} \left( \frac{1}{\kappa_T} \right)_T = \frac{2}{c \kappa_T} \left( \frac{\partial c}{\partial P} \right)_T + 1. \]

(7)


Table 1  Coefficients of ultrasonic velocity
for $c/\text{[m/sec]} = A_1 + A_2P + A_3P^2$  
[P in bar]

<table>
<thead>
<tr>
<th>Mole fraction of B</th>
<th>ULP*1</th>
<th>$20^\circ \text{C}$</th>
<th></th>
<th></th>
<th>$20^\circ \text{C}$</th>
<th></th>
<th></th>
<th>$20^\circ \text{C}$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$A_1$</td>
<td>$10A_2$</td>
<td>$-10^5A_3$</td>
<td>Max. dev. [%]</td>
<td>$A_1$</td>
<td>$10A_2$</td>
<td>$-10^5A_3$</td>
<td>Max. dev. [%]</td>
<td>$A_1$</td>
<td>$10A_2$</td>
</tr>
<tr>
<td>Benzene (A) - Toluene (B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>516*3</td>
<td>1325.6</td>
<td>4.7337</td>
<td>1.211</td>
<td>0.01</td>
<td>896*2</td>
<td>1277.5</td>
<td>4.9292</td>
<td>1.320</td>
<td>0.15</td>
<td>1289*1</td>
</tr>
<tr>
<td>0.10</td>
<td>928*1</td>
<td>1324.9</td>
<td>4.5945</td>
<td>1.073</td>
<td>0.15</td>
<td>1345*2</td>
<td>1279.5</td>
<td>4.6875</td>
<td>1.012</td>
<td>0.28</td>
<td>1862*3</td>
</tr>
<tr>
<td>0.25</td>
<td>1400</td>
<td>1324.4</td>
<td>4.5117</td>
<td>0.963</td>
<td>0.19</td>
<td>2000</td>
<td>1285.3</td>
<td>4.2973</td>
<td>0.623</td>
<td>0.25</td>
<td>2000</td>
</tr>
<tr>
<td>0.50</td>
<td>2000</td>
<td>1325.9</td>
<td>4.4557</td>
<td>0.856</td>
<td>0.20</td>
<td>2000</td>
<td>1283.1</td>
<td>4.3600</td>
<td>0.681</td>
<td>0.35</td>
<td>2000</td>
</tr>
<tr>
<td>0.70</td>
<td>2000</td>
<td>1327.1</td>
<td>4.4845</td>
<td>0.864</td>
<td>0.17</td>
<td>2000</td>
<td>1291.3</td>
<td>4.3565</td>
<td>0.665</td>
<td>0.33</td>
<td>2000</td>
</tr>
<tr>
<td>1.00</td>
<td>1500</td>
<td>1329.8</td>
<td>4.4736</td>
<td>0.828</td>
<td>0.26</td>
<td>1700</td>
<td>1289.8</td>
<td>4.5567</td>
<td>0.820</td>
<td>0.35</td>
<td>2000</td>
</tr>
</tbody>
</table>

| Benzene (A) - o-Xylene (B) |
| 0.00  | 516*3 | 1325.6 | 4.7337 | 1.211 | 0.01 | 896*2 | 1277.5 | 4.9292 | 1.320 | 0.15 | 1289*1 | 1236.2 | 4.8389 | 1.002 | 0.02 |
| 0.20  | 300   | 1330.9 | 4.1998 | 0.480 | 0.20 | 1834  | 1288.9 | 4.3780 | 0.723 | 0.35 | 300   | 1241.0 | 4.6612 | 0.440 | 0.07 |
| 0.40  | 300   | 1336.0 | 4.7336 | 1.386 | 0.19 | 2000  | 1300.8 | 4.3123 | 0.668 | 0.28 | 300   | 1250.2 | 5.3549 | 2.853 | 0.15 |
| 0.60  | 300   | 1346.7 | 4.4953 | 0.535 | 0.14 | 2000  | 1311.3 | 4.3380 | 0.680 | 0.18 | 300   | 1259.3 | 5.4954 | 2.211 | 0.13 |
| 0.80  | 300   | 1357.2 | 4.7212 | 1.300 | 0.05 | 2000  | 1323.4 | 4.3266 | 0.669 | 0.25 | 300   | 1273.9 | 5.4369 | 2.417 | 0.06 |
| 1.00  | 300   | 1368.0 | 3.8690 | 1.135 | 0.40 | 2000  | 1339.4 | 4.1021 | 0.569 | 0.53 | 300   | 1289.8 | 5.2912 | 2.310 | 0.14 |

*1): Upper limit of pressure  *2): Freezing pressure
From equations (6) and (7), the sum "n+m" may also be written by equation (8):
\[
\frac{\partial c}{\partial P} \frac{1}{\kappa_T} = \frac{1}{6} (n + m + 3).
\] (8)

This equation must be held at the arbitrary pressure, then, the author used the values of \(\frac{\partial c}{\partial P} \frac{1}{\kappa_T}\) and \(\kappa_T\) at the atmospheric pressure in order to calculate the value of "n+m". The values of \(\frac{\partial c}{\partial P} \frac{1}{\kappa_T}, p=1\) were newly determined applying the least square method on several experimental data obtained at every 25 bar up to about 200 bar, because the coefficients listed in Table 1 were not appropriate to calculate \(\frac{\partial c}{\partial P} \frac{1}{\kappa_T}, p=1\). Further, the values of \(\kappa_{T,n}\) for binary mixtures at atmospheric pressure were determined by equation (9):
\[
\kappa_{T,n} = \left[ \left( 1 + \frac{T \alpha \kappa c^2}{C_P} \right) \frac{1}{\rho c^2} \right]_{p=1},
\] (9)

where \(\alpha\) and \(C_P\) are the expansion coefficient and the specific heat at constant pressure, respectively. The value of \(\alpha\) was obtained using the measured densities \(\rho\) at several temperatures. And, \(C_P\) of the mixture was estimated from the equation of the ideal solution, namely:
\[
C_{P(mix)} = C_{P(A)X(A)} + C_{P(B)X(B)}.
\] (10)

where \(X\) is the mole fraction, and the subscripts \(A\) and \(B\) represent the liquid \(A\) and the liquid \(B\), respectively. In the literature, the value of \(C_P\) for benzene-toluene mixtures showed the behavior of nonideal solution. However, the maximum deviation of \(C_P\) between the literature value and the calculated value by equation (10) was only 0.12 percent at 30°C, and this deviation did not exercise a meaningful influence upon \(\kappa_{T,n}\) in equation (9).

Using the values \(\kappa_{T,n}\) and \([\partial c/\partial P]/c]\), the values of "n+m" and \(C\) for both binary mixtures were determined, and the result is given in Table 2. At each temperature, the values of the "n+m" at each composition for benzene-o-xylene mixtures are nearly constant, while, the values for benzene-toluene mixtures at 20°C are slightly higher than those at 30°C for low concentration of toluene. The values of \(C\) for pure liquids obtained at 30°C agree quite well with the values given from equation (2) using the literature values of \(\kappa_{T,\rho}\).

The isothermal compressibility at high pressure, \(\kappa_{T,P}\), can be calculated by equation (3), then, the following expression of the density, \(\rho\) is obtained using equation (4):
\[
\kappa_{T,P} \frac{1}{\rho_{(1)}} = \left( \frac{1}{\rho_{(1)}} \right)^C.
\] (11)

By the use of equation (11), the author already reported the densities for liquid n-alkanes at several temperatures and pressures which showed good agreement with the experimental values reported in the literature within 0.15 percent, in the range of pressures from 1 to 2000 bar.

As a preliminary work, the author has obtained the densities of pure benzene, toluene and o-xylene under high pressures. And the deviation of the literature values from the calculated values are shown in Fig. 4. As can be seen in this figure, the deviation for pure toluene or o-xylene

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Table 2 Determination of C and "n+m" from the ultrasonic velocity

<table>
<thead>
<tr>
<th>Mole fraction of B</th>
<th>(8c/8P) m [sec • bar]</th>
<th>n+m</th>
<th>C</th>
<th>(8c/8P) m [sec • bar]</th>
<th>n+m</th>
<th>C</th>
<th>(8c/8P) m [sec • bar]</th>
<th>n+m</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>0.504</td>
<td>21.7</td>
<td>9.2</td>
<td>0.504</td>
<td>21.7</td>
<td>9.2</td>
<td>0.554</td>
<td>21.8</td>
<td>9.2</td>
</tr>
<tr>
<td>0.10</td>
<td>0.504</td>
<td>22.4</td>
<td>9.4</td>
<td>0.517</td>
<td>21.9</td>
<td>9.3</td>
<td>0.554</td>
<td>22.4</td>
<td>9.4</td>
</tr>
<tr>
<td>0.20</td>
<td>0.501</td>
<td>22.5</td>
<td>9.5</td>
<td>0.521</td>
<td>22.3</td>
<td>9.4</td>
<td>0.555</td>
<td>22.9</td>
<td>9.6</td>
</tr>
<tr>
<td>0.30</td>
<td>0.509</td>
<td>22.6</td>
<td>9.6</td>
<td>0.529</td>
<td>22.9</td>
<td>9.6</td>
<td>0.569</td>
<td>23.8</td>
<td>9.9</td>
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<tr>
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<td>0.504</td>
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<td>9.6</td>
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<td>23.1</td>
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<td>10.0</td>
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<td>10.3</td>
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<td>30°C</td>
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<tr>
<td>0.00</td>
<td>0.504</td>
<td>21.7</td>
<td>9.2</td>
<td>0.504</td>
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<td>0.554</td>
<td>22.7</td>
<td>9.5</td>
</tr>
<tr>
<td>0.40</td>
<td>0.493</td>
<td>23.1</td>
<td>9.7</td>
<td>0.521</td>
<td>23.0</td>
<td>9.7</td>
<td>0.549</td>
<td>23.3</td>
<td>9.7</td>
</tr>
<tr>
<td>0.60</td>
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<td>23.2</td>
<td>9.7</td>
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<td>23.3</td>
<td>9.8</td>
<td>0.515</td>
<td>23.5</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Fig. 4 Comparison of the calculated density (base lines) with literature values for pure liquids

- a): Benzene
- b): Toluene
- c): o-Xylene

is larger compared with that for pure benzene. This may be arisen from the facts that the measured pressure interval was 1000 bar in the former case and 250 bar in the latter case. Moreover, to check the reliability of the present method, the densities of nitrobenzene-aniline mixture of which the P-V-T relations were given by Gibson et al. were calculated at 30°C, and the deviations are shown in Fig. 5. From the facts presented above, one can conclude that the densities calculated by the present method for the pure liquid and the binary mixture are found to coincide very well with respective literature values.
Therefore, in the similar manner, the densities for binary solutions of benzene-toluene and benzene-o-xylene were calculated using equation (11). And the specific volumes at atmospheric pressure were also determined. The results of specific volumes were in good agreement with the previous works by Rastogi et al.\(^\text{15}\) and Sumer et al.\(^\text{16}\)

From these values, the empirical coefficients of the Tait equation, \(J\) and \(L\) were determined and are listed in Table 3. For some pure liquids, it is empirically well known that the coefficient \(L\) is related linearly to \(1/T\). The same linear relation is also found in the present cases of the binary solutions. Therefore, it is thought that the density of both binary mixtures derived by use of the coefficients \(J\) and \(L\) are obtained with same accuracy.

\[ c^2 = \frac{1}{\rho \varepsilon_s}, \]  


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\[ \kappa_T \text{ and } \kappa_S \text{ for both liquid mixtures at each composition and temperature decrease smoothly with increasing pressure. The accuracy of the values of } \kappa_T \text{ and } \kappa_S \text{ would be better than the order of 2 percent.} \]

The expansion coefficient, \( \alpha \) is defined by equation (13),

\[ \alpha = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_{P}. \]  

Then, the values of \( \alpha \) at high pressure were calculated by differentiating the Tait equation which was given in Table 3.

Figures 8 and 9 show the effects of composition on \( \kappa_T, \alpha \) and \( \kappa_S \) for both binary mixtures at atmospheric pressure and 500 bar. The values for pure liquid at atmospheric pressure agree well with the values given in the literature\(^{17,18}\).

In the case of benzene-o-xylene mixtures, \( \kappa_T, \alpha \) and \( \kappa_S \) decrease monotonously with the decrease of the composition of benzene, while, \( \kappa_T \) and \( \alpha \) for benzene-toluene mixtures decrease sharply at first and become nearly constant as the concentration of benzene decreases, and \( \kappa_S \) are nearly constant at the whole composition range.


Composition dependency of $\kappa_T$, $\kappa_S$ and $\alpha$ for binary mixtures at 30°C and atmospheric pressure

- $\circ$: Benzene (A)-Toluene (B)
- $\bullet$: Benzene (A)-o-Xylene (B)

Fig. 8

Composition dependency of $\kappa_T$, $\kappa_S$ and $\alpha$ for binary mixtures at 30°C and 500 bar

- $\circ$: Benzene (A)-Toluene (B)
- $\bullet$: Benzene (A)-o-Xylene (B)

Fig. 9

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