

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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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 ($10^5 P_n$), 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, κ_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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1) R. E. Gibson and O. H. Loeffler, *J. Amer. Chem. Soc.*, **61**, 2877 (1939)

2) T. Takagi, *This Journal*, **48**, 10 (1978)

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 pressure³⁾. The result was in good agreement with that of the P - V - T data⁴⁾.

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 work³⁾, 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 I²⁾. The measurements were carried out at temperatures 20, 30 and 40°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 20cm³) with the reproducibility of $\pm 0.0003 \text{ g} \cdot \text{cm}^{-3}$, at every 5 degrees from 10 to 50°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°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°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^{5,6)} 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°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°C as shown in Fig. 1 are also found to agree with the results obtained by Vilcu *et al.*⁷⁾ Figures 2 and 3 show the relationships between the ultrasonic velocity and the pressure for benzene-toluene and benzene-*o*-xylene mixtures at 30°C. The velocity

3) T. Takagi, *Kagaku Kagaku Ronbunshu*, **4**, 1 (1978)

4) M. S. Benson and J. Winnick, *J. Chem. Eng. Data*, **16**, 154 (1971)

5) W. J. Snyder and J. R. Snyder, *J. Chem. Eng. Data*, **19**, 270 (1974)

6) D. D. Desphande and L. G. Bhatgadde, *J. Phys. Chem.*, **72**, 261 (1968)

7) R. Vilcu and A. Simon, *Revue Roumaine de Chimie*, **20**, 1359 (1975)

Binary Mixtures under High Pressures and Their Thermodynamic Properties II

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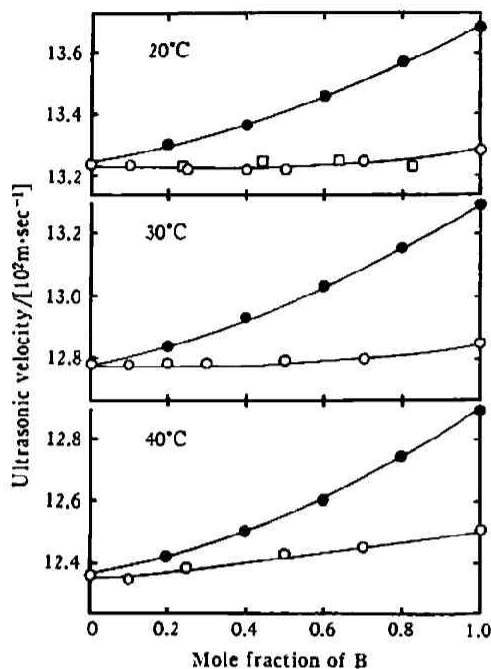


Fig. 1 Composition dependency of the ultrasonic velocity in binary mixtures at atmospheric pressure

○, □: Benzene (A)-Toluene (B)
●: Benzene (A)-*o*-Xylene (B)

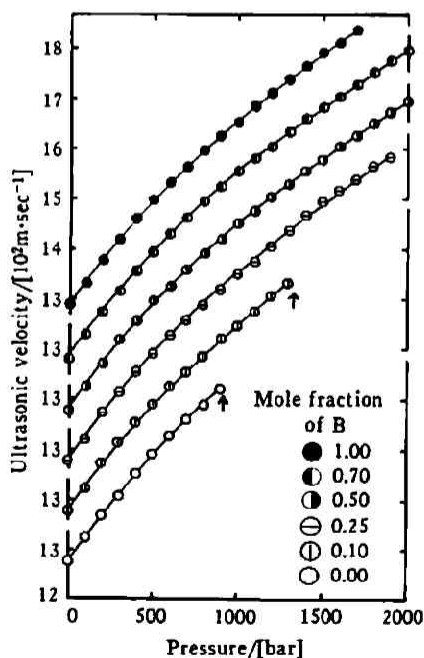


Fig. 2 Pressure dependency of the ultrasonic velocity in binary mixtures at 30°C
Benzene (A)-Toluene (B)

↑: Freezing pressure

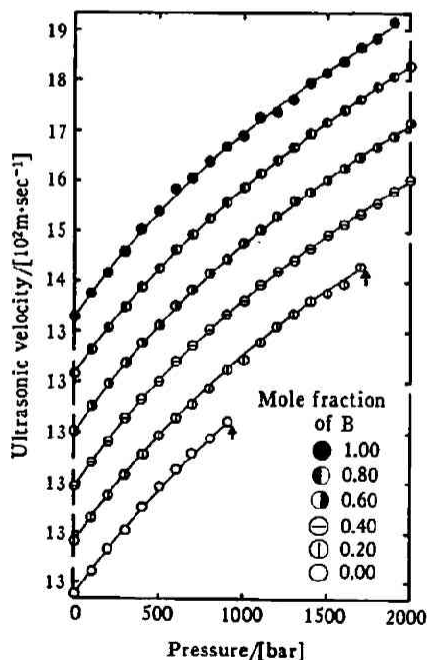


Fig. 3 Pressure dependency of the ultrasonic velocity in binary mixtures at 30°C
Benzene (A)-*o*-Xylene (B)

↑: 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 :

$$c = A_1 + A_2 P + A_3 P^2, \quad (1)$$

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, κ_T can be calculated as follows :

$$-\frac{1}{\kappa_T^2} \left(\frac{\partial \kappa_T}{\partial P} \right)_T = \frac{\partial}{\partial P} \left(\frac{1}{\kappa_T} \right)_T = C, \quad (2)$$

and the value of constant C is given as approximately $10.0^8, 9)$. Integration of this equation gives

$$\frac{1}{\kappa_{T(P)}} = \frac{1}{\kappa_{T(1)}} + CP, \quad (3)$$

where $\kappa_{T(P)}$ and $\kappa_{T(1)}$ are the isothermal compressibilities under the pressure, P and atmospheric pressure, respectively, and equation (3) is expressed as follows :

$$C = \frac{\partial}{\partial P} \left(\frac{1}{\kappa_T} \right)_T = \left(\frac{\partial \ln \kappa_T}{\partial \ln v} \right)_T, \quad (4)$$

where v is the specific volume.

From Mie's theory¹⁰⁾, equation (5) can be derived at the vicinity of the minimum potential energy :

$$\frac{\partial}{\partial P} \left(\frac{1}{\kappa_T} \right)_T = \frac{1}{3} (m + n + 6), \quad (5)$$

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) :

$$C = \frac{1}{3} (n + m + 6). \quad (6)$$

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.*¹¹⁾ have derived a relation between the ultrasonic velocity, c and the isothermal compressibility, κ_T standing on Mie's potential equation as follows :

$$C = \frac{\partial}{\partial P} \left(\frac{1}{\kappa_T} \right)_T = \frac{2}{c \kappa_T} \left(\frac{\partial c}{\partial P} \right)_T + 1. \quad (7)$$

8) E. Wilhelm, R. Schano, G. Becker, G. H. Findeng and F. Kohler., *Trans. Faraday Soc.*, **65**, 1443 (1969)

9) E. Wilhelm, *J. Chem. Phys.*, **63**, 3379 (1975)

10) E. A. Moelwyn-Hughes, "*Physical Chemistry*", Second Ed., p. 330, Pergamon Press, London (1964)

11) H. Nomura, A. Kuroki and Y. Miyahara, *J. Acoust. Soc. Japan*, **27**, 524 (1971)

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

Mole fraction of B	20°C			Max. dev. [$10^{-5}A_3$ %]	ULP*(1) /[bar]	30°C			Max. dev. [$10^{-5}A_3$ %]	ULP*(1) /[bar]	40°C			Max. dev. [$10^{-5}A_3$ %]	
	A_1	$10A_2$	10^5A_3			A_1	$10A_2$	10^5A_3			A_1	$10A_2$	10^5A_3		
Benzene (A) – Toluene (B)															
0.00	516*(3)	1325.6	4.7337	1.211	0.01	896*(3)	1277.5	4.9292	1.320	0.15	1289*(3)	1236.2	4.8389	1.002	0.02
0.10	928*(3)	1324.9	4.5945	1.073	0.15	1345*(3)	1279.5	4.6875	1.012	0.28	1862*(3)	1235.1	4.6748	0.853	0.24
0.25	1400	1324.4	4.5117	0.963	0.19	2000	1285.3	4.2973	0.623	0.26	2000	1238.8	4.5488	0.728	0.27
0.50	2000	1325.9	4.4557	0.856	0.20	2000	1283.1	4.3600	0.681	0.35	2000	1242.6	4.5593	0.734	0.33
0.70	2000	1327.1	4.4845	0.864	0.17	2000	1291.3	4.3365	0.665	0.33	2000	1245.1	4.5887	0.746	0.35
1.00	1500	1329.8	4.4736	0.828	0.26	1700	1289.8	4.5567	0.820	0.36	2000	1250.8	4.6739	0.832	0.48
Benzene (A) – o-Xylene (B)															
0.00	516*(3)	1325.6	4.7337	1.211	0.01	896*(3)	1277.5	4.9292	1.320	0.15	1289*(3)	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	4.8612	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	5.5499	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):

$$\frac{(\partial c/\partial P)_T}{c\kappa_T} = \frac{1}{6}(n+m+3). \quad (8)$$

This equation must be held at the arbitrary pressure, then, the author used the values of $(\partial c/\partial P)_T/c$ and κ_T at the atmospheric pressure in order to calculate the value of " $n+m$ ". The values of $(\partial c/\partial P)_{T,P=1}$ 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 $(\partial c/\partial P)_{T,P=1}$. Further, the values of $\kappa_{T(1)}$ for binary mixtures at atmospheric pressure were determined by equation (9):

$$\kappa_{T(1)} = \left[\left(1 + \frac{T\alpha^2 c^2}{C_P} \right) \frac{1}{\rho c^2} \right]_{P=1}, \quad (9)$$

where α and C_P are the expansion coefficient and the specific heat at constant pressure, respectively. The value of α was obtained using the measured densities ρ at several temperatures. And, C_P of the mixture was estimated from the equation of the ideal solution, namely:

$$C_{P(mix)} = C_{P(A)}X_{(A)} + C_{P(B)}X_{(B)}, \quad (10)$$

where X is the mole fraction, and the subscripts A and B represent the liquid A and the liquid B, respectively. In the literature¹²⁾, 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 $\kappa_{T(1)}$ in equation (9).

Using the values $\kappa_{T(1)}$ and $[(\partial c/\partial P)_T/c]_{P=1}$, 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 lower 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 κ_T ^{13,14)}.

The isothermal compressibility at high pressure, $\kappa_{T(P)}$, can be calculated by equation (3), then, the following expression of the density, ρ is obtained using equation (4):

$$\frac{\kappa_{T(P)}}{\kappa_{T(1)}} = \left(\frac{1/\rho_{(P)}}{1/\rho_{(1)}} \right)^C. \quad (11)$$

By the use of equation (11), the author already reported³⁾ 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^{13,14)} from the calculated values are shown in Fig. 4. As can be seen in this figure, the deviation for pure toluene or *o*-xylene

12) "International Critical Tables", V, 128, McGraw-Hill, New York (1928)

13) R. E. Gibson and J. F. Kincaid, *J. Amer. Chem. Soc.*, **60**, 511 (1938)

14) J. F. Skinner, E. L. Cussler and R. M. Fouss, *J. Phys. Chem.*, **72**, 1057 (1968)

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

Mole fraction of B	20°C			30°C			40°C		
	$(\partial c/\partial P)$	$n+m$	C	$(\partial c/\partial P)$	$n+m$	C	$(\partial c/\partial P)$	$n+m$	C
	$\left[\frac{m}{\text{sec} \cdot \text{bar}}\right]$	$[-]$	$[-]$	$\left[\frac{m}{\text{sec} \cdot \text{bar}}\right]$	$[-]$	$[-]$	$\left[\frac{m}{\text{sec} \cdot \text{bar}}\right]$	$[-]$	$[-]$
Benzene (A)–Toluene (B)									
0.00	0.50 ₄	21.7	9.2	0.50 ₄	21.7	9.2	0.55 ₄	21.8	9.2
0.10	0.50 ₄	22.4	9.4	0.51 ₇	21.9	9.3	0.55 ₄	22.4	9.4
0.25	0.50 ₂	22.5	9.5	0.52 ₁	22.3	9.4	0.55 ₅	22.9	9.6
0.50	0.50 ₆	22.6	9.6	0.52 ₅	22.9	9.6	0.56 ₉	23.8	9.9
0.70	0.50 ₄	22.8	9.6	0.52 ₉	23.1	9.7	0.57 ₂	24.1	10.0
1.00	0.54 ₂	24.7	10.3	0.55 ₉	24.6	10.2	0.58 ₈	24.9	10.3
Benzene (A)– <i>o</i> -Xylene (B)									
0.00	0.50 ₄	21.7	9.2	0.50 ₄	21.7	9.1	0.55 ₄	21.7	9.2
0.20	0.49 ₅	22.2	9.4	0.51 ₉	22.2	9.3	0.55 ₄	22.7	9.5
0.40	0.49 ₅	23.1	9.7	0.52 ₁	23.0	9.7	0.54 ₉	23.3	9.7
0.60	0.48 ₆	23.2	9.7	0.51 ₂	23.3	9.7	0.54 ₃	23.7	9.9
0.80	0.48 ₈	23.8	9.9	0.50 ₅	23.1	9.7	0.52 ₉	23.7	9.8
1.00	0.47 ₅	23.4	9.8	0.49 ₂	23.3	9.8	0.51 ₆	23.5	9.8

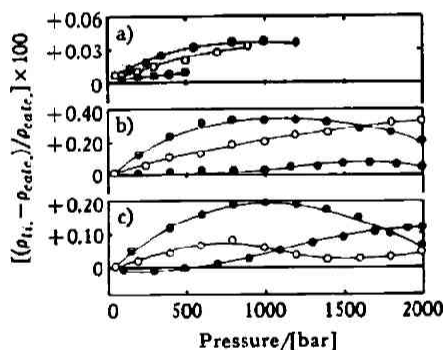
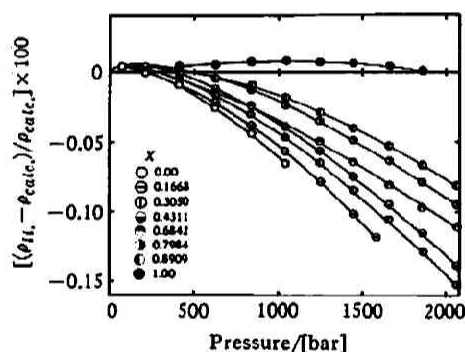


Fig. 4 Comparison of the calculated density (base lines) with literature values for pure liquids

●: 20, ○: 30, ⊗: 40°C
 a): Benzene¹³⁾, b): Toluene¹⁴⁾
 c): *o*-Xylene¹⁴⁾

Fig. 5 Comparison of the calculated density (base line) with literature value¹⁾ for nitrobenzene-aniline mixtures at 30°C
 X: Mole fraction of aniline

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 case¹⁰⁾ and 250 bar in the latter case¹³⁾. 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.*¹⁾ 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.

Table 3 Coefficients of the Tait equation

$$\text{for } v_P/[\text{cm}^3/\text{g}] = v_1 \left[1 - J \log \left(\frac{L+P}{L+1} \right) \right] \quad [P \text{ in bar}]$$

Mole fraction of B	20°C			30°C			40°C		
	$\frac{v_1}{[\frac{\text{cm}^3}{\text{g}}]}$	$\frac{L}{[\text{bar}]}$	$\frac{J}{[-]}$	$\frac{v_1}{[\frac{\text{cm}^3}{\text{g}}]}$	$\frac{L}{[\text{bar}]}$	$\frac{J}{[-]}$	$\frac{v_1}{[\frac{\text{cm}^3}{\text{g}}]}$	$\frac{L}{[\text{bar}]}$	$\frac{J}{[-]}$
Benzene (A)–Toluene (B)									
0.00	1.1380	1024.1	0.2190	1.1515	953.5	0.2207	1.1659	871.6	0.2193
0.10	1.1419	1030.7	0.2138	1.1536	965.9	0.2178	1.1671	876.2	0.2147
0.25	1.1449	1035.2	0.2131	1.1577	963.2	0.2145	1.1709	878.7	0.2119
0.50	1.1479	1028.3	0.2116	1.1613	962.5	0.2110	1.1735	867.1	0.2059
0.70	1.1508	1035.9	0.2110	1.1632	959.0	0.2097	1.1708	866.6	0.2042
1.00	1.1547	981.0	0.1995	1.1655	921.4	0.2011	1.1781	851.6	0.2000
Benzene (A)– <i>o</i> -Xylene (B)									
0.00	1.1380	1024.1	0.2190	1.1515	953.5	0.2207	1.1659	871.6	0.2193
0.20	1.1402	1052.0	0.2154	1.1523	970.3	0.2158	1.1657	886.7	0.2128
0.40	1.1419	1080.6	0.2089	1.1524	980.7	0.2098	1.1637	903.7	0.2092
0.60	1.1401	1093.5	0.2084	1.1516	1007.9	0.2078	1.1625	923.8	0.2063
0.80	1.1393	1103.1	0.2046	1.1494	1028.5	0.2092	1.1609	957.2	0.2062
1.00	1.1376	1137.6	0.2072	1.1471	1067.9	0.2077	1.1583	990.6	0.2069

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.*¹⁵⁾ and Sumer *et al.*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.

Derived thermodynamic properties

The adiabatic compressibility, κ_s can be calculated from :

$$c^2 = \frac{1}{\rho \kappa_s}, \quad (12)$$

where c is the ultrasonic velocity, and ρ is the density.

Using the experimental data of ultrasonic velocity and the derived density from the pressure dependency of the ultrasonic velocity, the pressure effects on the isothermal and adiabatic compressibilities have been determined by equations (3) and (12), as shown in Figs. 6 and 7. The values of

15) R. P. Rastogi, and K. T. R. Varma, *J. Chem. Soc.*, 2257 (1957)

16) K. M. Sumer and R. Thomson, *J. Chem. Eng. Data*, 13, 30 (1968)

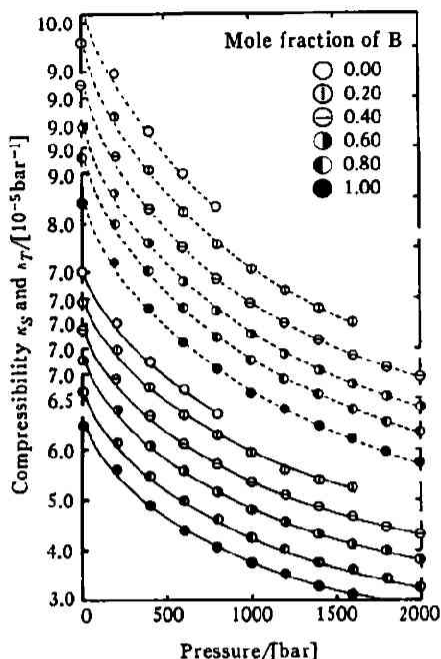


Fig. 6 Pressure dependency of the isothermal and adiabatic compressibilities for binary mixtures at 30°C

Benzene (A)-Toluene (B)

.....○.....: κ_T , —○—: κ_S

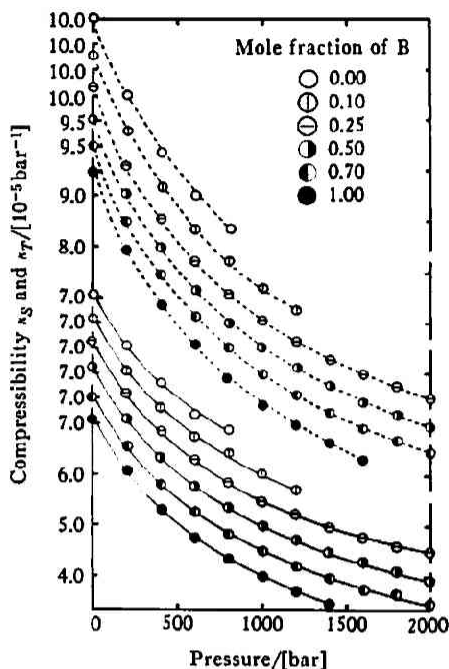


Fig. 7 Pressure dependency of the isothermal and adiabatic compressibilities for binary mixtures at 30°C

Benzene (A)-o-Xylene (B)

.....○.....: κ_T , —○—: κ_S

κ_T and κ_S for both liquid mixtures at each composition and temperature decrease smoothly with increasing pressure. The accuracy of the values of κ_T and κ_S would be better than the order of 2 percent.

The expansion coefficient, α is defined by equation (13),

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \quad (13)$$

Then, the values of α 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 κ_T , α and κ_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, κ_T , α and κ_S decrease monotonously with the decrease of the composition of benzene, while, κ_T and α for benzene-toluene mixtures decrease sharply at first and become nearly constant as the concentration of benzene decreases, and κ_S are nearly constant at the whole composition range.

17) R. K. Nigam and P. P. Singh, *Trans. Faraday Soc.*, **65**, 950 (1969)

18) J. A. Riddick and W. B. Bunger, "Organic Solvents", John Wiley and Sons, Inc., New York (1970)

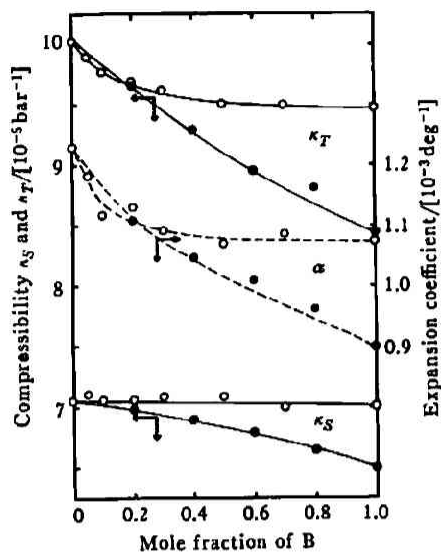


Fig. 8 Composition dependency of κ_T , κ_S and α for binary mixtures at 30°C and atmospheric pressure

○: Benzene (A)-Toluene (B)
●: Benzene (A)-o-Xylene (B)

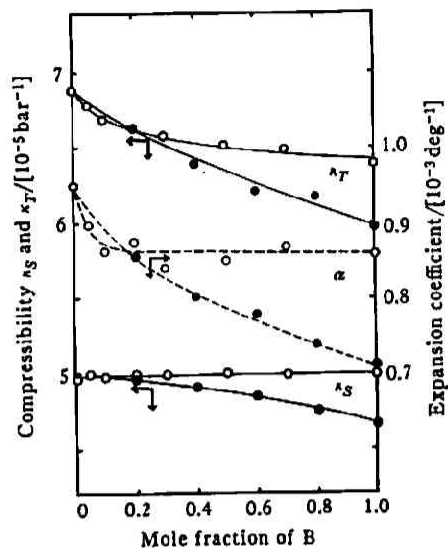


Fig. 9 Composition dependency of κ_T , κ_S and α for binary mixtures at 30°C and 500 bar

○: Benzene (A)-Toluene (B)
●: Benzene (A)-o-Xylene (B)

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