BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1224—1230(1971) [Vol. 44, No. 5

Ultrasonic and Thermodynamic Study on Solute-Solvent Interaction. Binary Mixtures of *t*-Butyl Chloride, *t*-Butyl Bromide and 1,1,1-Trichloroethane with Carbon Tetrachloride, Benzene and *p*-Xylene

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(Received September 7, 1970)

Sound velocity and density of binary mixtures of *t*-butyl chloride (*t*BC), *t*-butyl bromide (*t*BB), and 1,1,1-trichloroethane (TCE) with carbon tetrachloride (CT), benzene (B), and *p*-xylene (*p*X) were measured at temperatures, 25 and 35°C. The excess molar volume and excess compressibility of these systems were calculated. The temperature dependency of excess volume was negative for aromatic solutions and positive for CT solutions. The temperature coefficients of excess compressibility were negative for all systems. The relation between thermodynamic properties and intermolecular interactions in these systems were discussed. Two systems, B-TCE and CT-TCE, were found to be nearly ideal. The solute-solvent interactions in CT-*t*BC and *t*BC-TCE systems were found to be more attractive than in other systems.

Adiabatic compressibility of binary mixtures has been studied by a number of investigators using ultrasonic methods.[1–8] Though considerable data are found in literature, there are not many systematic studies on the dependency of compressibility upon the interaction between unlike molecules. It has been pointed out by several workers that the excess thermodynamic functions are sensitively dependent not only on the difference in intermolecular forces, but also on the difference in size of molecules.[9,10] It is obvious that the study of excess compressibility and excess molar volume gives important information on intermolecular forces determining the properties of mixtures.

The purpose of the present study is to investigate the solute-solvent interaction from ultrasonic velocity and density data, using the statistical theory of solutions.[9]

In this study, *t*-butyl chloride, *t*-butyl bromide, and 1,1,1-trichloroethane were used as solutes which are polar and nearly spherical in molecular shape, and carbon tetrachloride, benzene and *p*-xylene as solvents. Carbon tetrachloride was chosen as a typical solvent which is spherical in molecular shape.

Measurements of sound velocity and density were carried out at 25 and 35°C for nine binary mixtures.

Experimental

Samples of carbon tetrachloride (CT),[11] benzene (B), *p*-xylene (*p*X), *t*-butyl chloride (*t*BC), *t*-butyl bromide (*t*BB), and 1,1,1-trichloroethane (TCE) are guaranteed reagents obtained from Wako Pure Chemical Industry Co. Ltd., and used after purification.[12] Boiling points agreed with the values in literature. The purity of samples was examined by the measurements of density at 25°C.

Sample	Observed values of density at 25°C	Literature values[13]
Carbon tetrachloride	1.58446	1.58434
Benzene	0.87361	0.87362
p-Xylene	0.85663	0.85669
t-Butyl chloride	0.8356_1	$0.8354^{a)}$
t-Butyl bromide	1.2131_1	$1.2132_1{}^{a)}$
1,1,1-Trichloroethane	1.3293_3	$1.3293_5{}^{a)}$

a) Interpolated values

The sound velocity was measured at 3 Mc. The interferometer used is described in a previous paper.[7] The results are accurate within 0.3 m/sec. Density measurements were made using a pycnometer of the usual type. Its accuracy is within 0.01%. *t*-Butyl bromide is fairly unstable at ordinary temperatures and should be treated carefully. Thus, the accuracy of the sound velocity and density in the systems including *t*-butyl bromide is within 0.5 m/sec and 0.03%, respectively.

Results

The density d and sound velocity v were measured over the whole concentration range at 25 and 35°C for nine systems: CT-*t*BC, CT-*t*BB, CT-TCE, B-*t*BC, B-*t*BB, B-TCE, *p*X-*t*BC, *p*X-TCE, and *t*BC-TCE.

Excess Molar Volume on Mixing. Excess molar volume V^E was calculated from the density data, and its dependency of mole fraction is shown in Figs. 1(a)-(i) for each system. The abscissa x represents the mole fraction of solutes. The accuracy of V^E is about ±0.02 cc/mole, except for that of *t*-butyl bromide solutions, which is ±0.05 cc/mole.

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[1] G. A. Holder and E. Whalley, *Trans. Faraday Soc.*, **58**, 2108 (1962).

[2] H. Sackmann and A. Boczek, *Z. Phys. Chem.*, **29**, 329 (1961).

[3] E. A. Moelwyn-Hughes and P. L. Thorpe, *Proc. Roy. Soc.* (London), **A268**, 574 (1964).

[4] K. C. Reddy, S. V. Subrehmanyan, and J. Bhmasenachar, *J. Phys. Soc. Japan*, **19**, 559 (1964).

[5] R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **61**, 2102 (1965).

[6] L. A. Staveley, W. R. Tupman, and K. R. Hart, *ibid.*, **51**, 323 (1955).

[7] O. Kiyohara and K. Arakawa, This Bulletin, **43**, 3037 (1970).

[8] G. H. Findenegg and F. Kohler, *Trans. Faraday Soc.*, **63**, 870 (1967); E. Wilhem, R. Schano, G. Becker, G. H. Findenegg, and F. Kohler, *ibid.*, **65**, 1443 (1969).

[9] K. Arakawa and O. Kiyohara, This Bulletin **43**, 975 (1970).

[10] J. S. Rowlinson, "Liquids and Liquid Mixtures," 2nd ed., Butterworth, London (1969).

[11] Abbreviations are used for each substance.

[12] J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," Vol. II, 2nd edit., Interscience Publishers, Inc., New York (1967).

[13] J. Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Amsterdam, The Netherlands, Vol. I (1950) and Vol. II (1965).

All the systems except CT-TCE, B-*t*BB, B-TCE, and *p*X-TCE give negative values of V^E. The V^E *vs.* mole fraction curves in B-*t*BB and B-TCE systems are of nearly inverse S type, and that for CT-TCE system positive. The temperature dependency of V^E is negative for B-*t*BC, B-TCE, *p*X-*t*BC, and *p*X-TCE, and positive for CT-*t*BC and *t*BC-TCE systems. However, the temperature coefficients are very small, and those for CT-*t*BB, CT-TCE, and B-*t*BB are zero within experimental error.

Mathot and Desmyter[14] measured the V^E of CT-*t*BC and CT-TCE systems and obtained −0.26 cc/mol and 0.25 cc/mole for equimolar mixtures at 0°C, respectively. The values we obtained are −0.36 and 0.04 cc/mol for CT-*t*BC and CT-TCE at 25°C, respectively. There is a discrepancy between these values, which is larger in CT-TCE system.

The values of V^E can be represented by

$$V^E = x(1-x)\sum_{i=0}^{2} A_i \cdot (1-2x)^i \qquad (1)$$

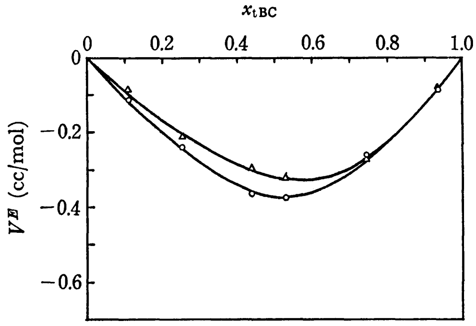

Fig. 1. 1(a). Excess molar volume of CT-*t*BC system.
○ 25°C, △ 35°C

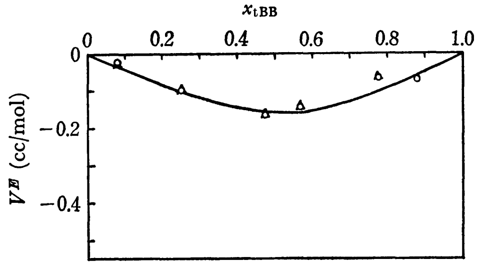

Fig. 1(b). Excess molar volume of CT-*t*BB system.
○ 25°C, △ 35°C

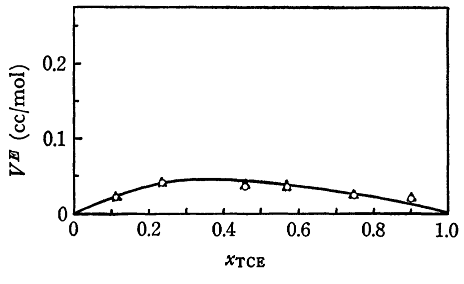

Fig. 1(c). Excess molar volume of CT-TCE system.
○ 25°C, △ 35°C

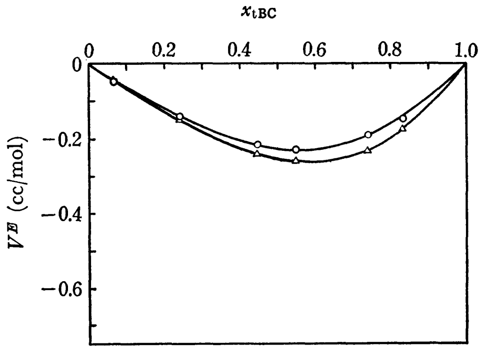

Fig. 1(d). Excess molar volume of B-*t*BC system.
○ 25°C, △ 35°C

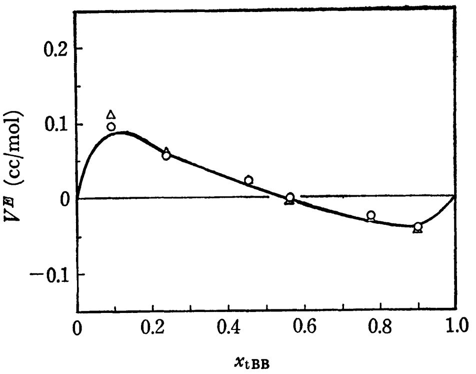

Fig. 1(e). Excess molar volume of B-*t*BB system.
○ 25°C, △ 35°C

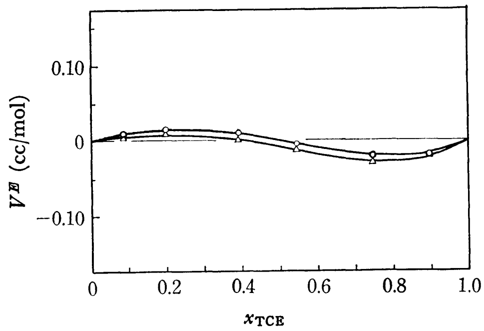

Fig. 1(f). Excess molar volume of B-TCE system.
○ 25°C, △ 35°C

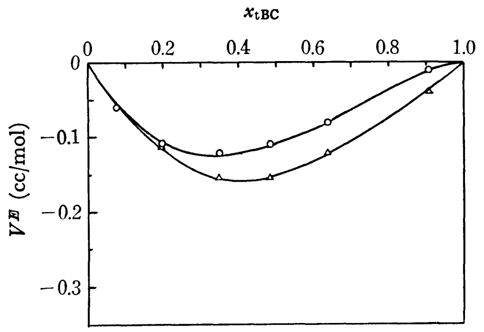

Fig. 1(g). Excess molar volume of *p*X-*t*BC system.
○ 25°C, △35°C,

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[14] V. Mathot and A. Desmyter, *J. Chem. Phys.*, **21**, 782 (1953).

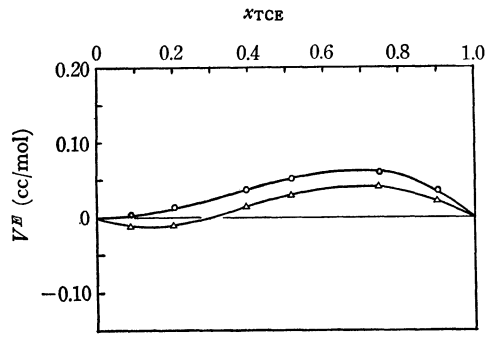

Fig. 1(h). Excess molar volume of *p*X-TCE system. ○ 25°C, △ 35°C

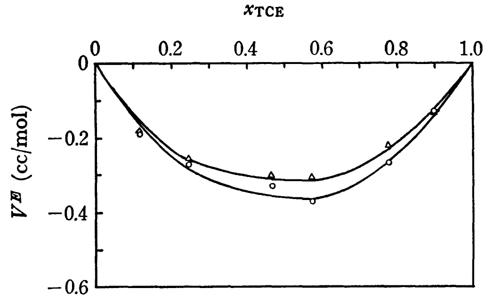

Fig. 1(i). Excess molar volume of *t*BC-TCE system. ○ 25°C, △ 35C°

where x is the mole fraction of solute. The coefficients A_i, which were determined for each system by the method of least squares, are given in Table 1(a).

Table 1(a). Values of the coefficients A_i

System	T (°C)	A_0	A_1 (cc/mol)	A_2
CT-*t*BC	25	−1.449	0.067	0.453
	35	−1.278	0.275	0.317
CT-*t*BB	25	−0.567	0.105	0.204
	35	−0.379	0.262	0.138
CT-TCE	25	0.146	0.010	0.154
	35	0.163	0.019	0.139
B-*t*BC	25	−0.903	0.191	−0.069
	35	−1.022	0.370	0.051
B-*t*BB	25	0.019	0.802	0.443
	35	−0.012	0.921	0.602
B-TCE	25	0.003	0.225	−0.109
	35	−0.033	0.209	−0.110
*p*X-*t*BC	25	−0.428	−0.418	−0.069
	35	−0.587	−0.239	−0.100
*p*X-TCE	25	0.199	−0.205	0.036
	35	0.111	−0.235	−0.070
*t*BC-TCE	25	−1.436	−0.212	−0.296
	35	−1.248	−0.212	−0.507

Sound Velocity. The values of sound velocity in pure components are given in column 3 of Table 2, together with literature values in the last column. The sound velocity of all these systems deviates negatively from linear addivity in mole fraction, and the deviation decreases with the rise of temperature. The sound velocity *vs.* concentration curves for CT-TCE, B-TCE, *p*X-TCE, and *t*BC-TCE systems at 25°C are shown in Fig. 2.

Adiabatic Compressibility. The values of adiabatic compressibility calculated from the values of v and d by means of the equation

$$\kappa_s = 1/(v^2 d) \tag{2}$$

are given in column 4 of Table 2 for pure liquids.

The excess compressibility $(V\kappa_s)^E$ is defined by means of the equation

$$(V\kappa_s)^E = V\kappa_s - (V_{AA}\kappa_{s,AA}x_A + V_{BB}\kappa_{s,BB}x_B) \tag{3}$$

where V, V_{AA} and V_{BB} are the molar volume of solution and pure liquids for species A and B, respectively, and $\kappa_{s,AA}$ and $\kappa_{s,BB}$ are the adiabatic compressibility of pure liquids A and B, respectively. The values of $(V\kappa_s)^E$ are shown in Figs. 3(a)—(i) for each system. $(V\kappa_s)^E$ becomes linear in mole fraction if a system behaves like an ideal solution.[7]

Table 1(b). Values of the coefficients B_i

System	T (°C)	B_0	B_1 (bar$^{-1}\times 10^{-6}$)	B_2
CT-*t*BC	25	−23.180	4.040	−0.668
	35	−25.268	2.530	1.961
CT-*t*BB	25	− 8.098	0.291	0.200
	35	—	—	—
CT-TCE	25	1.546	−1.770	1.613
	35	1.004	−0.470	−0.470
B-*t*BC	25	−28.104	1.333	−1.015
	35	−33.208	0.988	−1.384
B-*t*BB	25	− 9.176	−0.658	−0.453
	35	−11.099	−0.944	−1.020
B-TCE	25	− 0.691	−0.370	−1.182
	35	− 3.188	−1.464	−2.755
*p*X-*t*BC	25	− 9.962	1.982	−1.942
	35	−13.564	1.510	−0.602
*p*X-TCE	25	5.878	−1.089	0.061
	35	5.902	0.469	−1.044
*t*BC-TCE	25	−17.703	−1.475	1.502
	35	−20.784	−1.032	0.772

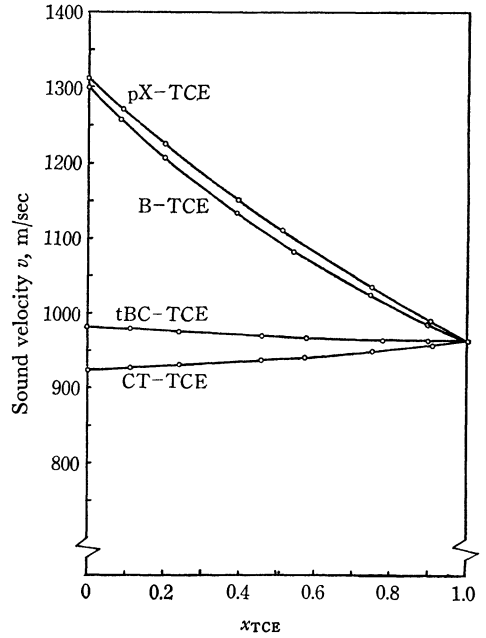

Fig. 2. Sound velocity of B-TCE, CT-TCE, *p*X-TCE and *t*BC-TCE systems.

TABLE 2. SOUND VELOCITY AND COMPRESSIBILITY OF PURE LIQUIDS

Substance	T (°C)	v (m/sec)	κ_s ($\text{bar}^{-1}\times 10^{-6}$)	Lit. values of sound velocity
Benzene	25	1299.1	67.8_3	1299,[a] 1307,[b] 1295[c]
	35	1251.3	74.0_1	1253,[a]
Carbon tetrachloride	25	921.2	74.3_7	923,[d] 927[b]
	35	890.4	80.6_0	892[d]
p-Xylene	25	1309.6	68.0_7	
	35	1268.0	73.3_5	
t-Butyl chloride	25	981.1	124.3_3	984[e]
	35	940.3	137.3_9	
t-Butyl bromide	25	$903._3$	101.0_3	
	35	$868._4$	110.7_5	
1,1,1-Trichloroethane	25	963.4	81.0_5	
	35	930.1	88.0_5	

a) A. Van Itterbeek and A. De Bock, *Physica*, **14**, 609 (1949).
b) Ref. 5.
c) D. D. Deshpande and L. G. Bhatgadde, *J. Phys. Chem.*, **72**, 261 (1968).
d) R. T. Legemann, D. R. McMillan, and W. E. Woolf, *J. Chem. Phys.*, **17**, 369 (1949).
e) G. W. Willard, *J. Acous. Soc. Amer.*, **19**, 235 (1947).

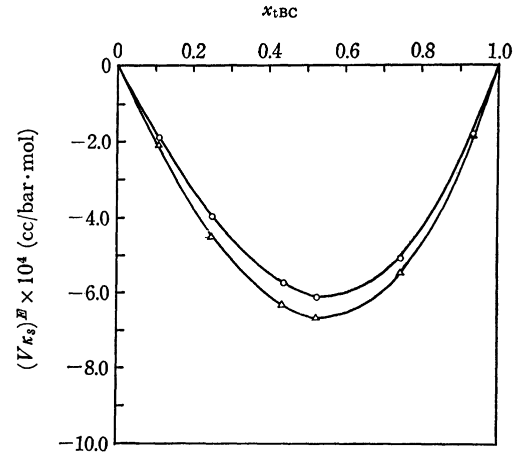

Fig. 3.(a). $(V\kappa_s)^E$ for CT-*t*BC system.
○ 25°C, △ 35°C

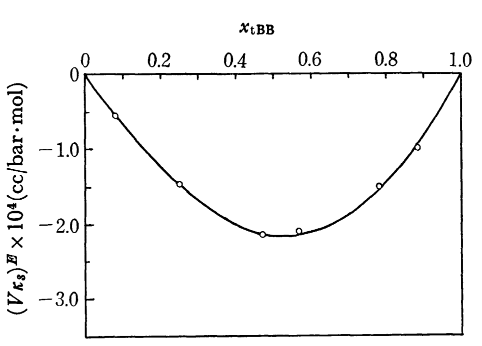

Fig. 3(b). $(V\kappa_s)^E$ for CT-*t*BB system at 25°C.

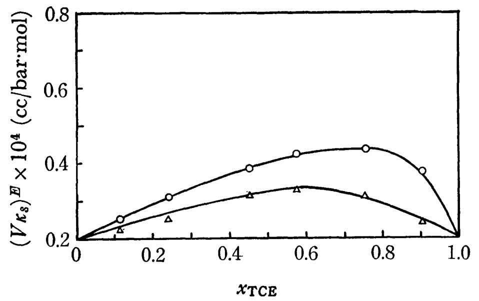

Fig. 3(c). $(V\kappa_s)^E$ for CT-TCE system.
○ 25°C, △ 35°C

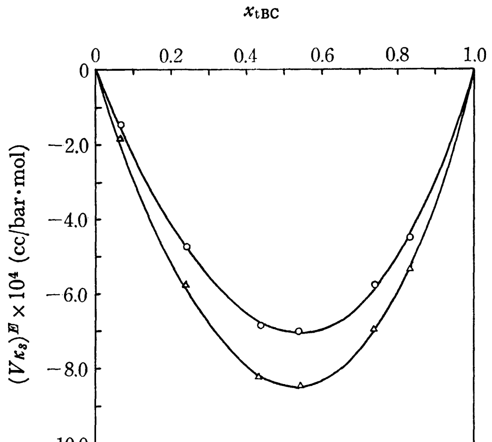

Fig. 3(d). $(V\kappa_s)^E$ for B-*t*BC system.
○ 25°C, △ 35°C

The $(V\kappa_s)^E$ values of all systems except CT-TCE have negative values and their dependency on temperature is negative for all systems except *p*X-TCE system, where it is zero within experimental error. The κ_s^E *vs.* mole fraction curves fit into the following equation.

$$\kappa_s^E = x(1-x)\sum_{i=0}^{2} B_i\cdot(1-2x)^i \tag{4}$$

Coefficients B_i are given in Table 1(b). The accuracy of κ_s^E is within 0.05%, and that for *t*-butyl bromide solutions within 0.1%.

Discussion

The curves of excess volume with respect to mole fraction differ from those of excess compressibility.

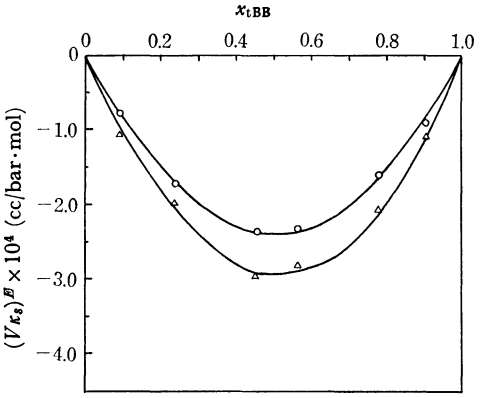

Fig. 3(e). $(V\kappa_s)^E$ for B-tBB system.
○ 25°C, △ 35°C

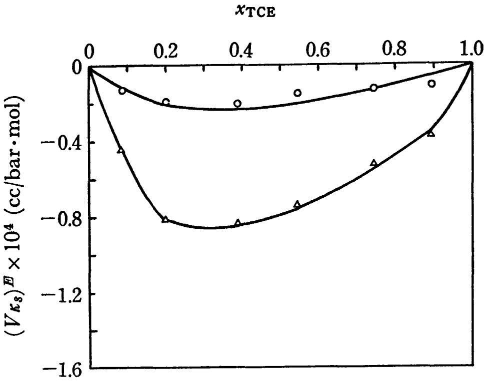

Fig. 3(f). $(V\kappa_s)^E$ for B-TCE system.
○ 25°C, △ 35°C

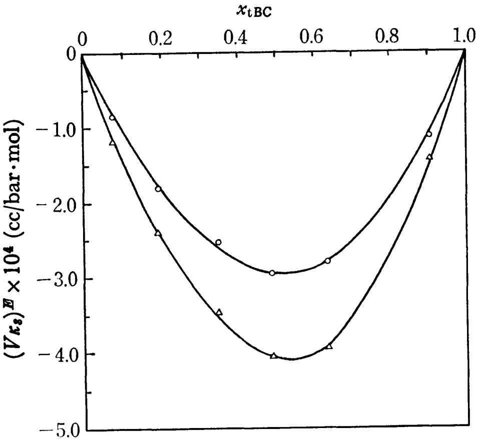

Fig. 3(g). $(V\kappa_s)^E$ for pX-tBC system.
○ 25°C, △ 35°C

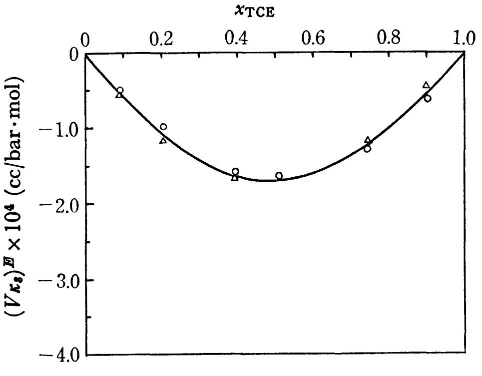

Fig. 3(h). $(V\kappa_s)^E$ for pX-TCE system.
○ 25°C, △ 35°C

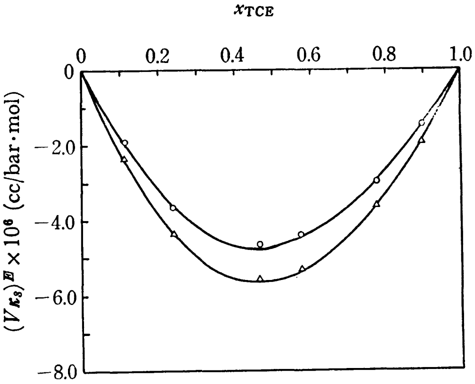

Fig. 3(i). $(V\kappa_s)^E$ for tBC-TCE system.
○ 25°C, △ 35°C

The latter are more symmetrical except for CT-TCE system. In particular, asymmetry of V^E is marked in aromatic systems.

It is seen that the temperature dependency of V^E has negative coefficients for aromatic solutions and positive ones for CT solutions, although the temperature coefficients are very small for all systems. The general trend in temperature dependency of $\kappa_s{}^E$ and $(V\kappa_s)^E$ seems to be negative.

The interaction between unlike molecules in these systems seems to be ascribed to dispersion forces and dipole-induced dipole interactions, considering the chemical nature of the species in these systems. Recently, Fort, Jr., and Lindstrom[15] reported that there is no complex formation.

Molecular size V^* for pure liquids was obtained from the values of molar volume V and thermal expansion coefficient α, by the equation[9].

$$V^* = V\times\left[(1+\alpha T)\Big/\left(1+\frac{4}{3}\alpha T\right)\right]^3. \qquad (5)$$

The values of these parameters are listed in Table 3, together with dipole moments of solute.

We showed that the V^E was expressed as the sum of two terms[9]: the one V^E_{size} associated with the size difference of molecules and the other $V^E_{\text{int.}}$ associated with the interaction forces between molecules. Thus, for a mixture composed of species A and B, we have

$$V^E = V^E_{\text{size}} + V^E_{\text{int.}} \qquad (6)$$

and

$$V^E_{\text{size}} = [(V^*_A - V^*_{AA})x_A + (V^*_B - V^*_{BB})x_B] \times [1-(9RT/\pi)(V^0/W_m)]^{-1} \qquad (7)$$

where $W_m = N^2\times(\gamma\varepsilon_A{}^* r_A{}^{*3}x_A + \gamma\varepsilon_B{}^* r_B{}^{*3}x_B)$, $V^* = N\beta r^{*3}$, $V^0 = V_{AA}x_A + V_{BB}x_B$, and pure components are denoted by AA and BB. γ, β, r^*, and ε^* have the same meaning as in the previous paper.[9] r^* and ε^* are related to those of pure liquids by means of the equations

$$r^*_A = r^*_{AA}x_A + r^*_{AB}x_B,\quad r^*_B = r^*_{AB}x_A + r^*_{BB}x_B,$$
$$r^*_{AB} = (r^*_{AA} + r^*_{BB})/2 \qquad (8)$$

and

$$\varepsilon^*_A = \varepsilon^*_{AA}x_A + \varepsilon^*_{AB}x_B,\quad \varepsilon^*_B = \varepsilon^*_{AB}x_A + \varepsilon^*_{BB}x_B \qquad (9)$$

The relation of molar volume and interaction energy

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[15] R. C. Fort, Jr., and T. R. Lindstrom, *Tetrahedron*, **23**, 3227 (1967).

Table 3. Molecular parameters of pure liquids (25 °C)

Substance	V (cc/mol)	$\alpha \times 10^3$ (deg.$^{-1}$)	V^* (cc/mol)	μ (D)
Benzene	89.41	1.223[a)]	69.22	
Carbon tetrachloride	97.09	1.226[b)]	75.13	
p-Xylene	123.93	1.013[c)]	99.11	
t-Butyl chloride	110.78	1.427[c)]	83.34	2.12[d)]
t-Butyl bromide	112.91	1.275[c)]	86.75	2.19~2.21[e)]
1,1,1-Trichloroethane	100.36	1.245[c)]	77.44	1.79[d)]

a) S. E. Wood and J. P. Brusi, *J. Amer. Chem. Soc.*, **65**, 189 (1943).
b) E. L. Washington and R. Battino, *J. Phys. Chem.*, **72**, 4496 (1968).
c) Estimated from the data on densities at various temperature summarized in Ref. 13.
d) Ref. 12.
e) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman Co., San Francisco and London (1963).

for a mixture is given by

$$W_m = (9RT/2\pi) \times [V^2/(V-V^*)] \tag{10}$$

where $V^* = V_A{}^*x_A + V_B{}^*x_B$ and V is molar volume of solution, and that for a pure liquid A by

$$N^2\gamma\varepsilon_{AA}^*r_{AA}^{*3} = (3RT/2\pi) \times [V_{AA}{}^{4/3}(V_{AA}{}^{1/3} - V_{AA}^*{}^{1/3})] \tag{11}$$

The value of θ, which is associated with intermolecular interaction energy $\varepsilon_{AB}{}^*$, is defined as follows.

$$\theta = [\varepsilon_{AB}^* - (\varepsilon_{AA}^* + \varepsilon_{BB}^*)/2]/\varepsilon_{AA}^* \tag{12}$$

The values $\varepsilon_{AB}{}^*$ for equimolar mixtures are calculated from the observed values of V^E and the molecular parameters in Table 3, using Eqs. (6)—(11). The values of θ are determined from $\varepsilon_{AB}{}^*$ and are given in Table 4. $\theta_{disp.}$, obtained using Bertholet's relation $\varepsilon_{AB}{}^* = (\varepsilon_{AA}{}^* \cdot \varepsilon_{BB}{}^*)^{1/2}$, and the values of V_{size}^E and $V_{int.}^E$ obtained for equimolar mixtures are also listed.

We see that the values of θ are negative and smaller than those of $\theta_{disp.}$, except for the systems CT-*t*BC and *t*BC-TCE which has positive values of θ. All the systems except these two have positive values of $V_{int.}^E$.

It is seen that the values of θ decrease in the order CT, B, and *p*X as solvents for a common solute and those of $V_{int.}^E$ increase in this order. The results are consistent with the idea that the attractive interaction between solute and solvent becomes stronger in the order *p*X, B, and CT as solvents.[9)]

Carbon tetrachlordie, *t*-butyl chloride, trichloroethane, and *t*-butyl bromide are similar chemically. They are regarded as derivatives of CH_4: in the first three compounds H atoms of CH_4 are replaced by Cl and CH_3 groups and in the last by Br and CH_3 groups. The molecular shape of these four compounds are nearly spherical. Carbon tetrachloride is non-polar and the other three have the dipole moment about 2D as given in Table 3.

In CT-TCE system, the observed values of V^E and $(V\kappa_s)^E$ are one order smaller than those in other systems, and the magnitude of θ is negative and small. Similar situations are found in B-TCE systems. Thus, it is concluded that these two systems are nearly ideal. Turner *et al.*[16)] reached the same conclusion from the measurements of dielectric relaxation times, boiling point diagram and heat of mixing of B-TCE system. From the fact that CT-B system is nearly ideal,[9)] it can be said that all binary mixtures consisting of CT, B, and TCE are regarded as ideal solutions.

As seen in Table 4, the observed values of V^E and $(V\kappa_s)^E$ in the systems including *t*BC are negative and comparatively larger in their absolute magnitude, compared with those in the systems including TCE. Moreover, the values of θ in CT-*t*BC and TCE-*t*BC systems are positive, which is in sharp contrast to the situation in CT-TCE and B-TCE systems. This means that the solute-solvent interactions in CT-*t*BC and *t*BC-TCE systems are more attractive than those in other systems.

The molecules of *t*BC and TCE have structures in which methyl groups and chlorine atoms are exchanged and have nearly the same dipole moments.

Table 4. Thermodynamic quantities of equimolar mixtures (25 °C)

System	$V^E{}_{obs.}$	$V^E{}_{size}$ (cc/mol)	$V^E{}_{int.}$	$(V\kappa_s)^E \times 10^4$ (cc/bar·mol)	θ (10^{-3})	$\theta_{disp.}$
CT-*t*BC	−0.36	−0.10	−0.26	-6.0_0	5.7	−0.5
CT-*t*BB	−0.14	−0.20	0.06	-2.1_2	−1.0	−0.0
CT-TCE	0.04	−0.01	0.05	0.3_8	−2.3	−0.0
B-*t*BC	−0.23	−0.31	0.08	-7.0_1	−7.7	−0.5
B-*t*BB	0.00	−0.46	0.46	-2.3_2	−16.5	−0.0
B-TCE	0.00	−0.11	0.11	-0.1_6	−4.2	−0.0
*p*X-*t*BC	−0.11	−0.31	0.20	-2.9_2	−16.1	−3.1
*p*X-TCE	0.05	−0.59	0.64	1.6_5	−21.2	−1.2
*t*BC-TCE	−0.36	−0.05	−0.31	-4.6_6	9.4	-0.4

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16) E. M. Turner, D. W. Anderson, L. A. Reich, and W. E. Vaughan, *J. Phys. Chem.*, **74**, 1275 (1970).

The molecular size V^* of CT, *t*BC, and TCE do not differ much. This is shown in Table 3. It might be concluded that the nature of more attractive interactions in CT-*t*BC and TCE-*t*BC systems is due to the interactions between methyl groups and chlorine atoms. This suggests that the interaction between these molecules can not be described by means of the central force field which is a function of the separation between molecular centers.10) This might be assumed to be an interaction through molecular surfaces.17)

The values of dipole moments of 1,2-dichloroethane (DCE) in pure liquid (2.1 D) and in benzene solution (1.7 D) are nearly equal in the order of magnitude to those of *t*BC and TCE, respectively. However, B-DCE system has positive values of V^E, $(V\kappa_s)^E$ and θ, which are in marked contrast to the negative values in B-*t*BC and B-TCE.7) A more refined treatment of a ternary mixture, which includes the conversion between gauche and trans forms in DCE, is desirable for B-DCE system.

In the systems including B and *p*X as solvents, the values of θ in *p*X solutions are more negative than those in B solutions. It indicates that the solutes studied are more attractive to B than to *p*X.

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17) P. J. Flory, *J. Amer Chem. Soc.*, **87**, 1833 (1965); A. Abe and P. J. Flory, *ibid.*, **87**, 1838 (1965).