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Ultrasonic and Thermodynamic Study on Solute-Solvent Interaction. Binary Mixtures of 1,2-Dichloroethane with Benzene, Toluene, *p*-Xylene and Cyclohexane

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The sound velocity and density of binary mixtures of benzene, toluene, *p*-xylene and cyclohexane with 1,2-dichloroethane (DCE) as a common component were measured at temperature 20—40°C, and the excess molar volume and excess compressibility of these systems were calculated. They were found to be positive. The excess compressibility is independent of temperature in the DCE-benzene system. Thermodynamical properties and the nature of intermolecular interaction in the systems were discussed. It has been shown that there is a certain weak attraction between DCE and aromatic molecules, and that there is no complex formation *viz.*, hydrogen-bonding or change transfer complex. It has been proposed that the interaction between *gauche* form of DCE and aromatic molecules is of electrostatic nature (dipole-induced dipole or hyper-polarizability).

Binary solutions consisting of a halogen-substituted ethane and an aromatic solvent have long been studied from various viewpoints, but complete information is still lacking.

One approach to the liquid structure of the system is in the field of the molecular structure theory by means of Raman and infrared spectroscopy,[1-3] dielectric measurements,[4-7] and NMR.[8] The solvent dependence of the conformational equilibrium in halogen-substituted ethanes in the solution has been studied.[1-8] It has been found that aromatic solvents exhibit an anomaly in the conformational equilibrium of halogen-substituted ethanes in contrast to non-aromatic solvents.[3-8]

In a second approach, *viz.*, a thermodynamical consideration, the 1,2-dichloroethane-benzene system has been regarded as a nearly ideal solution,[9,10] because the excess free energy, enthalpy and entropy resulting from mixing are small. However, excess molar volume is large in comparison with other excess thermodynamical quantities.[11-14] Measurements of thermodynamical quantities have been made on this "pseudo-ideal" solution.[9-16]

By the analysis using the solution theory,[17] it has been shown that this system is not ideal, and that a certain kind of order is present between two components.[17]

As a third approach for the 1,2-dichloroethane-benzene system, ultrasonic studies, which present a useful means for the study of liquid structure in general, have been made by Staveley *et al.*,[18]

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3) A. Wada and Y. Morino, *ibid.*, **22**, 1276 (1954).
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9) J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolyte," Third Ed., Dover Publications, Inc., New York (1964), Chapt. XIII, pp. 211, 216.
10) J. S. Rowlinson, "Liquids and Liquid Mixtures," 2nd Ed., Butterworth & Co. Ltd., London (1969), p. 137.
11) L. Sieg, J. L. Crutzen and W. Jost, *Z. phys. Chem.*, **198**, 263 (1951).
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16) L. A. K. Staveley, W. J. Tupman and K. R. Hart, *Discuss. Faraday Soc.*, **15**, 130 (1953).
17) K. Arakawa and O. Kiyohara, This Bulletin, **43**, 975 (1970).
18) L. A. K. Staveley, W. J. Tupman and K. R. Hart, *Trans. Faraday Soc.*, **51**, 323 (1955).

Kohler *et al.*[19] and others.[20]

This system is interesting as the object of studies of the interaction between polar molecules and π electrons, as well as that of studies of liquid structure.

We report here the results of an ultrsonic and thermodynamical investigation for the dichloroethane-aromatic systems and the dichloroethane-cyclohexane system which is taken as a reference system, and discuss the nature of the solute-solvent interactions in the systems.

Experimental

Samples of benzene, toluene, *p*-xylene, cyclohexane and 1,2-dichloroethane (DCE) were guaranteed reagents obtained from Wako Pure Chemical Industry Co. Ltd., and used on further purification.[21] The purity was examined by measurements of density at 20°C.

Sample	Density at 20°C	Lit. value[22]
Benzene	0.87904	0.87903
Toluene	0.86703	0.86696
p-Xylene	0.86105	0.68100
Cyclohexane	0.77853	0.77853
DCE	1.25297	1.25294

Sound velocity was measured using a usual crystal interferometer,[23] working at 3 Mc. The cell used is shown in Fig. 1. Measurements were made at 20, 30 and 40°C. The temperature was controlled within ±0.05°C. The measurement of sound velocity was reproducible within ±0.3 m/sec.

In order to test the apparatus, sound velocity was measured at 30°C for pure samples of benzene, *n*-hexane, cyclohexane and carbon tetrachloride. The results obtained were compared with data in literature.

Sample	Sound velocity at 30°C (m/sec)	Lit. value
Benzene	1275.4 (3 Mc)	1276.9,*1 1275.8*2
n-Hexnae	1062.8 (1 Mc)	1055.3*2
Cyclohexane	1228.6 (3 Mc)	1231.3,*3 1229.5*2
Carbon tetrachloride	908.6 (1 Mc)	905.9,*4 908*5

19) a) G. H. Findenegg and F. Kohler, *ibid.*, **63**, 870 (1967). b) E. Wilhelm, R. Schano, G. Becker, G. H. Findenegg and F. Kohler, *ibid.*, **65**, 1443 (1969).

20) R. J. Fort and W. R. Moore, *ibid.*, **61**, 2102 (1965).

21) J. A. Riddick and E. E. Toops, Jr., "Organic Solvent," Vol. II, 2nd Ed., Interscience Publishers, Inc., New York (1967).

22) J. Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Vol. I (1950) and Vol. II (1965).

23) H. Nomura and Y. Miyahara, *Nippon Kagaku Zasshi*, **88**, 22 (1967).

*1 Ref. 19a. *2 Ref. 24.

*3 Ref. 19b. *4 Ref. 25.

*5 K. C. Reddy, S. V. Subrahmanyam and J. Bhimasenacher, *J. Phys. Soc. Jap.*, **19**, 559 (1964).

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25) H. Sackmann and A. Boczek, *Z. Physik. Chem.*, **29**, 329 (1961).

The agreement is satisfactory on the whole.

The merit of this apparatus is that the quantity of samples needed for measurements is small, 15—20 cc.

Density measurements were made using a pycnometer of usual type, whose capacity was about 15 cc. Accuracy of the density obtained was ±0.01%.

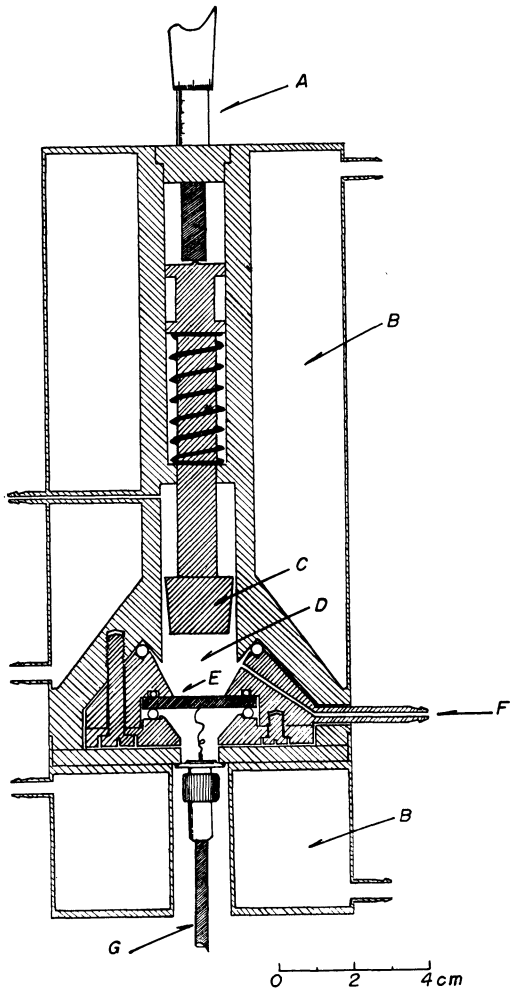

Fig. 1. Interferometer cell.
A: micrometer, B: double jacket, C: reflector, D: sample, E: crystal, F: liquid inlet, G: co-axial cable

Results

Density d and sound velocity v were measured over the whole concentration range at 20, 30 and 40°C for the four systems: DCE-benzene, DCE-toluene, DCE-*p*-xylene and DCE-cyclohexane.

Excess Molar Volume on Mixing. Excess molar volume V^E was calculated from density data which are given in Figs. 2(a), (b), (c) and (d) for each system. Abscissa x represents the mole fraction of DCE. The accuracy of V^E is about ±0.02 cc/mole. V^E values of DCE-benzene system agree

with literature values.[12–14,19a] The trend of its temperature dependence is also in agreement with the data.[13,14,19a] The values of V^E increase in the order: toluene<benzene<*p*-xylene<cyclohexane.

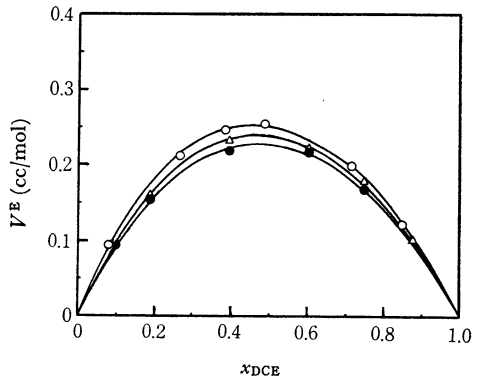

Fig. 2(a). Excess molar volume of DCE-benzene system.
Temperature: ○ 20°C, △ 30°C, ● 40°C

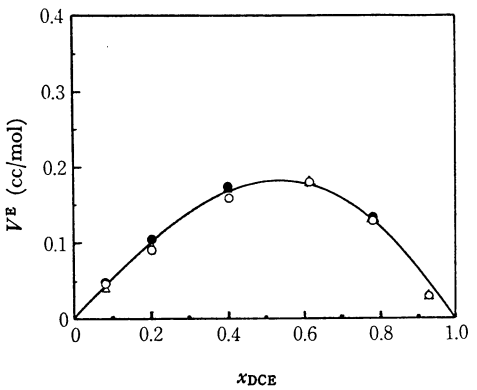

Fig. 2(b). Excess molar volume of DCE-toluene system.
Temperature: ○ 20°C, △30°C, ● 40°C

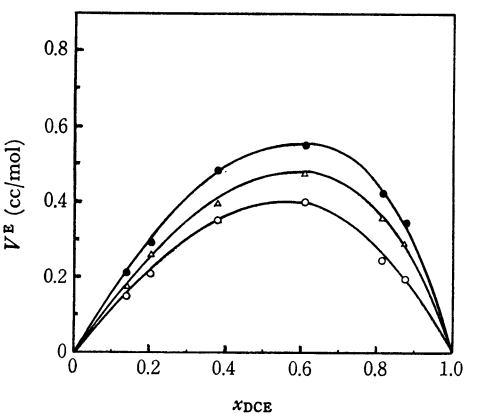

Fig. 2(c). Excess molar volume of DCE-*p*-xlyene system.
Temperature: ○ 20°C, △ 30°C, ● 40°C

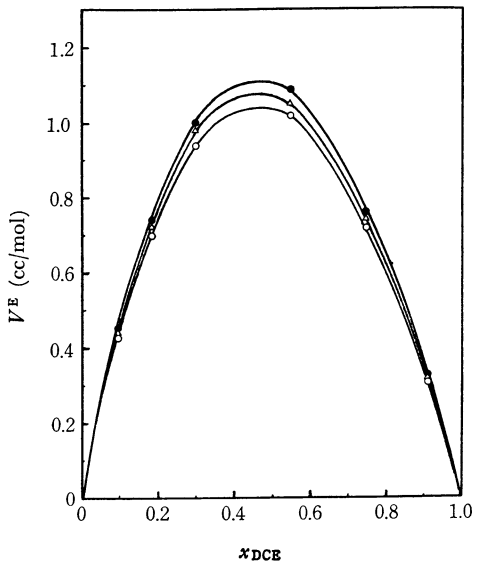

Fig. 2(d). Excess molar volume of DCE-cyclohexane system.
Temperature: ○ 20°C, △ 30°C, ● 40°C

Sound Velocity. Sound velocity v of all these mixtures deviates negatively from linear addivity in mole fraction, and the deviation decreases with rising temperature. Sound velocity *vs.* concentration curve of DCE-xylene system is shown in Fig. 3 as an example. The sound velocity of DCE-benzene system was measured by several workers,[18–20] and that of DCE-cyclohexane system by Kohler *et al.*[19b] Our data for these two systems are in good agreement with those of Kohler *et al.*

Compressibility. From the values of sound velocity v and density d, adiabatic compressibility

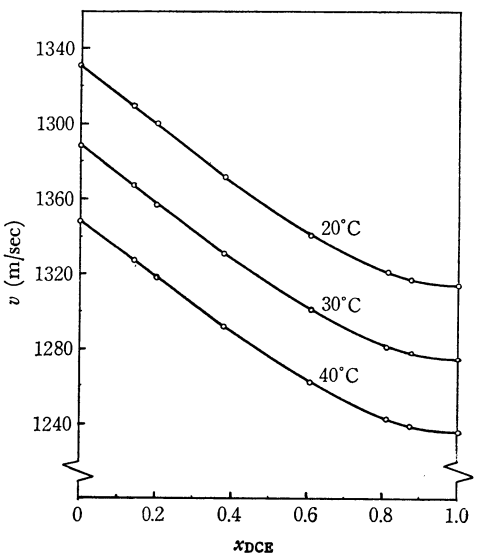

Fig. 3. Sound velocity for DCE-*p*-xylene system.

κ_s has been calculated by means of the relation

$$\kappa_s = \frac{1}{v^2 \cdot d} \tag{1}$$

The κ_s of the pure liquids obtained are given in Table 1. The uncertainty in κ_s is within $\pm 0.1\%$. Values of κ_s of pure liquids are in agreement with the values obtained by Kohler *et al.*[19]

The excess adiabatic compressibility κ_s^E and $(V\kappa_s)^E$ are calculated from κ_s and molar volume V of mixtures and pure components by the equations

$$\kappa_s^E = \kappa_s - \frac{1}{V}(x_A V_A \kappa_{s,A} + x_B V_B \kappa_{s,B}) \tag{2}$$

$$(V\kappa_s)^E = V \cdot \kappa_s - (x_A V_A \kappa_{s,A} + x_B V_B \kappa_{s,B}) \tag{2'}$$

$(V\kappa_s)$ becomes linear in mole fraction if a system behaves as an ideal solution.*6 $(V\kappa_s)^E$ *vs.* concentration curves are shown in Figs. 4(a), (b), (c) and (d) for each system.

All κ_s^E and $(V\kappa_s)^E$ are positive. The values increase in the order: benzene$\lesssim$toluene$<$xylene$<$cyclohexane. The temperature coefficients are all positive except for the DCE-benzene system, whose coefficient is found to be zero within experimental error.

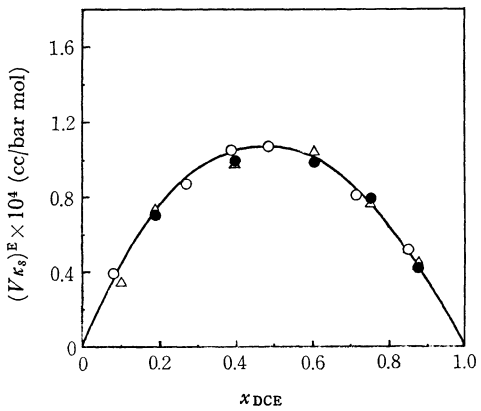

Fig. 4(a). $(V\kappa_s)^E$ for DCE-benzene system. Temperature: ○ 20°C, △ 30°C, ● 40°C

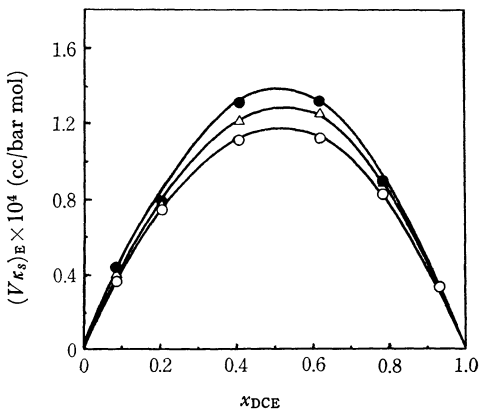

Fig. 4(b). $(V\kappa_s)^E$ for DCE-toluene system. Temperature: ○ 20°C, △ 30°C, ● 40°C

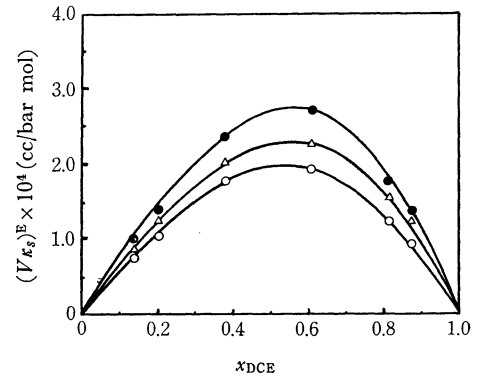

Fig. 4(c). $(V\kappa_s)^E$ for DCE-*p*-xylene system. Temperature: ○ 20°C, △ 30°C, ● 40°C

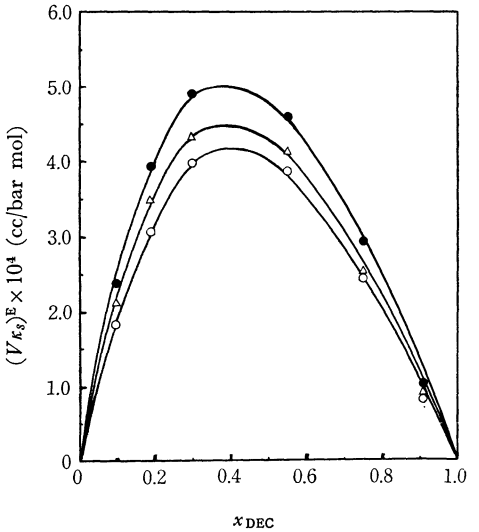

Fig. 4(d). $(V\kappa_s)^E$ for DCE-cyclohexane system. Temperature: ○ 20°C, △ 30°C, ● 40°C

The adiabatic compressibility of DCE-benzene system has been obtained by several workers.[18–20] Stavely *et al.*[18] reported that the temperature coefficient of κ_s^E for this system was slightly positive. However, in our measurements, the coefficient is almost zero within experimental error.

For each system, the data of excess adiabatic compressibility κ_s^E and the excess molar volume V^E

TABLE 1. ADIABATIC COMPRESSIBILITIES κ_s OF PURE LIQUIDS ($bar^{-1} \times 10^{-6}$)

T (°C)	Benzene	Toluene	*p*-Xylene	Cyclo-hexane	DEC
20	64.9_3	65.4_0	65.5_9	78.7_7	54.2_0
30	70.8_0	70.6_6	70.7_0	86.1_3	58.5_4
40	77.1_2	76.5_6	76.1_1	94.4_8	63.3_8

*6 See also Ref. 19a.

Table 2. Values of the coefficients in empirical equations for κ_s^E and V^E

System	T (°C)	A_0	A_1 (bar$^{-1}\times10^{-6}$)	A_2	B_0	B_1 (cm^3/mol)	B_2
DCE-Benzene	20	4.98	0.13	0.17	1.00	0.14	0.17
	30				0.97	0.07	0.05
	40				0.91	0.89	0.17
DCE-Toluene	20	5.01	−1.05	0.52	0.76	−0.03	−0.30
	30	5.44	−0.97	−0.26			
	40	5.49	−0.92	−0.29			
DCE-*p*-Xylene	20	7.80	−3.22	−0.23	1.61	−0.37	−0.21
	30	9.07	−2.80	−0.03	1.84	−0.78	0.50
	40	10.28	−5.03	−0.87	2.16	−0.88	0.55
DCE-Cyclohexane	20	17.32	4.57	−1.25	4.16	0.75	0.17
	30	18.33	5.77	−0.01	4.31	0.78	0.20
	40	20.46	6.66	−0.39	4.44	0.77	0.13

fit with the equation of the type

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

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

where x is the mole fraction of DCE. The coefficients A_i and B_i, which were determined for each system by the method of least squares using FACOM 270—20 Computer, are given in Table 2.

Discussion

Thermodynamical Function. Let us discuss thermodynamical properties of the systems by means of the statistical theory given previously.[17] Excess volume V^E, excess entropy S^E and an interaction energy parameter θ*[7] are calculated for equimolar

Table 3. Molecular parameters of pure liquids

Liquid	T (°C)	V (cc/mol)	$\alpha\times10^3$ (deg^{-1})	V^* (cc/mol)	C_p (cal/deg·mol)
Benzene	20	88.86	1.214	69.09	32.38[a]
	30	89.40	1.223	69.21	32.80[a]
	40	91.07	1.256	69.31	33.38[a]
Toluene	20	106.26	1.055	84.65	36.12[a]
p-Xylene	20	123.29	1.007	98.97	43.07[a]
Cyclohexane	20	108.10	1.180	84.21	36.67[b]
	30	109.41	1.232	84.33	37.48[b]
	40	110.79	1.285	84.51	38.35[b]
DEC	20	78.99	1.141	62.09	30.67[b]
	30	79.92	1.184	62.04	30.79[b]
	40	80.88	1.228	62.01	30.92[b]
DBE	20	86.18	0.943		

a) Ref. 22. b) Ref. 19b.

Table 4. Thermodynamical quantities of equimolar mixtures*

System	T (°C)	$H^E_{obs.}$ (cal/mol)	$V^E_{obs.}$ (cc/mol)	$V^E_{calc.}$ (cc/mol)	$TS^E_{obs.}$ (cal/mol)	$TS^E_{calc.}$ (cal/mol)	$\theta\times10^3$
DCE-C_6H_6	20	21[a]	0.25	−0.04	15[b]	6	3.3
	30	17[a]	0.24	−0.04	12[b]	6	3.6
	40	14[a]	0.23	−0.04	9[b]	5	3.9
DCE-$C_6H_5(CH_3)$	20	−10[c]	0.18	−0.50		4	15.3
DCE-*p*-$C_6H_4(CH_3)_2$	20	−17[c]	0.40	−1.21		9	32.5
DCE-*c*-C_6H_{12}	20	426[c]	1.04	0.86		127	−70.7
DBE-C_6H_6	20	72[d]	0.26[e]	0.01	29[d]	9	− 7.4
C_6H_6-*c*-C_5H_{10}	25	150	0.30	0.49		44	−30.7
C_6H_6-*c*-C_6H_{12}	25	195	0.65	0.50	117	61	−32.1
$C_6H_5(CH_3)$-*c*-C_6H_{12}	25	149	0.57	0.53		41	−25.1
C_6H_5F-*c*-C_6H_{12}	40	212	0.71	0.71	98	67	−36.7

a) Ref. 14.
b) Estimated values (see Ref. 14 and Ref. 11).
c) Ref. 13.
d) A. Neckal and H. Volk, *Monatsh.*, **89**, 754 (1958).
e) Ref. 19b.
* The values given in the 6th to 9th rows are cited from the preceding paper[17] for comparison.

*[7] $\theta=[\varepsilon_{AB}-(\varepsilon_{AA}+\varepsilon_{BB})/2]/\varepsilon_{AA}$, where ε_{AB} is a pair interaction energy between different species, and ε_{AA} and ε_{BB} that between the same species, respectively.

mixtures, using the molecular parameter listed in Table 3. They are given in Table 4, together with the observed values of excess enthalpy H^E (lit. values) and V^E. The values for the 1,2-dibromoethane (DBE)-benzene system and those for the other four binary systems containing an aromatic solvent as a component are also given in Table 4 for comparison.

We see appreciable differences between the three DCE-aromatic solvent systems and others. The values θ for these systems are all positive, and their magnitudes are in the order of aromatic basicity.[26,27] On the contrary, those for six other systems, in which the DCE-cyclohexane and the DBE-benzene systems are included, are all negative. The values of $TS^E_{obs.}$ for the DCE-aromatic solvent systems are found to be less than those for the DBE-benzene system and those for the aromatic-alicyclic systems. This supports the idea that a certain specific but weak attraction is present between DCE and aromatic molecules. The values of $TS^E_{calc.}$ for the aromatic-alicyclic systems are about half as much as $TS^E_{obs.}$. This might be ascribed to the presence of a certain ordered structure in aromatic liquids.[17] The fact that the values of $V^E_{calc.}$ for these DCE-aromatic systems are less than those of $V^E_{obs.}$ in contrast to the good agreement between $V^E_{calc.}$ and $V^E_{obs.}$ for other systems is also attributed to a certain attraction between DCE and aromatic molecules.

Compressibility. The values of κ_s^E obtained for the DCE-aromatic system are found to increase in the order : benzene, toluene, xylene and cyclohexane. The values of $(V\kappa_s)^E$ and κ_s^E of DCE-xylene system are about half as small as those of DCE-cyclohexane system in spite of the fact that molar volume of xylene is larger than that of cyclohexane. This shows that DCE molecules is more interacting with aromatic molecules than with cyclohexane.

Let us compare theoretical values $\kappa^E_{t,calc.}$ with experimental ones, using an approximate formula on excess compressibility[28] derived from the solution theory.[17] We have

$$\kappa_t^E = \frac{1}{3RT}\left[\frac{(V-V^*)^2}{V} - \frac{1}{V}\{(V_A-V^*_{AA})^2x_A+(V_B-V^*_{BB})^2x_B\}\right] \quad (3)$$

where V^* is $V^*_A \cdot x_A + V^*_B \cdot x_B$ and other notations are the same as those in the preceding paper.[17] From the values of sound velocity, we can get the adiabatic compressibility κ_s. κ_s^E can be transferred to excess isothermal compressibility κ_t^E, using the thermodynamical relation

$$\kappa_t = \kappa_s + \frac{V \cdot T \cdot \alpha^2}{C_p} \quad (4)$$

The values of excess specific heat C_p^E are available from literature. The values of κ_t^E obtained for equimolar mixtures are given in column 7 of Table 5, together with the values of $V^E_{obs.}$, $C^E_{p,obs.}$ and $\kappa^E_{s,obs.}$ used (those of pure components are given in Table 3.). On the other hand, κ_t^E can be calculated by Eq. (3) from the observed V^E. The $\kappa^E_{t,calc.}$ are listed in the last column of Table 5, and those for the DBE-benzene system are included for comparison.

The $\kappa^E_{t,obs}$ for all the systems are in good agreement with $\kappa^E_{t,calc.}$. The agreement is good also with respect to its temperature dependence for the DCE-benzene and DCE-cyclohexane system. This supports the idea that the interaction between DCE and aromatic molecules obeys the 6th power rule with respect to intermolecular distance.[17]

TABLE 5. THE EXCESS COMPRESSIBILITIES FOR EQUIMOLAR MIXTURES

System	T (°C)	$V^E_{obs.}$ (cc/mol)	$C^E_{p.obs.}$ (cal/deg·mol)	$\alpha_{obs.}\times10^3$ d) (deg^{-1})	$\kappa_s^E\times10^6$ (bar^{-1}) Obsd	$\kappa_t^E\times10^6$ (bar^{-1}) Obsd	$\kappa_t^E\times10^6$ (bar^{-1}) Calcd
DCE-Benzene	20	0.25	-0.0_7 b)	1.164	1.2_5	1.3	2.5
	30	0.24	-0.0_9 b)	1.195	1.2_5	1.3	2.5
	40	0.23	-0.1_3 b)	1.228	1.2_5	1.3	2.5
DCE-Toluene	20	0.19	-0.4_8 c)	1.089	1.2_5	2.9	4.6
DCE-*p*-Xylene	20	0.40	-0.4_1 c)	1.111	1.9_5	8.0	11.7
DCE-Cyclohexane	20	1.04	-0.6_2 a)	1.191	4.3_3	11.3	12.6
	30	1.08	-0.8_1 a)	1.231	4.5_8	12.1	13.0
	40	1.11	-1.0_1 a)	1.273	5.1_2	13.0	13.4
DBE-Benzene	20	0.26 a)				~-1.5 e)	2.1

a) Ref. 19. b) Ref. 18. c) Ref. 13.
d) Estimated values from the observed dV^E/dT and α of pure liquids (Table 3).
e) Value at 27°C (Ref. 19a).

26) M. Tamres, *J. Amer. Chem. Soc.*, **74**, 3375 (1952).
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Solute-Solvent Interaction. From the consideration on thermodynamical quantities and compressibility it is evident that there is a weak but specific interaction*[8] between DCE and aromatic molecules, which is too small and insufficient for the formation of a complex between solute and solvent molecules.

There have been two interpretations for the nature of this interaction. The first one was given by Ruiter,[14] Neckel and Volk[29] and others.[6,7] They proposed that it is a hydrogen-bonding (proton-donor-acceptor) interaction between the protons of *gauche* form of DCE and π electrons of aromatic molecules. However, the magnitude of $\varepsilon_{AB}-(\varepsilon_{AA}+\varepsilon_{BB})/2$*[8] is evidently too small to support the presence of a hydrogen-bonding between species A and B, where A is DCE and B is an aromatic. The situation is quite similar with respect to the presence of a charge transfer complex (electron-donor-acceptor). The hydrogen-bonding interaction can not explain the presence of "benzene effect" for the 2,3-dihalo-2,3-dimethylbutane-benzene system, in which all hydrogen atoms in DCE or DBE are replaced by methyl groups.[4]

This type of interaction, the so-called "benzene effect", is widely observed in binary mixtures of substituted dihaloethanes and haloketone with aromatic solvents.[5,30,31] The data on the shift of C–H stretching in Raman and infrared spectroscopy[6,32] do not support the presence of hydrogen-bonding in substituted dihaloethane-aromatic solvent systems.

It is concluded that there is no appreciable complex formation between DCE and aromatic molecules, and that the solute-solvent interaction is not ascribed to hydrogen-bonding or charge transfer.

There remains the second interpretation that it is an electrostatic interaction which is of a more general nature. The *gauche* form of DCE molecule has a large dipole moment and aromatic molecules are greatly polarizable. Thus, for the DCE-aromatic system the dipole-induced dipole interaction is considered to play an important role.

As seen in Table 4, the magnitudes of θ for DCE-aromatic systems are positive but at the most of the order of a few %. This shows that the interactions between DCE and aromatic molecules are of a similar nature to those between each identical molecules themselves, and supportes the results that it is the dipole-induced dipole interaction. The same idea was recently presented on the basis of NMR, dielectric and spectroscopy data.[30–33]

It is concluded that the interaction between DCE and aromatic molecules is not hydrogen-bonding and is of electrostatic nature (dipole-induced dipole or hyperpolarizability).

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*[8] The magnitude of $\varepsilon_{AB}-(\varepsilon_{AA}+\varepsilon_{BB})/2$ is of the order of several ten calories per mole, which is estimated from the values of θ given in Table 4.

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