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An Ultrasonic Method for Determination of the Difference in Hard-Sphere Volume of Conformational Isomers

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An ultrasonic method for determining the difference in hard-sphere volume of conformational isomers from sound velocity has been worked out, its accuracy being improved by taking the temperature dependence of the effective hard-sphere diameter into account. The difference for 1,2-dibromoethane, 1,1,2-trichloroethane, methylcyclohexane, and 1,2-dichloroethane was determined. The fractions of volume differences $\Delta V/V$ in these liquids were found to be $4._5$, 5, 11, and 19% for 1,2-dibromo-, 1,1,2-trichloroethane, methylcyclohexane, and 1,2-dichloroethane, respectively.

Determination of the effective hard-sphere volume of molecules in liquids is of interest from theoretical and practical points of view.[1)] In most studies on conformational isomerism, *e.g.*, halogenated ethanes and cyclohexane derivatives,[2–6)] the effect of difference in hard-sphere volume of conformers has been assumed to be negligibly small. Recently, questions with respect to this assumption have been raised.[1,7)] The lack of a good experimental method is the main reason for the volume difference not being considered in these studies. Wyn-Jones *et al.*[7)] adopted the ultrasonic absorption method, but its merit was restricted.

In the preceding paper,[1)] we proposed for 1,2-dichloroethane (DCE) a method for determining the volume difference from sound velocity based on the recent development of the theory of solutions.[8)] However, DCE is a special example: For the determination of ΔV it is necessary to know the magnitude of the hard-sphere volume for one of the two conformers from other sources. This is ascribed to the following property of the sample: The energy difference between the two isomers is zero in its liquid state,[2,4)] the population ratio of the two conformers remaining unchanged with varying temperature. Further, the effect of relaxational processes was not taken into consideration.

We have improved the method and applied it to cases in which the energy difference between conformers is not zero, enhancing the accuracy by taking the temperature dependence of the effective hard-sphere diameter[9)] into account. 1,2-dibromoethane (DBE), 1,1,2-trichloroethane (TCE), cyclohexane (CH), and methylcyclohexane (MeCH) were investigated. It was found that the method is useful for determining the difference in hard-sphere volume of conformers.

Method of Analysis

Formula for Isothermal Compressibility Derived from the Lebowitz Equation of Binary Mixtures.[1)] An equilibrium mixture of conformational isomers is considered to be a hard-sphere mixture with two components. We obtained a formula for isothermal compressibility of the equilibrium mixture by means of the Lebowitz equation. The outline of the theoretical procedure is given here, the details being reported.[1)] An analytical solution of the Percus-Yevick equation for binary hard-sphere mixtures[8)] is

$$\frac{p}{kT} = \frac{1}{(1-\xi)^3}\Big[(\rho_1+\rho_2)(1+\xi+\xi^2)-\frac{18}{\pi}\eta_1\eta_2(R_1-R_2)^2 \times \{R_1+R_2+R_1R_2(\eta_1R_1^2+\eta_2R_2^2)\}\Big],$$

$$\xi = \frac{\pi}{6}(\rho_1R_1^3+\rho_2R_2^3), \tag{1}$$

where p is pressure, k Boltzmann constant, T temperature, ξ packing fraction, $\rho_i=N_i/V$ number density, $\eta_i=\pi\rho_i/6$, and R_i hard-sphere diameter of the i-th component. Let us express R_i by

$$R_1 = R_0, \quad R_2 = R_0(1+\delta), \tag{2}$$

considering that δ is smaller than 0.1.[1)]

The isothermal compressibility $\kappa_T=-(1/V)(\partial V/\partial p)_T$ is derived from Eq. 1 as

$$\kappa_{T,0} = \frac{V(1-\xi)^4}{RT(1+2\xi)^2}\left(1-\frac{\pi x_1x_2R_0^3\rho\delta^2}{2(1+2\xi)^2}\left\{4+2\xi+\frac{\pi}{2}R_0^3\rho +\delta\left(2+\xi+\frac{\pi}{2}R_0^3\rho(1+2x_2)\right)+\delta^2\frac{3\pi}{2}R_0^3\rho x_2 +\delta^3\frac{\pi}{2}R_0^3\rho x_2\right\}\right]^{-1}, \tag{3}$$

where suffix 0 indicates κ_T for fluids consisting of hard-sphere molecules, R gas constant, V molar volume, and x_i mole fraction of the i-th component. The second term in square brackets is smaller than 0.01.[1)] Equation 3 can thus be approximated by

$$\kappa_{T,0} = \frac{V(1-\xi)^4}{RT(1+2\xi)^2}, \tag{4}$$

where ξ is the fraction of hard-sphere volumes of all molecules to molar volume of the liquid and is expressed by

$$\xi = \frac{\pi\rho(N_1R_1^3+N_2R_2^3)}{6N_A} = \frac{\rho(N_1v_1+N_2v_2)}{N_A} = \frac{\pi}{6}a^3\rho = \rho v_a,$$

$$\frac{N_1R_1^3+N_2R_2^3}{N_A} = a^3. \tag{5}$$

Here N_i is number of the i-th component, N_A Avogadro number, $\rho=N_A/V$, $v_i=\pi R_i^3/6$ hard-sphere volume of the i-th component, $v_a=\pi a^3/6$ average hard-sphere volume, and a the "average hard-sphere diameter."

For the usual fluids, it is necessary to take the effect of attractive forces into consideration. κ_T is expressed in this case by[1)]

$$\kappa_T = \left[\frac{RT(1+2\xi)^2}{V(1-\xi)^4}-\frac{2}{V}(\Delta H_v-RT)\right]^{-1}, \tag{6}$$

where ΔH_v is enthalpy of vaporization.

Determination of Average Hard-Sphere Volume and Volume, Difference between Conformers. From adiabatic compressibility κ_S determined from sound velocity and density data, we obtain

$$\kappa_T = \kappa_S + \frac{TV\alpha^2}{C_p}, \quad \kappa_S = \frac{1}{dv^2}, \tag{7}$$

where α is thermal expansion coefficient of the liquid, C_p molar heat capacity at constant pressure, d density, and v sound velocity. When the values of T, V, κ_T, and ΔH_v are substituted into Eq. 6, the value of ξ and subsequently the average hard-sphere volume can be evaluated.

The values of V and N_i in Eq. 5 vary with temperature. The population ratio of two conformational isomers, N_2/N_1, is given by

$$\frac{N_2}{N_1} = \exp(-\Delta G/RT) = A \exp(-\Delta H/RT), \tag{8}$$

where ΔG is free energy difference between conformers, ΔH enthalpy difference, and A constant. Thus, if we know ξ from sound velocity data at various temperatures, we can estimate the hard-sphere volumes of each conformer, combining the temperature dependence of N_2/N_1 with that of ξ.

The total compressibility for an equilibrium system is given by

$$\kappa_T = \kappa_{T,\infty} + \kappa_{T,r}, \tag{9}$$

where $\kappa_{T,\infty}$ is an instantaneous part and $\kappa_{T,r}$ a relaxational one.[6,10] According to the magnitude of ultrasonic relaxation frequency f_r, the procedure for determination of average hard-sphere volumes can be classified into: (a) for CH and MeCH[6,11,12] in which f_r is much smaller than the frequency f used for the measurement of sound velocity, and (b) for DCE, DBE, and TCE.[6,7,13,14]

When $f \gg f_r$, the contribution of $\kappa_{T,r}$ to κ_T can be ignored and Eq. 9 is reduced to

$$\kappa_T = \kappa_{T,\infty}. \tag{10}$$

Substituting the value of κ_T into Eq. 6, we can determine the magnitude of ξ. In Eq. 5, the value of the average hard-sphere volume is related to hard-sphere volumes of components v_1 and v_2, and also to the population ratio of isomers. The temperature dependence of the average hard-sphere volume is chiefly ascribed to the temperature dependence of the population ratio, and the molar volume difference ΔV can be evaluated from Eqs. 5 and 8, where

$$\frac{\Delta V}{V} = \frac{N_A}{\xi V}(v_2 - v_1) = \frac{v_2 - v_1}{v_a}. \tag{11}$$

When $f \ll f_r$, the contribution of $\kappa_{T,r}$ to κ_T should be considered. According to Hall,[15] $\kappa_{T,r}$ is given by

$$\kappa_{T,r} = \frac{V(\Delta V/V)^2}{2RT\{1+\cosh(\Delta G/RT)\}}, \tag{12}$$

where ΔV is identical with that defined by Eq. 11.[16] Substituting the right hand sides of Eqs. 6 and 12 into Eq. 9, the following expression of κ_T is obtained.

$$\kappa_T = \left[\frac{RT(1+2\xi)^2}{V(1-\xi)^4} - \frac{2}{V}(\Delta H_v - RT)\right]^{-1} + \frac{V(\Delta V/V)^2}{2RT\{1+\cosh(\Delta G/RT)\}}. \tag{13}$$

The procedure for determining hard-sphere volumes of isomers starting from Eq. 13 is the same as in the preceding case.

Temperature Dependence of the Effective Hard-Sphere Volume. For the determination of hard-sphere volumes for conformers described above, the temperature dependence of the average hard-sphere volume is attributed to that of the population ratio only. However, we should consider also the contribution from the temperature dependence of the effective diameter of hard-sphere.[9,17–19]

According to the perturbation theory of fluid by Barker and Henderson, the "softness" of the hard core of a molecule is taken into consideration[9] and the effective hard-sphere diameter becomes

$$a_t = \int_0^\sigma [1 - \exp\{-u(r)/kT\}]\mathrm{d}r, \tag{14}$$

where $u(r)$ is an intermolecular pair potential and $u(\sigma)=0$. The temperature coefficient of a_t, l, becomes

$$l = \frac{1}{a_t}\frac{\mathrm{d}a_t}{\mathrm{d}T} = -\frac{\int_0^\sigma \frac{u(r)}{kT^2}\exp\{-u(r)/kT\}\mathrm{d}r}{\int_0^\sigma [1-\exp\{-u(r)/kT\}]\mathrm{d}r}. \tag{15}$$

The Lennard-Jones (6—12) potential is chosen as $u(r)$, and $l(l<0)$ is computed numerically. Thus the effective hard-sphere volume at temperature T is expressed by

$$v_T = v_0(1+\alpha_t \Delta T) \quad \text{and} \quad \alpha_t = 3l, \tag{16}$$

where v_0 is the value at T_0 as reference temperature and ΔT the deviation from T_0.

Experimental

Sound velocity was measured with an interferometer working at 3 MHz[20] and density with a pycnometer. Measurements were carried out at temperatures in the range 15—45 °C, the temperature being controlled within ±0.05 °C. Samples were carefully purified before measurements. The accuracy of v is ±0.3 m/s. Values of d and v compared with other data[21] at 20 °C are given in Table 1.

Results

Values of d, v, κ_S, and κ_T determined in the present experiment for DBE, TCE, CH, and MeCH are summarized in Table 2. Values of thermodynamic quantities required for the determination of κ_T and v_a, C_p, α, and ΔH_v are summarized in Table 3, together with energy difference ΔH between conformers for these liquids.

In the case of CH, only the chair form exists at room temperature since the energy difference is as large as 22 kJ/mol.[3] It can be regarded as one component system in the temperature range of the present study.

The temperature coefficient of the effective hard-sphere diameter was calculated by Eq. 15 and is plotted against ε/k at 25 °C in Fig. 1 (ε: an energy parameter in $u(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]$). The curve is useful for

Table 1. Comparison of d and v with other data at 20 °C

	d / g cm^{-3}		v / m s^{-1}	
	This work	Ref.	This work	Ref.
DBE	2.1808_2	2.1804[a] 2.17988[b] 2.18002[b] 2.18006[d]	1006.8	1006.9[b] 1007.9[c]
TCE	1.4409_8	1.4405[a] 1.4411[a]	1166.0	1176[e]
CH	0.7783_8	0.7783[a] 0.77853[a] 0.77858[b] 0.77849[f]	1279.9	1280.5[b] 1279.1[c]
MeCH	0.7691_1	0.76944[a] 0.76936[a] 0.76925[a]	1237.0	1247[g]

a) Ref. 21. b) Ref. 26. c) R. Fischer, H. Posch, und F. Kohler, *Monatsh. Chem.*, **96**, 1865 (1965). d) A. Neckel und H. Volk, *Monatsh. Chem.*, **89**, 754 (1958). e) R.A. Padmanaban, *J. Sci. Industr. Res.*, **19B**, 336 (1960). f) H. Loiseleur, J-C. Merlin, et R.A. Paris, *J. Chim. Phys.*, **64**, 634 (1967). g) Ref. 11.

Table 3. Thermodynamic parameters at 25 °C

	α[a] / 10^{-3} K^{-1}	C_p / J mol^{-1} K^{-1}	ΔH_v / kJ mol^{-1}	ΔH / kJ mol^{-1}
DBE	0.9665	134.9[b,c]	43.27[c,d]	3.10[e,f]
TCE	1.0851	148.0[g,h]	40.28[d]	1.05[e,f]
CH	1.2318	155.3[b]	33.22[c]	22.0[i]
MeCH	1.1403	184.5[c,j]	35.38[c,k]	7.11[i]

a) Observed values in this study. b) Ref. 26. c) Ref. 21. d) J. Laynez and I. Wadsö, *Acta Chem. Scand.*, **26**, 3148 (1972). e) Ref. 2. f) Ref. 4. g) R. W. Crowe and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 4009 (1950). h) R.J. L. Andon, J. F. Counsell, D. A. Lee, and J. F. Martin, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1721 (1973). i) Ref. 3. j) Ref. 11. k) T. J. V. Findlay, *J. Chem. Eng. Data*, **14**, 229 (1969).

practical purposes. The variation of T from 0 to 100 °C shows a very slight difference in l, and l can be regarded as practically independent of the variation of T in the range 15—45 °C. The values of ε/k used for the estimation of l are 330, 430, 400, 330, and 330 K for DCE, DBE, TCE, CH, and MeCH,[22–24] respectively. When ε/k is larger than 300 K, the variation of l is small. The temperature dependence of the effective hard-sphere volume was estimated by using Eq. 16 (T_0: 25 °C) with the value of l given in Fig. 1.

The magnitudes of v_a, v_i, and $\Delta V/V$ for MeCH ($f \gg f_r \simeq 100$ kHz[6,11,12]) were determined by means of Eqs. 5, 6, 8, and 11. For DBE ($f \ll f_r$) and TCE ($f < f_r \simeq$ 16 MHz at 25 °C[6,7]), those of v_a, v_i, and $\Delta V/V$ were determined by means of Eqs. 5, 8, 11, and 13. In the case of DCE[25] ($f \ll f_r$), the values of v_a and $\Delta V/V$ were calculated by means of Eqs. 5, 11, and 13 and the reported data.[1] For CH which is regarded as one component system, the average hard-sphere volume v_a was determined by the use of Eqs. 5 and 6. The results

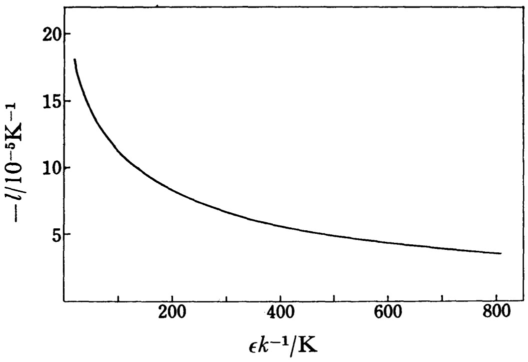

Fig. 1. The plot of l *vs.* ε/k at 25 °C.

Table 2. Values of d, v, κ_S and κ_T

		Temp/°C						
		15	20	25	30	35	40	45
d / g cm^{-3}	DBE	2.1912_0	2.1808_2	2.1703_7	2.1599_7	2.1493_8	2.1389_1	2.1287_2
	TCE	1.4487_3	1.4409_8	1.4332_8	1.4256_6	1.4178_1	1.4101_2	1.4022_9
	CH	0.7830_7	0.7783_8	0.7736_6	0.7689_9	0.7642_1	0.7594_7	0.7546_4
	MeCH	0.7734_3	0.7691_1	0.7647_7	0.7605_2	0.7561_3	0.7517_9	0.7473_9
v / m s^{-1}	DBE	1019.9	1006.8	993.9	981.2	968.4	955.5	942.7
	TCE	1183.6	1166.0	1149.2	1131.6	1114.4	1097.2	1080.1
	CH	1304.9	1279.9	1254.0	1229.1	1204.1	1181.4	1158.0
	MeCH	1259.5	1237.0	1214.9	1193.0	1171.2	1149.7	1128.9
κ_S / 10^{-11} Pa^{-1}	DBE	43.87	45.24	46.64	48.08	49.61	51.20	52.86
	TCE	49.28	51.04	52.83	54.77	56.80	58.91	61.12
	CH	75.00	78.42	82.20	86.08	90.26	94.34	98.82
	MeCH	81.51	84.97	88.59	92.39	96.41	100.64	104.99
κ_T / 10^{-11} Pa^{-1}	DBE	60.98	62.72	64.51	66.34	68.26	70.25	72.30
	TCE	70.38	72.63	74.90	77.34	79.86	82.48	85.20
	CH	105.97	109.75	113.90	118.15	122.69	127.14	132.00
	MeCH	107.88	111.65	115.56	119.65	123.96	128.46	133.09

Table 4. Average hard-sphere volumes and volume differences at 25 °C

	$\frac{v_a}{10^{-24}\,\text{cm}^3}$	$\Delta V/V$
DCE[a]	69.4_2	-0.19
DBE	76.4_0	-0.04_5
TCE	80.9_9	-0.05
MeCH	108.9_0	-0.11
CH	90.1_3	

a) Calculated by use of the previous data.

for v_a and $\Delta V/V$ thus obtained are summarized in Table 4.

Discussion

Examination of the Former Results Obtained by the Ultrasonic Absorption Method. In studies on conformational isomerism by means of the ultrasonic absorption method, it has been assumed so far that $(\Delta V/V)(C_p/\Delta H\alpha) \ll 1$,[6] and the effect of ΔV is negligible. However, we realized that there is no satisfactory evidence for the assumption, leading to an examination of the assumption. Wyn-Jones *et al.*[7] suggested that the assumption is not suitable when the value of $\Delta V/V$ is of the order of 0.1% or larger. For DBE, TCE, and MeCH, the magnitudes of $(\Delta V/V)(C_p/\Delta H\alpha)$ are estimated to be 2.0, 6.5, and 2.5, respectively, by using the data in Tables 3 and 4, indicating that the assumption is inadequate. For DCE, the value of ΔH in liquid state is zero;[2,4] the assumption does not hold.

According to Wyn-Jones *et al.*, the values of $\Delta V/V$ in conformational isomerism are *ca.* 1—3% for TCE in various solvents, and surmised to be 6% for pure liquid of TCE, the error of the estimation of ΔV being *ca.* 50%.[7] In the present study, the error might be small (<20%) as compared with that of the ultrasonic absorption method.

Consideration on the Magnitudes of v_i *and* ΔV. All the values of $\Delta V/V$ are negative (Table 4). The value of v_1 for a stable isomer is larger than that of v_2 for another isomer. v_1 corresponds to the *anti*-form for DCE, DBE, and TCE, and to the equatorial form for MeCH.

The value of $\Delta V/V$ for DCE is found to be larger than that for DBE. This is reasonable, according to the suggestion by Findenegg *et al.*[26] based on the cell theory. For TCE, it is 5% in the present study, 6% by means of the ultrasonic absorption method of Wyn-Jones *et al.*,[7] and 4% from the pressure effect of infrared spectroscopy reported by Christian *et al.*[27]

For MeCH, the value of $\Delta V/V$ becomes 11% and the hard-sphere volume for the equatorial form is larger than that for the axial one. No data for MeCH directly correlated with our present result has been reported so far. It was suggested from density data[7,11] of similar substances that the volume of the equatorial form is larger than that of the axial one. For instance, *cis*-1,3-dimethylcyclohexane has two equatorial methyl groups in its chair form and *trans*-stereoisomer has an equatorial group together with an axial methyl group. The difference in density between the *trans*- and *cis*-stereoisomers is supposed to correspond to the volume difference between the axial and the equatorial form of conformational isomers for MeCH. The volume difference between stereoisomers for 1,3-dimethylcyclohexane is estimated to be 2.2%.[7] Though the volume difference between separable stereoisomers is not the same as that between conformational isomers, it is certain that the volume of the equatorial form is larger than that of the axial one. Our present result for MeCH confirms this.[27]

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