An Ultrasonic Method for Determination of the Volume Change Due to Internal Rotation in 1,2-Dichloroethane

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A simple method for determining the volume change, ΔV, in conformational isomerism from sound velocity has been worked out from the theory of binary mixtures. The method was applied for obtaining the volume change due to internal rotation in 1,2-dichloroethane. The sound velocity was measured with an ultrasonic interferometer. The method was found useful.

The conformational equilibrium of halogenated ethanes has long been the subject of study from the viewpoint of molecular structure theory, the equilibrium between *trans* and *gauche* forms of 1,2-dichloroethane (DCE) having been clarified.[1-4] The energy difference between them is nearly zero in a liquid state,[1] while the ratio N_g/N_t in this state is 1.93 at room temperature, where N_g is the number of *gauche* molecules and N_t that of *trans* molecules.[3]

The molecular interaction in binary mixtures including DCE has been investigated by various methods such as the Raman effect, infra-red[2-5] and NMR[6] spectroscopy, and dielectric,[7-13] thermodynamic[14-20] and ultrasonic[21-25] methods.[26] However, the essential feature of the interactions between DCE and other compounds such as benzene has been a topic of controversy. Findenegg and Kohler[18,19] and Kiyohara and Arakawa[25] studied the DCE–benzene system by means of an ultrasonic method using theory of solutions, and Higasi *et al.*[12,13] by means of a dielectric method. Their conclusions did not agree.

In the above studies the volume change in conformational isomerism between *trans* and *gauche* forms of DCE[2,8,18,25] has not been taken into consideration, which seriously influences the determination of the magnitude of enthalpy difference ΔH and other thermodynamic quantities. This has been pointed out recently.[27-29]

Recent advancement in ultrasonic absorption technique made it possible to determine ΔV.[21] However, the determination is impossible when the frequency range does not cover the relaxation range of the system to be studied, the error being fairly large. ΔV has been usually neglected in studies of conformational equilibrium in which the assumption $(\Delta V/V)(C_p/\alpha) \ll \Delta H$ is valid.[21]

It has been reported[30] that the magnitude of $\Delta V/V$ in conformational isomerism for 1,1,2-trichloroethane (TCE) and other compounds in various solvents is 1—3%, but DCE was not included in the studies. We have undertaken to apply a simple method for obtaining ΔV from sound velocity on the basis of theory of solutions to DCE.

Method of Analysis

The solution of Percus-Yevick equation for binary liquid mixtures was given as follows.[31,32]

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

where R_i is the hard core diameter of i-th component, p pressure, T temperature, $\rho_i = N_i/V$ number density, $\eta_i = \pi\rho_i/6$, and ξ the volume fraction defined by

$$\xi = (\pi/6)(\rho_1R_1^3+\rho_2R_2^3). \tag{2}$$

We express here R_i as follows

$$R_1 = R,\ R_2 = R(1+\delta). \tag{3}$$

In actual cases of conformational equilibrium, δ is taken to be smaller than 0.1, thus Eq. (1) becomes

$$\frac{p}{kT} = \frac{1}{(1-\xi)^3}\Big[\rho(1+\xi+\xi^2) - \frac{\pi}{2}x_1x_2R^3\rho^2\delta^2\Big\{2+\frac{\pi}{6}R^3\rho + \delta\Big(1+\frac{\pi}{6}R^3\rho(x_1+3x_2)\Big) + \delta^2\Big(\frac{\pi}{2}R^3\rho x_2\Big) + \delta^3\Big(\frac{\pi}{6}R^3\rho x_2\Big)\Big\}\Big] \tag{4}$$

where $x_i = N_i/(N_1+N_2) = N_i/N$.

In order to obtain the isothermal compressibility κ_T defined by

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\left(\frac{\rho}{N}\right)\left(-\frac{N}{\rho^2}\right)\left(\frac{\partial\rho}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_T. \tag{5}$$

Equation (4) is differentiated with respect to pressure, and we obtain

$$\frac{1}{kT} = \left(\frac{\partial\rho}{\partial p}\right)_T\frac{(1+2\xi)^2}{(1-\xi)^4}\Big[1 - \frac{(\pi/2)x_1x_2R^3\rho\delta^2}{(1+2\xi)^2}\Big\{4+2\xi+\frac{\pi}{2}R^3\rho + \delta\Big(2+\xi+\frac{\pi}{2}R^3\rho(x_1+3x_2)\Big) + \delta^2\Big(\frac{3\pi}{2}R^3\rho x_2\Big) + \delta^3\Big(\frac{\pi}{2}R^3\rho x_2\Big)\Big\}\Big]. \tag{6}$$

The magnitude of ξ is the order of 0.5, and

$$(\pi/6)R^3\rho < 1, \quad x_1x_2 \leqq 0.25.$$

Thus

$$(\pi/2)x_1x_2R^3\rho/(1+2\xi)^2 < 0.2,$$

$$4 + 2\xi + (\pi/2)R^3\rho < 8.$$

The second term in the bracket [ ] in Eq. (6) is much smaller than 0.02, and can be neglected in comparison with the first term, 1.

Thus we get

$$\frac{1}{kT} = \left(\frac{\partial\rho}{\partial p}\right)_T\frac{(1+2\xi)^2}{(1-\xi)^4}. \tag{7}$$

$\kappa_{T,0}$ which is attributed to repulsive forces only is derived from Eqs. (5) and (7).

$$\kappa_{T,0} = \frac{1}{\rho kT}\frac{(1-\xi)^4}{(1+2\xi)^2} = \frac{\pi a^3}{6kT}\frac{(1-\xi)^4}{\xi(1+2\xi)^2}, \quad \delta<0.1 \tag{8}$$

Here, ξ is treated as follows

$$\xi = \frac{\pi}{6}(\rho_1 R_1^3+\rho_2 R_2^3) = \frac{\pi}{6}\frac{N_1R_1^3+N_2R_2^3}{V}$$
$$= \frac{\pi N(N_1R_1^3+N_2R_2^3)}{6V(N_1+N_2)} = \frac{\pi}{6}\rho\langle R_i^3\rangle = \frac{\pi}{6}\rho a^3,$$
$$\langle R_i^3\rangle \equiv a^3 \tag{9}$$

ξ is denoted by the "average hard core diameter" a, and indicates the "fraction of the hard core volumes of all molecules to whole volume of the mixture". Equation (8) is formally identical with the formula for a pure liquid derived by Reiss.[33]

Equation (1) is approximated as follows according to the above procedure.

$$\frac{p}{kT} = \left[\frac{1+\xi+\xi^2}{(1-\xi)^3}\right]\rho, \quad \delta<0.1 \tag{10}$$

This formula also agrees formally with that for a pure liquid,[33–36] ξ having the same expression and physical meaning as defined in Eq. (9).

It is necessary to consider the attractive forces, since the repulsive force only is considered in the above treatment. The average attractive potential is given by

$$-\langle U_N\rangle_{av.} = N\chi_0 = \Delta H_{vap.} - pV_{gas} = \frac{\text{const.}}{V^n} \tag{11}$$

where $\Delta H_{vap.}$ is enthalpy of vaporization and $n=1$ for van der Waals liquids.

The partition function for liquids is given by

$$Z = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} Q \exp(N\chi_0/kT) \tag{12}$$

where Q denotes the configurational integral.[17] It is well-known that

$$\left(\frac{\partial p}{\partial V}\right)_T = kT\left(\frac{\partial^2 \ln Z}{\partial V^2}\right)_T. \tag{13}$$

κ_T is obtained from Eqs. (5), (12), and (13) as follows.

$$\kappa_T = \left[-VkT\left(\frac{\partial^2 \ln Q}{\partial V^2}\right) - NV\left(\frac{\partial^2\chi_0}{\partial V^2}\right)\right]^{-1}$$
$$= \left[\frac{1}{\kappa_{T,0}} - \frac{2}{V}(\Delta H_{vap.}-RT)\right]^{-1}$$
$$= \left[\frac{RT}{V}\frac{(1+2\xi)^2}{(1-\xi)^4} - \frac{2}{V}(\Delta H_{vap.}-RT)\right]^{-1} \tag{14}$$

Adiabatic compressibility κ_S can be obtained from sound velocity, and isothermal compressibility κ_T from κ_S by means of the relation

$$\kappa_S = \frac{1}{\rho v^2}, \quad \kappa_T = \kappa_S + \frac{TV\alpha^2}{C_p} \tag{15}$$

where ρ is density in g/cm^3, v sound velocity, V molar volume of liquid, α thermal expansion coefficient, and C_p molar heat capacity.

When the values of κ_T and $\Delta H_{vap.}$ are substituted into Eq. (14), ξ can be evaluated, and we obtain the "average hard core diameter".

Thus, when the hard core diameter of one component in binary mixtures is known, that of another component is determined by Eq. (9).

Experimental

DCE (guaranteed reagent, Nakarai Chemicals Ltd.) was used with further purification.[37] Sound velocity was measured with an interferometer working at 3MHz.[25] Density was measured with a pycnometer. Measurements were carried out at 15—45 °C at 5 °C intervals. The temperature was controlled within ±0.05 °C. The results obtained were compared with the data in the literature (Table 1). The observed sound velocity agrees with the literature data, the accuracy being within 0.5 m/s.

TABLE 1. COMPARISON OF OBSERVED VALUES OF SOUND VELOCITY v (m/s) AND ADIABATIC COMPRESSIBILITY κ_S(10^{-12}cm^2/dyn) AT 20 °C WITH LITERATURE VALUES

	v	κ_S	Lit.
Obsd. value	1213.2	54.3_0	—
Lit. value	1213.4	54.2_1	18
	1213.2	54.2_3	19
	1213.5	54.2_0	25
		56.0	15

Results

The following values have been used in the calculation: α, 1.162×10^{-3} deg^{-1}; C_p, 129 J/mol deg; and $\Delta H_{vap.}$, 34.31 kJ/mol (Table 2). The value of N_g/N_t is taken to be 1.93 for DCE.[3]

The experimental values of κ_S and κ_T have been obtained from observed values of v. Values of hard core volume $\pi a^3/6$ have been determined from those of κ_T by Eq. (14) and are given in Table 3, the last row giving the average value of *trans* and *gauche* molecules.

TABLE 2. THERMODYNAMIC PARAMETERS OF DCE
Thermal expansion coefficient α (10^{-3} deg^{-1}), heat capacity C_p (J/mol deg), enthalpy of vaporization ΔH_{vap} (kJ/mol)

Temp. °C	α	C_p	ΔH_{vap}	Lit.
15—45	1.162			This work
20—40	1.132—1.190	129.0—131.5		15
20—40	1.183	130.1 (30 °C)		18
20—40	1.141—1.228	128.3—129.4		19
25—42			33.85—35.23	14
25			34.31	17

TABLE 3. EXPERIMENTAL AND CALCULATED RESULTS FOR DCE
v(m/s), κ_S and κ_T (10^{-12} cm^2/dyn), Hard core volume $\pi a^3/6$ (10^{-24} cm^3)

Temp °C	15	20	25	30	35	40	45
v	1232.6	1213.2	1194.6	1174.5	1155.4	1136.3	1116.9
κ_S	52.3_0	54.3_0	56.2_0	58.5_8	60.9_0	63.3_4	65.9_5
κ_T	76.0_1	78.5_6	81.0_9	83.9_4	86.8_4	89.8_6	93.0_6
$\pi a_3/6$	66.4_1	66.3_6	66.2_5	66.1_8	66.1_4	66.0_9	66.0_2

The hard core volume of *trans* molecule V_t has been determined from X-ray analysis of solid DCE,38) in which all molecules are known to be in the *trans* state,1) and also from other molecular structure data.39,40) The value of V_t obtained from various sources is found to be 78.5×10^{-24} cm^3 per molecule.

V_g is estimated to be 59.8×10^{-24} cm^3 from Eq. (9), and $\Delta V/V_t$ 23.8% from the values of $\pi a^3/6$ and V_t.

Discussion

ΔV was not considered in previous studies owing to the lack of data.2,8,18,25) Verma and others pointed out that the value of ΔV plays an important role in the determination of ΔH.27) According to their estimation, if $\Delta V/V$ in methylcyclohexane increases from 0 to 10%, ΔH varies from 2.9 to 6.0 kcal/mol and other thermodynamic quantities also vary drastically.

In studies on dipolar and multipolar interactions in liquid state having various forms of isomers,6) the influence of ΔV has often been neglected. The estimation of molecular interaction energy attributed to dipolar and quadrupolar fields is greatly affected by the estimation of ΔV. The difference of molecular volumes between various isomers affects the determination of molecular interaction energy a great deal. Thus the knowledge of ΔV in conformational isomerism is necessary to estimate ΔH and other thermodynamic variables exactly, and to explain the nature of the molecular interaction.

ΔV is determined by ultrasonic absorption technique.21) However, determination is impossible when the frequency range of the apparatus does not cover the relaxation range of the system under investigation. In many cases conformational equilibrium was studied on the assumption,21) $(\Delta V/V)(C_p/\alpha)\ll\Delta H$. In the case of DCE in liquid state, this does not hold since ΔH is nearly zero.1)

The $\Delta V/V$ in conformational isomerism for TCE and other compounds in various solvents has been reported to be 1—3%,30) but DCE was not included. The error is 50%.

In order to determine ΔV for liquid DCE, we should know the value of V_t. We can obtain V_t from the results of studies on solid DCE, in which all the molecules are known to be in the *trans* state.1) The value of V_t can be obtained from X-ray analysis of solid DCE and other data.38–40)

In solid DCE, the volume assigned to one molecule is found to be 106×10^{-24} cm^3 from its density.38) Taking the magnitude of packing parameter to be 0.740541) (face-centered cubic), we estimate the value of V_t to be 78.5×10^{-24} cm^3. This value is regarded as an "equivalent" hard core volume of the molecule in a close-packed state.

On the other hand, DCE is assumed to be a rotational ellipsoid having a major axis of 6.90 Å and a minor axis of 4.68 Å from diffraction data.38–40) The Cl–Cl distance estimated from X-ray data is 4.24 Å and the diameter of Cl atom 2.66 Å,42) and we can thus estimate the major axis of the ellipsoid to be 6.90 Å. The minor axis is estimated from (1, 0, 0) projected surface, the most dense one.38) V_t is thus calculated to be 79.1×10^{-24} cm^3 per molecule. This agrees with the value calculated from density. Thus the value 78.5×10^{-24} cm^3 is chosen for V_t.

The ratio N_g/N_t is also necessary for determining ΔV. The value is found from studies of molecular structure theory to be in the range 1.90—1.93 at room temperature.1,3) We have used the value 1.93.3) The fluctuation of ΔV for variation of N_g/N_t is very small, being of the order 0.1%.

The calculated hard core volume of DCE in the liquid state is held constant in the range 15—45 °C (Table 3), which shows the validity of the present method. It would be noted that the fraction N_g/N_t remains constant within the range of temperature in this study.

The value of $\Delta V/V_t$ is *ca.* 20%. The error is mainly due to the uncertainty in the determination of V_t. It is certain that the value for DCE is larger by one order than that for TCE, found to be 1—3% by Wyn-Jones *et al.*30)

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41) The value of V_t needed is that of the "equivalent" hard core volume in thermal motions which is statistically defined. Thus we chose the value of packing parameter to be 0.7405 for the closest packing in spite of the fact that the crystal form of solid DCE is known to be monoclinic.

42) The radius of Cl atom is assumed to be equal to that of K^+, 1.33 Å.[40)]