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Determination of the Difference in Hard-sphere Volume of Conformational Isomers from Sound Velocity

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Synopsis. The difference in hard-sphere volume of conformational isomers $\Delta V/V$ was determined from sound velocity data by a method proposed on the basis of the Lebowitz theory of solutions. The $\Delta V/V$ values between conformers were found to be 6, 9, 12, 7, and 12% for 1,1,2,2-tetrachloroethane, 1,1,2,2-tetrabromoethane, 1-chloropropane, 1-bromopropane, and ethylcyclohexane, respectively.

We proposed an ultrasonic method suitable for the determination of the difference in hard-sphere volume of conformational isomers ($\Delta V/V$) from sound velocity data,[1)] based on the Lebowitz theory,[2)] and applied the method to halogenoethanes and cyclohexane derivatives[1b)] as typical compounds with conformational isomerism.[3–6)]

In order to obtain further information on $\Delta V/V$ of conformational isomers, 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$), 1,1,2,2-tetrabromoethane ($CHBr_2CHBr_2$), 1-chloropropane ($CH_3CH_2CH_2Cl$), 1-bromopropane ($CH_3CH_2CH_2Br$), and ethylcyclohexane (c-$C_6H_{11}C_2H_5$) have been investigated.

An equilibrium mixture of conformational isomers we studied is considered to be a binary mixture of hard spheres. The formula for isothermal compressibility (κ_T) of the equilibrium mixture was derived from the equation of state for the binary mixture of hard spheres.[2)] Details of the procedure for analysis were described in the preceding paper,[1b)] notations used here being identical with those in it.

For the case of c-$C_6H_{11}C_2H_5$, the relaxation frequency f_r is smaller than the frequency f used for the measurement of sound velocity.[7)] In this case, κ_T is expressed by

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

For CHX_2CHX_2 and $CH_3CH_2CH_2X$[5,8,9)] ($f_r \gg f$), κ_T is given by

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

$\Delta V/V$ is expressed by

$$\frac{\Delta V}{V} = \frac{N_A}{\xi V}(v_2 - v_1) = \frac{v_2 - v_1}{v_a}, \tag{3}$$

where ξ is packing fraction ($=\rho v_a$), v_a average hard-sphere volume, and v_i hard-sphere volume of the i-th component. Putting the experimental values of κ_T into Eq. 1 or Eq. 2, we determine the magnitudes of v_a, v_i, and $\Delta V/V$. The temperature coefficient α_t of the effective hard-sphere volume was calculated in a similar manner to that reported.[1b)]

TABLE 1. RESULTS FOR d, v, κ_S, AND κ_T

		Temp/°C						
		15	20	25	30	35	40	45
d / 10^3 kg m^{-3}	$CHCl_2CHCl_2$	1.6049_0	1.5969_0	1.5891_4	1.5813_3	1.5734_1	1.5658_5	1.5579_8
	$CHBr_2CHBr_2$	2.9761_8	2.9649_8	2.9537_7	2.9424_5	2.9311_5	2.9199_6	2.9087_0
	$CH_3CH_2CH_2Cl$	0.8984_5	0.8921_8	0.8858_3	0.8795_4	0.8729_8	0.8668_3	0.8601_6
	$CH_3CH_2CH_2Br$	1.3618_9	1.3534_7	1.3450_8	1.3367_6	1.3281_8	1.3196_6	1.3110_6
	c-$C_6H_{11}C_2H_5$	0.7913_8	0.7873_6	0.7832_9	0.7793_0	0.7752_0	0.7711_3	0.7670_6
v / m s^{-1}	$CHCl_2CHCl_2$	1182.5	1166.1	1149.9	1134.1	1118.1	1102.3	1086.5
	$CHBr_2CHBr_2$	1051.3	1039.5	1029.1	1018.4	1007.6	997.2	986.7
	$CH_3CH_2CH_2Cl$	1109.8	1087.3	1066.6	1043.8	1024.1	1002.0	980.5
	$CH_3CH_2CH_2Br$	988.3	970.8	954.3	937.3	920.2	904.1	887.7
	c-$C_6H_{11}C_2H_5$	1312.0	1290.4	1269.1	1248.2	1227.3	1206.3	1185.6
κ_S / 10^{-11} Pa^{-1}	$CHCl_2CHCl_2$	44.56	46.05	47.59	49.17	50.84	52.56	54.37
	$CHBr_2CHBr_2$	30.40	31.21	31.97	32.77	33.60	34.44	35.31
	$CH_3CH_2CH_2Cl$	90.37	94.81	99.23	104.35	109.22	114.90	120.93
	$CH_3CH_2CH_2Br$	75.18	78.40	81.64	85.15	88.92	92.71	96.79
	c-$C_6H_{11}C_2H_5$	73.41	76.27	79.27	82.36	85.64	89.12	92.75
κ_T / 10^{-11} Pa^{-1}	$CHCl_2CHCl_2$	60.25	62.01	63.80	65.63	67.55	69.52	71.56
	$CHBr_2CHBr_2$	42.48	43.42	44.30	45.22	46.18	47.13	48.13
	$CH_3CH_2CH_2Cl$	131.25	136.27	141.28	147.00	152.47	158.74	165.38
	$CH_3CH_2CH_2Br$	105.60	109.23	112.89	116.82	121.01	125.22	129.74
	c-$C_6H_{11}C_2H_5$	94.78	97.88	101.10	104.43	107.93	111.62	115.46

TABLE 2. $\Delta V/V$ AND v_a AND THERMODYNAMIC PARAMETERS AT 25 °C

	$-\Delta V/V$	v_a 10^{-30} m^3	α[a] 10^{-3} K^{-1}	C_p J K^{-1} mol^{-1}	ΔH_v kJ mol^{-1}	ΔH kJ mol^{-1}
$CHCl_2CHCl_2$	0.06	95.7_5	0.9874	189.4[b,c]	45.78[d]	−4.60[e]
$CHBr_2CHBr_2$	0.09	114.9_6	0.7649	165.6[b]	70.00[b]	−3.45[e]
$CH_3CH_2CH_2Cl$	0.12	69.3_5	1.4494	132.1[b]	28.49[b]	−1.26[e]
$CH_3CH_2CH_2Br$	0.07	74.2_3	1.2668	140.0[b]	31.92[b,d]	−1.97[e]
c-$C_6H_{11}C_2H_5$	0.12	126.3_0	1.0406	211.8[f]	40.48[b]	7.53[g]

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Experimental

Sound velocity v was measured with an interferometer working at 3 MHz and density d with a pycnometer. The temperature was controlled within ±0.05 °C. Samples were carefully purified before measurements. The accuracy of v is ±0.3 m/s. Adiabatic and isothermal compressibilities (κ_S and κ_T) were estimated from density, sound velocity, and other thermodynamic quantities.

Results and Discussion

Values of d, v, κ_S, and κ_T determined for CHX_2CHX_2, $CH_3CH_2CH_2X$ (X=Cl and Br), and c-$C_6H_{11}C_2H_5$ are summarized in Table 1. The results for v_a and $\Delta V/V$ are given in Table 2, together with values of α, C_p, ΔH_v, and ΔH required for the determination of v_a and $\Delta V/V$. Values of α_t were estimated to be −1.6, −1.3, −2.0, −1.9, and -1.7×10^{-4} K^{-1} for $CHCl_2$-$CHCl_2$, $CHBr_2CHBr_2$, $CH_3CH_2CH_2Cl$, $CH_3CH_2CH_2Br$, and c-$C_6H_{11}C_2H_5$, respectively.

It was found from the negative value of $\Delta V/V$ (Table 2) that the value of v_1 is larger than that of v_2. For CHX_2CHX_2 and $CH_3CH_2CH_2X$, v_1 corresponds to the *anti* form, and to the equatorial form for c-$C_6H_{11}C_2H_5$. Wyn-Jones *et al.*[6] and Christian *et al.*[10] also reported similar results for $CHCl_2CH_2Cl$ by means of the ultrasonic absorption method and the pressure effect of infrared spectroscopy. In the case of CHX_2-CHX_2, the value of $|\Delta V/V|$ for chloro compound is smaller than that for bromo compound, while it is reversed for $CH_3CH_2CH_2X$ and CH_2XCH_2X.[1b]

For c-$C_6H_{11}C_2H_5$, the magnitude of $\Delta V/V$ (12%) is nearly equal to that of c-$C_6H_{11}CH_3$ (11%).[1b] It agrees with the results of c-$C_6H_{11}CH_3$[1b] and c-$C_6H_{11}X$ reported by Christian *et al.*[10] that the equatorial form was found to be larger than the axial one.

Our method is convenient and accurate for the determination of $\Delta V/V$ in conformational isomerism, as compared with the ultrasonic absorption method[6] used so far.

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