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Pressure and Temperature Effects on Conformational Equilibria between Rotational Isomers. II. Isobutyl and *s*-Butyl Halides in Hexane and Methanol

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The conformational changes in isobutyl halides (*i*-BuX) and *s*-butyl halides (*s*-BuX) in hexane and methanol have been analyzed by Raman spectroscopy as a function of temperature and pressure. The enthalpy and volume differences in the conformational changes from P_C (*trans*) to P_H (*gauche*) of *i*-BuX and from S_{HH}(*trans*) to $S_{HH'}$(*gauche* I) and to S_{CH}(*gauche* II) of *s*-BuX in the dissolved state have been obtained. The enthalpy and volume differences, ΔH and ΔV, of all the conformational changes depended on the solvents and the concentration in solution. In the solution of hexane, the ΔH ($P_C \rightarrow P_H$) of *i*-BuCl and *i*-BuBr both increased with a decrease in the concentration of *i*-BuX. The ΔV ($P_C \rightarrow P_H$) of *i*-BuCl increased with an increase in the contents of the solvents, hexane, but that of *i*-BuBr decreased. The concentration dependences of ΔH and ΔV were discussed on the basis of the intermolecular interactions. The relation between ΔH and ΔV was also discussed on the basis of thermodynamic consideration.

In our previous papers,[1,2] the conformational changes in some halogenoalkanes, such as 1,2-dihalogenoethane and butyl halides, in the pure liquid state have been analyzed by Raman spectroscopy as a function of temperature and pressure. The enthalpy and volume differences in the rotational isomers of these halogenoalkanes have been obtained.

In the dissolved state, it is well known that the enthalpy differences in the conformers are strongly related to some physical properties of the solvents, such as the dielectric constant and specific solute–solvent interactions in solutions.[3–5] It is also expected that the volume difference in the conformers in solution will depend on the solvent. There have been a few papers concerning this subject.[6,7] However, as their measurements were fragmentary and not systematic, they have not been sufficient to elucidate the solvent effects of the volume difference between the rotational isomers of a molecule.

In this paper, we will report the enthalpy and volume differences of the conformers of 1-halogeno-2-methylpropane and 2-halogenobutane (hereafter abbreviated as *i*-BuX and *s*-BuX; X=halogene) in hexane and methanol as obtained by Raman spectroscopy. These solvents, hexane and methanol, were chosen for the following reasons: (i) the dielectric constant of hexane is smaller than those of the halogenoalkanes investigated here, while that of methanol is larger, and (ii) hexane is an inert solvent for the halogenoalkanes, but the solvent methanol can be expected to interact with the halogenoalkanes.

We discussed the solvent effects and the concentration dependences of the enthalpy and volume differences of *i*-BuX and *s*-BuX in hexane and methanol. The relation between ΔH and ΔV was also discussed.

Experimental

The characteristic bands of the X-sensitive modes of each halogenoalkane have been well investigated and assigned to the rotational isomers.[8–13] The structures of the isomers concerned here are illustrated in Fig. 1, where their characteristic vibrational frequencies used are also given.

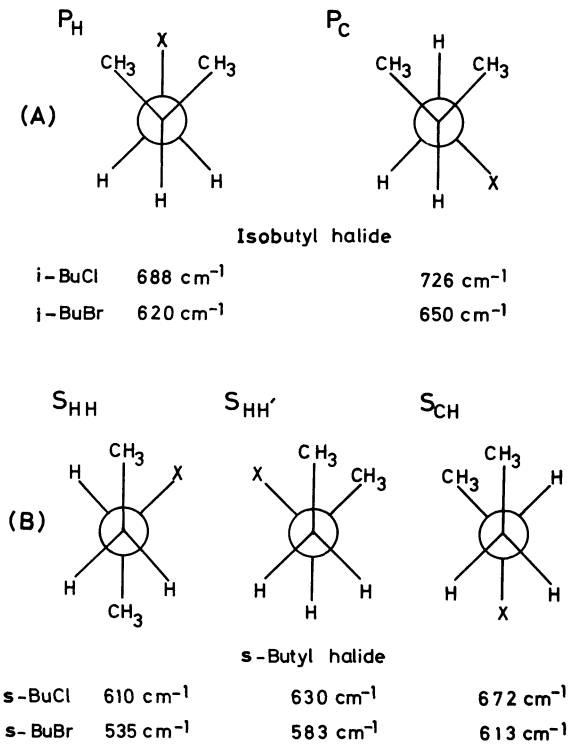

Fig. 1. Rotational isomers for butyl halides and the vibrational frequency of the C–X stretching mode, where X denotes Cl or Br.

Samples: The chemicals (commercial products) were purified by fractional distillation under reduced pressure. The solvents, hexane and methanol, were spectro-grade reagents (Nakarai Chemicals, Ltd.) and were used without further purification.

Raman Spectroscopy: The Raman spectra under high pressure were recorded using a laser Raman spectrometer, JEOL-Ul (manufactured by Japan Electron Optical Laboratory Co., Ltd.) and an argon-ion laser (NEC Co., Ltd.).

The pressure was measured by means of a Heise precision Bourdon-type gauge. The temperature dependence of the Raman spectra was measured at the atmospheric pressure, using a variable-temperature cell of the Harney-Miller type. The detailed experimental procedure and the data analysis have been described elsewhere.[1,2] The accuracy of the integrated intensities is within 3%.

Compressibility and Density Measurements: The densities of the solutions were measured by a pycnometer (20 cm^3) at temperatures from 15 to 30 °C. The adiabatic compressibility was determined from the density and the sound velocity data using the Laplace equation. The sound velocity measurements of the solutions were carried out using an ultrasonic interferometer operating at a constant frequency of 5.000 MHz.

Results

For the samples investigated here, the Raman frequency of the X-sensitive stretching vibrational modes of each conformer did not change in the solutions of hexane and methanol, and it was independent of the temperature and pressure changes in the temperature and pressure ranges concerning in this work.

The equilibrium constant, K, of the conformational equilibrium, A⇌B, can be expressed as:[3]

$$K = \frac{n_B}{n_A} = \frac{I_B \Omega_A}{I_A \Omega_B} \quad (1)$$

where n is the number of molecules, I is the Raman intensity, and Ω is the absolute scattering cross-section. The suffixes A and B refer to the conformers. Assuming that the Ω_A/Ω_B ratio is independent of the temperature and pressure changes in the whole range of measurements, we can estimate the enthalpy and volume differences between the two conformers on the basis of Arrhenius and van't Hoff equations;

$$\Delta H = -R\left[\frac{\partial \ln [I_A/I_B]}{\partial [1/T]}\right] \quad (2)$$

$$\Delta V = -RT\left[\frac{\partial \ln [I_A/I_B]}{\partial P}\right] \quad (3)$$

As an illustration of typical data, Figs. 2 and 3 show $\ln[I_{PH}/I_{PC}]$ *vs.* $1/T$ and P plots for *i*-BuCl in hexane at 40 and 80 mol% of the *i*-BuCl solute. The enthalpy and volume differences, ΔH and ΔV, are estimated, respectively, from the slopes in Figs. 2 and 3. The values thus obtained are summarized in Tables 1 and 2, along with the data of these samples in the neat state previously.[2] For comparison, the enthalpy differences of these compounds in the gaseous state are also shown in Table 1.

As may be seen in Table 1 and 2, strong solvent and concentration dependences of ΔH and ΔV were observed. Especially in the case of *i*-BuBr, the ΔH in the neat state showed a negative value, −0.7±0.1 kJ mol^{-1}. It seems unreasonable, but the ΔH of *i*-BuBr

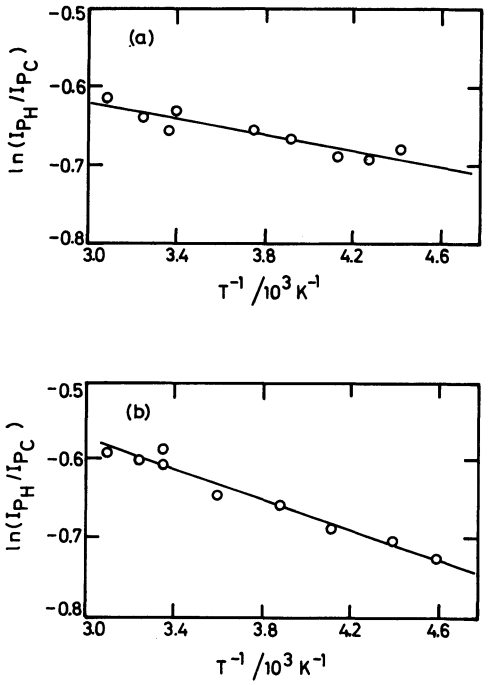

Fig. 2. Relationships between the logarithmic ratio of integrated intensities and temperature. (a) 80 mol% of *i*-BuCl in hexane. (b) 40 mol% of *i*-BuCl in hexane.

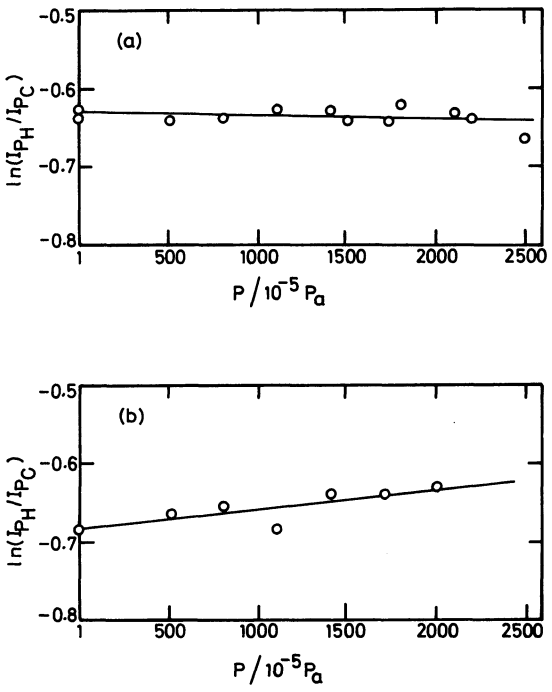

Fig. 3. Relationships between the logarithmic ratio of integarated intensities and pressure. (a) 80 mol% of *i*-BuCl in hexane. (b) 40 mol% of *i*-BuCl in hexane.

increased with a decrease in the contents of *i*-BuBr in solutions. Moreover, the positive volume difference of *i*-BuCl also decreased with an increase in the contents of hexane and changed to a negative value, −0.6$_2$±

Table 1. Conformational enthalpy differences, ΔH (kJ mol^{-1}) in hexane and methanol

	Neat[a]	In hexane			In methanol	Gas
		80 mol%	60 mol%	40 mol%	40 mol%	
i-BuCl						$0.6_1\pm0.4$
$P_C\rightarrow P_H$	0.0	$0.4_5\pm0.05$	$0.5_9\pm0.08$	$0.7_7\pm0.04$	$0.2_9\pm0.07$	$0.9_6\pm0.08$[b]
i-BuBr						
$P_C\rightarrow P_H$	-0.7 ± 0.1	$-0.1_9\pm0.04$	$-0.1_0\pm0.04$	$0.0_3\pm0.03$	$-0.2_5\pm0.06$	1.25 ± 1.3[b]
s-BuCl						
$S_{HH}\rightarrow S_{HH'}$	2.3 ± 0.4			2.3 ± 0.2	1.3 ± 0.1	
$S_{HH}\rightarrow S_{CH}$	2.5 ± 0.4			2.1 ± 0.1	1.9 ± 0.07	
s-BuBr						
$S_{HH}\rightarrow S_{HH'}$	2.7 ± 0.4			2.9 ± 0.2	3.0 ± 0.1	2.3 ± 0.2
$S_{HH}\rightarrow S_{CH}$	3.0 ± 0.4			2.5 ± 0.1	2.9 ± 0.1	1.5 ± 0.2

a) Ref. 2). b) Ref. 13).

Table 2. Conformational volume differences, ΔV (cm^3 mol^{-1}) in hexane and methanol

	Neat[a]	In hexane			In methanol
		80 mol%	60 mol%	40 mol%	40 mol%
i-BuCl					
$P_C\rightarrow P_H$	0.5 ± 0.1	$0.1_3\pm0.07$	$-0.3_9\pm0.07$	$-0.6_2\pm0.0_4$	$-0.4_6\pm0.04$
i-BuBr					
$P_C\rightarrow P_H$	-0.7 ± 0.2	$-0.7_9\pm0.08$	$-0.2_5\pm0.04$	$-0.5_3\pm0.04$	$-0.6_9\pm0.03$
s-BuCl					
$S_{HH}\rightarrow S_{HH'}$	-1.4 ± 0.4			$-1.8_0\pm0.2$	$-0.1_3\pm0.2$
$S_{HH}\rightarrow S_{CH}$	-0.8 ± 0.3			$-0.5_4\pm0.2$	0.0 ± 0.06
s-BuBr					
$S_{HH}\rightarrow S_{HH'}$	2.0 ± 0.4			$-1.4_5\pm0.2$	$0.8_2\pm0.2$
$S_{HH}+S_{CH}$	0.6 ± 0.2			$-0.9_1\pm0.1$	$0.1_8\pm0.2$

a) Ref. 2.

0.0_4 cm^3 mol^{-1} at the 40 mol% of *i*-BuCl.

For *s*-BuCl and *s*-BuBr, the enthalpy changes from S_{HH} to $S_{HH'}$ are nearly equal to those from S_{HH} to S_{CH} in the liquid and dissolved states. Therefore, the potential energies of the conformers, $S_{HH'}$ and S_{CH}, may be almost the same. The values of ΔH of *s*-BuBr in hexane and methanol are comparable to those in the gaseous state. This indicates that the intermolecular contribution to ΔH is small. In the cases of *s*-BuCl and *s*-BuBr, the signs of the ΔV of $S_{HH}\rightarrow S_{HH'}$ and $S_{HH}\rightarrow S_{CH}$ in hexane are both negative, but in methanol they are positive for *s*-BuBr and negative for *s*-BuCl. The signs of the ΔV of these conformational changes of *s*-BuCl and *s*-BuBr in methanol are the same as in the neat state. These results indicate that molecules of *s*-butyl halides in the neat state as well as those placed in methanol are in a strongly interacting field, as a result of the high dielectric constants of the media surrounding the central *s*-butyl halides. The absolute values of the volume changes caused by the $S_{HH}\rightarrow S_{HH'}$ transformation are about two or three times larger than those of $S_{HH}\rightarrow S_{CH}$, although the energy differences in the corresponding conformational changes are nearly equal in the two solutions.

Discussion

The origin of the enthalpy and volume differences, ΔH and ΔV, between the rotational isomers in solution can be divided into two factors. One is caused by the intermolecular interaction, and the other, by the intramolecular character. The solvent and concentration dependences of both ΔH and ΔV indicate that the intermolecular effects are predominant.

The changes in the intrinsic volume of each conformer were often estimated and compared with those obtained experimentally.[6,14] The intrinsic volume differences between the rotational isomers were calculated by the Bondi's method.[15] The results and van der Waals volumes are summarized in Table 3. The calculated volume changes are one or two orders of magnitude smaller than those obtained experimentally, but for *s*-BuCl and *s*-BuBr the order of the volume change of $S_{HH}\rightarrow S_{HH'}$ and $S_{HH}\rightarrow S_{CH}$ agrees with the experimental one.

The concentration dependences of the volume differences between the two conformers of *i*-BuCl and *i*-BuBr are shown in Fig. 4 as a function of the contents of the solute in hexane solutions. The concentration dependences are quite different for *i*-BuCl and *i*-BuBr. For *i*-BuCl, the volume difference, ΔV, decreased with an increase in the contents of hexane in solutions, but for *i*-BuBr, ΔV increased. As is shown in Fig. 4, the ΔV values of those two compounds seem to level off to a constant value at higher contents of hexane in solutions. On the other hand, the volume changes

Table 3. Calculation of volume differnce and van der waals volume by bondi method ($cm^3\ mol^{-1}$)

	Volume differences	van der Waals volume
i-BuCl		
$P_C \rightarrow P_H$	0.04	56.37
i-BuBr		
$P_C \rightarrow P_H$	0.05	58.47
s-BuCl		
$S_{HH} \rightarrow S_{HH}'$	0.03	56.37
$S_{HH} \rightarrow S_{CH}$	0	
s-BuBr		
$S_{HH} \rightarrow S_{HH}'$	0.12	58.47
$S_{HH} \rightarrow S_{CH}$	0.08	

The following parameters were used in the calculation:

Radii (Å)	Bond lengths (l/Å)		Bond angles (ϕ/°)
r(H)=1.20	C-H	1.10	C-C-C 112.2°
r(C)=1.70	C-C	1.53	C-C-H 110.4°
r(Cl)=1.77	C-Cl	1.77	C-C-Cl 110.0°
r(Br)=1.84	C-Br	1.95	C-C-Br 111.0°
			Cl-C-H 106.6°
			Br-C-H 105.4°

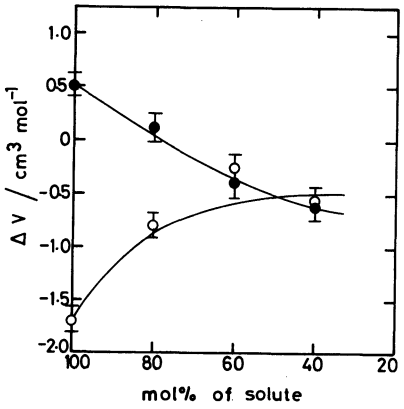

Fig. 4. Concentration dependence of ΔV of isobutyl halides in hexane. ●; *i*-BuCl ○; *i*-BuBr.

upon conformational change in the gaseous state are zero as is shown in Table 1. Therefore, ΔV becomes powerful measure of the changes in the packing of molecules in the liquid and dissolved states.

As may be seen in Table 1, the conformational enthalpy differences in *i*-BuCl and *i*-BuBr in hexane increase with an increase in the contents of hexane in solutions. In the neat state, such strong intermolecular interactions as dipole-dipole interactions are working. These strong intermolecular interactions will be reduced by the addition in solutions of hexane, which is an ineart solvent. Therefore, the enthalpy differences in these compounds increase with an increase in the concentration of hexane in solutions, and they tend to approach those in the gaseous state. The enthalpy difference in the gaseous state, ΔH_{gas}, corresponds to that of the intramolecular one. As a result, the enthalpy difference, $\Delta=\Delta H_{liq}-\Delta H_{gas}$, is a measure of the intermolecular interaction of the molecules in the liquid and dissolved states.

The enthalpy difference, $\Delta=\Delta H_{liq}-\Delta H_{gas}$, can be

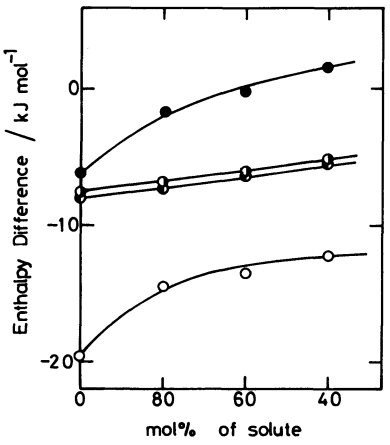

Fig. 5. Concentration dependence of enthalpy differences of isobutyl halides in hexane. $\Delta(=\Delta H_{liq}-\Delta H_{gas})$ of *i*-BuCl (●) and *i*-BuBr (○), obtained by the spectroscopic method. $\Delta H'$ of *i*-BuCl (○) and *i*-BuBr (○), calculated from Eq. 4.

estimated by the procedure proposed by Mizushima *et al.*,[16] using the reaction-field theory of Onsager:[17]

$$\Delta H' = \frac{\varepsilon-1}{2\varepsilon+1}\left[\left(\frac{\mu}{a^3}\right)_g - \left(\frac{\mu}{a^3}\right)_t\right] \quad (4)$$

where ε is the dielectric constant of the solvent and where μ and a are the dipole moment and the radius of the cavity of each conformer. The suffixes t and g refer to the states of *trans* and *gauche* respectively. The dipole moments of each conformer of the *i*-BuCl and *i*-BuBr were estimated by the method proposed by Miyagawa.[18] The radius of the cavity of these compounds was assumed to be the van der Waals radius of each conformer, whose value is indicated in Table 3. This assumption has been used by many investigators.[3,16] This dielectric constants of *i*-BuCl, *i*-BuBr, hexane, and methanol are found in the literature.[19] However, the dielectric constants of the solutions investigated here were not available; they were estimated using the following additivity rule of the molar polarization, $[p]$:

$$[p] = x_1[p_1] + x_2[p_2], \quad [p] = \frac{\varepsilon+1}{\varepsilon-2}\frac{M}{\rho}$$

where x_i refers to the mole fraction of the mixtures. The calculated values of the enthalpy difference, $\Delta H'$, are shown in Fig. 5, where the experimental values of $\Delta=\Delta H_{liq}-\Delta H_{gas}$ are also plotted. As may be seen in Fig. 5, the values of $\Delta H'$ increase with an increase in the contents of hexane in solutions. This trend well explains the experimental results, but the absolute numerical values of $\Delta H'$ are in very poor agreement with those obtained by experiments. This discrepancy between $\Delta H'$ and $\Delta(=\Delta H_{liq}-\Delta H_{gas})$ must be due to the poor estimation of the cavity radius, a, and the dipole moment, μ, of each conformer.

Equation 4 is the result of the first approximation, in which induced dipole moments were not taken into account. Besides, Eq. 4 involves only the long-range force; it does not take into account the short-range effects, especially the local packing effect of molecules. These short-range effects are all reflected in the term of the radius of the cavity. The estimation of the radius of the cavity of the rotational isomers is very important, but at present a precise estimation is very difficult.

Devauer and Lascombe[20] have thermodynamically related the enthalpy difference, Δ, to the volume change associated with the conformational change in liquids as following:

$$\Delta = \Delta H_{liq} - \Delta H_{gas} = RT^2\left(\frac{\partial f}{\partial T}\right)_V + \Delta V_{liq}\frac{\alpha T}{\beta_T} \quad (6)$$

where α and β_T are the expansion coefficient and compressibility respectively where f is $\ln[K/K_0]$, where K is the equilibrium constant for the liquid and/or dissolved state, K_0, that for gaseous state, and the other symbols have their usual meaning.

The thermodynamic parameters, α and β_T, of Eq. 6 for hexane solutions of *i*-BuCl and *i*-BuBr were determined as follows. The thermal expansion coefficient, α, was determined directly by the data of the temperature dependence of the density in solutions. The isothermal compressibility was calculated from the thermodynamic relation:

$$\beta_T = \beta_s + \frac{T\alpha^2 V}{C_p} \quad (7)$$

where the adiabatic compressibility, β_s, was determined with the aid of the Laplace equation, ($\beta_s = 1/(\rho u^2)$), from the data of density, ρ, and sound velocity, u, in solutions. The heat capacity of hexane and methanol was found in the literature,[19] but the halogenoalkanes investigated here no data were available. Therefore, the value for butyl chloride, 9.9 J/g.*K*.,[21] was adopted for the halogenoalkanes concerned in this work. The C_p's in solutions were estimated by assuming this relation

$$C_p = x_1 C_{p,1} + x_2 C_{p,2} \quad (8)$$

The values of $RT^2(\partial f/\partial T)_V$ thus obtained are summarized in Table 4. The values of $RT^2(\partial f/\partial T)_V$ are comparable in order with the values of Δ and $\Delta V_{liq}\alpha T/\beta_T$. Thermodynamically, the $RT^2\,(\partial f/\partial T)_V$ term corresponds to the internal energy difference between the liquid and gaseous states. The internal energy difference cannot be neglected in Eq. 6.

At this stage, it is difficult to calculate the physical properties concerning volume by statistical mechanical method. However, information about the internal energy of the solution is obtainable by the theoretical calculation on the basis of statistical mechanics and/or a computer-simulation experiment. The internal energy of the binary solution is calculated by the following equation:[22]

Table 4. The values of $RT^2(\partial f/\partial T)_V$ (kJ mol^{-1}) in Eq. 6.

		Hexane			Methanol
		80 mol%	60 mol%	40 mol%	40 mol%
i-BuCl					
$P_C \rightarrow P_H$	-0.7_6	-0.2_0	0.0_7	0.0_3	-0.1_8
i-BuBr					
$P_C \rightarrow P_H$	-1.4_1	-1.2_1	-1.2_8	-1.0_8	-1.2_9
s-BuBr					
$S_{HH} \rightarrow S_{HH}'$	0.2_3			0.9_5	0.9_5
$S_{HH} \rightarrow S_{CH}$	1.3_0			1.2_5	1.4_0

$$E = \frac{3}{2}NkT + \frac{2N^2}{V}\left[x_1^2\int_0^\infty u_{11}(r)g_{11}(r)r^2dr + 2x_1x_2\int_0^\infty u_{12}(r)g_{12}(r)r^2dr + x_2^2\int_0^\infty u_{22}(r)g_{22}(r)r^2dr\right]$$
$$x_1 = \frac{N_1}{N},\quad x_2 = \frac{N_2}{N},\quad N_1 + N_2 = N \quad (9)$$

where u_{ij} is the pair potential for molecules of i and j and g_{ij}, the radial distribution function. As may be seen in the equation, the short-range effects are involved in the term of the radial distribution function of each pair. We are now trying to calculate the internal energy using the theory of the reference interaction site model (RISM), which was proposed by Chandler *et al.*[23] We want to compare the calculated value with the experimental results obtained here.

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