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Concentration Fluctuation and the Light-scattering Spectrum

Kenji Iwasaki, Masami Tanaka, and Tsunetake Fujiyama
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158

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Light-scattering spectra were observed for binary solutions of carbon disulfide–chloroform at various concentrations. The relation between the Rayleigh-line intensity and the concentration fluctuation was derived. Using the proposed relation and the observed Rayleigh intensity, the concentration dependence of the concentration fluctuation was then determined. The results suggest that chloroform and carbon disulfide molecules have a tendency to get together in the binary solution.

Local fluctuation in the concentration is considered to afford information which is useful to understand the state of mixing from a molecular point of view. On the basis of this belief, we have planned a series of analyses of the temperature and concentration dependence of the concentration fluctuation in solutions. This, the first report of the series, will concern itself mainly with the determination of the concentration fluctuation through the observation of light-scattering spectra.

A light-scattering spectrum consists of a Rayleigh line, a pair of Brillouin lines, and a Rayleigh wing. Since the concentration fluctuation contributes to only the Rayleigh line, we can determine the concentration fluctuation from the Rayleigh intensity in a binary solution. We will derive an equation which relates the Rayleigh intensity of a light-scattering spectrum with the concentration fluctuation. Then the concentration dependence of the concentration fluctuation will actually be observed for the carbon disulfide–chloroform system through Rayleigh-intensity measurements. We chose the carbon disulfide–chloroform system because the concentration fluctuation of the system has been discussed previously on the basis of a band-width measurement of the infrared absorption spectra.¹⁾

Experimental

The light-scattering spectrometer used in the present study was designed and constructed in our laboratory.²⁾ Figure 1 shows the schematic layout of the spectrometer. The instrument is composed of a He-Ne gas laser source (NEC, GLG108, 50 mW), a Fabry-Perot interferometer, a lock-in amplifier (NF, LI573), and an X-Y recorder. The spacer between the interferometer etalons has a thickness of 6 mm, giving a free spectral range of 0.82 cm^{-1} and an overall instrumental half-width of about 0.042 cm^{-1}. The interferometer was pressure-scanned by evacuating the box enclosing the etalons and by allowing air to leak into the box slowly. The samples used in this experiment were commercially available reagents: carbon disulfide without further purification and chloroform purified by a column chromatography on alumina. The binary solutions of carbon disulfide and chloroform were made dust-free by the use of a Millipore-filter FG with a pore size of 0.2 μm. The test of a solution being dust-free can be done in principle by comparing the observed Rayleigh intensity with the true Rayleigh intensity of dust-free samples. As the true Rayleigh intensity is unknown, however, the dust-free test was done by comparing the observed Rayleigh intensity with the best data among the many Rayleigh intensities reported so far. In the case of the light-scattering spectrum, the L–P ratio, defined by $I_C/2I_B$, is the measure of being dust-free, because the Rayleigh intensity, I_C, is strongly influenced by the existence of dust, while the Brillouin intensity, I_B, is hardly influenced at all by the existence of dust. The observed L–P ratios are summarized in Table 1. It may be seen from the table that the present data agree well with those measured by Cummins *et al.*³⁾ The reason why our values are slightly larger than Cummins' is the difference in the methods by which the spectral components are separated. Because Cummins verified the dust-free state for water, whose L–P ratio is nearly zero, it seems that our optical purification and experimental techniques can realize a nearly dust-free state. Though a dust-free checking method like this is applicable only for pure liquids on which many intensity data are reported, we believe that mixture samples can be purified by the same method as that applied for pure liquids. The preparation (filtration and injection of a sample into a cell) of the sample was repeated five times or more, and the best value was chosen as the measured value. The refractive index of the sample was measured by means of a Shimadzu-Bausch Lomb Abbe refractometer 3L. The composition derivative of the refractive index at the mole fraction, x, was estimated from the difference between refractive indices measured at $x \pm 0.05$. All the measurements were performed at the temperature of 20±0.5 °C.

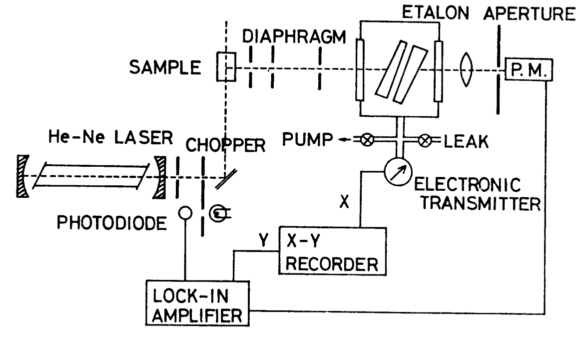

Fig. 1. Schematic layout of light scattering spectrometer.

Results and Discussion

Reduction of Rayleigh Intensity to Concentration Fluctuation. Miller presented an equation which relates the Rayleigh intensity of the light-scattering spectrum with the composition derivative of the chemical potential.⁴⁾ Following his theory, we derive an equation which directly relates the Rayleigh intensity of the light-scattering spectrum to the concentration fluctuation. Imagine a small-volume element which contains a constant number of moles, n_1, of one component in a binary solution at a constant temperature and

TABLE 1. OBSERVED INTENSITIES FOR PURE LIQUIDS

Liquid	Rayleigh intensity[a) Obsd (24.5 °C)	Rayleigh intensity[a) Calcd (24.5 °C)	L-P ratio Present (24.5 °C)	L-P ratio Reference[b) (20.0 °C)	Rayleigh wing intensity
Carbon disulfide	2.00	2.45	0.78	0.71	very strong
Benzene	1.31	1.02	0.93	0.84	medium
Chloroform	1.00	1.00	0.69	—	weak
Diethyl ether	0.82	0.80	0.41	0.35	very weak
Hexane	0.69	0.65	0.36	0.35	very weak
Acetone	0.60	0.57	0.48	0.44	weak
Ethanol	0.43	0.27	0.34	0.23	very weak

a) Relative values, the intensity of chloroform being chosen as a standard.
b) See Ref. 3.

pressure. If we consider the dielectric constant, ε, as a function of the entropy, S, the pressure, P, and the number of moles, n_2, of the other component, the mean-square fluctuation in the dielectric constant, $\langle(\Delta\varepsilon)^2\rangle$, is expressed by:

$$\begin{aligned}\langle(\Delta\varepsilon)^2\rangle &= (\partial\varepsilon/\partial P)^2_{S,n_2}\langle(\Delta P)^2\rangle + (\partial\varepsilon/\partial S)^2_{P,n_2}\langle(\Delta S)^2\rangle \\ &+ 2(\partial\varepsilon/\partial S)_{P,n_2}(\partial\varepsilon/\partial n_2)_{S,P}\langle\Delta S\Delta n_2\rangle \\ &+ (\partial\varepsilon/\partial n_2)^2_{S,P}\langle(\Delta n_2)^2\rangle \end{aligned} \tag{1}$$

because $\langle\Delta S\Delta P\rangle = \langle\Delta P\Delta n_2\rangle = 0$. Of the four terms on the right-hand side of Eq. 1, the first term contributes to a Brillouin intensity, while the remaining three terms contribute to a Rayleigh intensity. Thus, we can express Eq. 1 as:

$$\langle(\Delta\varepsilon)^2\rangle = \langle(\Delta\varepsilon_B)^2\rangle + \langle(\Delta\varepsilon_R)^2\rangle \tag{2}$$

where

$$\langle(\varepsilon_B)^2\rangle = (\partial\varepsilon/\partial P)^2_{S,n_2}\langle(\Delta P)^2\rangle \tag{3}$$

and

$$\begin{aligned}\langle(\Delta\varepsilon_R)^2\rangle &= (\partial\varepsilon/\partial S)^2_{P,n_2}\langle(\Delta S)^2\rangle \\ &+ 2(\partial\varepsilon/\partial S)_{P,n_2}(\partial\varepsilon/\partial n_2)_{S,P}\langle\Delta S\Delta n_2\rangle \\ &+ (\partial\varepsilon/\partial n_2)^2_{S,P}\langle(\Delta n_2)^2\rangle \end{aligned} \tag{4}$$

In these expressions, the $\langle\Delta S\Delta n_2\rangle$ term cannot be calculated from any observable quantities. Therefore, we express ε as a function of the temperature, T, the pressure, P, and the number of moles, n_2, of the other component. We thus obtain:

$$\begin{aligned}\langle(\Delta\varepsilon)^2\rangle &= (\partial\varepsilon/\partial T)^2_{P,n_2}\langle(\Delta T)^2\rangle + 2(\partial\varepsilon/\partial T)_{P,n_2} \\ &\times (\partial\varepsilon/\partial P)_{T,n_2}\langle\Delta T\Delta P\rangle \\ &+ (\partial\varepsilon/\partial P)^2_{T,n_2}\langle(\Delta P)^2\rangle + 2(\partial\varepsilon/\partial P)_{T,n_2} \\ &\times (\partial\varepsilon/\partial n_2)_{T,P}\langle\Delta P\Delta n_2\rangle \\ &+ (\partial\varepsilon/\partial n_2)^2_{T,P}\langle(\Delta n_2)^2\rangle + 2(\partial\varepsilon/\partial T)_{P,n_2} \\ &\times (\partial\varepsilon/\partial n_2)_{T,P}\langle\Delta T\Delta n_2\rangle \end{aligned} \tag{5}$$

instead of Eq. 1. Combining Eqs. 2, 3, and 5, we obtain the expression for $\langle(\Delta\varepsilon_R)^2\rangle$. In this expression, all the necessary terms can be calculated from the observable quantities. The mean square fluctuations[5)] of Eqs. 3 and 5 are calculated to be:

$$\left.\begin{aligned}&\langle(\Delta T)^2\rangle = kT^2/C_V, \quad &&\langle\Delta T\Delta P\rangle = kT^2\alpha/\beta_T C_V \\ &\langle(\Delta P)^2\rangle = kT/V\beta_S, \quad &&\langle\Delta T\Delta n_2\rangle = \langle\Delta P\Delta n_2\rangle = 0\end{aligned}\right\} \tag{6}$$

where k is the Boltzmann constant; C_V, the heat capacity at a constant volume; α, the thermal expansivity; β_T, the isothermal compressibility, and β_S, the adiabatic compressibility. Combining Eqs. 2, 3, 5, and 6, we get:

$$\langle(\Delta\varepsilon_R)^2\rangle = \frac{kT^2}{C_P}\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,n_2} + \left(\frac{\partial\varepsilon}{\partial n_2}\right)^2_{T,P}\langle(\Delta n_2)^2\rangle \tag{7}$$

where C_P is the isobar heat capacity. The first term of Eq. 7 is related to entropy fluctuation by:

$$\begin{aligned}\left(\frac{\partial\varepsilon}{\partial S}\right)^2_{P,n_2}\langle(\Delta S)^2\rangle &= \left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,n_2}\left(\frac{\partial T}{\partial S}\right)^2_{P,n_2}\langle(\Delta S)^2\rangle \\ &= \left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,n_2}\left(\frac{T}{C_P}\right)^2 kC_P \\ &= \frac{kT^2}{C_P}\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,n_2}\end{aligned} \tag{8}$$

The second term of Eq. 7, on the other hand, is the mean-square fluctuation of n_2 in a small volume containing a constant n_1. Therefore, Eq. 7 can be rewritten symbolically as:

$$\langle(\Delta\varepsilon_R)^2\rangle = \begin{pmatrix}\text{entropy fluctua-}\\ \text{tion term}\end{pmatrix} + \begin{pmatrix}\text{concentration fluctua-}\\ \text{tion term}\end{pmatrix} \tag{9}$$

Thus, we could express the concentration fluctuation, $\langle(\Delta n_2)^2\rangle$, in terms of $\langle(\Delta\varepsilon_R)^2\rangle$ and $\langle(\Delta S)^2\rangle$. It is important to emphasize that a small-volume element is chosen because it contains a constant number of moles, n_1. If the incident light, whose electric vector is polarized perpendicular to the scattering plane, passes through the fluctuation volume, V^*, in which mean mole number of one component, n_1, is confined, the intensity of light scattered perpendicularly to the incident light is given in terms of the Rayleigh ratio:

$$R_{90} = (\pi^2/\lambda_i^4)V^*\langle(\Delta\varepsilon)^2\rangle \tag{10}$$

where λ_i is the wavelength of the incident light. By combining Eqs. 7 and 10, the Rayleigh ratio for a Rayleigh line is expressed as:

$$\begin{aligned}(R_{90})_R = (\pi^2/\lambda_i^4)\Bigg\{&\frac{kT^2V^*}{C_P}\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,n_2} \\ &+ \left(\frac{\partial\varepsilon}{\partial n_2}\right)^2_{T,P} V^*\langle(\Delta n_2)^2\rangle\Bigg\}\end{aligned} \tag{11}$$

Now, we introduce three relations:

$$d\varepsilon = 2n\,dn$$

$$dx_2 = dn_2 x_1/(n_1+n_2)$$

$$C_P/V^* = C_{Pg}\cdot M/V^* = C_{Pg}\rho$$

where n is a refractive index; x_1 and x_2, the mole fractions of the 1 and 2 components; C_{Pg}, the isobar heat capacity per gram; ρ, the density, and M, the weight of V^*. Substituting these relations into Eq. 11, we find:

$$(R_{90})_R = (\pi^2/\lambda_i^4)\frac{4kn^2T^2}{C_{Pg}\rho}\left(\frac{\partial n}{\partial T}\right)^2_{P,x_2} + (\pi^2/\lambda_i^4)4n^2\left(\frac{\partial n}{\partial x_2}\right)^2_{T,P} V^*\langle(\Delta x_2)^2\rangle \tag{12}$$

Since the first term of Eq. 12 arises from the entropy fluctuation, the Rayleigh ratio for entropy fluctuation is expressed as:

$$(R_{90})_S = (\pi^2/\lambda_i^4)\frac{4kn^2T^2}{C_{Pg}\rho}\left(\frac{\partial n}{\partial T}\right)^2_{P,x_2} \tag{13}$$

Combine Eqs. 12 and 13, an equation which directly relates the observed Rayleigh intensity with the concentration fluctuation is obtained:

$$V^*\langle(\Delta x_2)\rangle = (\lambda_i^4/\pi^2)\frac{1}{4n^2(\partial n/\partial x_2)^2{}_{T,P}}\{(R_{90})_R-(R_{90})_S\} \tag{14}$$

From Eq. 14 we can determine $V^*\langle(\Delta x_2)^2\rangle$ experimentally, observing $(R_{90})_R$ and estimating $(R_{90})_S$ by the use of Eq. 13. The concentration fluctuation can be determined in the form of $V^*\langle(\Delta x_2)^2\rangle$ from the observation of the light-scattering spectrum. We cannot, however, determine the concentration fluctuation in the form of $\langle(\Delta x_2)^2\rangle$ from the light-scattering spectrum. We will call this $V^*\langle(\Delta x_2)^2\rangle$ the "fluctuation ability" hereafter.

Light-scattering Spectra. The observed spectra for the chloroform–carbon disulfide system are given in Fig. 2. It may be seen from the figure that the intensity of a Rayleigh line increases remarkably on passing from pure liquids to binary solutions. The intensity change in the Brillouin lines, on the other hand, is small in comparison with that of a Rayleigh line. The background intensity due to a Rayleigh wing is largest for pure carbon disulfide and smallest for pure chloroform.

Determination of the Rayleigh Ratio. The procedure for separating a Rayleigh line from Brillouin lines and from a Rayleigh wing is illustrated in Fig. 3. A Rayleigh wing is assumed to be almost flat along a frequency axis. The outer halves of the Brillouin lines are assumed to be equal to the non-overlapping line shapes. Thus, the intensity of a Rayleigh line was determined by eliminating the areas corresponding to the Rayleigh wing and the Brillouin lines.

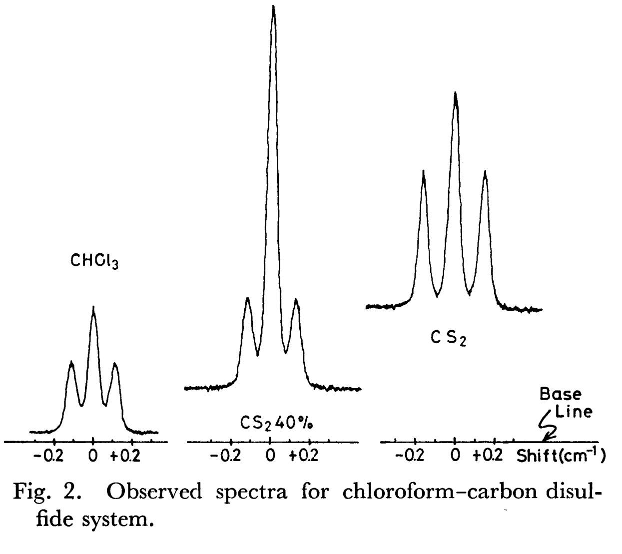

Fig. 2. Observed spectra for chloroform-carbon disulfide system.

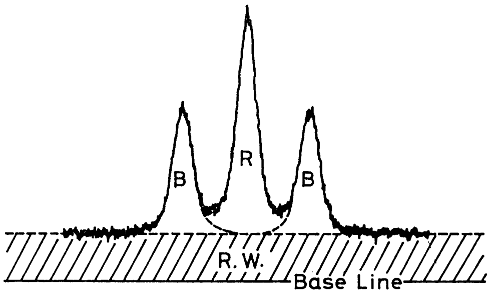

Fig. 3. Separation of Rayleigh line from light scattering spectra (schematic). R: Rayleigh line, B: Brillouin line, R.W.: Rayleigh wing.

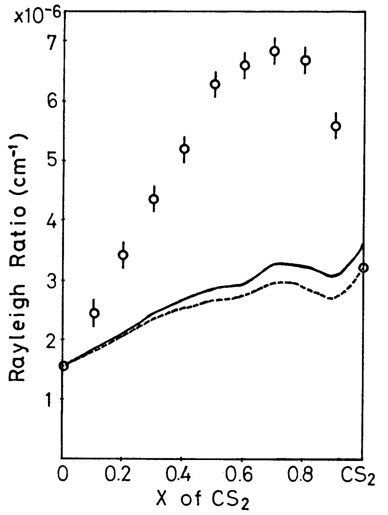

Fig. 4. Concentration dependence of Rayleigh intensity of chloroform-carbon disulfide system. The open circles correspond to $(R_{90})_R$, the solid line $(R_{90})_S$ and the broken line $(R_{90})_S{}^*$. Errors are indicated by the vertical lines.

The reliability of the observed Rayleigh ratios was checked by the use of Eq. 13. The observed Rayleigh ratios and the calculated Rayleigh ratios by Eq. 13 are compared in Table 1.

Since the observed Rayleigh intensities are relative values, we have to express the observed relative intensities, I_R, in terms of the Rayleigh ratios. We first calculate $(R_{90})_S$ for pure chloroform by the use of Eq. 13. We call this $(R_{90})_S{}^{CHCl_3}$. Then, the Rayleigh ratio for binary mixtures, $(R_{90})_R$, is calculated to be:

$$(R_{90})_R = I_R \times \frac{(R_{90})_S^{CHCl_3}}{I_R^{CHCl_3}} \tag{15}$$

where $I_R{}^{CHCl_3}$ is a relative Rayleigh intensity for pure chloroform.⁶⁾ The calculated Rayleigh ratios are plotted by open circules in Fig. 4.

Determination of the Concentration Fluctuation. The theoretical values of $(R_{90})_S$ at each mole fraction were

Table 2. Observed Rayleigh ratios for a Rayleigh line and Rayleigh ratios for entropy fluctuation in chloroform–carbon disulfide system

Mole fraction of CS_2	$(R_{90})_R$ (cm^{-1}) (20±0.5 °C)	$(R_{90})_S$ (cm^{-1}) (20 °C)	K	$(R_{90})_S^*$ (cm^{-1})
	$\times 10^{-6}$	$\times 10^{-6}$		$\times 10^{-6}$
0	1.55±0.06	1.55	1	1.55
0.105	2.43	1.82	0.987	1.80
0.203	3.42	2.11	0.975	2.05
0.301	4.34	2.42	0.963	2.33
0.398	5.20	2.65	0.951	2.52
0.495	6.31±0.24	2.83	0.939	2.66
0.599	6.61	2.90	0.926	2.69
0.693	6.86	3.24	0.914	2.96
0.799	6.71	3.21	0.901	2.90
0.898	5.59	3.04	0.889	2.70
1.000	3.18±0.05	3.63	0.876	3.18

calculated by substituting the observed values of λ_i, n, T, ρ, $(\partial n/\partial T)_{P,x_2}$, and the C_{Pg} values from the table[7] into Eq. 13 (see Table 2). The observed $(R_{90})_S$ for pure carbon disulfide was slightly different from that calculated from Eq. 13. This disagreement may be ascribed to the separation of a Rayleigh line from the light-scattering spectra. For the observation of the concentration fluctuation, however, the essential quantity is not $(R_{90})_S$ but $\{(R_{90})_R-(R_{90})_S\}$, that is, in intensity increment due to the concentration fluctuation. Therefore, the calculated $(R_{90})_S$ was corrected by means of a suitable parameter to:

$$(R_{90})_S^* = K \times (R_{90})_S$$

where K was chosen so that the calculated $(R_{90})_S$ for pure carbon disulfide was equal to the observed one. The K value for each concentration was thought to change continuously[8] from 1 to 0.876, the latter value of which is the correction factor for pure carbon disulfide (see the 4th column Table 2).

Using the Rayleigh ratios, $(R_{90})_R$, and the Rayleigh ratios for entropy fluctuations, $(R_{90})_S$, the fluctuation ability, $V^*\langle(\Delta x_2)^2\rangle$, was calculated from Eq. 14 at each concentration.

The reliability of the concentration fluctuations observed from Rayleigh intensities in the light-scattering spectra were examined with respect to two main factors:

1) the accuracy of the measured relative Rayleigh intensity, and

2) the observation of $(\partial n/\partial x)_{T,P}$.

The procedure of sampling is most important. As has been described in the previous paragraph, the samples were prepared so as to be almost dust-free. However, there was still a little doubt about the possibility of realizing a dust-free situation for all the samples observed. Therefore, we prepared a sample more than five times for one observation and took the best value as the observed value. We repeated the above procedure four times. The maximum deviation of the observed value from the averaged value was considered to be the error expected for the observed value (see the vertical lines of Fig. 4). The value of $(\partial n/\partial x)_{T,P}$ at the mole fraction x was obtained from the difference between the refractive indices at x±0.05. The precision of the refractive indices observed by means of an Abbe refractometer is about ±0.0001. As the determination of the concentration is precise enough, the precision of $(\partial n/\partial x)_{T,P}$ is about ±0.002. Taking into account the above two factors, the precision for the observed $V^*\langle(\Delta x_2)^2\rangle$ values is estimated to be about $\pm 0.174\times 10^{-23}\ cm^{-1}$ (see the vertical line of Fig. 5).

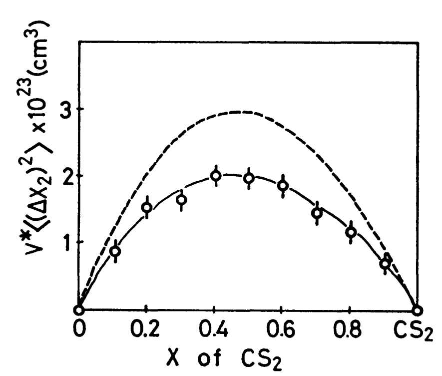

Fig. 5. Concentration dependence of concentration fluctuation for chloroform–carbon disulfide system. The open circules correspond to concentration fluctuation observed for chloroform–carbon disulfide system. The broken line shows concentration fluctuation expected for the ideal binary solution. Errors are indicated by the vertical lines.

Concentration Fluctuation. The concentration dependence of the concentration fluctuation observed for the chloroform–carbon disulfide system is shown in Fig. 5. Consider first the concentration fluctuation expected for the ideal binary solution, whose components are mixed with each other without intermolecular interaction. When a mixture of the 1 and 2 components behaves as a mixture of two simple particles, the chemical potential of the 2 component, μ_2, is given by:

$$\mu_2 = \mu_2^\circ + kT\ln x_2 \tag{16}$$

where μ_2° is the standard chemical potential. If the chemical potential is known, the fluctuation ability is calculated to be:

$$N\langle(\Delta x_2)^2\rangle = \frac{kTx_1}{(\partial\mu_2/\partial x_2)_{T,P}} \tag{17}$$

TABLE 3. EVALUATION OF FLUCTUATION ABILITIES FOR CHLOROFORM–CARBON DISULFIDE SYSTEM

Mole fraction of CS_2	$\{(R_{90})_R-(R_{90})_S{}^*\}$ (cm^{-1})	n_D^{20}	$(\partial n/\partial x_2)_{T,P}$ (20 °C)	$V^*\langle(\Delta x_2)^2\rangle$ (cm^3)
0	0 $\times 10^{-6}$	1.4452	—	— $\times 10^{-23}$
0.105	0.63	1.4474	0.117	0.89
0.203	1.37	1.4700	0.130	1.52
0.301	2.01	1.4830	0.150	1.65
0.398	2.68	1.4984	0.156	1.99
0.495	3.66	1.5143	0.181	1.98
0.599	3.92	1.5346	0.190	1.87
0.693	3.90	1.5525	0.212	1.47
0.799	3.82	1.5756	0.232	1.16
0.898	2.89	1.6000	0.254	0.71
1.000	0	1.6280	—	—

where N is the mean number of particles in V^*. Notice that the fluctuation ability is expressed in terms of N and $\langle(\Delta x_2)^2\rangle$ instead of V^* and $\langle(\Delta x_2)^2\rangle$. By combining Eqs. 16 and 17, we get:

$$N\langle(\Delta x_2)^2\rangle = x_2(1-x_2) \tag{18}$$

or

$$V^*\langle(\Delta x_2)^2\rangle = \frac{x_2(1-x_2)}{\rho_n} \tag{19}$$

where ρ_n is the number density and where $N=\rho_n V^*$. The broken line of Fig. 5 shows the fluctuation ability of a binary solution as predicted by Eq. 19. It may be seen from the figure that the observed fluctuation ability of the chloroform–carbon disulfide system is smaller than the prediction of Eq. 19 throughout all the mole fractions. This result suggests that there is a tendency inherent to the chloroform–carbon disulfide system which keeps the macroscopic concentration constant, even in a small volume. If we consider mixing from a microscopic point of view, the concept of concentration fluctuation corresponds to the variation in the concentration due to the thermal motion of molecules within a small volume. When there is no intermolecular interaction, the thermal motion of component molecules can be regarded as completely random. Therefore, the concentration fluctuation can be predicted by means of Eq. 18 or 19. Actually, however, the observed concentration dependence of the concentration fluctuation is different from that of Eq. 18 or 19, which indicates that the thermal motion of the component molecules is not random. This is probably to be ascribed to intermolecular interactions between the molecules of the same and/or different species. Instead of studying the nature of the intermolecular interactions directly, we introduce the concept of the association of molecules. If molecules of the same species have a tendency to get together in a binary solution, the concentration fluctuation takes a larger value than that of an ideal solution. In this case, a few molecules move in close association, therefore, the local concentration change due to thermal motion is much larger than that for the thermal motion of a single molecule. When molecules of different species have a tendency to get together, on the other hand, the concentration fluctuation takes a smaller value than that of an ideal solution. In this case, a complex molecule which is formed from molecules of different species behaves as a single molecule; therefore, the exchange of molecules between the inside and the outside of the small volume in question due to thermal motion brings about a much smaller concentration change inside the volume. The present results obtained for chloroform–carbon disulfide system suggest, therefore, that there is an inherent tendency in chloroform–carbon disulfide system which keeps the macroscopic concentration constant, even in a small volume. A more quantitative analysis of this problem will be made in the next report.

References

1) T. Fujiyama, M. Kakimoto, and T. Suzuki, *Bull. Chem. Soc. Jpn.*, **49**, 606 (1976); The $V^*\langle(\Delta x_2)^2\rangle$ values of the present report are slightly different from those reported in Ref. 1. Readers are invited to have more confidence in the present values.

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4) G. A. Miller, *J. Phys. Chem.*, **71**, 2305 (1967).

5) L. D. Landau and E. M. Lifshitz, "Statistical Physics," Pergamon Press, London (1958).

6) Table 1 shows that the ratio of the observed and calculated Rayleigh intensities is quite different from unity in carbon disulfide and in benzene, and almost unity for the other solvents. This singular phenomenon in carbon disulfide is considered to be due to the analytical process of separating the Rayleigh wing and the Rayleigh line. Therefore, chloroform was chosen as the intensity standard in the case of the binary solution of chloroform–carbon disulfide.

7) "International Critical Tables," McGraw-Hill, New York (1926).

8) The parameter, K, was introduced so as to correct the deviation between the observed and calculated intensities originating from the entropy fluctuation in carbon disulfide (see the first and second columns of Table 1). As the deviation is most obvious in carbon disulfide, it can also be expected in binary solutions of carbon disulfide and other solvents. In the case of a binary solution of carbon disulfide and chloroform, the effect is considered to be proportional to the concentration of carbon disulfide.