2988 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (11), 2988—2994 (1976) [Vol. 49, No. 11

Associated Complex Formation in a Binary Solution and the Concentration Fluctuation: The Chloroform-Diethyl Ether System

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(Received June 12, 1976)

The relations between the associated complex formation and the concentration fluctuation in a binary solution were derived. The concentration fluctuation of a chloroform–diethyl ether system was determined by observing light-scattering spectra at various concentrations. The theoretical values of the concentration fluctuation of this system were calculated from the proposed relation by the use of the shape and the number population of the associated complex, as determined from the infrared absorption intensity measurements. The observed and calculated concentration fluctuations agreed quite well.

The local fluctuation of the concentration is considered to afford information which is useful in understanding *mixing* from a molecular point of view. Based on this belief, a series of studies have been planned on analyses of the concentration dependence of the concentration fluctuation in solution through observation of the light-scattering spectra.[1)]

First, the relation between the concentration fluctuation and the Rayleigh intensities has been theoretically established.[2)] The concentration fluctuations for the chloroform–carbon disulfide system observed by this light-scattering method were compared with those obtained from the band-width of the infrared spectrum for the ν_1 fundamental of chloroform.[3)] The observed concentration dependence of the concentration fluctuation in the chloroform–carbon disulfide system indicated an associative tendency between the chloroform and carbon disulfide molecules.[2)]

The present report will concern itself with a study of the concentration dependence of the concentration fluctuation for a binary solution of the chloroform–diethyl ether system through the observation of light-scattering and infrared-absorption spectra. This system was chosen because (1: 1)-complex formation between chloroform and diethyl ether has been well established with this dissociation equilibrium:

$$\mathrm{CHCl_3{:}(C_2H_5)_2O} \rightleftharpoons \mathrm{CHCl_3 + (C_2H_5)_2O}$$

Our main interest lies in the relation between the complex formation and the concentration fluctuation.

Theoretical

Ideal Solution. We start by considering the concentration fluctuation in an ideal binary solution whose components, A and B, behave as simple particles. In order to express the concentration fluctuation in terms of the number fluctuation of Component A, the volume area containing a constant quantity of Component B is to be considered. The volume of such an area changes in magnitude momentarily around its mean value. Therefore, the fluctuation of the mole fraction, x_A, of Component A arises from two factors: The exchange of A molecules between the inside and the outside of the area due to thermal motion of A molecules and the volume change in the area due to thermal motion of the B molecules. As the molecular number, n_B, of Component B is constant within the area under consideration, the fluctuation of x_A is expressed by the fluctuation of n_A. The mean fluctuation in n_A, $\langle(\Delta n_A)^2\rangle$, has been given as:[4)]

$$\langle(\Delta n_A)^2\rangle = \frac{kT}{(\partial\mu_A/\partial n_A)_{T,P}} \tag{1}$$

where k is the Boltzmann constant; T, the temperature; μ_A, the chemical potential of Component A, and P, the pressure. By definition,

$$x_A = \frac{n_A}{n_A+n_B} \tag{2}$$

Therefore,

$$\mathrm{d}x_A = \frac{x_B}{n_A+n_B}\mathrm{d}n_A \tag{3}$$

because n_B is constant. If the mixture of Components A and B is considered to be ideal, the chemical potential of Component A is given by:

$$\mu_A = \mu_A^\circ + kT\ln x_A \tag{4}$$

where μ_A° is the standard chemical potential. Equations 1, 3, and 4 are combined to become:

$$N\langle(\Delta x_A)^2\rangle = x_A(1-x_A) \tag{5}$$

where

$$N = n_A + n_B$$

is the total number of molecules in the area under consideration.

Associated Complex Model. In the above discussion for an ideal solution, all the molecules in the solution are assumed to behave independently. In actual solutions, however, molecular species may be affected by a molecular species of the central molecule under consideration. This arises from the intermolecular interactions between the component molecules. In order to simplify the theoretical treatment, we wish to introduce the concept of an associated complex instead of considering intermolecular interactions explicitly. We will consider the formation of an associated complex, such as B_l or AB, in a binary solution of A and B components, where the suffix l indicates the number of molecules which form an associated complex. The associated complex, B_l or AB, is assumed to behave independently from the species A or B. In other words, the associated complex formation is considered to arise from strong intermolecular interactions, and the resultant complex is considered to have no interaction abilities with the other molecular species, A and B. Under these assumptions, we first calculate the concentration fluctuation in a system of complete association, because such a system can be treated as a two-component system of A and B_l or A and AB.

Case I (A and B_l): Consider a case where strong intermolecular interactions are expected between B molecules in a binary solution of A and B molecules. We assume that a mixture of Components A and B is a two-component system of A molecules and associated complex molecules, B_l. If the effect of the volume difference between A and B_l is neglected, the binary mixture of A and B_l is an ideal solution. Therefore, the following relation is obtained directly from Eq. 5:

$$N'\langle(\Delta x_A')^2\rangle = x_A'(1-x_A') \qquad (6)$$

where:

$$x_A' = \frac{n_A}{n_A+n_{B_l}} \qquad (7)$$

and:

$$N' = n_A + n_{B_l} \qquad (8)$$

and where n_A is the mean quantity of Component A in a small volume area which contains a constant number, n_{B_l}, of the B_l complex. As the $\Delta x_A'$, x_A', and N' which appear in Eqs. 6—8 are fictitious quantities, we have to rewrite these quantities in terms of real quantities, like Δx_A, x_A, and N. The true mole fraction, x_A, of Component A and the total number of molecules, N, in the volume range under consideration are expressed by these relations:

$$x_A = \frac{n_A}{n_A+ln_{B_l}} \qquad (9)$$

and:

$$N = n_A + ln_{B_l} \qquad (10)$$

From Eqs. 7—10, we obtain:

$$x_A' = \frac{lx_A}{(l-1)x_A+1}$$

or:

$$dx_A' = \frac{l}{\{(l-1)x_A+1\}^2}dx_A$$

and:

$$N' = \frac{(l-1)x_A+1}{l}N$$

Substituting the last three relations into Eq. 6, we finally obtain this relation:

$$N\langle(\Delta x_A)^2\rangle = -(l-1)x_A^3 + (l-2)x_A^2 + x_A \qquad (11)$$

In Fig. 1 the results obtained from Eq. 11 are illustrated for various l values. The result for $l=1$ is identical with the result for an ideal binary solution of Eq. 5. It may be seen from the figure that the concentration fluctuation increases in magnitude as the association number, l, increases. The maximum of the fluctuation curve moves to the larger-mole-fraction side as the association number increases, until it arrives at $x_A=2/3$ for an infinite l. This may be understood reasonably by the following intuitive image. When x_A is large, that is, when n_B is small, a local concentration fluctuates mainly as a result of thermal motion of associated species in and out of the volume area. When x_A is small, on the other hand, a local concentration fluctuates mainly as a result of motion of non-associated species. The effect on the local concentration of the coming in and going out of one species may be supposed to be much larger in the former case than in the latter.

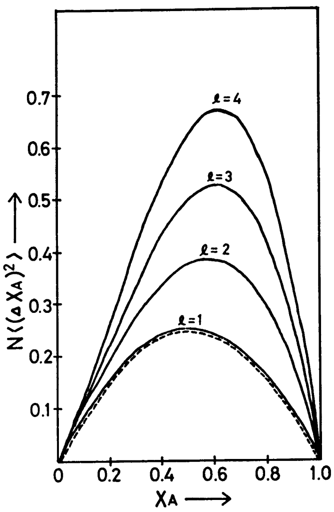

Fig. 1. Theoretical values of concentration fluctuation calculated from Eq. 11 for $l=1, 2, 3, 4$. The dashed line corresponds to the concentration fluctuation expected for an ideal binary solution.

Case II (A_l and B_l): Consider a case where strong intermolecular interactions are expected between A molecules and between B molecules. We assume that a mixture of Component A and B is a two-component system of associated complex molecules, A_l and B_l. Then, the calculation procedure is the same as that of Case I and the result is:

$$N\langle(\Delta x_A)^2\rangle = lx_A(1-x_A) \qquad (12)$$

In Fig. 2 the results obtained from Eq. 12 are illustrated for various l values. In this case, the value of the concentration fluctuation is l times as large as that for an ideal binary solution.

Case III (A and AB): Consider a case where (1:1) association between different species occurs in a binary mixture of Components A and B. The binary mixture of

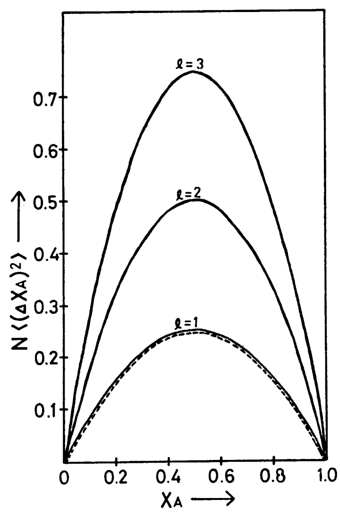

Fig. 2. Theoretical values of concentration fluctuation calculated from Eq. 12 for $l=1, 2, 3$. The dashed line corresponds to the concentration fluctuation expected for an ideal binary solution.

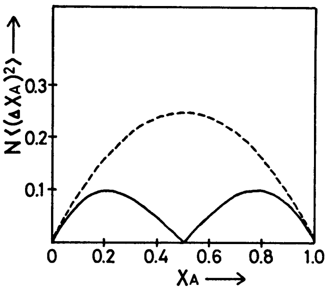

Fig. 3. Theoretical values of concentration fluctuation calculated from Eq. 13. The dashed line corresponds to the concentration fluctuation expected for an ideal binary solution.

A and B is composed of A and AB molecules for $x_A > 0.5$ and of B and AB molecules for $x_A < 0.5$. $N < (\Delta x_A)^2 >$ can be calculated similarly:

$$N\langle(\Delta x_A)^2\rangle = -2x_A^3 + 3x_A^2 - x_A \tag{13}$$

The results of Eq. 13 are shown in Fig. 3. It may be seen from the figure that the magnitude of the concentration fluctuation is smaller than that of an ideal solution for all the x_A values and that the concentration fluctuation has two maxima and takes a zero value at $x_A = 1/2$.

Thus, we can understand roughly the relation between the shape of the associated complex and the concentration dependence of $N < (\Delta x_A)^2 >$ from the calculation of $N < (\Delta x_A)^2 >$ for the system of complete association. Association between the same species brings a larger $N < (\Delta x_A)^2 >$ than that of an ideal solution, while association between different species brings a smaller $N < (\Delta x_A)^2 >$.

Complex Formation with Association Equilibrium. Thus far we have discussed the concentration fluctuation for the system of complete association. In actual solutions, however, we have to take into account the association equilibrium between an associated complex and the component molecules. Consider a case where an association equilibrium of the form:

$$A + B \rightleftharpoons AB$$

exists in a binary mixture of Components A and B. We assume that Components A and B and the AB complex behave as simple particles in the mixture. In other words, we consider an ideal ternary solution of A, B, and AB molecules. Under this assumption, we calculate the number fluctuation in the three-component system, and the result is reduced to the concentration fluctuation $N < (\Delta x_A)^2 >$.

Consider the fluctuations of the quantities, n_A and n_B, of A and B species in a small volume area which contains a constant number, n_{AB}, of the AB complex. The total number of molecules, N, in the volume area under consideration and the mole fraction, x_A, of Component A are expressed as:

$$x_A = (n_A + n_{AB})/N \tag{14}$$

and:

$$N = n_A + 2n_{AB} + n_B \tag{15}$$

From Eq. 14,

$$(\partial x_A/\partial n_A)_{n_B} = x_B/N \tag{16}$$

$$(\partial x_A/\partial n_B)_{n_A} = -x_A/N \tag{17}$$

Therefore,

$$\begin{aligned} dx_A &= (\partial x_A/\partial n_A)_{n_B} dn_A + (\partial x_A/\partial n_B)_{n_A} dn_B \\ &= (x_B/N) dn_A - (x_A/N) dn_B \end{aligned} \tag{18}$$

From Eq. 18, the mean square value of Δx_A is given as:

$$\langle(\Delta x_A)^2\rangle = \frac{x_B^2}{N^2}\langle(\Delta n_A)^2\rangle - 2\frac{x_A x_B}{N^2}\langle\Delta n_A \Delta n_B\rangle + \frac{x_A^2}{N^2}\langle(\Delta n_B)^2\rangle, \tag{19}$$

In order to calculate $< (\Delta n_A)^2 >$, $< \Delta n_A \Delta n_B >$, and $< (\Delta n_B)^2 >$, we define three imaginary mole fractions:

$$x_A' = n_A/N',\ x_B' = n_B/N',\ x_{AB}' = n_{AB}/N' \tag{20}$$

and:

$$N' = n_A + n_{AB} + n_B$$

In an ideal ternary solution of A, B, and AB, the corresponding chemical potentials are given as:

$$\mu_A = \mu_A^\circ + kT \ln x_A',$$

$$\mu_B = \mu_B^\circ + kT \ln x_B',$$

and:

$$\mu_{AB} = \mu_{AB}^\circ + kT \ln x_{AB}' \tag{21}$$

where μ_A°, μ_B°, and μ_{AB}° are the standard chemical potentials. Using the chemical potentials of Eq. 21, the number fluctuations are calculated to be:

$$\begin{aligned} &\langle\Delta n_A\rangle = \langle\Delta n_B\rangle = 0 \\ &\langle(\Delta n_A)^2\rangle = kTF_{BB}/(F_{AA}F_{BB} - F_{AB}^2) \\ &\langle(\Delta n_B)^2\rangle = kTF_{AA}/(F_{AA}F_{BB} - F_{AB}^2) \\ &\langle\Delta n_A \Delta n_B\rangle = -kTF_{AB}/(F_{AA}F_{BB} - F_{AB}^2) \end{aligned} \tag{22}$$

where:

$$F_{AA} \equiv \frac{\partial\mu_A}{\partial n_A},\ F_{BB} \equiv \frac{\partial\mu_B}{\partial n_B},\ F_{AB} \equiv \frac{\partial\mu_A}{\partial n_B} \tag{23}$$

Substituting Eq. 21 into Eq. 23, we obtain:

$$F_{AA} = \frac{kT(n_{AB} + n_B)}{n_A N'}$$

$$F_{BB} = \frac{kT(n_{AB} + n_A)}{n_B N'}$$

$$F_{AB} = \frac{-kT}{N'}$$

$$F_{AA}F_{BB} - F_{AB}^2 = \frac{(kT)^2 n_{AB}}{n_A n_B N'} \tag{24}$$

Now Eq. 22 can be rewritten as:

$$\langle(\Delta n_A)^2\rangle = \frac{n_A(n_A + n_{AB})}{n_{AB}}$$

$$\langle(\Delta n_B)^2\rangle = \frac{n_B(n_B + n_{AB})}{n_{AB}}$$

$$\langle\Delta n_A \Delta n_B\rangle = \frac{n_A n_B}{n_{AB}} \tag{25}$$

The combination of Eq. 19 and 25 leads to:

$$\langle(\Delta x_A)^2\rangle = \frac{1}{N} x_A(1 - x_A)(1 - 2n_{AB}/N)$$

Using the $x_{AB} = n_{AB}/N$ relation, we finally obtain the expression for the concentration fluctuation:

$$N\langle(\Delta x_A)^2\rangle = x_A(1 - x_A)(1 - 2x_{AB}) \tag{26}$$

The x_{AB} can take the values from 0 to 0.5. When no complexes are formed, x_{AB} should be zero. Put $x_{AB} = 0$, then Eq. 26 becomes:

$$N\langle(\Delta x_{\mathrm{A}})^2\rangle = x_{\mathrm{A}}(1-x_{\mathrm{A}})$$

which is identical with Eq. 5. In the case of a complete (1:1) complex formation, x_{AB} can be replaced by either x_{A} or x_{B}. Then Eq. 26 is reduced to:

$$N\langle\Delta(x_{\mathrm{A}})^2\rangle = x_{\mathrm{A}}(1-x_{\mathrm{A}})(1-2x_{\mathrm{A}})$$

which is identical with Eq. 13.

Experimental

In order to check the validity of the present theory, we have to observe the concentration fluctuation from the light-scattering spectra and the association equilibrium constant from infrared-absorption intensities.

Light-Scattering Measurements. The light-scattering spectra were recorded with a spectrometer designed and constructed in our laboratory.[1] The spectrometer is composed of a He-Ne gas laser source (NEC, GLG 108) and a pressure-scanning Fabry-Perot interferometer. The spacer between the interferometer etalons is 6 mm thick, giving a free spectral range of 0.82 cm^{-1} and an over-all instrumental half-width of about 0.042 cm^{-1}. The temperature inside the sample cell was maintained at 25.0±1.0 °C. The samples used in this experiment were commercially available reagents: Diethyl ether used without further purification and chloroform purified by column chromatography on alumina. The binary solutions of diethyl ether and chloroform were made dust-free by the use of a Millipore-filter FG (0.2 μm). The dust-free state was checked by comparing the observed L-P ratio of diethyl ether with the standard L-P ratio; the ratio of 0.41 was obtained by the present experiment, and that of 0.35 by Cummins.[5] The preparation (filtration and injection of a sample into cell) of the sample was repeated three times or more, and the sample which showed the best L-P ratio was used for further experiments. 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 refrative indices measured at $x \pm 0.05$.

Infrared-absorption Measurement. The chloroform-*d* was purchased from the Merck and Co., Ltd., and was dehydrated by zeorite A-3. The diethyl ether was purified by distillation with calcium hydride after the elimination of water by the use of zeorite A-3. The infrared-absorption spectra were recorded with a Perkin-Elmer 180 infrared spectrometer at the temperature of 25±1 °C. A sample cell with NaCl windows was used, and the thickness of a sample was determined by the interference-fringe method. The absorption spectra of the C-D stretching vibration for the frequency region of 2100—2400 cm^{-1} were measured under the resolution of 0.5 cm^{-1} and at the scanning speed of 7.0 cm^{-1}/min.

Results and Discussion

Light-scattering Spectra. The observed spectra for chloroform–diethy lether system are given in Fig. 4. It may be seem from the figure that the intensity of a Rayleigh line increases on passing from pure liquids to the binary solutions. The intensity of Brillouin lines, on the other hand, is largest for pure diethyl ether and smallest for pure chloroform. The intensity of a Rayleigh wing is weak and nearly constant along the frequency axis.

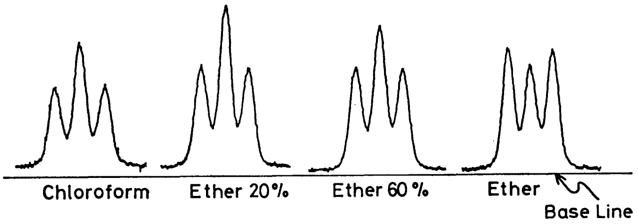

Fig. 4. Observed spectra for chloroform–diethyl ether system at 25 °C.

Concentration Fluctuation. Since the concentration fluctuation contributes only to a Rayleigh line, we can determine the concentration fluctuation from a Rayleigh intensity in a binary solution. In the previous report[2] we have shown the relation between the Rayleigh intensity of the light-scattering spectrum and the concentration fluctuation. The Rayleigh ratio for a Rayleigh line, $(R_{90})_{\mathrm{R}}$, can be written approximately as:

$$(R_{90})_{\mathrm{R}} = \begin{pmatrix}\text{entropy-fluctuation}\\ \text{term}\end{pmatrix} + \begin{pmatrix}\text{concentration-}\\ \text{fluctuation term}\end{pmatrix}$$

Therefore, the concentration fluctuation, $V^*\langle(\Delta x_2)^2\rangle$, is given by:

$$V^*\langle(\Delta x_2)^2\rangle = (\lambda_{\mathrm{i}}^4/\pi^2)\frac{1}{4n^2(\partial n/\partial x_2)^2_{T,P}}\{(R_{90})_{\mathrm{R}}-(R_{90})_{\mathrm{S}}\}, \quad (27)$$

where V^* is the fluctuation volume; x_2, the mole fraction of Component 2; λ_{i}, the wavelength of the incident light, and n, the refractive index. $(R_{90})_{\mathrm{S}}$ is the Rayleigh ratio for entropy fluctuation and is given by:

$$(R_{90})_{\mathrm{S}} = (\pi^2/\lambda_{\mathrm{i}}^4)\frac{4kn^2T^2}{C_{\mathrm{Pg}}\rho}(\partial n/\partial T)^2_{P,x_2} \quad (28)$$

where C_{pg} is the isobar heat capacity per gram, and ρ, the density.

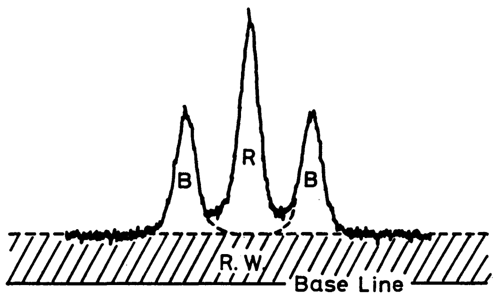

Fig. 5. Separation of Rayleigh line from light scattering spectra (schematic). R: Rayleigh line. B: Brillouin line. R.W.: Rayleigh wing.

The procedure of separating a Rayleigh line from Brillouin lines and a Rayleigh wing is illustrated in Fig. 5. 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 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.

Since the observed Rayleigh intensities are relative values, we have to express the observed relative intensities, I_{R}, in terms of Rayleigh ratios. A Rayleigh ratio is defined as Ir^2/I_0V_{S}, where I_0 is the incident-light intensity; I, the scattered-light intensity; r, the distance from scattering point to observing point, and V_{S}, the scattering volume. We first calculate $(R_{90})_{\mathrm{S}}^{\mathrm{CHCl_3}}$ for pure

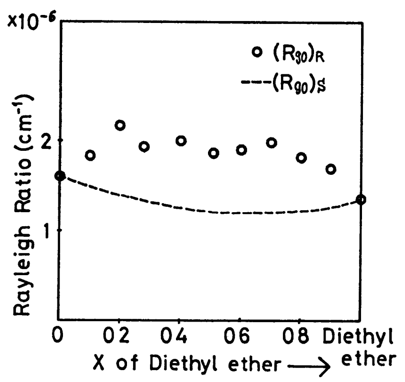

Fig. 6. Concentration dependence of Rayleigh intensity of chloroform–diethyl ether system. The open circles corresponds to $(R_{90})_R$ and the broken line $(R_{90})_S$.

chloroform by the use of Eq. 28. Then, the Rayleigh ratio for binary mixtures, $(R_{90})_R$, is calculated to be:

$$(R_{90})_R = I_R \times \frac{(R_{90})_S^{CHCl_3}}{I_R^{CHCl_3}} \tag{29}$$

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

The theoretical values of $(R_{90})_S$ at each mole fraction were calculated by substituting the observed values of λ_i, n, T, ρ, and $(\partial n/\partial T)_{p,x_2}$, and C_{pg} values from the standard table[6] into Eq. 28 (see Table 1). Then, the fluctuation ability, $V^*\langle(\Delta x_2)^2\rangle$, was calculated at each concentration from Eq. 27. The calculated $V^*\langle(\Delta x_2)^2\rangle$ values are plotted by open circles in Fig. 7. The dashed line of Fig. 7 corresponds to the concentration fluctuation expected for an ideal binary solution. The procedure of converting $N\langle(\Delta x_2)^2\rangle$ into $V^*\langle(\Delta x_2)^2\rangle$ will be described later. It may be seen from the figure that the observed concentration fluctuation is smaller than that expected for an ideal binary solution throughout all concentrations. This tendency indicates the existence of molecular association, not between the same species (see Case I and II), but between different species (see Case III), in this mixture. Therefore, we will try to explain the observed concentration-fluctuation curve by the use of Eq. 26, because association equilibrium is taken into account in Eq. 26.

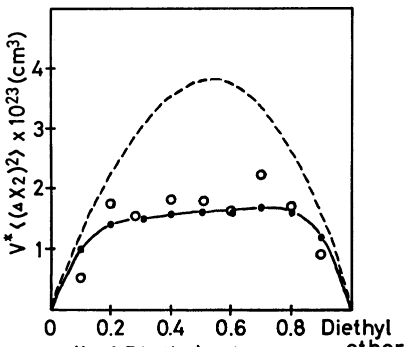

Fig. 7. Concentration dependence of concentration fluctuation for chloroform–diethyl ether system at 25 °C: ---; expected for an ideal binary solution, ○; observed by light scattering spectra, —●—●—; calculated from Eq. 26 by the use of the infrared data.

Determination of the Relative Population of (1: 1) Complex by Infrared-Absorption Measurements. The relative population of (1: 1) complex, x_{AB}, can be determined from the infrared-absorption-intensity measurement of the C-D stretching band (ν_1) of chloroform-*d*, because the ν_1 band increases in intensity in a diethyl ether solution by the formation of hydrogen bonding between chloroform-*d* and diethyl ether. The relative intensity of the ν_1 band of the chloroform-*d* in solution is defined as:

$$I_S = \frac{f_d}{l}\int_{\text{band}} \ln (I_0/I)\,\mathrm{d}(\ln \nu) \tag{30}$$

in cm^{-1}, and the absolute intensities of the ν_1 bands of free and bonded chloroform-d are defined, respectively, as:

$$\Gamma_F = \frac{f_d}{C_F l}\int_{\text{band}} \ln (I_0/I)\,\mathrm{d}(\ln \nu) \tag{31}$$

and:

$$\Gamma_B = \frac{f_d}{C_B l}\int_{\text{band}} \ln (I_0/I)\,\mathrm{d}(\ln \nu) \tag{32}$$

in (cm^2/mole), where l is the thickness of the sample; C_F and C_B, the concentrations in moles per cm^3; I_0, the energy of the incident light; I, the energy of the transmitted light, and ν, the frequency of the light, and where the integration covers the whole band area. The subscript "B" refers to the chloroform-*d* forming a complex or to an associated complex. The f_d factor is

TABLE 1. EVALUATION OF CONCENTRATION FLUCTUATION FROM LIGHT-SCATTERING SPECTRA FOR THE DIETHYL ETHER–CHLOROFORM SYSTEM

Mole fraction of $(C_2H_5)_2O$	$(R_{90})_R$ (cm^{-1}) (25°C)	$(R_{90})_S$ (cm^{-1}) (25°C)	$\{(R_{90})_R-(R_{90})_S\}$ (cm^{-1})	n_D^{25}	$(\partial n/\partial x)_{T,P}$ (24°C)	$V^*\langle(\Delta x_2)^2\rangle$ (cm^3)
0	1.60×10^{-6}	1.60×10^{-6}	$0\ \times10^{-6}$	1.4431	—	$—\times10^{-23}$
0.096	1.83	1.49	0.34	1.4345	0.105	0.60
0.198	2.16	1.40	0.76	1.4244	0.093	1.78
0.282	1.93	1.33	0.60	1.4168	0.089	1.54
0.395	1.99	1.26	0.73	1.4066	0.090	1.83
0.512	1.86	1.22	0.64	1.3980	0.086	1.79
0.597	1.90	1.22	0.67	1.3896	0.094	1.63
0.700	1.98	1.22	0.75	1.3810	0.085	2.23
0.802	1.82	1.24	0.58	1.3727	0.086	1.70
0.902	1.70	1.26	0.44	1.3621	0.106	0.88
1.000	1.35	1.27	0.08	1.3496	—	—

introduced to consider the intensity correction for the local-field effect,[7] which is defined as:

$$f_d = \frac{9n_D}{(n_D^2+2)^2} \tag{33}$$

where n_D is the refractive index of the sample. The three intensity parameters, I_S, Γ_F, and Γ_B, are related with each other as:

$$I_S = C_F\Gamma_F + C_B\Gamma_B \tag{34}$$

When chloroform-*d* and diethyl ether form a (1:1) complex, the analytical concentrations of free chloroform-*d* and diethyl ether, $C_F°$ and $C_E°$, are related to the equilibrium concentrations by:

$$C_F = C_F^\circ - C_B \tag{35}$$

$$C_E = C_E^\circ - C_B \tag{36}$$

where C_E is the equilibrium concentration of diethyl ether. Notice that weak hydrogen bonding between chloroform-d molecules is neglected. Equations 34 and 35 are then combined to give:

$$I_S = C_F^\circ\Gamma_F + (\Gamma_B - \Gamma_F)C_B \tag{37}$$

Γ_F is directly measured in pure chloform-*d*, and I_S, in solution. As the frequency shift of the ν_1 band due to hydrogen bonding is about 10 cm^{-1}, ν_1 bands corresponding to the free and the bonded states overlap greatly with each other. Therefore, Γ_B cannot be determined directly from the intensity measurement of the ν_1 band corresponding to the bonded state. The value of Γ_B was obtained from the slope of the plots of I_S against $C_F°$ in the low-concentration range of $C_F°$ (see Fig. 8). It is assumed here that all the chloroform-*d* molecules are hydrogen-bonded in the low-concentration range of $C_F°$. The Γ_B value of 1360 (cm^2/mol) and the Γ_F value of 109 (cm^2/mol) were obtained in the present work. As $C_F°$ is known, C_B can be determined from I_S, Γ_F, Γ_B, and $C_F°$ with the help of Eq. 37. C_B is reduced to x_{AB} as:

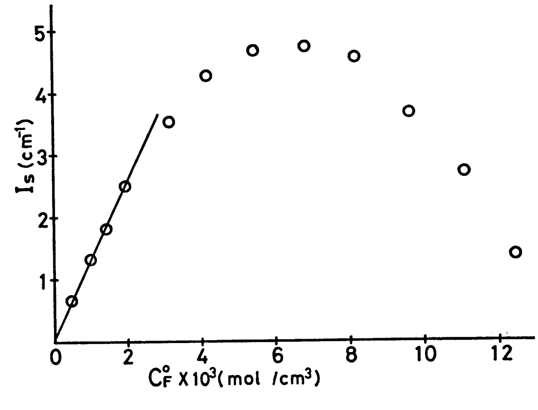

Fig. 8. I_S *vs.* $C_F°$ plot for the chloroform-*d*-diethyl ether system.

$$x_{AB} = \frac{C_B}{C_F^\circ + C_E^\circ} \tag{38}$$

Thus, we determined the relative population of the x_{AB} complex from the infrared-absorption measurements (see the 2nd column of Table 2).

TABLE 2. EVALUATION OF CONCENTRATION FLUCTUATION FROM Eq. 26 BY THE USE OF THE INFRARED DATA FOR THE DIETHYL ETHER–CHLOROFORM SYSTEM

x_A[a)]	x_{AB}	$N\langle(\Delta x_A)^2\rangle$	$V^*\langle(\Delta x_A)^2\rangle$ (cm^3)
0.10	0.10	0.072	0.99×10^{-23}
0.20	0.18	0.102	1.43
0.30	0.25	0.105	1.51
0.40	0.28	0.106	1.56
0.51	0.29	0.105	1.60
0.61	0.28	0.105	1.63
0.70	0.24	0.109	1.74
0.81	0.18	0.098	1.61
0.90	0.10	0.072	1.22

a) The subscript "A" refers to diethyl ether.

Comparison of Observed and Calculated $V^*\langle(\Delta x_2)^2\rangle$. As x_{AB} is obtained experimentally, $N\langle(\Delta x_2)^2\rangle$ can be calculated from Eq. 26. $N\langle(\Delta x_2)^2\rangle$ is related to $V^*\langle(\Delta x_2)^2\rangle$ by this relation:

$$V^*\langle(\Delta x_2)^2\rangle = \frac{N}{\rho_n}\langle(\Delta x_2)^2\rangle = \frac{N}{(\rho/M_{AV.})N_A}\langle(\Delta x_2)^2\rangle \tag{39}$$

and:

$$M_{AV.} = x_{ether}M_{ether} + x_{CHCl_3}M_{CHCl_3} \tag{40}$$

where ρ_n is the number density; N_A, Avogadro's number; x_{ether} and x_{CHCl_3}, the mole fractions of diethyl ether and chloroform respectively, and M_{ether} and M_{CHCl_3}, the molecular weights. In Fig. 7 the $V^*\langle(\Delta x_2)^2\rangle$ values calculated from Eqs. 39 and 40, using x_{AB} values determined by the infrared-intensity measurements, are compared with those obtained from the light-scattering data. It may be seen from the figure that these two sets of $V^*\langle(\Delta x_2)^2\rangle$ values agree quite well; this shows the validity of the present theoretical treatment of the concentration fluctuation.

Concluding Discussion. The present theoretical study has shown that the concentration dependence of the concentration fluctuation in a binary solution is quite sensitive to the formation of local structures or intermolecular interactions. If molecules of same chemical species have a tendency to get together, the concentration fluctuation takes larger values than those in an ideal binary solution. On the other hand, if molecules of different chemical species have a tendency to get together, the concentration fluctuation takes smaller values than those in an ideal binary solution. For a binary solution of chloroform–diethyl ether, the theoretical treatment corresponds to the calculation of the concentration fluctuation in a ternary solution. The pivotal point of the theory is the introduction of the shape and the number population of an associated complex. In the case of a chloroform–diethyl ether system, the shape and the number population can be determined by means of the infrared-absorption spectra. The very good agreement between the concentration fluctuation observed by the light-scattering spectra and the concentration fluctuation calculated using the infrared data shows that intensity measurements of light-scattering spectra can determine the shape and the number population of an associated complex which is formed in a binary solution. It must be emphasized that the concept of an associated complex was introduced so as to simplify the theoretical treatment; therefore, the concept of complex formation is a rather fictitious concept. In other words, the present theory postulates the usefulness of light-scattering measurements for the study of local structures which are formed in solutions by intermolecular interactions between component molecules.

References

1) K. Iwasaki, M. Tanaka, and T. Fujiyama, *Bunko Kenkyu*, **25**(3), 134 (1976).
2) K. Iwasaki, M. Tanaka, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **49**, 2719 (1976).
3) T. Fujiyama, M. Kakimoto, and T. Suzuki, *Bull. Chem. Soc. Jpn.*, **49**, 606 (1976).
4) L. D. Landau and E. M. Lifshitz, "Statistical Physics," Pergamon Press, London (1958).
5) H. Z. Cummins and R. W. Gammon, *J. Chem. Phys.*, **44**, 2785 (1966).
6) "International Critical Tables," McGraw-Hill, New York (1926).
7) S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **23**, 2376 (1955).