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Light Scattering Study of Local Structures in Solutions. Cooperative Translational Motion of Alcohol Molecules in Carbon Tetrachloride Solutions

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The concept of a "moving unit"—a group of molecules which move together for the time much longer than the velocity auto-correlation time, τ—was introduced in order to obtain information about cooperative translational motions of molecules in associated solution. The mutual diffusion coefficient was theoretically expressed in terms of the self diffusion coefficients and the number of moving units. The theoretical results were applied to the study of the mutual diffusion coefficients for methanol–carbon tetrachloride and ethanol–carbon tetrachloride solutions measured by Rayleigh scattering. It was shown that the mean number of alcohol molecules which constitute a moving unit is much smaller than the mean association number of alcohol, especially in the high concentration range of alcohol. This indicates that the hydrogen-bonded polymer of alcohol molecules cannot move without changing the polymer shape within the time τ.

Local fluctuations of concentration afford information which is useful for understanding the mixing of liquids from a molecular viewpoint. As the mean-square amplitude of concentration fluctuations is related to the spatial correlation between the positions of different molecules, it affords information about the local structure formation in solution. In the previous reports, we have discussed the local structures in various solutions on the basis of the quantitative analysis of the mean-square concentration fluctuation obtained from the Rayleigh scattering intensities.[1-8] The local structures were expressed in terms of the ordinary mean association number.

In order to discuss the state of mixing from a dynamical standpoint, however, the life-time of local structures should be taken into account in addition to the mean association number. Here, we define the "life-time" as the time during which the relative positions of molecules in a local structure change very little. The correlation time of concentration fluctuations, which is specified by a mutual diffusion coefficient, is considered to afford information about the life-time of the local structure. It is not possible, however, to obtain the life-time of the local structure directly from the mutual diffusion coefficient because too many parameters are necessary for the description of collective motions of molecules.

In the present report, we propose the existence of a group of molecules which move together for the time much longer than the velocity auto-correlation time of component molecules. We call this group of molecules a "moving unit." The mutual diffusion coefficient, which is obtained from the analysis of the Rayleigh scattering spectrum, can be expressed in terms of the number of moving units.

Binary solutions of methanol–carbon tetrachloride and ethanol–carbon tetrachloride were chosen as appropriate systems in which to determine the existence of such moving units. In these systems, the mean association numbers of hydrogen-bonded alcohol molecules increase with increasing alcohol concentration. Our main interest is to know whether these hydrogen-bonded alcohol molecules can be a moving unit particularly in the high concentration range of alcohols.

Theoretical

Mutual Diffusion Coefficient and Molecular Velocity Correlation. The spectrum of the Rayleigh light isotropically scattered by a binary solution can be approximated by two Lorentzian curves.[9] One of these corresponds to the scattering arising from the entropy fluctuations and the other to that from concentration fluctuations. Since the half-width of the latter spectrum is narrower than that of the former by a factor of about a hundred, these two curves can be identified separately, even though the band centers are overlapped. The spectrum for concentration fluctuations is expressed as[9]

$$I_c(k,\omega) \propto \frac{|k|^2 D}{\omega^2+(|k|^2D)^2} \tag{1}$$

where k is the scattering vector and D is the mutual diffusion coefficient. The time correlation function for concentration fluctuations is related to D:

$$\frac{\langle \Delta c(k,t)\Delta c(k,0)\rangle}{\langle|\Delta c(k)|^2\rangle} = \exp(-|k|^2Dt) \tag{2}$$

$$\Delta c(k,t) \equiv \int_v [c(r,t)-\langle c\rangle]e^{ik\cdot r}d^3r \tag{3}$$

when temperature and pressure fluctuations are disregarded.[10] In Eqs. 2 and 3, $c(r,t)$ is the concentration at the point r at time t in the scattering volume V and the pointed brackets indicate an equilibrium ensemble average.

D is expressed in terms of the time derivative of $\Delta c(k,t)$:[11]

$$D = \lim_{s\to 0}\lim_{k\to 0}\frac{1}{|k|^2}\frac{1}{\langle|\Delta c(k)|^2\rangle}\int_0^\infty \langle \Delta\dot{c}(k,t)\Delta\dot{c}(k,0)\rangle e^{-st}dt. \tag{4}$$

We now consider a binary solution whose components are molecules A and B. If the concentration is expressed in the mole fraction of A, $\Delta X_A(r,t)$ can be approximately expressed as

$$\Delta X_A(k,t) = -\frac{i}{\rho}k\cdot[X_B J_A(k,t) - X_A J_B(k,t)] \tag{5}$$

with

$$\boldsymbol{J}_{\mathrm{A}}(\boldsymbol{k},t)=\sum_{\mathrm{a}}^{n_{\mathrm{A}}}\boldsymbol{v}_{\mathrm{a}}(t)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{\mathrm{a}}(t)}$$

$$\boldsymbol{J}_{\mathrm{B}}(\boldsymbol{k},t)=\sum_{\mathrm{b}}^{n_{\mathrm{B}}}\boldsymbol{v}_{\mathrm{b}}(t)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{\mathrm{b}}(t)} \tag{6}$$

where ρ is the number density, X_{A} and X_{B} are the mean mole fractions of A and B, respectively, and n_{A} and n_{B} are the mean numbers of molecules A and B in V, respectively. $\boldsymbol{v}_{\mathrm{a}}(t)$ is the velocity of an a-th molecule of A, and $\boldsymbol{v}_{\mathrm{b}}(t)$ that of a b-th molecule of B at time t. In the limit of small $|\boldsymbol{k}|$, $\langle|\Delta X_{\mathrm{A}}(\boldsymbol{k})|^2\rangle$ can be written as

$$\lim_{\mathrm{k}\to 0}\langle|\Delta X_{\mathrm{A}}(\boldsymbol{k})|^2\rangle=\frac{V}{\rho}N\langle(\Delta X_{\mathrm{A}})^2\rangle \tag{7}$$

where N is the mean number of total molecules in a region which is very large compared to the distances between molecules and X_{A} is the concentration fluctuation in the region. Substituing Eqs. 5—7 into Eq. 4, we can obtain

$$D=Q[X_{\mathrm{B}}\{V_{\mathrm{aa}}+(n_{\mathrm{A}}-1)V_{\mathrm{aa'}}\}+X_{\mathrm{A}}\{V_{\mathrm{bb}}+(n_{\mathrm{B}}-1)V_{\mathrm{bb'}}\}-2(n_{\mathrm{A}}+n_{\mathrm{B}})X_{\mathrm{A}}X_{\mathrm{B}}V_{\mathrm{ab}}] \qquad (\mathrm{a}\neq\mathrm{a'}\ \ \mathrm{b}\neq\mathrm{b'}) \tag{8}$$

with

$$Q=\frac{X_{\mathrm{A}}X_{\mathrm{B}}}{N\langle(\Delta X_{\mathrm{A}})^2\rangle} \tag{9}$$

$$V_{\mathrm{ij}}=\frac{1}{3}\int_0^\infty\langle\boldsymbol{v}_{\mathrm{i}}(t)\cdot\boldsymbol{v}_{\mathrm{j}}(0)\rangle\mathrm{d}t \tag{10}$$

where i and j represent a, a', b, or b'. Q is a so-called thermodynamic factor expessed in terms of mean-square concentration fluctuations, $N\langle(\Delta X_{\mathrm{A}})^2\rangle$, which can be obtained by analyzing integrated intensities of Rayleigh scattering spectra.[1] $(X_{\mathrm{A}}X_{\mathrm{B}})$ is the magnitude of $N\langle(\Delta X_{\mathrm{A}})^2\rangle$ expected for an ideal binary solution. It can be seen from Eq. 10 that V_{aa} and V_{bb} correspond to the self diffusion coefficients of A and B, respectively;

$$V_{\mathrm{aa}}=D_{\mathrm{A}}\qquad V_{\mathrm{bb}}=D_{\mathrm{B}} \tag{11}$$

$V_{\mathrm{aa'}}$, $V_{\mathrm{bb'}}$, and V_{ab} are related to the velocity correlations between different molecules. In the case where these pair-correlations are negligible, D can be written as

$$D=Q(X_{\mathrm{B}}D_{\mathrm{A}}+X_{\mathrm{A}}D_{\mathrm{B}}). \tag{12}$$

Moving Unit and Diffusion Coefficient. We consider a solution in which strong intermolecular interactions such as hydrogen bonding exist. In such a solution, the velocities of these interacting molecules are expected to be strongly correlated, that is, $V_{\mathrm{aa'}}$, $V_{\mathrm{bb'}}$ and V_{ab} can not be neglected. It is very difficult to express these quantities in terms of microscopic parameters such as intermolecular forces. Instead of studying the details of these dynamical interactions, we assume that some numbers of molecules move together as a group for a time much longer than the velocity auto-correlation time. We call this group of molecules a "moving unit." In the binary solution of A and B molecules, moving units can be represented by A_l, B_m, and $\mathrm{A}_l\mathrm{B}_m$ where l or m is the number of molecules A or B which constitutes a moving unit. We further assume that the velocity correlation between molecules belonging to different moving units can be neglected, because it is much smaller than the velocity correlation between molecules belonging to the same moving unit. Then, the velocity correlation function can be written as

$$\langle\boldsymbol{v}_{\mathrm{i}}(t)\cdot\boldsymbol{v}_{\mathrm{i}}(0)\rangle=\sum_\alpha P_{\mathrm{i}}^\alpha\langle\boldsymbol{v}_{\mathrm{i}}^\alpha(t)\cdot\boldsymbol{v}_{\mathrm{i}}^\alpha(0)\rangle \tag{13}$$

$$\langle\boldsymbol{v}_{\mathrm{i}}(t)\cdot\boldsymbol{v}_{\mathrm{j}}(0)\rangle=\sum_\alpha P_{\mathrm{ij}}^\alpha\langle\boldsymbol{v}_{\mathrm{i}}^\alpha(t)\cdot\boldsymbol{v}_{\mathrm{j}}^\alpha(0)\rangle=\sum_\alpha P_{\mathrm{ij}}^\alpha\langle\boldsymbol{v}_{\mathrm{i}}^\alpha(t)\cdot\boldsymbol{v}_{\mathrm{i}}^\alpha(0)\rangle \tag{14}$$

(i, j=a, a', b, or b')

where P_{i}^α is the probability of finding an i-th molecule in a moving unit α ($\alpha=\mathrm{A}_l$ *etc.*), P_{ij}^α the probability of finding both the i-th and the j-th molecule belonging to α, and v_{i}^α is the velocity of an i-th molecule belonging to α. Under these assumptions, V_{ij} in Eq. 8 is expressed as

$$\begin{aligned}
V_{\mathrm{aa}}&=D_{\mathrm{A}}=\sum_l P_{\mathrm{a}}^{\mathrm{A}l}D_{\mathrm{A}l}+\sum_l\sum_m P_{\mathrm{a}}^{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\\
V_{\mathrm{bb}}&=D_{\mathrm{B}}=\sum_l P_{\mathrm{b}}^{\mathrm{B}l}D_{\mathrm{B}l}+\sum_l\sum_m P_{\mathrm{b}}^{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\\
V_{\mathrm{aa'}}&=\sum_l P_{\mathrm{aa'}}^{\mathrm{A}l}D_{\mathrm{A}l}+\sum_l\sum_m P_{\mathrm{aa'}}^{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\\
V_{\mathrm{bb'}}&=\sum_l P_{\mathrm{bb'}}^{\mathrm{B}l}D_{\mathrm{B}l}+\sum_l\sum_m P_{\mathrm{bb'}}^{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\\
V_{\mathrm{ab}}&=\sum_l\sum_m P_{\mathrm{ab}}^{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}
\end{aligned} \tag{15}$$

with

$$D_\alpha=\frac{1}{3}\int_0^\infty\langle\boldsymbol{v}_{\mathrm{i}}^\alpha(t)\cdot\boldsymbol{v}_{\mathrm{i}}^\alpha(0)\rangle\mathrm{d}t \tag{16}$$

$$\begin{aligned}
P_{\mathrm{a}}^{\mathrm{A}l}&=n_{\mathrm{A}l}\frac{l}{n_{\mathrm{A}}}\qquad P_{\mathrm{aa'}}^{\mathrm{A}l}=n_{\mathrm{A}l}\frac{l}{n_{\mathrm{A}}}\frac{l-1}{n_{\mathrm{A}}-1}\\
P_{\mathrm{b}}^{\mathrm{B}l}&=n_{\mathrm{B}l}\frac{l}{n_{\mathrm{B}}}\qquad P_{\mathrm{bb'}}^{\mathrm{B}l}=n_{\mathrm{B}l}\frac{l}{n_{\mathrm{B}}}\frac{l-1}{n_{\mathrm{B}}-1}\\
P_{\mathrm{aa'}}^{\mathrm{A}l\mathrm{B}m}&=n_{\mathrm{A}l\mathrm{B}m}\frac{l}{n_{\mathrm{A}}}\frac{l-1}{n_{\mathrm{A}}-1}\\
P_{\mathrm{bb'}}^{\mathrm{A}l\mathrm{B}m}&=n_{\mathrm{A}l\mathrm{B}m}\frac{m}{n_{\mathrm{B}}}\frac{m-1}{n_{\mathrm{B}}-1}\\
P_{\mathrm{ab}}^{\mathrm{A}l\mathrm{B}m}&=n_{\mathrm{A}l\mathrm{B}m}\frac{l}{n_{\mathrm{A}}}\frac{m}{n_{\mathrm{B}}}.
\end{aligned} \tag{17}$$

Substitution of Eqs. 15—17 into Eq. 8 yields the following equation:

$$D=Q\left[\frac{X_{\mathrm{B}}}{n_{\mathrm{A}}}\left(\sum_l l^2n_{\mathrm{A}l}D_{\mathrm{A}l}+\sum_l\sum_m l^2n_{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\right)+\frac{X_{\mathrm{A}}}{n_{\mathrm{B}}}\left(\sum_l l^2n_{\mathrm{B}l}D_{\mathrm{B}l}+\sum_l\sum_m m^2n_{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\right)-\frac{2}{n_{\mathrm{A}}+n_{\mathrm{B}}}\sum_l\sum_m lmn_{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\right] \tag{18}$$

and

$$\begin{aligned}
D_{\mathrm{A}}&=\frac{1}{n_{\mathrm{A}}}\left(\sum_l ln_{\mathrm{A}l}D_{\mathrm{A}l}+\sum_l\sum_m ln_{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\right)\\
D_{\mathrm{B}}&=\frac{1}{n_{\mathrm{B}}}\left(\sum_l ln_{\mathrm{B}l}D_{\mathrm{B}l}+\sum_l\sum_m mn_{\mathrm{A}l\mathrm{B}m}D_{\mathrm{A}l\mathrm{B}m}\right).
\end{aligned} \tag{19}$$

Moving Units in Alcohol–Carbon Tetrachloride System. In the binary solutions of methanol(A)–carbon tetrachloride(B) and ethanol(A)–carbon tetrachloride(B), the existence of the moving unit of A_l-type is expected. In this case, Eq. 18 is reduced to

$$D=Q(X_{\mathrm{B}}D'_{\mathrm{A}}+X_{\mathrm{A}}D_{\mathrm{B}}) \tag{20}$$

with

$$D'_{\mathrm{A}} \equiv \frac{\sum_l l^2 n_{\mathrm{A}l} D_{\mathrm{A}l}}{\sum_l l n_{\mathrm{A}l}} = \frac{\sum_l l^2 n_{\mathrm{A}l} D_{\mathrm{A}l}}{\sum_l l n_{\mathrm{A}l} D_{\mathrm{A}l}} D_{\mathrm{A}}. \tag{21}$$

$D_{\mathrm{A}l}$ is written as

$$D_{\mathrm{A}l} = \frac{1}{3}\langle|\boldsymbol{v}_{\mathrm{A}l}|^2\rangle\tau_{\mathrm{A}l} \tag{22}$$

with

$$\tau_{\mathrm{A}l} = \int_0^\infty \frac{\langle \boldsymbol{v}_{\mathrm{A}l}(t)\cdot\boldsymbol{v}_{\mathrm{A}l}(0)\rangle}{\langle|\boldsymbol{v}_{\mathrm{A}l}|^2\rangle} \mathrm{d}t. \tag{23}$$

In the above equations, $\langle|\boldsymbol{v}_{\mathrm{A}l}{}^2|\rangle$ is expected to be inversely proportional to l at constant temperature, because this relation holds:

$$\frac{1}{2}M_{\mathrm{A}l}\langle|\boldsymbol{v}_{\mathrm{A}l}|^2\rangle \propto T \tag{24}$$

where $M_{\mathrm{A}l}$ is the mass of the moving unit A_l ($\propto l$) and T is the temperature. If we assume $\tau_{\mathrm{A}l}$ is independent of l, we have

$$D_{\mathrm{A}l} \propto \frac{1}{l}. \tag{25}$$

Substituting Eq. 25 into Eq. 21, we obtain

$$D = Q[X_{\mathrm{B}}D_{\mathrm{A}}\langle l\rangle_{\mathrm{n}}^{\mathrm{d}} + X_{\mathrm{A}}D_{\mathrm{B}}] \tag{26}$$

$$\langle l\rangle_{\mathrm{n}}^{\mathrm{d}} \equiv \frac{\sum_l l n_{\mathrm{A}l}}{\sum_l n_{\mathrm{A}l}} \tag{27}$$

where $\langle l\rangle_{\mathrm{n}}^{\mathrm{d}}$ is the mean number of A molecules which constitute one moving unit. By substituting the experimentally observed values for D, Q, D_{A}, and D_{B} into Eq. 26, we can obtain the $\langle l\rangle_{\mathrm{n}}^{\mathrm{d}}$ value at each concentration.

Experimental

The light scattering spectrometer (heterodyne detection) used in the present study was designed and constructed in our laboratory.[12] The light source was an Argon ion laser (Spectra-Physics model 165-09) which produced 100-800 mW power at 488 nm. The scattering angle, θ, was defined by two pinholes approximately 50 cm apart and 0.5 mm in diameter. The laser beam was focused into a rectangular scattering cell. Scattered light and a local oscillator beam (scattered from the cell walls) were collected onto the surface of a photomultiplier tube (HTV R-374). The photocurrent was amplified and then fed to a spectrum analyzer (Takeda-Riken TR 4120S). This analyzer is designed for the analysis of the spectral region 50 Hz-30 MHz. Details of the spectrometer have been reported elsewhere along with the reliability of the observed data.[12]

Light scattering spectra were observed by using this spectrometer at the temperature of 24 ± 0.5 °C in the scattering angle range of $6°\leq\theta\leq11°$.

All the chemicals were commerical products. The sample solutions were made dust-free by the use of a millipore filter FG of 0.2 μm pore size.

Results and Discussion

Light Beating Spectra and Mutual Diffusion Coefficients. Figure 1 shows a typical example of an observed spectrum. All spectra were found to fit a Lorentzian. By plotting the observed half-widths against $|\boldsymbol{k}|^2$, the theoretical prediction of linear dependence of a half-width on $|\boldsymbol{k}|^2$ was confirmed. A mutual diffusion coefficient was obtained from the slope of the linear plot. The mutual diffusion coefficients thus obtained are plotted against the mole fractions of methanol and ethanol, respectively, in Figs. 2 and 3 (see the circles). The dashed lines in these figures indicate the mutual diffusion coefficients calculated for Eq. 12, where Q is obtained from the observed values of $N\langle(\Delta X_{\mathrm{A}})^2\rangle$ reported elsewhere.[8] Literature values were used for D_{A} and D_{B}.[13,14] It is seen from these figures that the observed values of diffusion coefficients are larger than those predicted from Eq. 12. This disagreement between the observed and theoretical values shows that velocity pair-correlation between different molecules cannot be neglected. As the observed values are larger than the

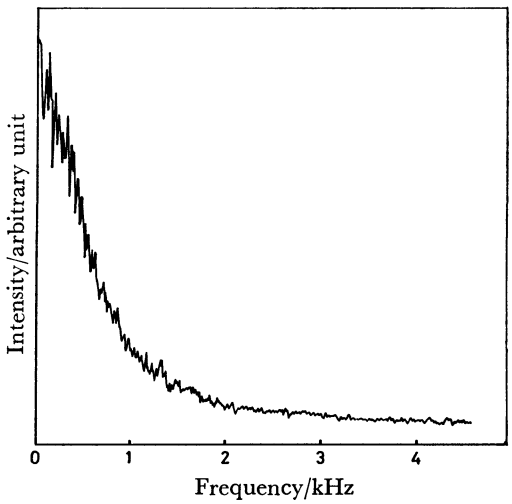

Fig. 1. Heterodyne beating spectrum of light scattered by methanol–carbon tetrachloride solution (0.3 mole fraction of methanol). Scattering angle is 7.25°.

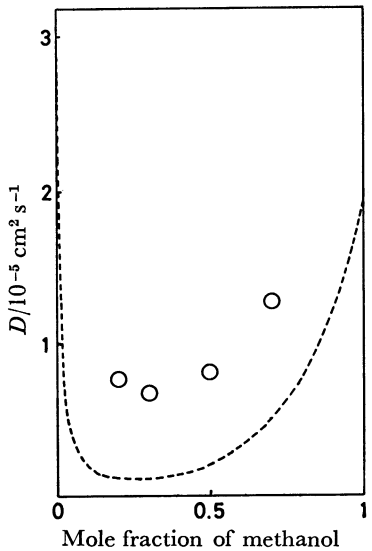

Fig. 2. Observed mutual diffusion coefficients for methanol–carbon tetrachloride system (○).
The dashed line corresponds to mutual diffusion coefficients calculated from Eq. 12.

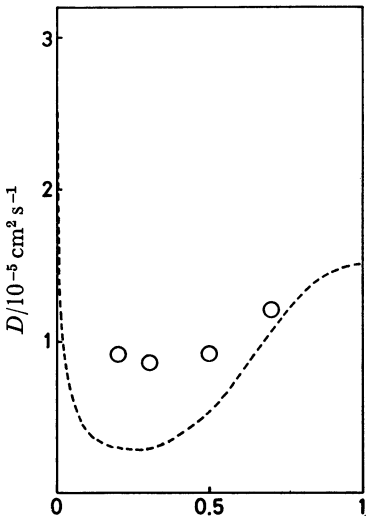

Fig. 3. Observed mutual diffusion coefficients for ethanol–carbon tetrachloride system (○). The dashed line corresponds to mutual diffusion coefficients calculated from Eq. 12.

theoretical ones, it can also be concluded that the velocity correlations between the molecules of the same species are stronger than between those of different species.

Moving Units and Mean Association Numbers in Alcohol–Carbon Tetrachloride System. The mean numbers, $\langle l\rangle_n^d$, were obtained from Eq. 26 using the observed mutual diffusion coefficients, D, the observed diffusion coefficients, D_A and D_B, and the observed mean-square concentration fluctuations, $N\langle(\Delta X_A)^2\rangle$. In Figs. 4 and 5 the mean numbers, $\langle l\rangle_n^d$, thus obtained are plotted against the mole fraction of alcohol for the methanol–carbon tetrachloride and ethanol–carbon tetrachloride systems, respectively.

In a previous paper,[8] we have analyzed the observed

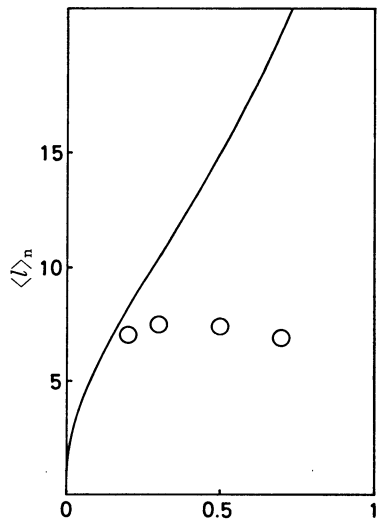

Fig. 4. Comparison of $\langle l\rangle_n^d$ (○) with $\langle l\rangle_n^p$ (——) for methanol–carbon tetrachloride system.

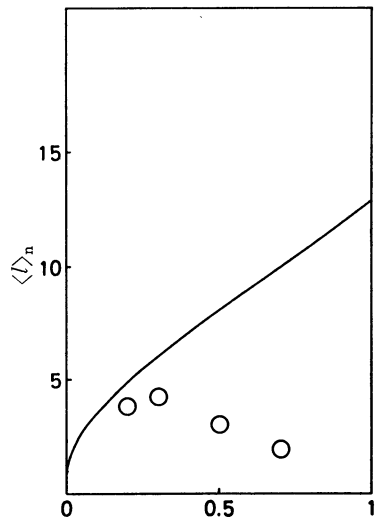

Fig. 5. Comparison of $\langle l\rangle_n^d$ (○) with $\langle l\rangle_n^p$ (——) for ethanol–carbon tetrachloride system.

mean-square concentration fluctuations, $N\langle(\Delta X_A)^2\rangle$, by using the polymer chain model. In this model, a group of hydrogen-bonded alcohol molecules is treated as a polymer chain whose length is proportional to the association number of alcohol molecules. The solid lines in Figs. 4 and 5 shows the mean association numbers[15]

$$\langle l\rangle_n^p = \sum_l l n_{Al}^p / \sum_l n_{Al}^p$$

obtained from the above analysis, where n_{Al} is the mean number of alcohol l-mers (A_l). An "l-mer" is defined here as a group of l number of alcohol molecules which are linked by $(l-1)$ hydrogen bonds. We cannot obtain information about the life-time of local structures from $\langle l\rangle_n^p$ because the definition of an "l-mer" does not include the concept of life-time. On the other hand, $\langle l\rangle_n^d$ is the mean number of alcohol molecules which can move together for a time much longer than the velocity auto-correlation time. Therefore, $\langle l\rangle_n^d$ may be called a "dynamical mean association number." These two quantities, $\langle l\rangle_n^d$ and $\langle l\rangle_n^p$, are not necessarily equal in magnitude, as can be understood from their definitions.

It is seen from Figs. 4 and 5 that $\langle l\rangle_n^d$ is only slightly smaller than $\langle l\rangle_n^p$ in the low concentration range of alcohol. As the alcohol concentration increases, however, the difference becomes very large. If all the hydrogen-bonded polymers of alcohol molecules can move for a time much longer than the velocity auto-correlation time without changing the polymer shape, each polymer can be regarded as a moving unit. Then, $\langle l\rangle_n^d$ is expected to be equal to $\langle l\rangle_n^p$. The above results indicate that a linear hydrogen-bonded polymer of alcohol molecules cannot always be a moving unit, especially in the high concentration range of alcohol. The difference between $\langle l\rangle_n^d$ and $\langle l\rangle_n^p$ may be explained as follows. Consider the velocity correlation between two alcohol molecules which form a polymer. If these two molecules are adjacent to each other, the

velocity correlation between them is expected to be strong. If these two molecules are not adjacent to each other, on the other hand, the velocity correlation between them becomes relatively weak. Therefore, it is expected that $\langle l\rangle_n^d$ cannot exceed a certain number, no matter how large the mean association number, $\langle l\rangle_n^p$.

From these results, the following picture may be drawn for the cooperative translational motion of alcohol molecules. In the low concentration range of alcohol, several alcohol molecules form a hydrogen-bonded polymer. The polymer can move for a time much longer than the velocity auto-correlation time without changing the polymer shape. The number of alcohol molecules moving together increases with the increase of the alcohol concentration in this concentration range. In the high concentration range, however, the polymer can no longer move without changing its shape as long as it could in the low concentration range. In other words, the number of molecules which can move together is much smaller than the mean association number.

Comparison with the Mean Association Number Obtained by Using an Ideal Associated Complex Model. In our previous paper,[8] the observed values of $N\langle(\Delta X_A)^2\rangle$ have been analyzed by using the ideal associated complex model. The model includes an assumption that alcohol molecules form an associated complex. The solution is regarded to be an ideal solution whose components are free molecules and the associated complexes. In other words, all the associated complexes are the same size as the carbon tetrachloride molecule and the internal degrees of the complexes are mutually independent. Under these assumptions, $N\langle(\Delta X_A)^2\rangle$ is expressed as

$$N\langle(\Delta X_A)^2\rangle = X_A(1-X_A)\{X_A+\langle l\rangle_w^c(1-X_A)\}$$
$$\langle l\rangle_w^c \equiv \sum_l l^2 n_{Al}^c / \sum_l l n_{Al}^c \qquad (28)$$

where n_{Al}^c is the mean number of associated complexes which are made up of l numbers of alcohol molecules. In the previous paper, it has been shown that this model cannot be applied to the present system (carbon tetrachloride solution of alcohols) especially in the high concentration range because the configurations of linear hydrogen-bonded polymers are not mutually independent. However, it has been also shown that $\langle l\rangle_w^c$ obtained from Eq. 28 is still a useful quantity, because the following expression can be obtained from the relation between $N\langle(\Delta X_A)^2\rangle$ and the spatial correlation of microscopic density:

$$\langle l\rangle_w^c - 1 = \int_{V^*} \rho_A g_{AA}(r)\mathrm{d}^3r - \int_{V^*} \rho_A g_{AB}(r)\,\mathrm{d}^3r$$

where A and B denote the alcohol and carbon tetrachloride molecules, respectively, ρ_A is the number density of alcohol, and $g_{\alpha\beta}(r)$ is the radial distribution function of α and β molecules (α, β=A or B). $\rho_\alpha g_{\alpha\beta}(r)\mathrm{d}^3r$ is the mean number of α molecules in a volume element d^3r, at a distance r from the center of a β molecule. Thus, $(\langle l\rangle_w^c - 1)$ represents the difference between the mean number of alcohol molecules in the neighborhood of a carbon tetrachloride molecule and that in a neighborhood of the same volume of an alcohol molecule. If the correlations between the positions of different alcohol molecules are rather strong in comparison with those between alcohol and carbon tetrachloride molecules, $\langle l\rangle_w^c$ takes larger values than unity according to the extent of the correlation. Therefore, $\langle l\rangle_w^c$ represents the number of alcohol molecules whose positions are strongly correlated.

In the case where the shape of each hydrogen-bonded species is spherical and their sizes are the same as the solvent molecules, $\langle l\rangle_w^c$ is expected to be equal to $\langle l\rangle_w^p$.[8]

$$\langle l\rangle_w^p \equiv \frac{\sum_l l^2 n_{Al}^p}{\sum_l l n_{Al}^p}.$$

This can be understood by considering that the positions of molecules which form a hydrogen-bonded species are strongly correlated in this case. In the case where the shape of each hydrogen-bonded species is like a polymer chain and various configurations are possible for the polymer chain, on the other hand, the correlation between positions of molecules which form an hydrogen-bonded species becomes relatively weak. Then, $\langle l\rangle_w^c$ is expected to be smaller than $\langle l\rangle_w^p$.

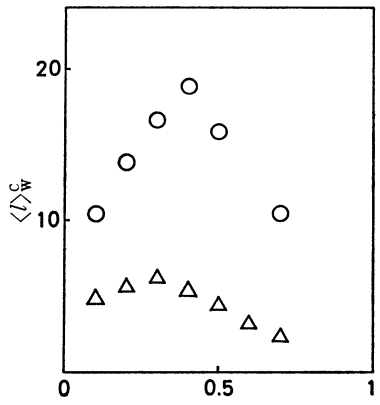

Fig. 6. Mean association numbers obtained from mean-square concentration fluctuation by using an associated complex model.
○: Methanol–carbon tetrachloride system, △: ethanol–carbon tetrachloride system.

Figure 6 shows the concentration dependences of $\langle l\rangle_w^c$ obtained from the observed $N\langle(\Delta X_A)^2\rangle$ values and Eq. 28. Comparison of $\langle l\rangle_n^d$ with $\langle l\rangle_n^p$ and $\langle l\rangle_w^c$ shows that the concentration dependence of $\langle l\rangle_n^d$ is more similar to that of $\langle l\rangle_w^c$ than to that of $\langle l\rangle_n^p$. These results can be understood by considering that the velocity time correlation between different molecules depends on the correlations of positions between these molecules.

Concluding Discussion. We have introduced the concept of a moving unit in order to obtain information about cooperative molecular motions. For the binary solutions of methanol–carbon tetrachloride and ethanol–carbon tetrachloride, we have compared the mean number of molecules which constitute an moving unit

(dynamical mean association number), $\langle l\rangle_n^d$, with two kinds of mean association number, $\langle l\rangle_n^p$ and $\langle l\rangle_w^c$. $\langle l\rangle_n^p$, the ordinary mean association number, is the mean number of molecules which are linked by hydrogen bonds. $\langle l\rangle_n^d$ is the number of molecules whose positions are strongly correlated. These parameters describe the local structure from different standpoints. We have shown that the concentration dependence of $\langle l\rangle_n^d$ is different from that of $\langle l\rangle_n^p$ for the present systems. This difference may be distinct for the solutions in which associated species of short life-time (the life-time is not much longer than the velocity auto-correlation time (10^{-12}—10^{-13} s)) exist. For the solutions in which associated species of long life-time exist, $\langle l\rangle_n^d$ is expected to approach $\langle l\rangle_n^d$. Incidentally, if all the associated species are spherical in shape and of the same size in addition to having long life-times, the relation that $\langle l\rangle_n^d \simeq \langle l\rangle_n^p \simeq \langle l\rangle_w^p \simeq \langle l\rangle_w^c$ is expected.

Although various techniques are available for studying statical structures of liquids or single molecular motions, there are few experimental methods which yield information about collective molecular motions. The measurement of mutual diffusion coefficients is useful for such study. In most of the reports on the mutual diffusion in associated solutions, however, little attention has been paid to the life-time of associated species. The observed mutual diffusion coefficients have usually been explained by using the mean association numbers such as $\langle l\rangle_n^p$ instead of $\langle l\rangle_n^d$.[18,19]

We have shown that the magnitude of the mutual diffusion coefficients depends on the life-time of the local structures formed in the solution. Though the moving unit is a fictitious concept at this stage, it is an important quantity for drawing pictures of the cooperative translational motions in associated solutions.

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15) In Ref. 8, the mean association number is expressed as
$$\langle l\rangle_w^p = \sum_l l^2 n_{Al}^p / \sum_l l n_{Al}^p.$$
Under the assumption of association equilibria described in Ref. 8, $\langle l\rangle_w^p$ is related to $\langle l\rangle_n^p$ by this relation: $\langle l\rangle_n^p = (\langle l\rangle_w^p + 1)/2$.
16) We cannot obtain information about the life-time of hydrogen bonds, because other molecular motions than the translational one may also break hydrogen bonds.
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