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Observation of Mutual Diffusion Coefficients and Cooperative Motions in Binary Solutions of *t*-Butyl Alcohol–Water and 2-Butoxyethanol–Water

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Rayleigh scattering spectra were observed for the binary solutions of t-butyl alcohol(TBA)–water and 2-butoxyethanol (BE)–water. The observed line-widths were reduced to mutual diffusion coefficients. The observed concentration dependencies of the mutual diffusion coefficients were well explained by postulating the existence of "moving units"— a group of molecules which move together for a time much longer than the velocity auto-correlation time. The structure of the moving units which are formed in the TBA–water solution was $(H_2O)_{20}TBA$ for $X_{TBA}\lesssim 0.05$, and $4(H_2O)_{20}TBA$ for $X_{TBA}\gtrsim 0.05$, where X_{TBA} is the mole fraction of TBA. For the BE–water solution, the structure was found to be $(H_2O)_{50}BE$ for $X_{BE}\lesssim 0.02$ and $3(H_2O)_{50}BE$ for $X_{BE}\gtrsim 0.02$. These results were compared with the results which had been obtained from the concentration dependencies of the mean-square concentration fluctuation values.

Local fluctuations of concentration afford information which is useful for understanding the mixing of liquids from a molecular viewpoint. Since the mean-square amplitude of concentration fluctuation is related to the spatial correlation between positions of different molecules, it affords information about the local structure formation in solution. In our 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—9)] The local structures were expressed in terms of the mean association number in the ordinary sense.

In order to discuss the state of mixing from a dynamical standpoint, however, the life-time of local structures should be taken into account along with 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. Instead of observing the life-time directly, we introduced the concept of a "moving unit"—a group of molecules which move together for a time much longer than the velocity auto-correlation time—in our preceding report[10)] as a useful concept for describing dynamical aspects of local structures. 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 systems obtained from the intensity distribution measurements of Rayleigh lines. It was shown that the mean number of alcohol molecules which constitutes a moving unit was much smaller than the mean association number of alcohol, especially in the high concentration range of alcohol. This indicated that the hydrogen-bonded polymer of alcohol molecules cannot move without changing shape within the velocity auto-correlation time.

The present report concerns itself with the extension of this line of approach to the aqueous solutions of *t*-butyl alcohol (TBA hereafter) and 2-butoxyethanol (BE hereafter). Our expectation is that the life-times of the local structures formed in these solution are much longer than those in the ordinary binary solutions like methanol–carbon tetrachloride and ethanol–carbon tetrachloride.[10)]

Recently, Iwasaki *et al.* have observed the light scattering spectra for the binary solution of *t*-butyl alcohol and water.[7,8)] They have concluded that clathrate hydrate-like structures of the type $g[(H_2O)_{21}TBA]$ ($g=1$—5) exist in the solution, from the analysis of the observed concentration dependence of the mean-square concentration fluctuation. By considering the results of X-ray diffraction analyses for the structure of solid clathrate hydrate, it has been suggested that a TBA molecule is surrounded by water molecules which form a polyhedron. This result indicates that the life-time of these local structures in the TBA–water solution might be much longer than those observed in the carbon tetrachloride solutions of alcohols.[10)] This expectation is confirmed by the measurement and analysis of the concentration dependence of the mutual diffusion coefficient, which is obtained from the line-width of Rayleigh line. The binary solution of water–BE is also included in the present study.

Experimental

The light scattering spectrometer (heterodyne detection) used in the present study was designed and constructed in our laboratory.[11)] The light source is an argon ion laser (Spectra-Physics model 165-09) which produced 0.1—1 W 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 is focused into a rectangular scattering cell. Scattered light and local oscillator beam (scattered from the cell walls) are collected onto the surface of a photomultiplier tube (HTV R-374). The photocurrent is amplified and then fed to a spectrum analyzer (Takeda-Riken TR 4120S). This analyzer is designed for use in the spectral region 50 Hz—30 MHz. The out-put of the analyzer is averaged by a signal averager (Kawasaki Electronica M50E-TMC 600). The averaged spectrum is squared prior to recording, so that the final output signal is proportional to the power spectrum of the scattered light. Details of the spectrometer have been reported elsewhere along with the reliability of the observed data.[11]

Light scattering spectra were recorded at the temperature of 25±1 °C in the scattering angle range of $5° < \theta < 21°$.

All the chemicals were commercial products (Tokyo Kasei's Extra Pure). 2-Butoxyethanol was purified by distillation and *t*-butyl alcohol was used without further purification. Water was triply distilled. The binary mixtures of TBA and water were made dust free by the use of a Nuclepore filter with a pore size of 0.1 μm.

Results and Discussion

Mutual Diffusion Coefficients and Velocity Correlation between Different Molecules. The procedure for obtaining the mutual diffusion coefficient from the Rayleigh scattering spectra is the same as that described in the preceding report.[10] Figures 1 and 2 show the concentration dependences of the mutual diffusion coefficients for the binary solutions of TBA–water and BE–water, respectively.

The mutual diffusion coefficient for the binary solution whose components are molecules A and B is expressed in terms of velocity correlation functions as

$$D = QL \tag{1}$$

with

$$L = X_B D_A + X_A D_B + X_B(n_A - 1)\, V_{aa'} + X_A\,(n_B - 1)\, V_{bb'} - 2X_A X_B\,(n_A + n_B)\, V_{ab} \tag{2}$$

$$Q = \frac{X_A X_B}{N\langle(\Delta X)^2\rangle} \tag{3}$$

$$V_{ij} = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_i(t)\cdot\mathbf{v}_j(0)\rangle \mathrm{d}t \tag{4}$$

$$(\mathrm{i, j,} = \mathrm{a, a', b\ or\ b'}).$$

The notations in these equations are the same as those used in the preceding report.[10]

In the case where velocity correlation between different molecules can be neglected, L is reduced to

$$L^\circ = X_B D_A + X_A D_B. \tag{5}$$

Equation 2 can be rewritten in terms of L° as

$$L \simeq L^\circ + X_A X_B (n_A + n_B)\,(V_{aa'} + V_{bb'} - 2V_{ab}), \tag{6}$$

where we have taken $n_4 - 1 \simeq n_A$ and $n_B - 1 \simeq n_B$ because $n_A, n_B \gg 1$. Equation 6 indicates that L is larger than L° when the velocity correlation between same species is stronger than that between different species, that is, $V_{aa'} + V_{bb'} > 2V_{ab}$. In the case where $V_{aa'} + V_{bb'} < 2V_{ab}$, on the other hand, L takes a smaller value than L°.

Figures 3 and 4 show the concentration dependences of L calculated from the observed values of D and $N\langle(\Delta X)^2\rangle$ for the binary solutions of TBA–water and BE–water. The observed values of $N\langle(\Delta X)^2\rangle$ for the BE–water system are shown in Fig. 12. The observed values for the TBA–water system were already reported.[7,8] It is seen from Figs. 3 and 4, that L takes a minimum value at $X \approx 0.05$ for the TBA–water system and $X \approx 0.02$ for the BE–water system, where X is the mole fraction of TBA or BE.

The broken line of Fig. 3 shows the concentration dependence of L° calculated from Eq. 5 where experimental values of the self diffusion coefficients found in the literature[12,13] was used (see Fig. 5). It is seen from

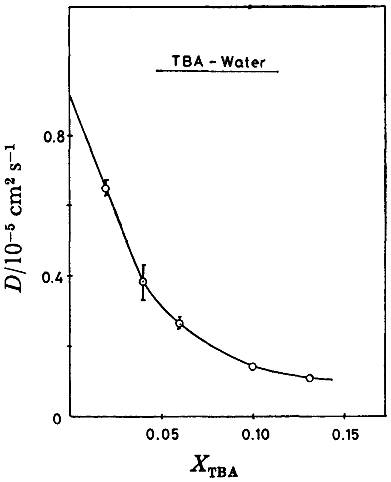

Fig. 1. Observed mutual diffusion coefficients for TBA–water system at 25 °C.

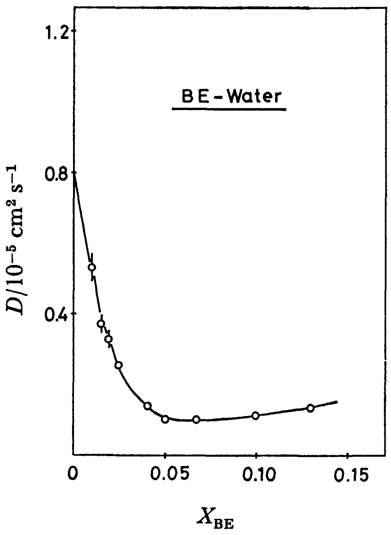

Fig. 2. Observed mutual diffusion coefficients for BE–water system.

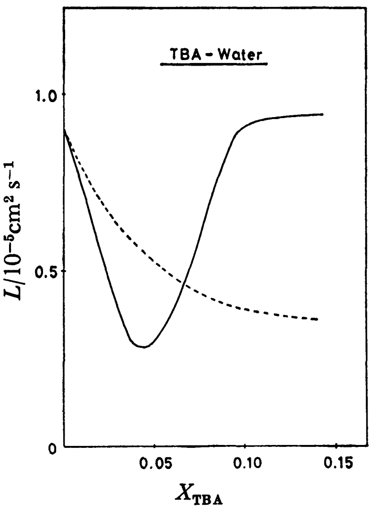

Fig. 3. Observed values of L (see Eqs. 1—3) for TBA–water system. The dashed line shows L° (see Eq. 5).

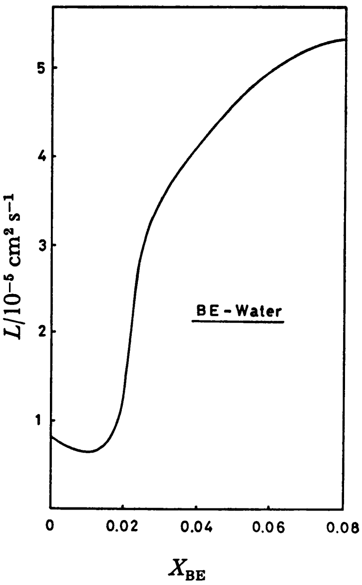

Fig. 4. Observed values of L (see Eqs. 1—3) for BE–water system.

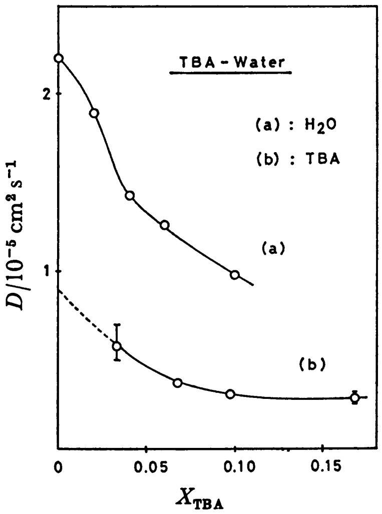

Fig. 5. Observed self diffusion coefficients for TBA–water system.

the figure that L is smaller than L° for $0<X<0.065$ and is larger than L° for $0.065<X$. These results suggest that $(V_{aa'}+V_{bb'}-2V_{ab})$ in Eq. 6 is not equal to zero for the present system.

Moving Unit in TBA–Water System. In the previous report,[10] we have introduced the concept of a moving unit in order to obtain information about the cooperative translational motion of molecules in solution. We will try to explain the observed concentration dependence of L by using this concept.

The analysis[7] of the Rayleigh intensities for the TBA–water system has shown the existence of clathrate hydrate-like structures of the type $(H_2O)_{21}$TBA for $0<X<1/22$ and of the type $5[(H_2O)_{21}$TBA] for $1/22<X$. Therefore, we consider first a moving unit of the A_lB-type where A and B represent water and TBA molecules, respectively. Then, L is expressed as

$$L=\frac{X_{\mathrm{B}}}{n_{\mathrm{A}}}\left[r^2 n_{\mathrm{A}_r}D_{\mathrm{A}_r}+l^2 n_{\mathrm{A}_l\mathrm{B}}D_{\mathrm{A}_l\mathrm{B}}\right]$$
$$+\frac{X_{\mathrm{A}}}{n_{\mathrm{B}}}\left[n_{\mathrm{B}_1}D_{\mathrm{B}_1}+n_{\mathrm{A}_l\mathrm{B}}D_{\mathrm{A}_l\mathrm{B}}\right]-2l\frac{n_{\mathrm{A}_l\mathrm{B}}}{n_{\mathrm{A}}+n_{\mathrm{B}}}D_{\mathrm{A}_l\mathrm{B}}, \tag{7}$$

where $n_\alpha(\alpha=\mathrm{A}_l\mathrm{B}$ *etc.*) is the number of moving units of α-type and D_α the self diffusion coefficient of a moving unit α. In Eq. 7, a moving unit of the A_l-type has also been assumed to exist. Since the relations

$$n_{\mathrm{A}}=rn_{\mathrm{A}_r}+ln_{\mathrm{A}_l\mathrm{B}}$$
$$n_{\mathrm{B}}=n_{\mathrm{B}_1}+n_{\mathrm{A}_l\mathrm{B}} \tag{8}$$

hold, Eq. 7 is reduced to

$$L=X_{\mathrm{B}}rD_{\mathrm{A}_r}+X_{\mathrm{A}}D_{\mathrm{B}_1}+X_{\mathrm{A}_l\mathrm{B}}\left[\frac{X_{\mathrm{B}}}{X_{\mathrm{A}}}l\left(lD_{\mathrm{A}_l\mathrm{B}}-rD_{\mathrm{A}_r}\right)\right.$$
$$\left.+\frac{X_{\mathrm{A}}}{X_{\mathrm{B}}}\left(D_{\mathrm{A}_l\mathrm{B}}-D_{\mathrm{B}_1}\right)-2lD_{\mathrm{A}_l\mathrm{B}}\right] \tag{9}$$

$$X_{\mathrm{A}_l\mathrm{B}}=\frac{n_{\mathrm{A}_l\mathrm{B}}}{n_{\mathrm{A}}+n_{\mathrm{B}}}. \tag{10}$$

(a) L for a Model System Composed of A_l, A_lB, and B_1. In order to determine the l-dependence of L, we consider the special case where $r=l$ and $D_{\mathrm{A}_l\mathrm{B}}=D_{\mathrm{A}_l}=D_{\mathrm{B}_1}\equiv\mathrm{D}^{\mathrm{s}}$. We further assume that for $0\leq X_{\mathrm{B}}\leq 1/(l+1)$ there exist only those moving units of the types A_l and A_lB and for $1/(l+1)\leq X_{\mathrm{B}}$ only those of the types A_lB and B_1. This corresponds to the conditions $X_{\mathrm{A}_l\mathrm{B}}=X_{\mathrm{B}}$ for $0\leq X_{\mathrm{B}}\leq 1/(l+1)$, and $X_{\mathrm{A}_l\mathrm{B}}=X_{\mathrm{A}}/l$ for $1/(l+1)\leq X_{\mathrm{B}}$. Figure 6 shows the concentration dependences of L for $D^{\mathrm{s}}=1$ and for various values. It is seen from the figure that there exists a specific concentration, X_l, at which L is zero. X_l is equal to $1/(l+1)$, which is the number ratio of B molecules to all the molecules in the moving unit A_lB. By comparing Fig. 6 with Fig. 3, we can see that the theoretical curve for $l=20$ in Fig. 6 explains the observed concentration dependence of L in the sense that L takes a minimum value at $X_{\mathrm{B}}\sim 0.05$. However, the observed value of L does not go to zero at any concentration. This suggests the existence of other types of moving units than A_lB even at $X_{\mathrm{B}}=$

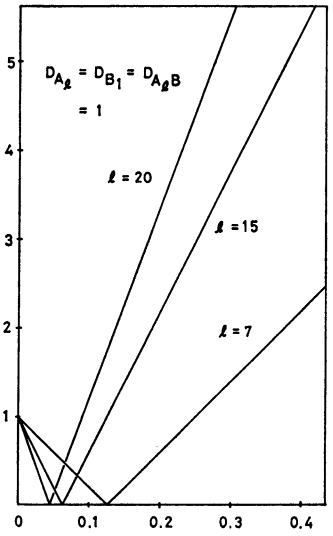

Fig. 6. Theoretical values of L calculated from Eq. 9 for $D_{\mathrm{A}_l\mathrm{B}}=D_{\mathrm{A}_r}=D_{\mathrm{B}_1}=1$ $(r=l)$ and for various l values.

$1/(l+1)$. Therefore, we consider the coexistence of the types A_l, A_lB, and B_1. In order to determine the concentration dependence of X_{A_lB}, we further assume the relation

$$\frac{n_{A_lB}}{N'} = K\frac{n_{A_l}}{N'}\frac{n_{B_1}}{N'}$$

$$N' = n_{A_l} + n_{A_lB} + n_{B_1}. \tag{11}$$

This corresponds to assuming the association equilibrium

$$A_l + B_1 \overset{K}{\rightleftharpoons} A_lB, \tag{12}$$

where K is an equilibrium constant. Then, X_{A_lB} can be expressed in terms of K as

$$X_{A_lB} = \frac{1}{2l}\left[\left(X_A + lX_B\right) - \left\{\left(X_A + lX_B\right)^2 - 4l\frac{K}{K+1}X_AX_B\right\}^{1/2}\right]. \tag{13}$$

Figure 7 shows the concentration dependences of L calculated from Eqs. 10 and 13 for $l=r=20$ and for various K values. It is seen from the figure that L takes a minimum value at $X_B \approx 0.05$.

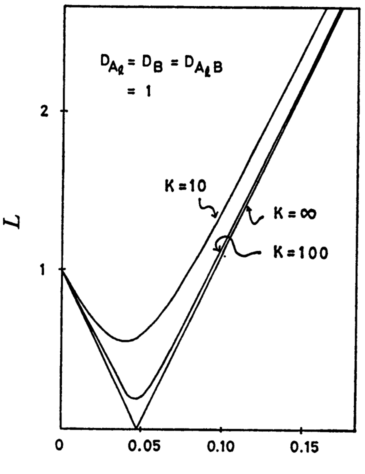

Fig. 7. Theoretical values of L calculated from Eqs. 10 and 13 for $l=r=20$ and for various K values.

(*b*) L *for a Model System Composed of* A_r, A_lB, *and* B_1. In the above analysis, we have assumed that the self diffusion coefficients of the moving units (D_{A_r}, D_{A_lB}, and D_{B_1}) are equal and independent on concentration. This assumption, however, is not quite reasonable, for the following reasons. The self diffusion coefficients, D_{A_r}, D_{A_lB}, and D_{B_1} can be related to the self diffusion coefficients, D_A and D_B, which correspond to the species A and B by the equations

$$D_A = \frac{rn_{A_r}}{n_A}D_{A_r} + \frac{ln_{A_lB}}{n_A}D_{A_lB}$$

$$D_B = \frac{n_{A_lB}}{n_B}D_{A_lB} + \frac{n_{B_1}}{n_B}D_{B_1}. \tag{14}$$

Therefore, the above assumption is equivalent to assuming $D_A = D_B$ at any concentrations. Actually, the observed D_A and D_B values are different and depend on concentration (see Fig. 5).

In order to take into account the observed concentration dependences of D_A and D_B properly, we rewrite Eq. 11 by using Eq. 14 as

$$L = rX_BD_A + X_AD_B - lX_{A_lB}D_{A_lB} \times \left[2 - \frac{X_B}{X_A}\left(l - r\right)\right]. \tag{15}$$

As Eq. 15 has four unknown parameters, l, r, X_{A_lB}, and D_{A_lB}, on the right hand side, it is difficult to determine these parameters from the observed data uniquely. Fortunately, however, we can restrict the probable magnitudes of these parameter values as follows.

As the sizes and weights of A_r and B_1 are both smaller than those of A_lB, the lower limit of the D_{A_lB} value may be defined as: $D_{A_lB} \leq D_{A_r}$ and $D_{A_lB} \leq D_{B_1}$. We can also define the upper limits of D_{A_lB} and D_{B_1}, so that the probable magnitudes of these parameters are restricted by the relations

$$D_{A_lB} \leq D_{A_r} \leq aD_{A_lB}$$

$$D_{A_lB} \leq D_{B_1} \leq bD_{A_lB}. \tag{16}$$

The constants a and b of Eq. 16 are arbitraly. However, it is improbable that D_{B_1} is larger than $10D_{A_lB}$ because the self diffusion coefficient of a moving unit is inversely proportional to its weight, approximately,[14] and because the weight of A_lB is about six times as large as that of B_1. So, we set $b=10$. Similarly, we may set $a=40/r$ because the weight of B_1 is about $4/r$ times as large as that of A_r. D_{A_r} and D_{B_1} can be expressed in terms of D_A, D_B, and D_{A_lB} as

$$D_{A_r} = \frac{D_AX_A - lX_{A_lB}D_{A_lB}}{X_A - lX_{A_lB}} \tag{17a}$$

$$D_{B_1} = \frac{D_BX_B - X_{A_lB}D_{A_lB}}{X_B - X_{A_lB}}. \tag{17b}$$

Combination of Eqs. 16 and 17 gives the relations

$$D_A \geq D_{A_lB} \geq \frac{X_AD_A}{a\left(X_A - lX_{A_lB}\right) + lX_{A_lB}} \tag{18a}$$

$$D_B \geq D_{A_lB} \geq \frac{X_BD_B}{b\left(X_B - X_{A_lB}\right) + X_{A_lB}}. \tag{18a}$$

Therefore, we can define the smallest value, L_{min}, and the largest value, L_{max}, of L as

$$L_{\text{min}} = M - X_{A_lB}D_AH \tag{19}$$

$$L_{\text{max}}^{a} = M - \frac{X_AD_AX_{A_lB}}{a\left(X_A - lX_{A_lB}\right) + lX_{A_lB}}H \tag{20a}$$

$$L_{\text{max}}^{b} = M - \frac{X_BD_BX_{A_lB}}{b\left(X_B - X_{A_lB}\right) + X_{A_lB}}H \tag{20b}$$

$$M = X_BrD_A + X_AD_B$$

$$H = l[2 - X_B(l-r)/X_A] \quad (a=40/r,\ b=10)$$

if $H>0$. The values of L_{max}^{a} and L_{max}^{b} are determined from Eqs. 18a and 18b, respectively. The values of L_{min} are determined from Eq. 18 and the relation that $D_A > D_B$ (see Fig. 5). For $H<0$, L_{min} in Eq. 19 becomes a maximum value and L_{max} in Eq. 20 becomes a minimum value. Figures 8—10 show the domain of L calculated from Eqs. 19 and 20 for some values of r and K, where the concentration dependence of X_{A_lB} is assumed to be determined by Eq. 13. It is seen from these figures that the observed L values satisfy the inequality represented by Eqs. 19 and 20 for $r=4$ in the

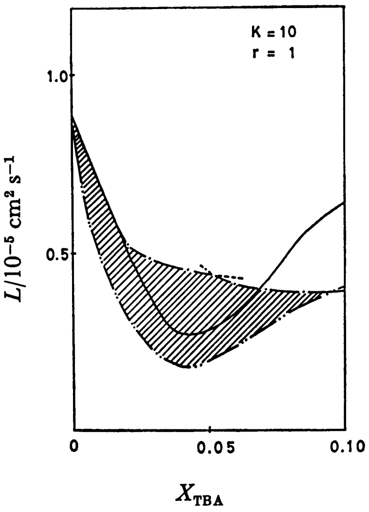

Fig. 8. Domain of L calculated from Eqs. 19 and for l=20, r=1, and K=10 (shaded area).

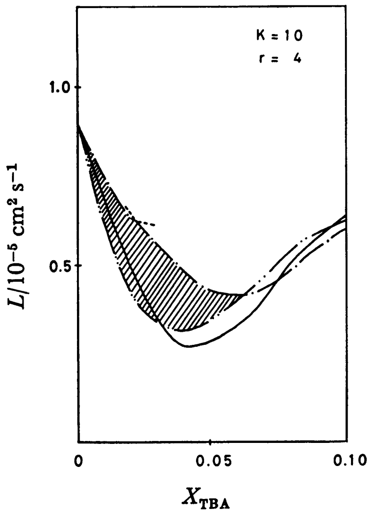

Fig. 9. Domain of L calculated from Eqs. 19 and 20 for l=20, r=4, and K=10 (shaded area).

low concentration range of TBA (X<0.03). In the high concentration range, however, the domain calculated for any r or K value does not cover the observed L values. This implies that the present model is not applicable in the high concentration range.

(c) L for a Model System Composed of A_r, gA_lB, and B_1. In the Rayleigh intensity analysis, the existence of the local structure of the type $5[(H_2O)_{l'}TBA]$ has been proposed for $1/(l'+1)<X_B(l'\approx 21)$. So we assume the coexistence of the moving units of the types gA_lB (g=2, 3,..), A_r, and B_1 for $X_B>1(l+1)$. Then, L is expressed as

$$L = M + X_{A_lB}D_{gA_lB}H'$$

$$H' \equiv l\left[2g - \frac{X_B}{X_A}\left(gl - r\right)\right] - \left[\frac{X_A}{X_B}\left(g - 1\right)\right]$$

$$X_{A_lB} = gX_{gA_lB}. \tag{21}$$

In this case the relations corresponding to Eq. 16 are

$$D_{gA_lB} \leq D_{A_r} \leq \frac{ag}{r} D_{gA_lB} \tag{22a}$$

$$D_{gA_lB} \leq D_{B_1} \leq bgD_{gA_lB}. \tag{22b}$$

Therefore,

$$L_{\rm min} = M - D_A X_{A_lB} H' \tag{23}$$

$$L^{\rm a}_{\rm max} = M - \frac{X_A D_A X_{A_lB}}{ag(X_A - lX_{A_lB}) + lX_{A_lB}} H' \tag{24a}$$

$$L^{\rm b}_{\rm max} = M - \frac{X_B D_B X_{A_lB}}{bg(X_B - X_{A_lB}) + X_{A_lB}} H' \tag{24b}$$

for $H'>0$. The domain of L calculated from Eqs. 23 and 24 for r=1, K=10, and g=4 is shown in Fig. 11, where the domain of L for $X_B<1/(l+1)$ is calculated from Eqs. 19 and 20. It can be seen from the figure that the calculated domain covers the observed values of X>0.02.

We could not find any other r and g values which give a domain of L which covers the observed values for X<0.1. However, for X<0.075, for example, the domain calculated for r=1 and g=3 also covers the observed L values. Similarly, for X<0.07, we can find

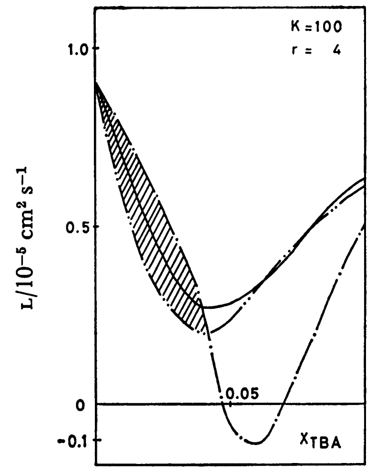

Fig. 10. Domain of L calculated from Eqs. 19 and 20 for l=20, r=4, and K=100 (shaded area).

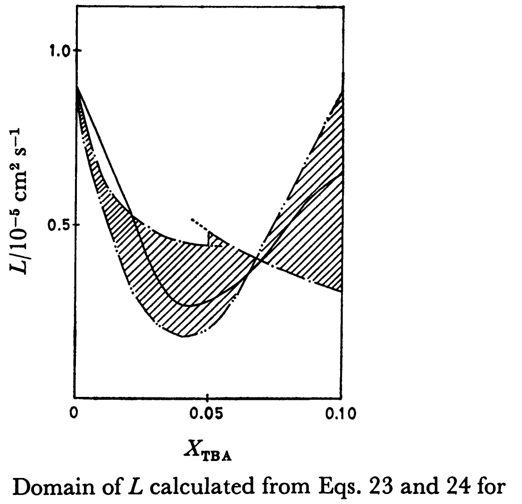

Fig. 11. Domain of L calculated from Eqs. 23 and 24 for l=20, r=1, K=10, and g=4 (X≥0.02) and that calculated from Eqs. 19 and 20 for l=20, r=1, and K=10 (X≤0.02).

that three sets of values: $(r, g) = (1, 4)$, $(1, 3)$, and $(2, 2)$, can produce domains which can cover the observed L. These results may suggest an increase of g and decrease of r with the increasing concentration of TBA.

From the above analysis, the following types of moving units can be expected in the TBA–water solution:

A_r $(r = 4\text{—}10)$, $A_{20}B$, and B_1 for $0 < X_B \lesssim 0.05$

A_1, $4A_{20}B$, and B_1, for $0.05 \lesssim X_B$.

An approximate l value can be determined from the concentration at which L takes a minimum value.

Moving Unit in BE–Water System. We have analyzed the observed mean-square concentration fluctuation for the BE–water system by the same way as was used for the TBA–water system.[7] Our conclusion is that there are local structures of the type $(H_2O)_{55}BE$ for $0 < X_{BE} < 1/56$ and of the type $3(H_2O)_{55}$ BE for $1/56 > X_{BE}$.

For the BE–water system, the self diffusion coefficients have not been reported. However, the observed concentration dependence of L in Fig. 4 suggests the existence of moving units similar to those in the TBA–water system, that is, the $(H_2O)_l BE$ type. From the concentration at which L takes a minimum value, the l value is obtained to be about 50.

Concluding Discussion. We have shown that moving units of the types $g[(H_2O)_{20}TBA]$ and $g'[(H_2O)_{50}BE]$ exist in the binary solution of TBA–water and BE–water, respectively. The analysis of the concentration dependences of the mutual diffusion coefficients gave these results. In the study of the mean-square concentration fluctuations for these systems, on the other hand, the existence of local structures of the types $g''[(H_2O)_{20}TBA]$ and $g'''[(H_2O)_{55}BE]$ has been suggested. With the help of the results of X-ray diffraction analyses for the structure of solid clathrate hydrate,[15] the following picture can be drawn for the mixing state of TBA–water mixtures. In the concentration range of $0 < X_{TBA} < 1/22$, a TBA molecule forms a polyhedron surrounded by water molecules and the polyhedra are dispersed in water. In the concentration range of $1/22 < X_{TBA} < 0.1$, the aggregates of five polyhedra are dispersed in TBA. Because the ratio of water molecules to a TBA molecule in a moving unit is nearly equal to that in the above polyhedron, it can be concluded that the life-time of the clathrate hydrate-like structure is much longer than the order of the velocity auto-correlation time (10^{-13}—10^{-12} s). This is in contrast with the results obtained for the binary solutions of methanol–carbon tetrachloride and ethanol–carbon tetrachloride. In these systems, a group of hydrogen-bonded alcohols cannot be a moving unit, especially in the high concentration range of alcohol ($X_{alcohol} \gg 0.1$). This result has been explained as follows. Consider the velocity correlation between two alcohols which form a linear hydrogen-bonded 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 the number of alcohols which form a moving unit cannot exceed a certain number, no matter how large the association number of hydrogen-bonded polymer is. In other words, the long hydrogen-bonded polymer cannot be a moving unit.

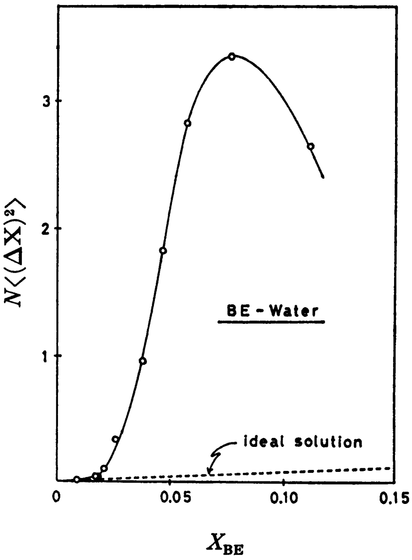

Fig. 12. Observed mean-square concentration fluctuation for BE–water system.

The present results are not inconsistent with this viewpoint. In the TBA–water solution, the distances between the TBA molecule and each water molecule which form a polyhedron are almost the same. Therefore, the velocity correlation between the TBA molecule and each water molecule is expected to be strong. For the BE–water system, no picture for the mixing state has been drawn. We suggest the picture is similar to that in the TBA–water systems, because the present study has shown that the local structure predicted by the Rayleigh intensity analysis can be a moving unit itself.

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