September, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **54**, *2573—2578 (1981)*

Determination of Local Structure and Moving Unit Formed in Binary Solution of *t*-Butyl Alcohol and Water

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(Received February 18, 1981)

The concentration dependences of the mutual diffusion coefficients at 24, 37, and 63 °C were observed for a binary solution of *t*-butyl alcohol (TBA) and water by the use of the light scattering method. The observed concentration dependences of the mutual diffusion coefficients were explained well by postulating the existence of a "moving unit"—a group of molecules which move together for a time much longer than the velocity correlation time. The structure of the moving units which are formed in the solution are $(H_2O)_{11}TBA$ at 24 °C and $(H_2O)_{20}TBA$ at 63 °C in the concentration range of $0<x_{TBA}<0.1$, where x_{TBA} is the mole fraction of TBA. Taking into account the local structures, which had been determined from the concentration dependences of the mean-square concentration fluctuation values, we could conclude that water molecules form a polyhedron which encages a TBA molecule and that these cages then gather together to form an aggregate. It is essential that these polyhedra do not share their faces with each other in the aggregate. It was also concluded that the number of cages which form an aggregate increases with an increase in the temperature. This suggests the existence of a pseudo-critical temperature for this system. That is to say, the TBA–water solution can separate into two phases under high pressures, a TBA-rich phase and a water-rich phase, in the latter of which almost all the molecules form polyhedra.

In our previous reports,[1,2] the mean-square concentration fluctuation observed by means of the light scattering spectra for TBA–water solution has been reported. From a quantitative analysis of the concentration fluctuation, it has been shown that the local structure of the type $g[(H_2O)_l TBA]$ exists in the solution. As the number ratio of TBA to water for this local structure was close to that of the solid clathrate hydrate of TBA,[3] we proposed that this local structure can be a clathrate hydrate-like structure.

It has been established, in the solid clathrate hydrate, that water molecules form polyhedra, each of which encages a guest molecule and that the several polyhedra share one of their faces (we will call this an "associated polyhedron" hereafter). We are interested in whether or not the same sort of associated polyhedra can be formed even in the solution phase, because we can draw another picture for the local structure formed in the solution phase. That is, the polyhedra gather together to form an aggregate without sharing faces with each other (we call this an "aggregated polyhedron" hereafter). The observation of the mean-square concentration fluctuation does not afford information which is accurate enough to judge which picture is correct, that is, whether "associated polyhedron" or "aggregated polyhedron." In addition to the mean-square concentration fluctuation, we have to know the life-time of the local structure in order to solve this problem.[4]

Recently, we have emphasized the importance of the concept of a "moving unit" — a group of molecules which move together for a time much longer than the velocity correlation time — in order to obtain information about the life-time of local structures. A moving unit can be determined by expressing the mutual diffusion coefficient theoretically in terms of the self-diffusion coefficients and the number of moving units.[5,6]

In the present study, we will discuss the above problem on the basis of an analysis of the mutual diffusion coefficients which are obtained from the correlation function of the electric field of Rayleigh light. It will be shown that the aggregated polyhedron picture is preferrable to the associated polyhedron picture. This conclusion will lead us to emphasize the fact that the mixing state of the TBA and water system is governed by a moving unit of the type $(H_2O)_l TBA$. We will also discuss the temperature effect on the mixing state on the basis of the "aggregated polyhedron" picture. It will be suggested that a binary solution of TBA and water may be separated into two phases under high pressure, a TBA-rich phase and a water-rich phase, in the latter of which almost all the water molecules form polyhedra.

Experimental

The light scattering spectrometer used in the present study was designed and constructed in our laboratory. The light source was 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 was focused into a rectangular cell with a path length of 1.5 cm. A 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 photo current was amplified by a factor of about 400 by means of a preamplifier and autocorrelated by a 400-channel correlation and probability analyzer (KANOMAX SAI-43A). The computed time auto-correlation function of the photocurrent was recorded on an X-Y recorder. At the same time, the auto-correlation function was transferred in a digital form from the correlator to a micro-computor (SHARP Mz-80C).

In our previous study,[7] a spectrum analyzer (Takeda Riken, TR-4120S) was used instead of a signal correlator. The signal correlator is superior to the spectrum analyzer for the observation of the current fluctuation in the low-frequency range (DC≈kHz) in the following respects. First the rate of data collection with the signal correlator is higher than that with the spectrum analyzer by a factor of more than 10^2. Second, we can compare the precision of the data sampling interval, τ. For the signal correlator used in the present work, the precision of τ is about 10^{-4} for the frequency range of DC≈50 kHz. In the case of the spectrum analyzer, on the other hand, the corresponding precision can be estimated from the precision of the observed frequency, $|\Delta f/f|$, because the $|\Delta\tau/\tau|=|\Delta f/f|$ relation holds between these two kinds of precision. The precision of the observed frequency is about 10^{-4} at 50 kHz and about 10^{-2} at 500 Hz. Thus, the signal correlator is more appropriate for the observation of the current fluctuation of the low-frequency signal (DC≈50 kHz). The characteristic frequency of the concentration fluctuation appears in this frequency range.

The time-correlation function of the electric field of Rayleigh light was observed at the temperatures of 24, 37, and 63 °C, with a temperature constancy of ±0.5 °C.

t-Butyl alcohol purchased from the Katayama Chemical Industries Co., Ltd., was used without further purification. Water was distilled after being passed through an ion-exchange resin. The binary mixture of TBA–water was made dust-free by the use of a Nuclepore filter with a pore size of 0.1 μm.

Results and Discussion

Light Scattering Measurement and Mutual Diffusion Coefficient. The time-correlation function of the electric field of the Rayleigh light isotropically scattered from a binary solution is composed approximately from two exponential functions.[8] One corresponds to the scattering due to entropy fluctuation, and the other, to that due to concentration fluctuation. Since the relaxation of the latter is slower than that of the former by a factor of 10^2, these two exponential curves can be identified separately. The correlation function for the concentration fluctuation is expressed as:

$$\frac{\langle\Delta c(\boldsymbol{q},t)\Delta c(\boldsymbol{q},0\rangle}{\langle\Delta c(\boldsymbol{q},0)^2\rangle}=\exp(-q^2Dt) \tag{1}$$

$$\Delta c(\boldsymbol{q},t)=\int_V(c(\boldsymbol{r},t)-\langle c\rangle)\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}}\mathrm{d}^3\boldsymbol{r}, \tag{2}$$

where $c(\boldsymbol{r},t)$ is the concentration at the point $\boldsymbol{r}$ at time t in the scattering volume, V, and where the pointed bracket represents an equilibrium ensemble average. Therefore, we can obtain the mutual diffusion coefficient, D, from the relaxation time of the time correlation function, $\tau_c\equiv 1/q^2D$.

Figure 1 shows a typical example of the observed photocurrent-correlation function, $\langle i(t)i(0)\rangle$, which corresponds to the correlation function of the scattered electric field. The observed correlation function was well expressed by a single exponential function. By plotting $1/\tau_c$ against q^2, the theoretical prediction of the linear dependence of $1/\tau_c$ on q^2 was confirmed. The mutual diffusion coefficients thus obtained are plotted against the mole fraction of TBA in Fig. 2.

The mutual diffusion coefficient for a binary solution composed of A and B components, D, is expressed in terms of the velocity correlation function as:[5]

$$D=QL \tag{3}$$

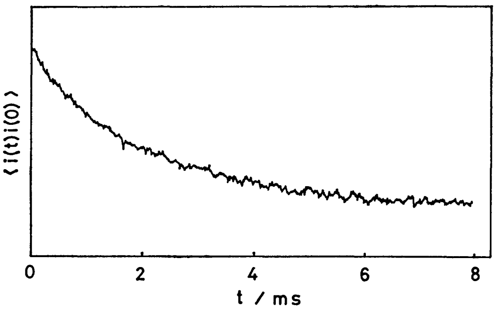

Fig. 1. Typical light scattering photocurrent autocorrelation function observed for TBA–water solution ($x_{\mathrm{TBA}}=0.13$, $\theta=9.62°$).

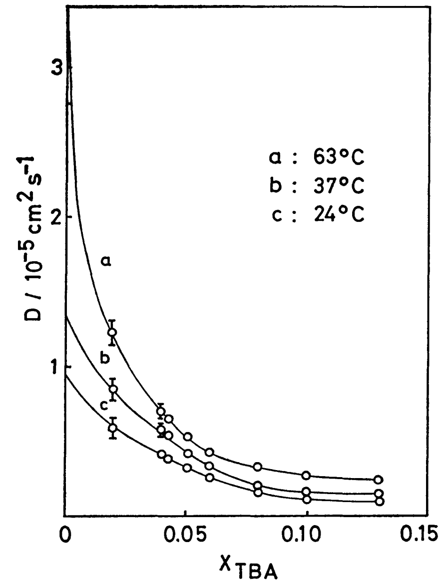

Fig. 2. Concentration dependence of the mutual diffusion coefficient for TBA–water solution at different temperatures.

$$L=L^\circ+(n_{\mathrm{A}}+n_{\mathrm{B}})x_{\mathrm{A}}x_{\mathrm{B}}(V_{\mathrm{aa'}}+V_{\mathrm{bb'}}-2V_{\mathrm{ab}}) \qquad (\mathrm{a}\neq\mathrm{a'},\ \mathrm{b}\neq\mathrm{b'}) \tag{4}$$

with

$$Q\equiv x_{\mathrm{A}}x_{\mathrm{B}}/N\langle(\Delta x_{\mathrm{A}})^2\rangle \tag{5}$$

$$L^\circ=x_{\mathrm{A}}D_{\mathrm{B}}+x_{\mathrm{B}}D_{\mathrm{A}} \tag{6}$$

$$V_{\mathrm{ij}}\equiv\frac{1}{3}\int_0^\infty\langle\boldsymbol{v}_{\mathrm{i}}(t)\boldsymbol{v}_{\mathrm{j}}(0)\rangle\mathrm{d}t \quad (\mathrm{i},\mathrm{j}=\mathrm{a},\mathrm{a'},\mathrm{b},\text{ or }\mathrm{b'}), \tag{7}$$

where $\boldsymbol{v}_{\mathrm{a}}(t)$ and $\boldsymbol{v}_{\mathrm{b}}(t)$ are the velocities of an a-th molecule of A and a b-th molecule of B respectively. x_{A} and x_{B} are the mole fraction of A and B, and n_{A} and n_{B} are the number of A and B molecules respectively. D_{A} and D_{B} are the self-diffusion coefficients of the A and B molecules respectively. L is called a kinetic diffusion coefficient. Figure 3 shows the concentration dependence of L for the water(A) and TBA(B) system, where Q is obtained from the observed mean-square concentration fluctuation, $N\langle(\Delta x_{\mathrm{A}})^2\rangle$, of Fig. 4.[9]

In order to calculate the L° value, the D_{A} and D_{B} values must be observed. Figure 5 shows the observed concentration dependences of D_{A} and D_{B} which

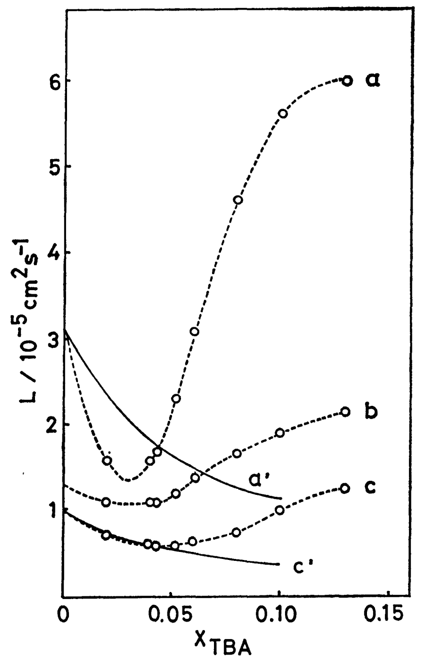

Fig. 3. Concentration dependence of L (curves a, b, and c) and L° (curves a' and c'); a, a': 63 °C, b: 37 °C, c, c': 24 °C (see Eqs. 4—6).

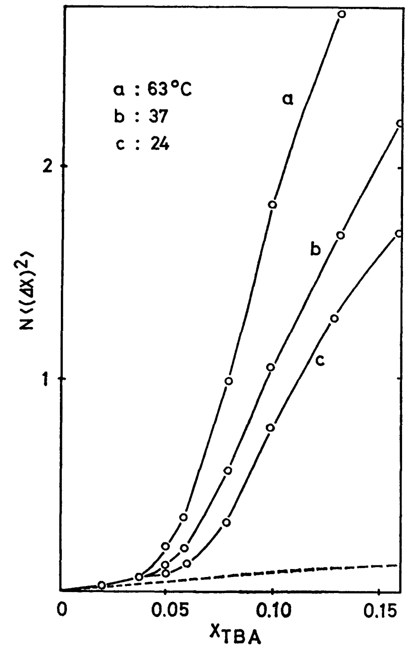

Fig. 4. Concentration dependence of the mean-square concentration fluctuation for TBA–water solution at different temperatures.[2] The dashed line corresponds to the concentration fluctuation expected for an ideal binary solution.

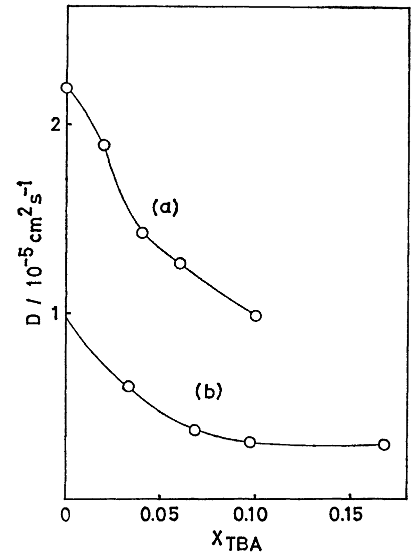

Fig. 5. Concentration dependence of the self-diffusion coefficients of: (a) water at 21 °C, (b) TBA at 25 °C.

are found in the literature.[10,11] Using these values, we have calculated the D_A and D_B values at 24 and 63 °C according to the following procedure. The temperature dependences of the self-diffusion coefficients, D_s, of pure water (0—55 °C) and TBA for a dilute aqueous solution (4—37 °C) have been reported.[12,13] The plots of $\ln D_s$ against $1/T$ are adequately approximated by straight lines, where T is the absolute temperature. If we assume that the temperature dependence of the self-diffusion coefficient is independent of the concentration, the D_s values at other temperatures can be estimated from these linear relations.

The concentration dependence of L° thus obtained for 24 and 63 °C are shown in Fig. 3. It may be seen from the figure that (L-L°) increases with the increase in the temperature in the concentration range of $0.05 < x_{TBA}$. This result indicates that the velocity correlation within the same species is larger for the higher temperature (see Eq. 4).

Analysis of Kinetic Diffusion Coefficient L. In the preceding report,[6] we have obtained the following expression for the kinetic diffusion coefficient, L, for the system composed of the moving units of the A_r, B_s, and gA_lB types:

$$L = M - x_{A_lB}HD_{gA_lB} \tag{8a}$$

and;

$$M = rx_BD_A + sx_AD_B \tag{8b}$$

$$H = l[2g-(x_B/x_A)(gl-r)]-(x_A/x_B)(g-s) \tag{8c}$$

$$x_{A_lB} = (1/2l)\left[x_A+lx_B-\{(x_A+lx_B)^2-\frac{4Kl}{K+1}x_Ax_B\}^{1/2}\right] \tag{8d}$$

$$K = (n_{A_lB}/N')/(n_{A_l}/N')(n_{B_1}/N') \tag{8e}$$

$$N' = n_{A_l} + n_{A_lB} + n_{B_1}, \tag{8f}$$

where D_{gA_lB} is the self-diffusion coefficient of the moving unit, gA_lB. In that preceding report, though, the value of D_{gA_lB} could not be determined uniquely.[6] In the present study, we have determined the parameters included in Eq. 8 in the following way. Table 1 shows the self-diffusion coefficients of pure liquids and the self-diffusion coefficients at an infinite dilution. It may be seen from the table that the ratio of the two diffusion coefficients corresponding to the two different solutes is almost the same for the three solvents. For example, the ratios of the self-diffusion coefficients of acetone and carbon tetrachloride are

TABLE 1. SELF-DIFFUSION COEFFICIENTS OF A FEW ORGANIC SUBSTANCES AT AN INFINITE DILUTION (25 °C)

Solute	Solvent		
	Acetone	Benzene	Carbon tetrachloride
Acetone	4.8*[a)]	2.8[b)]	1.7[e)]
Benzene	4.3[b)]	2.2*[a)]	1.5[e)]
Carbon tetrachloride	3.6[c)]	2.0[d)]	1.4*[f)]

* The self-diffusion coefficient value for the pure liquid.
a) F. A. L. Dullien, *AIChE J.*, **18**, 62 (1972). b) J. Leffler and H. T. Cullinan, *Ind. Eng. Chem. Fundam.*, **9**, 84 (1970). c) P. A. Hardt, D. K. Anderson, R. Ratchbun, B. W. Mar, and A. L. Babb, *J. Phys. Chem.*, **63**, 2059 (1959). d) J. K. Horrocks and E. McLaughlin, *Trans. Faraday Soc.*, **58**, 1357 (1969). e) W. Hayduk and S. C. Cheng, *Chem. Eng. Sci.*, **26**, 635 (1971). f) E. McLaughlin, *Trans. Faraday Soc.*, **55**, 28 (1959); *Quart. Rev.*, **14**, 236 (1960).

almost equal (1.33 in acetone, 1.4 in benzene, and 1.21 in carbon tetrachloride). This fact suggests that the ratio of the self-diffusion coefficients of two different species coexisting in a certain medium is almost constant, even if the physical properties of the medium are changed. Thus, we may assume that the magnitude of D_{gA_lB} is proportional to that of D_{A_r} or D_{B_s}; that is,

$$D_{gA_lB} = D_{B_s}/k_B \tag{9a}$$

or

$$D_{gA_lB} = D_{A_r}/k_A, \tag{9b}$$

where k_A and k_B are constans. On the other hand, the D_A and D_B self-diffusion coefficients have been expressed as:[6)]

$$D_A = \frac{(x_A - lx_{A_lB})}{x_A}D_{A_r} + \frac{lx_{A_lB}}{x_A}D_{gA_lB} \tag{10a}$$

$$D_B = \frac{(x_B - x_{A_lB})}{x_B}D_{B_s} + \frac{x_{A_lB}}{x_B}D_{gA_lB}. \tag{10b}$$

By substituting Eqs. 9a and 9b into Eqs. 10b and 10a respectively, we can obtain the expression of D_{gA_lB} in terms of D_A and D_B as:

$$D_{gA_lB} = \frac{x_B}{k_B(x_B - x_{A_lB}) + x_{A_lB}}D_B \tag{11a}$$

or

$$D_{gA_lB} = \frac{x_A}{k_A(x_A - lx_{A_lB}) + lx_{A_lB}}D_A. \tag{11b}$$

By substituting Eq. 11a or 11b into Eq. 8a, we can calculate L by the use of D_A and D_B. In order to obtain the parameters, K, l, r, s, q, and k_A (or k_B), the least-squares method was used.[14)] There is no strong reason for having which equation, Eq. 9a or 9b, is more appropriate. However, the better fit between the observed and the theoretical values for the concentration dependences of L could be obtained when we employed Eq. 9a.

Figure 6 shows the concentration dependences of the observed (dots) and the calculated (solid line) L values. For 24 °C, the best-fit parameters are: $K=39.0\pm7.7$, $l=11.1\pm0.3$, $r=6.0\pm0.8$, $s=4.0\pm1.2$, $g=0.9\pm0.03$, and $k_B=2.1\pm1.5$. These results show that the moving units of the $(H_2O)_{11}TBA$, $(H_2O)_6$, and $(TBA)_4$ types coexist in the concentration range of $0<x_{TBA}<0.1$ at 24 °C. For 63 °C, the best-fit parameters are $K=51.0\pm7.1$, $l=20.2\pm0.6$, $r=9.7\pm1.8$, $s=15.6\pm2.3$, $g=0.8\pm0.03$, and $k_B=0.3\pm0.09$. These results indicate the coexistence of the moving units of the $(H_2O)_{20}TBA$, $(H_2O)_{10}$, and $(TBA)_{16}$ types at 63 °C. The value of k_B at 63 °C is much smaller than that at 24 °C. This result seems quite reasonable, because these relations hold;

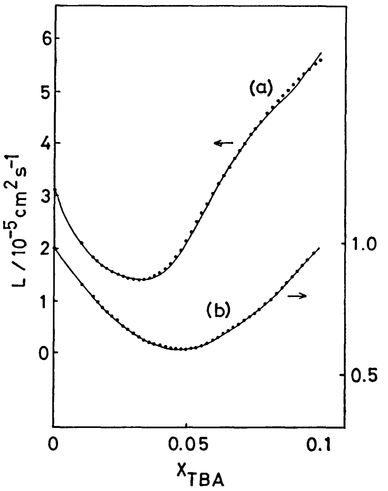

Fig. 6. The observed L values (······) and the best fit curve (——) calculated from Eqs. 8 and 11a: (a) 63 °C, (b) 24 °C.

$$D_{(H_2O)_{11}TBA} \simeq \frac{1}{2}D_{(TBA)_4}$$

and

$$D_{(H_2O)_{20}TBA} \simeq 3D_{(TBA)_{16}}.$$

A self-diffusion coefficient should increase with the decrease in a molecular weight.

Life-time of Local Structure and Mixing State of TBA–Water Solution. In the study of the mean-square concentration fluctuation for the TBA–water system, the existence of local structure of the $g[(H_2O)_lTBA]$, $(H_2O)_r$, and $(TBA)_s$ types has been suggested. In order to compare this result (local structure) with the present result (moving unit), the values of g, l, and s are summarized in Table 2. Hereafter, g, l, r, and s will refer to the parameters related with the local structure, while g^d, l^d, r^d, and s^d will refer to the corresponding parameters related with the moving unit.

In the preceding report,[6)] the g^d value was found to be 2—4 at 24 °C when the l^d value was fixed at 20. Based upon this result, we considered that the local structure obtained from the mean-square concentration fluctuation study can also be a moving unit. However, the estimation of the g^d value corresponding to an l^d value other than 20 has not been done. In the present study, the parameter values have been determined uniquely without fixing the

Table 2. The parameter values which characterize the sizes of the local structures and the moving units

Moving unit:

T/°C	l^{d}	g^{d}	s^{d}	r^{d}
24	11	1	3—5	5—7
63	19—21	1	13—18	8—11

Local structure (data from Ref. 2):

T/°C	l	$g^{a)}$		s	$r^{b)}$
		$x<x^{s}$	$x^{s}<x$		
24	15—19	2—3	4—8	4—16	—
63	21—25	2—3	12—22	2—20	—

a) $x^{s}=0.05$ (mole fraction of TBA). b) The r-value could not be determined uniquely, for the $N\langle(\Delta x)^2\rangle$ value was insensitive to the r-value (see Ref. 2).

l^{d} value. Therefore, we will be discuss about the moving unit in more detail in comparison with the local structure.

The number ratios of TBA to water molecules which form a moving unit, $g^{d}[(H_2O)_{l^d}TBA]$, are 1:11 and 1:20 at 24 and 63 °C respectively. It has been known that TBA molecules form a solid clathrate hydrate of the "17 hydrate" structure with water molecules.[3] In this solid clathrate hydrate, the water molecules form polyhedra, each of which encages a guest molecule. As the number ratio of TBA to water molecules in the moving unit is colse to that in the solid clathrate hydrate (1:17), the moving unit is considered to have a polyhedron-like structure.

It can also be seen from Table 2 that the g^{d} and l^{d} value are smaller than the g and l values respectively. This difference may be explained as follows. A moving unit is defined as a group of molecules which move together for a time much longer than the velocity-correlation time (10^{-13}—10^{-12} s), while a local structure is defined as an averaged local configuration of molecules, without considering its life-time. If the life-time of the local structure of the $g[(H_2O)_lTBA]$ type is as long as that of the moving unit, the g^{d} and l^{d} values should be equal to the g and l values respectively. As g^{d} and l^{d} are different from g and l, we can conclude that the life-time of the local structure of the $g[(H_2O)_lTBA]$ type is shorter than that of the moving unit of the $(H_2O)_{l^d}TBA$. In other words, the moving unit is relatively stable. As the g^{d} value is about 1 in the concentration range of $0<x_{TBA}<0.1$, the local structure determined from the mean-square concentration fluctuation study (*i e.*, $g[(H_2O)_lTBA]$) can be an aggregate of the moving units of the $(H_2O)_{l^d}TBA$ type. The difference between the local structure and the moving unit has already been pointed out in a previous study of the methanol–carbon tetrachloride system and of the ethanol–carbon tetrachloride system.[5]

Now we can answer the question raised in the introductory paragraph. The above results show that the translational motions of the polyhedra which form a local structure, $g[(H_2O)_lTBA]$, are mutually independent. If an "associated polyhedron" is formed in the solution, the motions of the component polyhedra may be considered to be mutually correlated, because the polyhedra share their faces with each other. Thus, the "aggregated polyhedron" is the more appropriate picture for the mixing state of the TBA–water solution.

The above conclusion is schematically visualized in Fig. 7. In the concentration range of $0<x_{TBA}<0.05$, the water molecules form a polyhedron which encages a TBA molecule and the aggregate of a few polyhedra is dispersed in water. In the concentration range of $0.05<x_{TBA}<0.1$, the aggregate of 4—8 polyhedra is dispersed in TBA. The aggregate of the polyhedra grow larger with the increase in the number of the moving units, $(H_2O)_{l^d}TBA$, formed in the solution.

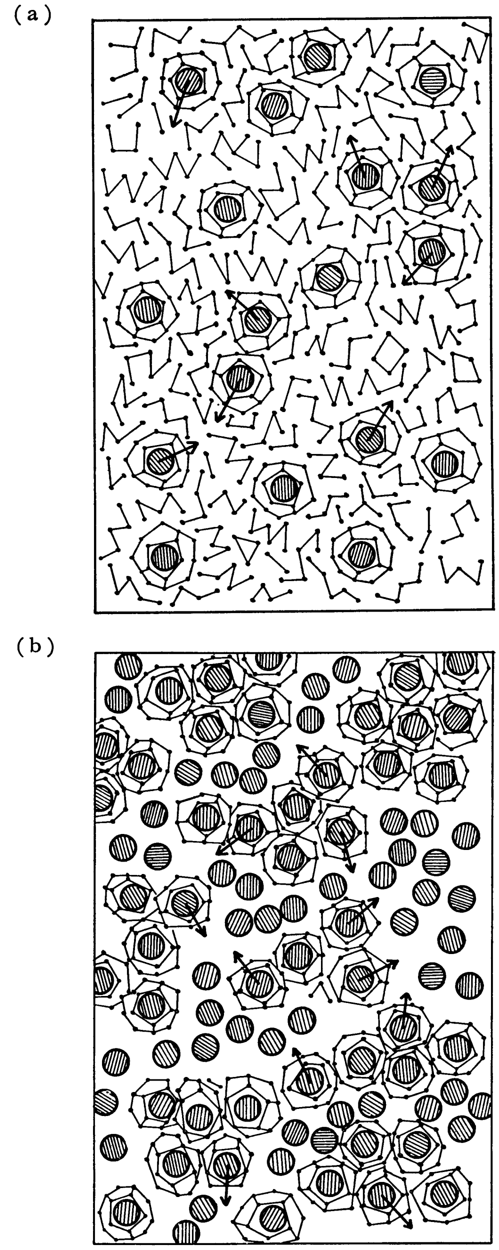

Fig. 7. Mixing state of TBA–water solution for: (a) $x_{TBA}\simeq 0.02$, (b) $x_{TBA}\simeq 0.09$ (schematic) at 24 °C. (●) and (◍) represent a water and a TBA molecule, **respectively.**

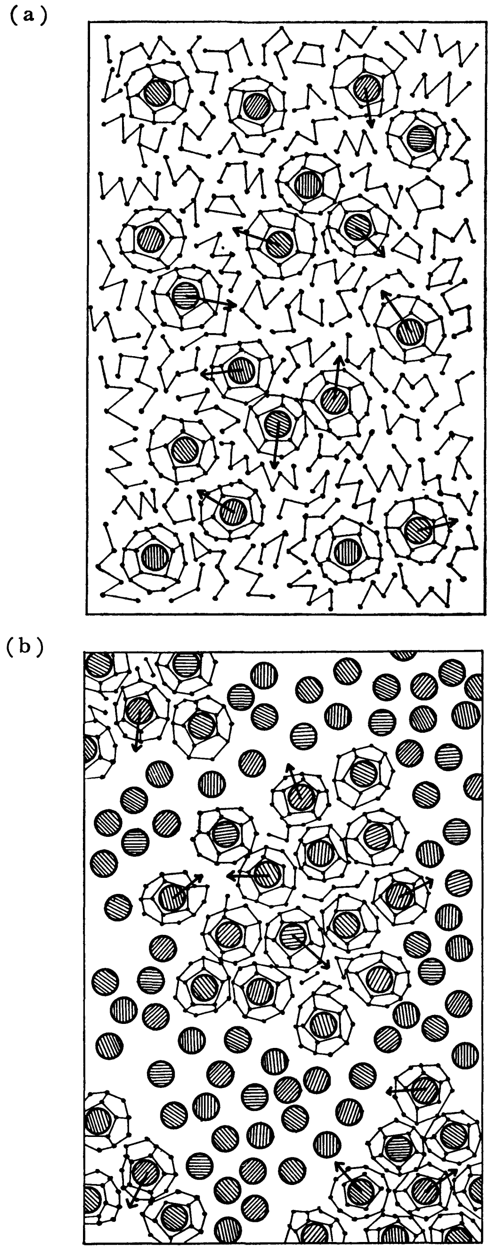

Fig. 8. Mixing state of TBA–water solution for: (a) $x_{\mathrm{TBA}} \simeq 0.02$, (b) $x_{\mathrm{TBA}} \simeq 0.09$ (schematic) at 63 °C. (●) and (◍) represent a water and a TBA molecule, respectively.

Temperature Effect on Mixing State. Next we will discuss the temperature effect on the mixing state of the TBA–water solution. As can be seen from Table 2, the g and l values increase with the increase of the temperature from 24 °C to 63 °C. The simultaneous increase in g and l brings about rapid increase in the total number of molecules which take part in the formation of the local structure of the $g[(\mathrm{H_2O})_l\text{-}\mathrm{TBA}]$ type. The increase in the l value shows that the number ratio of water to TBA molecules increases with the increase in the temperature. It can also be seen from Table 2 that the l^{d} value increases with the increase in the temperature, indicating that the polyhedron formed by water molecules becomes larger with an increasing temperature. It is important to emphasize that the g^{d} value is about 1 at both 24 °C and 63 °C, indicating that the moving unit of the $(\mathrm{H_2O})_{l^{\mathrm{d}}}\mathrm{TBA}$ type is a relatively stable unit and that these moving units gather together to form a local structure. These situations are visualized in Fig. 8, where the state of mixing at 63 °C is schematically drawn. When we drew Figs. 7 and 8, paying particular attention to the magnitudes of $x_{\mathrm{A}_{l^{\mathrm{d}}}\mathrm{B}}/x_{\mathrm{B}}$ and $l^{\mathrm{d}}x_{\mathrm{A}_{l^{\mathrm{d}}}\mathrm{B}}/x_{\mathrm{A}}$, which can be calucluated from Eq. 8d. The former is the number ratio of the moving unit, $(\mathrm{H_2O})_{l^{\mathrm{d}}}\mathrm{TBA}$, to all the TBA molecules in the system. The latter is the number ratio of the water molecules which take part in the formation of the moving unit, $(\mathrm{H_2O})_{l^{\mathrm{d}}}\mathrm{TBA}$, to all the water molecules in the system. In Figs. 7 and 8, arrows are attached to moving units in order to demonstrate that these units can move independently of one another.

In our previous report,[2] we suggested the existence of a pseudo-critical point for this system. If we compare Fig. 7 with Fig. 8, we can see that the state of mixing at 63 °C ($0.05 < x_{\mathrm{TBA}} < 0.1$) is very near to the phase separation into two phases: a water-rich phase and a TBA-rich phase. Moreover, all the water molecules in the water-rich phase may be expected to take part in the formation of polyhedra. Though the phase separation has not been observed at atmospheric pressure for this system, we will probably be able to see this sort of phase separation if we can elevate the temperature of this system under high pressure.

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