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Light Scattering Study of Local Structures in Solutions. Mean Association Numbers and Concentration Fluctuations for Alcohol-Carbon Tetrachloride Systems

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Light scattering spectra were observed for carbon tetrachloride solutions of methanol, ethanol, and 1-propanol. The Rayleigh intensities were reduced to concentration fluctuations. The observed concentration dependence of the concentration fluctuation was analyzed by using two distinct models: an ideal associated complex (IAC) model and a polymer chain (PC) model. In the IAC model, a group of hydrogen-bonded alcohol molecules is treated as a complex whose size is independent of the association number, l. In the PC model, on the other hand, the group of hydrogen-bonded molecules is treated as a linear polymer whose length is proportional to l. It was shown that the PC model can explain both the concentration fluctuation and the heat of mixing data, while the IAC model cannot be applied to the present systems. The mean association number obtained by the IAC model was discussed on the basis of the relation between the concentration fluctuation and the spatial correlation of microscopic density.

Local fluctuations of concentration afford information which is useful in understanding the mixing of a liquid from a molecular viewpoint. Thus we have carried out a series of studies to determine temperature and concentration dependences of concentration fluctuations through observation of light scattering spectra.

The relationship between the mean-square amplitude of concentration fluctuations and Rayleigh intensities has been theoretically established.$^{1)}$ A method has been proposed for determining local structures in associated solutions from the observed concentration fluctuations at various concentrations and various temperatures,$^{2,3)}$ and this method has been applied successfully for the studies of local structures in a few kinds of binary solutions.$^{4-9)}$

In the study of local structures which formed in the ethanol–carbon tetrachloride solution, it was found that the mean association number of ethanol increases up to about 7 with the increase of ethanol mole fraction up to 0.3 and then gradually decreases with the successive increases in ethanol concentration. On the other hand, the heats of mixing for this system have positive values at almost all the concentrations$^{10,11)}$ (See Fig. 14). This suggests that the mean association number increases monotonously with the increase of alcohol concentration, because the heat of mixing can be approximately related to the change of the number of hydrogen bonds on mixing. A similar conclusion has been suggested by the studies by spectroscopic methods.$^{12-15)}$ These results certainly suggest that our previous analysis of the concentration fluctuation values must be modified to some extent in the case of such associative solutions as the ethanol–carbon tetrachloride system.

In the present study, we will analyze the observed concentration fluctuations for the methanol–carbon tetrachloride and 1-propanol–carbon tetrachloride systems, in addition to the ethanol–carbon tetrachloride system, by using a model which can explain both the concentration fluctuations and the heat of mixing data. Then, the mean association number obtained by our previous analysis will be discussed on the basis of the relation between the concentration fluctuation and the spatial correlation of the microscopic density.

Experimental

The samples used in the present study were commercially available reagents. Methanol and 1-propanol were treated with zeorite A-3 in order to eliminate water. The binary solutions of methanol–carbon tetrachloride and 1-propanol–carbon tetrachloride were made dust-free by means of an Atago Abbe refractometer.

Light scattering spectra were observed at 24±1 °C by using a spectrometer which is composed of He–Ne gas laser source (NEC, GLG 108, 60 mW) and a pressure-scanning Fabry-Perot interferometer.$^{16)}$

Results and Discussion

Concentration Fluctuations. The procedure for obtaining the concentration fluctuation values from the observed light scattering spectra is the same as that described in the previous reports. In Fig. 1, the observed mean-square concentration fluctuations, $N\langle(\Delta X_A)^2\rangle$, are plotted against the mole fraction, x_A, of the alcohol for the carbon tetrachloride solutions of methanol, ethanol, and 1-propanol where N is the total number of molecules included in the field within which the concentration fluctuation is considered. The dashed line in the figure corresponds to $N\langle(\Delta X_A)^2\rangle$ expected for an ideal binary solution. It is seen from the figure that observed concentration fluctuations are larger than that of an ideal solution and take maximum values at $X_A=0.3$—0.4.

Analysis of $N\langle(\Delta X_A)^2\rangle$ by Using an Ideal Associated Complex Model. In our previous reports, a method has been presented for determining local structures from the observed $N\langle(\Delta X_A)^2\rangle$.$^{2,3)}$ In this method, we employed an ideal associated complex model$^{17)}$ (IAC model, hereafter). This model includes an assumption that the local structure can be treated as an associated complex; the solution is regarded as an ideal solution whose components are free molecules and associated complex molecules.

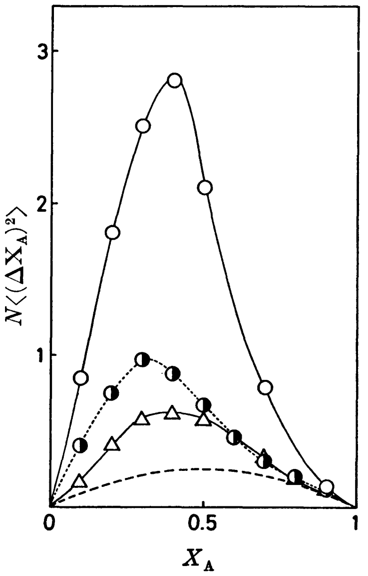

Fig. 1. Observed concentration fluctuation for methanol–carbon tetrachloride system (○), ethanol–carbon tetrachloride system (◑), and 1-propanol–carbon tetrachloride system (△).
The dashed line corresponds to the concentration fluctuation expected for an ideal binary solution.

In the present systems, we assume that associated molecules of the A_l type exist in the solution, where A represents the alcohol molecule and l is an association number. Then, $N<(\Delta X_A)^2>$ is expressed as[7,9)]

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

where n_{Al}^c is the mean number of A_l molecules. Thus, the mean association number of the alcohol, $<l>_w^c$, can be obtained from the observed values of $N<(\Delta X_A)^2>$ at each concentration. The results for the carbon tetrachloride solutions of methanol, ethanol, and 1-propanol are shown in Fig. 2. It is seen from the figures that $<l>_w^c$ increases with the increase of alcohol mole fraction up to 0.3—0.4 and then decreases with the successive increases in alcohol concentration.

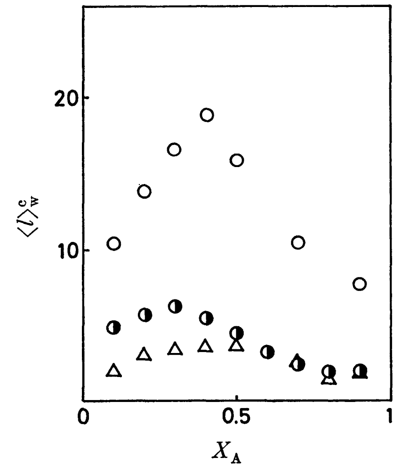

Fig. 2. Mean association numbers of methanol (○), ethanol (◑), and 1-propanol (△) in carbon tetrachloride solutions calculated from Eq. 1 and observed values of concentration flucutuation.

The heat of mixing per molecule, Δh^M, is expressed as

$$\Delta h^M = \frac{1}{n_A+n_B}\{\sum_l (l-1)n_{Al}^c \Delta h^c - \sum_l (l-1) n_{Al}^{c^\circ} \Delta h^c\}$$
$$= X_A \Delta h^c \left(\frac{1}{\langle l\rangle_n^{c^\circ}} - \frac{1}{\langle l\rangle_n^c}\right) \tag{2}$$
$$\langle l\rangle_n^c \equiv \sum_l l n_{Al}^c \Big/ \sum_l n_{Al}^c$$

by using the same model, where n_A and n_B are the numbers of the alcohol and carbon tetrachloride, respectively, Δh^c is the enthalpy change for the reaction

$$A_l + A_1 \longrightarrow A_{l+1}$$

and $n_{Al}^{c^\circ}$ is the mean number of A_l molecules for the pure state. In Eq. 2, Δh^d is assumed to be independent of l. $<l>_n^c$ and $<l>_n^{c^\circ}$ are the mean association numbers of the alcohol for the solution and the pure state, respectively. Although $<l>_n^c$ may differ from $<l>_w^c$ in magnitude, they will show, in principle, the same concentration dependences. The results in Fig. 2 suggest that $<l>_n^c$ is larger than $<l>_n^{c^\circ}$ in magnitude over almost all the concentration range and, therefore, Δh^M will take negative values. However, the experimental values of Δh^M in the literature[10,11,18)] are positive (see Fig. 14), which indicates that the IAC model cannot be applied to the present systems.

Analysis of $N<(\Delta X_A)^2>$ by Using Polymer Chain Model. In the IAC model, it is assumed that the configurations of associated complexes are mutually independent. However, this assumption may not be appropriate for the present systems because the shapes of the complexes may be chain-like in the high concentration range of the alcohol. So we make the following assumptions in this section for a binary solution composed of alcohol(A) and carbon tetrachloride(B) molecules:

(1) Alcohol molecules form linear, hydrogen-bonded polymers $A_l(l=1, 2, \ldots.)$, where l is an association number.

(2) The solution structure is treated by the quasilattice model.

(3) An alcohol l-mer, A_l, occupies the l numbers of cells in the lattice and a carbon tetrachloride molecule occupies one cell. The monomeric unit of the alcohol polymer can be exchanged with a carbon tetrachloride molecule in the lattice cells.

(4) The number of distinguishable ways of arranging the $(\sum_l n_{Al})$ numbers of polymers and n_B numbers of carbon tetrachloride molecules on the $(\sum_l n_{Al}+n_B)$ numbers of cells is given by Flory's equation for polymer solutions:[19)]

$$W = \frac{(\sum_l l n_{Al}+n_B)!}{\prod_l (n_{Al}!) n_B!} \frac{1}{2^{\sum_l n_{Al}}} \left(\frac{z-1}{\sum_l l n_{Al}+n_B}\right)^{\sum_l (l-1) n_{Al}} \tag{3}$$

where n_{Al} and n_B are the number of l-mers and carbon tetrachloride molecules, respectively, and z is the coordination number of the lattice.

(5) The internal motions of molecules belonging to different chemical species (*i.e.*, A_l and A_l', A_l and B,

etc.) are mutually independent.

Under these assumptions, the free energy for (n_A+n_B) molecules, F, in the present system is expressed as

$$F = n_A f_A^\circ + n_B f_B^\circ + \sum_l n_{Al} f_{Al}^E + kT \ln W \tag{4}$$

$$f_{Al}^E \equiv f_{Al} - l f_A^\circ$$

where f_A° and f_A° are the free energy per molecule for the hypothetical pure states of an alcohol and carbon tetrachloride, respectively. The hypothetical pure state is defined as the state where only monomers exist and molecules are arranged on the same lattice as that of the solution. f_{Al} is the free energy for l numbers of alcohol molecules forming an l-mer.

If association equilibria are assumed, the distribution of an association number can be determined by the equilibrium conditions:

$$\mu_{Al} = l\mu_{A_1} \text{ or } \mu_{Al+1} = \mu_{Al} + \mu_{A_1} \tag{5}$$

where

$$\mu_{Al} = \partial F / \partial n_{Al}.$$

Combination of Eqs. 4 and 5 gives the relation

$$\frac{X_{Al+1}}{X_{Al} X_{A_1}} = 2(z-1) \exp(-\Delta f_l / kT) \equiv K_l \tag{6}$$

$$\Delta f_l \equiv f_{Al+1}^E - f_{Al}^E$$

$$X_{Al} \equiv \frac{n_{Al}}{\sum_l l n_{Al} + n_B} \tag{7}$$

where Δf_l is the change of free energy due to the hydrogen bond formation:[20] $A_l + A_l \rightarrow A_{l+1}$. For simplicity, we assume that Δf_l is independent of l, that is

$$K_1 = K_2 = \cdots \equiv K. \tag{8}$$

Then, the X_{Al} can be expressed as

$$X_{Al} = K^{l-1} X_{A_1}^l. \tag{9}$$

The chemical potential of the alcohol is

$$\frac{\mu_A}{kT} = \frac{f_A^\circ}{kT} + \ln X_{A_1} + K X_A X_{A_1}. \tag{10}$$

Concentration fluctuations, $N\langle(\Delta X_A)^2\rangle$, are related to μ_A as

$$N\langle \Delta X_A)^2 \rangle = \left(\frac{X_B}{N}\right)^2 \langle (\Delta n_A)^2 \rangle \tag{11}$$

$$\langle (\Delta n_A)^2 \rangle = \frac{kT}{(\partial \mu_A / \partial n_A)_{n_B}} \tag{12}$$

where Δn_A is the fluctuation of n_A in the region which contains a constant number of B molecules. Combination of Eqs. 10, 11, and 12 gives the equation

$$N\langle (\Delta X_A)^2 \rangle = \frac{X_A(1-X_A)}{X_A + (1-X_A)/\langle l \rangle_w^p} \tag{13}$$

$$\langle l \rangle_w^p \equiv \frac{\sum_l l^2 n_{Al}}{\sum_l l n_{Al}} = \frac{1+KX_{A_1}}{1-KX_{A_1}}. \tag{14}$$

In order to compare the present model (the polymer chain model: PC model, hereafter) with the IAC model, the theoretical values of $N\langle(\Delta X_A)^2\rangle$ calculated for various $\langle l \rangle_w^c$ or $\langle l \rangle_w^p$ values are illustrated in Figs. 3 and 4. Apparently $N\langle(\Delta X_A)^2\rangle$ increases in magnitude as $\langle l \rangle_w^c$ or $\langle l \rangle_w^p$ increases in either model. However, the rate of increase in $N\langle(\Delta X_A)^2\rangle$ for the PC model is smaller than that for the IAC model especially in the

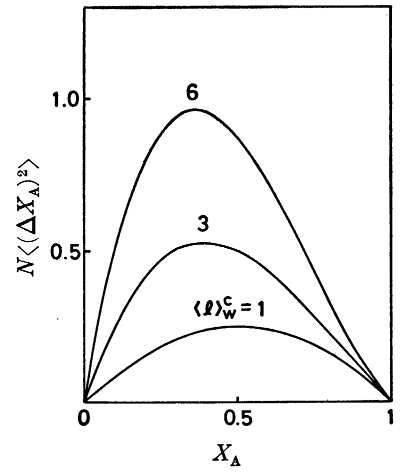

Fig. 3. Theoretical values of concentration fluctuation calculated from Eq. 1 for $\langle l \rangle_w^c = 1$, 3, and 6.

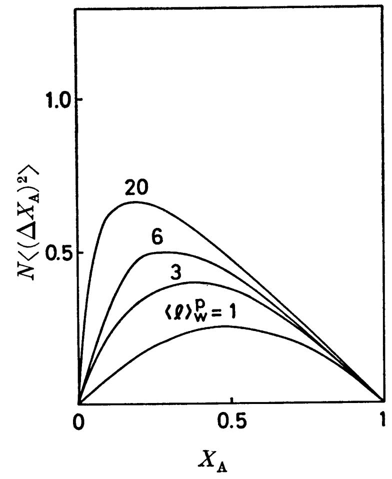

Fig. 4. Theoretical values of concentration fluctuation calculated from Eq. 13 for $\langle l \rangle_w^p = 1$, 3, 6, and 20.

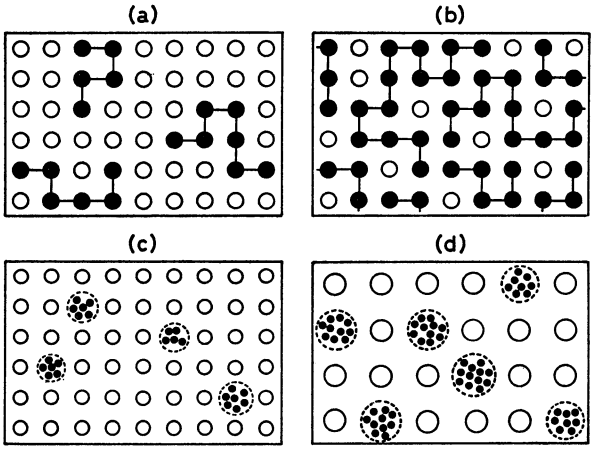

Fig. 5. Schematic representations of the ideal associated complex (IAC) model and the polymer chain (PC) model.

(a): PC model for $X_A \approx 0.3$, (b): PC model for $X_A \approx 0.8$, (c): IAC model for $X_A \approx 0.3$, (d): IAC model for $X_A \approx 0.8$. ● and ○ correspond to the alcohol molecule and the carbon tetrachloride molecule, respectively.

alcohol-rich solutions. The basic differences between the two models are schematically illustrated in Fig. 5. It may be seen from the figure that the two components mix with each other more homogeneously in the PC model than in the IAC model. Concentration fluctuations reflect sensitively the homogeneity of mixing, as can be seen from Figs. 3 and 4.

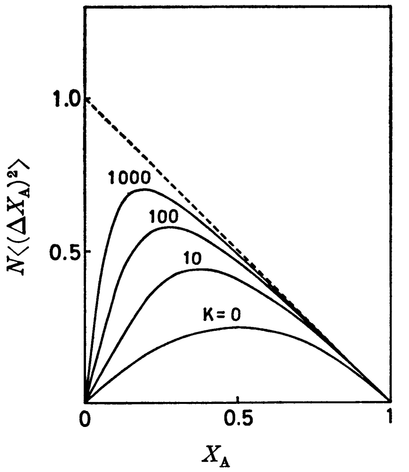

Fig. 6. Theoretical values of concentration fluctuation calculated from Eqs. 13 and 14 for $K=0$, 10, 100, and 1000.

Figure 6 shows the concentration dependences of concentration fluctuations calculated from Eq. 13 for various K values. Comparing the calculated results with the observed concentration fluctuation in Fig. 1, we can see that the PC model can explain the observed values of $N\langle(\Delta X_A)^2\rangle$ in the sense that $N\langle(\Delta X_A)^2\rangle$ takes maximum values at a mole fraction smaller than 0.5. However, the theoretical values of $N\langle(\Delta X_A)^2\rangle$ cannot exceed the values of $(1-X_A)$ even if $K=0$, which shows that the present model is still imperfect for explaining the alcohol solutions.

Modification of the PC Model. In the PC model, it is assumed that an alcohol l-mer occupies l cells in the lattice and, therefore, the number of different configurations of an l-mer is $Z(Z-1)^{l-1}$. In the IAC model, on the other hand, the sizes of associated complexes are all equal to that of a carbon tetrachloride molecule, regardless of their association numbers. It does not seem realistic to assume the ideal mixing of large linear polymers and small monomers, because the configurations of polymers are not mutually independent. In the previous calculation by using the PC model, however, these effects seem to be overemphasized because the hydrogen-bonded polymers are not entirely flexible, as we have assumed. Moreover, the sizes of an alcohol monomer and a carbon tetrachloride molecule are different. So we thought it better to assume that an alcohol l-mer occupies l/ρ cells. Then, the number of distinguishable ways of arranging molecules on the lattice becomes, instead of Eq. 3,

$$W=\frac{\{\sum_l(l/\rho)n_{Al}+n_B\}!}{\prod_l(n_{Al}!)n_B!}\frac{1}{2^{\sum_l n_{Al}}}\left(\frac{z-1}{\sum_l(l/\rho)n_{Al}+n_B}\right)^{\sum_l(l/\rho-1)n_{Al}} \tag{15}$$

and the relation among the mean number of polymers is

$$\frac{X'_{Al+1}}{X'_{Al}X'_{A1}}=2(z-1)\exp(-\Delta f_l/kT)\equiv K \tag{16}$$

$$X'_{Al}\equiv\frac{n_{Al}}{\sum_l(l/\rho)n_{Al}+n_B}. \tag{17}$$

Thus, $N\langle(\Delta X_A)^2\rangle$ is

$$N\langle\Delta X_A\rangle^2=\frac{X_A(1-X_A)\{X_A+\rho(1-X_A)\}^2}{X_A+(\rho/\langle l\rangle_w^p)(1-X_A)} \tag{18}$$

$$\langle l\rangle_w^p=\frac{\sum_l l^2n_{Al}}{\sum_l ln_{Al}}=\frac{1+KX'_{Al}}{1-KX'_{Al}}. \tag{19}$$

In the case where $\rho=\langle l\rangle_w^p$, Eq. 18 is identical with the expression of $N\langle(\Delta X_A)^2\rangle$ in the IAC model, that is, $\langle l\rangle_w^p=\langle l\rangle_w^c$.

Figures 7 and 8 show the concentration dependences of $\langle l\rangle_w^p$ and $N\langle(\Delta X_A)^2\rangle$, respectively, for $K=100$ and various ρ values. Figure 8 demonstrates that the maximum position of the curve moves to the larger-mole-fraction side as ρ increases. Now we can choose the sets of K and ρ values determined for the three systems. These are summarized in Table 1 and the theoretical values of $N\langle(\Delta X_A)^2\rangle$ calculated for the typical sets of parameter in Table 1 are illustrated in Figs. 9—11. Though the agreement between theoretical and observed values was not complete, we were satisfied with the present results and did not modified the model further. The concentration dependences of $\langle l\rangle_w^p$ calculated for these K and ρ values are illustrated in Fig. 12.

The magnitudes of ρ for the three systems studied are in the order methanol>ethanol>1-propanol, as can be seen from Table 1. As ρ has been defined as the number of alcohol molecules which occupy one cell in the lattice, its magnitude is expected to increase with decreasing

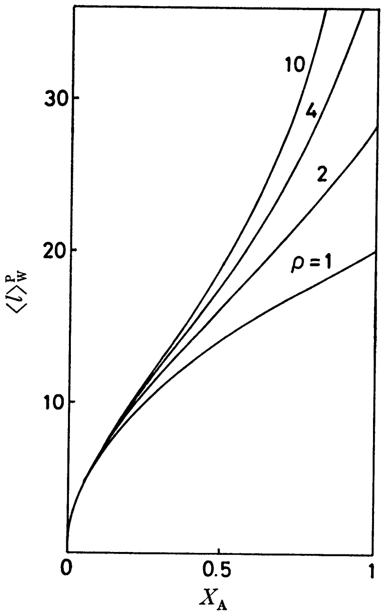

Fig. 7. Theoretical values of mean association numbers calculated from Eq. 19 for $K=100$ and $\rho=1$, 2, 4, and 10.

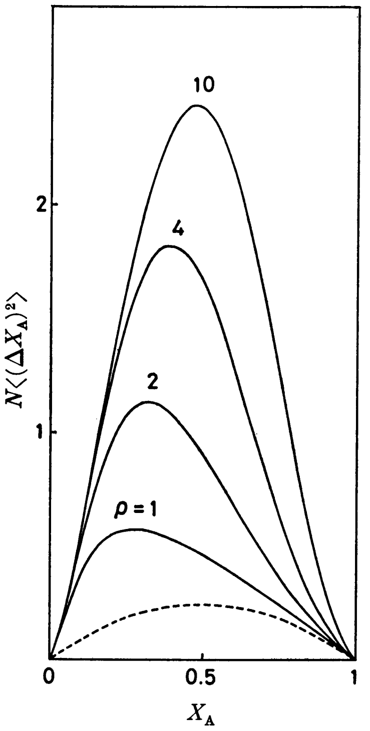

Fig. 8. Theoretical values of concentration fluctuation calculated from Eqs. 18 and 19 for $K=100$ and $\rho=1$, 2, 4, and 10.

Table 1. K and ρ values obtained in the present study for alcohol–carbon tetrachloride systems

	MeOH-CCl_4	EtOH-CCl_4	*n*-PrOH-CCl_4
K	200—300	50—150	10—20
ρ	5—6	1.6—2	1.3—1.6

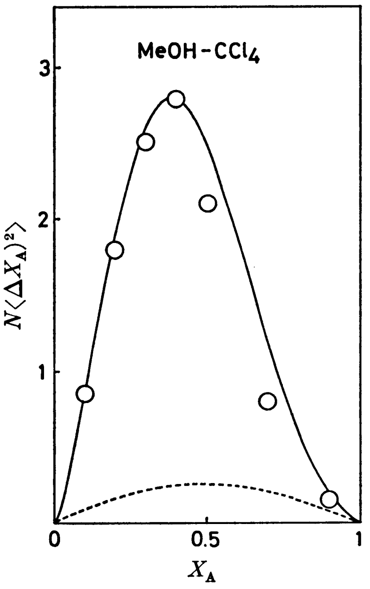

Fig. 9. Concentration fluctuation for methanol–carbon tetrachloride system.
○: Observed values, ——: calculated from Eqs. 18 and 19 for $K=250$ and $\rho=4.2$.

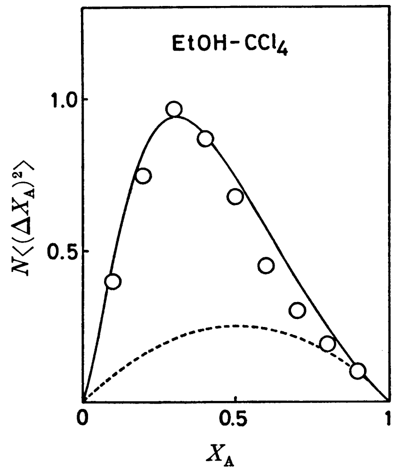

Fig. 10. Concentration fluctuation for ethanol–carbon tetrachloride system.
○: Observed values, ——: calculated from Eqs. 18 and 19 for $K=90$ and $\rho=1.7$.

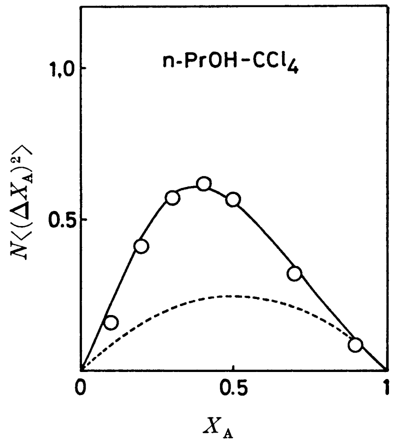

Fig. 11. Concentration fluctuation for 1-propanol–carbon tetrachloride system.
○: Observed values, ——: calculated from Eqs. 18 and 19 for $K=15$ and $\rho=1.45$.

the ratio of the molecular size of the alcohol to that of carbon tetrachloride.[21] The molecular sizes are in the order: carbon tetrachloride>1-propanol>ethanol> methanol. Therefore, the present results are consistent with the above expectation.

So far, ρ has been assumed to be independent of concentration. However, if its magnitude is influenced by the existence of carbon tetrachloride molecules, ρ should decrease its magnitude as the concentration of carbon tetrachloride decreases. Then, the theoretical values of $N\langle(\Delta X_A)^2\rangle$ in the high alcohol concentration range are expected to approach to the observed values, if the concentration dependence of ρ is taken into account.

Calculation of Heat of Mixing. The enthalpy for the (n_A+n_B) numbers of molecules, H, for the present system is expressed by using the PC model as

$$H = n_A h_A^o + n_B h_B^o + \sum_i n_{Ai} h_{Ai}^E \tag{20}$$

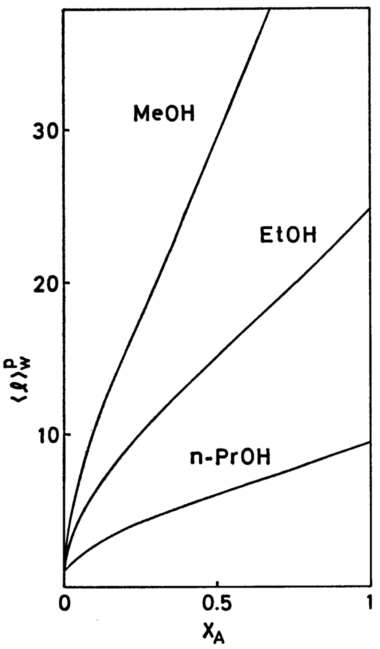

Fig. 12. Mean association numbers of methanol, ethanol, and 1-propanol in carbon tetrachloride solutions calculated from Eq. 19 for the parameters used in calculation of $N\langle(\Delta X_A)^2\rangle$ in Figs. 9—11.

$$h_\alpha^\circ \equiv kT^2 \frac{\partial(f_\alpha^\circ/kT)}{\partial T} \quad (\alpha = \text{A or B})$$

$$h_{Al}^E \equiv kT^2 \frac{\partial(f_{Al}^E/kT)}{\partial T}. \tag{21}$$

As we have assumed that Δf_{Al} of Eqs. 6 and 16 is independent of l, $\Delta h_l (\equiv h_{Al+1}^E - h_{Al}^E)$ is also independent of l, that is

$$\Delta h_1 = \Delta h_2 = \cdots \equiv \Delta h.$$

Then,

$$\sum_l n_{Al} h_{Al}^E = \sum_l n_{Al}(l-1)\Delta h$$

$$= \Delta h n_A \left(1 - \frac{1}{\langle l \rangle_n^p}\right) \tag{22}$$

where

$$\langle l \rangle_n^p = \frac{\sum_l l n_{Al}}{\sum_l n_{Al}} = \frac{1}{1 - KX'_{A_1}}. \tag{23}$$

Thus the heat of mixing per molecule, Δh^M, is

$$\Delta h^M = \Delta h X_A \left(\frac{1}{\langle l \rangle_n^{p\circ}} - \frac{1}{\langle l \rangle_n^p}\right) \tag{24}$$

where $<l>_n^{p\circ}$ is the mean association number in the pure alcohol. Figure 13 shows the values of $(\Delta h^M/\Delta h)$ calculated for the parameters used in the calculation of $N<(\Delta X_A)^2>$ in Figs. 9—11. Observed values of Δh^M at 20 °C are shown in Fig. 14 in the form of $\Delta h^M/kT$. Comparing Fig. 13 with Fig. 14, we can see that the calculated values explain the experimental results in the senses that Δh^M takes positive values and that its magnitude is in the order: 1-propanol>ethanol>methanol.[22)]

The calculation of $\Delta h^M/\Delta h$ in Fig. 13 is done by assuming that ρ is independent of concentration. We have also calculated $\Delta h^M/\Delta h$ for the ρ values which give the best fit between calculated and observed values of $N<(\Delta X_A)^2>$ without chaging the K value. For an example, the results for the methanol–carbon tetrachloride system are illustrated by the dashed line in Fig. 13.[23)] The observed concentration dependences of Δh^M seem to be explained well by the dashed line rather than the solid line in Fig. 13. By comparing the observed values of $\Delta h^M/\Delta h$ and the observed values of Δh^M, the value of Δh has been roughly obtained as 5 kcal mol^{-1} for methanol.

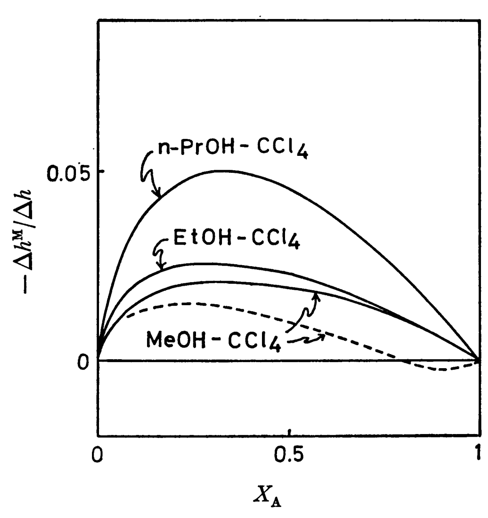

Fig. 13. Theoretical values of $-\Delta h^M/\Delta h$ calculated from Eq. 24 for the parameters used in calculation of $N\langle(\Delta X_A)^2\rangle$ in Figs. 9—11.

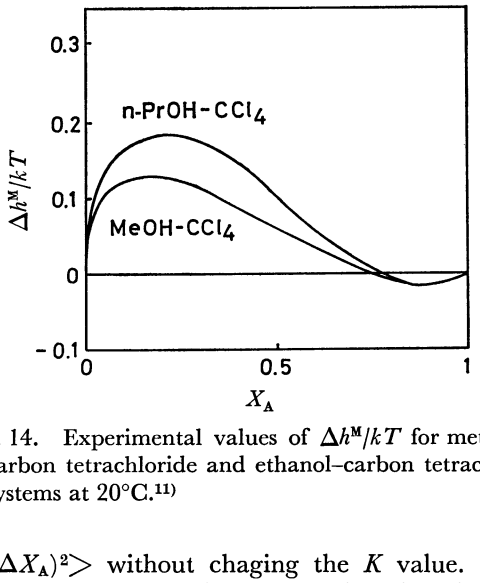

Fig. 14. Experimental values of $\Delta h^M/kT$ for methanol–carbon tetrachloride and ethanol–carbon tetrachloride systems at 20°C.[11)]

Interpretation for $<l>_w^c$. As previously described, the IAC model cannot be applied to the present systems. However, the concentration dependences of $<l>_w^c$ seem to reflect a certain aspect of the mixing state. In this paragraph, $<l>_w^c$ is interpreted based on the relation between $N<(\Delta X_A)^2>$ and the spatial correlation of the microscopic density.

The fluctuation of mole fraction ΔX_A in the constant volume V^* is expressed in terms of the number fluctuation of component molecules as

$$\Delta X_A = \left(\frac{\partial X_A}{\partial n_A}\right)\Delta n_A + \left(\frac{\partial X_A}{\partial n_B}\right)\Delta n_B. \tag{25}$$

Noting that

$$\Delta n_\alpha = \int_{V*} \rho_\alpha(r)\mathrm{d}^3r \qquad \Delta\rho_\alpha(\boldsymbol{r}) = \rho_\alpha(\boldsymbol{r}) - \rho_\alpha \tag{26}$$

where $\rho_\alpha(\boldsymbol{r})$ is the number density of α (α=A or B) at the point $\boldsymbol{r}$ and ρ_α the mean value of $\rho_\alpha(\boldsymbol{r})$, then $N<(\Delta X_\mathrm{A})^2>$ is[24)]

$$N\langle(\Delta X_\mathrm{A})^2\rangle = X_\mathrm{A}X_\mathrm{B}\{1+\rho X_\mathrm{A}X_\mathrm{B}(G_\mathrm{AA}+G_\mathrm{BB}-2G_\mathrm{AB})\} \tag{27}$$

$$G_{\alpha\beta} = \int_{V*}[g_{\alpha\beta}(r)-1]\mathrm{d}^3r \tag{28}$$

where ρ is the mean number density and $g_{\alpha\beta}(r)$ is the pair-distribution function of species α and β:

$$g_{\alpha\beta}(r) = \frac{\langle\rho_\alpha(0)\rho_\beta(r)\rangle - \langle\rho_\alpha\rangle\langle\rho_\beta\rangle\delta(r)\delta_{\alpha\beta}}{\langle\rho_\alpha\rangle\langle\rho_\beta\rangle}. \tag{29}$$

In our previously described treatment, the interactions between B molecules and between A and B molecules are neglected. This assumption corresponds to the relation

$$G_\mathrm{BB} = G_\mathrm{AB}. \tag{30}$$

Then, Eq. 27 is

$$N\langle\Delta X_\mathrm{A})^2\rangle = X_\mathrm{A}X_\mathrm{B}\{1+\rho X_\mathrm{A}X_\mathrm{B}(G_\mathrm{AA}-G_\mathrm{AB})\}. \tag{31}$$

On the other hand, Eq. 1 can be rewritten as

$$N\langle\Delta X_\mathrm{A})^2\rangle = X_\mathrm{A}X_\mathrm{B}\{1+(\langle l\rangle_\mathrm{w}^\mathrm{c}-1)X_\mathrm{B}\}. \tag{32}$$

By comparing Eq. 31 with Eq. 32, we obtain

$$\begin{aligned}\langle l\rangle_\mathrm{w}^\mathrm{c} - 1 &= \rho_\mathrm{A}(G_\mathrm{AA}-G_\mathrm{AB})\\ &= \int_{V*}\rho_\mathrm{A}g_\mathrm{AA}(r)\mathrm{d}^3r - \int_{V*}\rho_\mathrm{A}g_\mathrm{AB}(r)\mathrm{d}^3r.\end{aligned} \tag{33}$$

$\rho_\alpha g_{\alpha\beta}(r)$ 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, $\rho_\mathrm{A}(G_\mathrm{AA}-G_\mathrm{AB})$ is the difference between the mean number of alcohol molecules in the entire surrounding of a carbon tetrachloride molecule and that in the entire surrounding of an alcohol molecule. If the correlations between the positions of different alcohol molecules are rather strong in comparison with those between the positions of alcohol and carbon tetrachloride molecules, $<l>_\mathrm{w}^\mathrm{c}$ takes larger values than unity according to the extent of the correlation. Therefore, $<l>_\mathrm{w}^\mathrm{c}$ is considered to represent the number of alcohol molecules whose positions are strongly correlated.

In the case where the shapes of the hydrogen-bonded species are spherical and their sizes are the same as that of the solvent molecule, $<l>_\mathrm{w}^\mathrm{c}$ becomes equal to $<l>_\mathrm{w}^\mathrm{p}$. 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 hydrogen-bonded species is like a polymer chain and various configurations are possible for the polymer chain (*i.e.*, the polymer chain is flexible), on the other hand, the correlation between positions of molecules which form an hydrogen-bonded species becomes relatively weak. Then $<l>_\mathrm{w}^\mathrm{c}$ is expected to be smaller than $<l>_\mathrm{w}^\mathrm{p}$.

The concentration dependences of $<l>_\mathrm{w}^\mathrm{c}$ and $<l>_\mathrm{w}^\mathrm{p}$ may be interpreted as follows. In the low concentration range of alcohol, the hydrogen-bonded alcohols are isolated by carbon tetrachloride molecules. The correlation between positions of alcohol molecules increase with the increase of $<l>_\mathrm{w}^\mathrm{p}$. In the high concentration range, however, the highly-associated alcohol molecules form a continuous medium. Then the correlation between positions of alcohol molecules becomes weak because of the decrease in the number of carbon tetrachloride molecules which perform the task of isolating the associated alcohol molecules.

Conclusion. We have analyzed the concentration dependences of the mean-square concentration fluctuations observed for carbon tetrachloride solutions of three kinds of alcohols by using two distinct models. In the IAC model, the mean association number, $<l>_\mathrm{w}^\mathrm{c}$, can be obtained directly from the observed concentration fluctuation. However, the experimental values of heats of mixing cannot be explained by this model. On the other hand, the PC model can explain both the concentration fluctuation and the heat of mixing.

In previous reports, we have studied the local structures formed in various solutions by using the IAC model. The present study shows that this model cannot be applied to those solutions in which associative components form long chain-like local structures. For such solutions, the PC model should be used for obtaining the mean association numbers. It must be emphasized, however, that the mean association number, $<l>_\mathrm{w}^\mathrm{c}$, obtained from the IAC model is still a useful quantity, because it represents the extent of correlations between the positions of different associative molecules and because it can be easily and uniquely obtained by measuring the mean-square concentration fluctuation.

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20) The change of free energy related with the polymer configuration is ln $2(z-1)$ and is excluded from Δf_l.

21) If ρ is replaced by v_B/v_A, where v_A and v_B are the molar volumes of alcohol and carbon tetrachloride, K is expressed in terms of the molarity, C_{A_l} (mol dm^{-1}) and the volume fraction, ϕ_{A_l}, as

$$K = \frac{1}{v_B}\frac{c_{A_{l+1}}}{c_{A_l}c_{A_1}} = \frac{v_A}{v_B}\frac{l}{l+1}\frac{\phi_{A_{l+1}}}{\phi_{A_l}\phi_{A_1}}.$$

22) No observed values of $\Delta h^M/kT$ at 20 °C for ethanol–carbon tetrachloride could be found in the literature. However, observed values at 35 °C for the three systems presently studied are in the order: 1-propanol>ethanol>methanol.

23) The ρ value for pure methanol is about 1.8.

24) $G_{\alpha\beta}$ in Eq. 28 is identical with $G_{\alpha\beta}$ defined by Kirkwood and Buff. See J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, **19**, 774 (1951).