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Light Scattering Study of Local Structure in Solutions. Importance of Temperature Dependency Measurements

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Light scattering spectra have been observed for binary solutions of acetic acid and carbon tetrachloride at several concentrations and temperatures. The Rayleigh intensities were reduced to concentration fluctuations. The observed concentration and temperature dependencies of concentration fluctuation were interpreted by assuming association equilibria involving both cyclic dimers and linear polymers. The simultaneous measurement of concentration and temperature dependencies of concentration fluctuation are necessary to determine local structures in solutions where different types of local structure coexist.

The local fluctuation of concentration can aid understanding the mixing of liquids from the molecular viewpoint. Based on this, studies on the temperature and concentration dependencies of concentration fluctuation through observations of light scattering spectra have been initiated.[1)]

The relationship between concentration fluctuation and Rayleigh intensities have been theoretically established[2)] and a method proposed for determining the local structures[3)] existing in associated solutions from observed concentration fluctuation.[4,5)] The validity of the method has been checked for the diethyl ether–chloroform system in which local structures of the (A-B)type (A and B represent diethyl ether and chloroform molecules, respectively) are expected. The method has been extended to the systems in which several types of local structures are formed. The use of infrared and light scattering spectra is complementary and useful to determine local structures for the system in which local structures of the A_l and A_lB types are expected (A_l represents an aggregate which is made up of l molecules of A, and A_lB represents an aggregate which is made up of l molecules of A and one molecule of B). The simultaneous use of microscopic and macroscopic information is necessary to understand the state of mixing in solutions. In certain cases, however, microscopic information such as infrared spectra cannot be obtained for solutions, particularly at high concentration.

In the present report, it will be shown that the simultaneous measurement of concentration and temperature dependnecies of concentration fluctuation can determine local structures in solutions where different types of local structures coexist. The acetic acid–carbon tetrachloride system was chosen because acetic acid molecules have been known to form both cyclic dimers and linear polymers in nonpolar solvents.[7)]

Experimental

Light scattering spectra were observed at 22.5, 37, and 51 °C using a spectrometer designed and constructed in this laboratory.[1)] The spectrometer is composed of a He–Ne gas laser source (NEC, GLG 108) and a pressure scanning Fabry-Perot interferometer. The temperature of the samples was controlled by a high temperature cell developed in this laboratory. A temperature constancy of ±0.1 °C was obtained with the apparatus. The refractive indicies of the samples were measured by an Abbe refractometer (Atago).

The samples used in the present study were commercial products and used without further purification. The binary solution of acetic acid and carbon tetrachloride was made dust-free by the use of a milipore filter FG of 0.2 μm pore size.

Results and Discussion

Light Scattering Spectra and Concentration Fluctuation. Figure 1 illustrates the observed light scattering spectra for the acetic acid–carbon tetrachloride system at 22.5 °C. After separating the Rayleigh part from the observed spectra, the Rayleigh intensity was expressed relative to the Rayleigh intensity of pure carbon tetrachloride. The concentration fluctuation, $N\langle(\Delta X_A)^2\rangle$, was calculated from the relation,[2)]

$$N\langle(\Delta X_A)^2\rangle = \frac{N_A\rho}{M}\left(\frac{\lambda^4}{\pi^2}\right)\frac{1}{4n^2\left(\dfrac{\partial n}{\partial X_A}\right)^2}\{(R_{90})_R-(R_{90})_S\},$$

where N is the total number of molecules included in the field within which the concentration fluctuation is considered, N_A the Avogadro number, M the mean molecular weight, n the refractive index, ρ the density, λ the wavelength of the incident light, X_A the mole fraction of acetic acid, and $(R_{90})_R$ the Rayleigh ratio for a Rayleigh line. $(R_{90})_S$ is the Rayleigh ratio for entropy fluctuation and is expressed by the relationship:

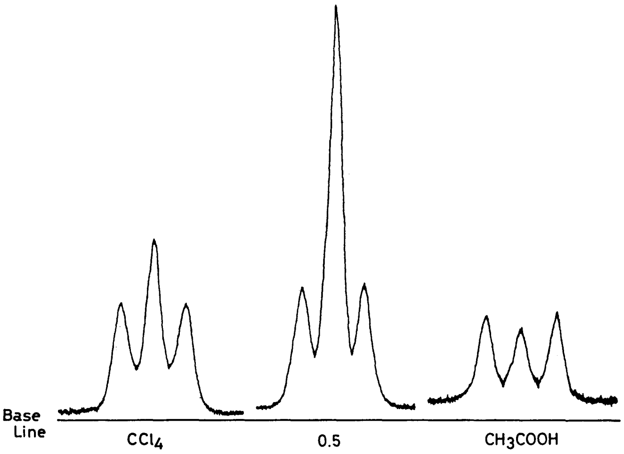

Fig. 1. Observed light scattering spectra for acetic acid-carbon tetrachloride system at 22.5 °C. Concentration is expressed in terms of mole fraction of acetic acid.

$$(R_{90})_S = \frac{\pi^2}{\lambda^4}\frac{4kn^2T^2}{C_{p_g}}\left(\frac{\partial n}{\partial T}\right)^2,$$

where k is the Boltzmann's constant, T the absolute temperature and C_{p_g} the isobaric heat capacity per gram. The values of $(R_{90})_S$ at each mole fraction were calculated from the physical quantities observed or obtained from the literature.[8]

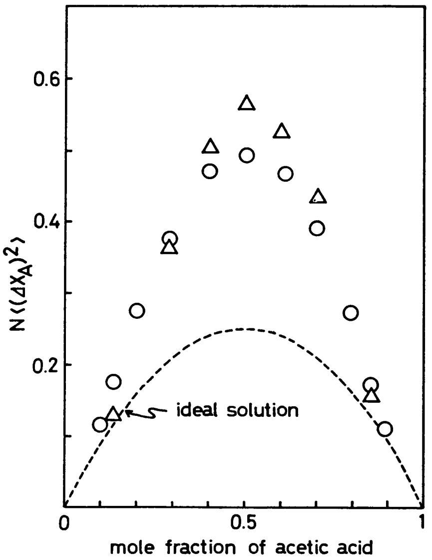

Fig. 2. Observed concentration fluctuation for acetic acid–carbon tetrachloride system at different temperatures: (○) 22.5 °C, (△) 51 °C.

In Fig. 2, the concentration fluctuations thus obtained are plotted against the mole fraction of acetic acid for different temperatures. The dashed line in Fig. 2 corresponds to the concentration fluctuation expected for an ideal solution. It is seen from the figure that the observed concentration fluctuation is larger than that of an ideal solution at all concentrations and the magnitude of concentration fluctuation increases with increasing temperature.

Analysis of Concentration Fluctuation. The method for determining local structures from the observed concentration fluctuation has been reported elsewhere.[4–6] In this method, an ideal associated complex model[9] was employed. This model assumes that the local structure can be treated as an associated complex and the solution regarded as an ideal solution whose components are free molecules and associated complex molecules.

As acetic acid molecules are associated with each other through hydrogen bonding, it may be assumed that associated molecules of the A_l type exist in the solution where A represents the acetic acid molecule and l is an association number. In this case, the concentration fluctuation is expressed by[6]

$$N\langle(\Delta X_A)^2\rangle = X_A(1-X_A)\{(1-X_A)\langle l\rangle+X_A\},$$
$$\langle l\rangle \equiv \frac{\sum_l l^2 n_{A_l}}{\sum_l l n_{A_l}}, \tag{1}$$

where n_{A_l} is the number of A_l molecules and $\langle l\rangle$ is the mean association number. Equation 1 qualitatively explains the present results in the sense that the concentration fluctuation is always larger than that of an ideal solution, $X_A(1-X_A)$. Therefore, the concentration and temperature dependencies of $\langle l\rangle$ may be determined by choosing an appropriate association equilibria model.

Acetic acid molecules are known to form both cyclic dimers and linear polymers. Therefore, $N\langle(\Delta X_A)^2\rangle$ will be calculated for the following types of model systems;

(a) cyclic dimer model,
(b) linear polymer model, and
(c) cyclic dimer-linear polymer model,

and calculated results will be compared with the observed values.

(a) Cyclic Dimer Model: It is assumed that the following species coexist in solutions;

$$A_1,\ A_2^c,\ B, \tag{2}$$

where A_1 and A_2^c represent a monomer and a cyclic dimer of acetic acid, respectively, and B represents a carbon tetrachloride molecule. In this model, the mean association number $\langle l\rangle$ is defined as

$$\langle l\rangle \equiv \frac{n_1+4n_2^c}{n_1+2n_2^c}, \tag{3}$$

where n_1 and n_2^c are the number of species A_1 and A_2^c, respectively. The mean concentrations of these species are related to each other by the equilibrium constant, K^c,

$$\frac{x_2^c}{x_1^2} = \frac{q_2^c}{q_1^2} \equiv K^c, \tag{4}$$

where q_i is a partition function of an i-th species,[6] which depends on temperature and not on concentration. x_i is the mole fraction of the i-th species, namely,

$$x_i = \frac{n_i}{n_1+n_2^c+n_B}, \tag{5}$$

where n_i is the number of carbon tetrachloride molecules. In the special case where $K^c=0$ and $K^c=\infty$, the mean association number may be written as

$$\begin{aligned}\langle l\rangle &= 1 \quad \text{for } K^c = 0,\\ \langle l\rangle &= 2 \quad \text{for } K^c = \infty.\end{aligned} \tag{6}$$

In Fig. 3, the $N\langle(\Delta X_A)^2\rangle$ values calculated for $K^c=0$ and $K^c=\infty$ are compared with the observed values. In the case where $0<K^c<\infty$, the concentration fluctuation takes the values between the values calculated for $K^c=0$ and $K^c=\infty$. It is seen from the figure that the observed values are generally larger than the calculated values for $K^c=\infty$ except for in the low concentration range indicating the existence of a polymer whose association number is larger than two.

(b) Linear Polymer Model: The coexistence of the following species is assumed:

$$\begin{matrix}A_1,\ A_2,\ A_3,\ \ldots,\ A_l,\ldots\\ B\end{matrix} \tag{7}$$

In this model, $\langle l\rangle$ is expressed as

$$\langle l\rangle = \frac{\sum_l l^2 n_l}{\sum_l l n_l} \tag{8}$$

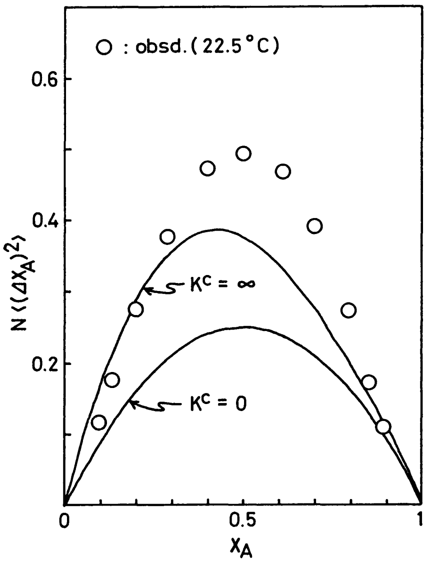

Fig. 3. Theoretical values of concentration fluctuation calculated from Eqs. 1, 3, and 4 for $K^c=0$ and $K^c=\infty$.

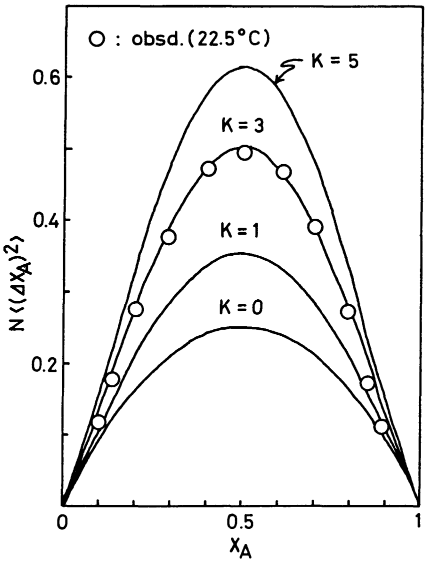

Fig. 4. Theoretical values of concentration fluctuation calculated from Eqs. 1 and 8—10 for $K=0$, 1, 3, and 5.

where n_l is the number of species A_l. The following equilibrium constants are thus defined;

$$\frac{x_3}{x_1^2} = \frac{q_2}{q_1^2} \equiv K_1,$$

$$\frac{x_3}{x_2 x_1} = \frac{q_3}{q_2 q_1} \equiv K_2,$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\frac{x_{l+1}}{x_l x_1} = \frac{q_{l+1}}{q_l q_1} \equiv K_l, \tag{9}$$

and it is assumed that

$$K_1 = K_2 = \ldots = K_l \equiv K. \tag{10}$$

In Fig. 4, the $N\langle(\Delta X_A)^2\rangle$ values calculated for different K values are compared with the observed values. From the figure it is apparent that the concentration fluctuation takes larger values for larger K. Therefore, the equilibrium constant, K, should increase with increasing temperature, since the observed concentration fluctuation increases as the temperature increases. This is inconsistent since the formation enthalpy of hydrogen bonding is negative. Therefore, this model cannot be applied to the present system, although the calculated values for $K=3$ agree well with the observed values at 22.5 °C.

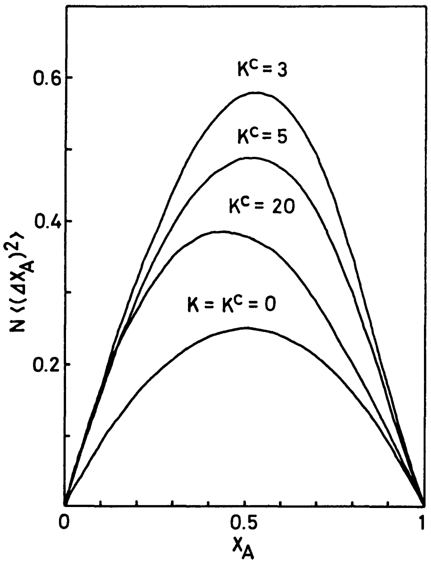

Fig. 5. Theoretical values of concentration fluctuation calculated from Eqs. 1, 12, and 13 for $K=10$ and various K^c values.

(c) Cyclic Dimer-Linear Polymer Model: It is assumed that cyclic dimers and linear polymers coexist in solution, that is, the following species:

$$\begin{array}{l} A_2^c \\ A_1,\ A_2,\ A_3,\ \ldots,\ A_l,\ \ldots. \\ B \end{array} \tag{11}$$

The mean association number and equilibrium constants are

$$\langle l \rangle = \frac{4n_2^c + \sum_l l^2 n_l}{2n_2^c + \sum_l l n_l}, \tag{12}$$

$$\frac{x_2^c}{x_1^2} = K^c,$$

$$\frac{x_2}{x_1^2} = \frac{x_3}{x_2 x_1} = \ldots = \frac{x_{l+1}}{x_l x_1} = \ldots = K. \tag{13}$$

Figure 5 demonstrates the concentration dependencies of the concentration fluctuation calculated for $K=10$ and several K^c values. It is seen from the figure that the concentration fluctuation increases in magnitude with decrease in K^c. This suggests that the observed temperature dependence of concentration fluctuation arises from a difference in temperature dependencies of K and K^c. The best fit between the calculated and observed concentration fluctuation was obtained by setting $K=13$ and $K^c=90$ for 22.5 °C and $K=8$ and $K^c=20$ for 51 °C. The final results for the theoretical calculation are shown in Figs. 6 and 7.

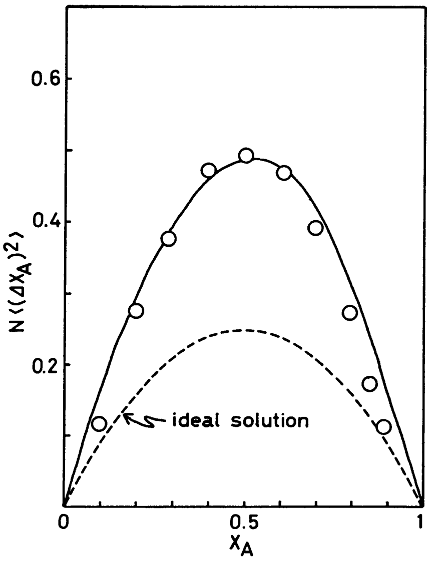

Fig. 6. Final results for theoretical calculations corresponding to experimental values at 22.5 °C.

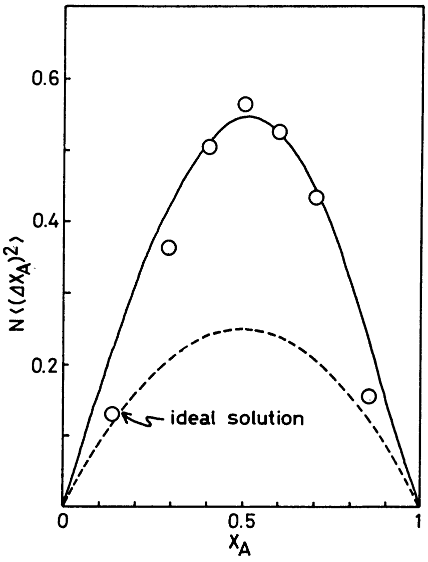

Fig. 7. Final results for theoretical calculations corresponding to experimental values at 51 °C.

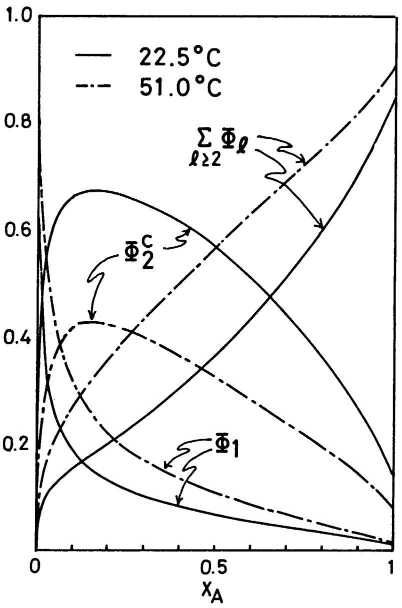

Fig. 8. Concentration and temperature dependencies of Φ^c and Φ_l calculated from Eq. 15.

The formation enthalpy of an associated complex may be calculated from the relationships;

$$\Delta H^c = RT^2\frac{\partial \ln K^c}{\partial T},$$

$$\Delta H = RT^2\frac{\partial \ln K}{\partial T}, \tag{14}$$

where ΔH^c and ΔH are the enthalpy change for the reaction, $A_1+A_1 \rightleftarrows A_2^c$ and $A_l+A_1 \rightleftarrows A_{l+1}$, respectively. The obtained values of ΔH^c and ΔH and the related entropy change, ΔS^c and ΔS, are given in Table 1.

The number ratio of the molecules forming an associated complex to the total acetic acid molecules,

$$\Phi_2^c = \frac{2n_2^c}{2n_2^c+\sum_l ln_l} \quad \text{(cyclic dimers)}$$

or

$$\Phi_l = \frac{ln_l}{2n_2^c+\sum_l ln_l} \quad \text{(linear polymers)} \tag{15}$$

may be calculated from Eq. 13. Figure 8 illustrates the temperature and concentration dependencies of Φ_2^c and Φ_l. It is seen from the figure that almost all the acetic acid molecules form cyclic dimers at low concentrations. At higher concentrations, however, the number of molecules forming linear polymers ($l>2$) is larger than the number of molecules forming cyclic dimers. As the temperature increases, the number of molecules forming cyclic dimers decreases and the molecules forming linear polymers increase. The number of monomers increases with the increase of temperature.

TABLE 1. THE ENTHALPY AND ENTROPY CHANGES CALCULATED FROM EQ. 14

The equilibrium constants at the temperatures of 22.5, 37, and 51 °C have been used in the calculation.

Enthalpy/kcal mol^{-1}		Entropy/cal deg^{-1} mol^{-1}	
ΔH^c	10.1	ΔS^c	25.1
ΔH	3.2	ΔS	5.9

Goldman and Emerson[10] have quantitatively analyzed the NMR chemical shift of the acid proton of acetic acid in carbon tetrachloride solution at several concentrations and temperatures. The present results are consistent with their results qualitatively, although they used three equilibrium constants.

Conclusions. In the preceding paragraphs, the observed concentration fluctuation has been analyzed using three different models of association equilibria. Model(a) is excluded because it could not explain the observed concentration dependence of concentration fluctuation whereas Model (b) and (c) could explain the observed concentration dependence of concentration fluctuation. The observed temperature dependence of concentration fluctuation could not however be explained by model (b). Only model (c) explained the observed concentration and temperature dependencies of concentration fluctuation, simultaneously. It must be emphasized that the mean association number itself can be determined directly from Eq. 1. The introduction of the concept of association equilibria will furnish additional information about the concentration and temperature dependencies of the concentration fluctuation. In determining local structures in solutions where various types of local structures are expected, however, an appropriate model of association equilibria has to be selected from the various plausible models which give the same mean association number. The present results indicate the possibility of determining local structures uniquely by observing both concentration and temperature dependencies for concentration fluctuation.

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3) "Local structure" is defined here as a group of molecules which form a specific local configuration with finite life-time by strong intermolecular interactions such as hydrogen bonding.

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