Light Scattering Study of Local Structures in Solutions. Structure-Forming Effect of Non-Associative Solvent on Ethanol Aggregate

Tsunetake FUJIYAMA and Masami TANAKA

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158

(Received, October 31, 1977)

Light scattering spectra were observed for binary mixtures of ethanol and carbon tetrachloride, and of ethanol and cyclohexane at various concentrations. The Rayleigh intensities were reduced to concentration fluctuation values. From the observed concentration fluctuation values, the mean association numbers of ethanol at each concentration were calculated. The results were compared with that observed in ethanol–chloroform system, where associative interaction between ethanol and chloroform molecules is expected. The concentration dependencies of the mean association numbers suggested that these non-associative solvent molecules (carbon tetrachloride and cyclohexane) promote the formation of large local structure in ethanol solution.

Local fluctuation of concentration is considered to afford information which is useful to understand the mixing of liquid from a molecular viewpoint. Based upon this belief, we have planned a series of studies on analysis of temperature and concentration dependencies of concentration fluctuation through observation of light scattering spectra.[1)]

First the relationship between concentration fluctuation and Rayleigh intensities has been theoretically established.[2)] Then, a theory has been proposed for determining local structures existing in associated solutions from the observed concentration fluctuation in various concentrations and at various temperatures,[3,4)] and the method has been applied successfully for the studies of local structures in a few kinds of binary solutions.[3–6)]

In the study of the local structures which are formed in ethanol–chloroform solution, it has been emphasized that the associative interaction between chloroform and ethanol molecules arrests the growth of the local structure of ethanol and keeps the mean association number of ethanol molecules constant for all the ethanol concentrations. It is of much interest, therefore, to see the effect of non-associative solvents like cyclohexane, in place of associative solvents like chloroform, on the local structure formation of ethanol. In the present report, we will discuss the formation of local structures in ethanol–cyclohexane and ethanol–carbon tetrachloride solutions on the basis of the quantitative analysis of the concentration fluctuation measured by the light scattering spectra.

Experimental

The samples used in the present study were commercially available reagents. Ethanol was purified by distillation after elimination of water by zeolite A-3. Carbon tetrachloride and cyclohexane were purified by distillation. The binary solutions of ethanol–carbon tetrachloride and ethanol–cyclohexane were made dust-free by the use of a millipore filter FG of 0.2 μm pore size. Mole fraction of sample solutions was determined from the weight and density of each component. The refractive indices of the samples were measured by means of a Shimadzu-Bausch Lomb Abbe refractometer 3L. Density data were found in the literature.[7)] The composition derivative of the refractive index at the mole fraction, x, was estimated from the refractive indices measured at $x \pm 0.05$. The temperature derivative of the refractive index at the temperature, T, was estimated from the refractive indices measured at $T \pm 10$ °C.

Light scattering spectra were recorded by using a spectrometer which is composed of a He–Ne gas laser source (NEC, GLG 108, 60 mW) and a pressure scanning Fabry-Perot interferometer. The spacer between the interferometer ethalon has a thickness of 6 mm, giving a free spectral range of 0.82 cm^{-1} and over-all instrumental half-width of about 0.042 cm^{-1}. Details of the spectrometer and the sampling technique have been reported elsewhere along with the reliability of the observed spectral parameters.[1,2)]

The temperature of the sample solutions was controlled by a high temperature cell which was made by the authors. A temperature constancy of ±1 °C was obtained with the use of the apparatus.

Results and Discussion

Light Scattering Spectra and Concentration Fluctuation. Figure 1 shows the light scattering spectra for the ethanol–carbon tetrachloride and ethanol–cyclohexane systems. It is seen from these figures that the Rayleigh intensity increases in magnitude on passing from pure liquids to binary solutions. After separating the Rayleigh part from the observed spectra, a Rayleigh intensity was expressed relative to a Rayleigh intensity of pure ethanol. Then the concentration fluctuation,

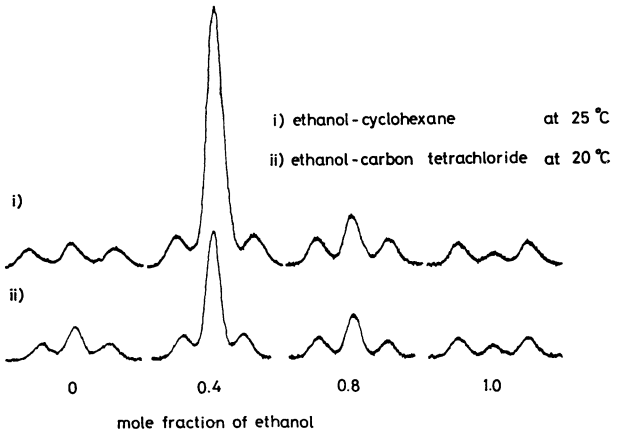

Fig. 1. Observed light scattering spectra for i) ethanol–carbon tetrachloride and ii) ethanol–cyclohexane systems. The concentration is expressed in terms of the mole fraction of ethanol.

$N\langle(\Delta x)^2\rangle$, was calculated from the relation,[2]

$$N\langle(\Delta x)^2\rangle = \frac{N_A\rho}{M}\left(\frac{\lambda_i^4}{\pi^2}\right)\frac{1}{4n^2\left(\frac{\partial n}{\partial x}\right)^2_{T,P}}\{(R_{90})_R-(R_{90})_S\}, \quad (1)$$

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_i the wavelength of the incident light, x the mole fraction of ethanol, 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 relation

$$(R_{90})_S = (\pi^2/\lambda_i^4)\frac{4kn^2T^2}{C_{pg}\rho}\left(\frac{\partial n}{\partial T}\right)^2_{P,x}, \quad (2)$$

where k is the Boltzmann constant, T the absolute temperature, and C_{pg} the isobar heat capacity per gram. The C_{pg} values were found in the literature[8] only for the pure liquids studied in this work. The C_{pg} values for the binary solutions were estimated from the C_{pg} values of the pure component liquids by assuming the relation

$$C_{pg} = x_1C^1_{pg} + x_2C^2_{pg}, \quad (3)$$

where C_{pg} and x_i are the isobar heat capacity and the mole fraction of the i-th component, respectively. The error expected to the C_{pg} values thus obtained was estimated to be about a few percent by considering the C_{pg} values observed for the binary solution of ethanol and methylcyclohexane.[9] As $(R_{90})_R$ is much larger than $(R_{90})_S$ in the present binary mixture, the over-all errors which should be attached to the concentration fluctuation values are mainly determined by the uncertainties expected for the observed composition derivatives fo refractive indices (see Eq. 1).

In Figs. 2 and 3, the concentration fluctuations thus obtained are plotted against the mole fraction, x, of ethanol for ethanol–carbon tetrachloride and for ethanol–cyclohexane systems, respectively. The dashed lines in these figures correspond to the concentration fluctuation expected for an ideal binary solution. The over-all errors which should be attached to the concentration fluctuations are indicated by the vertical lines. It is seen from these figures that the observed concentration fluctuations are generally larger than that of an ideal binary solution. The concentration fluctuation takes a maximum value at $x=0.5$ for an ideal binary solution, while the observed concentration fluctuation takes maximum values at the mole fraction smaller than 0.5 for both carbon tetrachloride and cyclohexane solutions. In ethanol–carbon tetrachloride solution, the concentration fluctuation assumes much larger value for all x than that of an ideal binary solution, and takes maximum value at $x=0.3$ at 20 °C.

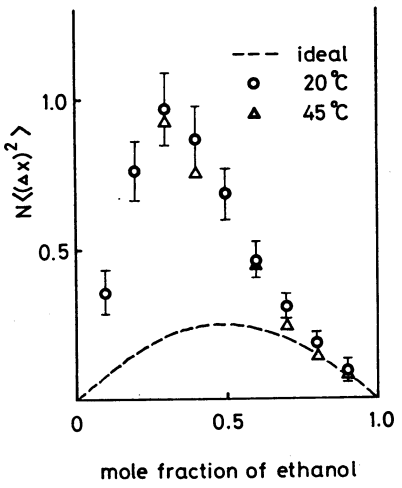

Fig. 2. Observed concentration fluctuation for ethanol–carbon tetrachloride system at the temperatures of 20 and 45 °C. Errors are indicated by the horizontal lines.

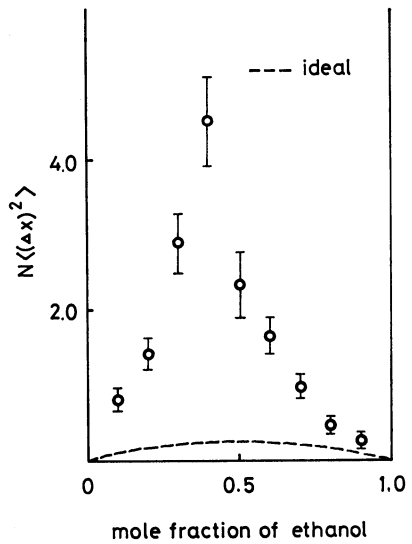

Fig. 3. Observed concentration fluctuation for ethanol–cyclohexane system at the temperature of 25 °C. Errors are indicated by the horizontal lines.

These specific concentration dependencis of the concentration fluctuation may arise from intermolecular interactions between component molecules. Taking into account the possible intermolecular interactions such as hydrogen bonding formation, we tried to estimate possible local structures expected in these ethanol solutions through theoretical consideration of the observed concentration dependencies of the concentration fluctuation.

Determination of Mean Association Number of Ethanol. In our previous reports[4,5] we have presented the associated complex model which can explain the relation between the associated complex formation and the concentration fluctuation in solutions. The associated complex formation in binary solutions would be classified into three cases: 1) the case where association between the same species occurs, 2) the case where association between different species occurs, and 3) the case where association between the same species and between different species occur simultaneously.

It has been shown that, the case 1), the concentration fluctuation takes a larger values than that of an ideal binary solution thoughout the whole concentration (see the systems "A and B_l" and "A_l and B_l" of the previous, report[4]). In the case 2), the concentration fluctuation

takes a smaller value than that of an ideal binary solution throughout the whole concentration (see the system "A and AB" or "B and AB" of the previous report[4]). In the case 3), on the other hand, the concentration fluctuation takes both larger and smaller values than that of an ideal binary solution (see the results for ethanol–chloroform system of the previous report[5]).

As the observed concentration fluctuations of Figs. 2 and 3 are always much larger than that of an ideal binary solution, the states of mixing of the solutions in question must belong to the case 1). In ethanol–carbon tetrachloride and ethanol–cyclohexane systems, it is hardly possible to imagine the associated complex formation between carbon tetrachloride molecules or between cyclohexane molecules. Therefore, we assume that l numbers of ethanol molecules associate with each other, and the resultant associated complex behaves as an independent molecule in these solutions. Then, the relation between the concentration fluctuation, $\langle(\Delta x)^2\rangle$, and the mean association number, l, of ethanol molecule is formulated to be[3,4]

$$N\langle(\Delta x)^2\rangle = x(1-x)\{x+l(1-x)\},$$

or

$$l = \frac{N\langle(\Delta x)^2\rangle - x^2(1-x)}{x(1-x)^2}, \qquad (4)$$

where x is the mole fraction of ethanol. Thus, the mean association number of ethanol can be obtained from Eq. 4 and the observed concentration fluctuation value at each concentration. The mean association numbers thus obtained for ethanol–carbon tetrachloride and ethanol–cyclohexane systems are plotted against the mole fraction of ethanol, respectively, in Figs. 4 and 5.

Local Structures in Ethanol Solutions. It is seen from Figs. 4 and 5 that the mean association number of ethanol molecules changes its magnitude with the change of the concentration. In the case of ethanol–carbon tetrachloride solution at 20 °C, the observed mean association number increases up to about 7 with the increase of ethanol mole fraction up to 0.3 and, then, gradually decreases with the successive increase in ethanol concentration. Almost the same concentration dependence can be seen in Fig. 5 for ethanol–cyclohexane solution. In this case, the maximum mean

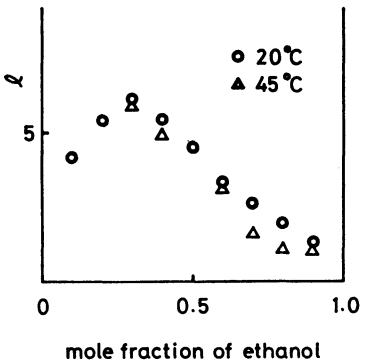

Fig. 4. Concentration dependence of mean association numbers of ethanol molecules observed in ethanol–carbon tetrachloride system.

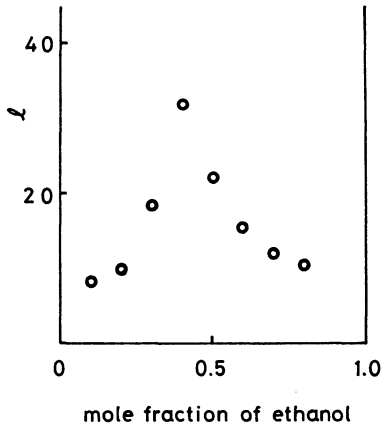

Fig. 5. Concentration dependence of mean association numbers of ethanol molecules observed in ethanol–cyclohexane system.

association number of ethanol is about 32 at 25 °C and is much larger than that observed in carbon tetrachloride solution. These results are in good contrast with the results obtained for ethanol–chloroform solution, namely, the mean association number of ethanol is about 3 for all the ethanol concentrations.[5]

It has been emphasized in the previous reports on the ethanol–chloroform system that the associative interaction between chloroform and ethanol molecules arrests the growth of the local structure of ethanol by truncating the successive growth of hydrogen bonding between ethanol molecules. The remarkable increase of the mean association number observed in the present systems is apparently consistent with this viewpoint, because the interaction between ethanol and cyclohexane or between ethanol and carbon tetrachloride is very weak in comparison with that between ethanol and chloroform molecules. However, the mean association number takes a maximum value in both cyclohexane and carbon tetrachloride solutions. At ceartain ethanol concentration the mean association number began to increase with the increase of ethanol concentration. It may be considered, therefore, that these non-associative solvent molecules promote the formation of larger local structure of ethanol molecules by surrounding and isolating the individual aggregate of ethanol molecules. Then, the decrease of the mean association number of ethanol molecules in the high ethanol concentration range can be understood reasonably, if we remind the fact that the mean association number in pure liquid ethanol is about 3—4.[10,11] As the mole fraction of ethanol increases, the number of carbon tetrachloride or cyclohexane molecules surrounding the ethanol aggregate becomes too small, and consequently neighbouring aggregates merge into more extensive aggregates, which assumes the character of pure liquid ethanol. As the mean association number of ethanol in pure liquid is about 3—4, the above situation is reflected upon the gradual decrease of the mean association number of ethanol from the maximum value down to 3—4, or the gradual breakdown of the local structure of ethanol in these solutions.

The difference between the maximum mean associa-

tion numbers observed in the ethanol–carbon tetrachloride and ethanol–cyclohexane solutions suggests the existence of very weak, but considerable degree of associative interaction between ethanol and carbon tetrachloride molecules in the binary solution of ethanol and carbon tetrachloride.

Concluding Discussion. From the discussion of the preceding paragraphs, the effects of the solvent molecules on a mean association number of ethanol may be summarized as the followings.

1) In the mixture of ethanol and the solvent which is associative with ethanol, the mean association number of ethanol does not exceed 3—4. The associative solvent molecule arrests the formation of large local structure of ethanol by truncating the seccessive hydrogen bond formation. In this sense, the associative solvent like chloroform has structure-breaking property.

2) The mean association number of ethanol increases remarkably in the mixture of ethanol and the solvent which is non-associative with ethanol. In this sense, the non-associative solvents like cyclohexane and carbon tetrachloride have structure-forming property.

The decrease of the mean association number with the increase of ethanol concentration in the ethanol-rich solution can be explained by the decrease of the structure-forming property of the non-associative solvent molecules with the decrease of the concentration of the non-associative solvent.

References

1) K. Iwasaki, M. Tanaka, and T. Fujiyama, *Bunko Kenkyu*, **25**, 134 (1976).
2) K. Iwasaki, M. Tanaka, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **49**, 2719 (1976).
3) T. Kato and T. Fujiyama, *J. Phys. Chem.*, **80**, 2771 (1976).
4) K. Iwasaki, Y. Katayanagi, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **49**, 2988 (1976).
5) T. Kato and T. Fujiyama, *J. Phys. Chem.*, **81**, 1560 (1977).
6) K. Iwasaki and T. Fujiyama, *J. Phys. Chem.*, **81**, 1908 (1977).
7) J. A. Barker, I. Brown, and F. Smith, *Discuss. Faraday Soc.*, **15**, 142 (1953); G. Scatchard and F. G. Satkiewicz, *J. Am. Chem. Soc.*, **86**, 130 (1964).
8) "International Critical Tables," McGraw-Hill, New York (1926). T. Nakamura, Y. Murakami, and R. Fujishiro, *Nippon Kagaku Kaishi*, **1976**, 1034.
9) S. C. P. Hwa and W. T. Ziegler, *J. Phys. Chem.*, **70**, 2572 (1966).
10) A. N. Fletcher, *J. Phys. Chem.*, **76**, 2562 (1972).
11) E. E. Tucker, S. B. Farnham, and S. D. Christian, *J. Phys. Chem.*, **73**, 3820 (1969).