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On the Critical Scattering Phenomena of a Nonpolar Binary Liquid Mixture

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Light scattering phenomena are discussed for a nonpolar binary liquid mixture composed of an optically active solute and an optically nonactive solvent in the critical region, using the Fisher theory. Comparing them with those in the case that the Ornstein-Zernike theory is satisfied, the appropriate analytic results are obtained and discussed.

Introduction

In 1987 we¹ have proposed a general theory of multiple scattering for a nonpolar fluid composed of chiral molecules. It is based on a general theory² of the dielectric tensor well suited, to study the dielectric behavior in the critical region. The theory of multiple scattering has been treated as the same way as that of single scattering in the phenomenological theory given by Einstein.^{3,4} The scattering intensity has been expressed in terms of the correlation function, which gives the information about the effect of fluctuations of the dielectric tensor in the sample fluid and nature of the incident light. The dielectric tensor fluctuates due to the fluctuations in density and other thermodynamic variables. We have considered the scattering only due to the density fluctuations, which plays the most dominant role in the critical region. In the subsequent paper⁵ we have for the first time, discussed the effect of the double scattering on the circular intensity differences in the critical region, where the Ornstein-Zernike theory holds.

The theory of the circular intensity differences has been extended a binary liquid mixture composed of an optically active solute and an optically nonactive solvent.⁶ The mixture is more suitable for experimental verification than the pure fluid. The basic difference with the latter is that there is one more extra variable in the mixture, *i.e.*, the concentration fluctuations. In fact, the concentration fluctuations play the central role in the critical region of a binary liquid mixture.⁷

The purpose of this paper is to analyze the light scattering in the critical region, where the Ornstein-Zernike theory does not hold. The correlation function of concentration fluctuations to be used is the Fisher theory of correlation function.^{8,9}

At first, a general formula for the single scattering intensity and the most dominant part of the double scattering intensity are given.⁶ Then, with the aid of the Fisher theory we obtain the sums and differences of components of the single and double scattering intensities approximately and discuss the circular intensity differences.

Theory

Let us consider a nonpolar binary liquid mixture composed of a chiral solute and an optically nonactive solvent denoted by 1 and 2, respectively. The single and most dominant part of double scattering intensities with the polarization \mathbf{u} in the liquid mixture are expressed as⁶

$$F_{ij}^S(\mathbf{r}, \omega_0) = (4\pi)^{-2} [(\epsilon_0 + 2)/3]^4 \rho_0^2 \omega_0^4 S_C(\mathbf{k}_0 - \mathbf{k}_S) V_S [\mathbf{u} \cdot \gamma'_C(\mathbf{k}_0, \mathbf{k}_S) \cdot \mathbf{E}_0] [\mathbf{u} \cdot \gamma'_C(\mathbf{k}_0, \mathbf{k}_S) \cdot \mathbf{E}_0]^* \quad (2.1)$$

$$F_{ij}^L(\mathbf{r}, \omega_0) = -i(8\pi)^{-2} [(\epsilon_0 + 2)/3]^4 \rho_0^2 \omega_0^4 \int V_0 dr_1 \int V_L dr_2 \int_{-\infty}^{\infty} k dk S_C(\mathbf{k}_0 - k\Omega) S_C(\mathbf{k}_S - k\Omega) [\mathbf{u} \cdot \{\gamma'_C(\mathbf{k}_S, k\Omega) \cdot K_C(k\Omega, \omega_0) \cdot \gamma'_C(k\Omega, \mathbf{k}_0)\} \cdot \mathbf{E}_0] [\mathbf{u} \cdot \{\gamma'_C(\mathbf{k}_S, k\Omega) \cdot K_C(r_{12}, \omega_0) \cdot \gamma'_C(k\Omega, \mathbf{k}_0)\} \cdot \mathbf{E}_0]^* \exp(ikr_{12}) \quad (2.2)$$

where

$$\begin{aligned} \epsilon_0 &= [1 + (2/3)\bar{\alpha}_0^0 \rho_0] / [1 - (1/3)\bar{\alpha}_0^0 \rho_0], \quad \bar{\alpha}_0^0 = \bar{\alpha}_1^0 x_1^0 + \bar{\alpha}_2^0 x_2^0, \\ \gamma'_C(\mathbf{k}_0, \mathbf{k}_S) &= \bar{\alpha}_0^0 + i\bar{\beta}_0^0 U \cdot (\bar{\mathbf{k}}_0 + \bar{\mathbf{k}}_S), \quad \bar{\alpha}_i^0 = (\alpha_i^0 \bar{V}_2 - \alpha_i^2 \bar{V}_1) / \bar{V}, \\ \bar{\beta}_0^0 &= \beta_0^0 x_1^0, \quad \bar{\beta}_i^0 = \beta_i^0 \bar{V}_2 / \bar{V}, \quad \bar{\mathbf{k}} = (1 - \frac{2}{3}\bar{\alpha}_0^0 \rho_0 \bar{x}_1^0), \quad \bar{x}_i^0 = x_i^0 (\bar{V} / \bar{V}_2), \\ \bar{\mathbf{k}} &= (1 - \frac{2}{3}\bar{\alpha}_0^0 \rho_0), \quad \bar{k}_s \cong \bar{k}_0 = n_0 \omega_0, \quad n_0 = \epsilon_0^{1/2}, \\ r_{12} &= r_1 - r_2 = r_{12}\Omega \end{aligned} \quad (2.3)$$

In the above equations ϵ_0 and ρ_0 and the dielectric constant and density of the liquid mixture at equilibrium, respectively; α_i^0 and β_i^0 are the second and third order molecular polarizability constants of the i -th species averaged over the molecular orientation, respectively, U being the Levi-Civita tensor; x_i^0 and \bar{V}_i are the mole fraction and molar volume of the i -th species at equilibrium, respectively; \bar{V} is the molar volume of the mixture; \mathbf{k}_0 and \mathbf{k}_S are the propagation vectors of the incident and scattered fields, respectively; V_S is the scattering volume, which is the cross section of the illuminated volume, V_L and observed volume, V_0 ; the explicit form of the renormalized propagator K_C in this paper may be obtained from K_C in Eq. (2.14) in ref. 5, replacing $\beta_0 \rho_0$ by $\bar{\beta}_0^0 \rho_0 \bar{x}_1^0$ and $S_C(k)$ is the static correlation function of concentration fluctuations. In the present paper we shall use the Fisher theory for the concentration fluctuation correlation function^[6], which is given as follows:^{8,9}

$$S_C(k) = k_B T \kappa / [1 + (\xi k)^2]^{1-\eta/2} \quad (2.4)$$

where $k_B T$ is the Boltzmann factor; ξ are the correlation length of the concentration fluctuations, η is the critical exponent for the correlation length and κ is defined as

$$\kappa = (\rho_0 g_{11})^{-1}; \quad g_{11} = \left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P} \quad (2.5)$$

Here, g is the mean molar Gibbs free energy of the mixture.

Let the direction of propagation of the incident monochromatic plane light be the z direction. Then, the field may be described as

$$E_0(\mathbf{r}, \omega) = E_0 \exp(ik_0 \cdot \mathbf{r}) 2\pi\delta(\omega - \omega_0) \quad (2.6)$$

with

$$k_0 = n(\omega_0)\omega_0, \quad E_0 \cdot k_0 = 0 \quad (2.7)$$

where ω_0 is the frequency of the incident light. For the circularly polarized light, we have

$$E_0 = (E_{0x}\hat{x} + E_{0y}\hat{y})/\sqrt{2}; \quad E_{0x} = \pm iE_{0y} \quad (2.8)$$

where \hat{x} and \hat{y} are the unit vectors of x and y directions, respectively and $+$ ($-$) sign applies for the left (right) polarized light.

Let the directions of the incident and scattered lights be z and y directions, respectively. The detector, on the y axis some $r = r\hat{y}$ far removed from the sample, measures the scattering intensity. Substituting Eqs. (2.7) and (2.8) into Eqs. (2.1) and (2.2), the components of sum and difference between the single scattering intensities for the circularly polarized lights may be given as follow

$$\begin{aligned} F_{Rz} + F_{Lz} &= A(\bar{\beta}_0^0/\bar{\alpha}_0^0)^2 A, \quad \Delta F_z = F_{Rz} - F_{Lz} = 0 \\ F_{Rz} + F_{Lz} &= A, \quad \Delta F_z = -2(\bar{\beta}_0^0/\bar{\alpha}_0^0) A \end{aligned} \quad (2.9)$$

where

$$A = (4\pi)^{-2} [(\epsilon_0 + 2)/3]^4 (\bar{\alpha}_0^0 \rho_0)^2 \omega_0^4 V_S S_C(2^{1/2}k_0) I_0 \quad (2.10)$$

In Eq. (2.9) the subscript $R(L)$ denotes the right (left) circularly polarized light and I_0 is the intensity of the incident light. Using Eqs. (2.2) and (2.6), we may obtain the following expressions for the double scattering

$$\begin{aligned} F_{Rz} + F_{Lz} &= -4\pi B \text{Im} \int V_0 dr_1 \int V_L dr_2 r_{12}^{-1} \int_{-\infty}^{\infty} k dk S_C \\ &\quad (k\Omega - k_0\Omega_y) S_C(k\Omega - k_0\Omega_z) [K_{XZ}(k\Omega, \omega_0) \\ &\quad K_{YZ}^*(r_{12}, \omega_0) + K_{YZ}(k\Omega, \omega_0) K_{XZ}^*(r_{12}, \omega_0)] \\ &\quad \exp(ikr_{12}), \\ F_{Rz} + F_{Lz} &= -4\pi B \text{Im} \int V_0 dr_1 \int V_L dr_2 r_{12}^{-1} \int_{-\infty}^{\infty} k dk S_C \\ &\quad (k\Omega - k_0\Omega_y) S_C(k\Omega - k_0\Omega_z) [K_{XZ}(k\Omega, \omega_0) \\ &\quad K_{XZ}^*(r_{12}, \omega_0) + K_{XZ}(k\Omega, \omega_0) K_{YZ}^*(r_{12}, \omega_0)] \\ &\quad \exp(ikr_{12}), \\ \Delta F_z &= -4B(\bar{\beta}_0^0/\bar{\alpha}_0^0) \int V_0 dr_1 \int V_L dr_2 r_{12}^{-1} \int_{-\infty}^{\infty} k dk S_C \\ &\quad (k\Omega - k_0\Omega_y) S_C(k\Omega - k_0\Omega_z) \{ \bar{k}_0\Omega_y [K_{XZ}(k\Omega, \omega_0) \\ &\quad K_{XZ}^*(r_{12}, \omega_0) + K_{YZ}(k\Omega, \omega_0) K_{XZ}^*(r_{12}, \omega_0)] \\ &\quad + \bar{k}_0\Omega_y [K_{XZ}(k\Omega, \omega_0) K_{XZ}^*(r_{12}, \omega_0) \\ &\quad - K_{XZ}(k\Omega, \omega_0) K_{YZ}^*(r_{12}, \omega_0)] \} \exp(ikr_{12}), \\ &\quad + 4B(\bar{\beta}_0^0/\bar{\alpha}_0^0) \int V_0 dr_1 \int V_L dr_2 r_{12}^{-1} \int_{-\infty}^{\infty} k dk S_C \\ &\quad (k\Omega - k_0\Omega_y) S_C(k\Omega - k_0\Omega_z) \{ [(\bar{k}_0 + \bar{k}_0)\Omega_y K_0(k\Omega, \omega_0) \\ &\quad - 2\bar{\alpha}_0^0 \rho_0 \bar{x}_1^0 \bar{k}_0\Omega_y K_1(k, \omega_0)] K_2(k, \omega_0) \} K_{YZ}^*(r_{12}, \omega_0) \\ &\quad + [(\bar{k}_0 + \bar{k}_0)\Omega_y K_0(k\Omega, \omega_0) - 2\bar{\alpha}_0^0 \rho_0 \bar{x}_1^0 \bar{k}_0\Omega_y K_1(k, \omega_0) \\ &\quad K_2(k, \omega_0)] K_{XZ}^*(r_{12}, \omega_0) \} \exp(ikr_{12}) \end{aligned}$$

$$\begin{aligned} \Delta I_z^d = & -4B(\bar{\beta}_0^1/\bar{\alpha}_0^1) \int V_0 dr_1 \int V_L dr_2 r_{12}^{-1} \int_{-\infty}^{\infty} k dk S_C \\ & (k\Omega - k_0\Omega_y) S_C(k\Omega - k_0\Omega_z) \{k_0\Omega_z [K_{XY}(k\Omega, \omega_0) \\ & K_{XY}^*(r_{12}, \omega_0) + K_{XX}(k\Omega, \omega_0) K_{XX}^*(r_{12}, \omega_0)] \exp(ikr_{12}) \\ & -4B(\bar{\beta}_0^1/\bar{\alpha}_0^1) \int V_0 dr_1 \int V_L dr_2 r_{12}^{-1} \int_{-\infty}^{\infty} k dk S_C \\ & (k\Omega - k_0\Omega_y) S_C(k\Omega - k_0\Omega_z) \{[(\bar{k}_0 + \bar{k})\Omega_z K_0(k\Omega, \omega_0) \\ & - 2\bar{\alpha}_0^1 \rho_0 \bar{x}_1^2 \bar{k}\Omega_z K_1(k, \omega_0)] K_2(k, \omega_0) \} K_{XX}^*(r_{12}, \omega_0) \} \\ & \exp(ikr_{12}) \end{aligned} \quad (2.11)$$

where Im denotes the imaginary part; K_{XY} and K_0 , K_1 , and K_2 are the XY component and scalar parts of the propagator K , respectively⁵ and B and \bar{k} are given as

$$B = (4\pi r)^{-2} [(\epsilon_0 + 2)/3]^4 (\bar{\alpha}_0^1 \rho_0)^4 \omega_0^4 I_0, \quad \bar{k} = [1 - (1/3)\bar{\alpha}_0^1 \rho_0] k \quad (2.12)$$

In the above equation I_0 is the intensity of the incident light.

Let us assume that the observed volume V_0 and illuminated volume V_L are concentric spheres and $V_0 > V_L$. Using the explicit forms of the renormalized propagator and the correlation function in Eq. (2.8) and integrating over k in the complex plane, we may express the z component of the sum of double scattering intensities as

$$I_{Rz}^d + I_{Lz}^d = C[S_c(\sqrt{2}k_0)]^2 F(b, \eta) \quad (2.13)$$

where

$$C = (32\pi r^2)^{-1} [(\epsilon_0 + 2)/3]^8 (\bar{\alpha}_0^1 \rho_0)^4 \omega_0^8 V_L d_0 I_0$$

$$F(b, \eta) = \int_0^\pi d\theta \frac{\sin^3 \theta \cos^2 \theta}{(1 - b \cos \theta)^{1-\eta/2}} \int_0^{2\pi} d\phi \frac{1}{(1 - b \sin \theta \sin \phi)^{1-\eta/2}}$$

$$b = 2p^2/(1 + 2p^2), \quad p = \xi k_0 \quad (2.14)$$

In the above equation d_0 is the radius of the observed volume. Unless the exponent η is zero or an integer, $F(b, \eta)$ cannot be computed analytically. When the system is far from the critical point, $F(b, \eta)$ are equivalent with $F(b, 0)$, since the exponent is much smaller than 1 in three dimension.⁹ As the system approaches to the critical point, the result obtained by Fisher's theory deviates from that of the case that the Ornstein-Zernike theory is satisfied.¹⁰ However, the deviation is very small. For an example, let us consider the ratio of $F(b, 0)/F(b, \eta)$ in the specific value of $b = 0.990$. The value means that when the magnitude of the propagation vector of the incident light, $k_0 \approx 105 \text{ cm}^{-1}$, the correlation length is about $7.040 \times 10^{-5} \text{ cm}$. This case is very close to the critical point. The ratio in the case of $\eta = 0.041^9$ is less than 1.040, which is not large enough compared to the experimental error. In any value of b and η , $F(b, 0)$ is the maximum limit of $F(b, \eta)$ and has of order 1.⁶ This indicates that the deviation from the Ornstein-Zernike theory is mainly due to the other terms in Eq. (2.13). Thus, we may substitute the integral by the case of $\eta = 0$ and the sum of the scattering intensity in the z direction can be written with the aid of Eqs. (2.9), (2.13) and (2.14)

$$I_{Rz}^d + I_{Lz}^d \approx D \quad (2.15)$$

where

$$D = (4r)^{-2} [(\epsilon_0 + 2)/3]^8 (2\epsilon_0)^{-2+\eta} (\bar{\alpha}_0^1 \rho_0)^4 (k_B T \kappa \xi^{-2+\eta})^2 \omega_0^{4+2\eta} V_L d_0 I_0 \quad (2.16)$$

The single scattering intensity in the z direction can be neglected compared with the double scattering, since the former is much less than the latter, if the system is very close to the critical point. The ratio of $I_{Rz} + I_{Lz}$ over the magnitude obtained from the Ornstein-Zernike theory is

$$\frac{I_{Rz} + I_{Lz}}{(I_{Rz} + I_{Lz})_{OZ}} \approx (2\rho^2)^\eta \quad (2.17)$$

The above result becomes concave, as the system approaches to the critical point.⁹ Using the more complicated procedure than above case and taking the most dominant terms, we may obtain

$$\begin{aligned} \Delta I_z \approx & -2D[\bar{\beta}_0^1 n_0 \omega_0 / 3\bar{\alpha}_0^1 (\epsilon_0 + 2)] [3\epsilon_0(9.2 + 0.1\epsilon_0) \\ & + \bar{\alpha}_0^1 \rho_0 \bar{x}_1^2 (2 + \epsilon_0)] 2.0 + 1.8\epsilon_0 \\ I_{Rz} + I_{Lz} = & A_1 [1 + 4D_1 G_2(n_0 \xi \omega_0)] \end{aligned} \quad (2.18)$$

$$\Delta I_x = -2A_1 [\bar{\beta}_0^1 n_0 \omega_0 / \bar{\alpha}_0^1 (\epsilon_0 + 2)] [4 - \epsilon_0 + \frac{D_1}{3} G_3(n_0 \xi \omega_0)]$$

where

$$A_1 = (4r)^{-2} [(\epsilon_0 + 2)/3]^4 (2\epsilon_0)^{-1+\eta/2} (\bar{\alpha}_0^1 \rho_0)^2 \omega_0^{2+\eta} k_B T \kappa \xi^{-2+\eta} V_L I_0$$

$$D_1 = \frac{1}{2} [(\epsilon_0 + 2)/3]^4 (2\epsilon_0)^{-1+\eta/2} (\bar{\alpha}_0^1 \rho_0)^2 \omega_0^{2+\eta} k_B T \kappa \xi^{-2+\eta} d_0$$

$$G_1 = 3\epsilon_0(9.2 + 0.1\epsilon_0) + \bar{\alpha}_0^1 \rho_0 \bar{x}_1^2 (2 + \epsilon_0) (2.0 + 1.8\epsilon_0) \quad (2.19)$$

$$G_2(n_0 \xi \omega_0) \approx \left[\frac{(n_0 \xi \omega_0)^{\eta-1}}{\eta} \right] - 0.1$$

$$\begin{aligned} G_3(n_0 \xi \omega_0) \approx & 3\epsilon_0 \left\{ 2(\epsilon_0 - 1.5) + (16 - \epsilon_0) \left[\frac{(n_0 \xi \omega_0)^{\eta-1}}{\eta} \right] \right\} \\ & - \bar{\alpha}_0^1 \rho_0 \bar{x}_1^2 (2 + \epsilon_0) \left\{ 0.8 + 1.1\epsilon_0 - 2(2 + 3\epsilon_0) \right. \\ & \left. \left[\frac{(n_0 \xi \omega_0)^{\eta-1}}{\eta} \right] \right\} \end{aligned}$$

It can be seen that as $\eta \rightarrow 0$, the above results are reduced to those obtained by the Ornstein-Zernike theory.⁶

The circular intensity difference, Δ is defined as^{5,6,10}

$$\Delta = (I_R - I_L)(I_R + I_L) \quad (2.20)$$

With the aid of Eqs. (2.15), and (2.18), we obtain

$$\Delta_z = -\frac{2\bar{\beta}_0^1 n_0 \omega_0}{3\bar{\alpha}_0^1 (\epsilon_0 + 2)} G_1 \quad (2.21)$$

$$\Delta_x = \frac{2\bar{\beta}_0^1 n_0 \omega_0 [3(4 - \epsilon_0) + D_1 G_3(n_0 \xi \omega_0)]}{3\bar{\alpha}_0^1 (\epsilon_0 + 2) [1 + 4D_1 G_2(n_0 \xi \omega_0)]} \quad (2.22)$$

The circular intensity difference in the x direction is due to the single and double scattering in the nominator and denominator, while it in the z direction is due to the double scattering. In this paper we only considered the single and double scattering, even though the system is very close to the critical point. In fact, the effects of the higher order multiple scattering than the double scattering, attenuation and etc. become important, as the system approaches to the

critical point.¹¹ In the not too distant future we shall discuss the above effects on the circular intensity differences.

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A Mechanistic Study on Acyl Transfer Reactions of Aryl Substituted Benzoates Between Aryloxides

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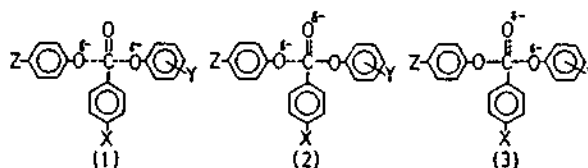
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Second order rate constants have been measured spectrophotometrically for reactions of 4-nitrophenyl substituted benzoates with various aryloxides and aryl benzoates with p-chlorophenoxide. The reactivity has exhibited significant dependences on the electronic nature of the substituent in the acyl moiety of the substrate and in the nucleophilic phenoxide, while the substituent in the leaving phenoxide has little influenced the reactivity. The Bronsted coefficient β values so obtained support that the present acyl transfer reaction proceeds *via* a stepwise mechanism in which the nucleophilic attack would be the rate-determining step. Interestingly, the magnitude of the β_{acyl} and β_{nuc} increases with increasing reactivity, implying that the reactivity selectivity principle is not operative in the present system. The failure of the reactivity selectivity principle is attributed to a change in transition state structure upon the substituent variation in the present acyl transfer reaction.

Introduction

Elucidation of reaction mechanism in chemical reactions has been a main goal for mechanistic chemists.^{1,2} Numerous types of linear free energy relationships (LFERs) have been performed to investigate reaction mechanism,³⁻⁶ especially for biologically important reactions such as acyl transfer reactions. However, acyl transfer reactions have not fully been understood. Two distinct mechanisms have been suggested, *i.e.*, one-step concerted pathway^{3,4} and stepwise addition-elimination pathways.^{5,6} The one-step pathway has been suggested to proceed with a single transition state (1) in which bond formation by nucleophile occurs concertedly with leaving group departure. This mechanism has been supported by the result of *ab initio* calculations for the reaction of CH_3COCl with Cl^- ion^{4a} as well as by experimental results for many types of acyl transfer reactions.^{3,4b} On the other hand, numerous evidences have been reported in favor of the formation of a tetrahedral intermediate in which the TS structure would resemble either 2 or 3 depending on the nature of the rate-determining step.^{5,6}

Therefore the following acyl transfer reactions have been chosen to investigate reaction mechanism systematically. Since the aryl acetates system has only two places (the aromatic rings of the leaving and attacking phenoxides) to place sub-



stituent without changing the structure significantly, limited information (β_{lg} and β_{nuc}) has been obtained from the LFER study. Unlike the effect of substituent on the nucleophile (β_{nuc}) and on the leaving group (β_{lg}), it has been suggested that the effect of substituent on the acyl moiety (β_{acyl}) would give information not just on the charge development but also the hybridization change upon reaching the TS.⁷ Thus, the present system would be considered to be better than the previous aryl acetate system for a systematic study of reaction mechanism, particularly on the nature of the TS structure.⁸ We report here the result of kinetic studies for reac-

