

BULLETIN OF THE KOREAN CHEMICAL SOCIETY

VOLUME 6, NUMBER 3, JUNE 20, 1985

On the Optical Activity of Critical Fluid

Dong Jae Lee

Department of Chemistry, Chonbuk National University, Chonju 520, Korea

Shoon Kyung Kim

Department of Chemistry, Temple University, Philadelphia, Pa. 19122, U.S.A. (Received October 11, 1984)

The optical activity of a fluid in the extreme critical region, where the Ornstein-Zernike theory does not hold, is explicitly obtained. We suggest new experimental methods to measure the critical exponent for correlation function by using the results of circular dichroism and optical rotation given in this paper.

In the previous paper¹ (hereafter referred to as I) we have proposed a general theory for optical activity of a pure fluid composed of chiral molecules. It is based on the model that a chiral molecule is represented by its induced dipole and quadrupole localized at the center of the molecule with the assumption that the applied electromagnetic field varies slowly over the molecular dimension. The theory is so effective that it enables us to calculate optical activity for a critical fluid with the aid of the Ornstein-Zernike theory of the correlation function of density fluctuations. In this paper we shall discuss optical activity for a critical fluid, which does not satisfy the Ornstein-Zernike theory.²

We shall start with eq.(1,4,3), which shows the difference between the refractive indices for the left(right) circularly polarized light

$$n_L(\omega) - n_R(\omega) = -\frac{1}{n_0} \left[\frac{1}{3} (\epsilon_0 + 2) \right]^2 M_{xy}(\vec{k}_0, \omega), \quad (1)$$

where we refer all the notations in this paper to I, since they are just the same as I. The correlation function to be used here, taking the most dominant term²

$$S_z(k) \approx k_B T \chi / (1 + k^2 \xi^2)^{1-\frac{\eta}{2}}, \quad (2)$$

where η is the critical exponent for correlation function. Substituting eq.(2) into eq.(1,4,5) and using the propagators and functions in I, we may calculate the optical rotations under the

condition of $\xi \gg a$ and circular dichroism.

The circular dichroism, $\Delta\alpha(\omega)$, is given as

$$\Delta\alpha(\omega) = 2\omega \text{Im}[n_L(\omega) - n_R(\omega)] = A_\alpha [\Delta\alpha]' \omega^2, \quad (3)$$

with

$$\begin{aligned} [\Delta\alpha]' = & \left(\frac{4 - \epsilon_0}{\epsilon_0 - 1} \right) \frac{1}{\eta(2+\eta)(4+\eta)p^2} [2(2+\eta)(4+\eta)p^2 + 2(4+\eta)p^2 \\ & + 1 - (1+4p^2)^{2+\frac{\eta}{2}}] + \frac{2}{\eta(2+\eta)p^2} \{ (2+\eta)p^2 + 1 \\ & - [(2-\eta)p^2 + 1](1+4p^2)^{\frac{\eta}{2}} \} + \left(\frac{\epsilon_0 + 2}{2\epsilon_0} \right) \left[\frac{1}{\eta} - \left(\frac{1}{\eta} \right. \right. \\ & \left. \left. - \frac{2p^2}{1+4p^2} \right) (1+4p^2)^{\frac{\eta}{2}} \right] + 0(t). \end{aligned} \quad (4)$$

The above result is so complicated that let us consider two limiting cases. If the system is far from the critical point but in the critical region, $\Delta\alpha(\omega)$ becomes

$$\Delta\alpha(\omega) \sim -\frac{4}{3} A_\alpha \left(\frac{4 - \epsilon_0}{\epsilon_0 - 1} \right) n_0^2 \xi^2 \omega^5, \quad \text{if } p \gg 1. \quad (5)$$

The above result, which is just the same as that in I, is proportional to ω^5 . When the system is extremely close to the critical point, we have

$$\begin{aligned} \Delta\alpha(\omega) \sim & A_\alpha \frac{1}{4\epsilon_0(\epsilon_0 - 1)\eta(2+\eta)(4+\eta)} \{ 2(2+\eta)(4+\eta) \\ & (\epsilon_0^2 + 13\epsilon_0 - 2) - 4(4 - 3\eta - 3\eta^2)\epsilon_0^2 + [(208 + 20\eta \end{aligned}$$

$$+4\eta^2 - \eta^3) \epsilon_0 - 2(2-\eta)(2+\eta)(4+\eta)] \\ (2p)^{\eta} \omega^3, \text{ if } p \gg 1. \quad (6)$$

The circular dichroism in the extreme critical region behaves $\sim \omega^3(n_0\xi\omega)^{\eta}$, whereas the circular dichroism of a fluid satisfying the Ornstein-Zernike theory shows logarithmic divergence, $\sim \omega^3$ in $(n_0\xi\omega)$.

The optical rotation, $\phi(\omega)$ may be separated into three parts

$$\phi(\omega) = \frac{1}{2}\omega \operatorname{Re}[n_L(\omega) - n_R(\omega)] \\ = \phi_0(\omega) + \phi_1'(\omega) + \phi_2'(\omega). \quad (7)$$

The first term, ϕ_0 is due to the molecular contribution and has been given in I. The second term, ϕ_1' is

$$\phi_1'(\omega) = - (81\pi^2)^{-1} (4 - \epsilon_0) (\epsilon_0 + 2) \beta_0 \rho_0 (k_B T \chi / \xi^3) \\ \left[\left(\frac{\xi}{a} \right)^{1+\eta} \psi(\eta, \alpha_0 \rho_0) - \frac{\pi}{2} \frac{(\epsilon_0 - 1)^2}{\epsilon_0} \right] \\ \omega^2 (1+p^2)^{\frac{\eta}{2}}, \text{ if } a \ll \xi, \quad (8)$$

with

$$\psi(\eta, \alpha_0 \rho_0) = \int dx x^{\eta} \frac{\theta(x)^2}{1 + \theta(x)}. \quad (9)$$

When $\xi=0$, ψ has been given in ref. 3 and is of the order 1 for $0 \leq \alpha_0 \rho_0 \leq 1$. The function, $\psi(\eta, \alpha_0 \rho_0)$ is also of the order 1 for $0 \leq \alpha_0 \rho_0 \leq 1.5$ and $0 < \eta < 1$. Owing to the condition $a \ll \xi$, the first part is dominant over the second term in the bracket of the right-handed side of eq.(8). The last term in eq.(7) is

$$\phi_2'(\omega) = \phi_2(\omega) (1+p^2)^{\frac{\eta}{2}}, \quad (10)$$

where $\phi_2(\omega)$ has been given in eq.(1,4,15). As discussed in I, ϕ_1' dominates over ϕ_2' in the case of $p < 1$. As the system approaches to the critical point, ϕ_2' becomes more important. If $1 < p \ll |t|^{-1}$, we have

$$\phi_2'(\omega) \approx \left[\frac{1}{3} (\epsilon_0 + 2) (\epsilon_0 - 1) \right]^2 (k_B T \chi / 16 \pi \epsilon_0 \xi^3) \\ \omega^2 p^{1+\eta} |t|. \quad (11)$$

The magnitude of ϕ_2' may be comparable to or larger than ϕ_1' . In the extreme case of $p|t| \gg 1$, ϕ_2' becomes

$$\phi_2'(\omega) \approx \left[\frac{1}{3} (\epsilon_0 + 2) (\epsilon_0 - 1) \right]^2 (k_B T \chi / 32 \epsilon_0 \xi^3) \omega^2 p^{\eta}. \quad (12)$$

The above result independent of β_0 may be comparable to or larger than ϕ_0 . We refer to I for the detailed discussion of the results.

Acknowledgement. One of the authors (D. J. Lee) would like to thank the Korean Science and Engineering Foundation for financial support.

References

- (1) Shoon K. Kim and Dong J. Lee, *J. Chem. Phys.*, **74**, 3597 (1981).
- (2) M. E. Fisher, *J. Math. Phys.*, **5**, 944 (1964).
- (3) D. Bedeaux and P. Mazure, *Physica (Utrecht)*, **67**, 23 (1973).

Kinetic Study on Bromine-Exchange Reaction of Antimony Tribromide with α -Phenylethyl Bromide in Nitrobenzene

Sang Up Choi[†], Young Il Pae* and Sok Hwan Rhyu*

Department of Chemistry, Sogang University, Seoul 121, Korea (Received November 3, 1984)

The kinetic study on the bromine-exchange reaction of antimony tribromide with α -phenylethyl bromide in nitrobenzene has been carried out, using Br-82 labelled antimony tribromide. The results show that the exchange reaction is first order with respect to α -phenylethyl bromide, and either second or first order with respect to antimony tribromide depending on its concentration. It is also concluded that α -phenylethyl bromide exchanges bromine atom with antimony tribromide much faster than other organic bromides previously examined. Reaction mechanisms for the exchange reaction are discussed.

Introduction

Previously we reported the results of the kinetic studies on the bromine-exchange reactions between some metal bromides and various organic bromides in nitrobenzene solution.¹⁻⁸ The systems of antimony tribromide with benzyl and *p*-xylyl bromides in nitrobenzene solution were studied for the bromine-exchange reactions,^{7,8} using radioactive tracer tech-

niques similar to those utilized in the systems of gallium bromide with various organic bromides.¹⁻⁶ The results of the studies on the systems of antimony tribromide with organic bromides indicated that the rates of the exchange reactions were first order with respect to the organic bromides, and either second or first order with respect to antimony tribromide depending on its concentrations. The experimental results also revealed that *p*-xylyl bromide exchanged bromine atom with antimony tribromide much faster than benzyl bromide. Hence, it was thought that

*Department of Chemistry, Ulsan University, Ulsan 690, Korea