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On the Optical Activity of Critical Fluid

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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 paper[1] (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

$$n_L(\omega) - n_R(\omega) = -\frac{1}{n_0}\{\frac{1}{3}(\varepsilon_0+2)\}^2 M_{xy}(\vec{k}_0, \omega),\qquad(1)$$

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 term[3]

$$S_7(k) \simeq k_B T_X / (1+k^2\xi^2)^{1-\frac{\eta}{2}},\qquad(2)$$

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

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

with

$$[\Delta\alpha]' = (\frac{4-\varepsilon_0}{\varepsilon_0-1})\frac{1}{\eta(2+\eta)(4+\eta)p^4}\{2(2+\eta)(4+\eta)p^4+2(4+\eta)p^2$$
$$+1-(1+4p^2)^{2+\frac{\eta}{2}}\}+\frac{2}{\eta(2+\eta)p^2}\{(2+\eta)p^2+1$$
$$-[(2-\eta)p^2+1](1+4p^2)^{\frac{\eta}{2}}\}+(\frac{\varepsilon_0+2}{2\varepsilon_0})\{\frac{1}{\eta}-(\frac{1}{\eta}$$
$$-\frac{2p^2}{1+4p^2})(1+4p^2)^{\frac{\eta}{2}}\}+0(t).\qquad(4)$$

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

$$\Delta\alpha(\omega) \sim -\frac{4}{3}A_\alpha(\frac{4-\varepsilon_0}{\varepsilon_0-1})n_0^2\xi^3\omega^4,\qquad if\ p \gg 1.\qquad(5)$$

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

$$\Delta\alpha(\omega) \sim A_\alpha\frac{1}{4\varepsilon_0(\varepsilon_0-1)\eta(2+\eta)(4+\eta)}\{2(2+\eta)(4+\eta)$$
$$(\varepsilon_0^2+13\varepsilon_0-2)-4(4-3\eta-3\eta^2)\varepsilon_0^2+[(208+20\eta$$

$$+4\eta^{2}-\eta^{3})\varepsilon_{0}-2(2-\eta)(2+\eta)(4+\eta)]$$

$$(2p)^{\eta})\omega^{3}, \text{ if } p\rangle\rangle1. \tag{6}$$

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

$$\phi(\omega)=\frac{1}{2}\omega \ Re[n_{L}(\omega)-n_{R}(\omega)]$$
$$=\phi_{0}(\omega)+\phi_{1}{}'(\omega)+\phi_{2}{}'(\omega). \tag{7}$$

The first term, ϕ_{0} is due to the molecular contribution and has been given in I. The second term, $\phi_{1}{}'$ is

$$\phi_{1}{}'(\omega)=-\ (81\pi^{3})^{-1}(4-\varepsilon_{0})\ (\varepsilon_{0}+2)\beta_{4}\rho_{0}\ (k_{B}Tx/\xi^{3})$$
$$[(\frac{\xi}{a})^{1+\eta}\psi(\eta,\ a_{0}\rho_{0})-\frac{\pi}{2}\frac{(\varepsilon_{0}-1)^{2}}{\varepsilon_{0}}$$
$$\psi(1+p^{2})^{\frac{\eta}{2}}]\omega^{3}, \text{ if } a\langle\xi. \tag{8}$$

with

$$\psi(\eta,\ a_{0}\rho_{0})=\int dx \ x^{\eta}\frac{\theta(x)^{2}}{1+\theta(x)}. \tag{9}$$

When $\xi=0$, ψ has been given in ref. 3 and is of the order 1 for $0\leqslant a_{0}\rho_{0}\leqslant1$. The function, $\psi(\eta,a_{0}\rho_{0})$ is also of the order 1 for $0\leqslant a_{0}\rho_{0}\leqslant1.5$ and $0\langle\eta\langle1$. Owing to the condition $a\langle\xi$, 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

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

where $\phi_{2}(\omega)$ has been given in eq.(1,4,15). As discussed in I, $\phi_{1}{}'$ dominates over $\phi_{2}{}'$ in the case of $p\langle1$. As the system approaches to the critical point, $\phi_{2}{}'$ becomes more important. If $1\langle p\langle|t|^{-1}$, we have

$$\phi_{2}{}'(\omega)\simeq[\frac{1}{3}(\varepsilon_{0}+2)\ (\varepsilon_{0}-1)]^{2}\ (k_{B}T_{x}/16\pi\ \varepsilon_{0}\xi^{3})$$
$$\omega^{3}p^{1+\eta}\ |t|. \tag{11}$$

The magnitude of $\phi_{2}{}'$ may be comparable to or larger than $\phi_{1}{}'$. In the extreme case of $p|t|\gg1$, $\phi_{2}{}'$ becomes

$$\phi_{2}{}'(\omega)\simeq[\frac{1}{3}(\varepsilon_{0}+2)\ (\varepsilon_{0}-1)]^{2}\ (k_{B}T_{x}/32\varepsilon_{0}\xi^{3})\ \omega^{3}p^{\eta}. \tag{12}$$

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.

References

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(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

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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

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