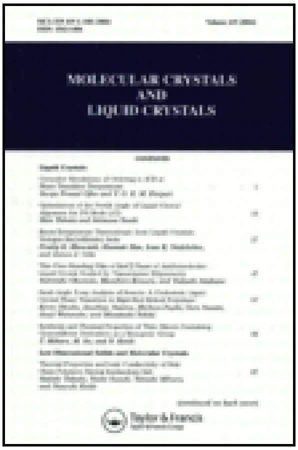

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

IONIC CONDUCTION IN NEMATIC AND SMECTIC A LIQUID CRYSTALS

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To cite this article: Shohei Naemura & Atsushi Sawada (2003): IONIC CONDUCTION IN NEMATIC AND SMECTIC A LIQUID CRYSTALS, Molecular Crystals and Liquid Crystals, 400:1, 79-96

To link to this article: http://dx.doi.org/10.1080/15421400390243066

Mol. Cryst. Liq. Cryst., Vol. 400, pp. 79–96, 2003
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390243066

IONIC CONDUCTION IN NEMATIC AND SMECTIC A LIQUID CRYSTALS

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Permittivity dispersion measurements in a very low frequency range were made on n-pentyl (5CB) and n-octyl (8CB) cyano biphenyls, providing characterization of mobile ions by the diffusion coefficient, or the mobility, and their temperature dependence in the nematic phase and/or the smectic A phase. Ionic conduction was confirmed in the nematic and the smectic A phases from the continuity of these temperature-dependent properties in the isotropic, the nematic, and the smectic A phases with reasonable changes at the transition temperatures. The Walden rule was found to be applicable to the ionic conduction in the nematic phase of 5CB without a pre-transitional phenomemon near the nematic-smectic phase transition, when appropriate mean values are taken for both the anisotropic mobility of ions and the anisotropic viscosity of the liquid crystal substance. It was also pointed out that care should be taken for the applicability of the Walden rule to liquid crystals in the case when the anisotropy of ionic conduction is argued, especially for liquid crystal materials containing mobile ions with a far less anisotropic shape than the liquid crystal molecules.

1. INTRODUCTION

Initiated by studies on Dynamic Scattering Mode, pioneer works to understand the behavior of ions in liquid crystals (LCs) have been devoted to nematic LCs in an early stage of the application of LCs to displays [1,2]. Already in 1972, there appeared an interesting report on smaller conductivity values parallel to the nematic director than those perpendicular to that [3].

The authors wish to express their appreciation to Mr. Ken-ichi Nishikawa and Ms. Ryoko Kimura of Atsugi Technical Center, Merck Japan Limited, for their ion chromatography analysis presented in this paper and their helpful discussions. Appreciation is also due to the other staff members of Atsugi Technical Center, Merck Japan Limited, for their continuous discussions.

Since the Twisted Nematic Mode has become the major player of Liquid Crystal Displays (LCDs), however, the ions in LCs went out of the minds of engineers in the LCD field. In other words, ions in LCs have become a minor player in LCDs and their effects on display performances have been considered to be negligible.

The situation changed when active-matrix (AM) LCDs appeared in the market. LC materials for uses in AM-LCDs are requested to be electrically resistive in a higher level compared to those in passive matrix LCDs. Partly being motivated by recognizing the importance of the behavior of ions even in modern LCDs, studies started again to understand ionic conduction in the nematic phase in details [4–7].

The authors have studies intensively on the behavior of mobile ions in nematic LCs, too, from a standpoint of practical application to LCDs [8–11]. First, we developed a novel method to characterize the mobile ions contained in LC materials with regard to their diffusion coefficients and also to estimate the density [12,13]. By applying this method, we identified the ion species in typical nematic LC materials [14–16].

Compared to these studies on nematic LCs, the studies on conductive phenomena in smectic LCs of nowadays are being focused on the part of electric conduction [17–21] starting from the pioneer works on electric properties of LCs by Kusabayashi and Labes [22].

There also exist limited number of studies on ionic conduction in smectic phases, many of which are on a basis of mobility measurements [23,24] or even conductivity measurements [25]. The arguments of ionic conduction made in some of these studies are based upon the Walden rule [26] and no arguments have been made on the validity of the Walden rule for the ionic conduction in mesophases. In other words, the Walden rule originated from isotropic liquids seems to have been considered to be applicable to ionic conduction in anisotropic LC phases.

Some arguments have also been made on the anisotropic diffusion coefficients of ions in the nematic [26] and the smectic [27] phases. In these studies, however, experiments were made on the systems composed of LC substances and intentionally added ionic compounds, which can not be an evidence of ionic conduction in LC phases of practical-use materials. That is, no measurements have been made directly on the anisotropic diffusion coefficients of ions intrinsically contained in LC materials.

In the following, studies on the behavior of ions in LCs will be expanded from the isotropic phase to the nematic and the smectic A phases, providing arguments on the anisotropic diffusion coefficients of ions in a LC matrix on a basis of measurements of the diffusion coefficients of ions, which were contained intrinsically in LC materials. These arguments together with considerations on the self-diffusion of LC molecules will clarify the validity of the Walden rule in the anisotropic ionic conduction in the nematic and the smectic phases.

2. MOBILE IONS IN LIQUID CRYSTALS

First, characterization was made on ions contained in practical-use LC materials from permittivity dispersion measurements, conditions of which are identical to our previous studies [8]. The LC materials examined are *n*-pentyl cyano biphenyl (5CB) and *n*-octyl cyano biphenyl (8CB). Measurements were made on the temperature dependence of the complex permittivity dispersion in a low frequency range between 10^{-4} Hz and 10^{3} Hz. The temperature ranges, in which the measurements were done, cover the nematic and the isotropic phases of 5CB and moreover the smectic A phase in case of 8CB. The phase sequences and the transition temperatures of these LC substances are listed in Table I.

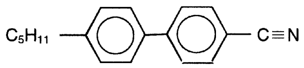
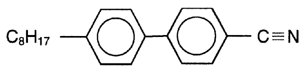
Examples of measured frequency dependence of the real part and the imaginary part of the complex permittivity are shown in Figures 1 and 2 for 5CB at 50°C in the isotropic phase [9]. These results provide an estimation of the diffusion coefficient D and the number density n of mobile ions as described in our previous paper [13] and as listed in Table II. Here in the speculation of the number density, the quantity of electricity of the ions argued in this paper is assumed to be equal to the elementary electric charge.

By using the Stokes-Einstein equation,

$$6\pi\eta R_S D = k_B T, \tag{1}$$

and the measured viscosity η of 5CB at $T = 323$ (50°C), the diffusion coefficient value can be converted into the Stokes radius R_S of the ions. Here, k_B is the Boltzmann constant. Thus, the majority of the mobile ions

TABLE I Chemical structures, Phase Sequences and the Transition Temperatures of LC Substances Examined; n-pentyl cyano biphenyl (5CB) and n-octyl cyano biphenyl (8CB)

	Chemical structure	Phase sequences (Transition temperature, °C)
5CB		C (24) N (35.3) I
8CB		C (21.5) S_A (33.5) N (40.5) I

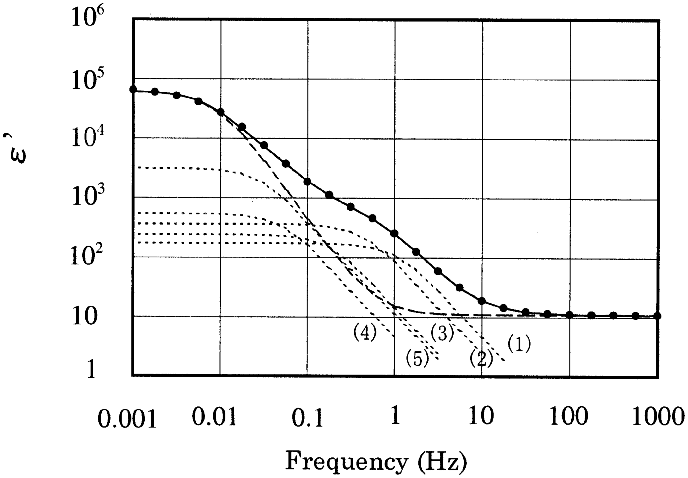


FIGURE 1 Frequency dependence of the real part ε' of the complex permittivity, measured and calculated for 5CB at 50°C; Symbols: measured, Dashed line: calculated contribution from electric double layers, Dotted lines: calculated contributions from 5 kinds of ions (1)–(5) with attributes listed in Table II, Solid line: Accumulation of the contributions from the electric double layers and the 5 kinds of ions.

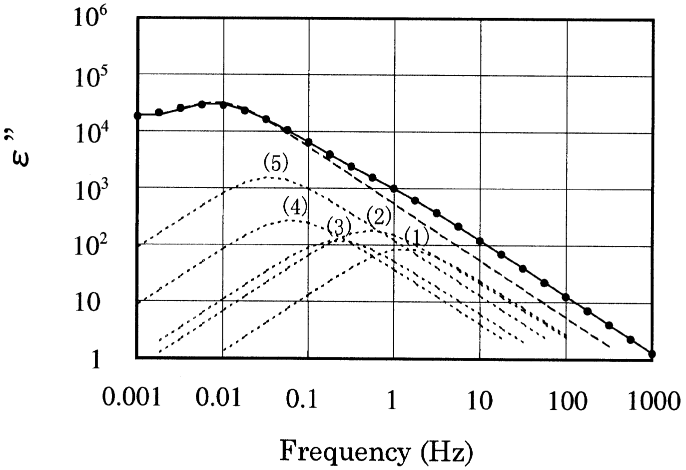


FIGURE 2 Frequency dependence of the imaginary part ε'' of the complex permittivity, measured and calculated for 5CB at 50°C; Symbols: measured, Dashed line: calculated contribution from electric double layers, Dotted lines: calculated contributions from 5 kinds of ions (1)–(5) with attributes listed in Table II, Solid line: Accumulation of the contributions from the electric double layers and the 5 kinds of ions.

TABLE II Attributes of Ions Contained in 5CB in the Isotropic Phase at 50°C; D: Diffusion Coefficient, n: Number Density, R_S: Stokes Radius

Ion	D (m^2/s)	n (m^{-3})	R_S (m)
(1)	7.1×10^{-11}	3.8×10^{19}	2.5×10^{-10}
(2)	2.9×10^{-11}	8.0×10^{19}	6.0×10^{-10}
(3)	1.2×10^{-11}	5.3×10^{19}	1.5×10^{-9}
(4)	3.4×10^{-12}	1.2×10^{20}	5.1×10^{-9}
(5)	1.9×10^{-12}	6.8×10^{20}	9.2×10^{-9}

observed are speculated to be in the size of 2.5×10^{-10} m to 1.5×10^{-9} m in terms of the Stokes radius as also listed in Table II, providing the idea that inorganic ions are playing an important role to form those ions in the structures of naked, hydrated and solvated ions with polar organic molecules [14]. Existence of free inorganic ions in LC materials were confirmed by ion chromatography measurements and the majority was found to be Br^- and SO_4^{2-} anions and NH_4^+ cations as shown in Figure 3. The major contributions of inorganic ions to the electric conduction of LC materials were also confirmed by the fact that LC materials with higher specific resistivity exhibit less concentration of free inorganic ions according to the ion chromatography measurements as shown in Figure 4. The permittivity dispersion measurements on 8CB in the isotropic phase also provided the similar attributes of contained ions as listed in Table III.

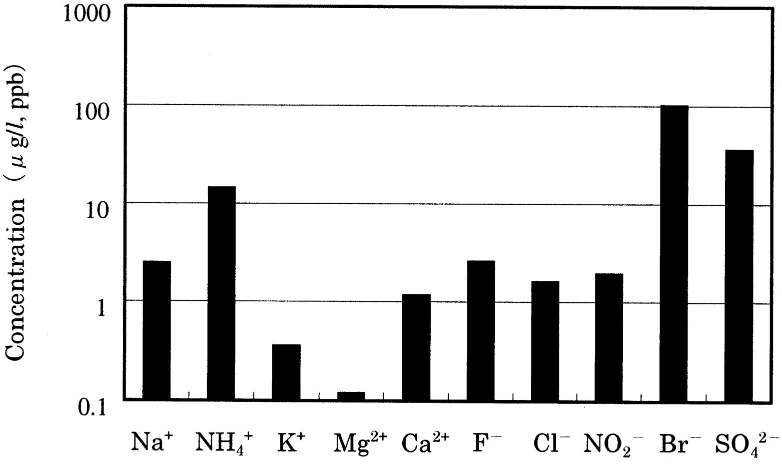


FIGURE 3 Inorganic ions in 5CB detected by ion chromatography.

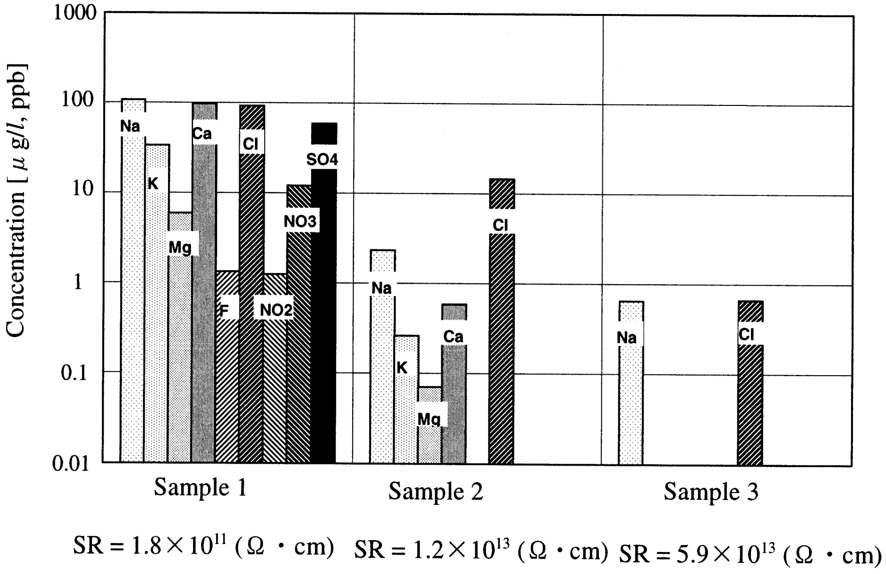


FIGURE 4 Inorganic ions in LC materials detected by ion chromatography.

TABLE III Attributes of Ions Contained in 8CB in the Isotropic Phase at 52°C; *D*: Diffusion Coefficient, *n*: Number Density, R_S: Stokes Radius

Ion	D (m^2/s)	n (m^{-3})	R_S (m)
(1)	9.9×10^{-11}	2.8×10^{18}	1.4×10^{-10}
(2)	5.1×10^{-11}	1.6×10^{19}	2.8×10^{-10}
(3)	1.8×10^{-11}	2.8×10^{19}	7.8×10^{-10}
(4)	7.8×10^{-12}	4.4×10^{19}	1.8×10^{-9}
(5)	1.8×10^{-12}	1.4×10^{20}	7.8×10^{-9}
(6)	2.7×10^{-13}	6.9×10^{20}	5.2×10^{-8}

3. IONIC CONDUCTION IN LIQUID CRYSTALS

3.1. 5CB in Isotropic and Nematic Phases

Figures 5 and 6 show the permittivity dispersion of 5CB measured by taking the temperature as a parameter [11]. At the temperatures (1) 23.1°C, (2) 26.1°C, (3) 29.2°C and (4) 32.3°C, 5CB exhibits the nematic phase and at the temperatures (5) 38.5°C, (6) 44.7°C and (7) 50.8°C, 5CB is in the isotropic phase. By applying the above method to characterize the mobile ions introducing the observed dispersion of the space charge

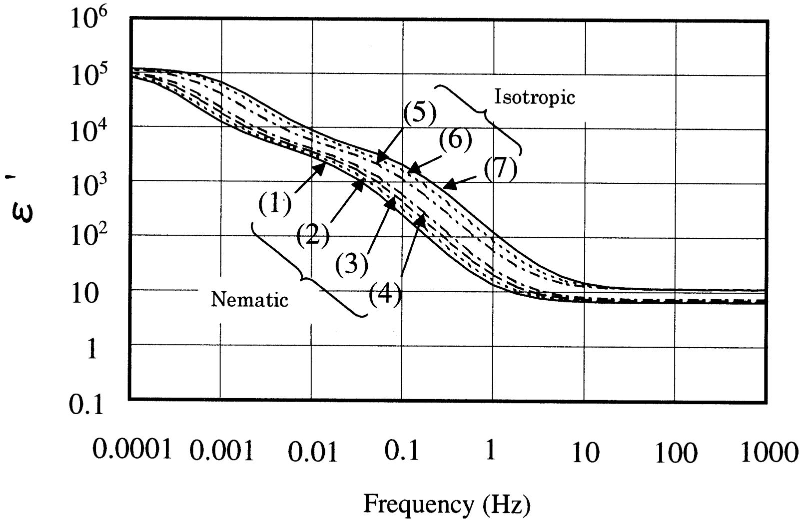


FIGURE 5 Measured frequency dependence of the real part ε′ of the complex permittivity, of 5CB with temperature as a parameter, (1) 23.1°C, (2) 26.1°C, (3) 29.2°C, and (4) 32.3°C in the nematic phase, (5) 38.5°C, (6) 44.7°C and (7) 50.8°C in the isotropic phase.

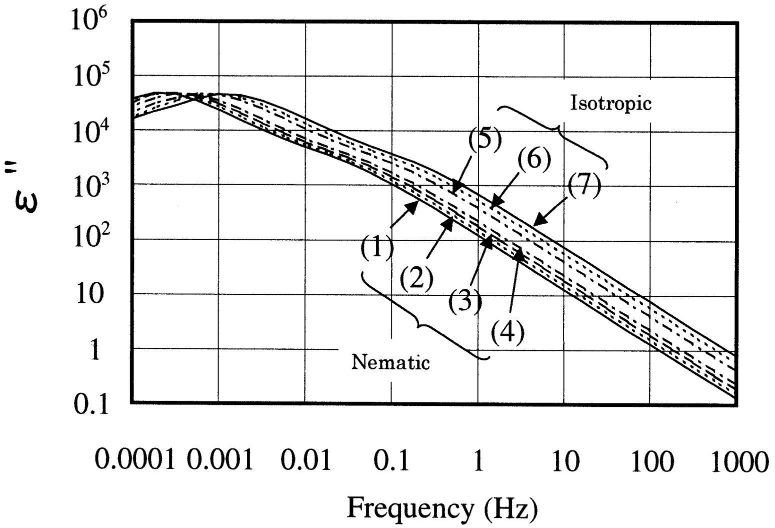


FIGURE 6 Measured frequency dependence of the imaginary part ε″ of the complex permittivity, of 5CB with temperature as a parameter, (1) 23.1°C, (2) 26.1°C, (3) 29.2°C, and (4) 32.3°C in the nematic phase, (5) 38.5°C, (6) 44.7°C and (7) 50.8°C in the isotropic phase.

TABLE IV Temperature Dependence of Attributes of an Average Kind of Ion in 5CB in the Nematic and the Isotropic Phases; Tr: Reduced Temperature, D: Diffusion Coefficient (Anisotropic Component $D_\perp$ Perpendicular to the Director in Case of the Nematic Phase, μ: Mobility (Anisotropic Component $\mu_\perp$ Perpendicular to the Director in Case of the Nematic Phase), n: Number Density

Temp. (°C)	Tr	$D_\perp$(m^2/s)	$\mu_\perp$(m^2/Vs)	n(m^{-3})
23.1	0.96	4.90×10^{-12}	1.92×10^{-10}	1.85×10^{20}
26.1	0.97	5.95×10^{-12}	2.31×10^{-10}	1.85×10^{20}
29.2	0.98	7.45×10^{-12}	2.86×10^{-10}	1.83×10^{20}
32.3	0.99	9.30×10^{-12}	3.53×10^{-10}	1.80×10^{20}
38.5	1.01	1.70×10^{-11}	6.33×10^{-10}	1.85×10^{20}
44.7	1.03	2.30×10^{-11}	8.39×10^{-10}	1.95×10^{20}
50.8	1.05	2.95×10^{-11}	1.06×10^{-9}	2.05×10^{20}

polarization, the diffusion coefficient and the number density of the ions at these temperatures were obtained as shown in Table IV.

In Table IV, the mobility of the ions are also listed, which were calculated by using the Nernst-Einstein-Townsend equation,

$$\mu = qD/k_BT. \tag{2}$$

Here, the characterization was made on an average kind of ions with regard to the diffusion coefficient and the number density. Actually, the curve fitting method was applied to the obtained permittivity dispersion by assuming that there exists only one kind of ions with regard to the diffusion coefficient and the number density. This was made for a simplicity reason, and it was also briefly confirmed that there appear no significant differences in the following arguments even if we make for each kind of ions classified in Table II.

The diffusion coefficient and the mobility values listed in Table IV at the temperatures within the nematic range of 5CB are the components, $D_\perp$ and $\mu_\perp$, perpendicular to the director. It is because a homogeneous alignment was confirmed for the test cell from the dielectric constant measurements in the nematic phase [11].

The parallel component of the mobility $\mu_\parallel$ was determined as follows. Assuming that the electric conduction of 5CB in the nematic phase is dominated by the ions characterized above, the conductivity σ is given by $nq\mu$, and therefore the following equation seems to be valid:

$$\sigma_\parallel/\sigma_\perp = \mu_\parallel/\mu_\perp. \tag{3}$$

The conductivity $\sigma_\perp$ of the LC bulk was obtained from the same measurement that was made on the permittivity by using the impedance

TABLE V Temperature Dependence of the Anisotropic Components ($\mu_{\parallel}$, $\mu_{\perp}$) of the Mobility of an Average Kind of Ions in 5CB in the Nematic Phase; Tr: Reduced Temperature, $\sigma_{\parallel}/\sigma_{\perp}$: Ratio of the Anisotropic Components ($\sigma_{\parallel}$, $\sigma_{\perp}$) of the Conductivity, Corresponding to $\mu_{\parallel}/\mu_{\perp}$

Temp. (°C)	Tr	$\mu_{\perp}$ (m^2/Vs)	$\frac{\sigma_{\parallel}}{\sigma_{\perp}}$	$\mu_{\parallel}$ (m^2/Vs)
23.1	0.96	1.92×10^{-10}	1.65	3.16×10^{-10}
26.1	0.97	2.31×10^{-10}	1.59	3.67×10^{-10}
29.2	0.98	2.86×10^{-10}	1.55	4.42×10^{-10}
32.3	0.99	3.53×10^{-10}	1.49	5.24×10^{-10}

analyzer as mentioned above, and the conductivity was precisely determined by eliminating the influence of the electric double layers [11]. The parallel component $\sigma_{\parallel}$ was determined from the conductivity measurement under a magnetic field application to the test cell and by employing an extrapolation procedure to the observed relation between $1/\sigma$ and $1/H$, where H is the strength of the applied magnetic field [11]. Thus, the parallel component of the mobility $\mu_{\parallel}$ can be calculated by using Eq. (3) and obtained $\sigma_{\parallel}$, $\sigma_{\perp}$ and $\mu_{\perp}$ values and is listed in Table V together with the $\sigma_{\parallel}/\sigma_{\perp}$ values corresponding to $\mu_{\parallel}/\mu_{\perp}$ [11]. This procedure to use one test cell without alignment layers was introduced in order to avoid the unfavorable influences from additional ions, which can be easily dissolved from alignment layers into the LC layer [28].

The Arrhenius plot was made for the obtained temperature dependence of the mobility μ in the isotropic phase and the components, $\mu_{\parallel}$ and $\mu_{\perp}$, in the nematic phase as shown is Figure 7. As is also indicated in Figure 7, the activation energy of the mobility was calculated as 0.36 eV for μ in the isotropic phase and 0.43 eV and 0.52 eV for $\mu_{\parallel}$ and $\mu_{\perp}$, respectively.

The temperature dependence of the viscosity η of 5CB in the isotropic phase and its Miesowicz viscous coefficients, η_1, η_2 and η_3, in the nematic phase are reported in Ref. 29 and are shown in Figure 8. The Arrhenius plot in Figure 8 provides the activation energy of the viscosity as 0.34 eV for η, 0.55 eV for η_1, 0.25 eV for η_2 and 0.33 eV for η_3.

The almost same activation energy values for μ and η in the isotropic phase suggest the validity of the Walden rule

$$\mu\eta = \text{constant} \tag{4}$$

in this temperature range, that is clearly shown in Figure 9. This is a clear evidence of the fact that ionic conduction is dominating the electric conduction of 5CB in the isotropic phase and the ions characterized above are the major charge carriers. In the isotropic phase, both ions and

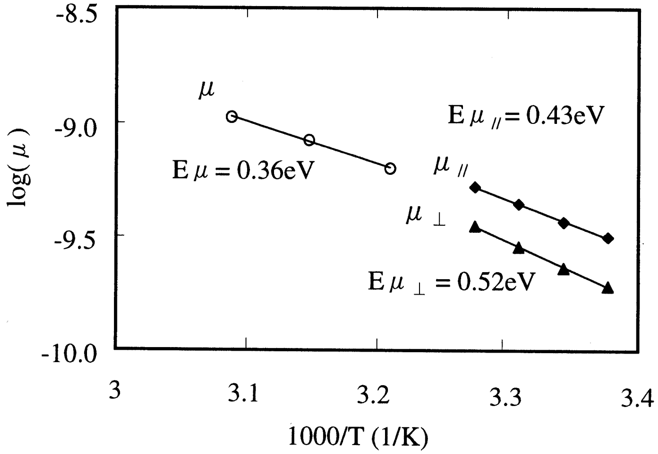


FIGURE 7 Arrhenius plot of the mobility μ in the isotropic phase and the anisotropic components, $\mu_{\parallel}$ and $\mu_{\perp}$, in the nematic phase of 5CB with the activation energy values $E\mu$.

LC molecules are reasonably considered as isotropic particles in their shape and the Eqs. (1) and (2) for isotropic liquids and spherical particles flowing isotropic liquids can be applied to the present system, resulting in Eq. (4).

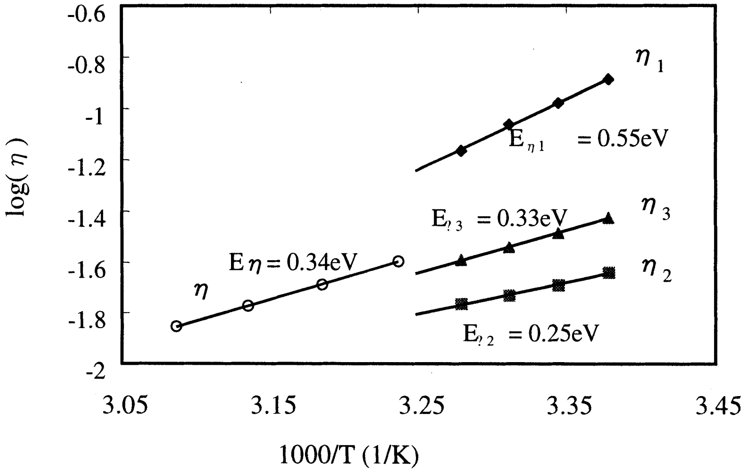


FIGURE 8 Arrhenius plot of the viscosity η in the isotropic phase and the Miesowicz viscosity coefficients, η_1, η_2 and η_3, in the nematic phase of 5CB (from Ref. [29]) with the activation energy values E_{η}.

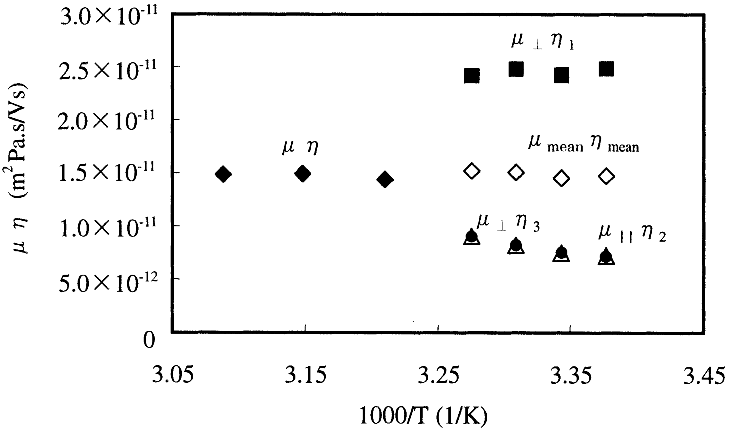


FIGURE 9 Temperature dependence of the products $\mu\eta$ in the isotropic phase and $\mu_\perp\eta_1$, $\mu_\parallel\eta_2$, $\mu_\perp\eta_3$ and $\mu_{\text{mean}}\eta_{\text{mean}}$ in the nematic phase of 5CB: $\mu_{\text{mean}} = (\mu_\parallel + 2\mu_\perp)/3$, $\eta_{\text{mean}} = (\eta_1 + \eta_2 + \eta_3)/3$.

The activation energy of the mobility $(\mu_\parallel, \mu_\perp)$ of ions and the Miesowicz viscous coefficients (η_1, η_2, η_3) of 5CB in the nematic phase are similar in the range of 0.25 eV and 0.55 eV, but show larger differences than both μ and η values in the isotropic phase. As the result, the product of corresponding components $(\mu_\perp\eta_1, \mu_\parallel\eta_2, \mu_\perp\eta_3)$ exhibits a small temperature dependence as shown in Figure 9. That means, the Walden rule is not necessarily valid for the present system in the nematic phase.

The anisotropic self-diffusion coefficients of nematic LC molecules are considered to be given by [30]

$$\begin{aligned} D_\perp &= \langle D\rangle\{1 - S(1-\gamma)/(2\gamma+1)\}, \\ D_\parallel &= \langle D\rangle\{1 + 2S(1-\gamma)/(2\gamma+1)\}. \end{aligned} \tag{5}$$

Here, $\langle D\rangle$ is the average diffusion coefficient, S is the orientational order parameter, and γ is equal to $\pi d/(4l)$ with d the diameter and l the length of the rod-like molecules. According to Parodi [31], those anisotropic self-diffusion coefficients can be related to the viscosity anisotropy $(\eta_\parallel, \eta_\perp)$ of LC materials as

$$\begin{aligned} D_\perp &= k_BT/(v\eta_\perp l), \\ D_\parallel &= k_BT/(v'\eta_\parallel l), \end{aligned} \tag{6}$$

where, v and v' are numerical factors of order one. This provides an idea that the following formula can be introduced to represent the Miesowicz viscosity coefficients in relation with the diffusion coefficients:

$$\begin{aligned}\eta_1 &= kT/(v_1 D_\perp l),\\ \eta_2 &= kT/(v_2 D_\parallel l),\\ \eta_3 &= kT/(v_3 D_\perp l).\end{aligned} \tag{7}$$

The mobility of particles in an LC matrix can also be related to diffusion coefficient components from an analogy to Eq. (2) for isotropic liquids as follows:

$$\begin{aligned}\mu_\parallel &= qD_\parallel/k_BT,\\ \mu_\perp &= qD_\perp/k_BT.\end{aligned} \tag{8}$$

What should be noted here is that the diffusion coefficients related to the mobility of ions in a LC matrix are not necessarily identical to the self-diffusion coefficients of LC molecules given by Eq. (5). It is because the majority of the ions under the present study are considered to be different from LC molecules in their shape and less anisotropic. That is, the geometrical anisotropy γ and the order parameter S included in Eq. (5) can be lower for ions than for LC molecules.

Consequently, the diffusion coefficients do not disappear from the product of a η component, Eq. (7), and a μ component, Eq. (8), leaving some temperature dependence of the product, $\mu_\perp \eta_1$, $\mu_\parallel \eta_2$ and $\mu_\parallel \eta_3$. However, if a mean value of the mobility μ_{mean} is considered in the form of

$$\mu_{\text{mean}} = (\mu_\parallel + 2\mu_\perp)/3, \tag{9}$$

Eqs. (5) and (8) yield

$$\begin{aligned}\mu_{\text{mean}} &= (q/3k_BT)(D_\parallel + 2D_\perp)\\ &= q\langle D\rangle/k_BT,\end{aligned} \tag{10}$$

where the influences of S and γ values of ions are eliminated. Thus, by taking a similar mean value of the viscosity of the LC matrix,

$$\eta_{\text{mean}} = (\eta_1 + \eta_2 + \eta_3)/3, \tag{11}$$

the product $\mu_{\text{mean}}\,\eta_{\text{mean}}$ seems to become temperature independent. This was found to be plausible from experimental results as shown in Figure 9. Figure 9 also shows that the product value $\mu\,\eta$ is continuously constant across the nematic-isotropic transition temperature if these mean values are taken for both the anisotropic mobility and the anisotropic viscosity. This result supports the idea that the ionic conduction is dominating the electric conduction and the mobile ions characterized in the isotropic phase are playing an important role even in the nematic phase.

3.2. 8CB in Isotropic, Nematic and Smectic A Phases

The same measurements were made on 8CB, which has the smectic A phase in addition to the nematic phase, as those made on 5CB. The Arrhenius plot of the temperature dependence of the mobility μ is given as shown in Figure 10. In the smectic A phase, however, the magnetic field was not strong enough to provide an accurate extrapolation in the relation between $1/\sigma$ and $1/H$ to calculate the component $\mu_{\parallel}$, parallel to the director or perpendicular to the smectic layer. This is why only the perpendicular component $\mu_{\perp}$ is plotted in Figure 10.

The activation energy of the mobility was also calculated for 8CB as 0.40 eV for μ in the isotropic phase and 0.63 eV and 0.72 eV for $\mu_{\parallel}$ and $\mu_{\perp}$ in the nematic phase, respectively. The activation energy is slightly larger for the mobility of ions in 8CB in the isotropic phase and a bit larger in the nematic phase. The activation energy was also calculated as 0.54 eV for the mobility component $\mu_{\perp}$ in the smectic A phase.

The temperature dependence of the viscosity η in the isotropic phase and its Miesowicz viscous coefficients, η_1, η_2 and η_3, in the nematic phase are reported for 8CB, too, in Ref. 29. The Arrhenius plot was made as shown in Figure 11, providing the activation energy of the viscosity as 0.33 eV for η, 0.65 eV for η_1 and 0.28 eV for η_3. The activation energy of the viscosity η_2 was also estimated as 0.39 eV very roughly due to the limited temperature range of normal temperature dependence.

In the isotropic phase of 8CB, the similar activation energy values for μ and η confirm the validity of the Walden rule as shown in Figure 12. It is

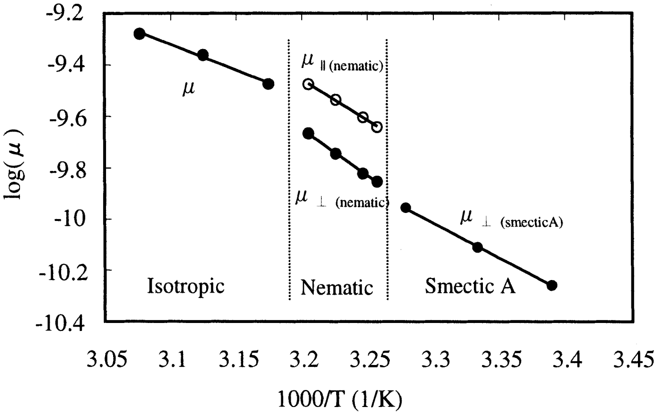


FIGURE 10 Arrhenius plot of the mobility μ in the isotropic phase and the anisotropic components, $\mu_{\parallel}$ and $\mu_{\perp}$, in the nematic phase and the smectic A phase of 8CB.

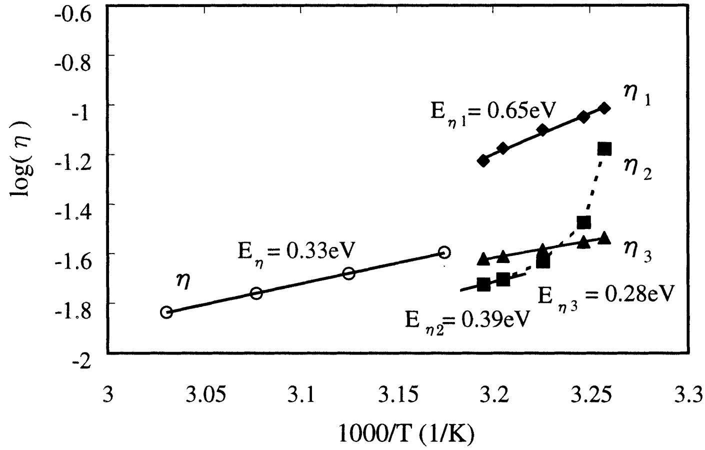


FIGURE 11 Arrhenius plot of the viscosity η in the isotropic phase and the Miesowicz viscosity coefficients, η_1, η_2 and η_3, in the nematic phase of 8CB (from Ref. [29]).

also the same as the case of 5CB, that, in the nematic phase, the product $\mu_{\mathrm{mean}}\eta_{\mathrm{mean}}$ is temperature independent and quantitatively similar to $\mu\eta$ in the isotropic phase, except the temperature region close to the nematic-smectic A phase transition temperature. In this pre-transitional

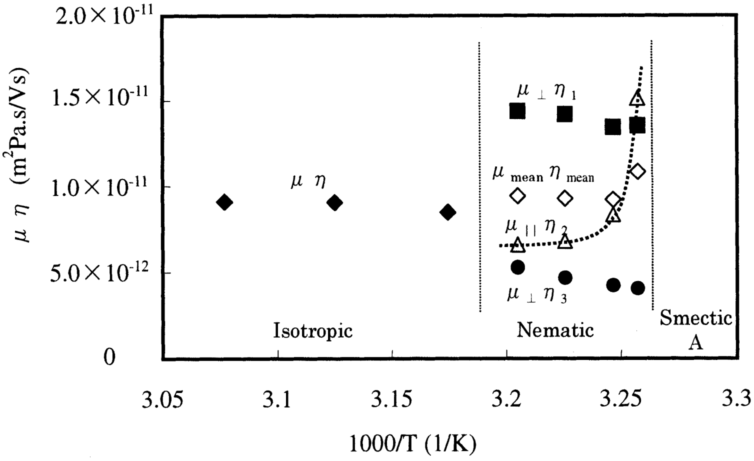


FIGURE 12 Temperature dependence of the products $\mu\eta$ in the isotropic phase and $\mu_{\perp}\eta_1$, $\mu_{\parallel}\eta_2$, $\mu_{\perp}\eta_3$ and $\mu_{\mathrm{mean}}\eta_{\mathrm{mean}}$ in the nematic phase of 8CB: $\mu_{\mathrm{mean}} = (\mu_{\parallel} + 2\mu_{\perp})/3$, $\eta_{\mathrm{mean}} = (\eta_1 + \eta_2 + \eta_3)/3$.

temperature region, the Miesowicz viscosity coefficient η_2 of 8CB exhibits a divergence as indicated in the Arrhenius plot in Figure 11. This abnormal pre-transitional phenomenon was not observed in the temperature dependence of the mobility $\mu_{\parallel}$ of ions in 8CB, resulting in the large temperature dependence or a divergence of the product $\mu_{\parallel}\eta_2$ shown in Figure 12.

As is well known, there appear cybotactic clusters with a smectic structure in the nematic phase in a temperature range close to the nematic-smectic phase transition. Therefore, the divergence of the Miesowicz viscous coefficient η_2 is considered to be due to the existence of cybotactic clusters and provides a speculation that η_2 is infinitely large in the smectic A phase. In other words, the amplitude of the periodic potential in the normal direction of the smectic layers, which is usually used when discussing the self-diffusion coefficient $D_{\parallel}$ of LC molecules in the smectic phase, is quite large. Judging from the fact that there can not be seen any influence of cybotactic clusters on the mobility $\mu_{\parallel}$ of ions, however, the amplitude of the periodic potential seems not to be so large for the diffusion of impurity ions in a smectic LC matrix.

There can be other explanations that ions flowing in cybotactic clusters are negligible in number and make no effective influence on the total flow of ions in the nematic phase containing cybotactic clusters, or the order of the smectic bilayers can be destroyed by the ions [29]. However, it seems more plausible to assume a difference of the amplitude of the periodic potential between LC molecules and ions contained in the present LC material. This speculation can also be supported by the measurements of anisotropic mobility of charge carriers in an LC material, exhibiting some finite values even for $\mu_{\parallel}$ of ions in the smectic A phase [32]. Our results on the basis of the diffusion coefficient measurements also agree well with the measurements of the conductivity of 8CB parallel to the director in the pre-transitional temperature range exhibiting no divergence [33].

The above arguments mean that the diffusion coefficient $D_{\parallel}$ for ions or the impurity-diffusion coefficient, which corresponds to that in the formula of the mobility Eq. (8), is significantly different from that for LC molecules or the self-diffusion coefficient, which appear in the formula of the viscosity coefficient Eq. (7). This is the reason why the Walden rule does not hold for the anisotropic ionic conduction in mesophases of LC materials.

4. SUMMARY

Mobile ions contained in LC materials, 5CB and 8CB, were characterized from measurements of permittivity dispersion in a very low frequency range with regard to their diffusion coefficient D and number density n in their isotropic phase. Here, the quantity of electricity q of the ions was assumed to be equal to the elementary electric charge, which was found to be reasonable after ion chromatography measurements showed that the major inorganic ions contained in these materials are monovalence ions.

It is a common way to confirm the ionic conduction in isotropic liquid dielectrics by the validity of the Walden rule, which teaches that the product of the mobility μ of ions and the viscosity η of the matrix liquid is constant independent from the temperature.

In the isotropic phase of the LC materials, the validity of the Walden rule was confirmed, providing the idea that the above ions are playing a decisive role in the electric conduction of LC materials in the isotropic phase.

In the nematic phase of the LC materials, the Walden rule also seems to be valid for both mean values of the viscosity η_{mean} and the mobility μ_{mean} with quite a similar value of the constant in the isotropic phase, which corresponds to $q/(6\pi R_s)$, where R_s is the Stokes radius of the ions. This result supports the idea that the conductive phenomenon in the nematic phase under present observation is mainly due to ionic conduction.

Nevertheless, the products of an anisotropic component of the mobility ($\mu_\parallel$, parallel to the nematic director, and $\mu_\perp$, perpendicular to that) of ions and the Miesowicz viscosity coefficient (η_1, η_2 and η_3) of the LC material, $\mu_\parallel\eta_1$, $\mu_\parallel\eta_2$, and $\mu_\perp\eta_3$, exhibit small temperature dependence, reflecting the difference of activation energies of the viscosity of the nematic LC material and the mobility of ions. This seems to be because the geometrical anisotropy γ and the order parameter S are lower for ions than for the LC substance, although the ion diffusion in a nematic media shows the same features as self-diffusion of nematic LC molecules, in principle, which can be represented by Eq. (5). That is, the Walden rule is not necessarily valid for the anisotropic ionic conduction in the nematic phase, when not mean values but the anisotropic components are considered for the mobility and the viscosity.

In the smectic A phase, it is easily expected that the anisotropy of ionic conduction will be extremely large, assuming that ions experience the similar potential barrier as the LC molecules when penetrating through smectic layers resulting in a quite small value of the diffusion coefficient $D_\parallel$, while the diffusion coefficient $D_\perp$ parallel to the layers is comparatively large.

Measurements of $D_\parallel$ and $D_\perp$ were performed for the ions in a higher temperature range in the nematic phase of 8CB, where the pre-transitional phenomenon can be observed for the viscosity. The pre-transitional phenomenon in the nematic phase at temperatures near the nematic-smectic A transition is known to be due to the appearance of cybotactic clusters with a smectic layer structure. Therefore, in this temperature range, the Miesowicz viscosity coefficient η_2 can exhibit a divergence.

If the Walden rule is valid for ionic conduction in the smectic A phase, this will provide the idea that the mobility value $\mu_{\|}$ of ions will become almost zero, which means that there will be no contribution from the ion movement in the electric conduction in the direction normal to smectic layers. This is also expected to be observed in the pre-transitional temperature range in the nematic phase.

As a result, however, our measurements of the diffusion coefficient $\boldsymbol{D}_{\|}$ or the mobility $\mu_{\|}$ in this pre-transitional temperature range still exhibit a normal temperature dependence as found in the nematic temperature range far from the nematic-smectic A transition. Thus we presume that there still remains contribution of ion movement in electric conductance in the smectic A phase even in the anisotropic component of the conductance $\sigma_{\|}$ in the direction normal to smectic layers. That means the diffusion coefficient $\boldsymbol{D}_{\|}$ of ions is not infinitely large as that of LC molecules.

The self-diffusion of LC molecules in the smectic A phase is related to the viscosity in a similar way as in the nematic and the isotropic phases for both $\boldsymbol{D}_{\|}$ and $\boldsymbol{D}_{\perp}$, and the anisotropy coefficients can be given by Eq. (6). Thus, the divergence of the viscosity coefficient as a pre-transitional phenomenon foresees that the diffusion coefficient $\boldsymbol{D}_{\|}$ of LC molecules is infinitely large in the smectic A phase.

These discussions provide the idea that impurity-diffusion coefficient is quite different from the coefficient for self-diffusion in case of the diffusion in the layer-normal direction in the smectic A phase.

In conclusion, the Walden rule is considered to be valid only for isotropic liquids or LC materials in the isotropic phase. Regarding the anisotropic conduction in mesophases of practical LC materials containing geometrically isotropic ions, the Walden rule holds only for mean values of the viscosity and the mobility in the nematic phase of LC materials without a pre-transitional phenomenon near the nematic-smectic A phase transition. The Walden rule can not be necessarily used to confirm the existence of contributions from mobile ions in the electric conduction in mesophases of LC materials.

Those results are in line with some previous reports on measurements of impurity diffusion using LC materials with intentionally added ionic compounds as impurities [27,34], the model of impurity diffusion in the smectic A phase [35], and measurements of the conductivity [33] or the mobility [24,32] for smectic LC materials. However, the present study confirmed the anisotropic conduction due to the intrinsic impurity ions contained in LC materials from direct measurements of anisotropic diffusion coefficients of ions. This paper also provided, for the first time, the argument on the validity of the Walden rule in the anisotropic ionic conduction from the standpoint of the difference between the ion diffusion in a LC matrix and the self-diffusion of LC molecules.

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