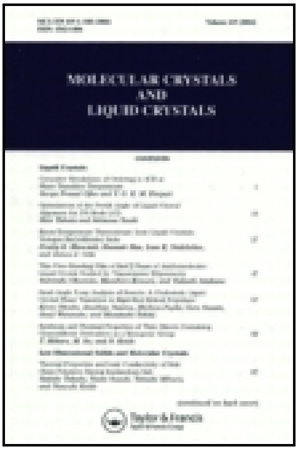

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The Anisotropic Electrical Conductivity of M.B.B.A. Containing Tetrabutyl-Ammonium Tetraphenyl-Boride

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The Anisotropic Electrical Conductivity of M.B.B.A. Containing Tetrabutyl-Ammonium Tetraphenyl-Boride[†]

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An investigation was made of the anisotropic electrical conductivity ($\sigma^{\parallel}$ and $\sigma^{\perp}$) of MBBA (p-methoxybenzylidene-p-n-butylaniline) containing tetrabutylammonium tetraphenylboride (henceforth denoted as AB where A^+ is the tetrabutylammonium cation and B^- is the tetraphenylboride anion). Alignment parallel and perpendicular to the applied electric field was accomplished by means of a 6000 Gauss magnetic field. The measurements were made at 22°C in a frequency range of 5,000 to 20,000 Hertz and at a sequence of nominal concentrations of AB up to about 10^{-4} moles/liter. The DC angularaverage conductivity $\bar{\sigma}(= 1/3\,\sigma^{\parallel} + 2/3\,\sigma^{\perp})$ was obtained by extrapolating plots of $\bar{\sigma}$ versus the square of the frequency to zero frequency. The experimental measurements fit apparently quite well by a simple dissociation model, $AB \rightleftharpoons A^+ + B^-$ with the results

$$K \text{ (the dissociation constant)} = \frac{C_A \times C_{B^-}}{C_{AB}} = (5.69\pm0.94)\times 10^{-6} \text{ moles liter}^{-1}$$

$$A_\sigma \text{ (the anisotropy ratio)} = \frac{\sigma^{\parallel} - \sigma^{\perp}}{1/3\sigma^{\parallel} + 2/3\sigma^{\perp}} = 0.305\pm0.015$$

$$A_0 \text{ (the specific conductance)} = \lim_{C_{A^+}=C_{B^-}\to 0}\left(\frac{1000\,\bar{\sigma}}{C_{A^+}}\right) = 0.398\pm032 \text{ mho cm}^{-1}\text{ moles}^{-1}\text{ liter}$$

[†] Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21-25, 1972.

From these results we obtain for the mobility sums

$$\mu_{A+\parallel} + \mu_{B-\parallel} = (4.94 \pm .41) \times 10^{-6}\ \text{cm}^2\ \text{sec}^{-1}\ \text{volt}^{-1}$$

$$\mu_{A+\perp} + \mu_{B-\perp} = (3.71 \pm .30) \times 10^{-6}\ \text{cm}^2\ \text{sec}^{-1}\ \text{volt}^{-1}$$

INTRODUCTION

Recent impetus of using room-temperature nematic liquid crystals for alphanumeric displays has stimulated studies of the electrical properties of MBBA (p-methoxybenzylidene-p-n-butylaniline) [1,2] Although Sussman[3] has recently reported on the conductivity of PAA (p-azoxyanisol), a hightemperature nematic liquid crystal containing ionic dopants, literature information on similar studies of MBBA is lacking. We present here the electrical conductivity of MBBA containing TBATPB (tetrabutylammonium tetraphenylboride) as the ionic dopant.

EXPERIMENTAL

Experimental techniques on measurements of the electrical conductivity of insulating liquids can be fraught with non-reproducible and non-linear effects. We quote typically the conductivity measurements of benzene by Forster.[4,5] His results may be summarized as follows: (a) The apparent conductivity increased with electrode spacing and decreased with voltage; (b) there were two space-charge regions, one near each electrode, and a bulk region where the field was constant; (c) the conductivity in the bulk region was independent of voltage and electrode spacing. Sussman[3] recently reported the a.c. conductivity measurements of PAA (p-azoxyanisole) containing TIPAN (tetra-iso-pentyl ammonium nitrate) at 60 Hz. He claimed that this frequency was high enough to avoid polarization effects, but below the frequency at which the capacitative effects would contribute to the current. We believe that electrode polarization and carrier injection are present at these low frequencies and must go beyond 5 to 10 KHz to avoid the implications of electrode effects.[†] At frequencies beyond 5 to 10 KHz, it is paramount to measure accurately the capacitative currents and make corrections of these currents. Lumping together all the relaxation and loss processes into one broad band having a single relaxation time τ, the total "permittivity" of the material can be written as,

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[†] For f = 10 KHz and representative conductivities, we have estimated the polarization voltage drop to be less than 10^{-4} of the total applied voltage.

$$\overleftrightarrow{\eta} = \frac{\overleftrightarrow{\epsilon}_0 - \overleftrightarrow{\epsilon}_\infty}{1 + i\omega\tau} + \frac{4\pi\,\overleftrightarrow{\sigma}_0}{i\omega} + \overleftrightarrow{\epsilon}_\infty \qquad (1)$$

$$\mathrm{Re}\,\overleftrightarrow{\eta} = \frac{\overleftrightarrow{\epsilon}_0 - \overleftrightarrow{\epsilon}_\infty}{1 + \omega^2\tau^2} + \overleftrightarrow{\epsilon}_\infty \qquad (2)$$

$$\mathrm{Im}\,\overleftrightarrow{\eta} = \frac{(\overleftrightarrow{\epsilon}_0 - \overleftrightarrow{\epsilon}_\infty)\omega\tau}{1 + \omega^2\tau^2} + \frac{4\pi\,\overleftrightarrow{\sigma}_0}{\omega} \qquad (3)$$

where the bars ↔ over ϵ_0 (low frequency-limit dielectric constant), ϵ_∞ (high frequency-limit dielectric constant) and σ_0 (dc conductivity) are used to indicate tensorial quantities appropriate for liquid crystals. At sufficiently low measuring frequences ($\omega^2\tau^2 << 1$)‡, Eq. (3) becomes replacing $\frac{4\pi}{\omega}\,\mathrm{Im}\,\overleftrightarrow{\eta}$ by $\overleftrightarrow{\sigma}$

$$\overleftrightarrow{\sigma} = \overleftrightarrow{\sigma}_0 + \frac{(\overleftrightarrow{\epsilon}_0 - \overleftrightarrow{\epsilon}_\infty)\omega^2\tau}{4\pi} \qquad (4)$$

Introducing the measuring frequency $f(= \omega/2\pi)$, Eq. (4) becomes,

$$\overleftrightarrow{\sigma} = \overleftrightarrow{\sigma}_0 + \pi(\overleftrightarrow{\epsilon}_0 - \overleftrightarrow{\epsilon}_\infty)\, f^2\tau \qquad (5)$$

When $\overleftrightarrow{\sigma}$ is plotted versus f^2, the data points should follow a straight line whose slope is $\pi(\overleftrightarrow{\epsilon}_0 - \epsilon_\infty^\parallel)\tau$ and intercept is $\overleftrightarrow{\sigma}_0$ if the above simplifying assumptions are correct.

If in a nematic liquid crystal we take a local coordinate frame in which the one axis is the local director $\vec{n}$, any of the above tensorial quantities are reduced to diagonal form with one parallel element and two equal perpendicular elements due to axial symmetry. We further define the following quantities:

$\sigma_0^\parallel$ = dc conductivity parallel to $\vec{n}$
$\sigma_0^\perp$ = dc conductivity perpendicular to $\vec{n}$
$\epsilon_0^\parallel$, $\epsilon_\infty^\parallel$ = dielectric constants (low and high frequency limits) parallel to $\vec{n}$
$\epsilon_0^\perp$, $\epsilon_\infty^\perp$ = dielectric constant perpendicular to $\vec{n}$
$\bar{\sigma}_0 = 1/3\sigma_0^\parallel + 2/3\sigma_0^\perp$ = angular average of the dc conductivity
$\bar{\epsilon}_0 = 1/3\epsilon_0^\parallel + 2/3\epsilon_0^\perp$ = angular average of the low frequency dielectric constant
$\bar{\epsilon}_\infty = 1/3\epsilon_\infty^\parallel + 2/3\epsilon_\infty^\perp$ = angular average of the high frequency dielectric constant
A_σ = conductivity anisotropy ratio = $(\sigma_0^\parallel - \sigma_0^\perp)/\bar{\sigma}_0$
A_{ϵ_0} = dielectric anisotropy ratio (low frequency-limit) = $(\epsilon_0^\parallel - \epsilon_0^\perp)/\bar{\epsilon}_0$
A_{ϵ_∞} = dielectric anisotropy ratio (high frequency-limit) = $(\epsilon_\infty^\parallel - \epsilon_\infty^\perp)/\bar{\epsilon}_\infty$

The measuring cell consists of two nesa-coated glass plates approximately 4 cm. by 1 cm. separated by two end mylar spacers (0.6 cm. by 1 cm.) of fixed

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‡ The result for $\omega << 1/\tau$ will be the same as that for many relaxation times if $\omega << 1/\tau_i$, $i = 1, \ldots, r$.

thicknesses giving an effective cell area of about 2.8 cm. by 1 cm. and from 50 to 200 microns thick. The cell is totally enclosed in a doublejacketed pyrex glass vessel with circulating water thermostatically controlled to ± 0.1°C. The narrow empty space between the cell and the pyrex-glass enclosure was flushed with a slow stream of dry nitrogen during measurements. The cell and water-cooled pyrex-glass enclosure were mounted at the center of a 6000 Gauss 4-inch electromagnet (Varian Associates) with a two-position control to orient the cell plates in either parallel or perpendicular configuration with respect to the magnetic field direction. A magnetic field of 3000 Gauss was shown to be sufficient to align the liquid crystal, but a 6000 Gauss field was maintained in actual measurements. The conductance and capacitance of the measuring circuit were measured by means of a Model 75C direct capacitance bridge (Boonton Electronics Corp.). The measured capacitance, after a correction of the parallel capacitance contribution from the mylar spacers and a negligible small correction of the capacitance of the lead wires, yields the capacitance of the liquid crystal film. The conductance correction from mylar inserts and lead wires was so negligibly small that the bridge reading yields directly the conductance of the liquid crystal film.

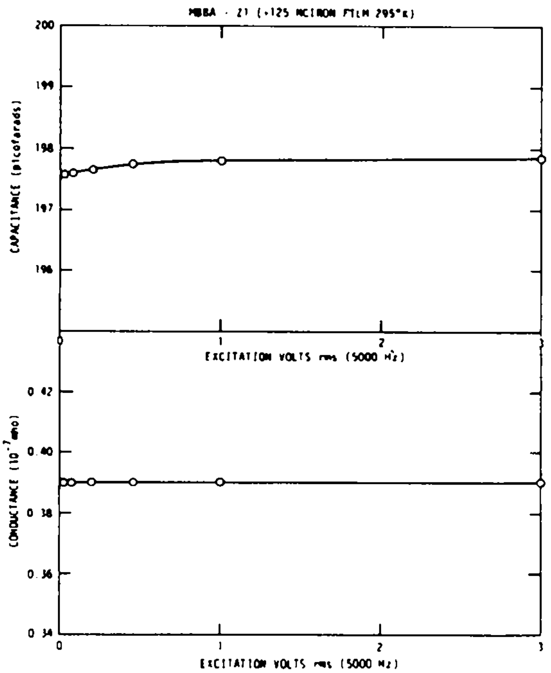

FIGURE 1 Conductance and capacitance data versus the excitation voltage for MBBA film at 5000 Hertz and 295.0°K.

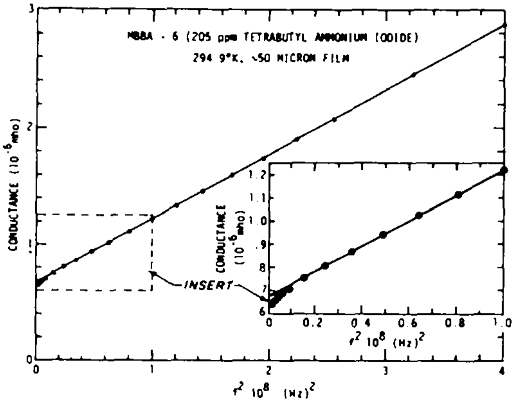

FIGURE 2 Conductance - (frequency)^2 plot for MBBA film at 294.9°K (zero magnetic field).

The experimental conductance is shown to be independent of the excitation voltage applied normal to the cell plates in the range 0.03 to 3 volts rms. Typical data are shown in Figure 1 where the excitation voltage was changed from 0.03 to 3.0 volts rms at 5000 Hertz. The conductivity results for a given liquid crystal material are independent of the cell thicknesses in the range 50 to 200 microns tested. The final test for our model and verification of Eq. (5) are illustrated in Figure 2 where the plot of experimentally measured conductance (no magnetic field applied) versus f^2 follows a straight line except at low frequencies (see insert of Figure 2) where electrode polarization and/or carrier injection may become appreciable to cause deviation from linearity.

Both zone-refined and distilled MBBA were used in this study. The TBATPB salt, made by mixing equal molal quantities of tetra-butyl ammonium bromide and sodium tetra-phenyl boride in aqueous solution and thoroughly washing and drying of the TBATPB precipitate, was weighed and dissolved in MBBA to give MBBA solutions containing up to about 50 ppm TBATPB. The dimensions of the empty cell were measured by means of a low power microscope at 50X and derived also indirectly from capacitance measurements of a standard liquid (Dow Corning Silicone Oil). Both the direct and indirect evaluation of the cell constants agree within experimental error of the cell area and thickness measurements (± 3 percent). The cell constant is expressed as the ratio of the average plate spacing to the plate area and falls within the range of 0.003 to 0.005 cm^{-1}. The product of the experimentally measured conductance and the cell constant yields the conductivity of the liquid crystal film.† Typical conductance -f^2 plots

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†In Figures 1, 2, 3, and 4 only conductances (direct experimental measurements) are plotted. The conductance multiplied by cell constant yields the conductivity.

for MBBA containing various amounts (0 to 22.5 ppm) of TBATPB near room temperature are shown in Figure 3. Since the slopes of the conductance -f^2 plots for a given liquid crystal composition are, within the limits of experimental error, identical the angular average conductance at each measuring frequency was calculated from the experimentally measured values (1/3 conductance H $\parallel$ $\vec{\eta}$ plus 2/3 conductance H $\perp$ $\vec{\eta}$) and plotted versus f^2 to yield an extrapolated angular average conductance at zero frequency; this, multiplied by the cell constant gives the angular average conductivity $\bar{\sigma}_0$ for the liquid crystal. The conductivity anisotropy ratio A_σ is computed as the difference in conductance for H $\parallel$ $\vec{\eta}$ and H $\perp$ $\vec{\eta}$ divided by the angular average conductance.

The temperature dependence of conductivity of MBBA containing TBATPB was studied by means of low frequency measurements at 200 Hertz employing a General Radio capacitance bridge (1616A, 1620A). No frequency corrections were made. The data are typically shown in Figure 4. An activation energy of 0.53 ev for the angular average conductivity was used to obtain small temperature corrections of the experimental $\bar{\sigma}_0$ values to the reference temperature

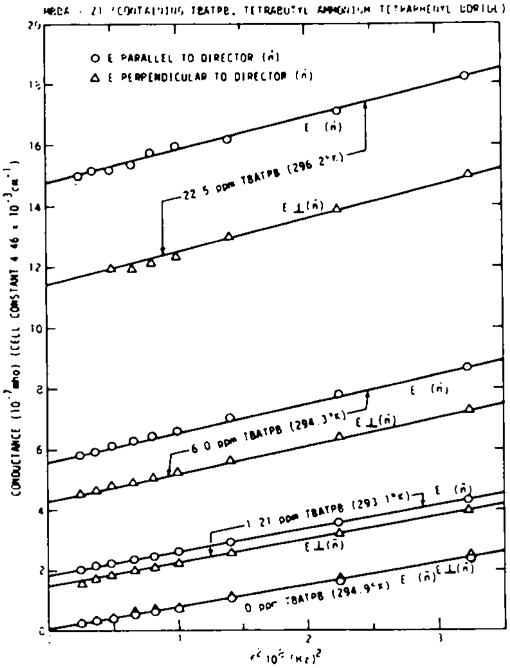

FIGURE 3 Conductance-(frequency)^2 plots for MBBA containing 0, 6.0 and 22.5 ppm TBATPB for E $\parallel$ $\vec{n}$ and E $\perp$ $\vec{n}$ at measuring temperatures indicated.

295.20°K. The complete data (after temperature corrections) for four separate sets of measurements are condensed in Table 1.

The data given in Table 1 are plotted as $\bar{\sigma}_0$ versus $\sqrt{C}$ in Figure 5 and A_R versus concentration of TBATPB in ppm in Figure 6. Figure 5 indicates that the conductivity varies linearly with the square root of concentration of TBATPB in MBBA except at very low concentrations. Figure 6 shows that the conductivity anisotropy ratio is independent of the concentration of TBATPB in MBBA in the range 0 to 50 ppm investigated. The results strongly suggest a simple dissociation model:

$$(C_4H_9)_4N(C_6H_5)_4B \rightleftharpoons (C_4H_9)_4N^+ + (C_6H_4)_4B^- \qquad (6)$$

or in short hand notation

$$AB \rightleftharpoons A^+ + B^- \qquad (7)$$

Let C_A+ be the concentration of A^+, C_B-that of B^-, C_{AB} that of undissociated AB, and C be the total concentration in MBBA, all expressed in moles/liter; it follows

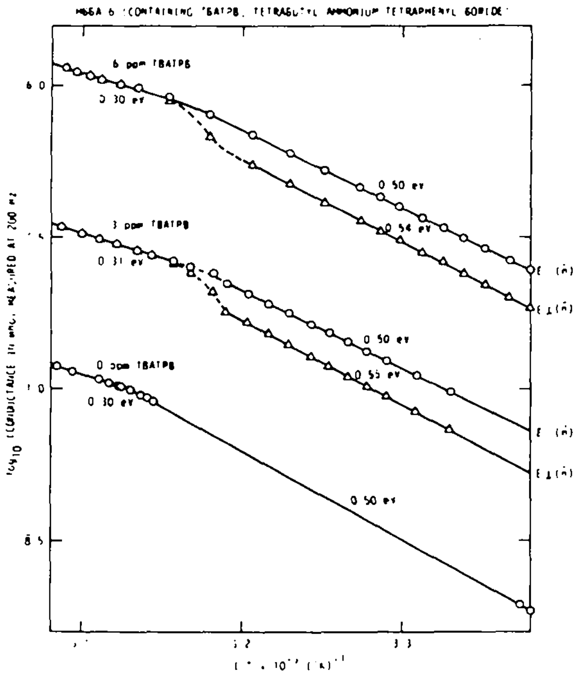

FIGURE 4 Log(conductance) $-\frac{1}{T}$ plots for MBBA containing various amounts of TBATPB for $E \parallel \vec{n}$ and $E \perp \vec{n}$ at 200 Hertz.

TABLE 1

A				B				C				D			
MBBA-Z1				MBBA-7				MBBA-Z1				MBBA-8			
ppm	C	$\bar{\sigma}_0$	A_σ	ppm	C	$\bar{\sigma}_0$	A_σ	ppm	C	$\bar{\sigma}_0$	A_σ	ppm	C	$\bar{\sigma}_0$	A_σ
0.317	0.587	2.46	0.290	0.202	0.369	1.10	0.282	0.476	0.889	1.58	-	4.32	8.08	19.3	0.297
0.557	1.03	4.37	0.301	0.830	1.512	7.15	0.320	1.212	2.26	7.97	0.331	11.32	21.12	32.7	0.335
0.891	1.65	5.33	0.297	1.201	2.37	7.21	0.275	2.565	4.79	12.93	0.302	16.2	30.3	43.0	0.307
1.63	2.96	8.68	0.284	1.994	3.63	9.40	0.322	6.00	11.20	22.46	0.300	26.2	49.0	55.1	0.317
2.63	4.96	10.82	0.295					7.30	13.63	23.80	0.302	30.9	57.8	59.9	0.324
								16.55	30.90	43.4	0.301	39.6	74.0	70.7	0.317
								22.50	42.00	52.5	0.307	49.6	92.8	80.6	0.303
								41.90	78.22	74.0	0.310				

$A_\sigma = 0.305 \pm 0.015$
ppm – concentration of TBATPB in MBBA in $^{\sigma}$parts/million
C – concentration in 10^{-4} moles/liter
$\bar{\sigma}_0$ – average angular conductivity in 10^{-10} (ohm-cm)$^{-1}$
A_σ – conductivity anisotropy ratio
MBBA-Z1 – zone refined
MBBA-7, 8 – distilled

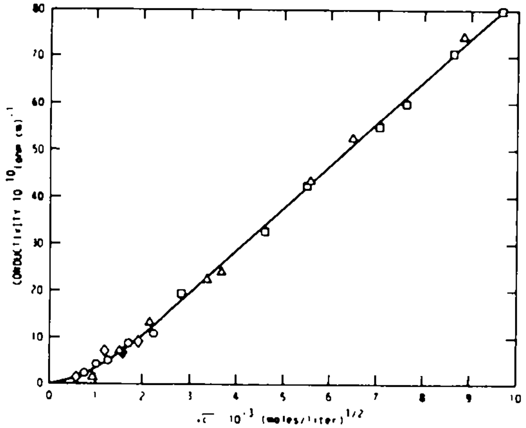

FIGURE 5 Conductivity-(concentration)$^{1/2}$ plot for MBBA containing various amounts of TBATPB - summary of data points at 295.2°K.

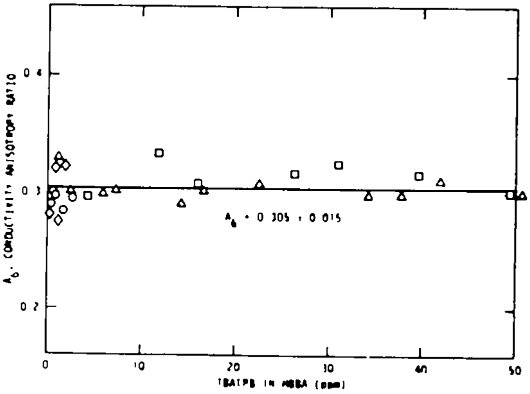

FIGURE 6 Conductivity anisotropy ratio for MBBA containing various amounts of TBATPB at 295.2°K.

$$K = \frac{C_{A^+} \cdot C_{B^+}}{C_{AB}} \tag{8}$$

$$C = C_{AB} + C_{A^+} \tag{9}$$

$$C_{A^+} = C_{B^-} \tag{10}$$

If Λ_A+ is the specific conductance of A^+, Λ_B- that of B^-, and $\Lambda_0 = \Lambda_{A^+} + \Lambda_{B^-}$ that of A^+ and B^-, it follows,

$$\frac{1000\,\bar{\sigma}_0}{C_{A^+}} = \Lambda \quad , \qquad \Lambda_0 = \lim_{c \to 0} \Lambda(c) \tag{11}$$

Combining Eqs. (8), (9), (10) and (11), it follows

$$C = \frac{10^3}{\Lambda_0} \bar{\sigma}_0 + \frac{10^6}{K\Lambda_0^2} \bar{\sigma}_0{}^2 \tag{12}$$

A least squares fit of the data shown in Table I yields,

$$K = (5.69 \pm 0.94) \times 10^{-6} \text{ moles liter}^{-1}$$

$$\Lambda_0 = (0.39 \pm 0.032) \text{ mho cm}^{-1} \text{ moles}^{-1} \text{ liter}$$

$$A_\sigma = 0.305 \pm 0.015$$

at the reference temperature 295.20°K. From these results one obtains for the apparent mobility sums,

$$\mu^{\parallel}_{A^+} + \mu^{\parallel}_{B^-} = (4.94 \pm 0.41) \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$$

$$\mu^{\perp}_{A^+} + \mu^{\perp}_{B^-} = (3.71 \pm 0.30) \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$$

Assuming that the mobilities of A^+ and B^- are nearly equal,[8] we can thereby give approximate values of the mobilities of the individual ions as

$$\mu^{\parallel} \cong 2.47 \times 10^{-6}, \mu^{\perp} \cong 1.86 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1} \text{ at } 295.20°\text{K}.$$

DISCUSSION

The slopes of the conductance-f^2 plots shown typically in Figure 3 (after insertion of the cell constant), is $(\bar{\epsilon}_0 - \bar{\epsilon}_\infty)$ according to Eq. (5), where $\bar{\epsilon}_0$ and $\bar{\epsilon}_\infty$ are, respectively, the low- and high-frequency limit dielectric constants and τ is the relaxation time. The angular average values $\pi(\bar{\epsilon}_0 - \bar{\epsilon}_\infty)\tau$ from our measurements on MBBA at 295°K fall within 3.1 to 3.6 x 10^{-18} mho cm^{-1} sec^2. Using angular average values of $\bar{\epsilon}_0 = 5.1$ and $\bar{\epsilon}_\infty = 2.4$ (the square of the refractive index at optical frequencies), the relaxation time τ calculated from our data is in the range 3.4 to 3.9 x 10^{-7} sec, agreeing within a factor of 2.5 with the values reported by Rondelez[1] *et al.* from dielectric loss peak studies. These authors identify the relaxation process with a rotational diffusion mechanism although the true relaxation spectrum may be a broad one composed of a number of yet-unresolved relaxation processes including rotational diffusion.

According to the theory of ionic conduction in unassociated electrolytes[9] our results are subject to a large correction due to interionic attraction effects. It must be noted that a large part of the interionic attraction effects are represented by the empirical treatment of dissociation. For example, at a total concentration C of 1.5 x 10^{-6} moles/liter the activity coefficients deviate from unity by about 7% and the further correction according to the theory of ionic conduction in associated electrolytes[10] is less than 2%. The total correction is within experimental error.

At higher total concentrations (i.e. $C >> 1.5 \times 10^{-6}$ moles/liter) the corrections would presumably be much larger. However, there is no well established theory that is sufficiently accurate in this regime. In respect to this question we can only retreat to the position that our simple dissociation model without additional corrections gives an excellent fit to the data from an empirical curve fitting point of view. In fact, we have tried more complex curves with more adjustable constants; however, these did not give an appreciably better fit and furthermore the additional constants were subject to an unduly large *a posteriori* variance. In any case, in the low concentration range where the theory of ionic conductance is valid the corrections are negligible as discussed in the last paragraph.

Both the cation and anion for the dopant TBATPB have nearly equal ionic radius of 3.63Å.[8] The angular average viscosity for MBBA at room temperature is 0.34 Poise according to the recent measurements of Martinoty and Candau.[6] Employing Walden's rule,[7] the specific conductance Λ_0 for TBATPB in MBBA is $\Lambda_0 = \frac{W}{\eta} = \frac{0.44}{1.34} = 1.3$† which is about a factor of three larger than our experimentally determined value of 0.40. The TBATPB dopant we synthesized analyzed about 500 ppm of sodium as a cation impurity. Since the dopant was made by means of precipitation from equal molar quantities of tetrabutyl ammonium bromide and sodium tetraphenyl boride in aqueous solution, an equivalent amount of bromide ion must be present as the anion impurity. These ionic impurities may cause the observed specific conductance to be lower than the theoretical value. We estimate the contribution of these ions to be less than 5%. A more accurate evaluation of the specific conductance as well as the dissociation constant must await similar measurements of higher purity doping material than what is presently achieveable. The purification and characterization methods for trace impurities, though difficult and laborious, are being attempted in our laboratory.

We would like to close by mentioning some experimental difficulties. As has been discussed by others,[1, 2] MBBA is very sensitive to environment, particularly moisture. Although our dry nitrogen gas was obtained by passing the nitrogen vapor from a liquid nitrogen storage over a long column of drierite, changes in physical properties of the liquid crystal begin to take place in the cell after about 12 hours at room temperature. We therefore used fresh samples and completed the measurements within an hour or so to avoid these difficulties. It is our belief

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† The parameter W is given by $0.8147 \times 10^{-8} \left(\frac{1}{r_{A^+}} + \frac{1}{r_{B^-}}\right)$ were r_{A^+} and r_{B^-} are the respective cation and anion radius.

that quantitative measurements for sustained time periods and at higher temperatures should be made in permanently sealed cells.

Acknowledgement

The authors wish to thank Prof. John McTague, UCLA, who suggested TBATPB as the ionic dopant, and Dr. Freeman Jones, Jr., who synthesized both the TBATPB and MBBA used in this study.

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