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Crown Ether Complex Salts as Conductive Dopants for Nematic Liquids†

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Abstract—A series of crown ether complex salts was demonstrated to increase significantly the electrical conductivity of mesomorphic liquids for the purpose of inducing dynamic scattering. The cations of these salts, synthesized by well-known procedures, were the complexes of sodium and potassium primarily with dicyclohexyl-18-crown-6, and organic anions of varying size, shape and flexibility were employed. The salts exhibited both satisfactory solubility and degree of dissociation to be useful as charge carries in chlorostilbenes, Schiff bases and azoxybenzenes. The conductivity, cut-off frequency and threshold voltage for the (low frequency) electrohydrodynamic instability were measured for several combinations. The concentration dependence of the equivalent conductivity indicates that a large portion of the charge is carried by associated (triple) ions. In chlorostilbenes, the available range of conductivities with these dopants is about 10^{-12} to 10^{-7}ohm^{-1}cm^{-1}.

1. Introduction

It is well known that electrical conduction in nematic liquids is due to ionic charge carriers. In order to study and to utilize the electro-optical properties of these liquids it is desirable to have a selection of dopants which, by virtue of the differing size, shape, association constant and redox potentials of the resulting ions, can impart different electrical properties to the nematic solution. Dopants

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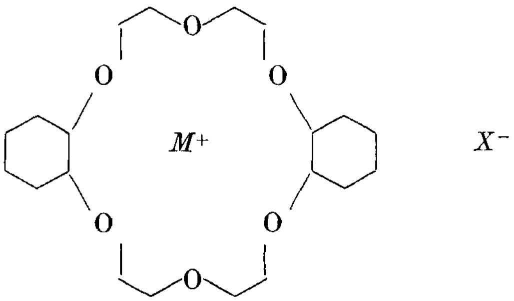
reported(1,2) up to the present have all utilized a quaternary nitrogen atom as the site of the positive charge; a broader range of physical properties can be expected by using complexed metal salts as dopants.

The ion concentration in low dielectric constant solvents, such as the usual nematic liquids, is limited by solubility and ion association. Both these factors are optimized by selecting structures in which a centrally located charge is surrounded by flexible organic moieties. Solubility is enhanced by the destabilization of the crystal lattice, and ion association is decreased due to a lowering of the Coulomb forces by the steric separation of centers of opposite charge. Some alkali metal complexes of macrocyclic polyethers, first described by Pedersen,(3) adequately fulfill these requirements. Here we wish to report on their use as conductive dopants in several nematic liquids.

2. Results

Twelve complex salts of dicyclohexyl-18-crown-6 (1a) and dibenzo-18-crown-6 (1b) were prepared. The syntheses were a modification of the method of Pedersen.(3a) For the measurement of the solute electrical properties of the complex salts, a 60 : 40 (by weight) mixture of 4-butyl-4′-ethoxy-α-chlorostilbene and 4-octyl-4′-ethoxy-α-chlorostilbene(4) was chosen as nematic solvent for the majority of the tests primarily for the ease of obtaining highly resistive samples. The undoped solvent was nematic between 8° and 59°C, had a



1a—6-membered rings saturated
1b—6-membered rings aromatic

negative dielectric anisotropy, but did not exhibit continuous dynamic scattering either under DC or AC excitation as the conductivity was 1.0×10^{-12} ohm^{-1} cm^{-1}.

All of the complex salts had sufficient solubility and degree of dissociation to permit dynamic scattering in the chlorostilbene solvent. Some representative examples of the conductivities, cut-off frequencies and threshold voltages of filtered solutions of dopants in chlorostilbene solvent are listed in Table 1. Solutions containing excess solid complexes had higher and less reproducible conductivities than filtered saturated solutions of the same dopant. Complex salts successfully used as dopants to induce dynamic scattering but whose electrical properties were not all measured included the following anions: 4-(2-ethyl-hexyloxy)benzoate, dodecylsulfate and hexylxanthate.

The use of the crown ether complexes as ionic dopants is not limited to the chlorostilbenes. For example, dopant No. 6 increased both the conductivity and the cut-off frequency of a freshly purified MBBA sample from 3×10^{-11} ohm^{-1} cm^{-1} and 12 Hz, respectively, by a factor of 10. A 1% concentration of the same dopant in a distilled sample of Licristal Nematic Phase IV⁽⁵⁾ resulted in an increase in conductivity from 3×10^{-10} to 7×10^{-8} ohm^{-1} cm^{-1} and in cut-off frequency from 270 Hz to 40 kHz.

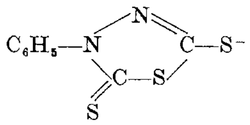
The concentration dependence of the conductivity and the cut-off frequency was investigated using dopant No. 6 in the chlorostilbene mixture. In these experiments, the resistance measurements were carried out in the presence of a magnetic field (6 KOe) to establish alignment,⁽⁶⁾ and the AC voltage imposed on the sample was kept low (1.0 volt, 157 Hz) to avoid interference by the hydrodynamic instability. The results are shown in Fig. 1.

3. Discussion

CONDUCTIVITY VS. NATURE OF DOPANT

The variations in the conductivity data of Table 1 can be qualitatively interpreted as effects due to the size and symmetry of the constituent ions. It is apparent that the highest conductivities are associated with dopants containing large and flexible aliphatic anions which are amply soluble in the chlorostilbene solvent. For example,

Table 1 Electrical properties of the chlorostilbene mixture containing various dopants. Solutions are saturated (except as noted) and filtered, $T = 23°C$

Dopant No.	Ligand	M	X^-	σ (ohm^{-1}cm^{-1})	f_c (Hz)	V_{th} (V rms)
1	1a	Na	$(C_6H_5)_4B^-$	1×10^{-8}	680	8
2	1b	Na	$(C_6H_5)_4B^-$	3×10^{-10}	170	10
3	1a	K	SCN^-	3×10^{-10}	300	8
4[a]	1a	K	$C_4H_9(C_2H_5)CHCOO^-$	1×10^{-7}	4500	7
5[b]	1a	K	$[C_4H_9(C_2H_5)CHCH_2]_2PO_4^-$	5×10^{-9}	500	6
6[a]	1a	K	$C_4H_9(C_2H_5)CHCH_2SO_3^-$	2×10^{-8}	7100	7
7	1a	K		3×10^{-9}	——	5·5
8	1a	K	$CH_3O—C_6H_4—CHCH—C_6H_4O^-$	4×10^{-9}	——	4

[a] conc = 5% by weight
[b] conc = 1% by weight

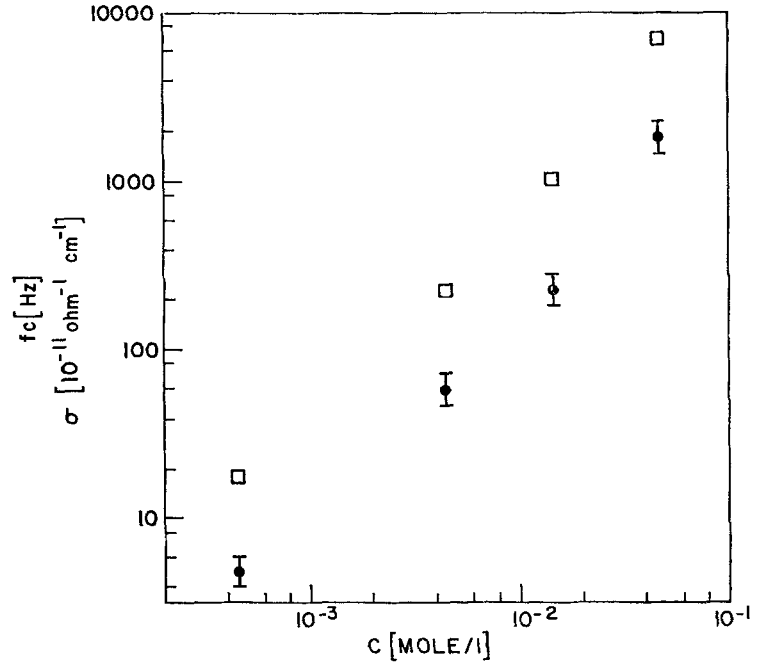


Figure 1. Log-log plot of conductivity (circles) and cut-off frequency (squares) vs. concentration of dopant No. 6 in chlorostilbene solvent.

dopant No. 2 with the planar dibenzo-18-crown-6-sodium cation is less effective than its saturated counterpart.

Cut-Off Frequency

The cut-off frequency for electrohydrodynamic instability is given by the Helfrich–Dubois-Violette–de Gennes–Parodi theory(7,8) as

$$f_c = (\zeta^2 - 1)^{1/2}/2\pi\tau$$

with $\zeta^2 = (1 - \sigma_\perp \epsilon_\parallel / \sigma_\parallel \epsilon_\perp)\alpha$ and $\tau = \epsilon_\parallel / 4\pi\sigma_\parallel$.

Here $\sigma_\parallel$, $\sigma_\perp$, $\epsilon_\parallel$, and $\epsilon_\perp$ are the conductivities and dielectric constants parallel and transverse to the alignment direction, and α is a quantity depending only on the dielectric constants and the viscosity coefficients of the nematic liquid. For a given solvent the dielectric constants and α should be independent of the concentration and nature of the charge carriers; hence the cut-off frequency is expected to be proportional to the conductivity and show also a weak dependence on the conductivity anisotropy.

The data of Table 1 show the expected trend in the cut-off frequencies albeit the quality of the conductivity data here does not warrant quantitative comparisons. The more precise data of Fig. 1 show good proportionality between f_c and $\sigma_\perp$.

ION ASSOCIATION

In Fig. 2 we have replotted the concentration dependence of the conductivity of the dicyclohexyl-18-crown-6-potassium-2-ethylhexylsulfonate solutions in chlorostilbene in terms of equivalent conductance, $\Lambda \equiv 10^3\ \sigma/c$. The fact that the log-log plot exhibits a positive (instead of a $-1/2$) slope indicates(9,10) that in this system we are dealing with ion association higher than pairwise, and leads to the important conclusion that the majority of the charge is carried by ions more complicated (triple ions) than those pictured by the stoichiometric formula.

An order of magnitude estimate of the mean degree of dissociation (number of ions of any kind/twice the number of molecules of salt dissolved), $\gamma = \Lambda/\Lambda_0$, can be made by the use of Walden's rule(11) which

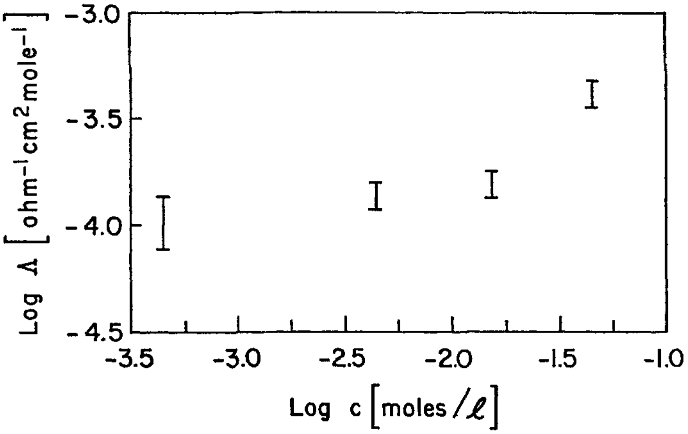


Figure 2. Equivalent conductance of dopant No. 6 in chlorostilbene solvent as a function of concentration.

states that the equivalent conductance of any ion at infinite dilution is given by $\Lambda_0 = W/\eta$. Here η is the solvent viscosity in poise, and W a constant which for most large ions is about 0.56. With a reasonable number (1.5 poise) for the appropriate viscosity of the chlorostilbene solvent the mean degree of dissociation of dopant No. 6 appears to be 10^{-3} to 10^{-4} over the entire concentration range studied.

THRESHOLD VOLTAGE

The threshold voltage for the onset of the electrohydrodynamic instability in the absence of a magnetic field is given by theory(7) in the low frequency limit as

$$V_{\text{th}} = V_0/(\zeta^2 - 1)^{1/2}$$

where V_0 depends only on the dielectric and elastic constants of the nematic liquid. From the definition of ζ it is apparent that an increase in the ratio of the parallel to transverse conductivities should lower the threshold voltage. Since $\sigma_{\parallel}/\sigma_{\perp}$ was expected to depend not only on viscosity coefficients of the nematic liquid but on the shape of the ions as well, we designed the elongated anions of dopants Nos. 7 and 8 with the aim of lower threshold voltages. In view of the conclusions of the previous section it appears that the success of this design was largely fortuitous, and should be interpreted as indicating that triple ions containing these anions are also more elongated than those built of more spherical constituent ions.

UTILITY

As seen from Table 1, some of the dopants described here allow a variation of five orders of magnitude in the conductivity of a nematic liquid.

While under DC conditions chlorostilbene mixtures with any of the dopants decompose rapidly (minutes), the stability under AC excitation varies from dopant to dopant. Under the accelerated conditions of 120 V 60 Hz AC, in an open cell protected(12) from ultraviolet light the best measured lifetime was found(13) to be 2500 hours (dopant No. 6).

4. Experimental

Preparation of Crown Ether Complex Salts

An equimolar amount of dicyclohexyl-18-crown-6 (Aldrich Chemical Company) or dibenzo-18-crown-6 (Aldrich) and an appropriate potassium or sodium salt of an organic moiety was dissolved in an excess of methanol. The solution was allowed to reflux for 2 h after which the solvent was removed on a rotary evaporator. The residue was taken up in an excess of benzene, and the resulting solution was filtered to remove any uncomplexed salt that may have remained. The benzene was removed from the filtrate on a rotary evaporator to afford the residual product, a light-colored thick gum. Sodium or potassium analyses by atomic absorption spectroscopy(14) indicated the products to be 50–90% pure; the impurities most likely contained predominant amounts of unreacted crown ether ligand.

In those instances where potassium or sodium salts were not commercially available for use in the above reaction, they were prepared by allowing equivalent amounts of potassium carbonate and an organic acid to reflux in aqueous methanol. The resulting alkali salt could be isolated by solvent removal, or, alternatively, its solution in aqueous methanol could be directly employed as a reagent to be combined with a methanol solution of dicyclohexyl-18-crown-6.

Preparation of Crown Ether Salt Solutions in Nematic Solvents

Known amounts of a crown ether complex salt and a nematic liquid were combined in a vial which was then heated to isotropic. After cooling, the mixture was filtered by suction through a medium-porous sintered glass funnel to afford a stock solution. The actual concentration of the complex salt in the solution was determined by potassium or sodium atomic absorption spectroscopy.(14) Samples of known higher dilution were made by combining pure nematic fluid with a known amount of the above stock solution and heating to isotropic.

Measurements

The data in Table 1 were obtained by enclosing the solutions between indium-oxide coated glass plates separated by 25 μm teflon spacers.

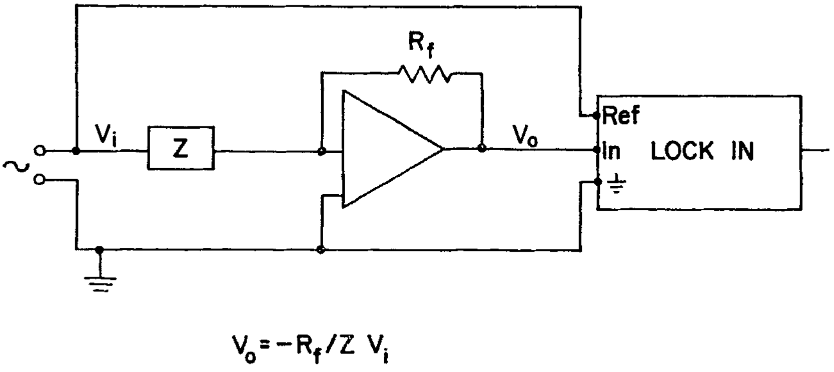


Figure 3. Circuit for measurement of the components of the impedance of nematic samples.

The cell area was defined by an etched pattern of a circle of 0.51 cm diameter and a lead line to the edge of the cell. Resistances were measured at 120 V 60 Hz across the cell by observing the voltage drop across a series resistor. Threshold voltages refer to the appearance of the hydrodynamic instability (not the dynamic scattering) and were measured at 60 Hz. Cut-off frequencies denote the disappearance of dynamic scattering at 30 V rms.

The conductivities reported in Fig. 1 were determined in cells whose circumference, except for two filling holes, was sealed with glass frit. The electrode area was defined as above, and the cell thicknesses were individually measured. The resistivities were measured with a circuit shown in Fig. 3. Cut-off frequencies refer to 35 V rms.

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