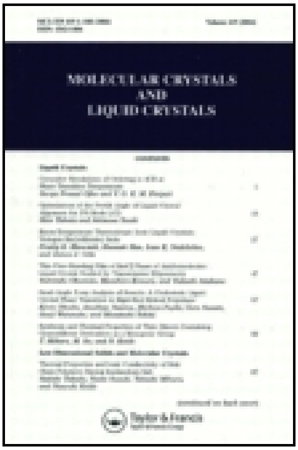

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Study of the Nature of Charge Carriers through Bilayer Lipid Membranes in the Presence of External Agents

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Version of record first published: 13 Dec 2006.

To cite this article: Ruma Datta , Papiya Nandy & Benoy B. Bhowmik (1987): Study of the Nature of Charge Carriers through Bilayer Lipid Membranes in the Presence of External Agents, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 150:1, 325-333

To link to this article: http://dx.doi.org/10.1080/00268948708074807

Mol. Cryst. Liq. Cryst., 1987, Vol. 150b, pp. 325–333
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Printed in the United States of America

Study of the Nature of Charge Carriers through Bilayer Lipid Membranes in the Presence of External Agents

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(Received February 9, 1987; in final form April 22, 1987)

The semiconducting property of planar bilayer lipid membrane (BLM) is well known and the nature of conduction through this phase has been generally accepted to be ionic. However, our experiments on the effect of several salts, electron acceptors and donors on the electrical conductivity of BLM have explored interesting phenomena which were never observed earlier. This can be properly interpreted on the assumption of electronic conduction through this system. The calculated value of electron mobility is 1.4×10^2 cm^2–volt^{-1}–sec^{-1}.

INTRODUCTION

The semiconducting property of lipids has been firmly established by several authors.[1,2] The exact nature of charge carrier through the bilayer lipid membrane (BLM) which is in the liquid crystalline phase and is used as a model for the biological membrane, is still a controversial one, though ionic conduction seems to be accepted in general.[3] However, our experiments on the effect of several salts, electron acceptors and donors on the electrical conductivity of BLM can be properly interpreted on the assumption of electronic conduction through this system.

The electrical resistance across an orifice in the aqueous medium increases manifold when BLM is formed on it. Under this condition the bulk resistance of the solution may be neglected compared to that of BLM.[4–6] These resistances become comparable when an electron acceptor or a donor is present in the medium and then the specific conductance of BLM (σ_m) can be calculated from the measured values of resistances in presence and in absence of BLM. Nature of variation of σ_m with the concentration of an electrolyte, added in the bathing solution containing the electron acceptor, shows peculiar behaviour, not explored earlier and these results can only be explained on the basis of electronic conduction through BLM, which behaves as an intrinsic semiconductor. Similar experiments in presence of electron donors also support our assumption.

MATERIALS AND METHODS

The electrolytes used in the experiment were HCl, LiCl, NaCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, $ZnCl_2$, K_2SO_4 and Na_2SO_4 (concentration: 0–2 mM). The electron acceptors used were iodine, picric acid and 2,4-dinitrophenol (concentration: 1 mM) and the electron donors used were bipyridyl and acridine (concentration: 1 mM). These AR grade chemicals supplied by BDH and E. Merck were used after proper purification according to the standard methods. Oxidized cholesterol in *n*-decane was used as BLM forming material. For this purpose, cholesterol supplied by Eastman Organic Chemical was oxidized[7] and then recrystallized from *n*-octane. AR grade *n*-decane and *n*-octane were supplied by E. Merck and were used without further purification. Double distilled water was used in all experiments.

BLM was formed by brushing a saturated solution of oxidized cholesterol in *n*-decane on a 1.5 mm diameter hole in a teflon cup separating two bathing solutions.[4] The experiments were done under symmetric conditions. A constant potential difference of 50 mV was applied across a pair of platinum electrodes placed about 1 cm apart on opposite sides of the orifice and the current was measured with the help of a Keithley electrometer (model No. 614). The whole experimental arrangement was enclosed in a Faraday cage in order to minimize the external electrical disturbance.

RESULTS AND DISCUSSION

If R_1 and R_2 denote the electrical resistance across the platinum electrodes in presence and in absence of BLM respectively, then R_1 is of the same order of magnitude as R_2 when an external agent like iodine is present in the aqueous bathing solution (otherwise $R_1 >> R_2$). Under this condition, the resistance of BLM is $R = R_1 - R_2$

(otherwise $R = R_1$). Figure 1 shows the variation of R_1, R_2 and the calculated values of R with concentration of the electrolyte KCl in presence of iodine (concentration 1 mM). The specific conductivity of BLM (σ_m) is calculated from R (which is equal to $R_1 - R_2$ in the present experimental condition containing electron acceptor or donor otherwise it is equal to R_1) and the dimension of BLM (diameter ~1.5 mm and thickness ~100 Å).

Initial value of σ_m in aqueous medium increases by several orders of magnitude in presence of iodine[5] (See Table I). When KCl is added in this solution, then with the rise in electrolyte concentration, σ_m lowers initially and attains a minimum around 0.2 mM concentration

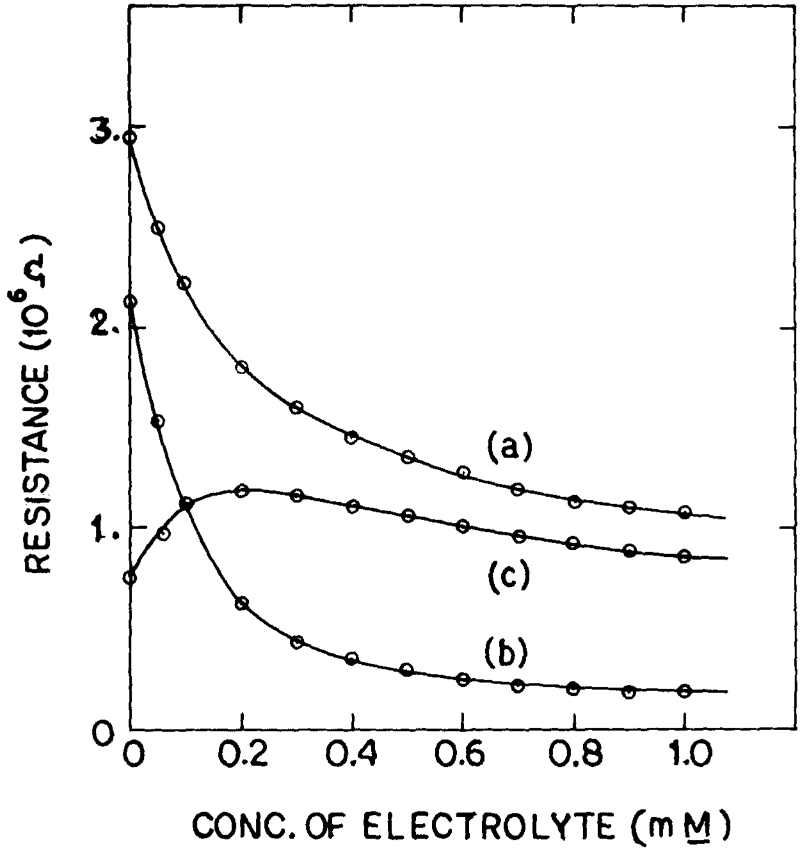

FIGURE 1 Variation of resistance of the system across the orifice with electrolyte concentration (Electrolyte used: KCl and iodine concentration: 1 mM): (a) with BLM, (b) without BLM, and (c) calculated value for BLM ($c = a - b$).

TABLE I

Semiconducting properties of oxidized cholesterol BLM in bathing solution of electron acceptor and donor

Solution	Ea (eV)	σ_m (Ω^{-1}-cm^{-1})	Semiconducting characteristics	Comments
H_2O	2.02	4.5×10^{-15}	Intrinsic	Conduction by electron & holes n_i = 115/cc
KCl (1 mM)	2.02	4.6×10^{-14}	Intrinsic	charge injection at BLM/electrolyte interface
I_2 (1 mM)	0.98	7.0×10^{-11}	p-type	holes are majority charge carriers. $n_p = 3.6 \times 10^6$/cc
I_2 (1 mM) + KCl (0.2 mM)	0.98	3.7×10^{-11}	p-type	hole–electron recombination reduces number of charge carriers
I_2 (1 mM) + KCl (1 mM)	0.98	6.8×10^{-11}	p-type	equilibrium attained
Acridine (1 mM)	1.16	8.0×10^{-13}	n-type	electrons are majority charge carriers. $n_n = 4.1 \times 10^4$/cc
Acridine (1 mM) + KCl (0.2 mM)	1.16	1.2×10^{-12}	n-type	more electrons are injected at BLM/electrolyte interface
Acridine (1 mM) + KCl (1 mM)	1.16	2.75×10^{-12}	n-type	equilibrium attained

Data presented here are the mean of 5–6 separate measurements with standard deviation of 5% Ea and σ_m denote activation energy and specific conductivity of BLM respectively.

of KCl (Figure 2a). The value then rises again and reaches a saturation value for electrolyte concentration ≥ 1 mM. The same qualitative pattern is followed by all the electrolytes, except with slight variation in the values. The representative curves for variation of σ_m with electrolyte concentration are given in Figure 2 for KCl, $CaCl_2$ and K_2SO_4. Curves of similar nature are obtained with other electron acceptors like picric acid and 2,4-dinitrophenol (Figure 3). In presence of an electron donor, however, a very different behaviour is obtained. In Figure 4, the variation of σ_m with KCl concentration is plotted in presence of (a) bipyridyl and (b) acridine (donor concentration 1 mM). Here the decrease in σ_m at low concentration of electrolyte is not observed, instead σ_m increases until a saturation value is reached.

The values of activation energy for each set were obtained by

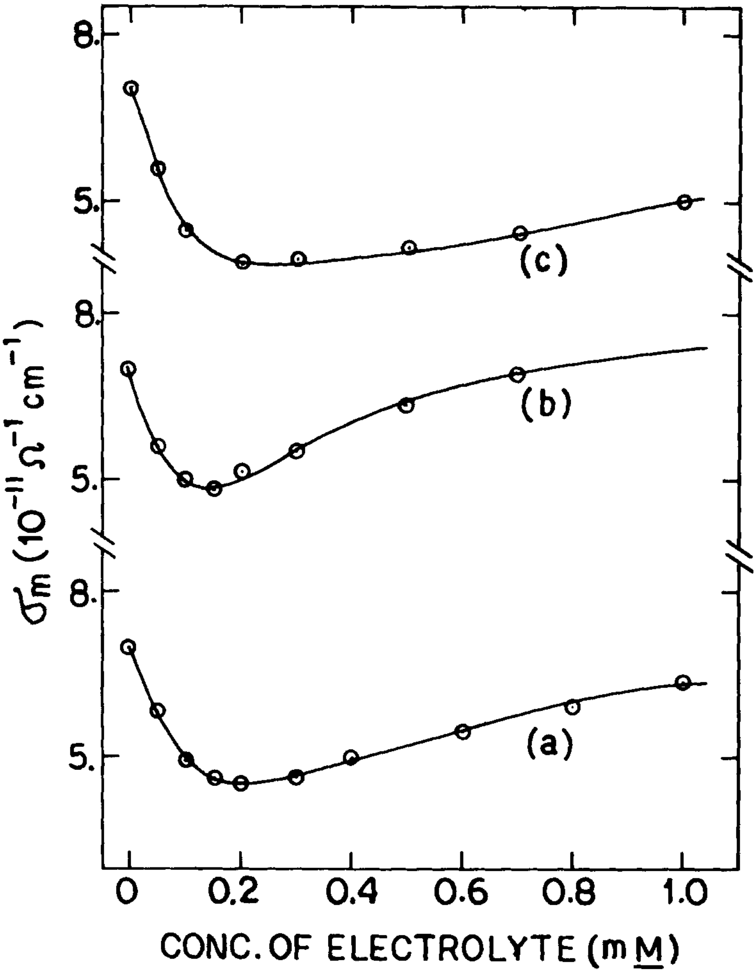

FIGURE 2 Variation of specific conductivity of BLM (σ_m) in presence of iodine with concentration of different electrolytes (a) KCl, (b) $CaCl_2$ and (c) K_2SO_4.

measuring the variation of σ_m with temperature[2] and using the formula

$$\sigma_m = \sigma_o \exp(-E_a/2kT)$$

where E_a is the activation energy and σ_o is the extrapolated value of conductivity at infinite temperature. All the experimental results are presented in Table I.

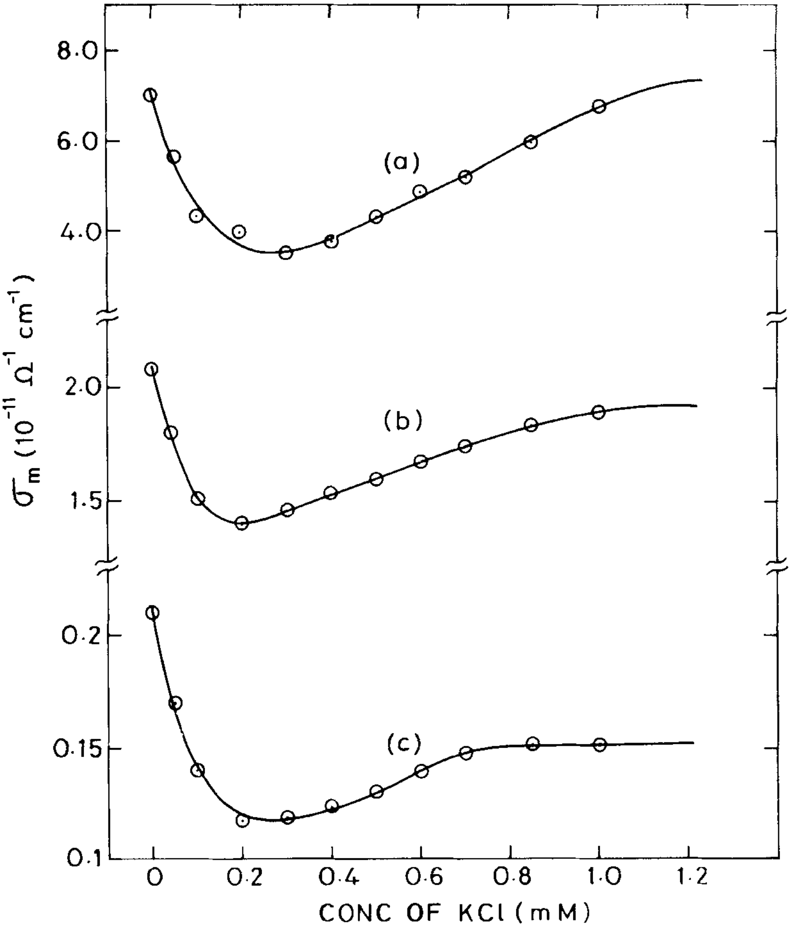

FIGURE 3 Variation of specific conductivity of BLM (σ_m) in presence of different electron acceptors with concentration of KCl. Acceptors (concentration: 1 mM): (a) iodine, (b) picric acid and (c) 2,4-dinitrophenol.

Lipids are intrinsic semiconductors[1,2] and the conduction through such material is generally due to mobility of both holes and electrons.[8] Using standard formula[8] and the measured band gap energy of 2.02 eV, the density of intrinsic charge carrier in BLM in aqueous medium can be calculated to be ~115/cc. Assuming equal mobility for holes and electrons, the value of mobility is calculated to be 1.4 × 10^2 cm^2/volt-sec. When iodine is added in the bathing solution, the effect of these electron acceptor molecules in BLM is equivalent to introducing

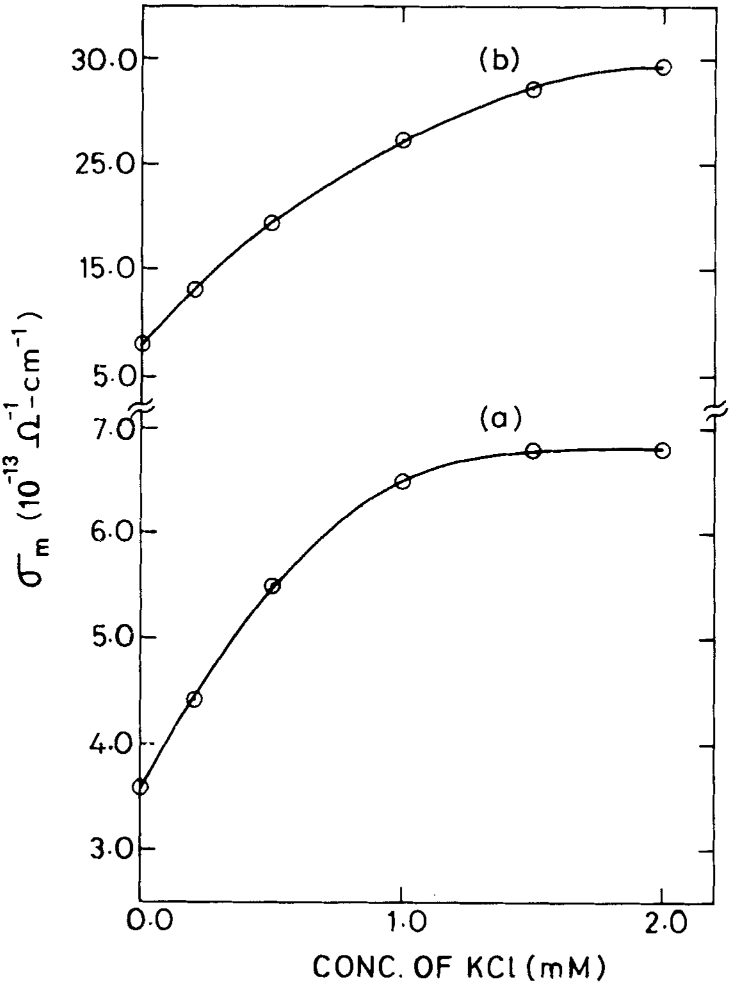

FIGURE 4 Variation of specific conductivity of BLM (σ_m) in presence of different electron donors with concentration of KCl. Donors (concentration: 1 mM): (a) bipyridyl and (b) acridine.

hole donating impurities into it,[9] causing the manifold rise in the conductivity due to the increment in the number of holes. Comparing the BLM conductivity values in presence and in absence of iodine, the number of holes created in presence of iodine can be approximately calculated to be 3.6×10^6/cc. The number density of iodine molecules for 1 mM concentration is 6.0×10^{17}/cc, which is much larger compared to the hole density, suggesting that only a very few iodine molecules penetrate into the BLM.

If an electrolyte like KCl is now added to the bathing solution, the electron injection at the interface of the electrolyte and BLM, which acts as a double electrode,[5,6,10,11] will depend on (a) the standard electrode potential of the anions and cations at the interface and (b) the activation energy of the system. Thus at the same electrolytic concentration of KCl, the probability of electron injection is expected to be more for a BLM with less activation energy (here in presence of iodine) than for a BLM with higher activation energy (in case of aqueous bathing solution or in presence of acridine). At low concentration of the electrolytes, in presence of an electron acceptor when the BLM behaves as a *p*-type semiconductor, these injected electrons partially recombine with the holes, reducing the number of charge carriers and consequently the conductivity decreases. As the electrolyte concentration increases, more and more electrons pass through the BLM and the conductivity increases till the saturation value is reached. Hence the electronic conduction through BLM along with its double electrode behaviour explain the qualitative nature of the conductivity–concentration curve in presence of an electron acceptor (iodine, picric acid, 2,4-dinitrophenol) satisfactorily.

In presence of the electron donor (acridine, bipyridyl) in the bathing solution, the conductivity increases (see Figure 4b) as the donor molecules introduce some electrons in the BLM system. Comparison of measured values of conductivity in presence and in absence of acridine gives an approximate number of such electrons, 4.1×10^4/cc. Now when an electrolyte is added in the bathing solution, more and more ions are available for injecting electrons at the BLM interface and hence the conductivity goes on increasing until a saturation value is obtained. Also a close look at Table I reveals that the addition of electron donors or acceptors in the bathing solution change the activation energy whereas addition of electrolytes do not. That would not have been the case if ions were the majority charge carriers through BLM.

Thus the assumption of electronic conduction through BLM allows us to interpret the variation of BLM conductivity with electrolyte concentration in presence of an electron acceptor as well as in presence of an electron donor in the bathing solution. It is interesting to note that while preparing this manuscript, we had the opportunity to come across the very recent literature,[12] where similar conclusion has been drawn with different experimental systems.

Acknowledgments

This work is supported by a DAE grant, Govt. of India. We are thankful to Prof. H. Ti Tien for the gift of the BLM chamber. Helpful discussion with Prof. Alfred Saupe is gratefully acknowledged.

References

1. B. Rosenberg, B. B. Bhowmik, H. Harder and E. Postow, *J. Chem. Phys.*, **49**, 4108 (1968).
2. B. Rosenberg and B. B. Bhowmik, *Chem. Phys. Lipids.*, **3**, 109 (1969).
3. K. O'Shaughnessy and S. B. Hladky, *Biochim. Biophys. Acta.*, **724**, 381 (1983).
4. H. T. Tien, Bilayer Lipid Membrane (BLM) Theory and Practice (Mercel Dekker, 1974).
5. B. B. Bhowmik and P. Nandy, *Chem. Phys. Lipids.*, **34**, 101 (1983).
6. P. Nandy, R. Datta and B. B. Bhowmik, *J. Coll. Interf. Sc.*, **115**, 277 (1987).
7. H. T. Tien, S. Carbone and E. A. Dawidowicz, *Nature*, **212**, 718 (1976).
8. C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., 1976), pp. 300–313.
9. M. A. Slifkin, *Charge Transfer Interaction of Biomolecules*, (Academic Press, 1971), p. 1.
10. H. T. Tien, B. Karvaly and P. K. Shich, *J. Coll. Interf. Sci.*, **62**, 185 (1977).
11. B. B. Bhowmik, R. Datta and P. Nandy, *J. Coll. Interf. Sci.*, in press.
12. H. T. Tien, J. Kutnik, P. Krysinski and Z. K. Lojewska, *Electrical Double Layer in Biology*, (Plenum, 1986), pp. 1–20.