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PHYSICAL STUDIES OF PHOSPHOLIPIDS

VII. THE D.C. ELECTRICAL CONDUCTIVITY PROPERTIES OF SOME MEMBRANE PHOSPHOLIPIDS*

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SUMMARY

1. The variation of the d.c. electrical conductivity with temperature has been studied for a range of phospholipids in the polycrystalline solid condition and also in various mesomorphic states. The lipids examined include diacylphosphatidylethanolamines, phosphatidylcholines (lecithins), phosphatidylserines and phosphatidic acids. At the onset of each mesomorphic phase, a change in the conduction parameters occurs. Fully saturated 1,2-diacylphosphatidylethanolamines possess 2 distinct mesomorphic phases. At the transition temperature from crystalline to the first mesomorphic phase, the activation energy for conduction changes from approx. 2.0 eV to approx. 3.0 eV. At the second transition temperature the activation energy falls to about 0.8 eV. Phosphatidylcholines have a higher activation energy of approx. 3.5 eV in the crystalline state which decreases at the first transition temperature to 0.7–1.4 eV depending upon the degree of unsaturation in the hydrocarbon chain.

2. With the lecithins and phosphatidylserines an unusual conductivity effect is observed which might be associated with the formation of a cubic mesomorphic phase.

3. Correlation of the conductivity results with results obtained using other techniques, *e.g.* NMR spectroscopy, X-ray diffraction and thermal studies, suggest that the observed conductivity may be an intrinsic property associated with the polar end groups.

4. The specific resistance of the phospholipids is lowered by several orders of magnitude by the addition of small quantities of water.

5. These results are discussed with relevance to some biophysical problems of contemporary interest.

Abbreviation: DTA, differential thermal analysis.

* An account of this study was presented at the 2nd International Biophysics Congress, Vienna, 5–9th September, 1966.

INTRODUCTION

Phospholipids are important components of many cell membranes. They have been considered to be involved in a whole range of biological processes, including nerve excitability, membrane permeability and mitochondrial oxidative phosphorylation[1]. It has been suggested that their electrical properties may have relevance in a number of membrane processes, including the excitation properties of axons[2], and coupled oxidation–reduction processes[3,4] across membranes.

Advances in techniques for the separation, purification, characterisation and synthesis of phospholipids are making it increasingly possible to obtain well characterised materials for the study of many of their physical properties. Recent studies have shown that phospholipids can exist in a number of mesomorphic phases[5–8] and we have explored this in earlier papers in this series. Here we present the results of some studies on the d.c. electrical conductivity of various types of phospholipids.

EXPERIMENTAL

Materials

The following samples were prepared synthetically in our laboratories by methods previously described[6].

*1,2-Diacyl-*DL*-phosphatidylethanolamines*. Dimyristoyl; distearoyl; dipalmitoyl; 1-stearoyl-2-elaidoyl; dioleoyl.

*1,2-Diacyl-*L*-phosphatidylcholines* (*lecithins*). Distearoyl; dipalmitoyl; dioleoyl. A sample of egg-yolk lecithin was prepared from fresh eggs according to the procedure outlined by SINGLETON *et al.*[9].

Other phospholipids. Dimyristoyl phosphatidic acid; 1,2-distearoylphosphatidylserine and a natural sample of phosphatidylserine (Mann Research) were also used.

(All samples were in the acid form except the phosphatidylserines, which were present as sodium salts.)

The purity of the samples was assessed by the techniques of thin-layer chromatography and differential thermal analysis (DTA).

Apparatus and experimental procedures

The determination of electrical conduction parameters of poorly conducting organic materials, such as phospholipids, can be complicated by a variety of factors such as adsorbed gases, variable hydration, the crystalline or polycrystalline state of the sample, and electrode material. We have attempted, as far as possible, to eliminate or allow for these factors. The basis of the present technique was to measure the d.c. electrical resistance of a highly compressed microcrystalline powder, as a function of temperature under carefully standardised conditions. All measurements reported in this paper were carried out with the cell shown in Fig. 1.

The cell was fabricated from a rod of Teflon, and the central electrode lead passed through a hollow quartz insulating rod. An electrode separation of approx. 1 mm was maintained by a Teflon spacer. The cell components were mounted on 2 threaded brass rods and positioned by nuts such that light pressure was applied to the electrodes by the spring.

In the circuit the sample is connected in series with a standard resistor. A known

d.c. voltage (which could be varied between 0 and 240 V) was applied across the sample and the standard resistor. The voltage drop across the standard resistor was measured by means of a high impedance electrometer (Vibron model 62A; input impedance $>10^{15}\ \Omega$). Extensive shielding precautions, including an earthed Faraday cage, were found to be necessary. The temperature of the sample was determined by means of a copper–constantan thermocouple situated in close proximity to the sample. The sensitivity of the circuitry was such that, using an applied voltage of 100 V, the maximum resistance which could be measured with confidence was about $5 \cdot 10^{14}\ \Omega$. For a sample of thickness 1.0 mm, diameter 5.0 mm, this corresponds to a specific resistance of $10^{15}\ \Omega \cdot$cm. The conductivity cell was attached to a conventional high-vacuum line, enabling evacuation to 10^{-5}–10^{-6} mm Hg. This ensured thorough outgassing and the elimination of any free water associated with the sample.

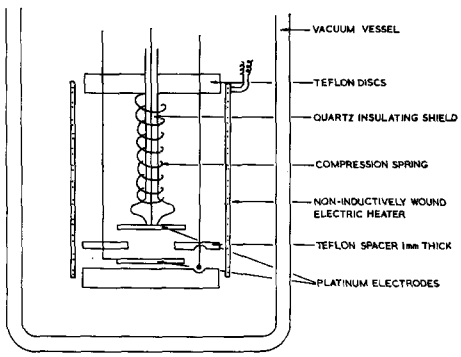


Fig. 1. The d.c. conductivity cell.

Before each determination of resistance the cell was allowed to attain thermal equilibrium. Regulation of the temperature was achieved by changing the voltage supplied to a small heating coil surrounding the sample and within the vacuum system (Fig. 1). Resistance readings were taken at intervals of approx. 3° and approx. 1° in the region of phase transitions. The efficacity of this procedure was demonstrated by the complete reversibility and lack of hysteresis on both heating and cooling, using synthetic samples of cholesterol and polyamide 6-6. After thermal equilibrium had been established at a convenient temperature (usually after 1 h) Ohm's law plots were determined by changing the applied voltage in 10 V increments and measuring the current at each voltage.

Several attempts were made to detect possible polarisation effects (*i.e.* a change in the sample resistance with time, often indicative of an ionic conduction mechanism). To avoid possible complications with the circuit time constant, a convenient temperature was selected at which the sample resistance was less than $10^{10}\ \Omega$. The resistance of the sample was observed for periods up to an hour after switching on the applied voltage. Investigation of the use of a range of electrodes, evaporated silver films, 'Aquadag' colloidal graphite, silver paint and platinum showed no artefacts due to electrode variation. Bright platinum electrodes were used to obtain the results in this paper.

The phospholipids were highly compressed at about 6000 kg/cm^2 into discs of

5 mm diameter and 1 mm thickness to obviate intercrystalline resistance and capacity effects. Prior to each resistance–temperature run, the discs were placed in liquid N_2 for at least 16 h in an attempt to ensure that the samples were in a crystalline form. The disc was then inserted in the conductivity cell which was then assembled to the vacuum line. The thermocouple and heater leads were taken out at the top of the conductivity cell through Apiezon wax seals in B10 silica cones. The cell was evacuated to 10^{-6} mm Hg for 24 h, or until the resistance of the sample had become constant at a given temperature, when all adsorbed oxygen and free water were assumed to have been removed.

The resistance of the sample was measured as a function of temperature for cycles of heating and cooling to the desired temperature. Current–voltage characteristics and polarisation effects were then studied. Finally, the apparatus was dismantled and the thickness of the disc measured.

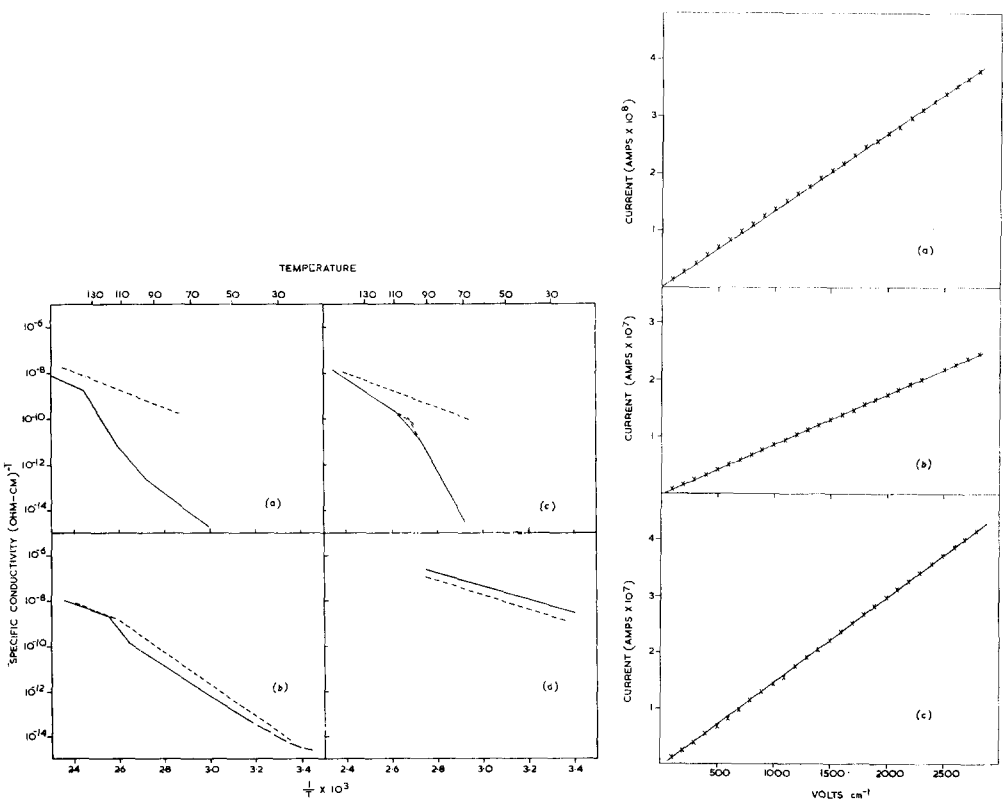


Fig. 2. Temperature dependence of the d.c. conductivity of various 1,2-diacyl-DL-phosphatidylethanolamine derivatives. ———, heating; - - - - -, cooling; a, distearoyl; b, 1-stearoyl-2-elaidoyl; c, dipalmitoyl; d, dioleoyl.

Fig. 3. Current–voltage characteristics for: a, 1-stearoyl-2-elaidoyl-DL-phosphatidylethanolamine (87°); b, 1,2-dioleoyl-DL-phosphatidylethanolamine (24°); c, 1,2-distearoyl-phosphatidylserine (24°).

RESULTS

The temperature dependence of the d.c. electrical conductivity for a solid dielectric, irrespective of the detailed conduction mechanism, can often be represented by the Arrhenius equation for an activated process. In its simplest form the equation may be written

$$\sigma = \sigma_0 \exp - E/kT \qquad (1)$$

In the equation, σ is the measured specific conductivity, T is the absolute temperature, k is Boltzmann's constant, and E is the activation energy for the conduction process.

The results obeyed the Arrhenius equation between various transition temperatures characteristic for each phospholipid, and are presented as plots of the logarithm of the specific conductivity against the inverse absolute temperature. The temperature dependence of the conductivity for both heating and cooling runs for 4 diacylphosphatidylethanolamines are shown in Fig. 2. Current–voltage characteristics of some other phospholipids are shown in Fig. 3.

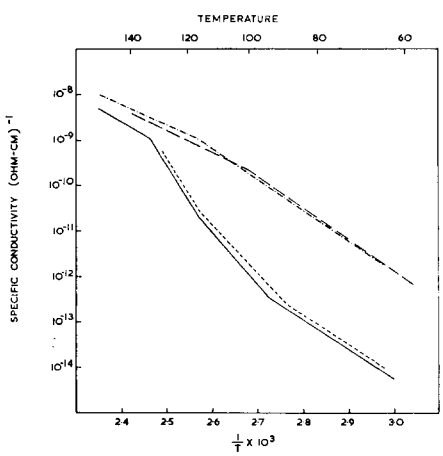


Fig. 4. Temperature dependence of the d.c. conductivity of dimyristoylphosphatidylethanolamine. · · · · ·, sample A, cooling from 130° (*i.e.* below second transition temperature); ———, sample A, reheating; - - - - -, sample A, recooling from 140° (*i.e.* above second transition temperature); — · — · —, sample B, cooling from 160°.

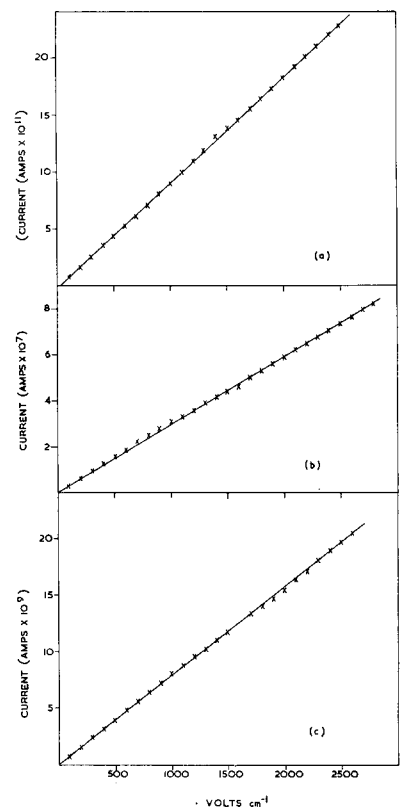


Fig. 5. Current–voltage characteristics of dimyristoylphosphatidylethanolamine in different temperature regions: a, 96°, below first transition temperature; b, 120°, between first and second transition temperatures; c, 86°, experiment performed after heating sample above second transition temperature (135°) and then cooling. The sample was still in liquid crystalline state (see text).

In an attempt to understand various features of the conductivity results, 1,2-dimyristoylphosphatidylethanolamine was investigated in some detail. Different electrode materials, heating and cooling runs to and from different temperatures, and current–voltage characteristics at a range of temperatures were investigated. A representative sample of the Arrhenius plots is shown in Fig. 4. Current–voltage plots for the dimyristoyl derivative at various temperatures are shown in Fig. 5.

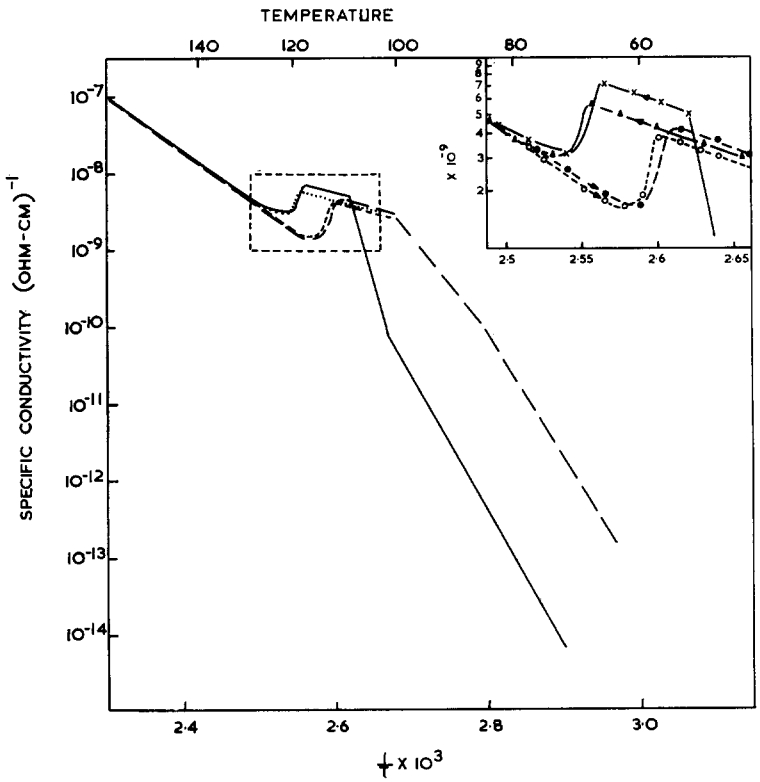


Fig. 6. Temperature dependence of the d.c. conductivity of 1,2-distearoyl-L-phosphatidylcholine; ———, heating to 150° (insert ×—×); - - - -, cooling from 150° to 100° (insert ○- - - -○); · · · · ·, heating from 100° to 135° (insert ———); — — —, cooling from 135° to 50° (insert ●- - -●).

Arrhenius plots for cycles of heating and cooling for distearoyl- and dipalmitoyllecithin are shown in Figs. 6 and 7. Shown in the insert of Fig. 6 is an unusual effect which was observed with the phosphatidylcholines and with distearoylphosphatidylserine. On the first heating run a sudden drop in conductivity occurs over a very small temperature range (1°). On cooling a corresponding increase in conductivity occurs with a small temperature hysteresis. Cycles of heating and cooling indicated that the effect was reproducible and reversible. This effect was not observed with the diacylphosphatidylethanolamines. Arrhenius plots for heating and cooling of distearoylphosphatidylserine and dimyristoyl phosphatidic acid are shown in Fig. 8.

Attempts to observe polarisation phenomena were indecisive. If polarisation phenomena are present then they must be small.

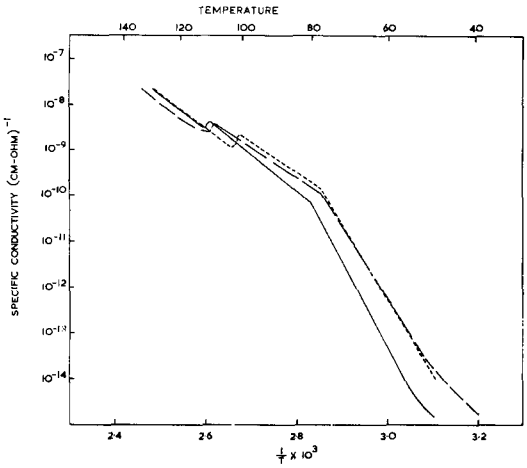


Fig. 7. Temperature dependence of the d.c. conductivity of 1,2-dipalmitoyl-L-phosphatidylcholine; ———, heating, - - - - -, cooling; — — —, reheating.

DISCUSSION

The conductivity–temperature results, though differing in detail, have certain overall similarities. With the exception of dioleoylphosphatidylethanolamine, dioleoylphosphatidylcholine and egg-yolk lecithin, abrupt changes in the slope of the Arrhenius plots occur at definite temperatures. Other physical studies[5–8] have indicated that mesomorphic phase changes occur at these same transition temperatures. This correlation (Fig. 9) shows that the d.c. electrical conductivity and mesomorphic phase behaviour of phospholipids are intimately related.

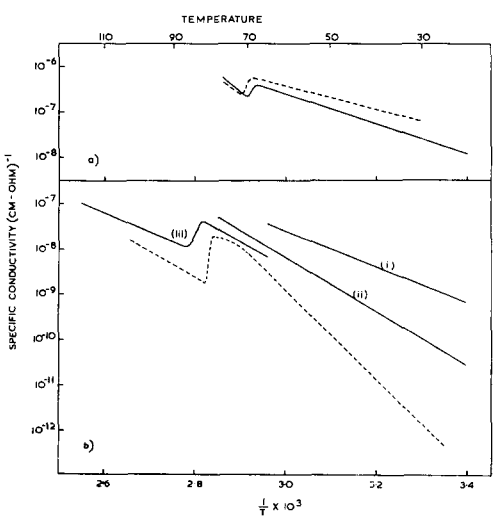


Fig. 8. Temperature dependence of the d.c. conductivity of other phospholipids. a, dimyristoyl phosphatidic acid; ———, heating; - - - - -, cooling; b, distearoylphosphatidylserine; ——— (I), first heating; ——— (II), second heating; ——— (III), third heating; - - - - - cooling.

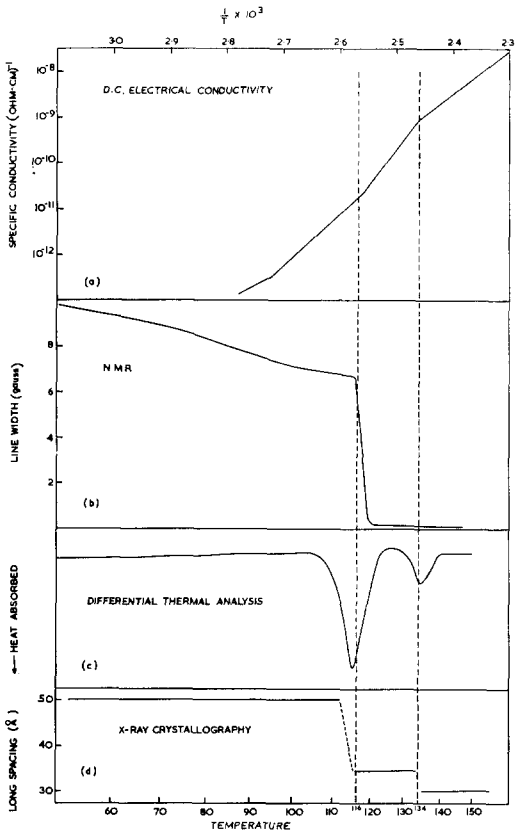


Fig. 9. A comparison of the d.c. conductivity behaviour with temperature of 1,2-dimyristoyl-DL-phosphatidylethanolamine with other measurements (NMR, X-ray and DTA measurements).

The relevant activation energy for the conduction process can be calculated from the slope of the Arrhenius plots between the various transition temperatures and the values are presented in Table I. The transition temperatures obtained by DTA studies and the specific conductivity at the highest transition temperature for each sample studied are also shown.

The nature of the charge carriers

The linear current–voltage characteristics and the absence of polarisation phenomena suggest either an electronic or very efficient protonic charge-transfer mechanism.

The phosphatidylethanolamines on heating show first an increase in activation energy followed by a pronounced decrease at the second transition temperature. This is difficult to reconcile with either a purely protonic or electronic mechanism, but discounts conduction by adventitious impurities. A consistent explanation may follow from considering the majority carriers to be electrons in the low-temperature regions and protons at higher temperatures, where reorientational processes, necessary for

TABLE I

PHASE TRANSITION TEMPERATURES, d.c. CONDUCTIVITY ACTIVATION ENERGIES AND SPECIFIC CONDUCTIVITIES OF A RANGE OF PHOSPHOLIPIDS

Sample	*Observed transition temperature*		*Activation energy (eV) for d.c. conductivity* $\sigma = \sigma_0 \exp -\frac{E}{kT}$			*Specific conductivity at highest transition temperature* $(\Omega \cdot cm)^{-1}$
	DTA	*Conductivity*	*Temperature range*	*Heating*	*Cooling*	
Phosphatidylethanolamines						
1,2-DL-Dimyristoyl	115	115	90–115	2.3	1.4	$1 \cdot 10^{-9}$
			115–135	3.1		
			>135	1.3	0.9	
1,2-DL-Distearoyl	118	114	<114	2.1		
			114–136	3.3	0.8	$2 \cdot 10^{-9}$
	137	136	>136	0.8		
1-Stearoyl-2-elaidoyl	109	105	<105	1.3	1.4	
			105–120	2.7		$2.5 \cdot 10^{-9}$
	129	120	>120	0.6	0.6	
1,2-DL-Dioleoyl	(about 42°?)	—	—	0.7	0.7	about 10^{-9} (40°)
Phosphatidylcholines						
1,2-L-Distearoyl	90	102	<102	3.5	2–3	
			102–108	(7.0?)	—	about $4 \cdot 10^{-9}$
		108	108–120	0.5	—	
	105	118–120	>120	1.4	0.5	
1,2-L-Dipalmitoyl	70	80	<80	3.7	3.1	
			80–110	1.6	—	10^{-9}–10^{10}
	95	110–112	>110	1.4	1.4	
1,2-L-Dioleoyl	<0	—	—	0.7	0.7	about $3 \cdot 10^{-9}$ (40°)
Miscellaneous						
Distearoylphosphatidylserine			<80	0.8–1.1	—	
	86–87	80–86	>86	0.7–0.8	0.7–0.8	$6 \cdot 10^{-8} \rightarrow 2 \cdot 10^{-9}$
Dimyristoyl phosphatidic acid	—	63–67	<63	0.65	0.65	$5 \cdot 10^{-7} \rightarrow 2 \cdot 10^{-9}$
			>67			
Egg-yolk lecithin	<0	—	—	0.7	0.7	about 10^{-9} (40°)
Polyamide 6-6 this work		118	>118	1.0	1.0	$2.2 \cdot 10^{-10}$ (127°)
			<118	2.0	2.0	
ref. 15		115	>115	1.12	—	$2.6 \cdot 10^{-10}$ (127°)
			<115	1.9-2.6	—	
Chlosterol this work		—		2.2	2.2	$2 \cdot 10^{-11}$ (127°)
ref. 25		—		2.4	—	$2 \cdot 10^{-12}$ (127°)

conduction by a Grotthus-type mechanism (Fig. 11a) are more easily visualized. Controlled electrolysis experiments are needed to evaluate these possibilities[10]. In the low-temperature regions, however, where the charge-carrier problem is most acute, the high resistance of anhydrous phospholipids precludes such experiments. Protonic conduction has been postulated and fairly well established in ammonium dihydrogen phosphate[11,12], long-chain alcohols[13,14] and certain polyamides[15]. As these compounds also show structural and mesomorphic properties[16] similar to the phospholipids, protonic conductivity in the latter may be anticipated.

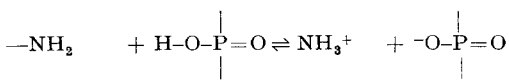
Structural mechanisms

A hydrogen-bonded polar region is a common structural feature of the phospholipids and similar hydrogen bonded networks found in ice, polyamides, and long-chain alcohols are known to be favourable to proton conduction. The conduction pathway in phospholipids is, therefore, probably associated with this polar region. This is supported by the similarity of the specific conductivity in corresponding mesomorphic states and the enhanced conductivity following absorption of water by the polar region.

Several representations of the polar head group region of phosphatidylethanolamines showing H-bonded networks are possible. One such schematic model is shown in Fig. 11b. In direct analogy with the Grotthus model for ice, shown in Fig. 11a, proton conductivity would be dependent on: (a) The rate of generation of free protons. (b) The apparent mobility of the protons. This will be controlled by the rate of reorientational processes leading to favourable hydrogen-bonded chains, and the potential energy barrier to be surmounted by the proton on transfer from the phosphate to the ammonium site.

The generation of 'free' protons is probably independent of the lipid phase since it reflects equilibria (Eqns. 3–5), analogous to those which occur with ice or water (Eqn. 2)

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \tag{2}$$



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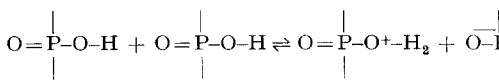

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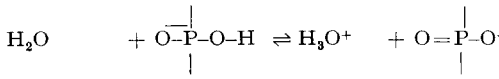


(5)

The mobility of the charge carriers, whether protons or electrons is, however, likely to be strongly dependent on the detailed lattice structure. With the phosphatidylethanolamines at the first transition temperature, NMR spectroscopic evidence shows a sudden increase in hydrocarbon chain mobility, whilst X-ray diffraction studies show a decrease in the crystal long spacing from 50 to 34.5 Å in the case of the dimyristoyl derivative. The polar head groups are still maintained by coulombic interactions in ionic sheets. There may also be an increase in the lateral spacing and a decrease in the vertical spacing between polar groups. The X-ray long spacings decrease slightly at the second transition point, and the NMR results suggest that some additional motion of the polar head group may be taking place (Fig. 10).

In the high-temperature region, the high-molecular motion of the hydrocarbon chains enables the conducting pathway to be considered as a relatively freely interacting chain of polar groups. A relatively low activation energy for charge-carrier mobility is thus to be anticipated.

In the low-temperature region those processes, leading to charge-carrier mobility will be subjected to quite different constraints because of the crystallinity of the hydrocarbon chains and the restricted rotation of the polar end groups about the C–O,

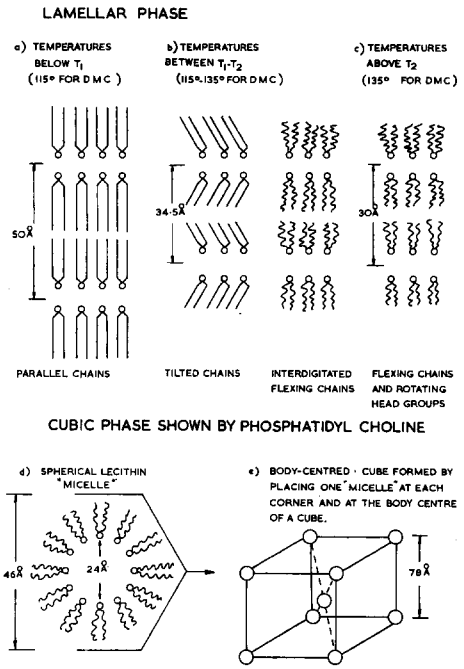
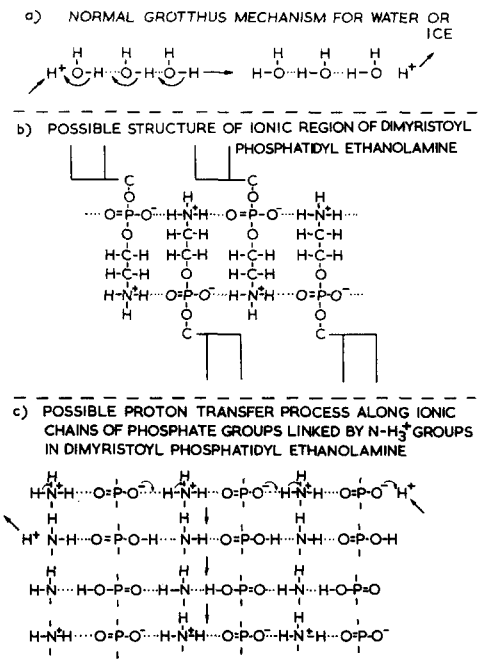


Fig. 10. Schematic representations of the phases exhibited by phospholipids at different temperatures. DMC, 1,2-dimyristoyl-DL-phosphatidylethanolamine.

P–O or C–N bonds. This will produce a higher activation energy in this region. The intermediate temperature region is the most difficult to interpret. The lipid hydrocarbon chains are fluid, but polar group rotation about the C–O, P–O and C–N bonds is probably still restricted. The polar group separations have changed from those of the low-temperature region; their precise nature and effect cannot be assessed, but they may result in a system very unfavourable to charge-carrier mobility and hence a high activation energy is observed.

Alternatively, the conductivity in the low and intermediate temperature regions could be considered to be electronic. The polar groups may be aligned closely enough to give electron mobility through chains of phosphate groups. The activation energy for generation of a conducting electron is half the energy gap between the ground state and the conduction band. Values of the activation energy in the low and middle temperature regions, however, correspond to extremely high energy gaps of approx. 4 eV and approx. 6 eV respectively which would militate against an electronic mechanism. The energy required by an electron to surmount the potential energy barrier between phosphate groups, will be very sensitive to changes in the polar group separation. The increase in activation energy occurring at the first transition temperature could be due to an increase in separation between the phosphate groups occurring simultaneously with the 'melting' of the hydrocarbon chains.

At the second transition temperature, the onset of polar end group rotation makes protonic conduction efficient and energetically the more favourable mechanism. The decrease in activation energy at the second transition temperature may be due to a change from electronic to protonic conduction.



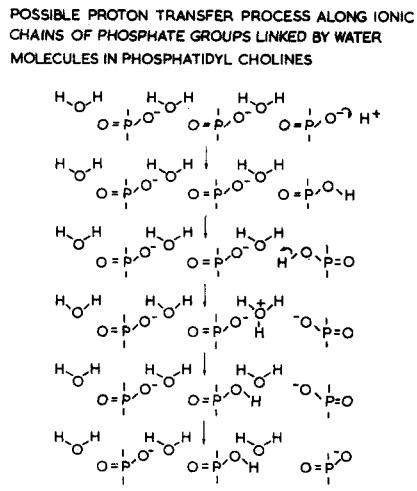


Fig. 11. Schematic model illustrating possible proton conduction in hydrogen-bonded phosphatidylethanolamines.

Fig. 12. Schematic model illustrating possible proton conduction in the diacylphosphatidylcholines.

If proton conductivity is involved, the conductivity mechanism cannot be the same for the phosphatidylcholines as for the phosphatidylethanolamines, as the former do not have hydrogen atoms bonded to nitrogen available for forming hydrogen-bonded networks. An alternative path can, however, be formulated involving water molecules and these are known to be strongly bound to phosphatidylcholines (Fig. 12). Reorientation of the polar head group or molecule as a whole is still required to obtain the continuous transfer of protons. Whatever the conduction mechanisms, it must also be inferred that the polar head groups in phosphatidylethanolamines behave differently from those in phosphatidylcholines at the first phase transition since, with the former, the activation energy increases, whereas, with the latter it decreases.

The lecithins also show the unusual but reproducible effect illustrated in Fig. 6. This effect is not due to the reversible adsorption or desorption of water molecules, because the system is continuously pumped to a high vacuum throughout the heating and cooling cycle. It seems more likely to be associated with the occurrence of a cubic mesomorphic phase (Fig. 10)[17,18]. A sample of 1,2-dipalmitoylphosphatidylcholine monohydrate, observed under the polarised light microscope, shows a cubic-type phase at 125° and gives a conductivity effect (between 120 and 130°) similar to that shown in Fig. 6. The detailed structure of the cubic phase is still uncertain and hence we cannot be certain of the structural processes involved in conductivity in this phase.

To conclude this discussion we mention some general features of the conductivity results.

The hysteresis observed on heating and cooling

This is most clearly seen in the case of 1,2-dimyristoylphosphatidylethanolamine, as shown in Fig. 4, where examples of Arrhenius plots of heating and cooling to temperatures 5° above and 5° below the second transition temperatures are given. Provided the second transition temperature is not exceeded, then heating and cooling plots are essentially free of hysteresis. The diacylphosphatidylcholines, in general, show considerably less hysteresis than the diacylphosphatidylethanolamines. This observation agrees with conclusions reached on the basis of other physical techniques[6].

The effect of the hydrocarbon chain structure

As a result of unsaturation in the hydrocarbon chain, the temperature for mesomorphic or liquid crystalline transitions is lowered. Hence the conductivity at a given temperature is increased from that of the crystalline phase to that of the mesomorphic phase as in dioleoylphosphatidylethanolamine, dioleoylphosphatidylcholine and egg-yolk lecithin, where the conductivity is characteristic of the high-temperature region of fully saturated phospholipids (Fig. 2, Table I).

The effect of hydration

Some observations suggest that hydration greatly lowers the specific resistance of the sample by several orders of magnitude. The effects are reversible and are associated with the polar head group region. The first adsorbed water molecules are probably incorporated into the hydrogen bond network associated with the polar groups, increasing the concentration and effective path length of mobile protons. Alternatively, adsorbed water may increase the electronic conductivity by acting as an electron donor[19,20], or by changing the dielectric constant[21] of the system.

Recently STRAUB (K. D. STRAUB AND W. S. LYNN, personal communication) has observed d.c. conductivity with an activation energy of 0.4–0.5 eV in a presumably highly hydrated egg-yolk lecithin gel. Linear current–voltage characteristics, stable currents and absence of electrolysis products were observed. These results are in agreement with our results for phospholipids in a mesomorphic condition.

Cholesterol

Cholesterol is often found as a major constituent of membranes, and for completeness its conductivity properties were also studied. The activation energy and specific resistance are given in Table I; both were considerably higher than those of phospholipids in the liquid crystalline condition. Our values are in agreement with those reported by WOBSCHALL AND NORTON[22]. It is unlikely that intrinsic conductivity associated with cholesterol plays any role in membrane function.

Phospholipid conductivity in biology

In this section we shall point to areas in biology where the conductivity properties of phospholipids may be relevant. The extrapolations to these systems are rather speculative and uncertain in character.

Mitochondrial and many other membranes are characterised by phospholipids

containing a high degree of unsaturation[23]. Membrane phospholipids at room temperature are therefore in a mesomorphic liquid crystalline condition[6]. The conductivity of phospholipids in their mesomorphic phase will be appropriate to the biological situation. Unsaturated lipids have a specific resistance of approx. $10^9\ \Omega \cdot cm$ at physiological temperature, a value not very different from those for ice or water. The average value for the total activation energy is 0.7 eV (or about 16 kcal/mole). This energy requirement is higher than that normally associated with ATP hydrolysis for example, but this may be available in certain specialised cases.

(a) The co-ordinated flow of electrons through and between the various complexes of the electron transfer chain appear to have an absolute requirement for the presence of unsaturated phospholipids[23]. The reactions, which take place in the essentially hydrophobic, anhydrous milieu of the mitochondrion, are formally oxidation–reduction reactions involving in some parts of the chain, both 2 protons and 2 electrons and in others only single electrons. It is usually stated that at the required positions, protons are injected into, or taken up from 'the medium'. If the medium consisted of phospholipids, the phosphate groups could play a functional role in proton or electron transfer.

(b) In theoretical studies of the excitation properties of axons, certain phospholipid molecules are considered to change their orientation and combining properties under the influence of an electrical field[2]. Changes in polar-group configuration may be partly responsible for some of the observed conductivity results in our experiments.

(c) JAHN[3], COPE[4] and ROBERTSON[24] have developed theories to relate enzymatic redox processes on two sides of a biological membrane with protonic or electronic charge transport through the membrane, and the active transport of ions. Charge transport processes associated with phospholipid polar groups may play a role to offset charge inequality brought about by active transport of anions.

(d) The resistance values for phospholipid model membranes in the bilayer form have been established to lie in the range 10^6–$10^9\ \Omega/cm^2$ (see ref. 25). At the present time a difficulty in these studies is that, whilst phospholipid bilayers appear to be freely permeable to water[26,27], they are very impermeable to ions. Ion-exchange phenomena followed by electron or proton migration associated with the phospholipids could possibly be involved in the overall conductivity. If this were so no net ion transfer would occur, but resistance values comparable with bulk water would be expected.

CONCLUSIONS

Phospholipids, such as 1,2-diacylphosphatidylcholines and ethanolamines, have been shown to have a significant electrical conductivity. Discontinuities are observed in the conduction parameters at various temperatures which correspond to those at which structural changes have been shown to occur by other techniques, such as X-ray, DTA and NMR spectroscopy. The charge-carrier mobility, probably associated with the polar head groups, appears strongly dependent upon the hydrocarbon chain fluidity within each mesomorphic phase. Conductivity processes involving phospholipids may be important in a variety of biophysical situations.

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