Dielectric Studies of Ionic Interactions in Aqueous Lamellar Amphiphilic Systems

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The behaviour of counterions in aqueous lamellar systems is strongly dependent on the electrostatic interactions with the lamellar surfaces. This was observed in the frequency-dependent electric properties of such systems. Alteration of the interlamellar distances gives rise to very pronounced effects in the electric behaviour of the systems. Different lamellar systems and different counterions all show the same qualitative effects. This indicates that the observed effects are of a rather general nature. A simple qualitative physical model is presented.

Recently, much attention has been directed towards the dielectric behaviour of lyotropic liquid crystalline systems. They are good model systems because of their strict geometries. These systems also have considerable practical applications. Recently reported model calculations on lyotropic liquid crystalline systems are one part of a larger project aimed at an explanation of surfactant aggregation in general.[1-3] It has been shown that the existence of lamellar microstructures and the extension of lamellar liquid crystalline phases in multicomponent systems consisting of a surface active agent, water and semipolar additive can be explained by means of electrostatic interactions.[4,5] A proper understanding of the mechanisms in lamellar mesophases is of special importance since these systems are used as models for concentrated colloidal dispersions[6,7] and for biomembranes.[8,9] Direct practical applications of lamellar mesophases in as diverse fields as display systems and emulsion stability show the importance of detailed investigations of the structures.

Some years ago, it was demonstrated that the conductivity of lamellar Aerosol OT/water phases had a pronounced maximum at a given water layer thickness.[10,11] In these experiments, the lateral conductivity was specifically measured, i.e., the conductivity along the water layers and parallel to the Aerosol OT surfaces. The conductivity maximum was explained as occurring when the Helmholtz planes of two opposite Aerosol OT surfaces coincided. One important question is whether the observation of a conductivity maximum is limited to the Aerosol OT system or whether it occurs also in other lamellar liquid crystalline systems and for counterions other than sodium. We have therefore extended our study to involve the system alkali octanoate/decanol-1/water, the counterion being sodium, potassium or lithium. The direct advantage of studying ternary systems of this kind is the possibility of varying the surface charge density keeping the water layer thickness approximately constant.

In the earlier studies, the Aerosol OT samples were aligned between two glass slides with two gold wires acting as spacers and electrodes. In this way, mainly the conductance along the water layers was measured. However, it is of interest to investigate how the orientation of the sample influences the measured electrical properties. Samples with the lamellae aligned perpendicular to the electric field and fully isotropic samples were therefore studied in this investigation.

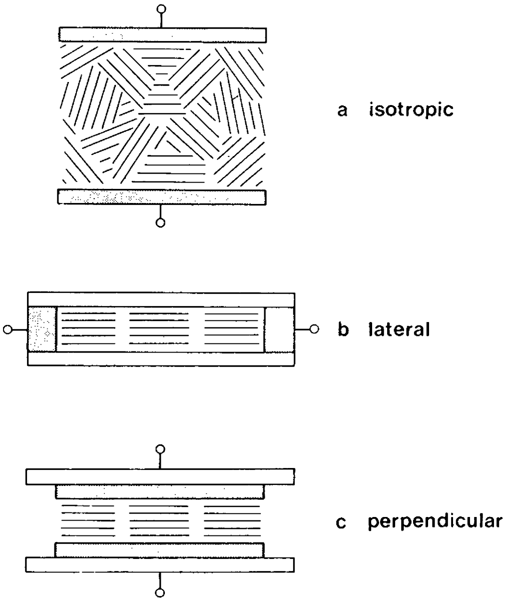
Some qualitative theoretical models are proposed which may account for the observed frequency dependencies and the behaviour of the average ion mobility for thin and thick water layers.

Dedicated to Professor Per Ekwall on his 90th birthday.

Materials and methods

Preparations of the samples (Bis-di-2-ethyl hexylsulphosuccinate sodium salt; Aerosol OT) (Fluka, Switzerland)/water and sodium, potassium or lithium octanoate/n-decanol/water were made by weighing the components in test tubes. These were subsequently sealed and heated until equilibrium was attained (not above 70–80 °C). The samples were always stored at least 1 week at room temperature before the electrical measurements were undertaken. The measurements were carried out with two standard sine wave impedance bridges, Wayne Kerr B 601 (15 kHz to 5 MHz) or Wayne Kerr 801 B (1–100 MHz). The preparation of the salts has been described earlier,[12] decanol was obtained from Ega-Chemie and was reported to be 99.5 % pure.

The measurements on isotropic or unoriented samples (Fig. 1a) were performed with a cell consisting of two brass blocks separated by a plastic spacer giving a 2 mm thick 1 ml cavity. This cell was calibrated with air, *n*-alcohols and water.


a isotropic

b lateral

c perpendicular

Fig. 1. Schematic illustration of the three types of measurement cells used in the study. (a) Isotropic sample between two metal electrodes. (b) Sample aligned between two glass slides. The metal spacers serve as electrodes. The electric field is in this configuration is parallel to the lamellae. (c) Sample aligned between two glass slides onto which thin metal films have been deposited. The electric field in this configuration is perpendicular to the lamellae.

The measurements on ordered samples (Fig. 1c) were undertaken with another type of cell. Here we used glass plates onto which a strip of gold was deposited by evaporation in a standard high vacuum system. The adhesion of gold to the glass plate was facilitated by a thin intermediate layer of chromium. Two such plates were put together with plastic spacer slides and the sample in between, so that the gold strips crossed each other, hence forming a parallel plate capacitor at the crossover. The capacitor had an area of 0.25 cm^2 and a thickness of 50 μm. The area outside the gold strips could easily be checked with a polarization microscope.

For the lateral conductance measurements, glass plates were used with 20 μm thick aluminium strips as spacers and electrodes (Fig. 1b). The glass plates were 2 cm wide. The order of the system was checked with a polarization microscope.

Values for the water layer thickness in the lamellar liquid crystalline structures were taken from the literature,[13] or determined by X-ray diffraction. The water layer thickness d_w is obtained according to

$$d_w = \varnothing_w d_{tot} \qquad (1)$$

where $\varnothing_w$ is the volume fraction of water, and d_{tot} is the total repetition distance for the lamellae according to X-ray diffraction.

The electrical measurements were performed either as a function of frequency in the range 15 kHz – 100 MHz or at a constant frequency of 100 kHz. Polarization effects at the electrodes should be rather small in the chosen frequency range compared to the influence of the lamellar structure of our samples on the measured electrical properties.[10]

Special care had to be taken, however, when measuring on the laterally oriented samples due to the relatively high conductivity in this case. Disordered regions at the electrodes give rise to a significant contact resistance and series capacitance. Measurements were therefore performed at several different distances between the electrodes and the true conductivity and dielectric constant calculated as in Ref. 10

Results

Admittance versus frequency

The experimental results were obtained as the parallel capacitance and conductance of the samples. Although the dielectric constant and the mobility are microscopic quantities which vary with location in the sample, we have chosen to present the experimental results as the apparent dielectric constant and the average mobility of the ions in the sample. The apparent dielectric constant was calculated from the measured capacitance and the geometry of the sample. The average mobility per ion was calculated from the measured conductance and the geometry of the sample assuming that all the counterions contribute to the measured conductance. We gave no microscopic significance to the presented parameters, but they allowed us to compare the electric properties of the different samples studied. The calculation of an average mobility means that we have compensated for the decrease in counterion density (ions/m^3) with increasing water layer thickness. The comparison is thus made per counterion instead. The use of an apparent dielectric constant makes it possible to compare polarization effects in samples with the different geometries described below. Several systems and sample orientations were studied. All measurements were performed at room temperature (25 °C).

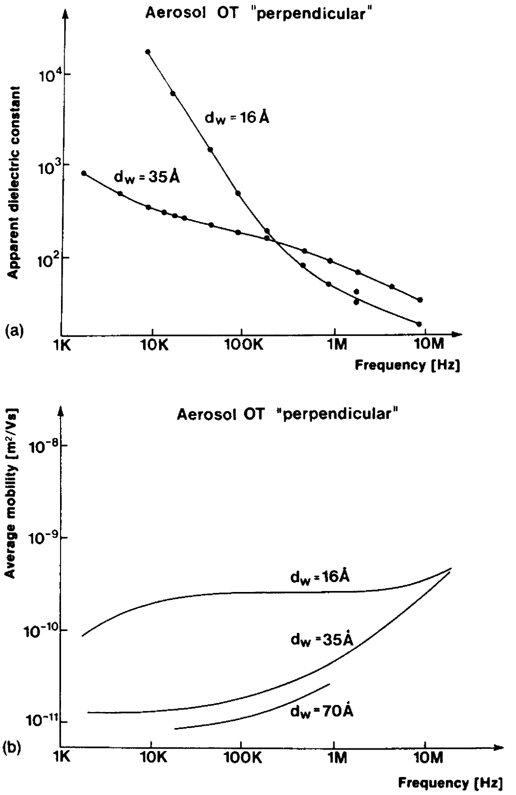


Fig. 2. Apparent dielectric constant (a), and average mobility (b) versus frequency for two different Aerosol OT/water mixtures. d_w denotes the thickness of the water layers between the lipid bilayers. The measurements were performed using the configuration in Fig. 1c.

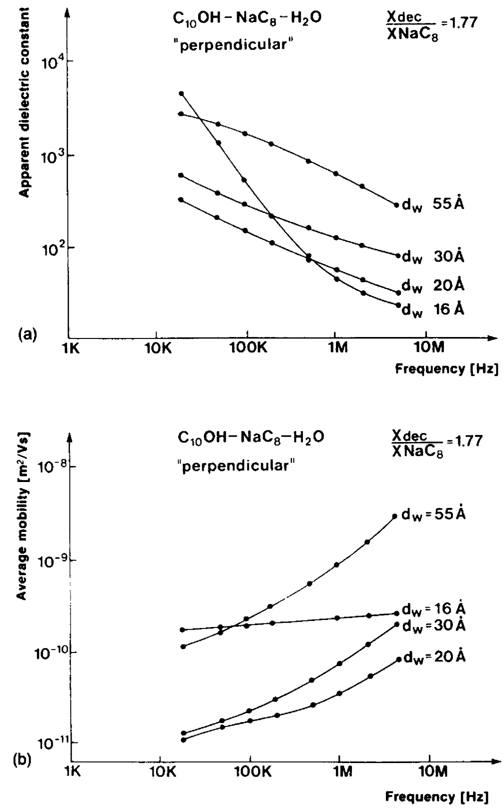


Fig. 3. Same as Fig. 2 but for different sodium octanoate/*n*-decanol/water compositions, where the alcohol/surfactant ratio is kept constant at 1.77.

For the Aerosol OT/water system, samples with the lamellae aligned perpendicular to the

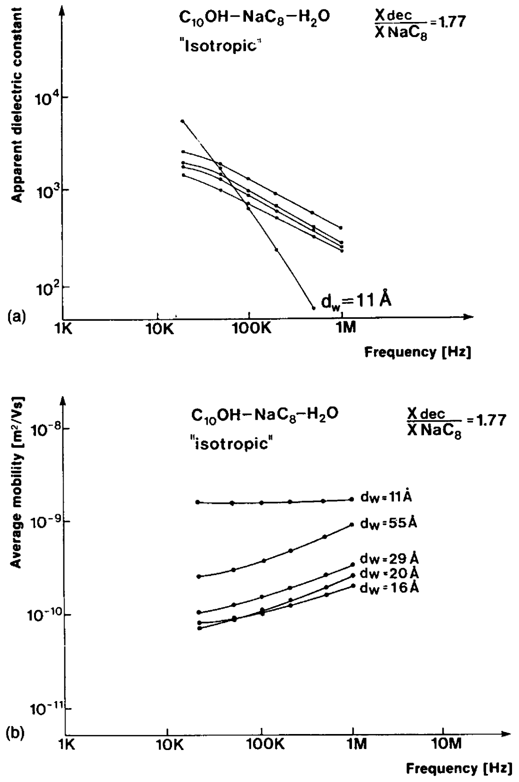


Fig. 4. Same as Fig. 3 but with the measurements performed with the configuration in Fig. 1a.

electrodes were studied extensively in order to facilitate comparison with earlier measurements on laterally orientated systems. Fig. 2 shows results for a system with thin (d_w = 1.6 nm) and thick (d_w = 3.5 nm) water layers, respectively. A water layer thickness of 1.6 nm is close to that at which the maximum in conductivity was observed in earlier measurements on laterally oriented samples.[10]

Figs. 3 and 4 show results for several sodium octanoate/decanol/water samples with different water content and different water layer thicknesses. In Fig. 3, the lamellae were arranged perpendicular to the electric field, whereas Fig. 4 describes the results for isotropic (unoriented) systems.

Average mobility versus water layer thickness

One observation for Aerosol OT/water samples was that a pronounced maximum occurred in the measured conductivity of the thin water layers.[10]

A maximum in the apparent mobility per ion at 100 kHz was also observed in the octanoate/decanol/water samples as indicated in Fig. 5. The figure also illustrates results obtained for different counterions, and in the case of Na^+, for two different decanol/octanoate ratios. It is observed that in all cases, the maximum average mobility occurs at a water layer thickness about 0.2 nm

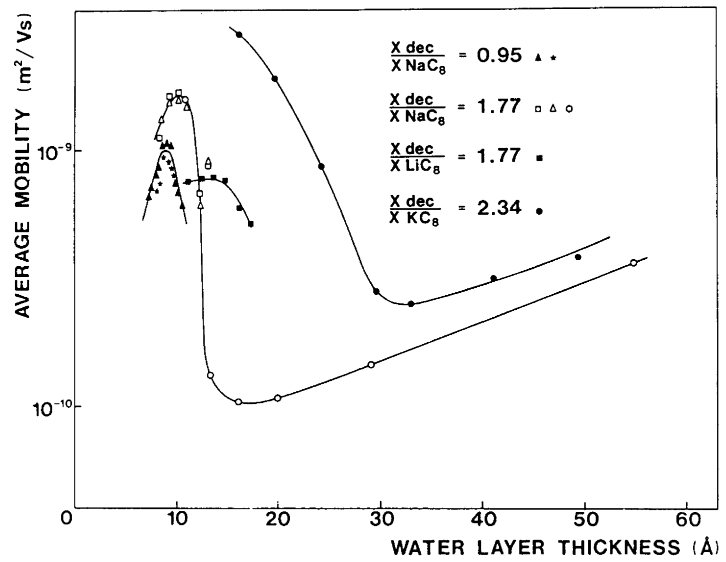


Fig. 5. Average mobility per ion as a function of water layer thickness measured at 100 kHz for samples with different counterions. In the case of sodium as a counterion two different alcohol/surfactant ratios were investigated

larger than the minimal value obtained at the water-poor phase boundary towards the gel phase G. It was not possible to obtain the maximum conductivity of the K^+-octanoate system with the measurement equipment used. The results shown in Fig. 5 were obtained from the conductivity measured at 100 kHz on unoriented samples.

Different sample orientations

The influence of sample orientation is shown in Figs. 3 and 4. The figures indicate that only the magnitudes of the mobility and the apparent dielectric constant, but not their qualitative frequency dependence are affected by mechanical sample orientation. We also made test measurements on laterally oriented samples (Fig. 1c). The average mobility and apparent dielectric constant were largest with this orientation.

The frequency dispersion and water layer thickness dependence of, for example, the average mobility are still the same, however. For the laterally oriented samples, the contact resistance between the electrodes and the sample can be significant. Measurements at several electrode distances were therefore made for each system. However, in order to obtain qualitative information, it is not necessary to measure the laterally oriented samples. As will be shown in the discussion below there are actually very small differences between the mobility measured in an isotopic and a laterally oriented sample.

Discussion

Orientation effects

It is observed from the experimental results that there is no qualitative difference between samples with different orientations. The conductivities (or average mobilities) are, however, smaller in the perpendicularly oriented samples. The fact that no qualitative differences are observed between different orientations may appear strange at first, but a simple argument indicates that we should expect only quantitative differences. For a given water content, we have, of course, the same amount of mobile ions with the same local mobility irrespective of how the sample is oriented.

For thin water layers, we would also expect that the conductivity at 100 kHz would be very small for a perfectly perpendicularly oriented sample due to the hindered motion in the water layers. It is, however, easy to realize that there is a finite conductivity arising due to slightly misaligned lamellae. Assuming that the mobility perpendicular to the water layer is zero and assuming that the lateral mobility is μ_l, we find that in a region where the misalignment of the lamellae from being perfectly perpendicular to the electrical field is θ, the resultant mobility is

$$\bar{\mu} = \mu_l \,\mathrm{sine}^2\,\theta. \tag{2}$$

A misalignment of a few degrees hence creates a detectable resultant mobility. For a completely isotropic sample, one expects an average total mobility

$$\bar{\mu} = \tfrac{2}{3}\,\mu_l \tag{3}$$

from simple statistical arguments.

The conclusion from this simple calculation is that, in order to obtain a marked difference between samples of different orientations, an almost perfect perpendicular sample has to be made. Furthermore, it appears that at least as far as the conductivity is concerned, a lateral oriented and isotropic sample give about the same result. An important result is thus that we can also draw fundamental conclusions from isotropic samples. The unoriented isotropic samples generally had a mobility that was an order of magnitude smaller than that of the lateral samples. This indicates there is still an orientational effect at the electrodes even when the samples are thick, making the probability of the occurrence of perpendicular water layers larger than that of parallel ones. The fact that the measured dielectric constant was largest for the laterally oriented samples is rather natural since a larger part of the sample was shorted by the ionic conductivity the more parallel the water layers were to the electric field.

Average mobility

The average mobilities shown in Fig. 5 have some interesting features. If we compare the Aerosol OT/water and the octanoate/decanol/water system we find an increase in average mobility with increasing water layer thickness (to the right of the maximum) for the latter system. Furthermore, in this region, the ratio between the mobilities for K^+ and Na^+ is almost equal to the ratio of the mobilities of the two ions in bulk water, i.e. μ_{K^+}/μ_{Na^+}.

However, the mobilities observed in the thick water layers are much smaller in all lamellar systems we have studied than the mobilities of respective ions in bulk water. This suggests that only a small fraction of the ions move freely in the water layers of amphiphilic lamellar liquid crystalline systems. For the systems studied in Fig. 5 were see that when the water layer thickness is increased the *average* mobility increases. Furthermore, if the mobility versus water layer thickness (at 100 kHz) is compared for a perpendicularly oriented and an isotropic sample, respectively, we observe that the mobility increases more rapidly for the perpendicular samples than for isotropic samples. This suggests that it is the increase in mobility and/or number of freely moving ions in the water layers and not of ions moving along the interfaces, which is the reason for the increase of mobility for the thick water layers in this case. A similar increase in mobility was not observed for the Aerosol OT/water samples[10] indicating that the charge density and binding of ions to the surfaces are also important parameters. Furthermore, the observed peak in the conductivity is not sharp for the Aerosol OT system. It is interesting to note that the mobility at the maximum in Fig. 5 also depends on the charge density on the lamellae; a larger relative concentration of NaC_8 reduces this maximum mobility. The effects of orientation should be rather small at large water layer thicknesses. If we assume that the ions which are in the water layers, and not bound to the surface, have their normal bulk mobility (an assumption which is substantiated by the ratio of the K^+ and Na^+ mobilities discussed above) then we find at a water layer thickness of 5 nm that only about 1 % of the ions are free to move in the water phase.

Another observation, which might be of interest, is that the maximum mobility is obtained for very thin water layers (for sodium around 0.9 nm in one of the examples). These layers can approach the same dimensions as ionic channels in cell membranes and, therefore, the studied ternary system and other similar ones can be used as models to study the conduction mechanism through channels in cell membranes.

Frequency dispersion

A tentative model for the observed frequency dispersions and especially the qualitative changes with changes in water layer thickness will be discussed below. We observe that the apparent dielectric constants are rather large indicating a large internal polarization. In thick water layers, we assume that the ions are drifting as "normal" ions in bulk water until they reach a water-nonpolar interface where they move along this interface due to the component of the electric field in this direction (Fig. 6a). The equivalent circuit for each lamellae would then be a surface impedance in series with a parallel RC circuit describing the conductivity and dielectric constant in the water layer. Since the system is not homogeneous, there are several such circuits, with different parameter values, parallel and series coupled. Therefore, the experimentally observed frequency dependence will not follow any simple frequency dependence model. The internal po-

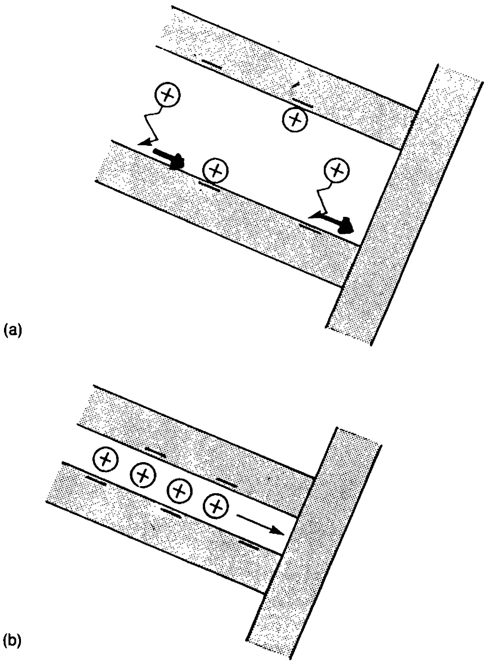


Fig. 6. A model for how ions move in the aqueous region in the lamellar system at large and small water layer thicknesses. See text for further details.

larization is a result of the counterions reaching the polar/nonpolar interface as suggested in Fig. 6a.

The high apparent dielectric constant at low frequencies and its frequency dependence for thin water layers indicate that the ions move in another way in these water layers. This is also substantiated by the maximum of the average mobility in layers with small water layer thicknesses. We suggest that instead of the normal random motion of the ions in the thick water layers, the ions move mainly along the lamellae within thin water layers, probably through a pulsating mechanism (Fig. 6b). The measured conductance and capacitance are determined by the series and parallel coupling of a number of elemental circuits. These consist of a resistor in series with a capacitor. A difference between thin and thick water layers is that the polarization effects in the former occur mainly at "grain boundaries" and in the latter within each lamellae. It should be pointed out that the frequency dependence is not similar to that of a simple electrode polarization neither for thick nor for thin water layers.

The measured dielectric constant is smaller at the highest frequencies in samples with thin water layers. This is simply due to the fact that the system behaves more and more like a dielectric medium (compare the discussion of the conductance above) at higher frequencies and that a system with thin water layers contains less water (with high dielectric constant).

The qualitative change in the frequency dispersion at a critical water layer thickness (observed in all lamellar liquid crystalline systems we have studied so far) can be explained in the following way. In thick water layers where the ions move mainly by diffusion (i.e., normal drift in the electrical field) polarization takes place at the normal lipid-water interfaces (Fig. 6a). In thin water layers, the ions are constrained to move along the lipid surfaces in a concerted movement. Polarization effects take place therefore mainly at defects in the sample (Fig. 6b). A larger part of the sample is "short circuited" by the ions. Hence, larger conductances and capacitances are measured at low frequencies for the thin water layers.

Conclusions

The results presented in this communication have extended the earlier findings on Aerosol OT/water mixtures to other lamellar systems. We have verified the observation that the conductivity of such systems has a maximum at a given water layer thickness. Furthermore, it was demonstrated that the frequency dependence of the conductivity and dielectric constant of the lamellar system changes at the same water layer thickness. We have also found that it is very difficult to obtain a perpendicularly oriented sample "perfect" enough to yield the electrical properties perpendicular to the lamellae. A slight deviation in the direction of the lamellae causes large changes in the measured electrical parameters. A conclusion is therefore that isotropic samples are well suited for studies of the observed phenomena.

We have demonstrated that simple admittance measurements yield interesting information about lyotropic liquid crystalline systems. The study of the electrical properties of these systems is of interest for several reasons. One intriguing fact is that the thin water layers come very close to the ion channels in cell membranes. The fact that a special conducting mechanism exists in the thin water layers could then be directly related to conductance through an ion channel. There are several experiments which can be done to further elucidate the behaviour of ions in these systems. Measurements of the capacitance and conductance as functions of temperature and frequency at a constant water layer thickness will be reported in a forthcoming publication.

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