References and Notes

(1) (a) K. Scheffler and H. B. Stegmann, "Elektronenspinresonanz", Springer-Verlag, Berlin, 1970; (b) L. Kevan and L. D. Kispert, "Electron Spin Double Resonance Spectroscopy", Wiley, New York, N.Y., 1976, and references cited therein.
(2) L. J. Berliner, Ed., "Spin Labeling", Academic Press, New York, N.Y., 1976.
(3) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
(4) K. P. Dinse, K. Möbius, R. Biehl, and M. Plato, *Magn. Reson. Relat. Phenom.*, *Proc. Congr. AMPERE, 17th*, 419 (1973).
(5) K. Hinrichs, B. Kirste, H. Kurreck, and J. Reusch, *Tetrahedron*, **33**, 151 (1977).
(6) (a) W. Broser, B. Kirste, H. Kurreck, J. Reusch, and M. Plato, *Z. Naturforsch., B*, **31**, 974 (1976); (b) W. Gierke, W. Harrer, B. Kirste, H. Kurreck, and J. Reusch, *ibid.*, **31**, 965 (1976); (c) H. van Willigen, M. Plato, K. Möbius, K. P. Dinse, H. Kurreck, and J. Reusch, *Mol. Phys.*, **30**, 1359 (1975).
(7) W. Harrer, H. Kurreck, J. Reusch, and W. Gierke, *Tetrahedron*, **31**, 625 (1975).
(8) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).
(9) R. M. Dupeyre, H. Lemaire, and A. Rassat, *J. Am. Chem. Soc.*, **87**, 3771 (1965); R. Brière, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 3290 (1965).
(10) (a) J. H. Freed, *J. Chem. Phys.*, **43**, 2312 (1965); (b) *J. Phys. Chem.*, **71**, 38 (1967); (c) J. H. Freed, D. S. Leniart, and J. S. Hyde, *J. Chem. Phys.*, **47**, 2762 (1967); (d) J. H. Freed, *ibid.*, **50**, 2271 (1969); (e) J. H. Freed, D. S. Leniart, and H. D. Connor, *ibid.*, **58**, 3089 (1973).
(11) A. G. Redfield, *Adv. Magn. Reson.*, **1**, 1 (1965).
(12) W. Lubitz, K. P. Dinse, K. Möbius, and R. Biehl, *Chem. Phys.*, **8**, 371 (1975).
(13) H. R. Schütte, "Radioaktive Isotope in der Organischen Chemie und Biochemie", Verlag Chemie, Weinheim, 1966; K. Schubert, Diplomarbeit, Freie Universität Berlin, 1976.
(14) R. Biehl, M. Plato, and K. Möbius, *J. Chem. Phys.*, **63**, 3515 (1975).
(15) H. J. Fey, Diplomarbeit, Freie Universität Berlin, 1977; to be published.
(16) R. Biehl, K. Hinrichs, H. Kurreck, W. Lubitz, U. Mennenga, and K. Roth, *J. Am. Chem. Soc.*, **99**, 4278 (1977).
(17) N. M. Atherton, "Electron Spin Resonance", Ellis Horwood, Chichester, 1973.
(18) K. Mukai, T. Kamata, T. Tamaki, and K. Ishizu, *Bull. Chem. Soc. Jpn.*, **49**, 3376 (1976).
(19) N. Hirota in "Radical Ions", E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N.Y., 1968; J. H. Sharp and M. C. R. Symons in "Ions and Ion Pairs in Organic Reactions", M. Szwarc, Ed., Vol. 1, Wiley, New York, N.Y., 1972.
(20) N. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).
(21) B. Kirste, H. Kurreck, K. Möbius, M. Plato, and H. van Willigen, to be published.
(22) This case was realized in a very recent ENDOR study using a ^{13}C labeled phenoxyl type radical, to be published.
(23) W. Lubitz, thesis, Freie Universität Berlin, Germany, 1977.

Ion Binding Studied Using Quadrupole Splittings of [23]Na+ Ions in Lyotropic Liquid Crystals. The Dependence on Surfactant Type

G. Lindblom,* B. Lindman,* and G. J. T. Tiddy*

Contribution from Physical Chemistry 2, Chemical Center, P.O.B. 740, S-220 07 Lund, Sweden, and Unilever Research, Port Sunlight Laboratory, Port Sunlight, Wirral, Merseyside L62 4XN, England. Received August 26, 1977

Abstract: Sodium-23 NMR quadrupole splittings (Δ) are reported for sodium ions in lyotropic liquid crystals prepared from a range of surfactants. The results are consistent with the hypothesis that the splittings are caused by distortion of the sodium ion hydration due to a thin layer of bound water at the lipid/water interface. Nonionic surfactants show no binding of sodium ions at the surface. For the anionic surfactants sodium octyl sulfate and sodium octyl sulfonate, the Δ values are consistent with diffuse layer binding. It is necessary to postulate a specific binding to describe the binding in sodium octanoate systems. The behavior of splittings at high water content in systems anionic surfactant–decanol–water indicates that there is no first-order phase transition between B and D lamellar phases. Instead, the B phase seems to be a continuation of the D phase.

Introduction

The lipid bilayer is an essential component of biological membranes. To understand membrane properties, and in particular the role of counterions, it is necessary to investigate the binding of ions to bilayers. The lamellar phase, which is formed in simple amphiphile–water mixtures, is an excellent model system for this purpose. In addition, sodium NMR is a good technique to investigate interactions between ions and surfactant head groups because of the observation of quadrupole splittings in these systems.[1] To date, studies of these systems have dealt mainly with spectroscopic problems, and have given little detailed information on the nature of the binding between counterions and head groups. In this paper we report the changes in [23]Na quadrupole splittings caused by surfactant concentration and chemical structure. The results enable more information to be obtained on the mechanisms responsible for the splittings, and also give some insight into counterion binding in different systems.

We have investigated the magnitudes of splittings in lamellar phases formed from both charged and uncharged lipids. The phase diagrams of the systems chosen have been mostly studied previously by Ekwall et al.,[2] and in general the liquid crystal structures are well established. However, our results suggest that the "B" lamellar phase reported for several of the systems studied is not a separate phase from the normal D lamellar phase, and should not be represented by a separate area on the phase diagram.

Experimental Section

Most chemicals used were commercially available, and were used without further purification. Sodium di(2-ethylhexyl)sulfosuccinate (Aerosol OT, Fluka) was purified according to Park et al.[3] Samples were usually prepared by mixing a weighed amount of the components in sealed tubes at elevated temperatures. For alkyl sulfates this can cause degradation, and in these cases mixing was achieved by agitation/centrifugation at room temperature. Phase homogeneity was checked by deuterium NMR for samples containing D_2O, and by x-ray diffraction for a number of other samples. NMR measurements were made as described previously,[4,5] using wide line and pulsed NMR spectrometers. Large splittings ($>\sim$15 kHz) were measured on the wide-line spectrometer (15.82 MHz) and small splittings on the pulsed spectrometer (23.81 MHz). The latter was used in conjunction with a Varian C-1024 CAT. Generally, the measurements are accurate
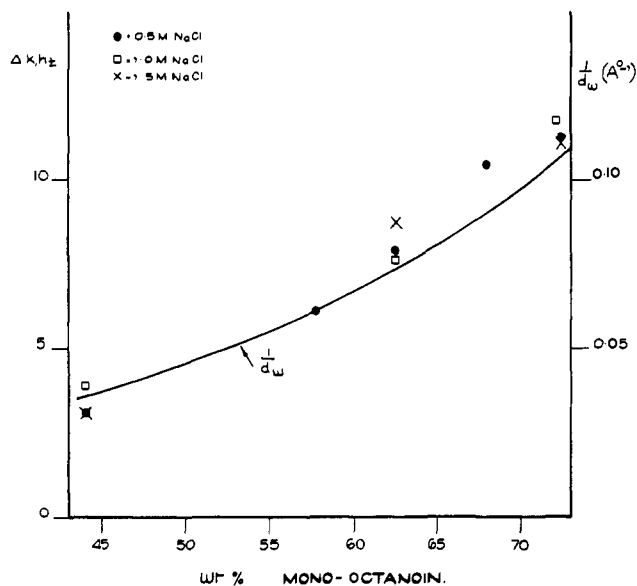
Figure 1. Dependence of Δ on salt and water content of lamellar phase prepared from 1-monooctanoin. The line shows the inverse of the water layer thickness (d_w), based on the results of ref 8.

to 5% or 0.1 kHz, whichever is the greater. For samples with high water contents, where splittings are indistinct, then the error rises to 20%.

Theory and General Considerations

The environment of ions in lyotropic liquid crystals is anisotropic, and in noncubic phases this gives rise to the observation of resonance splittings for quadrupolar nuclei. The anisotropy causes an electric field gradient at the nucleus and some orientations of this field gradient (with respect to the liquid crystalline axis) are favored over others. Theoretical descriptions of NMR resonance splittings due to this orientation have been given in a number of articles[6,7] and only a brief outline is presented here.

The orientation gives rise to the presence of nonaveraged electric field gradients, and nuclei having electric quadrupole moments (spin quantum numbers $I > \frac{1}{2}$) interact with the field gradient at the nucleus, resulting in the splitting of the NMR resonance into $2I$ peaks. The frequency difference between adjacent peaks is termed the quadrupole splitting (Δ), and its magnitude is given by eq 1 for a powder sample.

$$\Delta = \left| \sum_i p_i \nu_{Qi} S_i \right| \tag{1}$$

The values of Δ are a weighted average of the values at the i different sites, due to rapid exchange. S_i, the order parameter describing the field gradient orientation of the fraction of molecules at site $i(p_i)$, is given by $S_i = \frac{1}{2}(3 \cos^2 \theta_{DMi} - 1)$. θ_{DMi} is the angle between the liquid crystal axis (the director) and the electric field gradient at site i. $4\nu_Q$ is equal to the quadrupole coupling constant (for $I = \frac{3}{2}$, like ^{23}Na). For an aligned sample (a sample where the director has a single orientation) the splitting is given by

$$\Delta = \left| (3 \cos^2 \theta_{LD} - 1) \sum_i p_i \nu_{Qi} S_i \right| \tag{2}$$

θ_{LD} is the angle between the magnetic field and the director.

For species with cubic or higher symmetry such as hydrated counterions, the electric field gradient at the nucleus may arise both from the electric field gradients due to the charged amphiphile head groups and the distortions of the hydration sheath.[7] Equations 1 and 2 are generally applicable, and

therefore still valid, since there is no a priori reason to suppose that the electric field gradient lies along the director. However, the interpretation of Δ values is difficult since values of ν_{Qi} are not known. In this paper we compare Δ values for lamellar phase samples containing charged lipids, zwitterionic lipids, and nonionic lipids in an attempt to investigate the different contributions.

The usual model for the binding of counterions to a charged surface is one involving a Gouy-Chapman "diffuse" double layer plus a Stern layer of specifically adsorbed ions. These two types could be regarded as two different "sites" in eq 1. Ions in the diffuse layer are not associated with any one specific surfactant group, and would be expected to have the electric field gradient along the director. Ions in the Stern layer could be located between head groups, adjacent to a particular charged anion. These ions could experience electric field gradients at an angle to the director. The presence of both types of ions could give rise to complex composition/temperature dependences of the splitting.

Results and Discussion

1. Nonionic and Zwitterionic Lipids. The ^{23}Na splittings for various concentrations of sodium chloride in the lamellar phase of the 1-monooctanoin-water system are shown in Figure 1. Similar values were measured on addition of sodium bromide and sodium iodide. The splittings increase sharply with decreasing water content, and are practically independent of salt concentration or temperature, decreasing slightly at higher temperatures. It is unlikely that the splittings are due to specific binding to the surface since they do not depend on sodium ion concentration. A more reasonable hypothesis is based on the idea that splittings are due to distortion of the ion hydration sheath. Water between the lipid layers consists of two types, free water with no net orientation, and a layer of oriented water one or two molecules thick at the lipid/water surface. This oriented water can be expected to induce distortions of the sodium hydration sheath for sodium ions entering the layer. Assuming a uniform distribution of ions, the observed splittings will be proportional to the fractional thickness (t) of the two bound layers of water compared to the total water thickness (d_w) as given in the equation

$$\Delta_{obsd} = \frac{t}{d_w} \Delta_0 \tag{3}$$

Δ_0 = quadrupole splitting in bound water layer. This equation predicts that the observed splitting is dependent on the inverse water layer thickness, and the agreement with experiment, illustrated in Figure 1, is quite good. (The thickness of the water layer was found to be independent of the salt content[8].)

An estimate of Δ_0 can also be made using eq 3 by plotting Δ_{obsd} against $1/d_w$. This was made for the 1-monooctanoin-water-NaCl system. A straight line was obtained with the slope $t\Delta_0 = 100$ Å kHz. If it is assumed that the thickness of the interface water layer is equal to about 2 Å, then $t = 4$ Å and $\Delta_0 = 25$ kHz. This value of Δ_0 is in very good agreement with that calculated in ref 7 for a displacement by 0.1 Å of one of the water molecules in the first hydration layer of the sodium ion.

The above results indicate that a major contribution to the splittings arises from distortion of the ion hydration sheath, and show that the presence of charged surfactants is not necessary to produce splittings. We have also observed splittings in lamellar phases prepared from octylamine-water and n-alkyl polyoxyethylene ether-water systems. In the latter case the magnitudes of the splittings were not measured because the resonances were too broad. These results confirm that the presence of charged surfactants is not required for the observation of ^{23}Na quadrupole splittings.
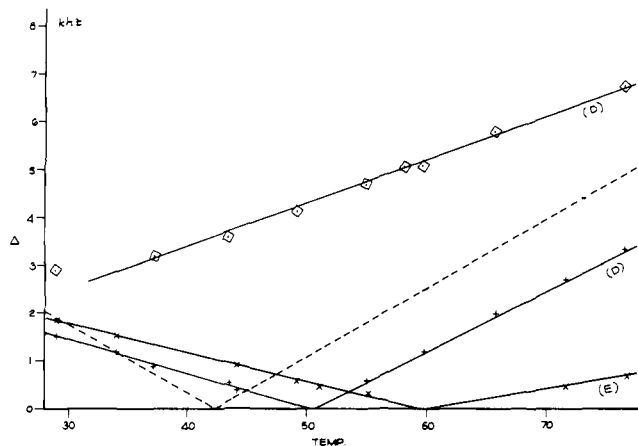
Figure 2. Dependence of Δ on composition for sodium octyl sulfate-decanol-water system. (Phase diagram after Ekwall et al.[2])

Figure 3. Dependence of Δ on composition for sodium octyl sulfonate-decanol-water system. (Phase diagram after Ekwall et al.[2])

For zwitterionic surfactants, measurements on lecithin–salt solution systems have been published elsewhere,[9] and are described here only briefly. The splittings have a complex dependence on chain length, temperature, and concentration of added cholesterol. However, they lie in the range 2–12 kHz, similar to the magnitudes of splittings in uncharged bilayers. The lecithin–water interface is complex because of the penetration of water between choline groups. Thus there is not a simple layer of bound water perpendicular to the liquid crystal axis and this could result in the complex patterns of splittings observed. However, there is no evidence to indicate that the presence of the charges gives any enhanced basic splitting.

2. Charged Surfactants. Sulfate and Sulfonate Head Groups. Sodium octyl sulfate and sulfonate both from lamellar phases when mixed with decanol in the presence of water. The measured Δ values for these systems are shown in Figures 2 and 3. The values are similar in both systems, being remarkably insensitive to the fraction of added decanol or to water content, unlike the results for the monooctanoin lamellar phase. The splittings are also insensitive to temperature changes. Some difficulty was experienced in measuring Δ values at high water contents (e.g., in the B phase, Figure 2), because the "beats" occurring on the ^{23}Na free induction decay (pulsed NMR) became indistinct as water content increased. Indeed, it was not possible to measure Δ values at high water contents in the sodium octyl sulfonate system. This has implications for the structure of "B" phase and is discussed below.

Since the values of Δ are insensitive to the various parameters, the splittings may be explained by either a distortion of the ion hydration layer because of the bound water layer or by head group-counterion specific complex formation. The latter is considered unlikely because of the large binding energy required. The total water thickness lies in the range 8–100 Å, but the bound water layer is probably ~2–3 Å thick, and is independent of d_w. If it is assumed that ions more than 2–3 Å from the surface have zero splittings, then the reduction in counterion concentration at the surface is less than 30% at high water content. The decrease may be less than this, since the whole bilayer becomes less ordered at high water content and this would also reduce Δ. Unfortunately, there are no double layer calculations of ion concentrations at the surface in these *closed* systems for comparison with the present conclusions. The lack of variation in the ion distribution should be contrasted to that of the monooctanoin systems where the distribution was dependent on total water content.

3. Charged Surfactants. Carboxylate Head Group. Sodium octanoate forms a lamellar phase with decanol in the presence of water, and some Δ values for this phase have been published previously.[4,5,10,11] New results are shown in Figure 4. The

Figure 4. Dependence of Δ on composition for sodium octanoate-decanol-water system. $\otimes$, samples where Δ is almost invariant with increasing temperature, or increases with increasing temperature; X, samples where Δ decreases strongly, passes through zero, and then increases with increasing temperature. Dotted line indicates uncertainty in boundary position.

phase diagram differs from that given by Ekwall et al.[2] because the "C" phase, at first thought to be a "tetragonal" phase, appears[5,12,13] to be an emulsion of D + L$_1$, and has been eliminated from the diagram. The values are generally similar to those of the sulfate and sulfonate systems at water contents greater than ~60%, although the splittings are reduced by ~30%. These splittings are almost insensitive to temperature and become more indistinct as water concencentration increases. No splittings could be measured for the higher water content B phase samples (see below). For samples with water contents less than ~60% the splittings were temperature dependent, as illustrated in Figure 5. Those of samples containing ~38–60% water increased with temperature; those with $\lesssim$38% water decreased to zero, and then increased with increasing temperature.

The effect of decanol content appears to be small. The strong temperature dependence of Δ values is not due to decanol-octanoate interactions since similar effects are observed in the lamellar phase of the sodium octanoate–octanoic acid system (Figure 6) and in pentanol–sodium octanoate.[14] The temperature dependence also occurs in the octanoate–water system

Figure 5. Illustration of different dependences of Δ on temperature observed at different parts of the phase diagram. (Dotted curve is theoretically calculated; see text.)

Figure 6. Dependence of Δ on composition for the sodium octanoate–octanoic acid–water system.

alone. The samples shown in Figure 6 all have Δ values that initially decrease with increasing temperature, pass through zero, and then increase.

In previous publications[5,14] we used a model based on the variation of Θ_{DM} (eq for S_i) with composition to explain the results. At low water contents, it was proposed that sodium ions were held between head groups, and that S was negative. Increasing the temperature or the addition of water caused S to become more positive. The zero splitting observed for some samples corresponds to an average Θ_{DM} of $54°$ $44'$, the magic angle. Splittings that decrease strongly with temperature correspond to negative S values, while those that increase with temperature have positive S values. We now propose to detail the model further. We assume that there are two groups of bound counterions, one a diffuse layer and the second a more specific site perhaps corresponding to a Stern layer. The diffuse layer is assumed to have a positive order parameter. The second group consists of specifically adsorbed counterions that have negative order parameters. Both of these order parameters are approximately temperature invariant. We assume a free-energy difference ΔG between the two groups; thus the ratio of ions in the "specific" group (P_{sp}) and diffuse layer (P_{dif}) is given by

$$P_{sp}/P_{dif} = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left[-\frac{(\Delta H - T\Delta S)}{RT}\right]$$

For the negative order parameters observed at low water content $P_{sp} > P_{dif}$ while at high temperatures or high water concentrations $P_{dif} \gg P_{sp}$. Without Δ values for the two states it is difficult to test the model. However, assuming values of $P_{sp} = 0.9$ at 0 °C and $P_{sp} = 0.1$ at 150 °C, with $\Delta_{sp} = -7$ kHz and $\Delta_{dif} = +12$ kHz, the dotted curve in Figure 5 was calculated. The curve does reproduce the minimum in Δ, and the dependence of Δ on temperature is approximately correct. However, experimental curves appear to have different slopes before and after zero, and this is not reproduced. It seems pointless at this stage to attempt further curve-fitting procedures, because of the many unknown variables. For samples with >60% water, where little or no specific binding is observed, the Δ values are somewhat smaller than those of the sulfate and sulfonate lamellar phases. In the sodium octanoate–pentanol system,[14] the temperature invariant splittings are much smaller, being ~1–4 kHz. The suggestion given earlier,[14] that this is due to counterion dissociation from the surface, is only one possibility in view of the fact that similar results are not observed in the present study. An alternative explanation is possible in terms of the overall order of the system. The duration of the proton free induction decay of the
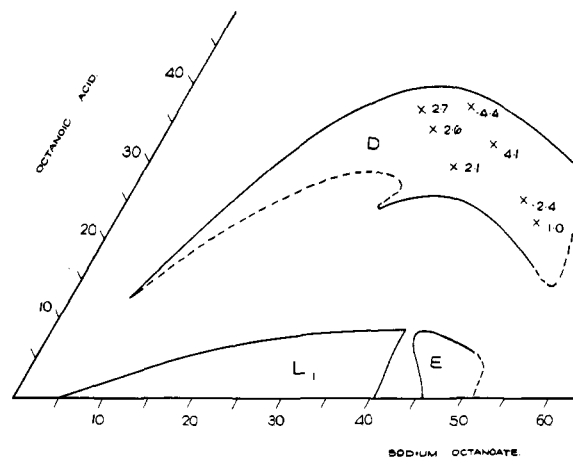
octanoate–decanol lamellar phase increases by a factor of 2 at high water contents,[12] indicating a drop in the alkyl chain order parameter by 50%. It is not immediately obvious how this reduction would alter the sodium ion S values, but certainly they would be expected to fall, in agreement with the observed results. The very low Δ values for the pentanol system may be a consequence of an extra low alkyl chain order for this system, because of the very short alkyl chains.

4. Hexagonal (E) Phase. Only a few results have been obtained for the E phase, but they are generally similar to those of the lamellar phase. The Δ values of sulfate samples are almost temperature invariant, while those of octanoate samples show the temperature dependence given in Figure 5. Other things being equal, theory predicts that Δ values in the E phase will differ by a factor of $-\frac{1}{2}$ from those in the D phase. (Of course, the sign of Δ is not normally obtained in an experiment.) This means that the temperature dependence of the type shown in Figure 5 for the E phase sample implies a positive order parameter with respect to the director lying along the rod axis,[17] whereas a negative order parameter is deduced for the same behavior in the D phase. The observed values are consistent with this prediction.

5. Structure of B Phase. In all the systems studied here it was difficult or impossible to measure Δ values at the highest water contents because the "beat" pattern observed on the ^{23}Na free induction decay became difficult to observe. However, intensity measurements showed that the observed signal corresponded only to 40% of the intensity predicted for an isotropic solution having the same number of sodium ions present. The most likely explanation of these facts is that rapid sodium ion exchange occurs between crystallites having different orientations in the powder sample. Kléman et al. have reported that the number of defects increases with added water in lecithin lamellar phase.[15] If the same occurs for the present systems, then the crystallite size will decrease with increasing water content. Exchange of sodium ions between regions with different macroscopic orientations would result in the coalescence of the outer lines of the sodium resonance. At an intermediate rate of transfer of sodium ions, i.e., when the lifetime in a region with a particular orientation is longer than the inverse Larmor frequency but shorter than the inverse splitting, the lines of the $m = \frac{3}{2} \to \frac{1}{2}$ and $m = -\frac{1}{2} \to -\frac{3}{2}$ transitions would become too broad for Δ to be measured, but would not contribute significantly to the central observed resonance. To average the splitting, exchange must occur on a time scale of $1/2\pi\Delta$, i.e., of ~10^{-4} s. This gives the size of the microcrystallites as ~0.5 μm if we assume that the sodium ion self-diffusion coefficient is 5×10^{-10} m^2/s. It is well known that "B" phase samples are "cloudy", i.e., scatter light, in agreement with the presence of

particles of this size. Also, it is impossible to align "B" phase samples using microscope cover slips, as for D phase samples. This also indicates the presence of many defects in the samples (i.e., small crystallite size). Where it was possible to measure Δ values for the B phase, the values are similar to those in the D phase and do not reflect the presence of a first-order phase change. Since similar NMR behavior was observed for systems containing "B" phase (sodium octanoate, sodium octyl sulfate) and the one without a B phase (sodium octyl sulfonate) it seems likely that "B" phase is simply a continuation of D phase at high water content, and that no first-order B/D phase change exists. In the original paper,[16] Ekwall et al. concluded that the x-ray evidence for the coexistence of B + D phases was not unequivocal. The boundaries shown in Figure 4 were obtained by analysis of separated samples after prolonged centrifugation. It is possible that the gravity gradient along the centrifuge tubes caused the separation observed. Certainly it is hard to find a physical reason why lamellar phase samples with ∼64 Å water layer should separate from samples with ∼72 Å water layers as was observed. There appears to be a case for the reexamination of low-angle x-ray scattering on samples in the B + D two-phase region.

References and Notes

(1) Å. Johansson and B. Lindman in "Liquid Crystals and Plastic Crystals", Vol. 2, G. W. Gray and P. A. Winsor, Ed., Ellis Horwood, Chichester, England, 1974, p 192; G. Lindblom, *Acta Chem. Scand.*, **25**, 2767 (1971); M. Shporer and M. M. Civan, *Biophys. J.*, **12**, 114 (1972); D. M. Chen and L. W. Reeves, *J. Am. Chem. Soc.*, **94**, 4384 (1972); H. J. C. Berendsen and H. T. Edzes, *Ann. N.Y. Acad. Sci.*, **204**, 459 (1973); D. M. Chen, K. Radley, and L. W. Reeves, *J. Am. Chem. Soc.*, **96**, 5251 (1974); K. Radley, L. W. Reeves, and A. S. Tracey, *J. Phys. Chem.*, **80**, 174 (1976).
(2) P. Ekwall, L. Mandell, and K. Fontell in "Liquid Crystals 2", Vol. II, G. H. Brown, Ed., Gordon and Breach, London, 1969, p 325; P. Ekwall in "Advances in Liquid Crystals", Vol. 1, G. H. Brown, Ed., Academic Press, New York, N.Y., 1975, p 1.
(3) D. Park, I. Rogers, R. W. Toft, and P. A. Winsor, *J. Colloid Interface Sci.*, **32**, 81 (1970).
(4) G. Lindblom and B. Lindman, *Mol. Cryst. Liq. Cryst.*, **22**, 45 (1973).
(5) G. Lindblom, B. Lindman, and G. J. T. Tiddy, *Acta Chem. Scand.*, Ser. A, **29**, 876 (1975).
(6) A. D. Buckingham and K. A. McLauchlan, *Prog. Nucl. Magn. Reson. Spectrosc.*, **2**, 63 (1967).
(7) H. Wennerström, G. Lindblom, and B. Lindman, *Chem. Scr.*, **6**, 97 (1974).
(8) Estimates based on results in W. E. Peel, Ph.D. Thesis, Sheffield Polytechnic, 1972; P. Ekwall, L. Mandell, and K. Fontell, *Acta Chem. Scand.*, **22**, 1543 (1968); M. Persson, K. Fontell, and G. Lindblom, unpublished.
(9) N.-O. Persson, G. Lindblom, B. Lindman, and G. Arvidson, *Chem. Phys. Lipids*, **12**, 261 (1974); G. Lindblom, N.-O. Persson, B. Lindman, and G. Arvidson, *Ber. Bunsenges. Phys. Chem.*, **78**, 955 (1974); G. Lindblom, N.-O. Persson, and G. Arvidson, *Adv. Chem. Ser.*, **No. 152**, 121 (1976).
(10) H. Gustavsson, G. Lindblom, B. Lindman, N.-O. Persson, and H. Wennerström in "Liquid Crystals and Ordered Fluids", Part 2, J. F. Johnson and R. S. Porter, Ed., Plenum Press, New York, N.Y., 1974, p 161.
(11) G. Lindblom, N.-O. Persson, and B. Lindman in "Chemie Physikalische Chemie und Anwendungstechnik der Grenzflächenaktiven Stoffe", Vol. II, Carl Hanser Verlag, München, 1973, p 925.
(12) G. J. T. Tiddy, *J. Chem. Soc., Faraday Trans. 1*, **68**, 379 (1972).
(13) N.-O. Persson, K. Fontell, B. Lindman, and G. J. T. Tiddy, *J. Colloid Interface Sci.*, **53**, 461 (1975); A. Forge, J. Lydon, and G. J. T. Tiddy, *ibid.*, **59**, 186 (1977).
(14) J. B. Rosenholm and B. Lindman, *J. Colloid Interface Sci.*, **57**, 362 (1976).
(15) M. Kléman, C. Colliex, and M. Veyssie, *Adv. Chem. Ser.*, **No. 152**, 71 (1976).
(16) L. Mandell and P. Ekwall, *Acta Polytech. Scand.*, 1 74 (1968).
(17) In ref 14 the sign of the order parameter is referenced to the normal to the lipid–water surface.

Ultraviolet Photoelectron Studies of Biological Pyrimidines. The Valence Electronic Structure of Cytosine

C. Yu, S. Peng, I. Akiyama, J. Lin, and P. R. LeBreton*

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. Received September 15, 1977

Abstract: UV photoelectron spectroscopy and CNDO/S molecular orbital calculations have been employed to investigate the electronic structure of cytosine (I), 1-methylcytosine (II), *N*,1-dimethylcytosine (III), *N,N*,1-trimethylcytosine (IV), 3-methylcytosine (V), 1,5-dimethylcytosine (VI), 1,6-dimethylcytosine (VII), 5-methylcytosine (VIII), and 6-methylcytosine (IX). The resolution of the spectra obtained for different members of this series of molecules varies markedly. Of all the molecules investigated the photoelectron bands arising from the five uppermost orbitals are well resolved only for *N*,1-dimethylcytosine. The variation in the resolution arises partially from the overlapping of bands. Furthermore, spectra obtained for molecules in which labile H atoms are replaced by methyl groups exhibit much better resolution than spectra for other molecules. This observation is probably related to hydrogen bonding effects. For cytosine the spacing of bands occurring in the spectrum is accurately reproduced in the results of CNDO/S calculations carried out on the 1(H) aminooxo tautomeric form of the molecule. In compounds II–IV and VI–IX the spacing of bands and the shifts observed in the spectra are also well predicted by calculations carried out on the aminooxo tautomers. However, for 3-methylcytosine the results indicate that an imino tautomeric form is most stable. For all compounds the CNDO/S calculations indicate that three of the five uppermost orbitals are π orbitals and that two are lone-pair orbitals. In cytosine the first and fifth bands arise from π orbitals while the fourth band arises from a lone-pair orbital. The second and third bands arise from a π and a lone-pair orbital which are strongly overlapping and their ordering remains uncertain.

Introduction

The valence molecular orbital structure of biological purines and pyrimidines plays an important role in determining the biochemical properties of these molecules.[1] Energies and electron distributions associated with the valence orbitals of these molecules influence the manner in which purines and pyrimidines participate in weak bonding interactions as well as in chemical reactions.[2-4]

The valence structure of biological purines and pyrimidines

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