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Deuterium Magnetic Resonance Study of α,ω-Dicarboxylic Acid Guests in Disk Micelles of Varied Bilayer Thickness

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Type II DM lyotropic liquid crystals are composed of large disk-shaped micelles of bilayer thickness[1,2] which are orientationally correlated with one another in an aqueous matrix. The bilayer thickness depends on the amphiphile selected to prepare the mesophase. Several important questions remain with respect to the bilayer chemistry of these micelles. An independent measure of the bilayer thickness should be possible, using deuterium magnetic resonance of the deuteriated CD$_2$ segments of a guest α,ω polar or ionic substituted amphiphile, by noting the characteristics expected for the degree of order profile when the α,ω amphiphile exactly spans the bilayer. Counting the segments stretched across the bilayer then gives an estimate of the bilayer thickness. The thickness of the disk micelles has been estimated by low-angle X-ray diffraction methods in the case of decyl sulfate/decanol micelles.[1] The thickness obtained, 38 Å, evidently must include the hydration and counterion layer on the micelle, because this is too long for a 10-carbon-chain bilayer.[3] In finite micelles there is a mechanism of exchange between amphiphiles that span the bilayer and those that turn back on themselves to expose their ionic groups to the same side of the micelle by simply diffusing to the edge of the disk and reentering the body of the micelle in an exchanged configuration. Seelig and co-workers[4,5] used spin labels for similar experiments on lamellar phases some years ago, but in lamellar phases the only mechanism of exchange between the "U" form and the stretched form of the α,ω amphiphiles requires passage of the ionic head group through the bilayer. The micelles of type II DM mesophases are of large diameter (~1000 Å).[6] The exchange rate between the U-shaped chains and spanning chains must be less than ~10^4 s^{-1} in order to resolve them separately in the deuterium NMR spectrum. The large size of the individual micelles greatly reduces the velocity of this new mechanism of diffusion to the edge, with exchange. This communication reports successful experiments with α,ω-dicarboxylic acids. The long-chain dicarboxylic acids were prepared by the method of Hünig et al.[7] and perdeuteriated essentially as described in the literature.[8] ^{2}H NMR spectra were registered at 25 °C on a Bruker WM 250 spectrometer.

Figure 1 shows an example of the three possible situations. The diacid may span the bilayer more or less exactly as in Figure 1A, have an equilibrium between the U form and the stretched form as in Figure 1B, or be entirely in the U form as in Figure 1C. In the stretched form the degree of order profile will be more or less

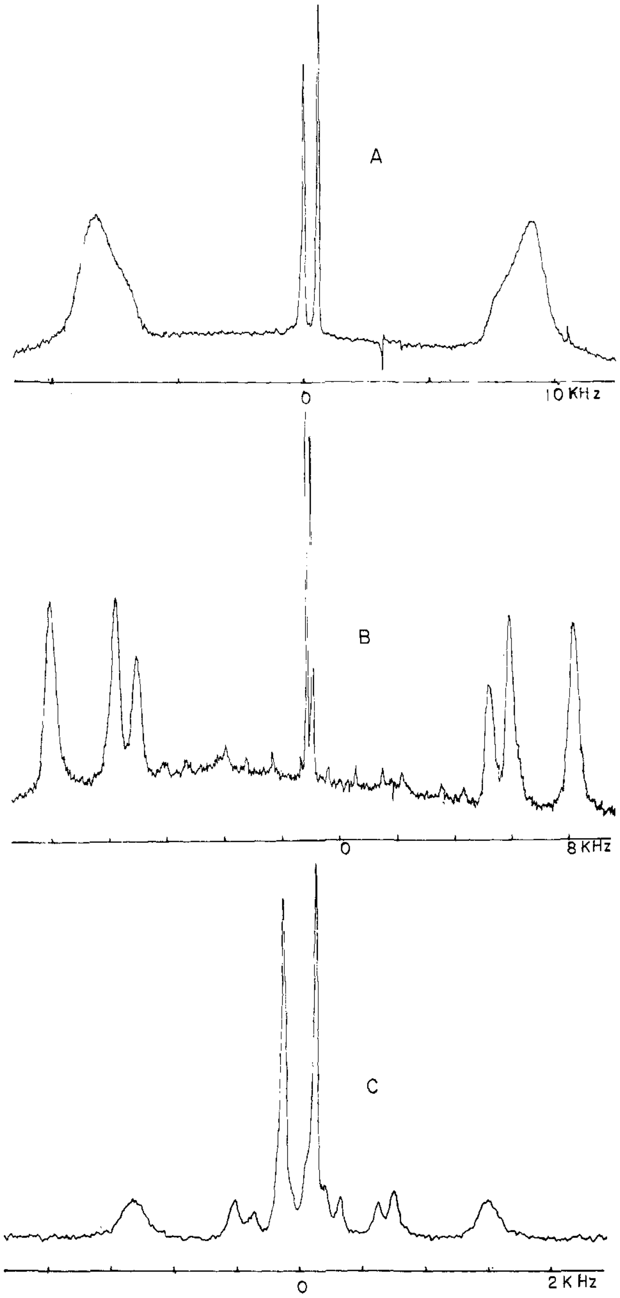

Figure 1. ^{2}H NMR spectra of mesophase type II DM. (A) Weight percent composition: 35.31:7.40:6.61:50.17:0.51 potassium decanoate–KCl–1-decanol–H$_2$O (0.1% D$_2$O, pH 7)–C$_{22}$ α,ω-dicarboxylic acid (perdeuteriated ~50%). The 0.1% DOH doublet is at the center of the deuterium magnetic resonance spectrum. The deuterium magnetic resonance quadrupole doublet of all segments in the chain is almost coincident with splitting 17.36 kHz. The dicarboxylate therefore spans a bilayer with a distance from head group to head group of ~1.54 cos 35.2 × 21 = 26.4 Å. C$_{18}$ perdeuteriated α,ω-dicarboxylic acid in a similar system (not shown) adopts a U shape only since its extended length is not great enough to span the bilayer. (B) Weight percent composition: 38.67:2.80:57.88:0.64 decylammonium chloride–NH$_4$Cl–H$_2$O (pH ~2)–C$_{18}$ α,ω-dicarboxylic acid (perdeuteriated). The 0.1% DOH doublet is at the center of the spectrum. The intense doublets with the largest splittings (17.6, 13.20, and 11.76 kHz) are assigned to a spanning configuration which contains some kinks and jogs, indicating that it is too long and does not therefore take up the all-trans form A small quantity of U-shaped chains is present and six doublets of equal intensity are resolved. It is presumed that the other two lie under the outer intense peaks. The individual assignments await specific deuteriation of the diacid. The six inner doublets have quadrupole splittings 0.96, 2.80, 4.64, 6.00, 8.64, and 10.16 kHz. The bilayer thickness as in A must be less than 21.4 Å, excluding head groups and adsorbed species. (C) Weight percent composition: 32.42:6.33:6.09:54.97:0.18 sodium lauroylsarcosinate–Na$_2$SO$_4$–1-decanol–H$_2$O (pH ~12)–C$_{18}$ dicarboxylate (perdeuteriated). The chain of C-18 exists only in the U-shaped form and the peaks have quadrupole splittings 0.252, 0.482, 0.963, 1.259, and 2.759 kHz.

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constant along the chain, since freedom of trans/gauche motions, which shorten the chain, is minimal. The overall degree of order will then be determined by other motions, such as those of the micelle as a body, which are equal in their effect on all stretched segments. In the U form there may be constraint angle effects, making individual assignments uncertain,[9] but there will be a falloff in degree of order toward the base of the U-shaped hydrocarbon chain. In our previous formulation[10]

$$S_{\text{exptl}(i)} = S_{\text{MO}(i)} \cdot S_{\text{CO}(i)} S_{k/j(i)} S_{\text{diff}(i)} \tfrac{1}{2}(3\cos^2\Omega - 1) \qquad (1)$$

where, for a given segment i along the chain, S_{exptl} is the experimentally determined degree of order of the C–D bond vector and S_{MO}, S_{CO}, $S_{k/j}$, and S_{diff} are the contributions to the degree of order which arise from micelle oscillation, oscillation of the long axis of a chain which carves out a cone, kink/jog-type segmental motions, and diffusion of amphiphiles around the edges of the large micelles, respectively.[10] Ω is the angle between the director and the applied magnetic field. For type II DM mesophases, $\Omega = 90°$, $S_{k/j(i)} \simeq 1$ for a stretched chain, $S_{\text{CO}(i)} \sim 1$ for the noncooperative motions of the stretched chain about the micelle normal, and, as usual, we assume for large micelles $S_{\text{diff}(i)} \sim 1$. Thus, for the degree of order of segments in a chain spanning the bilayer exactly, in the all-trans form

$$S_{\text{exptl}(i)} = -\tfrac{1}{2} S_{\text{MO}(i)} \qquad (2)$$

This interesting simplification of the general expression for the degree of order of the C–D bonds gives us direct access to the contribution due to micelle motion. In this formalism, however, we have not considered cooperative wavelike undulations of the bilayers. Since the effects of this type of rigid body motion have been shown to be appreciable,[6] further experiments are required with disk-micelle phases in thermodynamic equilibrium with the parent phase[6,10] in order to compare the reduction of degree of order because of the wave motions in the infinite bilayers of lamellar phases with micelle motions.[6,10]

In addition, since increasing numbers of gauche rotations of hydrocarbon chains decrease the effective bilayer thickness,[3] it is interesting to note that a 22-carbon chain fits almost exactly across of bilayer of potassium decanoate, while an 18-carbon chain may span a bilayer of decylammonium chains. Even when the different size of the head groups is taken into account, it is obvious that kink/jog motions of the two amphiphiles are quite different. By taking ratios of the quadrupole splittings of any position i along the chain relative to that of the terminal methyl group, the contributions of rigid body motions in eq 1 may be eliminated.[2] This method of ratios was used to predict that bilayers of potassium decanoate are more extended than those of decylammonium chains,[6,10–12] a fact that has been proven directly by the NMR results presented here. This technique is being extended to many different bilayer systems, using a large variety of dicarboxylic acids enabling the study of the effects of such variables as temperature, chemical composition, water content, and the nature of the head group and counterions upon bilayer thickness.

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Book Reviews

Radiation Chemistry of Carbohydrates. By N. K. Kochetkov, L. I. Kudrjashov, and M. A. Chlenov (USSR Academy of Sciences, Moscow). Translation Editor, G. O. Phillips (North E. Wales Institute of Higher Education). Pergamon Press, Oxford. 1979. xiii + 247 pp. $43.00.

As the authors point out in their prefatory section, this book provides a mechanistic viewpoint on the chemical nature of major degradation pathways associated with the action of ionizing radiation on carbohydrates in solution. There follows a brief chapter on the radiation chemistry of water and aqueous solutions that lists reactive products encountered as intermediates during decomposition of the aqueous phase. The remaining chapters, three in all, cover methodology, radiolysis of various classes of carbohydrates, and the radiation-induced transformations produced by γ irradiation.

The book covers a period of research between 1961 and 1977, relying upon an earlier review (G. O. Phillips, *Adv. Carbohydr. Chem.*, **16**, 13–58 (1961)) for studies prior to 1961. G. O. Phillips has appended a list of 98 additional references spanning the period 1975–1978, each reference accompanied by a brief sentence in which the document under consideration is summarized. The appendix also includes several schemes in which reactions of radicals derived from irradiated aqueous solutions of erythritol, *scyllo*-inositol, D-glucose, D-ribose-5-phosphate, 2-amino-2-deoxy-D-glucose, cellobiose, thymidine, and DNA are summarized. These schemes are from a review on free-radical reaction of carbohydrates by C. von Sonntag that has now appeared in print (*Adv. Carbohydr. Chem. Biochem.*, **37**, 7–77 (1980)). In an independent review of this book, J. C. Arthur, Jr. (*Carbohydr. Res.*, **84**, C17–C18 (1980)) has gathered together several editorial comments that will be useful to anyone who consults this work.

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Fundamentals of Enzyme Kinetics. By Athel Cornish-Bowden (University of Birmingham, U.K.). Butterworths, Boston. 1979. x + 230 pp. $19.95

This text, an outgrowth of the author's "Principles of Enzyme Kinetics (1976)", is designed to provide the serious student of enzymology with a background of principle and experimental strategy at a level not commonly found in the current general biochemistry texts.

The ten chapters are arranged to include an introduction to basic principles of chemical kinetics (1) and enzyme kinetics (2), followed by some practical aspects dealing with purification and measurement (3). The student is introduced to the derivation of steady-state rate equations (4), inhibitors and activators (5), and two-substrate reactant systems (6), then led into a discussion of the effects of pH and temperature on enzymes (7). The last third of the book is given over to a consideration of the phenomenon of cooperativity (8), fast reactions and the limitations of steady-state measurements (9), and comments on the estimation of kinetic constants and statistical methods of data analysis (10). Six pages of selected references are provided at the end of the text. Problems (and solutions) are given.

The author and the work are of the school of enzyme kinetics we have come to associate with Boyer/Alberty/Dalziel/Cleland and their many co-workers. The text invites comparison with the author's earlier work and others of this genre that have appeared within the past few years.

My impressions? I recommend it. The writing is clear, and the rigor is evident but it does not intrude on the smooth flow of ideas. The text is attractively packaged and priced (by today's standards) and fills the gap cited above. It provides in a single source excellent ingress to the more substantive literature of enzyme kinetics.

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