THE INTERACTION OF D AND L-ALANINE WITH AN OPTICALLY ACTIVE MODEL MEMBRANE SYSTEM

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1. Introduction

The study of lyotropic liquid crystalline bilayer phases by nuclear magnetic resonance has been receiving ever increasing attention because these systems have many of the properties of naturally occurring membranes. One facet of these materials which has received no attention is the effect that a centre of optical activity within the bilayer might have on the ordering of other optically active materials with which it comes into contact.

In an effort to gain some information concerning such interactions we have prepared an optically resolved sodium decyl-2-sulfate which was used, together with the amino acids D and L-alanine, for the preparation of nematic lyotropic phases.

2. Materials and methods

Sodium decyl-2-sulfate (d,l) was prepared from decane-2-ol by reacting the decanol with concentrated sulfuric acid (1:3 mole ratio) at −10°C for 24 h. The solution was neutralized with sodium hydroxide, all the while maintaining it at 0°C. The sodium decyl-2-sulfate was obtained from ethanol and the sodium exchanged for the (−)2-phenylethylammonium ion. One component of the racemic mixture crystalized readily from light petroleum ether. Final recrystalization provided long, very fine needles with m.p. 83.5–84°C. The (−)2-phenylethylammonium was then exchanged for sodium to provide the optically resolved sodium decyl-2-sulfate ($[\alpha]_D^{20} = -4.4$ (c = 4, H_2O)) used in this study. A typical phase composition used is given below.

Sodium *n*-decylsulfate, 20.8 wt%. Sodium decyl-2-sulfate, 11.9. Sodium sulfate, 4.5. *n*-Decanol, 5.8. D-alanine, 2.1. D_2O, 54.9.

The straight chain decylsulfate component was used in conjunction with the other since, with the pure decyl-2-sulfate, problems were encountered with phase formation and with crystallization. The nematic phase instead of a smetic phase was prepared since it orders spontaneously in a magnetic field and sharp n.m.r. transitions are provided.

Results and discussion

In fig.1(A) shows the partial proton spectrum of D-alanine in the phase whose composition is given above. Only the methyl group resonance is shown. The overall triplet pattern results from the dipolar coupling within the methyl group, the doubleting from the dipolar and scalar couplings between the methyl group and the adjacent proton. The spectrum shown in fig.1 (B) was obtained by preparing a phase containing both D and L-alanine, but in different proportions. Of major interest are the eight outer transitions. The most intense peak of each pair is from the L-alanine in the phase, the less intense peak is from the D-alanine. No splitting is observed in the central pair since the chemical shift between the D and L methyls is extremely small. Any difference in dipolar couplings to the adjacent proton must also be small and hidden in the line-width. In order to insure that this spectrum was not an artifact resulting, perhaps, from the coexistence of more than one nematic material, a further phase with opposite proportion of D and L-alanine was prepared. The expected spectrum was obtained.

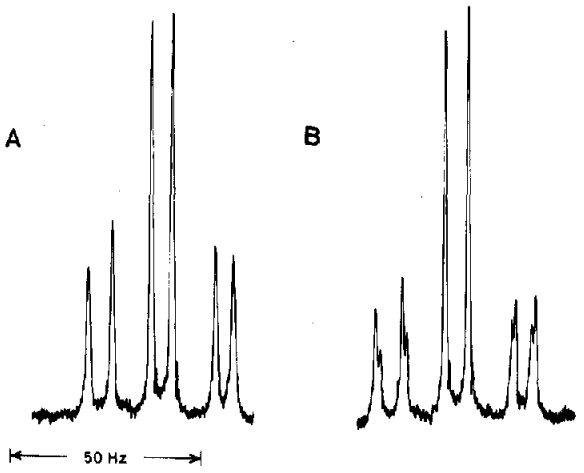

Fig. 1. (A) The methyl resonance from D-alanine (2.1 wt%) in the phase described in the text. (B) The methyl resonance from a similar phase but containing L-alanine (1.3 wt%) and D-alanine (0.8 wt%). The spectrum clearly shows that the D and L amino acids are ordered differently.

The dipolar coupling within the methyl group is directly proportional to the degree of order of the C_3 axis of this group, S_{C_3}, and is given by the following expression

$$D_{HCH} = \frac{h\gamma^2 H}{8\pi^2 r_{HH}^3} \quad S_{C_3}$$

As a consequence, from the dipolar splittings observed for D and L-alanine, it was found that the L-alanine is ordered 6% more highly than the D-alanine. In an attempt to determine if this represented the maximum difference in order for this phase, a phase which contained one-half as much alanine was prepared. Here also the L-alanine was ordered 6% more than the D.

Two mechanisms by which the two orders arise suggest themselves. The alanine molecules, being very soluble in water, may reside almost entirely in the interstitual water of the phase. They would be ordered differently by seeing an asymmetry in the interface region of the phase superstructure. This does not seem a good explanation since the two observed orders would arise mainly as a result of electrostatic interactions. Such interactions should affect both alanines similarly.

A second explanation is that the molecules reside mainly in the interstitual water, indicated by the small D_{HCH} ($\sim$ 5.5 Hz), but penetrate into the highly ordered regions of the phase, that is, into the electrical double layer region. While in the electrical double layer the D and L-alanines would be strongly influenced by the asymmetry of their environment and undergo substantially different ordering forces. The observed spectrum is then a weighted average from the molecules in the interstitual water and those in the electrical double layer.

It is interesting to note that when the concentration of sodium decyl-2-sulfate in the total decyl-sulfate was decreased the difference in order between the D and the L-alanine was found to be roughly proportional to the square of the concentration. This indicates that the ordering results from a more complex situation than a simple one to one interaction. A cumulative effect, perhaps a result of the packing of one decyl-2-sulfate with respect to another, is possible.

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