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ON THE FLEXIBILITY GRADIENT OF FATTY ACID SPIN LABELS

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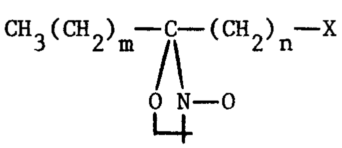
Intrinsic flexibility of fatty acid and ester spin label probes in the nematic MBBA is investigated. The "flexibility gradient" in the absence of such a gradient in the supporting medium is remarkably strong. The ordering of flexible labels is compared with that of more rigid labels in MBBA and with the molecules of MBBA themselves.

INTRODUCTION

Recently, systematic studies have begun to be made on the behavior of solute molecules dissolved in nematic phases.[1-3] These studies, carried out by a wide variety of techniques, seek to extend the understanding of the effect or orienting pseudo potentials on solute molecules and conversely, the effect of impurities on the thermodynamic properties of the liquid crystal. We have used EPR to study nitroxide radicals in nematics, partly motivated by the possibility of understanding better the analogy between nematics and the biological membrane, and have begun to extend these studies to flexible nitroxide radicals. Our first studies have been carried out with the six nitroxides I(12,3), I(5,10), I(1,14), II(12,3), II(5,10), II(1,14) where the general structure is as follows:



I(m,n) X = CO_2H

II(m,n) X = CO_2M_e

The labels I(m,n) have been employed extensively in biological systems and model systems.[5-7] A recurring result

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in a wide range of systems incorporating lipid bilayers or similar structures is the so-called "flexibility gradient" which is a decrease in the order parameter of the oxazolidine ring as n increases. Generally the flexibility gradient is understood as follows: the acid head group more or less is firmly fixed at the lipid-water interface. As n increases, the oxazolidine ring is increasingly deeper into the lipid bilayer where S decreases with n because intra- and intermolecular forces allow more molecular motion. The order parameter of the label is supposed to reflect somewhat the order of the supporting medium thus the flexibility gradient of the label is said to indicate a corresponding flexibility gradient in the medium and this view is supported qualitatively but not quantitatively by other methods.[4] Qualitatively one might understand the discrepancy in terms of an intrinsic flexibility gradient in the labels themselves that dominates the envisioned cooperative order that is supposed to exist in a lipid bilayer. We wanted to shed light on such an intrinsic gradient in these labels by studying them in a system with no flexibility gradient, a nematic liquid.

A similar problem of the effect of the flexible end chains attached to the more rigid aromatic cores of the nematic molecules themselves has received theoretical and experimental attention.[8-12] Flexibility gradients have been observed and in some cases[10,11] interpreted in terms of order parameter referred to a single molecular-fixed axis system.

EXPERIMENTAL

MBBA purchased from Eastman Kodak and spin labels purchased from Syva Associates, Palo Alto, CA. were used as received. Air saturated samples approximately 1 mM were placed in 3 mm quartz tubes and studied at x-band after checking that neither degassing nor using lower concentrations changes the results reported here. The EPR were recorded and the temperature was controlled and measured as before.[7]

The order parameters were determined by

$$S = \frac{A_{11} - A_{\perp}}{A_{zz} - A_{xx}} \; \frac{a_N}{a'_N}$$

$$= 0.83\,(A_{11}/a'_N - 1) \qquad (1)$$

where the first line of equation (1) is due to Hubbell and McConnell[5] and the second line is derived using the molecular fixed parameters A_{zz}, A_{xx}, and a_N given by Gaffney[13] where A_{11} is the line separation of the three-line nitroxide spectrum in the nematic phase and a_N' is the separation in the isotropic phase. For details see, for example, reference 5.

RESULTS AND DISCUSSION

The labels I(m,n) and II(m,n) in MBBA gave typical, simple three-line nitroxide EPR spectra in the temperature range 25-60°C. The line spacings and linewidths were such that the rapid motion formalism necessary to make equation (1) valid is applicable. Details concerning the rotational motion and the magnetic parameters will be given elsewhere. Here we concentrate on the value of S as a function of n which is shown for the labels I(m,n) in Figure 1 together with order parameters of other non-flexible labels and of the MBBA molecule itself. Also shown are data from the literature for I(m,n) in two model membrane systems. Remarkable is the fact that in spite of the lack of translational order in the nematic liquid crystal that might lead to a collective flexibility gradient in the medium, the labels do show a gradient comparable to that in other systems. One does not expect the values of S to be the same in these very different systems. Indeed near the acid head group (low n) one expects S to be larger in the model membrane systems because of the anchoring effect mentioned above. This would be absent in the nematic and this is clearly observed in Figure 1. There is some specific interaction of the acid head group with MBBA which is apparent when the order parameter of I(12,3) is compared with that of II(12,3). See Table 1.

TABLE 1. Order parameters in MBBA[a]

T(°C)	I(1,14)	II(1,14)	I(5,10)	II(5,10)	I(12,3)	II(12,3)
36	.11	.11	.14	.11	.18	.14
31	.13	.13	.21	.22	.31	.16
26	.15	.15	.33	.33	.43	.29
21	.17	.17	.46	.43	.51	.39

[a] Temperature, ± 1°C. The EPR order parameters are accurate to ± .01.

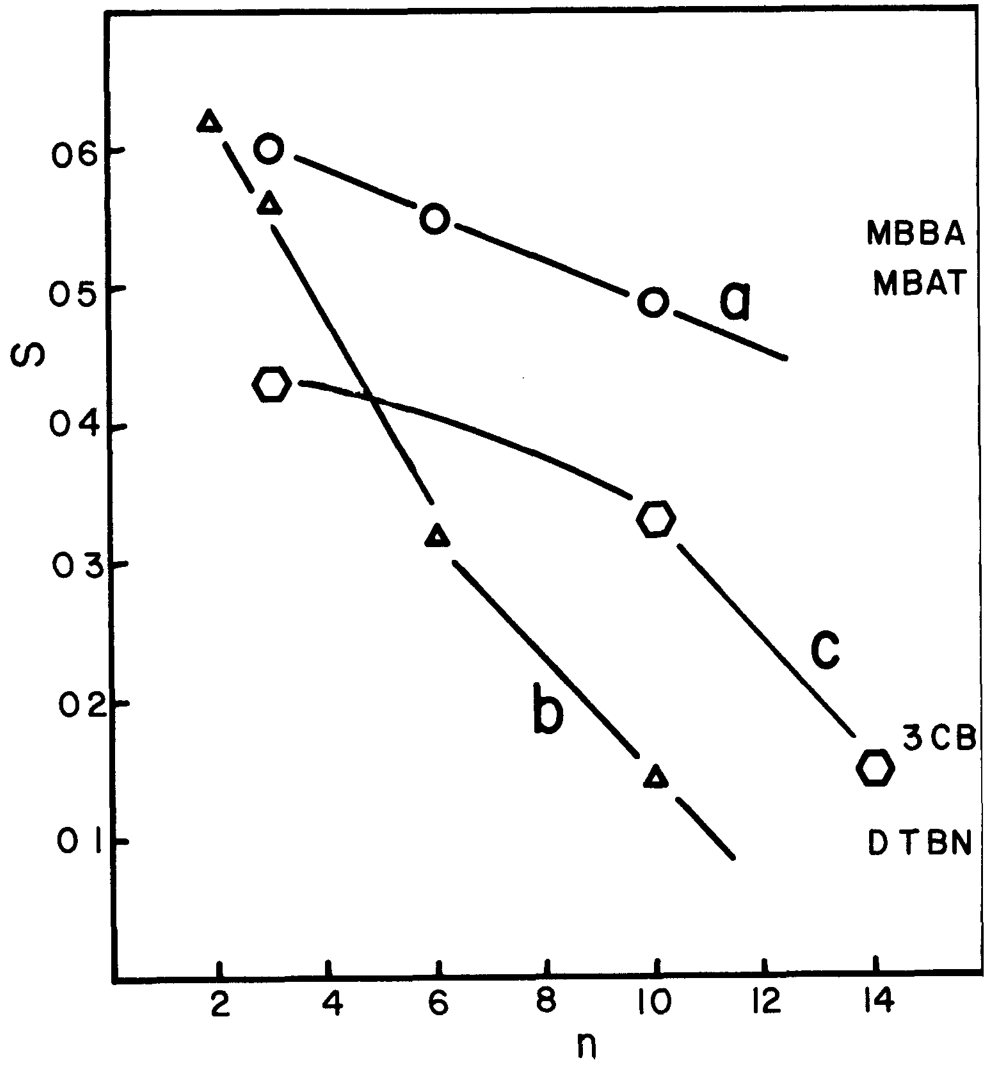

FIGURE 1. The order parameter, S, vs the bond number, n, for spin labels I(m,n) in (a) aqueous dispersions of egg lecithin-cholesterol (2:1 mole ratio), reference 4, (b) decanol-sodium decanol bilayers, reference 6, (c) MBBA, T = 26°C, this work. Along the right hand edge are indicated order parameters in MBBA at 26°C of DTBN, di-tert-butylnitroxide; 3CB, tricholorobenzene, reference 1; MBAT, N-(p-methoxy benzylidene) -4-amino-2,2,6, 6-tetramethylpiperidino-1-oxyl, a rod-like nitroxide, reference 3; and MBBA, reference 1.

Further away from the head group, the order of the acids and esters is essentially the same which shows that the specific interaction with the acid does not affect the intrinsic flexibility gradient of interest here.

To facilitate our discussion of flexible molecules in an orienting medium, we imagine two idealized cases. In the first, we envision a perfect bilayer of flexible molecules in which long range cooperative effects and the intrinsic flexibility of individual molecules interplay to produce the observed flexibility gradient. Presumably deuteron magnetic resonance of deuterated soap molecules and lipids measures this.[14,15] In the second, we imagine a flexible molecule, perhaps anchored at one end, that is subjected to a mean orienting field that is spatially invarient, i.e., all portions of the flexible molecule are subjected to the same mean orienting potential. This is probably approximately true for the flexible end chains of nematic molecules in the nematic mesophase and we assume that it describes the situation of the fatty acid spin labels in MBBA. What about the fatty acid spin labels in the lipid bilayers?

Of central importance here, is that the flexibility gradient and the order of these labels are large--comparable to those observed in oriented bilayers. This being the case, it seems inescapable that the flexibility gradient observed for these labels in bilayer systems is dominated by the type of interactions envisioned in the second idealized case mentioned above. In other words, the contribution of cooperative phenomena to the flexibility gradient in lipid bilayers would only weakly affect the observed spin label flexibility gradient. This is the view of Seelig and Niederberger.[9] We have eliminated uncertainties associated with macroscopically disordered systems with the possible attendant difficulties due to slow motion,[16] so these results seem to support their view.

The second idealized case mentioned above, leads to an exponential decrease of the order parameter with the number of bonds separating the nitroxide group from the anchor point. The anchor point provides a reference frame from which to measure the segmental order parameters but in the present case, there is no such reference frame; however, Bos and Doane[11] and Dong et al.[10] have suggested referring all segmental order parameters to a single molecular fixed axis system. With only three experimental points, we can not carry out a detailed analysis to estimate the molecular fixed order parameter but it is interesting to suppose that the measured order parameters of II(m,n) varys exponentially with the bond numbers from the center of mass (which would be the reference frame of the molecular order parameter). Thus $S = S_0 S_1^k$ where k is the number of bonds between the center of mass and the oxazolidine ring and S_0 is the molecular fixed order parameter. This would require that II(m, n) be symmetric and that the center of mass not depend on n, neither of which obtains, but surprising this model fits pretty well with $S_0 = 0.57$ and $S_1 = 0.80$ at 25°C taking the center of mass to be at carbon number 9. Obviously more values of n are necessary to establish the exponential dependence but it does seem clear that the rigid body order of these flexible molecules approaches that of MBBA at 25°C, S = 0.58 and that of a nematic-like spin probe, N-(p-methoxybenzylidene)-4-amino-2,2,6,6-tetramethypiperidino-1-oxyl dissolved in MBBA, S = .54.

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