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TCNE$^{\cdot -}$: AN ANIONIC SPIN PROBE FOR THE STUDY OF POLAR ANISOTROPIC SYSTEMS

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Abstract The radical anion of tetracyanoethylene (TCNE), when produced in the presence of the macrocyclic polyether dibenzo-18-crown-6, was found to be a convenient spin probe for studying amphiphilic liquid crystals. Both the value of the isotropic nitrogen hyperfine splitting constant and the broadening induced on the ESR lines by the addition of the paramagnetic salt $NiCl_2$ to the lyotropic mixture, seem to indicate that TCNE resides in the polar interfacial region of the liquid crystal.

Ordering and reorientation of spin probes in anisotropic media can be studied from their electron resonance spectra. Indirect information on the anisotropic environment itself can also be inferred from the experimental results for the radical. This method has been widely used to investigate thermotropic and lyotropic liquid crystals as well as biological systems. Lyotropic liquid crystals are particularly interesting substrates, partly because of their everyday occurrence as soaps and, more important for us, since they constitute useful model systems for membrane type structure. For instance some of them give lamellar phases formed of bilayers with the aliphatic chains inside and the polar head groups at the interface with the water phase separating one bilayer from another.[1] For such inhomogeneous systems, and even more for real membranes, it is important to be able to assess a variety of radicals as probes. The reason is that suitable changes in the structure and characteristics of the probe can favour its residence in various regions of the substrate, which can therefore be studied in turn.

The most widely used spin probes are certainly nitroxide radicals. These are neutral species whose structure can be changed in a number of ways. It should be noted, however, that normally the NO group is, for reasons of chemical stability, part of a piperidine or oxazolidine ring and what is actually modified are the functional groups attached to these rings. For example the very different cholestane and stearic probes contain the nitroxide function at the same oxazolidine ring. These probes have revealed data useful in the elucidation of the structure of the hydrophobic core of the bilayer;[2] however it is fairly difficult with an ordinary nitroxide to investigate one of the most interesting regions of lyotropic and biological systems, that is the polar heads' interface.

Natural candidates to sit in this region seem to be electrically charged radicals. Unfortunately the use of these species as spin probes is normally prevented by their poor stability in ordinary experimental situations. Thus we are faced with the problem of increasing the stability of these ionic radicals. An advantageous method to do this, in the case of the radical anions, is to complex the alkali counterion with macrocyclic polyethers.[3] As a matter of fact we have recently found that the radical anion of tetracyanoethylene (TCNE) is very long lived even at high temperatures in the presence of small amounts of dibenzo-18-crown-6 ether, and can be used as a probe for thermotropic liquid crystals.[4] With respect to nitroxide spin probes, $TCNE^{\cdot-}$, besides being ionic, has the advantage that the ESR lines do not hide unresolved proton hyperfine structure and that its smaller size, together with the reduced anisotropy of the hyperfine and g tensors, imply that slow motion ESR spectra will be obtained in more viscous systems than with conventional probes.

The scope of this letter is to report on the feasibility of

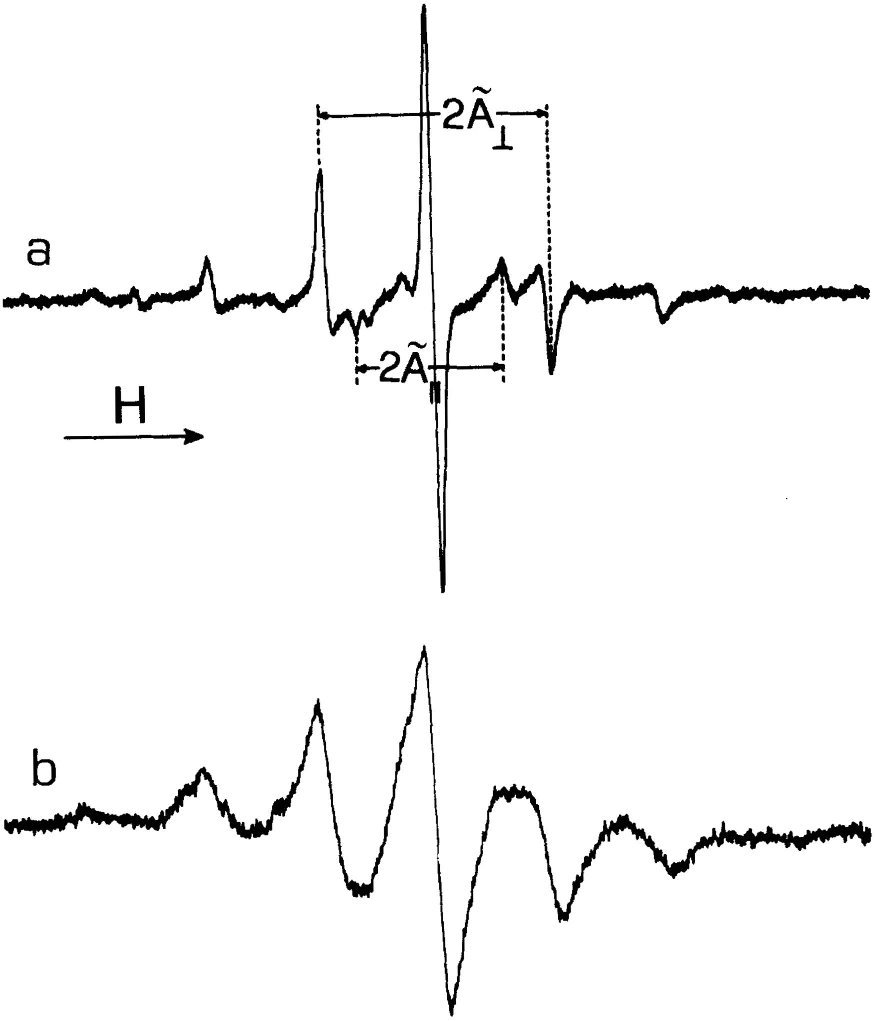
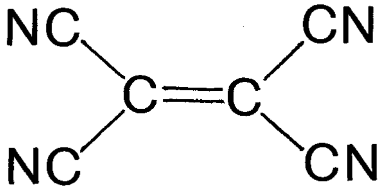
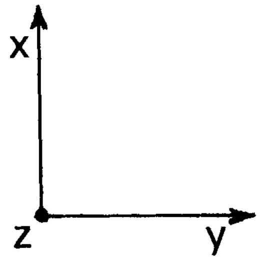


FIGURE 1 ESR spectra of TCNE$^{\overline{\cdot}}$ dissolved in a lyotropic liquid crystal (a) before and (b) after the addition of $NiCl_2$.

using TCNE$^{\overline{\cdot}}$ as a probe also for amphiphilic liquid crystals. Moreover we shall hint that TCNE$^{\overline{\cdot}}$ does actually reside in the polar head region, thus making an attractive candidate for further spin probe studies of model and real systems.

For this investigation we have chosen a lyotropic mesophase composed of sodium caprylate 28 wt%, decanol 42 wt% and water 30 wt%. Such a mixture is known to possess a bilayer structure.[1] The radical was obtained by dissolving in the liquid crystal a 1:1:1 mixture of TCNE, KI and dibenzo-18-crown-6 ether in a nitrogen atmosphere and by gently heating to favour homogenization. The ESR spectrum, recorded at room temperature, is shown in Fig. 1a. The appearance is that of a powder type spectrum; however the lines are very narrow, thus hinting that the system is rather a poly-liquid crystalline one. In other words the probe is rapidly tumbling in ordered domains, but the domains are in turn isotropically distributed since the sample is, as a whole, unoriented. From the separation between the lines due to the orientations of the director of the liquid crystal parallel and perpendicular to the magnetic field, it is possible to extract the order parameter inside the domains. Due to the D_{2h} symmetry of TCNE, the principal axes of the ordering matrix are determined to be those shown below.





The difference between the components of the partially average hyperfine tensor is

$$\tilde{A}_{\parallel} - \tilde{A}_{\perp} = A_{zz} - \frac{1}{2}(A_{xx}+A_{yy})\ \overline{\mathscr{D}^{2}_{00}} + \frac{3}{8}(A_{xx}-A_{yy})(\overline{\mathscr{D}^{2}_{02}} + \overline{\mathscr{D}^{2}_{0-2}}),$$

where A_{xx}, A_{yy}, A_{zz} are the principal values of $\underset{\sim}{A}$. Since the nitrogen hyperfine tensor here has cylindrical symmetry, we find

$$\tilde{A}_{\parallel} - \tilde{A}_{\perp} = (A_{\parallel} - A_{\perp})\ \overline{\mathscr{D}^{2}_{00}}$$

Similar expressions hold for the $\underset{\sim}{g}$ tensor. The measured values of $A_{\parallel}$ and $A_{\perp}$ in ethanol solution are known to be 5.77 and -0.47 gauss respectively, while $g_{\parallel}$ = 2.0024 and $g_{\perp}$ = 2.0029.[5] By introducing in the above equation these components and the values determined from the spectrum of Fig. 1a, _i.e._ $\tilde{A}_{\parallel}$ = = 1.18 and $\tilde{A}_{\perp}$ = 1.83 gauss, we have at once $\bar{P}_2 = \mathscr{D}^{2}_{00} = -0.104$. A slightly greater value of $\bar{P}_2$ (-0.12) can be calculated from $\tilde{g}_{\parallel}$ = 2.00277 and $\tilde{g}_{\perp}$ = 2.00271. The latter value, however, is certainly less accurate than the one determined from the anisotropy of the hyperfine tensor. The negative sign of $\bar{P}_2$ shows that TCNE is preferentially oriented with its _z_ axis perpendicular to the director. It may be noticed that the ESR spectrum exhibits some low intensity peaks near the central line. We attribute these to "forbidden" transitions which become partially allowed when the director of the liquid crystal makes an angle with the magnetic field intermediate between 0 and 90 degrees.[4]

The existence of a non-vanishing order parameter shows that this anionic spin probe is resident in an ordered region. This could be the hydrophobic core or the polar head interface As a third possibility we may conceive the probe being ordered by purely steric effects, even if it is dissolved in the water phase. In fact the thickness of the water layer may be as small as 7 Å,[6] thus comparable with the size of the probe. To test this last hypothesis, monodomain samples were prepared by homeotropic alignment of the liquid crystal between two closely spaced parallel glass plates.[6] Spectra were then taken with the magnetic field parallel and perpendicular to the plate normal, and therefore to the director. The larger value of the hyperfine splitting, which was coincident with A measured in the polydomain sample, was found with the applied field perpendicular to the director. Since in the water phase the TCNE$^{\cdot-}$ radical, which is lath-like, should prefer to be, on average, oriented with its _z_ axis perpendicular to the layer, we would expect the larger component of A to be found when the director is parallel to the magnetic field. We may then conclude that the probe does not reside in the water layer. The most attractive hypothesis is that the radical sits at the polar interface rather than in the inner hydrophobic region. Strong indication in this direction comes from the observation that the isotropic splitting constant $\underline{a} = (A_{\parallel} + 2A_{\perp})/3 = 1.61$ gauss, is closer to the value measured in a polar solvent, eg ethanol (1.607), than in MeTHF (1.575).[5] To try a verification of this guess we have dissolved a paramagnetic salt, $NiCl_2$, in the lyotropic mixture. The Ni^{2+} paramagnetic ions are expected to provide an extra relaxation mechanism for the electron spin of $TCNE^{\cdot-}$, provided ions and probe can come in close contact. In Fig. 1b we show the ESR spectrum after the addition of $NiCl_2$. We can see that the lines are noticeably broadened thus indicating that the extra relaxation mechanism is effective. Since $NiCl_2$ is most probably contained in the water phase, it seems confirmed that $TCNE^{\cdot-}$, which interacts with the Ni^{2+} ions, resides in the polar interfacial region. If this is the case, the $TCNE^{\cdot-}$ anionic probe can possibly be used to investigate variations at the polar interface in model or real membranes.

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