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Chemical reactivity within a smectic B liquid crystalline phase: a model of enzyme catalysis?

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The rearrangement of allyl *p*-dimethylaminobenzenesulphonate (ASE) to form a zwitterionic product has already been recognized as an effective probe for the study of reactivity within the smectic B phase [4, 5, 19]. We have used deuterium NMR, linear dichroism and X-ray diffraction techniques to investigate the phase diagram of the ASE-OS35 reaction system. The partitioning of the reactant molecules between coexisting smectic, nematic and/or isotropic phases and the structural organization of the smectic catalytic host at different temperatures and reactant guest concentrations have been characterized. On the basis of these measurements, a model of ASE reactivity in smectic solvents has been developed. The reaction takes place provided that coexisting isotropic or nematic phases are present to act as a reservoir for the ASE reactant molecules prior to their entering the smectic phase; they then react and leave the smectic phase as a zwitterionic product. The analogy between this model of reactivity within smectic phases and the Michaelis–Menten enzyme processes is discussed. This relationship opens up the intriguing possibility of designing new experiments with which to investigate further liquid crystalline models of enzyme catalysis.

1. Introduction

Guest molecules dissolved in a liquid crystalline host are orientationally ordered and in smectic phases also translationally ordered [1] as a result of solute–solvent interactions. The host may also deform the structure of the guest molecules to make them more compatible with the molecular organization within the ordered host [2, 3]. In addition to the influence of the liquid crystal solvent on the static behaviour of the guest molecule, the rates of molecular motion may also be changed, and, more significantly, the anisotropy of the host will induce an anisotropy in the dynamics of the guest. The influence of the solute–solvent interactions in liquid crystalline solutions on the behaviour of the guest might be expected to modify its chemical reactions and this is indeed the case. Smectic phases are the most interesting and promising mesomorphic solvents for studying reactivity control by orientational effects. The orientational

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ordering of nematic solvents is smaller and so this is less efficient in inducing these effects in guest reactions [4, 5]; perhaps more importantly, the orientional order in a nematic is not coupled to the translational order as it is in a smectic phase.

Experiments able to display reactivity control need to be designed with great care. The efficiency of smectic solvents in controlling chemical reactions has been found to be very critically dependent upon minor changes of the experimental conditions and subtle details of the reactant molecular structure [6–18]. Problems of precision [15] or indeed conflicting data [13, 15] have also been found. These problems are no longer surprising, given the observation that the smectic phase of the reaction mixture can coexist with either isotropic or nematic phases, depending on both the solute structure and concentration [19]; such coexisting phases are now known to influence the overall kinetics of the reaction taking place in the smectic phase. Indeed it has been shown how the complex phase behaviour of these reacting systems can lead to discontinuities in the reaction pattern [19]. Very significant insights were then given into this aspect by the groups of Leigh and Weiss using deuterium NMR spectroscopy. A paper [18], by Leigh and his colleagues, was submitted to the *Journal of the American Chemical Society* almost in coincidence with a preliminary communication by us reporting the use of the same NMR approach but applied to the ASE-OS35 system (see figure 1). These NMR data, which were not published at that time and have now been included in the present report, demonstrated that under the reaction conditions, the host smectic phase coexists with either isotropic or nematic phases.

OS35 (4-propylcyclohexane-1-carboxylic acid 4-*n*-pentylcyclohexyl ester) (see figure 1 (*a*)) was chosen as the solvent for the reaction studies because it provides a smectic B phase transparent to UV light, thus making it easier to perform temporal spectroscopic measurements on the reactions of the guest. We chose as a reaction for our studies the rearrangement of allyl *p*-dimethylaminobenzenesulphonate (ASE) (see figure 1 (*b*)) to a zwitterionic product because the necessary reactant orientation could be induced by the host structure. This reaction is a very sensitive probe of reactivity in smectic phases. ASE is in fact indefinitely stable in its solid state and also in isotropic or nematic solutions. The reaction kinetics for the rearrangement in the smectic B phase of

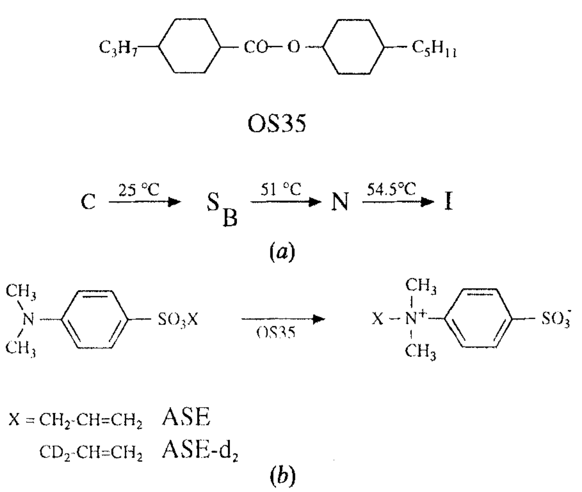


Figure 1. The chemical structures of (*a*) the mesogenic solvent OS35 (4-*n*-propylcyclohexane-1-carboxylic acid 4-*n*-pentylcyclohexyl ester) and (*b*) the reactant solute ASE (allyl *p*-dimethylaminobenzenesulphonate).

OS35 were found to be strictly second order, thus suggesting an intermolecular reaction. As a result of such insights, the reactivity in smectic B solvents is finally becoming a phenomenon which is reasonably well understood.

2. The coexistence of the smectic B phase of the ASE-OS35 mixture with nematic or isotropic phases

Observation of the orientational order of ASE molecules in the reaction mixture provides a convenient method with which to determine the form of the phase diagram, as well as to assign the phases in which the ASE is dissolved. The orientational order can be evaluated most easily in aligned or monodomain systems by measuring the components of physical properties defined by tensors of rank two parallel to the director. These properties include light absorption measured as linear dichroism (LD) (see later), and nuclear spin interactions determined by means of NMR spectroscopy. The quadrupolar spin interaction of deuterium nuclei provides one of the simplest NMR approaches with which to study orientational ordering. In a monodomain sample of a uniaxial liquid crystal, the degeneracy of the two Zeeman transitions for deuterium is removed and the single line characteristic of the isotropic phase is split into a doublet [20]. The magnitude of this quadrupolar splitting is determined by the order parameter S_{CD} of the C–D bond direction [21]

$$S_{CD}=(3\overline{\cos^2\beta_{CD}}-1)/2,$$

where β_{CD} is the angle made by the C–D bond with the director, provided the small biaxiality in the quadrupolar tensor is neglected.

Deuterons can be inserted into the molecular structure either of the liquid crystalline host or of the guest reactant. We have chosen to deuteriate the reactant ASE in the allyl group [22] (see figure 1). Deuterium NMR spectra of ASE-d_2 in OS35 were then recorded as a function of both concentration and temperature. On cooling a 1×10^{-2} M (0·31 mol per cent) solution from the isotropic phase, the single deuterium peak splits at the nematic–isotropic transition (54·5°C) into a doublet (see figure 2 (*a*)). This coexists with a single, sharper line from the isotropic phase for a narrow temperature range during which its intensity is gradually reduced to zero. As the temperature is lowered further throughout the nematic phase, the doublet splitting increases monotonically corresponding to the expected enhancement of the orientational order. The quadrupolar splitting reaches a maximum at the temperature (52°C) corresponding to the appearance of the smectic B phase in equilibrium with the nematic; then, slowly, the splitting decreases and the linewidth slightly increases. At about 48°C a single line appears suddenly, which rapidly replaces the doublet, presumably as a result of the formation of a disordered phase.

On increasing the solute concentration, the temperature range for the existence of the doublet decreases (see figure 2 (*b*)) until, for a concentration of 10^{-1} M, only a single narrow peak is obtained for the entire range of the pure mesogen (see figure 2 (*c*)). The change of the spectrum from a doublet to a single peak implies an isotropic distribution of ASE-d_2 and therefore, according to Fahie *et al.* [18], it is interpreted as evidence for a reentrant isotropic phase in coexistence with the smectic B phase. This interpretation of the NMR spectra in terms of the coexistence of the smectic B with nematic or isotropic phases is not unambiguous in this case because the deuterium NMR experiment does not give spectra which could be associated with ASE dissolved in the smectic B phase

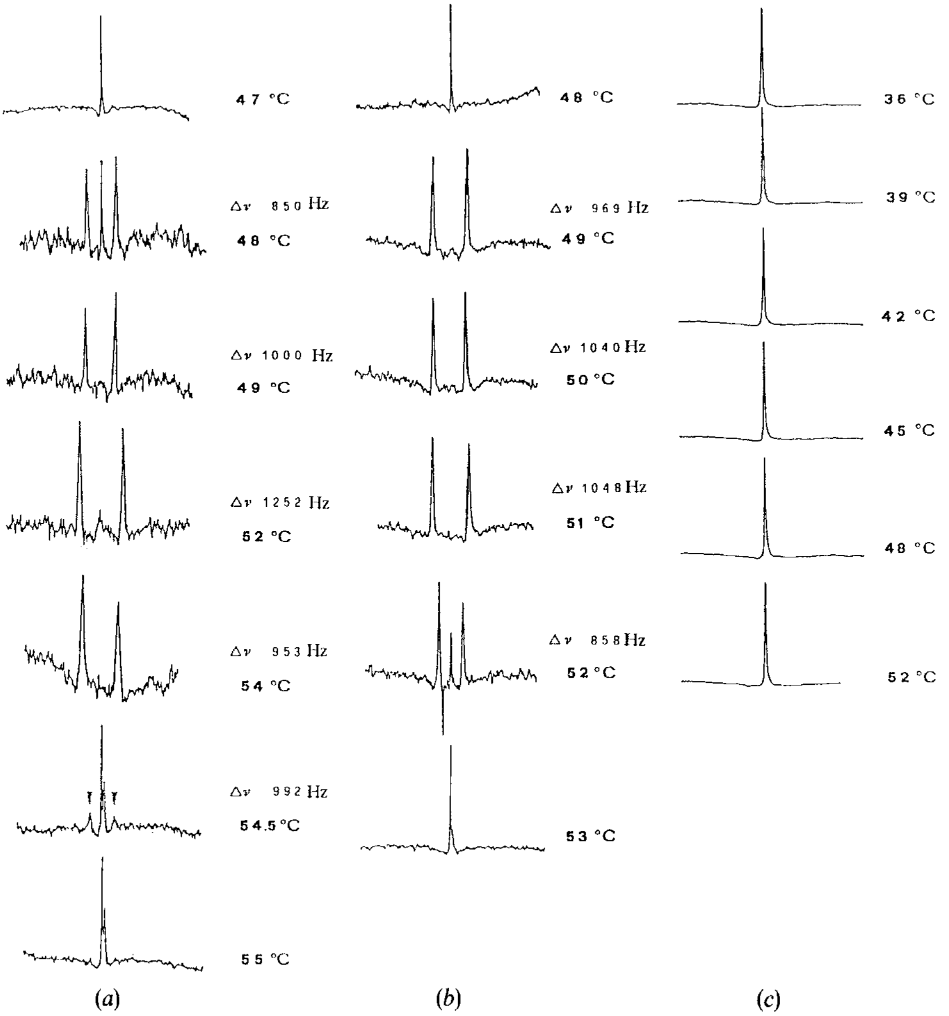
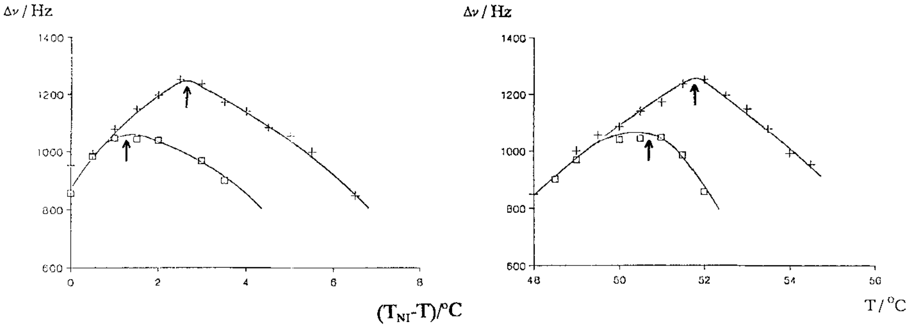


Figure 2. Deuterium NMR spectra of ASE-d_2 dissolved in OS35 at different concentrations and at different temperatures, (*a*): 1×10^{-2} M (0·31 mol per cent); (*b*): 3×10^{-2} M; (*c*): 10×10^{-2} M.

(see later). The NMR technique in this case apparently only observes guest ASE molecules when they are dissolved in nematic or isotropic phases; we shall return to this point later.

Support for the consistency of this interpretation is provided by plotting the quadrupolar splittings in two different ways, as shown in figure 3. In one, the quadrupolar splitting is plotted versus the shifted temperature, i.e. the difference between the temperature corresponding to the complete isotropization of the mixture from the nematic phase (T_{NI}) and the experimental temperature (T) (see figure 3 (*a*)). By this kind of scaling procedure, we allow for the simple fact that addition of a solute changes the nematic–isotropic transition temperature. As a result of using a shifted temperature scale, the quadrupolar splittings of nematic samples with different compositions are compared under similar conditions and so are expected to be the same. Thus in figure 3 (*a*), the quadrupolar splittings obtained by cooling two mixtures



(*a*) (*b*)

Figure 3. The quadrupolar splitting determined from deuterium NMR as a function of temperature for different concentrations of ASE-d_2 (+, 1×10^{-2} M, □, 3×10^{-2} M) are plotted (*a*) *versus* the shifted temperature ($T_{NI}-T$) where T_{NI} is the nematic–isotropic transition temperature and (*b*) *versus* the sample temperature (T).

at different ASE concentrations, fall, to within experimental error, on the same curve until they reach the two different maxima indicated by arrows; at these points the coexisting smectic B phase is first formed. After these maxima the points from each mixture fall on different curves. This behaviour supports our assignment of pure nematic phases for the rising part of the curves on the left hand side of the plot; in fact the ordering of the solute in this phase depends upon the bulk composition and the temperature, although the use of the shifted temperature effectively removes the composition dependence. The maxima mark temperatures after which the systems change drastically and the scaling is no longer appropriate; in other words the ordering of ASE within the nematic phase is not a universal function of the shifted temperature ($T_{NI}-T$) when the nematic coexists with the smectic B phase.

On the other hand, by plotting the same splittings simply *versus* temperature (see figure 3(*b*)) the reverse behaviour was obtained for the two sets of data. The points which we have just identified as corresponding to the pure nematic phase are now separated and this is what we actually expect, because the scaling provided by the shifted temperature is no longer operative. In contrast, the points which fall on two different curves on the right hand side of the figure 3(*a*) lie on the same line on the left hand side of this plot. In fact, when the nematic is in equilibrium with another phase, namely the smectic B, its ordering does not appear to depend any longer upon the composition but only on the absolute temperature. This universal behaviour of the order parameter for ASE-d_2 dissolved in the nematic phase coexisting with the smectic B phase can be understood in the following way. At a given absolute temperature, the concentration of the solute dissolved in the nematic phase is given by the position of the phase boundary between S_B+N and N. This concentration is independent of the total amount of ASE-d_2 and so is determined solely by the temperature. Since the orientational order of the solute is determined by its concentration at the phase boundary, the order must be a function of the absolute temperature, but not the total solute concentration, as we observe.

By plotting the transition temperatures identified by these deuterium NMR experiments, together with those obtained by DSC (see figures 2 and 3 of [19]) we obtain the phase diagram for this binary mixture shown in figure 4. In the definition of the phase diagram, two points still need to be clarified; first, the range of existence of the single smectic phase and secondly, the discontinuity at about 44°C in the smectic

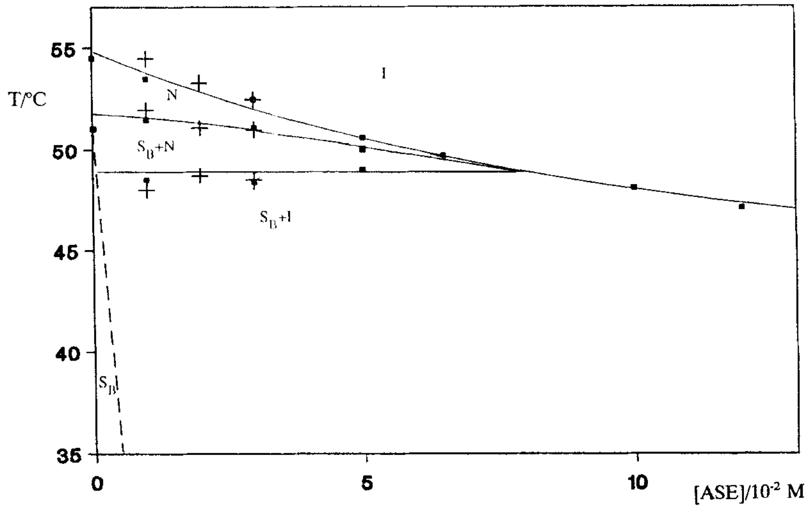


Figure 4. The phase diagram of the binary mixture ASE-d_2/OS35 at low reactant concentrations. The transition temperatures were determined by NMR spectroscopy (+) and DSC (■). The pure smectic B region, whose existence was demonstrated by LD, is tentatively indicated by a dotted line (see text).

structure suggested by peak 3 in the DSC pattern of figure 2 [19]. We were able to clarify the former point by NMR and LD techniques, and the latter by X-ray scattering.

3. The range of existence of the smectic B phase in the ASE-OS35 system

Our inability to observe peaks in the deuterium NMR spectra, which could be associated with ASE-d_2 dissolved in the smectic B phase of OS35, did not allow the boundary between the smectic B and the other phases to be defined and, more importantly, did not provide any evidence for its existence. However, the smectic B phase must exist for the mixtures with ASE, otherwise no reaction would take place. In addition the smectic phase of this system must also coexist with either an isotropic or a nematic phase, otherwise this would contradict all of the reactivity results obtained so far [23]. The inability to detect ASE-d_2 dissolved in a smectic environment by deuterium NMR spectroscopy can have two physical origins. It could simply be because the ASE concentration is too small to be detected, given the relatively low sensitivity of the NMR technique. Alternatively, it could result from line broadening effects which reduce the height of the spectral lines. In fact these lines can be unobservably broad either when a good monodomain has not been obtained or when the solute rotational motion is so slow as to make the reorientational rates of a similar magnitude to the quadrupolar splitting [24].

In order to help discriminate between these two different possibilities we have repeated the deuterium NMR experiments, but with fully deuteriated *p*-xylene as the solute. This molecule has a similar structure to ASE-d_2 but as it is more soluble in OS35 and contains more deuterons per molecule, the experiment necessarily has a higher sensitivity. Typical deuterium NMR spectra of *p*-xylene-d_{10} (1 per cent by weight) dissolved in OS35 are given in figure 5. The nematic spectrum (see figure 5(*a*)) is characterized by the appearance of two doublets, the more intense from the set of aliphatic deuterons and the other from the aromatic deuterons. There is, in addition, a pair of lines in the centre of the spectrum with a barely discernible separation resulting

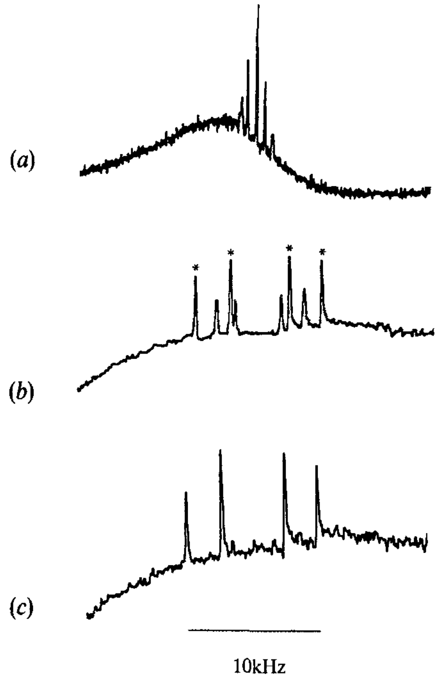


Figure 5. Deuterium NMR spectra of fully deuteriated p-xylene (1 per cent by weight) dissolved in OS35. (a): the nematic–isotropic transition region at 49·3°C is characterized by the two central lines from the isotropic phase and the two quadrupolar doublets from the nematic phase. (b): the nematic starts to be converted into the smectic phase at 36·8°C, new peaks appear, indicated by *, and then grow at the expense of the two nematic doublets until spectrum (c) is obtained. (c): deuterium NMR spectrum assigned to p-xylene-d_{10} dissolved in the smectic phase of the mixture at 21·8°C.

from the chemical shift difference of the aliphatic and aromatic deuterons; this special feature is associated with the coexisting isotropic phase at the nematic–isotropic transition. The quadrupolar splittings increase with decreasing temperature within the nematic range, as expected. When the nematic starts to be converted into the smectic B phase, the quadrupolar splittings stop increasing; in addition, four new peaks marked with stars appear with larger splittings and grow in intensity at the expense of the two nematic doublets (see figure 5 (b)). At lower temperatures (see figure 5 (c)) the spectrum associated with the nematic phase has vanished leaving just two doublets with their larger splittings. These new peaks are assigned to p-xylene-d_{10} dissolved in the smectic B phase with its higher orientational order. This positive result gives strong support to the view that the absence of ASE-d_2 spectra associated with the smectic B phase is most likely due to the very low concentration of ASE-d_2 in this phase. Hence, if, as we believe, this smectic B phase does exist, given the good signal to noise ratio of the spectra, we can estimate that the amount of ASE in this phase must certainly be less than 0·5 per cent (2×10^{-2} M).

Further evidence for this smectic B region when ASE is dissolved in OS35 was subsequently provided by the linear dichroism (LD) and X-ray techniques. The optical analogue of the deuterium NMR experiments which we have described was produced in an optical spectrometer. We placed a 12 kG electromagnet into the cell compartment of a JASCO-J500 dichrograph together with a temperature controlled sample holder between the poles of the magnet. The dichrograph had been adapted to record LD spectra using a modulation technique [25–27]. We were, as a consequence, able to reveal the presence of ASE in the smectic B phase, with a sensitivity greater than that of NMR spectroscopy by at least two orders of magnitude. LD corresponds to the differential absorption (A) of two perpendicularly polarized light components, parallel ($\parallel$) and perpendicular ($\perp$) to the director. The LD signal associated with a transition polarized along the ith molecular axis of the oriented, absorbing chromophores provides the order parameter S_i for the axis via

$$(A_\parallel - A_\perp)/(A_\parallel + A_\perp) = 3S_i/(2+S_i).$$

As with NMR spectroscopy, this technique gives a quantitative picture of the orientational order of the guest molecules within aligned liquid crystal solvents. The strength of the LD signal ($A_\parallel - A_\perp$) is determined by the extent of the macroscopic alignment of the sample and by the anisotropy of the local ordering of the absorbing molecules. When two phases are present, the observed signal is the weighted average of the contributions from the appropriate molecules in both phases. We have studied the LD signals of the band at 277 nm for ASE molecules dissolved in and oriented by the host liquid crystal OS35. This lowest energy electronic band is due to a charge transfer transition from the donor amino group to the sulphonate acceptor and is, therefore, polarized along the molecular long axis. Several LD spectra of ASE dissolved in OS35 have already been reported [19].

On the basis of our NMR results, the LD spectra were partially reinterpreted and integrated with the results of the methylcyclohexane experiment (see later) which mimics the effect on the ordering of increasing the ASE up to the values used in the NMR experiments. These high ASE concentrations are not possible in the LD experiments, because of experimental limitations of the technique which are described later. LD spectra of a previously oriented sample containing $4{\cdot}3 \times 10^{-4}$ M of ASE in OS35 were recorded during a heating cycle. In figure 6, the LD intensities at the maximum of the absorption band investigated are plotted against the sample temperature. The LD signal (full line) does not change on heating the sample to about 40°C. The signal then gradually decreases; this is likely to take place because of the

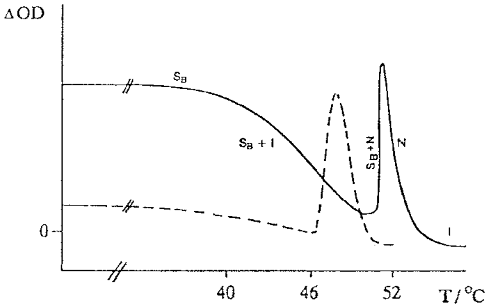


Figure 6. A sample (ASE $4{\cdot}3 \times 10^{-4}$ M) previously oriented inside a 12 kG magnetic field was heated, from room temperature up to the isotropic phase, and the LD signal at 277 nm (full line) recorded continuously. Methylcyclohexane was then injected into this sample (up to a total concentration of about 0·1 M for the two solutes) and the LD signal of the oriented solution recorded at the same wavelength during a cooling cycle is shown as the dashed line.

appearance of the reentrant isotropic phase in equilibrium with the smectic B phase. Since the LD intensity from the isotropic phase is necessarily zero, the reduction of the signal results from a decrease in the amount of the smectic B phase and also in the concentration of ASE in this ordered phase. The minimum at about 50·8°C corresponds to the transition of the coexisting isotropic phase into a nematic; on further heating, the LD signal grows very rapidly because of the increasing amount of the phase with its non-zero LD intensity. At about 51·5°C, corresponding to the highest LD values, the nematic no longer coexists with the smectic phase. The orientational order then goes rapidly to zero because, on increasing the temperature further, the orientational order in the nematic phase decreases until the transition to a pure isotropic takes place. We therefore attribute the maximum in ΔOD, shown in figure 6, to the pure nematic phase. The intensity of this peak from the nematic is slightly larger than the LD of ASE dissolved in the smectic B phase; this difference could indicate a higher orientational order of ASE in the nematic, but it most likely results from a poorer macroscopic order for the smectic B phase. In fact, samples suitable for these LD experiments have to be very thin (see the experimental section) and surface alignment is known to reduce the ability of a magnetic field to create a monodomain as the thickness decreases.

The range of concentrations which could be probed with this extremely sensitive technique is very narrow and far lower than that investigated by deuterium NMR spectroscopy. The LD signal must, in fact, be recorded at a sample optical density of approximately unity and the cell part cannot be reduced because of surface effects on the macroscopic alignment. This limitation in the range of concentrations did not allow the phase boundary of the existence for the smectic phase with either isotropic or nematic phases to be defined. In addition, the relevant transition temperatures for the mixture studied are closer to those of the pure solvent than the mixtures studied by NMR spectroscopy. In order to check in some way, therefore, the effect of increasing the solute concentration up to the range used in the NMR experiments (i.e. from 1×10^{-2} to 10×10^{-2} M) another solute, which does not absorb in the UV region, was added to the mixture. This new solute was methylcyclohexane and it was injected into an isotropic sample of the ASE solution in OS35 up to a total concentration of the two solutes of about 10×10^{-2} M. The LD was recorded while the mixture was cooled in the magnetic field (see the dashed line in figure 6). The new peak in this figure corresponds to the nematic phase and was found to be shifted to lower temperatures with respect to the experiment without methylcyclohexane. The high plateau found for temperatures down to room temperature in the experiment with ASE alone and associated with the smectic B phase was not reached. The LD signal remains very low, and this may reveal that at this higher solute concentration the smectic phase coexists with the isotropic phase down to room temperature, thus reducing the effective orientational order of ASE. This result is totally consistent with the persistent isotropic signals observed by deuterium NMR at the lowest temperatures investigated (see figure 2). This strong complementary role played by deuterium NMR and LD for this particular mixture is due to their ability to detect different sets of ASE molecules; those dissolved in nematic and isotropic environments are seen by the former technique, while the latter technique only observes those in aligned nematic and smectic phases. In contrast to NMR spectroscopy, the LD method is not able to differentiate between the guest molecules in coexisting phases.

So far we have investigated the phase diagram of the ASE-OS35 system by using techniques which focus on the guest molecules alone. However, a sound explanation of all the boundaries and discontinuities found in the reactivity pattern [19] of ASE requires a more detailed knowledge of the catalytic smectic phase throughout the region of the ASE-OS35 phase diagram in which the kinetic experiments were carried out. To obtain this information we have performed an X-ray investigation of the mixtures since this concentrates on the solvent and is also able to identify the nature of the phase.

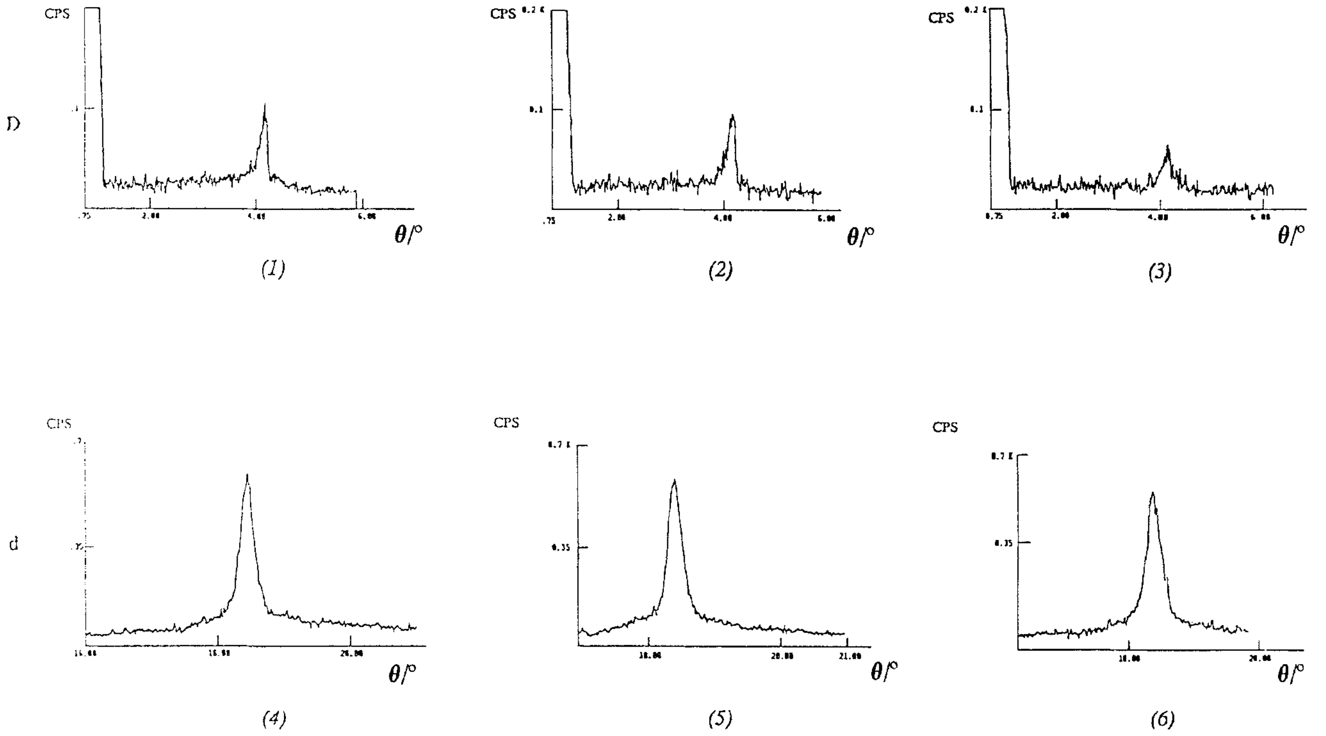
4. The structure of the smectic phase for the ASE-OS35 system

X-ray diffraction patterns of 0·01 and 0·5 M solutions of ASE dissolved in OS35 were recorded at different temperatures and are reported in figures 7 and 8. They provide evidence that in all cases the structure of the smectic phase formed by this mixture is smectic B-like. The intermolecular and the interplanar distances obtained from the wide angle and narrow angle peaks, respectively, are plotted as a function of temperature in figure 9. The shapes of the diffraction peaks for the smectic B phase of the mixture with the lowest concentration of ASE are practically identical to those obtained with pure OS35 and do not change with temperature. Furthermore, the interplanar and intermolecular distances (21·2 Å and 5·54 Å, respectively) are very close to those for pure OS35 which are 20·9 Å and 5·51 Å, respectively. The perturbation on the host structure by the solute ASE is, therefore, very limited at this range of guest concentration and no discontinuity was found in the smectic B pattern on changing temperature. The temperature at which the mixture becomes isotropic (56°C) fits the phase diagram given in figure 4 perfectly. In contrast, the smectic structure of the 0·5 M mixture is significantly different from that of the pure solvent. The peaks, and particularly the narrow angle peak, are less regular (although not larger) and shifted. For this mixture only the intermolecular distances can be determined and these are plotted in figure 9: their value are slightly larger than those found for the 0·01 M sample, but their dependence on temperature seems to be very similar.

In conclusion the NMR, LD and X-ray diffraction techniques have allowed us to determine the phase diagram for the mixture of ASE and OS35. Its smectic B phase, at the ASE concentrations used in the reactivity experiments, was found to be in equilibrium with either an isotropic or a nematic phase. The structure of the smectic phase was found to maintain, without discontinuities, the periodicities of pure OS35 far beyond the concentration of ASE employed in the kinetic measurements (see figure 5 of [19]. The deuterium NMR and LD results enabled the distribution of the guest reactant molecule between the coexistent phases to be demonstrated, while the X-ray diffraction technique probed directly the structure of the smectic catalytic host. On the basis of these studies the reactivity of ASE can now be described in the following way.

5. A model for reactivity in smectic solvents

The reactant is partitioned between the smectic and either the coexistent isotropic or nematic phases. The reaction of ASE takes place in the smectic phase, but only as long as the other cophases act as a reservoir for the reactant molecules which enter the smectic phase; they react and then leave it as a zwitterionic product. This sort of pre-equilibrium situation is in accord with the very unusual upward curvature of the Arrhenius plot [19, 23] and is able to account for the two most peculiar aspects of the ASE reactivity in OS35. First, the collapse of the second order kinetic constant with increasing concentration of ASE (see figure 5 in [19]) and secondly, the decrease of the concentration value at which the depression of the reaction rate starts (i.e. the threshold concentration) with increasing temperature, until no reaction takes place above 44°C.



(1) (2) (3)

(4) (5) (6)

Figure 7. Narrow angle (upper) and wide angle (lower) X-ray diffraction patterns of 0·01 M ASE in OS35. The temperatures were 30°C for (1) and (4), 44°C for (2) and (5) and 53°C for (3) and (6).

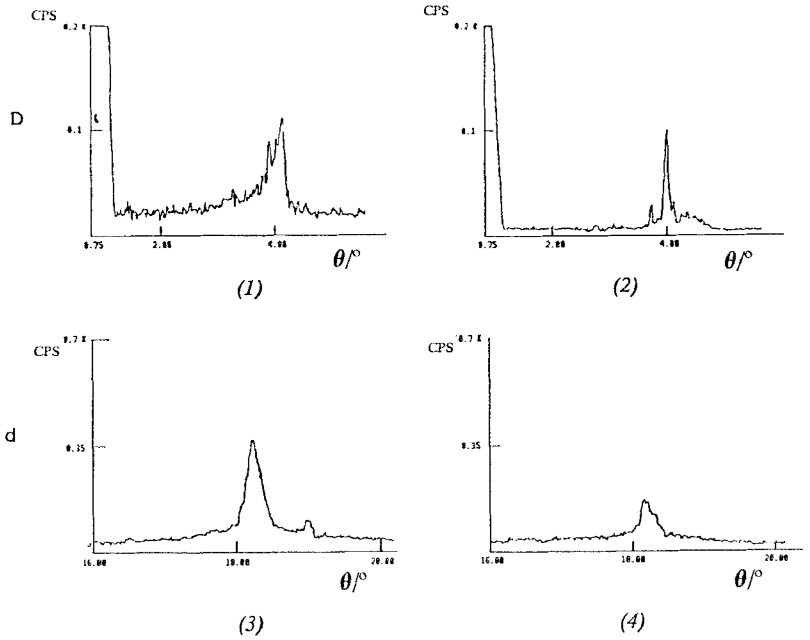


Figure 8. Narrow angle (upper) and wide angle (lower) X-ray diffraction patterns of 0·5 M ASE in OS35. The temperatures were 30°C for (1) and (3) and 44°C for (2) and (4).

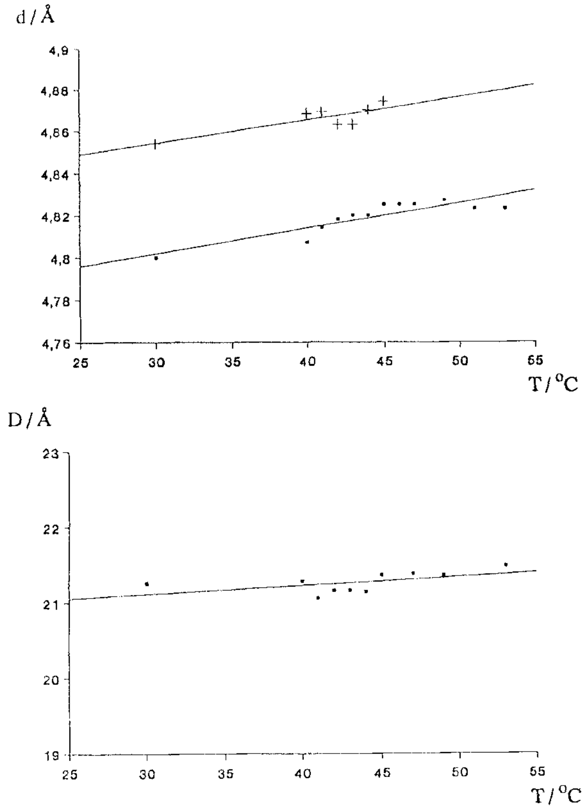


Figure 9. The intermolecular (*d*) and interplanar (*D*) distances obtained from the X-ray patterns of figures 7 and 8 plotted as a function of temperature for 0·1 M ASE (■) and 0·5 M ASE (+).

The first behaviour is due to a decrease of the relative volume of the coexisting smectic phase with increasing ASE concentration; the kinetic constant, being referred to the total concentration, therefore appears to be reduced. The second observation is likely to be determined by the disappearance, at temperatures above 44°C (see figure 4), of the region in which the coexisting smectic phase is a solution of ASE; after that the coexisting smectic phase consists essentially of pure OS35 solvent. The partition equilibrium no longer takes place and so the reactivity is blocked.

This rationalization, based on the pre-equilibrium process, suggests an analogy with the Michaelis–Menten description of the enzyme catalytic processes. In enzyme catalysis, the initial step is a complex formation between the enzyme E and the substrate S. Reaction then occurs within the ES complex. The product molecule leaves the enzyme and another reactant molecule takes its place,

$$\mathrm{E}+\mathrm{S}\rightarrow[\mathrm{ES}]\rightarrow\mathrm{E}+\mathrm{P}.$$

This scheme can be transferred to ASE reactivity where the reactant partition pre-equilibrium between the reservoir of coexisting isotropic or nematic phases and the smectic phase leads to the catalytic 'complex' $\mathrm{S_B}$-ASE

$$\mathrm{S_B}+\mathrm{ASE}\rightarrow[\mathrm{S_B}\text{-}\mathrm{ASE}]\rightarrow\mathrm{S_B}+\mathrm{ZWI}.$$

A flow of reactant molecules which enter the smectic phase, where they are dissolved, properly aligned and forced to react, takes place. As soon as they become the ionic product ZWI they are expelled from the smectic solution. In this picture, the smectic host is thus basically acting as an enzyme. At least two strict parallels between the two processes can be drawn. First, the pre-equilibrium in both cases is not rate determining; the equilibrium concentration of the 'complex' is reached before a significant fraction of the reactant is converted into the product. This sort of steady state approximation is certainly possible with a rate constant for the ASE quaternization which at 40°C is $9{\cdot}8\times10^{-5}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [23]. Secondly, the fraction of the reactant involved in the 'complex' is low. For enzymes, this occurs because of their usually very low concentration; for ASE it occurs because of its very low solubility in the coexisting smectic catalytic phase. As we have seen, concentrations below 0·5 per cent were in fact estimated from the deuterium NMR data.

However, one basic difference can be expected. The hyperbolic function of the initial velocity of an enzyme catalysed reaction versus the substrate concentration (see figure 9.14 and equation (9.171) of [28]) is not expected for ASE dissolved in OS35. In this case, in fact, the concentrations of ASE and of the coexisting smectic phase are not experimentally independent as are the concentrations of substrate and enzyme in the enzyme catalysis case.

In conclusion, by studying the mixture of ASE in OS35 with the aid of several complementary techniques such as deuterium NMR, linear dichroism, DSC, kinetic measurements and X-ray diffraction, a thorough understanding of the reactivity in smectic solvents seems, finally, to be achieved. As a result, correlations between this reactivity process and enzyme catalysis are suggested, thus opening perspectives for new experiments with liquid crystalline models of enzyme reactivity.

6. Experimental

ASE and ASE-d_2 were obtained as described previously [19, 22]. OS35 was supplied by E. Merck (Darmstadt) and used without further purification.

LD measurements were performed using a JASCO-J500 dichrograph. Samples were oriented by a magnetic field of 12 kG generated by an electromagnet placed in the cell compartment of the dichrograph, with the magnetic field perpendicular to the direction of the light beam. A thermostatted quartz cell (optical path length 1 mm) was used for the experiments. Deuterium NMR spectra were recorded on a Bruker CPX-200 spectrometer with variable temperature unit which controlled the temperature to ± 0·1°C. Standard conditions were used: 0·1 s delay between pulses; the average of at least 2500 scans and a single pulse of a few μs duration. X-ray diffraction experiments were performed by using a rotating anode generator Rigaku Denki RV300 equipped with a powder diffractometer: Ni-filtered CuKα radiation ($\lambda = 1{\cdot}54$ Å) was used. The samples, prepared at specific concentrations and left for some minutes above the melting temperature to avoid inhomogeneous mixtures, were held in a vacuum-tight cylindrical cell, fitted with two thin mica windows. The temperature was controlled with an accuracy of ± 0·5°C by using a circulation thermostat.

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