where $\phi_i$ is the angle formed by the lines joining the oxygen atom of a given molecule and those of its four nearest neighbours $j$ and $k$ ($i \neq j \neq k$). This definition is a rescaled version of the parameter introduced in ref. 4, in such a way that the average value of $\phi$ varies between 0 (in an ideal gas) and 1 (in a perfect tetrahedral network). If a molecule is located at the centre of a regular tetrahedron whose vertices are occupied by its four nearest neighbours, $\cos \phi = -1/3$. Thus, in a perfect tetrahedral network, $q = 1$. If, on the other hand, the mutual arrangement of molecules is random, as in an ideal gas, the six angles associated with the central molecule are independent, and the mean value of $\phi$ vanishes:

$$q = 1 - \frac{9}{8} \cos^3 \frac{\phi}{1} \sin \phi d \phi = 0$$

Alternative measures of order can be used. They do not change the general picture shown in Fig. 4. We have tested the ‘tetrahedrality parameter’ of ref. 31 as an alternative measure of orientational order, and the two-body excess entropy of ref. 32 as an alternative which the properties of interest were sampled every 40 ps.

Molecular dynamics simulations

Our results are based on constant temperature and density molecular dynamics simulations of 256 particles interacting via the shifted-force SPC/E potential in a cubic box with periodic boundary conditions. The Ewald summation was used to account for electrostatic interactions. The Lennard–Jones potential and real-space part of the Ewald summation were cut and linearly shifted to bring the energy and force to zero at a distance of 7.9 Å. The temperature was maintained using a Berendsen rescaling of the velocities and the density was within 1.7% of that of liquid water.

Isochores of the transport and thermodynamic anomalies occur over the broadest range of densities and temperatures and anticipate the occurrence of transport and thermodynamic anomalies.

Location of diffusivity extrema

Isochores of the $T \geq 300$ K data were fitted to the power law $D(T) = D_0(T - T_0)^{-\gamma}$, where $D_0$, $T_0$, and $\gamma$ are density-dependent adjustable parameters. Subsequently, the diffusivity minima were located from spline fits to isotherms generated by the power-law functions, and the diffusivity maxima were obtained from fifth-order polynomial fits to the isotherms. The temperatures of maximum density (squares in Fig. 4) were obtained from a Berendsen rescaling of the velocities with a relaxation time of 0.5 ps, and the equations of motion were solved using the velocity-Verlet and the RATTLE algorithm with a time step of 2 fs (ref. 33). For each of the densities examined, initial configurations were generated randomly and equilibrated using Monte Carlo techniques at the highest temperature considered in this study. 400 K Molecular dynamics simulations were started using the final particle positions of a previous simulation at a state point as near as possible to the new one. Each system was equilibrated for between 0.5 and 15 ns, depending on the state point, followed by a production phase (of length greater than or equal to the equilibration phase), during which the properties of interest were sampled every 40 ps.

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**Transparent nematic phase in a liquid-crystal-based microemulsion**

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Complex fluids are usually produced by mixing together several distinct components, the interactions between which can give rise to unusual optical and rheological properties of the system as a whole. For example, the properties of microemulsions (composed of water, oil and surfactants) are determined by the microscopic structural organization of the fluid that occurs owing to phase separation of the component elements. Here we investigate the effect of introducing an additional organizing factor into such a fluid system, by replacing the oil component of a conventional water-in-oil microemulsion with an intrinsically anisotropic fluid—namely liquid crystal. As with the conventional case, the fluid phase-separates into an emulsion of water microdroplets (stabilized by the surfactant as inverse micelles) dispersed in the ‘oil’ phase. But the properties are further influenced by a significant directional coupling between the liquid-crystal molecules and the surfactant tails that emerge (essentially radially) from the micelles. The result is a modified bulk-liquid crystal that is an ordered nematic at the mesoscopic level, but which does not exhibit the strong light scattering generally associated with bulk nematic order; the bulk material here is essentially isotropic and thus transparent.

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Complex fluids\textsuperscript{1,2} are generally multi-component mixtures. They sometimes possess mixed physical properties of their elements, but in many cases new properties emerge, reflecting the new structural organization of their elements. This aspect of complex fluids has recently been investigated using colloidal particles in liquid crystals\textsuperscript{3}, ferrosmectics\textsuperscript{4} and polymer-doped liquid crystals\textsuperscript{5}. Here we focus on microemulsion, a typical complex fluid. Microemulsion is defined as a mixture of three essential components: two immiscible liquids and surfactant molecules. Typical examples are water-in-oil or oil-in-water emulsions. In the former, microdroplets of water (inverse micelles) are dispersed in oil, while in the latter microdroplets of oil are dispersed in water. The rheological properties of two liquids and the microstructure of phase-separating liquids (size and shape of domains and their spatial distribution) strongly affect the physical properties of the resulting microemulsions\textsuperscript{6}.

Recently, the physical properties of spatially confined nematic liquid crystals\textsuperscript{7,8} and nematic elastomers (ref. 13 and references therein, and ref. 14) have been intensively studied to reveal the elastic distortion effects induced by spatial confinement and random disorder on phase transitions of liquid crystals. We expect a nematic microemulsion to provide a new random disorder effect on nematic ordering, essentially different from nematic emulsions and microemulsions.

We study here a lyotropic inverse micelle phase composed of water, oil (thermotropic liquid crystal, pentylenecyanobiphenyl, 5CB) and surfactant (dodecyl dimethyl ammonium bromide, DDAB). When 5CB is in the isotropic phase, this system is equivalent to conventional water-in-oil microemulsions. However, when nematic ordering occurs below an isotropic to nematic (I–N) transition temperature (\(T_{\text{IN}}\)), inverse micelles disperse in the nematic medium disturb long-range nematic order. Thus, we expect that a new type of superstructure may be produced by the strong anchoring effects of inverse micelles on nematic directors.

The composition of a mixture can be characterized by the weight fraction of DDAB in the lyotropic liquid crystal (DDAB+water), \(\phi_{\text{am}}\) and the weight fraction of 5CB to the total sample weight, \(1 - \phi\). Two characteristic lengths, the radius of an inverse micelle \(a\) and the intermicellar distance \(d\), can then be controlled independently by changing two concentrations, \(\phi_{\text{am}}\) and \(\phi\), respectively, as \(a = \delta(3 - 2\phi)d\phi_{\text{am}}\) and \(d = (4\pi/3\delta)^{1/3}a\), where \(\delta\) is the length of a DDAB molecule. In our experiments, we fixed \(\phi_{\text{am}}\) to be 85\%, so that \(\phi\) is kept constant (\(\phi \approx 0.19\ mm\)). By changing \(\phi\) from 0.02 to 0.5, we can vary \(d\) from \(~1\ mm\) to the inverse micelle size (\(~2a\)). For large \(\phi\), the average distance between inverse micelles is thus only a few times longer than the length of a 5CB molecule. It should be noted that for \(\phi > 0.3\) there may be a shape transition of inverse micelles from spherical to rodlike (cylindrical) micelles. The results for \(\phi > 0.3\) will be presented elsewhere.

To study the phase behaviour of liquid-crystal microemulsions, we performed differential scanning calorimetry (DSC) measurements. The results are shown in Fig. 1. For mixtures, there appear two distinct peaks, indicating the existence of two thermodynamic transitions. We observed the phase behaviour with polarizing microscopy. The results are shown in Fig. 2. We can clearly see phase separation accompanying the appearance of birefringent nematic droplets below the onset temperature of the second DSC peak (\(T_{\text{PS}}\)) (see Figs 2c and d). Thus, the second DSC peak is assigned to this phase separation. The first peak is assigned to the I–N transition because it becomes the I–N transition peak in the limit of \(\phi \rightarrow 0\). A mixture always looks isotropic in visible light above \(T_{\text{PS}}\) and there is no visible change across the I–N transition under polarizing microscopic observation (see Figs 2a and b); this strongly indicates that in the temperature region between the onset temperature of the first peak (\(T_{\text{IN}}\)) and that of the second one (\(T_{\text{PS}}\)), there exists a new phase, which is isotropic at a large length scale, but locally has nematic order. This optically isotropic nature may be realized because nematic fluctuations are pinned as in the case of nematic elastomers. We call this new phase the transparent nematic (TN) phase. A typical distance between inverse micelles is much shorter than visible light wavelengths, and inverse micelles do not aggregate in this phase, so that there is no true long-range nematic order in the usual sense. At the same time, however, the distinct DSC peak just below \(T_{\text{IN}}\) indicates that this phase has a nematic order, at least locally. Thus we conclude that the TN phase macroscopically exhibits isotropic nature, but locally possesses nematic order. Below \(T_{\text{PS}}\), the system phase separates into nematic (N) and TN phases. The nematic droplets emerging from the TN phase are strongly birefringent (see Figs 2c and d), as expected.

To unambiguously establish that the TN phase is optically transparent, we also made direct visual observation of a macroscopic sample in a glass tube with a diameter of 10 mm, immersed in a temperature-controlled bath. The temperature was calibrated by using the I–N transition of pure 5CB. We confirm that the sample is optically transparent and does not have any turbidity even below \(T_{\text{IN}}\) as long as the temperature is above \(T_{\text{PS}}\). At \(T_{\text{PS}}\), the system becomes completely turbid upon cooling. This conclusion is supported below.

We made dynamic polarized light scattering measurements of a macroscopic sample whose dimensions are about 10 mm \times 10 mm \times 30 mm. We note that the system is completely homogeneous on the macroscopic scale and there is no noticeable change in the scattering intensity above \(T_{\text{PS}}\). The temperature dependence of the scattered intensity for \(\phi = 0.071\) is shown in Fig. 3. Thus, we re-confirm that the TN phase is optically transparent and completely homogeneous above \(T_{\text{PS}}\). The transparency of the TN phase is comparable to that of the isotropic phase. The time correlation

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**Figure 1** Concentration dependence of differential scanning calorimetry scans. The cooling rate was fixed at 0.3°C min\(^{-1}\). Although only one peak is observed at \(T_{\text{IN}}\) for pure 5CB, two distinct peaks are detected for mixtures. The heat flow is scaled by the total amount (weight) of 5CB in a mixture. We take the onset of the increase of heat flow upon cooling as a transition temperature (\(T_{\text{PS}}(\phi)\)). The lower temperature transition (\(T_{\text{PS}}(\phi)\)) is assigned to phase separation by comparing it with the polarizing microscopic observation (see Fig. 2), while the higher temperature one is assigned to the isotropic–nematic transition as it is extrapolated to \(T_{\text{PS}}\) of pure 5CB in a dilute limit of the inverse micelle concentration.
function of composition fluctuations, \( S(q,t) \) (where \( q \) is wave number) is well described by a single exponential function: 
\[
S(q,t) = S(q,0) \exp(-2\Gamma t)
\]
where \( \Gamma \) is the decay rate of composition fluctuations. Thus, we obtain \( \Gamma \) by fitting an exponential function to the observed time correlation function. The temperature dependence of \( \Gamma \) for \( \phi = 0.071 \) is shown in Fig. 3. \( \Gamma \) decreases upon cooling till \( T_{IN} \) but increases below \( T_{IN} \). We found that this distinct minimum of \( \Gamma \) is located at \( T_{IN} \), independently determined by DSC. This feature is also observed for \( \phi = 0.063 \). Thus, we suppose that the observed minimum of \( \Gamma \) reflects the phase transition between the two optically transparent phases, the isotropic phase and the TN phase. We speculate that the increase of \( \Gamma \) below \( T_{IN} \) is due to long-range repulsive interactions between micelles mediated by medium-range liquid-crystalline order. In relation to this, we briefly discuss the origin of the decay of composition fluctuations. The diffusion constant \( D \) estimated from the relation \( D = \frac{k_bT}{6\pi\eta a} \), where \( k_b \) is Boltzmann’s constant and \( \eta \) is the shear viscosity. This suggests that the decay is primarily due to the diffusional motion of inverse micelles in 5CB. However, we need to study the \( q \) dependence of \( \Gamma \) for a conclusive argument. In particular, we need such information to clarify the dynamics of inverse micelles in a transparent nematic phase below \( T_{IN} \), which may not be described by simple diffusion. This point will be studied in the near future. Because dynamic light scattering experiments are made in an equilibrium state (we wait about an hour at each temperature for equilibration), we can say that there exists a well defined thermodynamic transition between the isotropic and TN phases. That is, the TN phase is not a metastable phase (such as a supercooled isotropic phase), but a new thermodynamic phase with local nematic order. Below \( T_{PS} \), the system becomes turbid because of phase separation. After several hours, it macroscopically phase-separates into two phases, the transparent TN phase (top) and the milky nematic phase (bottom), due to gravity.

To summarize all the experimental observations, a phase diagram is constructed as shown in Fig. 4. Here we also include the transition temperatures determined from the change in the temperature dependence of the intensity of static depolarized light scattering (data not shown). It demonstrates the \( \phi \) dependence of \( T_{IN}(\phi) \) and \( T_{PS}(\phi) \), observed by various methods. The \( N-\cdot TN \) phase separation may be induced by competition between the elastic energy due to distortion and the entropy associated with the spatial configuration of inverse micelles. With decreasing \( T \), the deformation costs more elastic energy, owing to further nematic ordering. Thus, a homogeneous transparent nematic phase becomes unstable and eventually phase-separates into an almost pure nematic phase and an isotropic TN phase filled with concentrated inverse micelles. The physical mechanism responsible for the new TN phase, or the \( I-\cdot TN \) transition, is not clear, although it may be true that the distortion of the director fields by inverse micelles is crucial to the appearance of the TN phase.

Now we propose an internal structure of this new phase, provided that liquid-crystal molecules are strongly anchored normal to the surface of an inverse micelle and that nematic directors are thus locally distorted by randomly dispersed inverse micelles. It is known that the relevant length of anchoring is given by \( a_s \sim K/W \) (where \( W \) is molecular anchoring strength)\(^1\). Thus, \( W \) should be of the order of \( 10^{-8} \text{N m}^{-1} \) to realize strong anchoring in our system, provided that the characteristic length scale \( a_s \) is the order of 10 nm. This value corresponds to the upper limit of \( W \) reported so far\(^1\). We note that \( W \) for the interface between water and 5CB in the presence
Figure 4 The $\phi - T$ phase diagram determined by experiment. Shown are experimental data from microscopic observation, static depolarized and dynamic polarized light scattering, and DSC measurements, together with the theoretical prediction (solid line) for $T_{IN}$. $N$ and $PS$ stand for isotropic–nematic phase transition and phase separation, respectively. The horizontal axis represents the characteristic quantity, $\phi^{2/3}$ (see text). A dotted line represents the phase-separation boundary and is drawn as a guide to the eye. We also show schematic figures of the states of microemulsion above $T_{IN}(\phi)$, below $T_{IN}$ but above $T_{TN}(\phi)$, and below $T_{PS}(\phi)$. We assume that nematic liquid crystal is strongly anchored to inverse micelles (see text).

of the surfactant sodium dodecyl sulphate has been shown to be larger than $10^{-3}$ m$^{-1}$. According to ref. 15, the control parameter $W_a/k$ is proportional to $Q^{-1}$ (where $Q$ is the orientational order parameter) and increases as $Q \rightarrow 0$. It should be noted that $Q$ may be small in the TN phase, as it is located near the $I-N$ transition temperature. Thus, a strong-anchoring situation might be possible for our TN phase, although it seems rather too strong if we note that the inverse micelle itself is stabilized by the surface energy of the similar strength. If we focus on the random disorder effects of inverse micelles on nematic director fields through such strong anchoring, we can speculate that the $I-N$ transition temperature decreases as a result of the disturbance to the nematic ordering induced by inverse micelles, as the system has to pay an extra energy cost associated with the distortion of nematic director fields around inverse micelles. The characteristic curvature associated with the deformation of director fields may be roughly the inverse of the intermicellar distance, which is estimated as $(3\phi/(4\pi a^3))^{1/3}$. Following ref. 18, the $I-N$ transition temperature, $T_{IN}(\phi)$, is expected to be shifted downward from $T_{IN}$ of the pure system, $T_{IN}(0)$, by $(K/A)(3/(4\pi a^3)\phi)^{2/3}$, where $K$ is the Frank elastic constant and $A$ is a constant. As shown in Fig. 4, the agreement between the prediction that $T_{IN}(0) - T_{IN}(\phi) \propto \phi^{2/3}$ and the experimental results is satisfactory. However, the validity of this simple argument should be checked more carefully, as (1) the assumption of the strong anchoring might not be the case, as mentioned above, and (2) the applicability of the mean-field coarse-grained model to our system, which is characterized by the mesoscopic length scale, is not obvious. Here we point out another possible scenario, which focuses on topological ordering effects instead of disorder effects. A 'topologically ordered' isotropic phase has been predicted to form between the conventional isotropic and nematic phase at large suppression of topological defects and weak nematic interactions. Our new phase may be connected to this 'topologically ordered' isotropic phase. Further experimental and theoretical studies are necessary to elucidate the physical mechanism responsible for the appearance of the TN phase.

We hope that this study will provide a new way of constructing useful exotic complex fluids. We speculate that external shear deformation or magnetic fields induce global nematic order, or the breakdown of the rotational symmetry in a length scale smaller than light wavelengths. Such a field-induced transition has recently been predicted theoretically for frustrated systems such as nematic elastomers and spin glass.

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Increased thermohaline stratification as a possible cause for an ocean anoxic event in the Cretaceous period

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Ocean anoxic events were periods of high carbon burial that led to drawdown of atmospheric carbon dioxide, lowering of bottom-water oxygen concentrations and, in many cases, significant biological extinction. Most ocean anoxic events are thought to be caused by high productivity and export of carbon from surface waters which is then preserved in organic-rich sediments, known as black shales. But the factors that triggered some of these events remain uncertain. Here we present stable isotope data from a mid-Cretaceous ocean anoxic event that occurred 112 Myr ago, and that point to increased thermohaline stratification as the probable cause. Ocean anoxic event 1b is associated with an increase in surface-water temperatures and runoff that led to decreased bottom-water formation and elevated carbon burial in the restricted basins of the western Tethys and North Atlantic. This event is in many ways similar to that which led to the more recent Plio-Pleistocene Mediterranean sapropels, but the greater geographical extent and longer duration (~46 kyr) of ocean anoxic event 1b suggest that processes leading to such ocean anoxic events in the North Atlantic and western Tethys were able to act over a much larger region, and sequester far more carbon, than any of the Quaternary sapropels.

The mid-Cretaceous is associated with ocean anoxic events (OAEs)—periods of elevated carbon burial in marine sediments known primarily from Tethyan basins, the Atlantic and equatorial Pacific. These events have been interpreted as the result of increased surface-water productivity caused by nutrient leaching of flooded lowlands during transgressions and/or increased continental runoff due to an accelerated hydrological cycle. Recent high-resolution stable isotope studies suggest an intensified vertical mixing and warming of the water column as a cause for the observed productivity increase during early Aptian OAE 1a and late Albian OAE 1d. For OAE 1d, this intensified mixing is expressed by decreased vertical isotopic gradients and a warming of the entire water-column. High-resolution stable isotope studies on planktic and benthic foraminifers indicate that a bathyal warming and vertical mixing may have caused OAE 2 and its associated extinctions. Or some of the OAEs may reflect decreased vertical mixing and the development of euxinic conditions throughout the water column that permits organic carbon to accumulate on the sea floor.

Ocean Drilling Program (ODP) Leg 171 B drilled mid-Cretaceous black shales of Albian age in the western subtropical Atlantic, off Florida. ODP Hole 1049C recovered Aptian to Eocene sediments, including a 46-cm-thick succession of laminated black shale, representing early Albian OAE 1b (ref. 13). Total organic carbon (TOC) contents in laminated black shales range from 0.5 to 13.2% (ref. 14). The record of OAE 1b at Site 1049 is unusual for most OAE sediments because the foraminifera are extremely well preserved and can be used to study the geochemical record of the event. Both planktic and benthic species have glassy shells with preserved surface ornamentation and without infilling calcite. In addition, the stable isotope signature of individual species suggests that stable isotopic ratios were not homogenized, which would be expected for diagenetically altered calcite.

Oxygen isotope values for the planktic species Hedbergella aff. Hedbergella trocoudae are consistently more negative by 0.7 to 0.1% than oxygen isotope values heavier by 0.60 to 0.05% than for the planktic species Hedbergella specotenosis tuviensis, suggesting a deeper habitat for the latter (see Supplementary Information). Benthic species show a constant offset of carbon isotopes with heavier values for Osangularia schloenbachii and negative values for Gyrodinoides nitidus. This suggests an infaunal habitat for G. nitidus and an epifaunal mode of life for O. schloenbachii, as infaunal forms tend to yield more negative signals owing to the enrichment of the pore waters with isotopically negative carbon that is derived from oxygenized organic carbon.

We identified four intervals (events I to IV, Fig. 1) that represent significant changes in ocean temperature, salinity and carbon flux during the OAE.

Event I is characterized by stable carbon and oxygen isotope values. Oxygen isotope values are surprisingly positive, suggesting either very cool surface and deep-water temperatures (around 12°C for surface water and 9°C for bottom water of an upper bathyal water depth around ~1,000 m) and/or high salinities before the black shale. In addition, oxygen and carbon isotope gradients between the surface and bottom water are very small, indicating a uniform water mass in the upper 1,000 m of the water column during this phase.

Event II marks a large 1.6%o negative oxygen isotopic shift in planktic foraminifers below the base of the black shale. This decrease is paralleled by a 0.9%o increase of planktic 813C values, followed by a decrease of the same magnitude at the base of the black shale. Benthic values in this interval remain relatively constant for the carbon isotopes, but oxygen isotopic values of benthic foraminifers show a slight decrease in the lowermost part of the black shale that occurs later than the negative shift of planktic foraminifers. The steep decrease in oxygen isotope values below the black shale is difficult to explain with a rise of sea surface temperatures only, as it would reflect a geologically rapid and significant rise of approximately 10°C. However, this decrease could be explained by a combination of salinity decrease and temperature increase of surface waters. The small increase in the vertical carbon gradient may point to an increase of surface-water productivity before the black shale, leading to increased carbon export and greater carbon isotope gradients between surface and bottom water. This interpretation is supported by the synchronous presence of benthic foraminifers that indicate high organic carbon fluxes to the sea floor. The decrease of carbon isotope values at the base of the black shale is difficult to explain, but might be connected to the presence of negative organic carbon in the black shale. However, constant sedimentation rates and the lack of compositional changes...