Electrolyte Effects on the Stability of Nematic and Lamellar Lyotropic Liquid Crystal Phases: Colligative and Ion-Specific Aspects

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Received: February 26, 2009; Revised Manuscript Received: June 12, 2009

We investigated the electrolyte effects on the stability of nematic and lamellar lyotropic liquid crystalline (LLC) phases formed by the simple anionic surfactant cesium pentadecafluorooctanoate (CsPFO) in water. To the lyotropic guest phase, at the constant CsPFO-mass fraction of 0.55, the series of electrolytes LiCl, NaCl, KCl, CsCl, CsI, and Cs_2SO_4, respectively, was added at concentrations ranging from 0.5 to 2.5 mol %. With increasing electrolyte concentration two substantially different effects were observed. At low concentrations all added electrolytes caused an increase of the thermal stability of the LLC phases, favoring the lamellar phase over the nematic phase. This behavior is, at least qualitatively, understood within the packing parameter model. The extent of the stabilization clearly depends on the chemical nature of the added cation. For a given cation, however, the effect is colligative, i.e., independent of the chemical nature of the added anion. At higher salt concentrations a salting-out-like phase separation was induced. This effect is clearly ion-specific as the salting-out concentration varied for each cation following the order of the Hofmeister series for cations.

Introduction

Lyotropic liquid crystalline (LLC) phases occur in solutions of amphiphiles in isotropic solvents depending on temperature and amphiphile concentration. In the present work we focus on aqueous solutions of ionic amphiphiles, i.e., amphiphiles with ionic head groups. With increasing concentration the amphiphiles aggregate in such a way that only the ionic head groups are in contact with the water making the whole aggregate soluble. The apolar amphiphile parts constitute the core of the aggregate. In a nematic LLC phase (N) the aggregates are discrete anisometric micelles of rod-like or disk-like shape which exhibit long-range orientational order of their principal axes along a preferred direction, the so-called director **n** (see Figure 1). At lower temperature or higher amphiphile concentrations a lamellar phase (L_α) can form which consists of stacks of flat elongated aggregates, amphiphile double-layers, separated by water layers. The index α indicates that the apolar tails are in a fluid-like state.

Ions added to an aqueous micellar amphiphile solution act via basically two mechanisms.[1] The strong hydration tendency of the added ions reduces the amount of "free water" available for the solvation of head groups at the aggregate surface. The electrostatic properties of the added ions modify the dielectric properties of the isotropic solvent and thereby the repulsion interaction between equally charged aggregates as well as the electrostatic repulsion between adjacent head groups at the micelle surface. Both processes involve a rich variety of enthalpic and entropic contributions, making it difficult to pre-estimate the net salt effect or at least the dominant salt effect in a given system. In any case, substantial changes of the phase
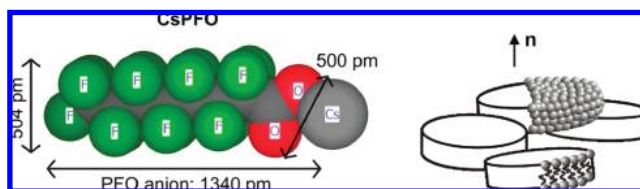

Figure 1. Left: Calotte model of the cesium perfluorooctanoate (CsPFO) molecule, geometrically optimized. The approximate diameters of the perfluoro chain and the carboxylate head group are given, as well as the approximate length of the perfluorooctanoate (PFO^-) anion. The atoms without labels are carbon atoms. Right: schematic drawing of disk-like micelles in a nematic phase with orientational order along the director **n**.

properties can be expected due to added salts. In fact, it has been found that adding electrolytes to a LLC phase significantly influences the thermal stability[2] as well as various other properties, like, e.g., structural parameters,[3] the orientational order,[4] or the properties of the nematic−isotropic phase transition.[5] The effects of additional salt on the stability of the LLC state of matter are of particular interest since they provide a deeper understanding of the role and nature of electrostatic interactions in this complex form of soft matter.

Already in the 1920s McBain and co-workers studied salt effects in soap/water systems in which several LLC phases are present.[2,6] The authors' interest was rather directed toward the applicability of Gibb's phase rule and the understanding of the soap-boiling process. Nevertheless, their data provide the first documentation of electrolyte effects on the stability of LLC phases. An analysis of their ternary phase diagrams for the lyotropic system composed of sodium palmitate/H_2O/NaCl at various temperatures reveals that, for a fixed soap/water ratio, the lamellar L_α-phase (formerly called "neat phase") is thermally stabilized for low concentrations of the added NaCl.[6] At higher salt concentrations phase separation occurs. The hexagonal phase ("middle phase") is destabilized even at low salt concentrations. The latter finding was also reported by Gault et al.[7] for the

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addition of electrolytes to the hexagonal phases formed by various cationic amphiphiles in water.

In the present work, we concentrate on the LLC phases occurring in aqueous solutions of the simple anionic amphiphile cesium pentadecafluoro-octanoate (CsPFO); see Figure 1 for the molecular structure. The CsPFO/water phase diagram—first investigated by Boden et al. in 1979[8] and refined in numerous subsequent investigations, e.g., refs 9–12—possesses with decreasing temperature or increasing CsPFO concentration an isotropic micellar phase of disk-like micelles,[13–15] a nematic phase of again disk-like micelles as well as a lamellar phase, which is discussed to bear defects in the lamellae ("water holes")[11] or even to consist of positionally ordered disk-like aggregates.[13] The nematic phase is stable over a remarkably large range of temperatures and amphiphile concentrations compared to other LLC systems. In addition, the system exhibits the rare case among lyotropic systems of a thermal transition between the lamellar phase and the nematic phase allowing the investigation of electrolyte effects on both phases. Previous studies on the influence of adding salt to the CsPFO/water system[3,16–19] revealed that the added electrolytes lead to a thermal stabilization in both the lamellar and the nematic phase, while at high salt concentrations the nematic phase vanishes in favor of the lamellar phase.[3,18] However, the nature of the salts was barely varied since only CsCl or CsOH were added.

The thermal stabilization of the L_{α}-phase with increasing electrolyte concentration is described by Mukherjee et al. with a phenomenological theory on the lamellar-nematic phase transition using a Landau free energy expansion which included a coupling between electrolyte-concentration variables and the orientational order parameter.[20] Within a similar theoretical approach to the salt effect on the nematic–isotropic transition Mukherjee et al. found a quadratic increase of the clearing temperature, i.e., the temperature of the isotropic–nematic transition, with increasing electrolyte concentration.[21] Both theories fit experimental data quite well; however, they do not provide any mechanistic model via which the added ions are supposed to act on a molecular scale. Nor does Mukherjee's theoretical approach account for chemically different electrolytes or for the salt effects observed at high salt concentration, like, e.g., the phase separation[3,6] or the destabilization of the nematic phase.[3]

An intuitive model to understand the salt-induced thermal stabilization of the nematic and the lamellar phase on a molecular scale can be derived from the well-known packing parameter, first proposed by Tartar[22] and further developed by Tanford,[23] which Israelachvili[24] introduced into his thermodynamic theory on isotropic micellar solutions to explain the existence of nonspherical micelles. The packing parameter accounts for the average geometry of an aggregated amphiphile expressed as ratio of the head group diameter and the diameter of the apolar amphiphile tail. Israelachvili related a change in this size ratio to a change of the aggregate shape. For the addition of salts he discussed that added counterions screen the intra-aggregate repulsions, i.e., electrostatic repulsions between ionic head groups at the same aggregate surface. This makes smaller head group diameters possible and, thus, favors the growth of disk-like micelles and aggregates with less curved geometries, like, e.g., lamellae. We will discuss the packing parameter later in more detail and show that it also accounts for the salt-induced thermal stabilization of the nematic and lamellar LLC phases since, according to Boden and Gelbart,[25] the growth of the micelle concerning its size and its anisotropy thermally stabilizes the LLC state.

As the electrostatic screening is mainly a function of charge and concentration of the added counterions the electrolyte-induced thermal stabilization of LLC phases could be expected to be independent of the chemical nature of the added counterion. In the light of these considerations this salt effect could most interestingly bear characteristics of a colligative effect, like, e.g., the well-known freezing point depression. To clarify this issue, careful investigations of the influence on LLC phases induced by systematically varied electrolytes at different concentrations are required. However, to our knowledge there are only few such studies, none of which deals with a simple ionic amphiphile like is CsPFO.

Attard et al. investigated the influence of a series of different electrolytes added over a broad concentration range to the lamellar phase of a cationic amphotropic amphiphile in water.[26] The issue of a colligative character of the salt-induced thermal stabilization of the lamellar phase unfortunately remains unresolved within Attard's work as mainly kinetic penetration scans and not equilibrium phase diagrams were recorded. Rather interesting, however, is another finding of the authors. For higher electrolyte concentrations they observed a destabilization of the LLC state in terms of a phase separation similar to the "salting-out" phenomenon known for protein solutions. The salting-out concentration was found to depend on the chemical nature of the added counterions which thereby could be ordered following the well-known Hofmeister series established for the salting-out strength of anions in protein solutions.[27] This particular salt-induced phase separation is obviously not a colligative effect. Similar ion-specific influences of electrolytes are known and exploited for the synthesis of mesoporous materials.[28] Focused on this important application Leontidis has reviewed the Hofmeister anion effects of electrolytes added to lyotropic systems with cationic and non-ionic amphiphiles. The electrolytes are found to generally increase the stability of the calcinated material but the possibly colligative or ion-specific mechanisms behind are barely discussed, apparently due to insufficient data.

Evidence that salt effects can bear both colligative and ion-specific characteristics at the same time was reported by Kostko and co-workers.[29] They studied the influence of a remarkable diversity of electrolytes on the stability of a chromonic nematic LLC phase formed by an anionic amphiphile in water. With increasing salt concentration a thermal stabilization of the LLC phase was found to be, on the one hand, dependent on the salt concentration but independent of the chemical nature of the added anion, thus indicating a colligative effect. On the other hand, the extent of the stabilization differed for each cation (i.e., the counterion to the amphiphile). Since this ion-specific salt effect did not follow the Hofmeister series for cations it was interpreted by the authors with respect to the particular inner structure of the chromonic nematic phase where disk-shaped amphiphiles are stacked into columns which order in a nematic way. According to Kostko et al. the added cations stabilize the LLC phase if they improve the stack aggregation by coordinating the amphiphiles.

Recently, Park et al.[30] reported a detailed study of the salt effects on the nematic phase in another chromonic LLC with anionic amphiphiles. Like Kostko they found an increase of the clearing point due to added salt, which was attributed to a salt-induced screening of the intra-aggregate repulsion and a subsequent growth of the aggregates. In contrast to Kostko, however, the nature of added anions showed an influence on the extent of the thermal stabilization, at least in the case of $MgSO_4$ compared to $MgCl_2$. Park et al. discuss the higher

hydration tendency of the sulfate ion as the origin behind this ion-specific effect. Via X-ray scattering Park could further identify another electrolyte effect onto their system. The correlation length was found to increase with added salt concomitant with a decrease of the inter-aggregate distance. This microstructural salt effect was interpreted as screening of inter-aggregate repulsions. A strong salt effect on the inter-aggregate interaction is also apparent from a substantial increase (by 3 orders of magnitude) of the viscosity reported by Prasad et al.[31] who added only 20 mM NaCl to a nematic chromonic LLC. It remains an open question to what extent the observations on chromonic LLCs apply also to LLCs from simple ionic amphiphiles.

To elucidate the possible colligative and ion-specific contributions to the thermal stabilization in nematic and lamellar LLC phases of simple ionic amphiphiles, we here present investigations of the influence of a series of electrolytes on the lyotropic phase behavior of the simple anionic amphiphile cesium pentadecafluoro-octanoate (CsPFO) in water. The electrolytes LiCl, NaCl, KCl, and CsCl were added to systematically vary the potential counterion of the amphiphile anions. We further selected CsI and Cs_2SO_4 to study the effect of varying the added anion and its valency. For all added salts quasi-binary phase diagrams were recorded for a fixed CsPFO–water ratio and various electrolyte concentrations. The results reveal that two electrolyte effects (thermal stabilization and phase separation) occur. The stabilization of the LLC state at low salt concentrations is not a simple colligative effect but mainly depends on the chemical nature of the added counterion (here the cation). At higher electrolyte concentration an ion-specific destabilization in terms of a salting-out like phase separation takes place.

Experimental Section

CsPFO was prepared by neutralizing the corresponding acid with an aqueous solution of cesium hydroxide monohydrate. After filtration, the aqueous solution was twice washed with hexane and the water was evaporated. The pulverized off-white product was dried overnight at 105 °C. Its purity was confirmed by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA), both methods showing a single decomposition point at 228 °C (literature: ~222 °C[32]).

Samples were prepared by carefully weighing out the electrolyte, CsPFO, and bidistilled water into small cylindrical glass vials. The CsPFO/H_2O mass ratio was kept constant at 55/45 for all samples while the electrolyte concentration was varied from $x = 0$ to 2.5 mol %. Homogeneous liquid crystalline solutions were obtained after equilibrating the samples at 40 °C for 24 h. These were then filled into rectangular capillaries (Camlab Microslides, thickness: 100 μm) by capillary action. The capillaries were sealed with an epoxy glue.

Transition temperatures and the nature of the present phase(s) were determined by means of temperature dependent texture observations using a polarizing microscope (Olympus BH-2) and a hot stage (Mettler FP 52). The samples were continuously heated at a rate of 1 K/min from room temperature to the isotropic phase while changes of the texture were recorded with a digital video camera (Sony Handycam DCR-HC85E). The temperatures determined via this efficient technique are in accordance with those obtained by very slow heating. This confirms that the chosen heating rate provides equilibrium conditions. The estimated total accuracy of the transition temperatures including effects due to concentration uncertainties is about ±2.0 K.

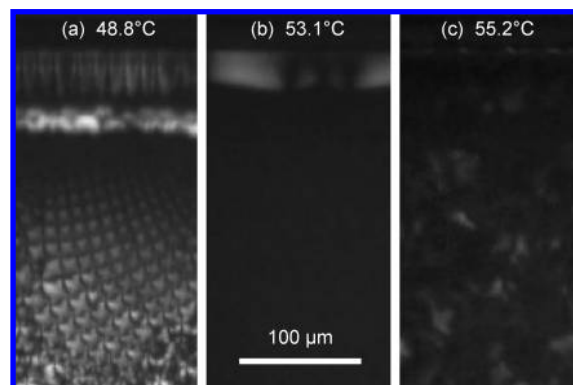To derive the molecular dimensions the CsPFO molecule was geometrically optimized using the MM2 force field method and

Figure 2. Textures observed in the salt free CsPFO/H_2O sample (mass ratio 55/45). The dark stripe in the upper part of the photographs is the capillary edge. (a) The lamellar phase with typical focal-conic defects. (b) While the nematic phase aligned mainly homeotropically, a characteristic Schlieren texture developed at the capillary edge. (c) In the nematic isotropic two-phase region the homeotropic alignment breaks up and circular isotropic droplets start to grow.

the van-der-Waals radii implemented into Chem3D Pro (Cambridge Soft).

Results and Discussion

In the salt-free CsPFO/H_2O reference sample a lamellar and a nematic LLC phase as well as a small nematic–isotropic two-phase region could be identified from the texture micrographs (see Figure 2). Similar textures were observed in the other samples, allowing the identification of the phases and of the phase transitions for each composition. The phase behavior of all investigated lyotropic solutions for different electrolytes and electrolyte concentrations are given in Figure 3 in the form of quasi-binary phase diagrams, i.e., plots of the measured transition temperatures against the electrolyte concentration. A qualitative analysis of the phase diagrams reveals several effects induced by the electrolytes.

(i) In general, with increasing concentration all added salts lead to an increase of the clearing points, thus, to a stabilization of the liquid crystalline state. At moderate electrolyte concentrations, i.e., 1.0 mol % $\leq x$(salt) $\leq$ 1.5 mol %, all transition temperatures are raised by some 10 K.

(ii) With increasing salt concentration the lamellar phase is stabilized at the expense of the nematic phase as observed for potassium chloride and the three cesium electrolytes. The nematic phase even disappears at higher concentrations of the cesium salts.

(iii) The phase diagrams for CsCl, CsI, and Cs_2SO_4 are rather similar, provided that one takes into account that Cs_2SO_4 contributes twice as many cations per mole than CsCl and CsI.

(iv) At higher electrolyte concentrations, phase separation similar to the salting-out phenomenon[27] occurs; i.e., the LLC phases are completely destabilized. The resulting phases are an isotropic liquid and a birefringent turbid gel, the nature of which is still unclear. This destabilization of LLC phases was observed for LiCl, NaCl, and KCl. For CsCl the maximum concentration was obviously not reached but it can well be assumed that phase separation would also occur for CsCl at a concentration higher than 2.5 mol %.

(v) The electrolyte concentration necessary to induce the salting-out effect described in (iv) is obviously a function of the chemical nature of the added cations. For the chlorides the salting-out concentration increases in the order $Li^+ < Na^+ <$
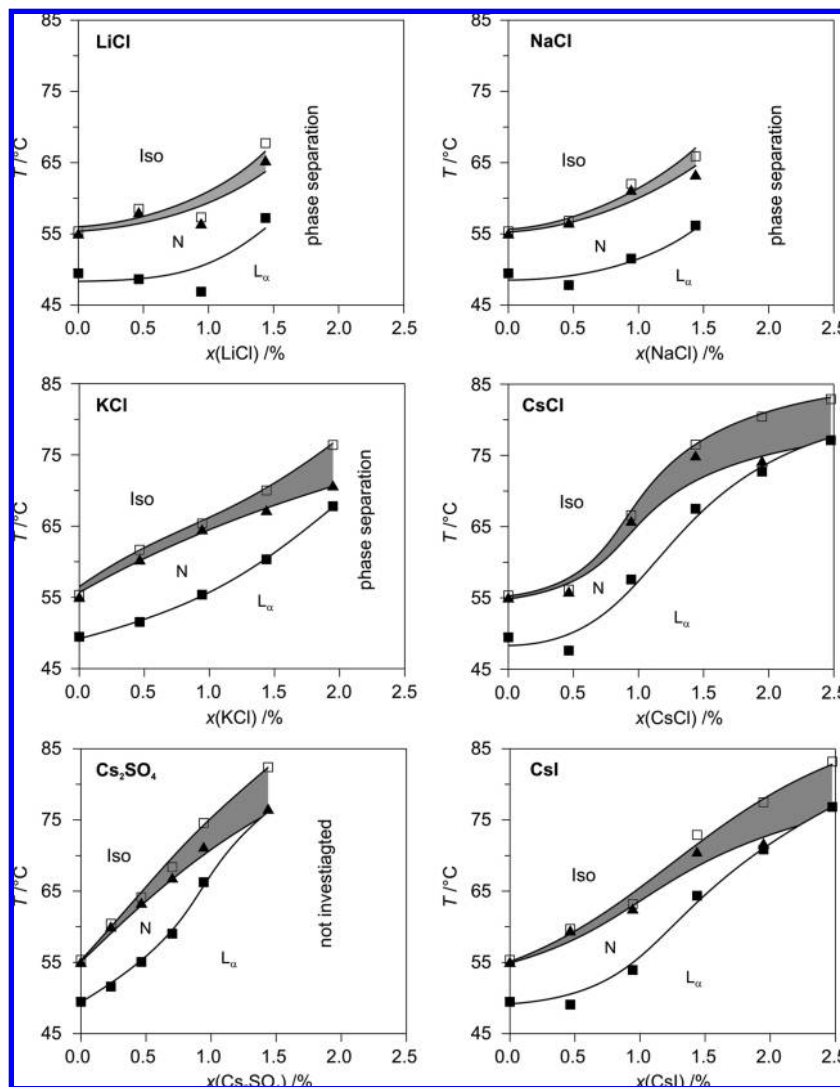
Figure 3. Quasi-binary phase diagrams of the ternary systems CsPFO/H$_2$O/salt with LiCl, NaCl, KCl, CsCl, CsI, and Cs$_2$SO$_4$ as salts and the constant CsPFO/H$_2$O mass ratio of 55/45. Phase separation was observed in the mixtures with x(LiCl) = 2 and 2.5%, x(NaCl) = 2 and 2.5%, and x(KCl) = 2%. L$_\alpha$-N two-phase regions could not be observed due to homeotropic orientation. The curves are guides to the eye. I: Isotropic phase. N: Nematic phase. L$_\alpha$: Lamellar phase. Gray: Two-phase regions. Open squares: Clearing temperature. Filled triangles: Beginning of the two-phase region. Filled squares: L$_\alpha$-N transition.

K$^+$ < Cs$^+$. (For the cesium salts, the salting-out concentration was not reached within the investigated concentration range).

To explain these observations, we come back to the possible mechanisms via which the added ions influence the phase: on the one hand dehydration of the whole phase, i.e., the reduction of the amount of free water due to the hydration of the added ions, and on the other hand screening of intra- and inter-aggregate repulsions, i.e., the electrostatic repulsions between head groups at the same aggregate surface and between aggregates, respectively. We will first treat the hydration argument. Then we will demonstrate how the screening of intra-aggregate repulsion can be revealed as an important salt effect. Therein, colligative and ion-specific aspects will be discussed. Finally, the role of inter-aggregate interactions in LLCs and the salt effect on these interactions is considered.

The hydration of the added ions leads to an increase of the effective amphiphile concentration considering the binary amphiphile−water ratio. Neglecting other influences of the added ions, the phase behavior of the ternary phase with added salt should therefore be equivalent to the phase behavior of the binary amphiphile-water phase with the increased amphiphile

concentration. Comparing the salt-induced changes of the phase behavior described in (i) and (ii) with the binary phase diagram for the CsPFO−water system recorded by Boden et al.,[9] we find that, in fact, the LLC transition temperatures are increased by both, adding electrolytes and increasing the amphiphile concentration. This qualitative analogy appears to confirm the importance of the dehydrating influence of added salts. However, a more quantitative comparison of the phase behavior found when adding CsCl−here any effects of changing the counterion to the amphiphile are absent−with the binary phase diagram reveal that the dehydration mechanism alone cannot account for the observed phase behavior. For instance, in the sample with 1.5 mol % CsCl the transition temperatures are found to be increased by some 20 K (see Figure 3) while the amount of water bound by the cesium and chloride ions would increase the CsPFO−water ratio only such that the temperatures are raised by 10 K, even if full static hydration numbers of eight for Cs$^+$ and six for Cl$^-$ are assumed (see Table 1).[33] In addition, the differences in the hydration numbers of the cations Li$^+$, Na$^+$, K$^+$, and Cs$^+$ are not reflected by the thermal stabilization of the lamellar phase nor can the stabilization of the nematic phase

TABLE 1: Enthalpy of Solution $\Delta H_{solv}{}^a$, Mean Ionic Activity Coefficient $\gamma_{\pm}{}^b$ and Ion Hydration Number n_1 (and n_2) for the First (and Second) Solvation Sphere^c for the Added Electrolytes in Aqueous Solution

	electrolyte					
	LiCl	NaCl	KCl	CsCl	CsI	Cs_2SO_4
ΔH_{solv}/kJ mol^{-1}	−37.03	3.88	17.22	17.78	33.35	
$\gamma_{\pm}$ (for 0.6 mol/kg)	0.746	0.676	0.640	0.595	0.588	0.275
cation M$^+$	Li$^+$	Na$^+$	K$^+$	Cs$^+$		
n_1 (n_2)	4 (12)	4−8	4−8	6−8		
anion X$^-$				Cl$^-$	I$^-$	SO$_4{}^{2-}$
n_1				5−8	4−10	7−10

^{a} ΔH_{solv} at 25 °C from ref 34. ^{b} $\gamma_{\pm}$ at 25 °C from ref 34 interpolated for 0.6 mol/kg, which is consistent with the salt concentration in the LLC samples with 1 mol % added salt. ^{c} n_1 and n_2 from scattering experiments ref 33.

observed for small salt concentration be explained by the dehydration argument.

Investigations on the influence of added salts on an isotropic micellar phase,[1] revealed that dehydration by added electrolytes and their effect on the long-range repulsion between micelles is largely less important for the properties of the micellar isotropic phase than the enhanced electrostatic screening of adjacent head groups. The observation indicates the important role of electrolytes in the self-assembly process of amphiphiles, especially of ionic amphiphiles, since the screening of electrostatic repulsion between equally charged head groups at the aggregate surface is a necessary condition for the aggregation. The screening is achieved by hydration spheres around each head group and by present counterions. Details of the self-assembly process are treated by Israelachvili[24] in his thermodynamic theory on isotropic micellar solutions in which he also discussed the role of added salt. Israelachvili deduced that screened repulsions between the head groups at the aggregate surface via added electrolytes lead to micellar growth.

To relate this result with the thermal stability of the LLC state, it is necessary to consider the driving forces for the ordering of micelles into LLC phases. An approach for the CsPFO/water system was provided by Boden, Gelbart, and co-workers.[25] The authors demonstrated that the isotropic−nematic transition temperatures in cesium perfluoroalkyloate/water systems can be calculated with high accordance to experimental data via a combination of a hard-particle theory with a self-assembly theory. Starting point of the procedure is a result from Onsager's hard particle theory[35] applied to disk-like micelles: At the isotropic−nematic transition, the product of the amphiphile volume fraction φ and the micellar anisotropy b/a (with disk diameter b and thickness a) is constant at the transition temperatures on cooling and heating, i.e., the phase transition temperatures T_{IN} and T_{NI}, respectively:

$$\varphi \frac{b}{a} = \begin{cases} 1.67 \text{ at } T_{IN} \\ 1.80 \text{ at } T_{NI} \end{cases}$$

Via this Onsager criterion the nematic alignment is coupled to both the anisotropy of the micellar shape and the size of the micelle. The temperatures, at which the critical Onsager values are reached, i.e., the transition temperatures, were determined by Boden and Gelbart using a dilute solution self-assembly theory for disk-like micelles based on a theory of McMullen et al.[36] This approach yields an important result for elucidating the origin of the salt-induced thermal LLC stabilization. At

TABLE 2: Structural Parameters in the Nematic and Lamellar Phases of CsPFO/D$_2$O with Mass Ratio 55/45: Aggregation Numbers n_{agg}, the Micellar Axis of the Discoid Ellipsoid b (Long), the Diameter of the Effective Head Group Area d_{polar}, and the Packing Parameter Π^a

	T_{NI}	T_{NL}	$T_{NL} - 5$ K
n_{agg}	113	140	150
b/nm	5.95	6.67	6.88
d_{polar}/nm	0.952	0.909	0.829
Π	0.53	0.55	0.61

^{a} Derived from ref 13 with the micellar short axis $a = 2.20$ nm^{13} and the diameter of the apolar tail $d_{apolar} = 5.04$ nm from Figure 1.

constant amphiphile volume fraction, an increase of the micelle diameter b leads to an increase of the nematic−isotropic transition temperatures, and thus to a thermal stabilization of the LLC state. According to Israelachvili added electrolytes induce micellar growth and, indeed, evidence for the micellar growth in the LLC phases of the CsPFO/water system due to added CsCl was found by Holmes et al.[19] and Leaver et al.[3] This means that Isrealachvili's theory on isotropic solutions applies well on LLC phases provided the validity of the approach done by Boden and Gelbart. Concerning our findings in observation (i) the combined theories indicate that increased screening of intra-aggregate repulsions accounts for the salt-induced stabilization of the nematic and lamellar phases in the CsPFO/water system at low salt concentrations.

We still need to explain observation (ii), i.e., the stronger stabilizing influence of added electrolytes on the lamellar phase than on the nematic phase as the salt concentration is increased. Since it was shown above that Israelachvili's considerations on self-assembly in micellar solutions are not restricted to the isotropic phase but apply equally well for LLC phases it is straightforward to address the issue with another aspect of Israelachvili's theory: the packing parameter,[24] which correlates the aggregate shape and the effective amphiphile geometry. The latter is reflected by the dimension-free packing parameter Π

$$\Pi = \frac{V_{eff}}{l_{max}A_{eff}}$$

where V_{eff} denotes the effective volume of the hydrophobic tail, l_{max} the maximum length of the hydrophobic tail, and A_{eff} the effective cross section of the hydrophilic head group at the aggregate surface. The value $\Pi = 1$ corresponds to a cylindrical molecular shape, packing best into large disk-like or lamellar aggregates, whereas smaller values represent more conical amphiphile shapes resulting in curved aggregates, like, e.g., disk-shaped micelles ($1/2 \leq \Pi < 1$) or rod-shaped micelles ($1/3 \leq \Pi < 1/2$).

To illustrate the situation in the CsPFO/water system the packing parameter values were derived from the diameter of the perfluoro chain, which was calculated using a force field geometry optimization and including the van-der-Waals radii of the fluorine atoms, and from the diameter of the effective head group area estimated from the aggregation numbers and structural parameters for the aggregates given by Boden et al.,[13] assuming the aggregates to be discoid ellipsoids in all three phases as proposed by the authors. The results are summarized in Table 2 and reveal the increase of the packing parameter throughout the nematic phase into the lamellar phase.

The packing parameter can be used to illustrate the effect of changing the parameters that affect the amphiphile geometry

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in the LLC state provided that the Onsager criterion described above is fulfilled. The effective hydrophobic volume and length mainly depend on molecular parameters and the temperature. The effective head group area includes the solvation sphere around the bare head group and, thus, is expected to strongly depend on the nature of the solvent, the solvent concentration, and the amount and nature of added electrolytes. This way, the influence of added electrolytes on the thermal stability of an LLC phase and on the kind of LLC phase formed, since LLC phases are characterized via the shape and arrangement of their building blocks, can be illustrated with the intuitive steric model of the packing parameter.

Applied to our experimental findings sketched (i), (ii), and (iii), the following picture can be drawn using the packing parameter model. The added cations electrostatically screen the repulsion between adjacent anionic head groups, thus reducing their effective size. According to the packing parameter the amphiphiles adopt a more cylindrical average shape that favors a growth of the disk-like micelles and enhances, as shown by Boden and Gelbart,[25] the thermal stability of both nematic and lamellar phases (observation i). At increasing salt concentration the packing parameter increases toward one, i.e., flat lamellar-like aggregates, and the lamellar phase is stabilized more strongly than the nematic phase (as described in observation ii). The almost colligative behavior of the three cesium salts (observation iii) can also be illustrated with the packing parameter since for the intra-aggregate interactions between the anionic head groups the concentration and chemical nature of the added cation, the counterion, is certainly dominant over anion effects.

To demonstrate the general use of the packing parameter model, we also applied it to the published salt effects in LLC phases with rod-like aggregates. McBain[6] and Gault[7] reported a destabilization of the hexagonal LLC phase, which is built up by elongated cylindrical micelles. The model accounts for the finding since the diameter of rod-shaped aggregates is restricted by the amphiphile length and cannot grow to allow less curved aggregates. In nematic LLC phases of rod-like micelles, however, the growth of the initially short micelles in length reduces the average curvature of an aggregate and thermally stabilizes the phase as was found experimentally by Mukherjee et al.[21]

Figure 4 reveals aspects of the role of the chemical nature of the added salts. In Figure 4a, the increase of the clearing temperature ΔT_{cl} is plotted against the concentration of added cesium cations. Within the experimental error all three cesium salts increase the clearing point in the same way as shown by the solid line in Figure 4a. For a certain added counterion, here the cation, the LLC stabilization depends on the cation concentration only but not on the chemical nature of the added anion.

Concerning the different added cations the situation is changed, i.e., rather ion-specific than colligative. Figure 4b shows the increase of the clearing temperature as a function of the cation concentration for different alkali metal chlorides. The quadratic increase of the clearing temperature with increasing salt concentration was also found in other experimental studies[5,21] and could be derived in theoretical calculations.[21] The effect of varying the cations is clearly not colligative. Apparently, the efficiency of the head group screening by added counterions depends on counterion properties, like, e.g., size and charge density. Thus, the LLC stabilization induced by low salt concentrations is dominated by the chemical nature and the concentration of the added counterion.
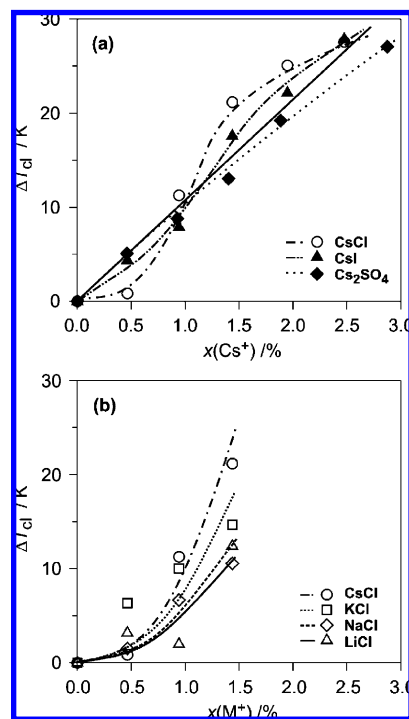

Figure 4. Salt-induced increase of the clearing temperature ΔT_{cl} versus the molar fraction of added cations. (a) The three cesium salts induce rather similar behavior. The dashed curves are guide to the eyes. The solid line represents the average tendency. Note that cesium sulfate contributes with twice as many cations as the monovalent salts. (b) For the four different alkali-metal chlorides MCl, the stabilization of the LLC phase is obviously ion-specific. The ΔT_{Cl} values are neglected for higher salt concentrations as salting-out behavior or phase change occurred in some cases. The curves are guides to the eye. Their parabolic shape is motivated by both experimental results[5,21] and theoretical considerations,[21] which make the ΔT_{cl} value for $x(K^+) = 0.5\%$ appear as an experimental error.

For our case of alkali cations, the salting-out strength decreases within the first period from Li^+ to Cs^+, which means that the salting-out concentration increases following the order $Li^+ < Na^+ < K^+ < Cs^+$. Since we have found in (v) that the same order applies for the ion specificity of the phase separation induced by added salts in LLC phases, it can be assumed that both phenomena are of similar origin. From chemical intuition it is obvious to connect (iv) and (v) with the high solvation tendency of electrolytes since this reduces the effective amount of free water available for the solubilization of the amphiphile aggregates. Furthermore, solvation properties of ions are well-known to highly depend on their chemical nature. Another electrolyte property that could account for the ion-specificity of the phase separation is the activity of the electrolytes in aqueous solution. The mean ionic activity coefficient and the solvation enthalpy for each added salt are given in Table 1 together with the hydration numbers of the added ions. We need to stress that these values are measured in dilute aqueous solutions and do not include possible influences of the dissolved amphiphilic molecules and the charged aggregates present in the LLC phases. However, since the relative concentration of amphiphile was kept constant for the different added salts, the values in Table 1 provide a sensible basis for the discussion of the ion-specific salt effect.

From Li^+ to Cs^+, i.e., following the observed tendency for the salting-out strength, the solvation enthalpy develops continuously from an exothermic solvation process for LiCl to an endothermic process for CsCl. In the same order the mean

activity coefficient of the added chloride salts decreases, indicating that ion solvation and activity play a role in the salting-out process. This is also reflected, though to a smaller extent, by the hydration numbers that slightly increase from Li^+ to Cs^+. It is interesting to note that the different properties of the added anions (see Table 1) have apparently only a weak influence since all cesium salts showed almost the same salt-effect—see discussion above. These phenomenological considerations reflect our findings quite well. Further understanding of the interactions governing such Hofmeister-like ion-specific phenomena was developed on a theoretical base by Ninham et al.[37] These authors found that at high salt concentrations (around and above 0.1 M) ion-specific dispersion interactions can become dominant compared to the rather non-ion-specific electrostatic ones.

Another aspect that is worth further attention is the role of inter-aggregate interactions between adjacent aggregates in LLCs as well as the influence of added salt on inter-aggregate interactions. Some authors found experimental evidence that added electrolytes emphasize an attractive character of inter-aggregate interactions in LLCs.[30,31,38] For example, added electrolytes increase the correlation length of aggregates in the lamellar phase of the CsPFO/water system and at the same time induce a periodic undulation of the lamellar spacing allowing partly reduced aggregate distances.[38] Most interestingly, already Israelachvili correlated the role of attractive inter-aggregate forces in the structural transition from isotropic micellar solutions to phases with higher ordered and larger aggregates, e.g., LLC mesophases, with phase separation and present electrolytes: "When the structural transitions are caused by *attractive* forces the larger structures may now either separate out from, or coexist with, the smaller aggregates or monomers in solution. Such attractive forces arise between uncharged amphiphilic surfaces, e.g., those having non-ionic or zwitterionic head groups, and for charged head groups in high salt where the electrostatic repulsion is screened."[24] These considerations represent an important hint, stimulating further investigations, that inter-aggregate interactions may play an unexpectedly important part in both the almost colligative thermal stabilization of LLC phases at low salt concentration and for the ion-specific phase separation at high salt concentration.

Conclusions

Electrolytes added to nematic and lamellar LLC phases of anionic amphiphiles in water induce two pronounced effects with substantially different characteristics. These compete with each other, the balance being shifted by tuning the electrolyte concentration. At low concentration the salt increases the thermal stability of the LLC phases. The effect is ion-specific with respect to the added cation which interacts directly with the anionic amphiphile-head groups. The chemical nature of the added anions, on the other hand, barely influences the quality and quantity of the stabilization. Considering electrolytes with the same cation the salt effect is therefore colligative.

Beyond a certain electrolyte concentration, which depends on the chemical nature of the added counterion, a substantial destabilization of the LLC state occurs in terms of a phase separation. The similarity of this behavior to the salting-out phenomenon known for aqueous protein solutions, together with the fact that it is ion-specific in the same way, i.e., according

to the Hofmeister series for ions, strongly suggests that both effects are of the same origin. Thereby, simple ionic LLC systems like the one studied here could be very useful as model system for a more general understanding of electrolyte effects in soft matter, e.g., in biological systems like membranes.

References and Notes

(1) Sein, A.; Engberts, J. B. F. N. *Langmuir* **1995**, *11*, 455.
(2) McBain, J. W.; Burnett, A. J. *J. Chem. Soc.* **1922**, *121*, 1320.
(3) Leaver, M. S.; Holmes, M. C. *J. Phys. II* **1993**, *3*, 105.
(4) Kuzma, M.; Saupe, A. *Mol. Cryst. Liq. Cryst.* **1983**, *90*, 349.
(5) Rosenblatt, C. N.; Zolty, J. *J. Phys. Lett.* **1985**, *46*, 1191.
(6) McBain, J. W.; Lazarus, L. H.; Pitter, A. V. *Z. Phys. Chem.* **1930**, *A147*, 87.
(7) Gault, J. D.; Leite, M. A.; Rizzatti, M. R.; Gallardo, H. *J. Colloid Interface Sci.* **1988**, *122*, 587.
(8) Boden, N.; Jackson, P. H.; McMullen, K.; Holmes, M. C. *Chem. Phys. Lett.* **1979**, *65*, 476.
(9) Boden, N.; Jolley, K. W.; Smith, M. H. *J. Phys. Chem.* **1993**, *97*, 7678.
(10) Iijima, H.; Kato, T.; Soderman, O. *Langmuir* **2000**, *16*, 318.
(11) Jolley, K. W.; Boden, N.; Parker, D.; Henderson, J. R. *Phys. Rev. E* **2002**, *65*, 041713.
(12) Jolley, K. W.; Smith, M. H.; Boden, N.; Henderson, J. R. *Phys. Rev. E* **2002**, *65*, 041713.
(13) Boden, N.; Corne, S. A.; Holmes, M. C.; Jackson, P. H.; Parker, D.; Jolley, K. W. *J. Phys. (Paris)* **1986**, *47*, 2135.
(14) Johannesson, H.; Furo, I.; Halle, B. *Phys. Rev. E* **1996**, *53*, 4904.
(15) Iijima, H.; Kato, T.; Yoshida, H.; Imai, M. *J. Phys. Chem. B* **1998**, *102*, 990.
(16) Plumley, S.; Kuzma, M. R. *Mol. Cryst. Liq. Cryst.* **1991**, *200*, 33.
(17) Holmes, M. C.; Sotta, P.; Hendrikx, Y.; Deloche, B. *J. Phys. II* **1993**, *3*, 1735.
(18) Cull, B.; Heino, M.; Lee, S. H.; Kumar, S.; Keast, S. S.; Neubert, M. E. *Liq. Cryst.* **1994**, *17*, 507.
(19) Holmes, M. C.; Leaver, M. S.; Smith, A. M. *Langmuir* **1995**, *11*, 356.
(20) Mukherjee, P. K.; Bhattacharya, J. *J. Chem. Phys.* **2007**, *126*, 024901.
(21) Mukherjee, P. K.; Lagerwall, J. P. F.; Giesselmann, F. *Liq. Cryst.* **2005**, *32*, 1301.
(22) Tartar, H. V. *J. Phys. Chem.* **1956**, *59*, 1195.
(23) Tanford, C. *J. Phys. Chem.* **1972**, *76*, 3020.
(24) Israelachvili, J. N. *Intermolecular and surface forces*; Academic Press: New York, 1991; pp 1−450.
(25) Boden, N.; Harding, R.; Gelbart, W. M.; Jolley, K. W.; Heerdegen, A. P.; Parbhu, A. N. *J. Chem. Phys.* **1995**, *103*, 5712.
(26) Attard, G. S.; Fuller, S.; Tiddy, G. J. T. *J. Phys. Chem. B* **2000**, *104*, 10426.
(27) Hofmeister, F. *Arch. Exp. Path. Pharmakol.* **1888**, *25*, 1.
(28) Leontidis, E. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 81.
(29) Kostko, A. F.; Cipriano, B. H.; Pinchuk, O. A.; Ziserman, L.; Anisimov, M. A.; Danino, D.; Raghavan, S. R. *J. Phys. Chem. B* **2005**, *109*, 19126.
(30) Park, H. S.; Kang, S. W.; Tortora, L.; Nastishin, Y.; Finotello, D.; Kumar, S.; Lavrentovich, O. D. *J. Phys. Chem. B* **2008**, *112*, 16307.
(31) Prasad, S. K.; Nair, G. G.; Hegde, G.; Jayalakshmi, V. *J. Phys. Chem. B* **2007**, *111*, 9741.
(32) Boden, N.; Corne, S. A.; Jolley, K. W. *J. Phys. Chem.* **1987**, *91*, 4092.
(33) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.
(34) Linde, D. R. (ed.) *CRC Handbook of Chemistry and Physics 89th ed.;* CRC Press, Taylor & Francis Group: Boca Raton, FL, 2008.
(35) Onsager, L. *Ann. N. Y. Acad. Sci.* **1949**, *51*, 627.
(36) McMullen, W. E.; Ben-Shaul, A.; Gelbart, W. M. *J. Colloid Interface Sci.* **1984**, *98*, 523.
(37) Ninham, B. W.; Yaminsky, V. *Langmuir* **1997**, *13*, 2097.
(38) Holmes, M. C.; Smith, A. M.; Leaver, M. S. *J. Phys. IV* **1993**, *3*, 177.