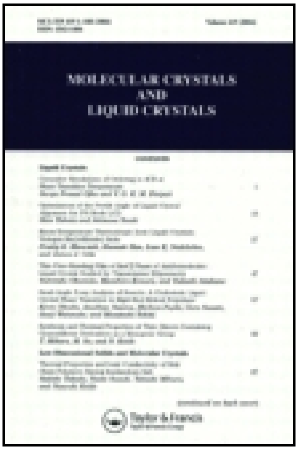

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Lytropic Liquid Crystals of D-(2)-Octylammonium Chloride

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D-(2)-octylammonium chloride has been observed to form lyotropic liquid crystals in aqueous solutions. Cholesteric, nematic, and smectic phases will form depending on concentration, co-amphiphile content, ionic environment and temperature. The cholesteric textures displayed by aqueous mixtures of 1:2:1 D-(2)-octylammonium chloride:decylammonium chloride:salt (NH_4Cl, KCl, LiCl, NaCl) were investigated for the dependence of the pitch upon such variables as the nature of the salt cation, salt concentration, pH and temperature. The investigative methods used include magnetic field orientation, differential scanning calorimetry, laser diffraction and optical microscopy. The results obtained include the dependence on the concentration of chiral dopants and compensation effects.

INTRODUCTION

Cholesteric lyophases are an important class of materials with potential for application in fiber technology, surfactant and colloid problems and display concepts. In complete analogy with thermotropic mesophases, their chirality can originate from either doping a nematic lysophase with chiral additives or from intrinsic chirality. Solutions of chiral rod-like polymers such as poly-(γ-benzyl-L-glutamate) in appropriate solvents,[1] are the best known example of intrinsic chirality. Typical studies of low molecular weight species which form extended cylindrical micelles that can be doped to form cholesteric lyophases include those by Radley and Saupe[2] of such systems as the ternary mixture cesium decylsulphate, salt, and water doped with D-tartaric acid. Such systems typically have a small induced chirality, i.e. the pitch of the cholesteric array is very large. Short pitch can however be achieved in some instances by doping the nematic lyophase of disodium cromoglycate in water with amino acids.[3–7]

Lyotropic systems in which chiral amphiphilic anions are responsible for the intrinsic chirality have been reported by Covello et al.[8] Their approach involved acylating amino acids, and they prepared potassium-n-laurylalaninate, -serinate and -valinate, all of which showed cholesteric behaviour in some region of their phase diagrams.

In this article, an example is reported of the formation of a cholesteric lyophase by a chiral cationic amphiphile; namely, D-(2)-octylammonium chloride. To our knowledge, only one such system has been reported previously.[9]

EXPERIMENTAL

Investigation methods include temperature controlled microscopy, differential scanning calorimetry (Perkin-Elmer DSC-2C/TADS), pH measurements and laser diffraction. Temperature controlled environments were obtained with a Mettler FP-52 Hot Stage. When long equilibration times were desired or temperatures lower than room temperature required, a Lauda temperature controlled circulating bath with a brass sampling chamber was used. Optical microscopic observations were made with a Nikon LKE stereomicroscope fitted with a Polaroid MP-3 Land camera. Additional observations were made with a Nikon Optiphot-pol fitted with a Nikon camera system. A 20 Kilogauss electromagnet (Ventron Instruments HS-1365C) was used for magnetic alignment purposes. The air gap in this instrument is sufficiently wide to permit insertion of slides such that the magnetic field can be either parallel or perpendicular to the face of the preparation or the long axis of the capillary tube.

Reagents (decylamine and L-octanol obtained from Aldrich) were used unpurified as obtained from the suppliers. D-(2)-octylammonium chloride was synthesized from L-octanol according to the method of Streitweiser et al[10] and was verified to have 99% optical purity by polarimetry. Decylammonium chloride and D-(2)-octylammonium chloride were recrystallized from 100% ethanol and dried under vacuum. D-(2)-octylammonium chloride is hygroscopic so care must be taken in order to keep it in the anhydrous state. Solids were weighed on an analytical balance and transferred to resealable airtight vials made of either polypropylene or glass. Water or salt solutions were introduced with a Hamilton syringe. Occasionally dopants were weighed into a sealable polypropylene vial (Sarstedt) and aliquots of a lyotropic stock solution were introduced with an Eppendorf pipette. The vials were stoppered and heated repeatedly on a water bath, then left for a minimum of 24 hours at room temperature. The solutions in the stoppered vials were observed to be stable for several weeks. Acidified stock solutions stored in 5 mm i.d. 2 dram vials were stable for 6 months.

Slides were prepared using flat glass capillary tubes of .2 × 2 mm and .3 × 3 mm inner diameter (Vitro Dynamics Inc.). The tubing was cut into 3/4 inch lengths, and the lyotropic mixture was introduced by capillary action. The outside of the capillary tube was then cleaned, sealed, and mounted on a microscope slide. The sealant most frequently used was Devcon five-minute epoxy.

RESULTS

D-(2)-octylammonium chloride is a white crystalline solid with an endothermic melting point at 89.4°C ($\Delta H = -17$ cal/g). A mixture of 17.7% D-(2)-octylammonium chloride (D-oac), 36.6% decylammonium chloride (dac), 5.9% ammonium chloride and 39.8% water (by weight) was found which displays a cholesteric phase with negative diamagnetic anisotropy and a pitch of 60 μm at room temperature. This mixture shows two temperature dependent phases. A lamellar phase is observed for −5°C to 16°C. A cholesteric phase is observed above this temperature which undergoes a transition to an isotropic liquid at 32.5°C. The smectic to cholesteric transition occurs very slowly. Several hours may be necessary for thermal equilibrium in an aligned preparation when cooled from the cholesteric phase. The pitch of the above mixture was observed to decrease as the concentration of salt was increased, i.e. a stock solution of 17.7% D-oac, 36.6% dac, 5.9% NH_4Cl and 39.8% H_2O was doped with salt. Table I shows the pitch dependence on salt concentration at 20°C. The pitch was also observed to be linearly dependent on temperature. Figure

TABLE I

Pitch at 20°C of a 17.7% D-oac, 36.6% dac, 5.9% NH_4Cl and 39.8% H_2O Cholesteric Lyophase Doped with Additional NH_4Cl

NH_4Cl Wt %	Pitch μm
5.9	60
7.9	40
9.0	30

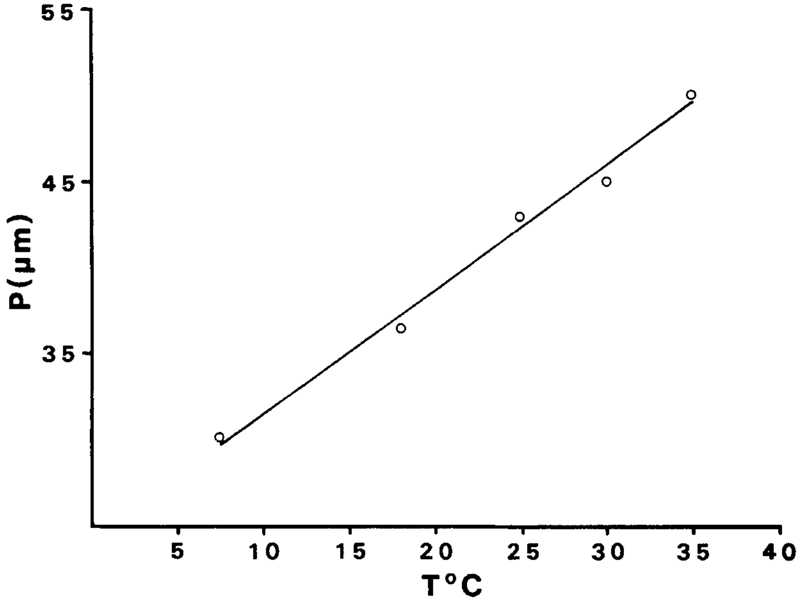

FIGURE 1 Pitch vs temperature for 17.7:36.6:7.9:39.8 D-oac:dac:NH_4Cl:H_2O by weight.

1 shows the pitch dependence upon the temperature for a mixture of 17.7:36.6:7.9:39.8 (by weight).

The sensitivity of the system to the addition of salt prompted a more thorough look at the effects of salt in these mixtures. Cholesterics with fingerprint textures were observed to form with salts other than ammonium chloride when combined in the same molar ratio. The molar rations of these lyotropic phases were calculated to be 1.0:1.8:1.0:20.5 D-oac:dac:salt:water. Significant deviations from this ratio (excepting salts) usually results in the destruction of the chiral mesophase. Table II gives the observed pitch at 20°C, clearing points

TABLE II

Pitch and Clearing Point Transitions for 1:0:1.8:1.0:20.5 Molar Ratios D-oac:dac:salt:water

Salt	Pitch, μm,20°C	T_{m-i} (°C)	ΔH_{m-i} (cal/g)
NH_4Cl	60	32.5	.02
KCl	45	45.0	.02
LiCl	42	40.0	.05
NaCl	110	57.0	.07

TABLE III

Pitch at 20°C of Acidified and Unacidified 1.0:1.8:1.0:20.5 Molar Ratios D-oac:dac:water

Salt	Unacidified Pitch (μm)	Pitch at Low pH (μm)
NH_4Cl	60	38
KCl	45	45
LiCl	42	42
NaCl	110	48

and clearing point enthalpies (from dsc) for equimolar compositions utilizing four salts.

A shortening of the pitch occurs when the mixtures are acidified. Table III compares the pitch when the salt solution is acidified to pH = 1 with the unacidified mixtures. This was accomplished by adding a small amount of equimolar HCl to the standard salt solutions, thereby keeping the chloride concentration constant. Note that the "twisting power" of the unacidified cations is $Li^+ > K^+ > NH_4^+ > Na^+$. When the pH is lowered, the relationship becomes $NH_4^+ > Li^+ > K^+ > Na^+$.

An additional study was performed to examine the dependence of the pitch on the pH. Several salt solutions of varying pH were prepared and the pH of the resulting lyophases measured with a microelectrode. Sodium and ammonium cations yield a linear pitch dependence on the pH (see Figure 2). The accuracy of the pH measurements at high ionic strengths of salt is, however, rather poor. When the pH is lowered there is also an extension of the cholesteric temperature range. In the case of the ammonium cation, the clearing point at pH = 4.5 is 32.5°C while the clearing point is 58°C when the pH is lowered to 1.5.

A number of chiral dopants were examined for their ability to decrease or alter the pitch of the cholesteric phase. Most merely succeeded in destroying the cholesteric phase. Chiral sugars, however, could be added and the cholesteric phase often remained stable up to 20 wt% of added sugar. Figure 3 shows the results for 100 μl aliquots of a mixture of 1.0:1.8:1.0:20.5 D-oac:dac:NH_4Cl:H_2O doped with D-(+)-glucose. Similar results were observed when fructose was used as a dopant.

Compensation studies were initiated in order to investigate the interaction between the D-(2)-octylammonium chloride induced cholesteric lyophase and a chiral dopant with the opposite sense of optical rotation. Anomeric L-glucose (Sigma, 98%) was selected as the do-

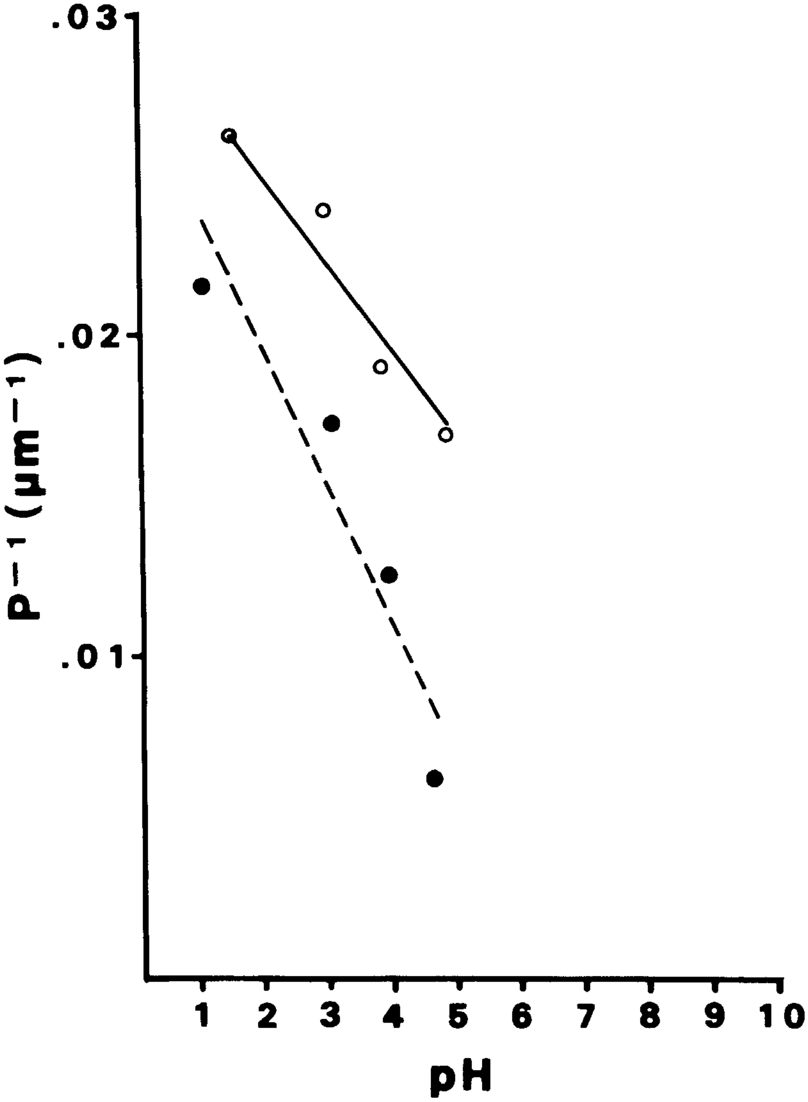

FIGURE 2 Pitch variation with pH of salt solutions in cholesteric lyophases of alkylammonium mixtures with sodium chloride (○) and ammonium chloride (●).

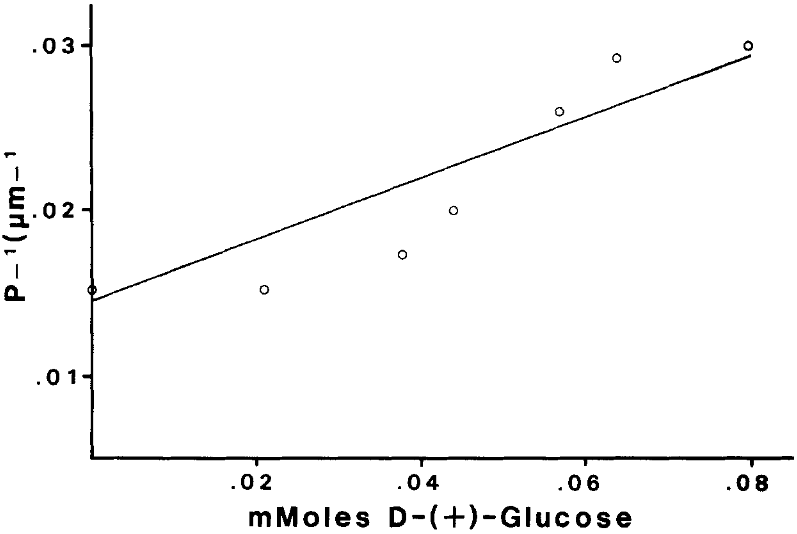

FIGURE 3 1.0:1.8:1.0:20.5 D-oac:dac:NH_4Cl:H_2O (m:m) [17.7:36.6:59:39.8 wt:wt] doped with anhydrous D-(+)-Glucose. Inverse pitch (μm^{-1}) at 20°C vs m Moles D-(+)-Glucose.

pant because the lyophase exhibits a high tolerance to sugars. Aliquots of approximately 100 µl of a standard mixture of 17.7:36.6:5.9:39.8 by weight of D-oac, dac, NH_4Cl and H_2O were weighed into vials and doped with various amounts of anomeric L-glucose. After thorough mixing the pitch was measured in the usual fashion. As shown in Figure 4, there is a linear dependence between the pitch and the amount of anomeric L-glucose. A further compensation study was undertaken by preparing a stock solution of 17.7:36.6:5.9:39.8 racemic D,L-(2)oac:dac:NH_4Cl:H_2O and a similar stock solution containing 17.7% D-(2)-oac. Aliquot of the two solutions were combined in various proportions and the pitch measured in the usual manner. The results, shown in Figure 5, show that there is a linear relationship between the pitch and the amount of uncompensated (or active) D-(2)-octylammonium chloride.

CONCLUSIONS

The pitch of cholesteric lyophases of D-(2)-octylammonium chloride can be modulated in similar ways to those found effective for thermotropic liquid crystals. It is observed to increase with increasing

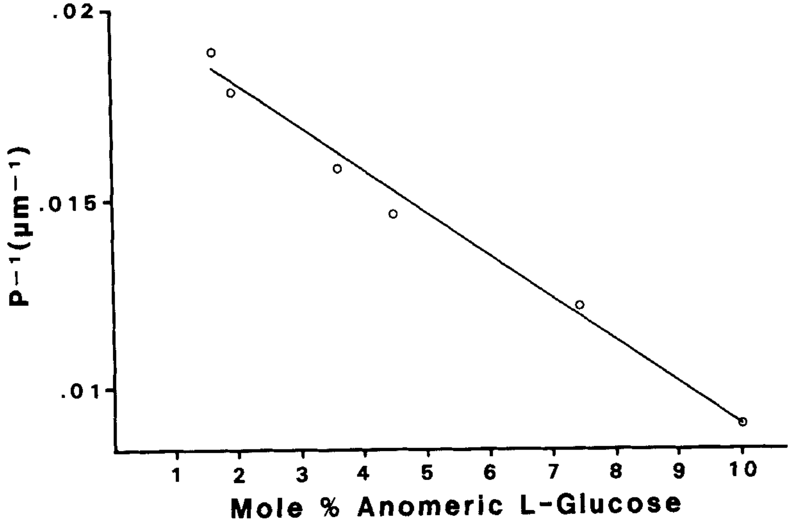

FIGURE 4 Inverse pitch at 20°C vs mole % anomeric L-Glucose in 17.7% D-oac, 36% dac, 5.9% NH_4Cl and 39.8% H_2O cholesteric lyophase.

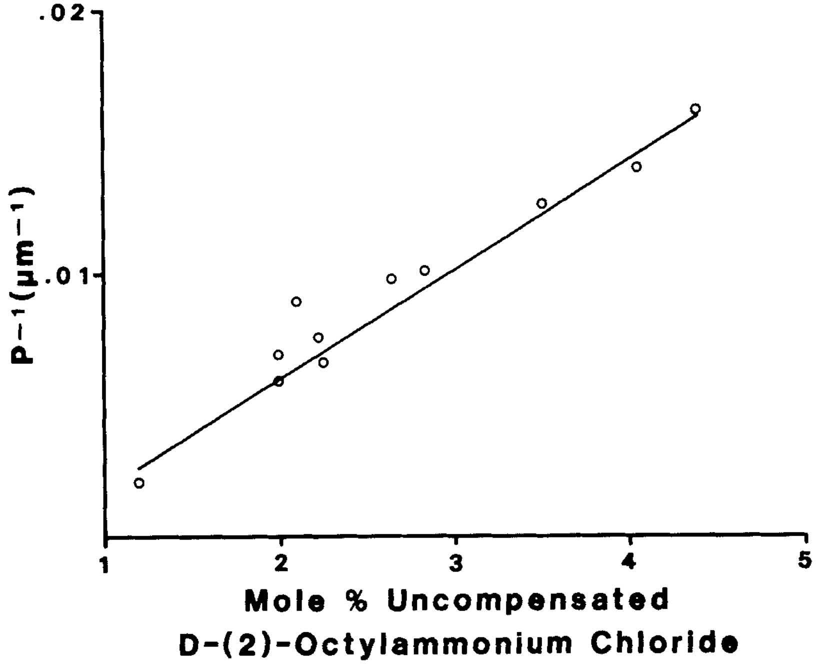

FIGURE 5 Compensation of a cholesteric lyophase of 17.7% D-oac, 36.6% dac, 5.9% NH_4Cl and 39.8% H_2O with its racemic nematic analog. Inverse pitch (μm^{-1}) at 20°C vs mole % uncompensated D-(2)-octylammonium chloride.

temperature, and to decrease with increasing pH. The pitch is also dependent on the nature of the salt cation (Li^+, K^+, NH_4^+, Na^+), and decreases linearly with salt concentration. It is apparently independent of the amphiphile concentration within the cholesteric regime, but the existence of the mesophase is dependent on a specific ratio of the constituents. The cholesteric mesophase is thermally stable if properly handled. Boundary conditions (capillary type, seal, storage, etc.) are quite crucial. When the texture does degrade, a parabolic focal conic texture is frequently the result. These textures can be highly regular, especially for samples contained in a planar capillary aligned in a magnetic field. The pitch decreases with the addition of D-glucose and D-fructose, but increases with the addition of anomeric L-glucose. The cholesteric lyophase can be compensated by the addition of an identical mixture containing racemic (2)-octylammonium chloride, to yield a nematic lyotropic liquid crystal. The cholesteric lyophase shows negative diamagnetic anisotropy which allows the direct measurement of pitch through the fingerprint textures.

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