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LIQUID CRYSTALLINE AND SURFACTANT PROPERTIES OF ALKYL PYRIDINIUM SALTS

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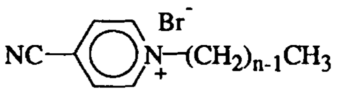
Abstract Several new alkyl pyridinium salts, namely 1-*n*-alkyl-4-cyanopyridinium bromides with alkyl chains containing 14, 16, and 18 carbon atoms, were synthesized, and their mesomorphic and micellar properties were studied. For compounds with 16 and 18 carbons in the alkyl chain, a thermotropic smectic A phase is present. The compounds also behave as surfactants in dilute aqueous solutions, and the Krafft temperature and the critical micelle concentration of each compound were determined.

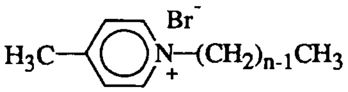
INTRODUCTION

Most thermotropic liquid crystals are neutral compounds. On the other hand, many lyotropic liquid crystals, especially those in aqueous systems, are composed of compounds with ionic head groups and hydrocarbon or fluorocarbon chains. Little work has been done on thermotropic liquid crystals possessing ionic cores. Earlier research on ionic thermotropic liquid crystals focused on metal alkanoates.[1,2] More recently, ionic thermotropic liquid crystals in which the head groups are aromatic, namely pyridinium salts, have been investigated.[3-6] The structures of these compounds are more similar to the traditional thermotropic liquid crystals than the alkanoates. For example, Tabrizian *et al.* studied 4-methyl and 4-tolyl pyridinium bromides of various alkyl chain lengths in order to compare the properties of the single and double ring compounds as a function of alkyl chain length.[5]

The cyano group is well known for its property to promote mesogenic function.[7] Therefore, we have synthesized 1-*n*-alkyl-4-cyanopyridinium bromides with different alkyl chain lengths and compared their mesogenic properties with those reported for the 1-*n*-alkyl-4-methylpyridinium bromides.[5] Because these compounds also possess surfactant characteristics, their properties in dilute aqueous solutions have been studied as well.



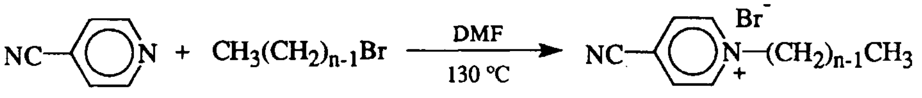
1-*n*-alkyl-4-cyanopyridinium bromide
(PCN-n)



1-*n*-alkyl-4-methylpyridinium bromide
(PMe-n)

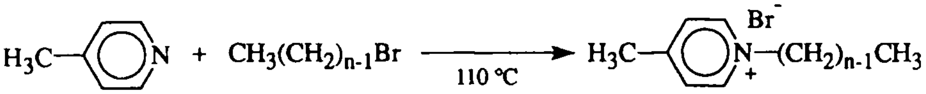
EXPERIEMNTAL

4-Cyanopyridine and the appropriate alkyl bromides were obtained from Aldrich Chemicals. Synthesis of the 1-*n*-alkyl-4-cyanopyridinium bromides was accomplished through the use of straightforward quaternization reactions. However, because the electron-withdrawing property of the cyano group reduces the nucleophilic character of the pyridinium nitrogen, the reaction did not proceed using ethanol as solvent, and a higher reaction temperature was required. Therefore, dimethylformamide (DMF) was selected as the solvent. 1-*n*-Octadecyl bromide and 4-cyanopyridine were heated in DMF at 130 °C with stirring for twelve hours. The reaction mixture was cooled to room temperature and poured into diethyl ether to precipitate the product. The product was filtered, washed, dried, and re-precipitated from a 1:4 mixture of methanol and water, and recrystallized four times in the same solvent. The final product was a slightly yellow powder. Anal.: Calculated for $C_{24}H_{41}N_2Br$: C 65.89; H 9.44; N 6.40; Br 18.26. Calculated for $C_{24}H_{41}N_2Br \cdot \frac{1}{2}H_2O$: C 64.56; H 9.48; N 6.27; Br 17.90. Calculated for $C_{24}H_{41}N_2Br \cdot H_2O$: C 63.28; H 9.51; N 6.15; Br 17.54. Found: C 64.12; H 9.43; N 6.10; Br 17.16. Therefore, the product was likely a hemihydrate. Mass spectrum: m/e = 357.4 ($C_{24}H_{41}N_2^+$).



1-*n*-Hexadecyl-4-cyanopyridinium bromide and 1-*n*-tetradecyl-4-cyanopyridinium bromide were synthesized and purified in the same manner. ^1H NMR was used to identify the products. For 1-*n*-hexadecyl-4-cyanopyridinium bromide: (300 MHz, $CDCl_3$): δ [ppm] = 0.85 (t, J = 6.7 Hz, 3H, CH_3), 1.23 and 1.32 (m, 26H, aliphatic CH_2), 2.04 (m, 2H, $CH_2CH_2N^+$), 5.10 (t, J = 6.5 Hz, 2H, CH_2N^+), 8.33 (d, J = 6.2 Hz, 2H, $2CHCHN^+$), 9.75 (d, J = 6.6 Hz, 2H, $2CHN^+$).

1-*n*-Alkyl-4-methylpyridinium bromides were prepared by heating the alkyl bromide directly in 4-methylpyridine (picoline) at 110 °C with stirring for twelve hours without the use of solvent.[5] The reaction mixture was cooled to room temperature and poured into hexane to precipitate the product, which was filtered, washed, and dried. It was then recrystallized four times from a mixture of 1:4 methanol and water. The final product was a white powder. ^{1}H NMR was used to identify the products. For 1-*n*-hexadecyl-4-methylpyridinium bromide, mass spectrum: m/e = 318.5 ($C_{22}H_{40}N^+$); ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.84 (t, J = 6.7 Hz, 3H, aliphatic CH_3), 1.19, 1.21 and 1.28 (m, 26H, aliphatic CH_2), 1.96 (m, 2H, $CH_2CH_2N^+$), 2.64 (s, 3H, aromatic CH_3), 4.86 (t, J = 7.4 Hz, 2H, CH_2N^+), 7.85 (d, J = 6.1 Hz, 2H, $2CHCHN^+$), 9.20 (d, J = 6.6 Hz, 2H, $2CHN^+$).



An Olympus polarizing optical microscope with a Linkham heating stage was used to determine the transition temperatures and to observe the microscopic textures of the compounds. The Krafft temperatures were determined by visual observation of laser light scattering of the aqueous solutions of the compounds. A YSI Model 35 conductance meter was used to determine the critical micelle concentrations of the compounds that were studied.

RESULTS

In this section, the 1-*n*-alkyl-4-cyanopyridinium bromides are abbreviated as PCN-n, and the 1-*n*-alkyl-4-methylpyridinium bromides abbreviated as PMe-n, for the sake of brevity, with n representing the length of the alkyl chain.

When examined under the polarizing optical microscope, PCN-16 and PCN-18 showed two transition temperatures after melting, indicative of the presence of a mesophase. The mesophase displays a focal conic texture with uniaxial conoscopic crosses, which indicate a smectic A phase. In addition, both of the compounds display a crystal-crystal transition below the melting point. However, PCN-14 does not exhibit a liquid crystalline phase.

The corresponding methyl compounds, PMe-16 and PMe-18, also display two transition temperatures. Both have focal conic texture and regions with uniaxial conoscopic crosses, characteristic of the smectic A phase.[5] The transition temperatures of the two series of compounds are listed in Table I.

TABLE I. Transition temperatures of 1-*n*-alkylpyridinium bromides in °C. Values in parentheses are those reported in reference 5.

Compound	K_1		K_2		S_A		I
PCN-14	•		•	184			•
PCN-16	•	61	•	192	•	196	•
PCN-18	•	65	•	195	•	201	•
PMe-14	•		•	76 (74)			•
PMe-16	•		•	88 (84)	•	113 (109)	•
PMe-18	•		•	95 (92)	•	162 (158)	•

Attempts to formulate eutectic mixtures of the corresponding cyano and methyl compounds were made by determining the melting points of the mixtures PCN-14/PMe-14, PCN-16/PMe-16, and PCN-18/PMe-18. The mole fractions of the mixtures ranged from 9:1 to 1:9. However, it was found that the two kinds of compounds did not dissolve in each other well when one compound was in the solid phase and the other was in the S_A or liquid phase. Therefore, they did not form eutectic mixtures.

Initial efforts to characterize the critical micelle concentrations (CMC's) of the compounds at room temperature did not yield definitive results. It was subsequently discovered that the Krafft temperature, the temperature below which the solubility of a surfactant is not high enough to form micelles, was above room temperature for all the compounds studied (Table II).

TABLE II. Krafft temperatures of 1-*n*-alkylpyridinium bromides.

Compound	Krafft Temperature, °C	Compound	Krafft Temperature, °C
PCN-14	66	PMe-14	33
PCN-16	88	PMe-16	42
PCN-18	72	PMe-18	45

The compound PCN-16 possessed the highest Krafft temperature, 88 °C, which necessitated performing the CMC measurements at a temperature larger than this value.

In order to compare the CMC data for all the compounds in the two homologous series, the CMC of each compound was determined at 90 °C using conductance measurements. The results are shown in Table III.

TABLE III. Critical micelle concentrations of 1-*n*-alkylpyridinium bromides at 90 °C.

Compound	CMC, mM	Compound	CMC, mM
PCN-14	7.23	PMe-14	7.91
PCN-16	2.55	PMe-16	3.13
PCN-18	0.81	PMe-18	0.96

DISCUSSION

Previous studies of 1-*n*-alkylpyridinium halides have demonstrated a strong dependence of the S_A-isotropic transition temperature on the alkyl chain length.[3-5] The present study is in accordance with this observation, and the results indicate that a terminal chain longer than fourteen carbons is required for the manifestation of liquid crystal behavior. When the 4-substituent is changed from a methyl group to a cyano group, the melting point increases and the mesophase temperature range decreases (Table I).

A common feature in various models for the mesophase structure of alkylpyridinium halides is that the packing is considered to be interdigitated, with the anions sandwiched between the pyridinium rings.[3-6] The main reasoning for this modeling is that the location of the anion relative to the pyridinium ring would place the anion near the concentration of positive charges. Thus, electrostatic attractions would tend to stabilize the layers of molecules in the mesophase.

According to this model, because the presence of the strongly electron-withdrawing cyano group in the 1-*n*-alkyl-4-cyanopyridinium compounds would increase their polarity, their clearing temperatures would be raised with respect to the corresponding 1-*n*-alkyl-4-methylpyridinium compounds. This was indeed observed (Table I). Unfortunately, the increase in the polarity causes the melting points to increase even more, leading to a decrease in the mesophase ranges (Table I). This is in direct contrast to non-ionic thermotropic liquid crystals, for which the presence of a terminal cyano group usually enhances the liquid crystalline property and increases the mesomorphic range.[7]

The much higher Krafft temperatures of the 1-*n*-alkyl-4-cyanopyridinium compounds compared to the corresponding 1-*n*-alkyl-4-methylpyridinium compounds

(Table II) are probably also caused by the increased lattice energy of the former due to the polarity of the cyano group. However, the CMC's of the corresponding compounds in the two homologous series do not differ by appreciable amounts (Table III). Considering that the cyano group is more hydrophilic than the methyl group, the slightly lower CMC's for the 1-*n*-alkyl-4-cyanopyridinium series is somewhat surprising. Because the CMC values of surfactants are often determined at or near room temperature, it is not easy to compare our data with those listed in the literature.[8] The only CMC value obtained for a comparable cationic surfactant at an elevated temperature is for 1-*n*-hexadecylpyridinium chloride, which has a CMC of 2.3 mM at 80 °C.[9] The data listed in Table III compare favorably with this value.

In summary, the 1-*n*-alkyl-4-cyanopyridinium bromides, the 1-*n*-alkyl-4-methylpyridinium bromides and some other alkylpyridinium salts[3-5] exhibit a thermotropic smectic A phase and behave as normal surfactants in aqueous solutions, bridging the gap between thermotropic and lyotropic liquid crystals.

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