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The Thermotropic Liquid-Crystalline Behavior of Alkylammonium Benzenesulfonates and Related Salts

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Alkylammonium benzene-, pyridine-3-, *p*-toluene-, and *p*-ethylbenzenesulfonates were found to be smectogenic when the cation carries an octyl or longer alkyl group. The thermal stability of the mesophase usually reaches its maximum at the octadecylammonium salt. The temperature range of stable existence is in the following order: pyridine-3-sulfonate>*p*-toluenesulfonate>benzenesulfonate>*p*-ethylbenzenesulfonate, suggesting the presence of a specific interaction between the ammonium ion and the nitrogen atom in the pyridine ring.

Several series of long-chain alkylammonium salts have been known to exhibit liquid-crystalline phases. They include salts containing counter ions as simple as halide ions and also two-dimensional sheets of tetrahalometallate ions.[1-5] In our previous paper, the thermotropic liquid-crystalline properties of alkylammonium alkanesulfonates were described.[6] Because the thermal stability of the mesophase in these salts was considerably affected by the counter ions, we then decided to extend our study of alkylammonium salts employing a wide range of aromatic anions. As will be described below, the picrate ion was found to be of limited use; however, benzenesulfonic acid was discovered to form mesomorphic salts with many long-chain alkylamines. As a large number of derivatives of the latter acid are readily available, we may be able to examine the effects on the mesomorphic behavior of various substituents carried by the aromatic nuclei. This paper will present the results of our work on the benzenesulfonates and three related series of salts.

Experimental

Materials. The benzene-, pyridine-3-, *p*-toluene-, *p*-ethylbenzenesulfonic acids, picric acid, and 2,4-dinitro- and 2,6-dinitrophenols are commercially available. Equimolar amounts of an alkylamine and an acid dissolved in boiling methanol were mixed. The salt thus precipitated was purified by recrystallization until a sharp mesomorphic–isotropic transition was recorded on the calorimetric curve during the processes of heating and cooling at the same temperature. For example, Found: C, 67.27; H, 10.52; N, 3.33; S, 7.59%. Calcd for $C_{18}H_{37}NH_3^+\cdot C_6H_5SO_3^-$: C, 67.40; H, 10.60; N, 3.28; S, 7.50%.

Measurements. The calorimetric and X-ray diffraction measurements were carried out as described in our previous paper.[6]

Results and Discussion

Many benzene-, pyridine-3-, *p*-toluene-, and *p*-ethylbenzenesulfonates can produce a smectic phase. Table 1 presents their melting and clearing points, the associated enthalpies, and the layer spacings as measured within 10 °C above the melting points. The

Table 1. Transition Temperatures (°C), Enthalpy Changes (kJ mol^{-1}), and Layer Spacings (nm) of Alkylammonium Salts[a]

n[b]	Melting	Clearing	Layer spacing
	Benzenesulfonates		
9	102(32)	—	—
10	98(35)	99(2.9)	2.06
11	89—92(32)	107(2.7)	2.19
12	88—92(33)	114(2.4)	2.31
13	89—92(40)	120(2.3)	2.41
14	91—96(21)	124(2.2)	2.57
15	97(21)	127(2.2)	2.65
16	95(26)	130(2.1)	2.77
17	94—96(62)	130(2.0)	2.90
18	98—100(23)	133(2.0)	3.01
	Pyridine-3-sulfonates		
11	102(46)	—	—
12	97(85)	106(0.6)	2.51
13	103(53)	134(0.8)	2.66
14	96(44)	152(0.9)	2.76
15	100(62)	154(1.0)	2.89
16	99(56)	173(1.0)	3.05
17	105(66)	178(1.0)	3.14
18	103(65)	186(1.0)	3.27
	p-Toluenesulfonates		
8	131(17)	—	—
9	130(18)	127(3.6)	2.07
10	128(19)	129(3.4)	2.19
11	118(14)	133(3.3)	2.30
12	105(14)	137(3.1)	2.44
13	100(16)	140(3.0)	2.54
14	98(17)	144(2.8)	2.65
15	99(19)	145(2.8)	2.78
16	98(21)	146(2.9)	2.86
17	98(22)	146(2.7)	2.94
18	98(23)	144(2.5)	3.01
	p-Ethylbenzenesulfonates		
7	136(17)	—	—
8	129(18)	129(3.4)	—
9	121(18)	125(2.8)	2.01
10	123(21)	120(2.5)	2.16
11	121(19)	119(2.4)	2.28
12	111—114(17)	119(2.6)	2.39
13	104(16)	122(2.7)	2.49
14	101(18)	123(2.7)	2.58
15	101(19)	124(2.6)	2.69
16	101—103(22)	125(2.6)	2.78
17	101(23)	126(2.5)	2.87
18	101(23)	127(2.4)	2.99

a) The second quantities are in parentheses. b) The number of carbon atoms in the alkyl group.

rather broad peak due to melting recorded for several salts, mostly benzenesulfonates, suggests the presence of a solid-solid transition just below the melting point. In these cases, the temperature range estimated by taking into consideration the normal peak width due to melting is presented in the table; the value of enthalpy change is given for the whole peak. Solid-solid transitions well separated from the melting were also recorded quite often, but they are not included in this table.

In Fig. 1, the melting and clearing points of the benzene- and pyridine-3-sulfonates are plotted against the number of carbon atoms (*n*) in the cation. In this diagram, the upper limit of the temperature range indicated in Table 1 is taken as the melting point. The narrow temperature range of the mesophase found in the decylammonium salt in the former series is widened by the destabilization of the crystalline phase and by the stabilization of the mesophase with an increase in the alkyl chain length. While the melting point ceases to fall soon and then gradually rises (see Curve a), the clearing point continues to rise (see Curve b). In the hexadecyl-, heptadecyl-, and octadecylammonium salts, the mesophase exists over 35 °C. The pyridine-3-sulfonate exhibits a mesophase when the cation carries a dodecyl group. The melting point shows a marked even-odd alternation, but it remains within a range of only a few degrees (see Curve c). The mesophase is rapidly promoted by the increase in the number of carbon atoms in the alkyl group with a marked even-odd alternation, providing an additional check on the purity (see Curve d). The temperature range of the stable existence of the mesophase exceeds 80 °C in the octadecylammonium salt.

As is depicted in Fig. 2, the alkyl group attached to the aromatic nucleus significantly influences the thermal stability of the mesophase. The phase is metastable in nonylammonium *p*-toluenesulfonate, but it becomes stable in the next homologous member. The melting point is lowered with an increase up to n=14, but thereafter it remains at almost the same temperature (see Curve a). On the other hand, the clearing point is raised to n=17 (see Curve b). The mesophases in the hexadecyl-, heptadecyl-, and octadecylammonium salts are stable over 48 °C. The melting point and clearing point in octylammonium *p*-ethylbenzenesulfonate are not distinguishable from each other in the process of heating, but the two can easily be separated in the process of cooling. The mesophase is stable in the next member, but again metastable in the following two. The melting point then changes nearly in parallel to that of the *p*-toluenesulfonate in a slightly higher temperature range (see Curve c). As the clearing point increases only slowly with *n* (see Curve d), even the widest temperature range of stable existence achieved with the octadecylammonium salt is no more than 26 °C, the narrowest among the four series examined in the present work.

In the benzene-, *p*-toluene-, and *p*-ethylbenzenesulfonates, the enthalpy change at the clearing point decreases with the number of carbon atoms in the alkylammonium ion. Such a tendency is in agreement with what we found for the alkanesulfonates studied previously.[6] The value tends to be high in the *p*-toluenesulfonates. On the other hand, the pyridine-3-sulfonate is transformed into an isotropic

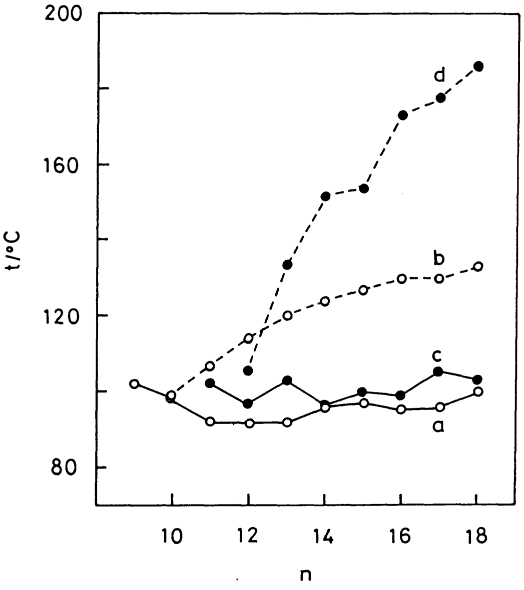

Fig. 1. Plots of transition temperatures against the number of carbon atoms in the alkyl group (*n*). (a) Melting point, (b) clearing point of alkylammonium benzenesulfonates, (c) melting point, and (d) clearing point of the pyridine-3-sulfonates.

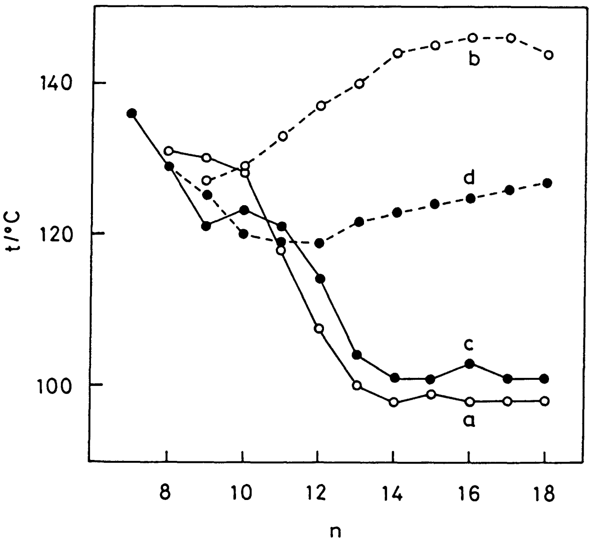

Fig. 2. Plots of transition temperatures against the number of carbon atoms in the alkyl group (*n*). (a) Melting point, (b) clearing point of alkylammonium *p*-toluenesulfonates, (c) melting point, and (d) clearing point of the *p*-ethylbenzenesulfonates.

liquid with a rather small enthalpy change. Besides, the value increases as the homologous series ascends.

In all the salts, the X-ray diffraction pattern recorded for the mesophase consists of a sharp inner peak and a diffuse outer one, indicating that the phase is of the smectic A or C type. The inner peak is accompanied by a weaker one assignable to the second-order reflection. The plot of the layer spacing in the mesophase of the benzenesulfonates against the number of carbon atoms in the cation gives a slope of 0.125 nm per methylene unit, in conformity with the fully-extended configuration of the alkyl group (see Line a in Fig. 3). The same slope is obtained by the plot for the pyridine-3-sulfonates. The latter salts give layer spacings longer by about 0.2 nm than the corresponding benzenesulfonates, even though the two anions are of nearly the same size (see Line b).

When the alkyl group in the cation is relatively short, the layer spacing in the *p*-toluenesulfonate is longer by about 0.1 nm than that of the corresponding benzenesulfonate; however, the deviation from the slope of 0.125 nm per methylene in the higher homologous members is so appreciable that the octadecylammonium salt exhibits essentially the same spacing as that given by the corresponding benzenesulfonate. The spacing shown by the *p*-ethylbenzenesulfonate comes intermediate between the benzene- and *p*-toluenesulfonates and deviates from the slope of 0.125 nm per methylene on ascending the homologous series. The mesophases given in these sulfonates may be concluded to be of the smectic A type on the basis of the observed slope of 0.125 nm per methylene and also the pseudo-isotropic texture, with oily streaks. The lateral spacing is about 0.45 nm for all the series.

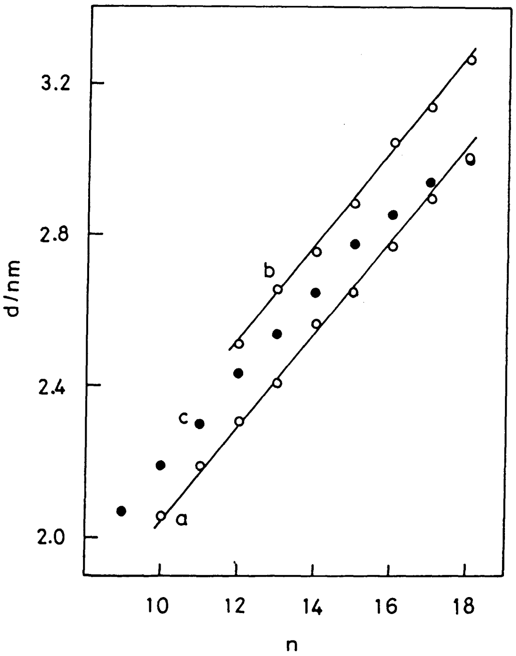

Fig. 3. Plots of layer spacings (d) in mesophases against the number of carbon atoms in the alkyl group (*n*) for alkylammonium benzenesulfonates (a), pyridine-3-sulfonates (b), and *p*-toluenesulfonates (c).

Previously, we showed that the layer spacing measured for the alkylammonium methanesulfonates agrees well with the sum of the lengths of the cation and anion and proposed a structure in which ion-pairs are alternatively oriented so that the long alkyl chains can be interdigitated with each other.[6] Similar models have been employed to represent the mesophases of alkylammonium chlorides by Busico et al., 1-methyl-4-dodecylpyridinium salts by Sudhölter et al., and 1-alkyl-4-methylpyridinium halides by Bazuin et al.[1,7,8]

The octadecylammonium ion in the most extended configuration is estimated to be about 2.60 nm long, employing a van der Waals radius of the methyl group of 0.20 nm, a C–C bond length of 0.154 nm, a C–N bond length of 0.147 nm, a tetrahedral angle, and a thermochemical radius of the ammonium ion of 0.14 nm. The difference between the calculated length of the cation and the spacing in the octadecylammonium benzenesulfonate, 3.01 nm, is no more than 0.41 nm. This value is much shorter than the estimated length of the anion, 0.95 nm, but it is long enough to accommodate the charged head group of the anion. Apparently, the long axis of the rigid anion cannot be in line with the alkylammonium ion orthogonally oriented to the layer plane. The length of the anion may be calculated on the basis of the following data; a van der Waals radius of hydrogen atom in C–H bond of 0.12 nm, a C–H bond length of 0.110 nm, an aromatic C–C bond length of 0.140 nm, a C–S bond length of 0.182 nm, and a thermochemical radius of the sulfate ion of 0.26 nm. The required thermochemical radii were taken from a table compiled by Jenkins and Thakur.[9]

As to the pyridine-3-sulfonates, the longer spacing and also the higher thermal stability of the mesophase relative to that in the benzenesulfonates may imply the presence of a specific interaction between the ammonium ion and the nitrogen atom in the anion. Indeed, the formation of a hydrogen-bonded complex cation between triethylammonium ion and pyridine has been shown by the work of Masri and Wood.[10] Therefore, the side-by-side hydrogen bonding in the sheet of ion-pairs may promote the smectic thermal stability, thus providing additional lateral intermolecular attraction. The layer structure may be destroyed only when the long alky chains are conformationally more disordered—in other words, more liquid-like, as is suggested by the relatively small enthalpy changes at the clearing point.

The fact that the spacing in the *p*-toluenesulfonate is longer by 0.1 nm than that in the corresponding benzenesulfonate may be explained by the difference between the sum of the van der Waals radius of the methyl group and the C–C bond length, 0.35 nm, and the sum of the van der Waals radius of the hydrogen atom and the C–H bond length, 0.23 nm. The shorter spacing in the *p*-ethylbenzenesulfonates may be an indication that the alkyl group attached to the anion is dissolved into the layer formed by the paraffinic parts of the cations. We have shown that the layer spacing decreases as the alkyl group on the anion becomes longer in the alkanesulfonates and that the spacings in the 1-propanesulfonates are shorter by 0.30 nm than those in the corresponding methanesulfonates.$^{6)}$

As the temperature range of the stable existence of the mesophase is wide in the octadecylammonium pyridine-3-sulfonate, we examined the layer spacing as a function of the temperature. The spacing decreases monotonously from 3.27 nm at 110 °C to 3.12 nm at 170 °C, suggesting that the increased conformational disorder gives rise to some decrease in the layer spacing. The deviations in the spacing from the linear relationship observed for the *p*-toluene- and *p*-ethylbenzenesulfonates are within the abovementioned change caused by the temperature increase and might be ascribed to the extensive conformational disorder of the long paraffinic chains.

Octadecylammonium and heptadecylammonium picrates are smectogenic. While the former solid salt is transformed into a smectic phase at 120 °C with an enthalpy change of 66 kJ mol^{-1}, and then into an isotropic liquid at 135 °C with a change of 0.6 kJ mol^{-1}, the mesophase given by the latter is metastable. When the melt formed at 114 °C with an enthalpy change of 51 kJ mol^{-1} is cooled, a smectic phase appears at 113 °C with 0.4 kJ mol^{-1}. The layer spacing of 3.33 nm found for the octadecylammonium salt is the longest among those recorded in this work, but it is still not long enough to position the long axis of the anion perpendicular to the layer plane. No mesophase was observed with the hexadecylammonium salt which melts at 113 °C. Neither the octadecylammonium 2,4-dinitrophenolate nor the 2,6-dinitrophenolate was found to be mesogenic.

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