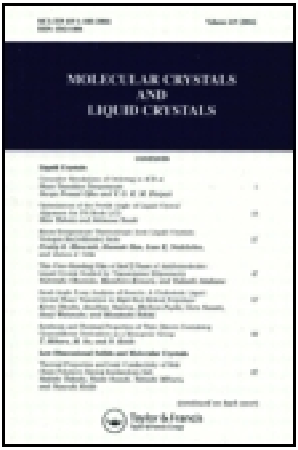

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The Thermotropic Liquid-Crystalline Behavior of Alkylammonium Naphthalenesulfonates

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A smectic A phase was observed for a number of alkylammonium naphthalene-1- and 2-sulfonates. The former series needs undecyl or longer alkyl groups to be mesogenic and the latter needs heptyl or longer ones. The clearing point is generally raised ascending the homologous series, but it is found within a rather narrow range; namely, 30°C in the case of 1-sulfonates and 21°C in the case of 2-sulfonates. The 1-naphthol-4-sulfonates are mesogenic only when the ammonium ion carries a tridecyl or longer alkyl group. The clearing point is rapidly promoted by the increase of the chain length.

Keywords: Smectic, alkylammonium salts, naphthalenesulfonates

INTRODUCTION

In our previous paper,[1] the thermotropic liquid-crystalline properties of alkylammonium benzenesulfonates and picrates were described. A large difference in the ability of forming a mesophase was noted between these two acids. While picric acid forms mesogenic salts only with heptadecyl and octadecylamines, benzenesulfonic acid forms mesogenic salts with decyl to octadecylamines. In this paper, we report an extension of our work to the naphthalenesulfonates in order to see the influence of counter ions. Furthermore, we showed that the smectic A phase given by the pyridine-3-sulfonate is markedly more stable than that given by the corresponding benzenesulfonate.[1] Since it seemed highly likely that the hydrogen-bonding between the ammonium ion and the nitrogen atom in the anion promotes the smectic thermal stability, the 1-naphthol-4-sulfonates were included in the present work.

EXPERIMENTAL

The naphthalene-1- and 2-sulfonic acids were commercially available. The 1-naphthol-4-sulfonic acid was prepared by an ion exchange (Dowex 50W-X8) from the sodium salt. Equimolar amounts of an alkylamine and an acid dissolved in boiling methanol or methanol-ethanol mixtures were mixed. The salt thus precipitated was purified by recrystallization from the same solvent until a sharp smectic-isotropic transition was recorded on the calorimetric curve during the processes of heating and cooling at the same temperature. For example, Found: C, 70.40; H, 9.88; N, 3.04; S, 6.69%. Calcd. for $C_{18}H_{37}NH_3^+$ $C_{10}H_7SO_3^-$ (1-sulfonate): C, 70.40; H, 9.92; N, 2.93; S, 6.71%. Found: C, 66.96; H, 9.28; N, 3.07; S, 6.90%. Calcd. for $C_{16}H_{33}NH_3^+$ $C_{10}H_6$ $(OH)SO_3^-$: C, 67.06; H, 9.31; N, 3.01; S, 6.89.%

Calorimetric and X-ray diffraction measurements were carried out as described in our previous paper.[1]

RESULTS AND DISCUSSION

A number of the naphthalene-1- and 2-sulfonates and also 1-naphthol-4-sulfonates can form a smectic phase. Their melting and clearing points, the associated enthalpies, and the layer spacings are summarized in Table I. Solid-solid transitions exhibited by some lower homologous members of the 2-sulfonates are not included in this table.

As is shown in Figure 1, the clearing point of the naphthalene-1-sulfonates continuously rises with increasing the alkyl chain length, whereas the melting point of the relatively lower members falls and that of the higher members gradually rises. As a result, the mesophases appearing in the first three members are metastable and the two transition temperatures coincide with each other at the tetradecylammonium salt. Then, the mesophase has a temperature range of the stable existence though it is 10°C at most. While the melting point of the naphthalene-1-sulfonate is higher only by several degrees than that of the corresponding benzenesulfonate, the clearing point is significantly depressed by the replacement of the anion. The enthalpy changes at the clearing point are similar to those reported for the benzenesulfonates. The value tends to decrease ascending the series. This tendency is in agreement with what we found for the benzenesulfonates and also for the alkanesulfonates.[1,2]

The X-ray diffraction pattern measured for the mesophase consists of a sharp inner peak and a diffuse outer one. The former peak is accompanied by a weaker one assignable to the second-order reflection. The pattern is of the smectic A or C type. The strong tendency of the mesophase to be homeotropic excludes the latter possibility. The relationship between the layer spacing (d) in the mesophase and the number of carbon atoms (n) in the alkylammonium ion is approximated by $d = 0.103n + 1.08$. The increment per methylene group is smaller than the value expected for a fully-extended conformation of alkyl chain: 0.125 nm, suggesting that the chain is in an extensive conformational disorder. The molecular length of a naphthalene-1-sulfonate ion along the line connecting the sulfur atom attached to the 1-position and the hydrogen atom attached to the 4-position of the naphthalene nucleus is estimated to be 0.95 nm on the basis of the following data: a van der Waals radius of the 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

TABLE I

Transition temperatures (°C), enthalpy changes (kJ mol^{-1}) and layer spacings (nm) of alkylammonuim salts[a]

n[b]	Melting	Clearing	Layer Spacing
		Naphthalene-1-sulfonates	
10	109 (21)	—	—
11	100 (32)	78 (3.3)	2.23
12	99 (32)	85 (2.7)	2.31
13	97 (27)	91 (2.5)	2.39
14	96 (33)	96 (2.4)	2.51
15	97 (34)	103 (2.2)	2.63
16	97 (27)	104 (2.0)	2.72
17	99 (37)	107 (2.0)	2.83
18	98 (38)	108 (2.1)	2.93
		Naphthalene-2-sulfonates	
6	139 (22)	—	—
7	157 (25)	152 (6.4)	—
8	161 (26)	153 (5.5)	2.02
9	157 (24)	151 (4.6)	2.13
10	154 (25)	152 (4.6)	2.23
11	142 (20)	155 (4.6)	2.38
12	137 (21)	161 (4.5)	2.53
13	132 (22)	166 (4.1)	2.60
14	129 (21)	168 (4.0)	2.74
15	129 (27)	171 (4.0)	2.89
16	127 (29)	173 (3.6)	2.95
17	127 (29)	174 (3.5)	3.05
18	128 (30)	173 (3.5)	3.14
		1-Naphthol-4-sulfonates	
12	156 (48)	—	—
13	149 (39)	95 (—)[c]	2.62
14	144 (42)	128 (—)[c]	2.76
15	136 (40)	172 (—)[c]	2.79
16	131 (41)	225 (—)[c]	2.87
17	128 (42)	>240(decomp)	2.93
18	130 (47)	>240(decomp)	3.03

[a] The enthalpy changes are in parentheses.
[b] The number of carbon atoms in the alkyl group.
[c] Less than 0.1 kJ mol^{-1}.

length of 0.182 nm, and a thermochemical radius of the sulfate ion of 0.26 nm. The last value was taken from a table compiled by Jenkins and Thakur.[3] If the ammonium ion, the van der Waals diameter of which is 0.28 nm,[3] and the sulfonate ion are arranged in a line, the space of 1.08 nm is too small to accommodate the cation. However, there is an open space which is large enough to place the positively-charged head group of the alkylammonium ion on the shoulder of the negatively-charged head group and above the hydrogen atom attached to the 8-position of the naphthalenesulfonate ion (see Figure 2a).

The melting point of the naphthalene-2-sulfonate is higher by 28 to 45°C than that of the corresponding 1-sulfonate (compare Curves a and c in Figure 1). The temperature decreases ascending the homologous series except for the first three members. The S_A-I transition is located at a temperature higher by 65 to 77°C than

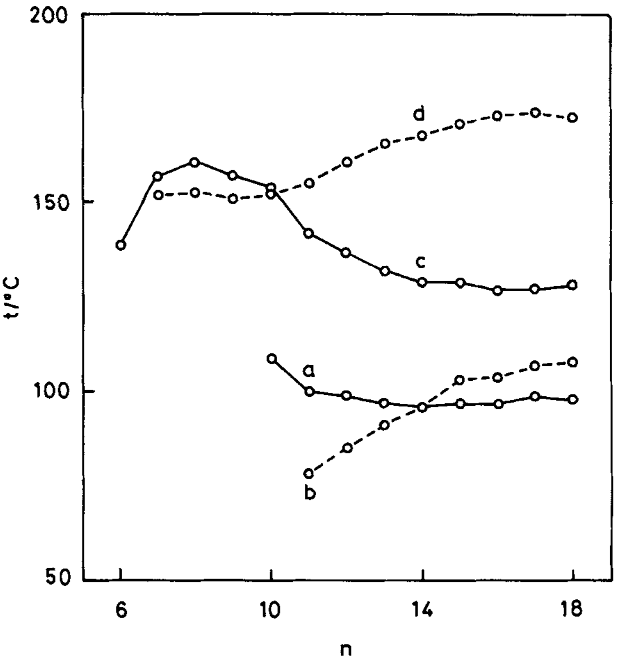

FIGURE 1 Plots of transition temperatures against the number of carbon atoms in the alkyl group (n). (a) Melting point and (b) clearing point of alkylammonium naphthalene-1-sulfonates and (c) melting point and (d) clearing point of the 2-sulfonates.

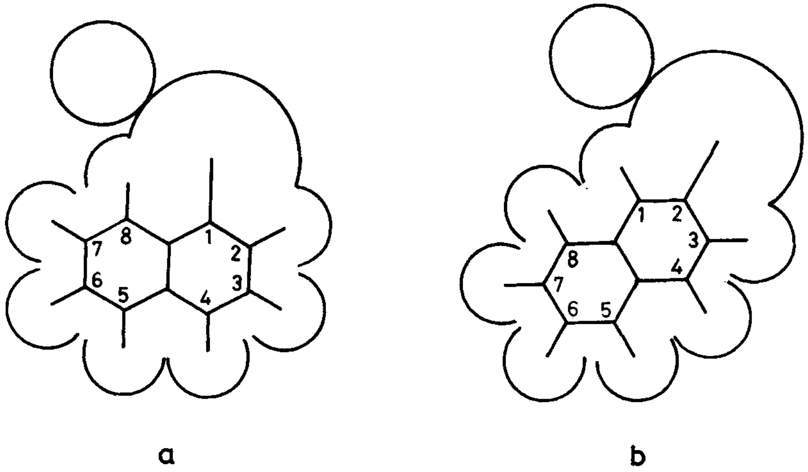

FIGURE 2 Schematic representation of the proposed arrangements of the cationic head of the alkylammonium ion and (a) the naphthalene-1-sulfonate ion and (b) the napthalene-2-sulfonate ion.

that of the 1-sulfonate. As is depicted in Figure 1, this temperature tends to rise with an increase of the alkyl chain length (see Curves b and d). Because of these tendencies, the heptyl to decylammonium salts give a metastable smectic A phase. The temperature range of the stable existence is widened from 13°C in the undecylammonium salt to 45°C in the octadecylammonium salt. The enthalpy change associated with the S_A-I transition in this series is almost twice as large compared with that in the 1-sulfonate series and decreases ascending the homologous series.

Since the mesophase is stable over a fairly wide temperature range in the last member of the naphthalene-2-sulfonate series, the layer spacing was examined at several temperatures. A slight decrease by raising the temperature was recorded; that is, 3.25 nm at 130°C, 3.17 nm at 150°C, and 3.08 nm at 170°C. The values given in Table I were measured in the middle of the range of the stable existence. They are expressed by $d = 0.113n + 1.14$. The increment per methylene group is larger than that in the 1-sulfonates but is still smaller than that expected for a fully-extended alkyl chain. The molecular length in the direction along the short axis of the naphthalene nucleus is 0.80 nm; therefore, the cation and anion can be arranged in a line with each other, leaving an open space of 0.06 nm. Besides, the width of the anion along the long axis of the naphthalene nucleus is as much as 1.12 nm and may be too wide to be efficiently packed in the mesophase. If the molecular axis is turned by 90°, the height increases to 1.13 nm. The space left on the shoulder of the negatively-charged head group is so small that the positively-charged head group of the alkylammonium ion cannot be accommodated without expanding the spacing. When the short axis is tilted by 30° to the layer normal, the height of the anion becomes about 1.00 nm as depicted in Figure 2b, allowing the positively-charged ammonium moiety to be accommodated into an open space on the shoulder of the negatively-charged head group. This arrangement may be more plausible for the naphthalene-2-sulfonates.

Regarding the smectic A phases of the above-mentioned two series, we propose a structure in which the ion-pairs are alternatively oriented so that the long alkyl chains can be interdigitated with each other. Similar models have been employed to represent the mesophases of alkylammonium benzene- and alkanesulfonates by us and also those 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.*[4-6]

The introduction of a hydroxyl group to the naphthalene-1-sulfonate ion drastically modifies the liquid-crystalline behavior. Although the observation of a smectic phase is limited to the tridecyl to octadecylammonium salts, the thermal stability is rapidly and increasingly enhanced ascending the homologous series. On the other hand, the melting point is raised by 29 to 57°C compared with that of the corresponding naphthalene-1-sulfonate. The smectic phase is metastable in the first two members and the enantiotropic transition occurs only for the next two. Thermal decomposition is observed far below the clearing point when the heptadecyl and octadecylammonium ions are employed. Similar but less pronounced dependence of the S-I transition temperature on the number of carbon atoms in the alkyl group was noted for the pyridine-3-sulfonates.

According to the table compiled by Demus *et al.*, the enthalpy changes at the non-ordered smectic-isotropic transition are usually found in the range from 2.9 to 42.7 kJ mol^{-1}.[7] Therefore, the 1-naphthol-4-sulfonates are anomalous in the sense that the endothermic peaks are too small (less than 0.1 kJ mol^{-1}) to be determined on our calorimeter. In this aspect too, the pyridine-3-sulfonates resemble, to some degree, the present series. The enthalpy changes at the S_A-I transition of the pyridine-3-sulfonate series were in the range of 0.6 to 1.0 kJ mol^{-1} which may be compared with 2.0 to 2.9 kJ mol^{-1} measured for the benzenesulfonates. Moreover, the increase of enthalpy change at the clearing point with increasing the chain length was observed, a tendency opposite to the case of benzene- and naphthalenesulfonates. Unfortunately, it is not possible to confirm whether such a tendency is shown by the 1-naphthol-4-sulfonates or not.

The X-ray diffraction pattern of the 1-naphthol-4-sulfonates is clearly of the smectic A type and the mesophase shows a strong tendency to be homeotropic. The layer spacing of the octadecylammonium 1-naphthol-4-sulfonate was recorded to be 3.03 nm at 140°C and the same at 170°C. For the other members, the measurements were made just below the S_A-I transition when the mesophase is metastable and just above the K-S_A transition when the phase is stable. The dependence of layer spacing on the number of carbon atoms in the alkyl chain is represented by $d = 0.075n + 1.67$, indicating that the chains are not orthogonal to the smectic layer. The arrangement of the positively- and negatively-charged head groups in this mesophase are, no doubt, not simple, judging from the large space left for them. A terminal hydroxyl group is known to markedly promote the mesophase of ordinary thermotropic liquid-crystalline compounds through intermolecular hydrogen bonding.[8] Moreover, a greatly enhanced mesomorphic temperature range through the formation of intermolecular hydrogen bonds in some binary mixtures such as 4-butoxybenzoic acid and trans-4-(4-ethoxybenzoyloxy)-4′-stilbazole has been disclosed.[9,10] Therefore, the dimerization or polymerization of the anions by the hydrogen-bond formation in the mesophase of the 1-naphthol-4-sulfonates seems very probable.

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