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Thermotropic Liquid Crystal Properties of Alkylammonium Alkanesulfonates

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Alkylammonium methane-, ethane-, 1-propane-, and 1-butanesulfonates exhibit a smectic A phase when the cation carries a dodecyl or longer alkyl group. The temperature range of the existence decreases in the following order: methanesulfonates > 1-propanesulfonates > ethanesulfonates > 1-butanesulfonates. In the last series, the mesophase is entirely metastable. The layer spacing in the 1-propanesulfonate is shorter by about 0.30 nm than that of the corresponding methanesulfonate, even though the alkyl chain length in the anion is increased by 0.25 nm.

Several series of long-chain alkylammonium salts have been known to exhibit mesophases. For example, alkylammonium tetrahalometallates, $(RNH_3)_2MX_4$, in which the alkylammonium ions form a double layer between MX_4 sheets, have been extensively examined and often considered as crystalline models of lipid bilayers.[1] Furthermore, the isotropic liquid of some alkylammonium chlorides is known to be preceded by a smectic A phase.[2] Since the role of a counter ion in the liquid crystal formation must be important in a system as simple as the above-mentioned salts, we have undertaken studies regarding the influence of the range of anions on the thermal properties of alkylammonium salts. Various sulfonic acids are readily available and form mesomorphic salts when combined with many long-chain alkylamines; therefore, these salts seemed to be particularly suitable for our purpose. This paper, the first of this series, reports on the properties of four series of alkanesulfonates.

Experimental

Materials. Equimolar amounts of an alkylamine and an alkanesulfonic acid dissolved in boiling alcohol were mixed. The precipitated salt was purified by recrystallization and kept in a vacuum desiccator. For example, Found: C, 59.40; H, 11.59; N, 4.33%. Calcd for $C_{15}H_{31}NH_3^+CH_3SO_3^-$: C, 59.40; H, 11.53; N, 4.33%.

Measurements. Calorimetric curves were recorded on a Rigaku Thermoflex differential scanning calorimeter at a heating or cooling rate of 5 K min^{-1}. The mesomorphic-isotropic transition was well defined on the curve; its reversal at the same temperature assured us of the purity of our salts. Enthalpy changes were estimated by comparing the peak areas with that due to the melting of indium, 3.26 kJ mol^{-1}. Phase diagrams were determined by the calorimetric curves of mixtures. X-Ray diffractions were measured with a Rigaku auto-diffractometer, model RAD IVB, using filtered copper radiation. The temperature of the sample holder was regulated as described in our earlier paper.[3]

Results and Discussion

The melting and clearing points and the associated enthalpies are summarized for alkylammonium methane-, ethane-, 1-propane-, and 1-butanesulfonates in Table 1. In the case of the methanesulfonates, the melting point decreases according to the sequence from dodecyl to tetradecylammonium and, then, remains at 143 °C. A plot of the clearing point against the number of carbon atoms (n) in the cation produces a curve which is slightly convex upwards. Conse-

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

n[b]	Melting	Clearing	Layer Spacing
	Methanesulfonates		
12	150(25)	—	—
13	147(24)	150(1.1)	—
14	142(21)	157(0.9)	2.76
15	143(24)	159(1.0)	2.85
16	143(25)	159(0.9)	3.05
17	143(26)	159(0.9)	3.12
18	143(25)	156(1.0)	3.26
	Ethanesulfonates		
13	84(23)	—	—
14	85(24)	82(0.9)	—
15	89(29)	88(1.1)	—
16	88(31)	93(1.1)	2.75
17	95(33)	97(1.1)	2.89
18	95(35)	98(1.0)	3.00
	1-Propanesulfonates		
11	77(18)	—	—
12	76(22)	71(1.8)	—
13	73(21)	80(1.8)	2.39
14	77(21)	81(1.7)	2.50
15	79(22)	87(1.8)	2.59
16	85(25)	88(1.7)	2.75
17	88(27)	93(1.7)	2.83
18	90(34)	92(1.7)	2.96
	1-Butanesulfonates		
11	74(21)	—	—
12	76(21)	65(2.3)	—
13	73(23)	68(2.3)	2.31
14	80(24)	74(2.2)	2.41
15	85(28)	75(2.2)	—
16	85(29)	77(2.2)	2.68
17	90(34)	79(2.0)	—
18	88(37)	—	—

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

quently, the widest temperature range of stable existence is achieved when the cation carries pentadecyl to heptadecyl groups. The clearing point of the ethanesulfonate is lower by 58 to 75 °C than that of the corresponding methanesulfonate and increases smoothly with the number of carbon atoms in the alkyl group; the melting point is lower by 48 to 63 °C. As a result, the mesophase is metastable when n is fifteen or less. Even when the phase is stable the temperature range of stable existence is no more than 5 °C. Both the melting and clearing points of the 1-propanesulfonates are located at temperatures several degrees lower than those of the ethanesulfonates. The mesophase given by the 1-propanesulfonate is stable when n is thirteen or more but the existence range is merely two to eight degrees. It may be noted that the clearing point of this series shows a marked even-odd alternation which provides an additional check on the purity. The transition temperatures are further lowered in the 1-butanesulfonates. As the depression of the clearing point is more pronounced than that of the melting point, all the mesophases observed for this series are metastable. The enthalpy change at the clearing point increases slightly with the number of carbon atoms in the sulfonate ion, but not with that in the ammonium ion.

The X-ray diffraction pattern recorded for the mesophases of the methane- and 1-propanesulfonates within or a little below the temperature range of the stable existence 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 sometimes accompanied by weak peaks assignable to second- and third-order reflections, since the specimen spread in the form of a thin layer over an aluminum holder is not free from orientation. The layer spacing measured for the methanesulfonates (see Table 1) agrees well with the sum of lengths of the cation and anion. For example, Found: 3.26 nm. Calcd for $C_{18}H_{37}NH_3^+ + CH_3SO_3^-$: 2.59+0.64=3.23 nm. The former length is estimated for an all-trans conformation of the alkyl group, employing a C-C bond length of 0.154 nm, a C-N bond length of 0.147 nm, a tetrahedral angle, a van der Waals radius of methyl group of 0.20 nm, and a thermochemical radius of ammonium ion of 0.14 nm (the latter employing a C-S bond length of 0.182 nm and a thermochemical radius of sulfate ion of 0.26 nm). The thermochemical radii were taken from a table compiled by Jenkins and Thakur.[4] Therefore, one may conclude that the mesophase given by the methanesulfonates is of the smectic A-type and that the schematic representation given in Fig. 1a may be a reasonable model. Here, the large circle represents the ionic end of methanesulfonate ion, the small circle that of the alkylammonium ion, and the wavy line the alkyl chain. This conclusion is consistent with the strong tendency shown by the mesophase to be homeotropic. The smectic phases of 4-alkylpyridinium

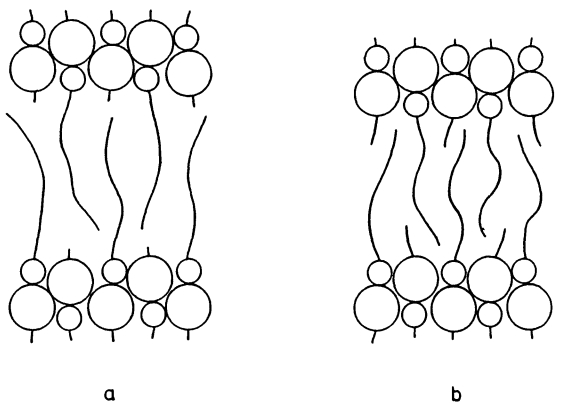

Fig. 1. Schematic representation of the proposed structure for (a) the smectic A phase of the methanesulfonate and (b) that of the 1-propanesulfonate. Large circle: the ionic end of the anion; small circle: the ionic end of the cation; wavy line: alkyl chain.

hydrochloride and 1-alkyl-4-methylpyridinium halides have been proposed to be represented by similar models by Sudhölter et al. and by Bazuin et al. respectively.[5,6] A plot of the layer spacing in the mesophase of the methanesulfonates against the number of carbon atoms in the alkylammonium ion can be fit to a slope of 0.125 nm, agreeing with the value calculated for a fully-extended configuration. The same slope appears to be applicable to a plot for the 1-propanesulfonates; however, the layer spacings, themselves, are shorter by about 0.30 nm than those of the corresponding methanesulfonates. Since the observed slope, and also the tendency to be homeotropic, strongly indicate that the mesophases are of the smectic A-type, the alkyl group attached to this anion (the whole length of which is estimated to be about 0.89 nm) must be dissolved into the layer formed by the paraffinic parts of the cations as sketched in Fig. 1b. The stable or metastable mesophases of the remaining alkanesulfonates also exhibit diffraction patterns of the same type. Although the data are scanty, the spacing seemingly decreases as the alkyl group on the anion becomes longer. The lateral spacing shrinks from about 0.47 nm for the methanesulfonates to about 0.45 nm for the 1-propanesulfonates. This change may indicate a crowding of the alkyl chains in the latter series.

The identification of the mesophases given by the ethane- and 1-butanesulfonates was supplemented by a demonstration of complete miscibility with the smectic A phase of hexadecylammonium methanesulfonate. Phase diagrams of the binary systems, consisting of hexadecylammnium ethane- and 1-butanesulfonates and a reference compound, are presented in Figs. 2a and b, respectively. In these diagrams, K, M, and I stand for crystalline, mesomorphic, and isotropic phases, respectively, and the reference compound is placed on the left-hand side. The complete miscibility between the two mesophases in the former system is

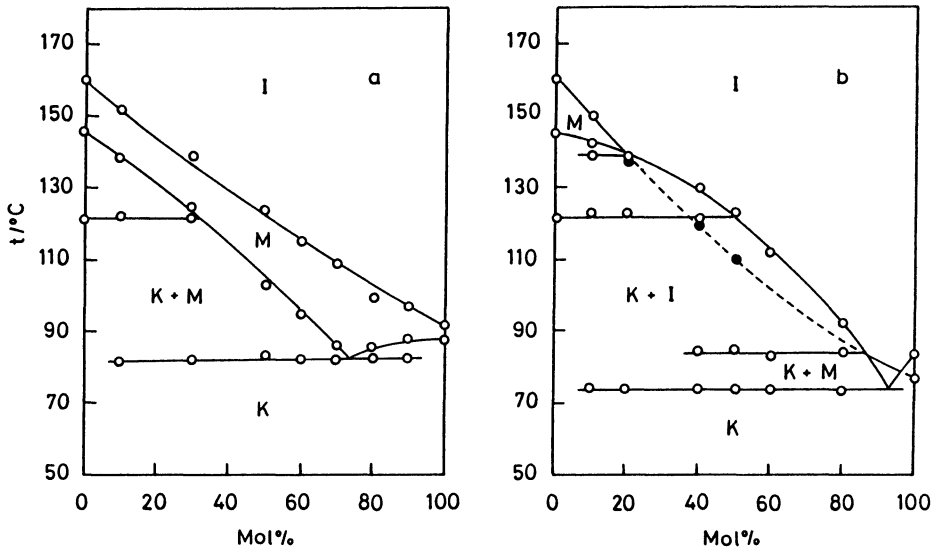

Fig. 2. Phase diagrams of (a) the hexadecylammonium methanesulfonate–ethanesulfonate and (b) the hexadecylammonium methanesulfonate–1-butanesulfonate systems. The reference compound is located on the left-hand side. The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

shown by the fact that the curve smoothly connects the two clearing points. The eutectic is located at 82 °C and 73 mol% of the ethanesulfonate. The horizontal line at 121 °C on the left-hand side is due to the solid-solid transition of the reference compound. The mesophase of the 1-butanesulfonate in Fig. 2b is metastable and the major part of the M–I transition point curve is beneath the freezing-point curve of the reference compound. The shaded circles are the I–M transitions observed during the process of cooling. The intersections between these transition point curves give rise to the appearance of horizontal lines at 84 and 138 °C. The eutectic in this system is located at 73 °C and 93 mol% of the 1-butanesulfonate. The mesophase is stable only in two small regions near the melting point of the reference compound and above the eutectic point. The crystalline phase of the methanesulfonate coexists with the mesophase in the temperature range from 73 to 84 °C, with the isotropic melt in the range from 84 to 138 °C, and again with the mesophase in the range from 138 °C to the melting point (143 °C).

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