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Liquid crystals derived from multi-cationic azamacrocyclic alkylsulphates

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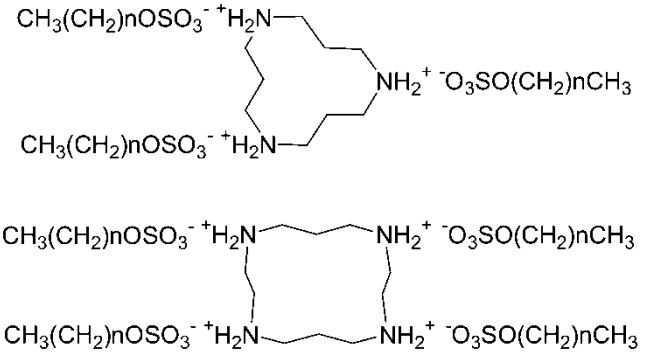
Two homologous series of azamacrocyclic *n*-alkylsulphates were synthesized and characterized. Their thermotropic liquid crystalline behaviour was studied by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. At room temperature both series exhibited lamellar crystalline phases. For the tetraazacyclotetradecane alkylsulphate salts a highly ordered smectic phase was observed following their melting. The triazacyclododecane derivatives however melted into disordered smectic A phases, apparently due to the less symmetric polar group which does not favour in-layer organization. Extensive hydrogen bonding was observed in the crystalline phases of both series of compounds as well as above their melting into smectic phases, albeit rather weak in the case of the triaza derivatives.

1. Introduction

The thermotropic liquid crystalline behaviour of amphiphilic molecules [1, 2] with one polar head group has been extensively studied. A wide range of polar heads, including ammonium [3], aliphatic quaternary ammonium [4], carboxylate [5], sulphonate [6], pyridinium [7] and quaternary phosphonium [8] groups have been introduced. The type of liquid crystalline phases exhibited by these compounds depended on an interplay of the length and number of lipophilic chains, the nature of the polar heads and the counter ions. Quaternization of tertiary aliphatic amines, using a range of organic halides, proved especially fruitful for producing various liquid crystalline phases [4]. On the other hand protonated ammonium salts [3], as expected, lack this possibility and liquid crystalline polymorphism was less rich than that seen for the quaternized salts [1]. In this case only the length of the aliphatic chain affects the liquid crystalline behaviour of the salts.

Dipolar amphiphilic compounds also exhibit various liquid crystalline phases which are also dependent on the polar head groups, and the type and the length of the spacer between the polar heads. Thus, early examples of dipolar amphiphiles with two pyridinium head groups, attached on a biphenylene core with the appropriate chain length spacers, exhibited smectic liquid crystalline phases [9]. All aliphatic bis(quaternary) amphiphilic ammonium salts [10] exhibited smectic phases, one of which, at least, resembled the smectic T phase [11]. When a hydrophilic oligo(oxyethylene) spacer was introduced in *gemini* dialkylammonium surfactants, depending on the length of this spacer and temperature, L_β and L_α phases were exhibited [12]. For 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromides [13] an aliphatic bicyclo moiety was inserted between two long aliphatic chains resulting also in a smectic T phase. Recently, ordered smectic phases were established for piperazinium *n*-alkylsulphates, while smectic A phases were exhibited by homopiperazinium derivatives [14]. The differences in the mesophases observed were attributed to the symmetry of the piperazinium di-cation as opposed to the non-symmetric homopiperazinium group.

In the present investigation the effect of the triaza and tetraaza multi-cations on the liquid crystalline character of their amphiphilic alkyl sulfate salts is investigated (see scheme below). In this context it is



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worth mentioning that investigations containing macrocyclic moieties focused on the formation and characterization of liquid crystalline compounds in which the long alkyl chains were covalently attached on these azamacrocyclic cores [15]. Differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) identified the liquid crystalline character of these salts while X-ray diffraction (XRD) established their supramolecular structures.

2. Experimental

2.1. *Materials and synthesis*

1,4,8,11-Tetraazacyclotetradecane and 1,5,9-triazacyclododecane trihydrobromide were purchased from Aldrich. 1,4,8,11-tetraazacyclotetradecane was used without further purification; 1,5,9-triazacyclododecane trihydrobromide was purified by dissolving it in water and precipitating with acetone. Sodium decyl sulfate and sodium dodecyl sulphate were purchased from Janssen while sodium tetradecyl sulphate and sodium hexadecyl sulphate were purchased from Merck. All alkyl sulphates were recrystallized from ethanol before use.

2.1.1. *Synthesis of 1,4,8,11-tetraazacyclotetradecane tetrahydrobromide*

1,4,8,11-Tetraazacyclotetradecane was dissolved in chloroform and protonated by adding excess of aqueous hydrobromic acid under intense agitation. The protonated product spontaneously precipitated, and was filtered and recrystallized from ethanol/water (4:1 v/v). The material was exhaustively dried under vacuum over phosphorus pentoxide.

2.1.2. *Synthesis of tetrakis-n-alkyl sulphates of 1,4,8,11-tetraazacyclotetradecane (n=10,12,14,16)*

To 0.1 mol of 1,4,8,11-tetraazacyclotetradecane tetrahydrobromide, dissolved in water, 0.42 mol of *n*-alkyl sodium sulphate dissolved in water was added. For dissolving the higher members of the series slight heating was required. The precipitated salts were filtered, washed with hot water, recrystallized from ethanol and dried under vacuum over phosphorus pentoxide. Their structures were established by ^{1}H NMR and elemental analysis. ^{1}H NMR (500 MHz, DMSO-d_6, $T=50^\circ$C): $\delta=6.25$ (s, NH_2^+), 3.70 (t, $^-OSO_3C\underline{H}_2CH_2$), 2.85 (broad s, $^+H_2NC\underline{H}_2C\underline{H}_2+$ *H_2NC*), 2.75 (broad s, $^+H_2NC\underline{H}_2CH_2C\underline{H}_2NH_2^+$), 1.70 (broad s, $^+H_2NCH_2C\underline{H}_2CH_2NH_2^+$), 1.40 (t, $^-OSO_3CH_2C\underline{H}_2$), 1.20 (m, $^-OSO_3CH_2CH_2(C\underline{H}_2)_nCH_3$), 0.75 (t, CH_3).). Elemental analysis: $C_{50}H_{112}N_4S_4O_{16}$: calc. C 52.05, H 9.79, N 4.86, S 11.12; found C 51.74, H 9.80, N 4.88, S 11.25%. $(C_{58}H_{128}N_4S_4O_{16})H_2O$: calc. C 54.26, H 10.21, N 4.36, S 9.99; found C 54.27, H 10.39, N 4.53, S 10.36%. $(C_{66}H_{144}N_4S_4O_{16})(H_2O)_2$: calc. C 56.06, H 10.55, N 3.96, S 9.07; found C 56.20, H 10.62, N 3.98, S 9.58%. $C_{74}H_{160}N_4S_4O_{16}$: calc. C 59.64, H 10.82, N 3.76, S 8.60; found C 59.39, H 10.93, N 3.91, S 8.75%.

2.1.3. *Synthesis of tris-n-alkyl sulphates of 1,5,9-triazacyclododecane (n=10,12,14,16)*

To 0.1 mol of 1,5,9-triazacyclododecane trihydrobromide, dissolved in water, 0.32 mol of *n*-alkyl sodium sulphate salt, also dissolved in water, was added. For dissolving the hexadecyl sodium sulphate salt slight heating was required. The mixture was allowed to react for several hours at room temperature. The products obtained were separated from the reaction mixture by centrifugation, then dissolved in methanol, precipitated with water, centrifuged and exhaustively dried under vacuum over phosphorus pentoxide. The structures of the resulting salts were established by ^{1}H NMR and elemental analysis. ^{1}H NMR (500 MHz, DMSO-d_6, $T=50^\circ$C): $\delta=7.50$ (s, NH_2^+), 3.70 (t, $^-OSO_3C\underline{H}_2CH_2$), 3.10 (broad s, $^+H_2NC\underline{H}_2CH_2C\underline{H}_2NH_2^+$), 1.95 (broad s, $^+H_2NCH_2C\underline{H}_2CH_2NH_2^+$), 1.50 (t, $^-OSO_3CH_2C\underline{H2}$), 1.25 (m, $^-OSO_3CH_2CH_2(C\underline{H}_2)_nCH_3$), 0.85 (t, CH_3). Elemental analysis: $(C_{39}H_{87}N_3S_3O_{12})H_2O$: calc. C 51.80, H 9.92, N 4.65, S 10.64; found C 51.68, H 9.85, N 4.58, S 10.53%. $(C_{45}H_{99}N_3S_3O_{12})_2H_2O$: calc. C 55.18, H 10.29, N 4.29, S 9.82; found C 55.22, H 10.45, N 4.44, S 9.63%. $C_{51}H_{111}N_3S_3O_{12}$: calc. C 58.08, H 10.61, N 3.98, S 9.12; found C 57.91, H 10.86, N 3.82, S 9.19 %. $(C_{57}H_{123}N_3S_3O_{12})_2H_2O$: calc. C 59.65, H 10.89, N 3.66, S 8.38; found C 59.65, H 11.13, N 3.62, S 8.05%.

2.2. *Characterization*

Liquid crystal textures were observed using a Leitz–Wetzlar polarizing microscope equipped with a Linkam hot-stage. Thermotropic polymorphism was investigated by differential scanning calorimetry employing a DSC-10 calorimeter (TA instruments) at heating/cooling rates of 10°C min^{-1}. Thermal stability was assessed by thermogravimetry employing a TGA 2050 analyser (TA instruments) at a heating rate of 10°C min^{-1}. Liquid crystalline phases were investigated by X-ray diffraction using $CuK_{\alpha1}$ radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-AXIS IV image plate. Powder samples were sealed in Lindemann capillaries and heated using an INSTEC hot stage. FTIR studies were performed using a Nicolet Magna 550 spectrometer coupled with a VLT-2 variable temperature cell (Research & Industrial Instruments Company).

Table 1. Melting temperatures and enthalpies for the triazacyclododecane derivatives.

n	T/°C	ΔH/kJ mol^{-1}
10	51.3	23.5
12	63.8	33.9
14	65.5	43.7
16	71.8	50.3

Table 2. Melting temperatures and enthalpies for the tetraazacyclotetradecane derivatives.

n	T/°C	ΔH/kJ mol^{-1}
10	57.4	16.6
12	69.4	41.6
14	80.3	54.4
16	92.0	64.0

3. Results and discussion

3.1. *Thermal and optical studies*

The triaza derivatives were thermally stable up to 130°C when heated at a rate of 10°C min^{-1}. At higher temperatures they began to decompose, especially at temperatures above 200°C, i.e. at temperatures below their isotropization temperatures. The tetraaza derivatives exhibited essentially the same behaviour. At 140°C the weight loss was less than 0.7% for the triaza and 0.6% for the tetraaza derivatives.

Upon heating under the polarizing microscope the triaza derivatives melted into fluid birefringent phases with ill developed focal-conic domains at temperatures ranging from 51 to 72°C (table 1). On the other hand, the tetraaza derivatives melted to birefringent, highly viscous phases with marbled textures (figure 1) at somewhat higher temperatures (table 2), suggesting the presence of highly ordered mesophases. Since both series of compounds degrade before their isotropization temperatures, it was not possible to obtain well developed liquid crystalline textures. The transitions observed by POM were confirmed by DSC, which also revealed, in certain cases, crystal–crystal transitions at lower temperatures, which however were not observed during the second heating. Both the transition temperatures and transition enthalpies depend rather strongly on the length of the alkyl chains, suggesting that the crystal stability is dominated by the packing of the alkyl chains and that the transitions mainly result from the melting of the aliphatic chains (see also discussion of XRD results).

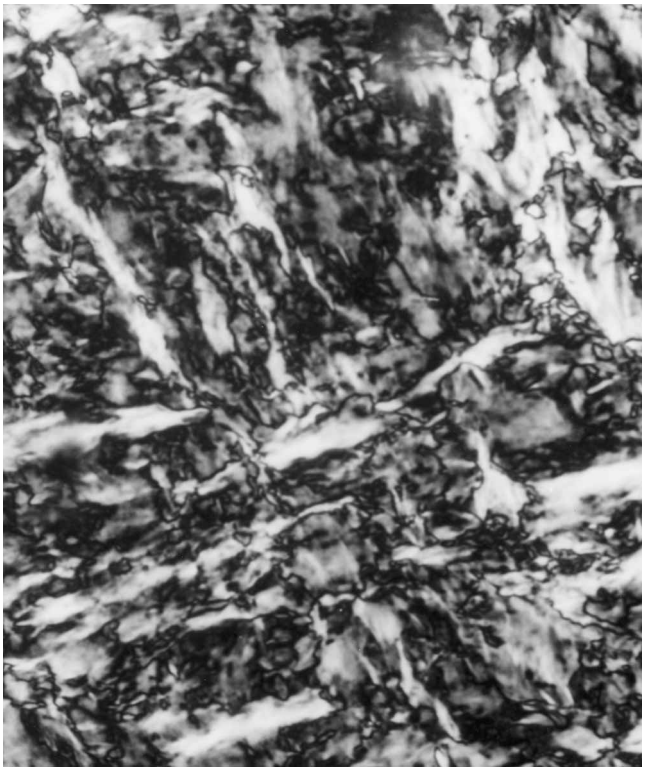

Figure 1. Texture of tetraazacyclotetradecane hexadecylsulphate observed under POM.

3.2. *Structural investigation of the smectic phases*

Before investigating the structural characteristics of the phases, it should be noted that although the di-protonated or neutral tetraazacyclotetradecane (cyclam) molecules adopt an endodentate conformation the tetraprotonated cyclams adopt a centrosymmetric exodentate conformation. The protonated amino groups are directed away from the macrocycle, being located as far away as possible from each other to minimize electrostatic interactions [16]. As a result of the tendency to adopt this conformation, the molecule can simultaneously hydrogen bond up to eight different hydrogen bond acceptors such as carboxylate or sulphate groups [16–18]. Additionally in the case of the cyclam tosylate salt, the tosyl moieties arrange themselves to form hydrophobic regions above and below the hydrogen-bonded sheet comprising the polar layer [18].

FTIR spectroscopy was used to investigate hydrogen bonding in both series of compounds as a function of increasing temperature. For the tetraaza derivatives in the crystalline phase, the spectra of the compounds contain in the N–H stretching region four bands at 3130, 3244, 3376 and 3465 cm^{-1} that are in agreement with those reported in the literature for guanidinium benzensulphonate [19] or for guanidinium benzene sulphonates [20], suggesting the formation of a hydrogen-bonded pattern between the sulphate and the amino groups. Although not explicitly stated in the literature, these bands can be assigned to the symmetric

and antisymmetric stretching vibrations of the NH_2^+ groups hydrogen-bonded to two different oxygen atoms of the sulphate ion located at different distances; this was established crystallographically in the case of cyclam tosylate or cyclam sulphate [16, 18]. At temperatures just above the thermal transition detected by DSC, the absorption bands in the infrared spectra decrease in intensity, becoming broader while retaining their peak positions. A hydrogen bonding network is therefore present even after the melting of the compounds to a less ordered phase.

The FTIR spectra of the triaza derivatives exhibit similar characteristics at room temperature. In the same N–H stretching region, four bands are observed at 3250, 3365, 3440 and 3528 cm^{-1}, i.e. at higher wave numbers than for the tetraaza derivatives, suggesting that the hydrogen bonding pattern is weaker. On heating above the melting temperature, only two low intensity broad bands are discernible at 3250 and 3440 cm^{-1} suggesting that weak hydrogen bonding is present between the NH_2^+ groups with only one oxygen atom of the sulphate ion.

The XRD patterns of the tetraaza derivatives at temperatures above the transition temperatures contain in the small angle region four sharp equidistant reflections, revealing the lamellar ordering of the molecules. The *d*-spacings vary linearly with the number of carbon atoms in the alkyl chains according to the equation $d\ (\text{Å}) = 8.5_{\pm 0.5} + 1.82_{\pm 0.04}\ n$ at 100°C (figure 2). The *Y*-intercept, which is a measure of the thickness of the polar sublayer, is very close to the crystallographically determined distance between the sulphate groups in the hydrophilic layer of the cyclam tosylate salt [18] and therefore the tetraaza groups are almost orthogonal in the polar sublayer.

In the wide angle region the X-ray patterns contain a diffuse band centred at about 4.5 Å, indicative of the liquid-like conformation of the alkyl chains; a number of low intensity reflections (figure 3) reveal the existence of a high order of molecules within the layers as well as that the layers are correlated with each other. With increasing chain length the number of sharp reflections decreases, evidently due to the increase in separation of the ionic charges. Additionally, the width at half-height of the most intense wide angle reflections suggests that the correlation extends to about 250–300 Å, depending on the length of the alkyl chains, which corresponds to approximately seven successive layers for the hexadecyl up to about ten layers for the decyl derivative. The three-dimensional correlations between the sublayers arise from the long range electrostatic interactions of the ionic moieties periodically distributed inside the polar layers [21]. This phase is therefore, formally, a genuine crystal exhibiting three-dimensional positional order, although it is soft and fluid. The electrostatic interactions are however stronger within the polar layers than between them, and therefore the smectic layers are able to slip over each other. From a morphological point of view therefore, this phase can be considered as a highly ordered smectic liquid crystal.

Although XRD data of monodomains are not available, it was possible to assign, at least tentatively, the reflections observed (table 3) to a three-dimensional monoclinic lattice. As shown in table 3 the cell parameters are almost identical for all the tetraaza compounds ($a = 13.3$ Å, $b = 10.0$ Å). The angles of the monoclinic cells, $\beta \cong 88°$, have values very close to 90°, i.e. the cell is close to orthorhombic. The number of

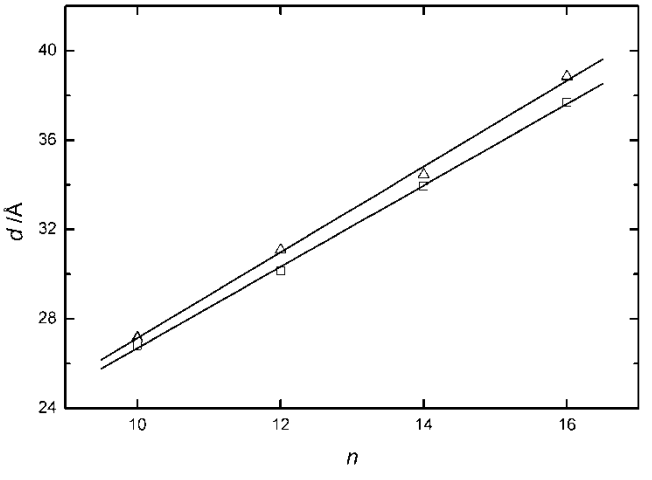

Figure 2. Smectic periodicities of the triaza (triangles, 80°C) and tetraaza (squares, 100°C) derivatives as a function of the number of carbon atoms in the alkyl chains.

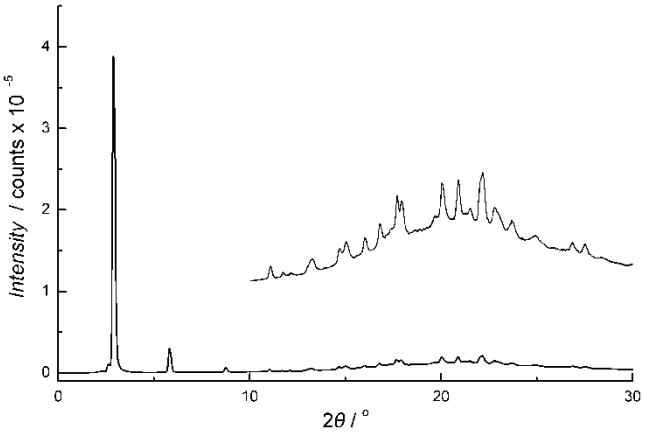

Figure 3. XRD pattern of tetraazacyclotetradecane dodecylsulphate in the smectic phase at 100°C. For clarity, the diffractogram is also shown at angles $2\theta > 10°$ with its intensity multiplied by a factor of 15.

Table 3. XRD data for the C_{10}–C_{16} tetraazacyclotetradecane alkylsulphate salts at 100°C; d_{obs} and d_{calc} are the observed and calculated spacings, respectively, of the ($h\,k\,l$) reflections of the monoclinic cells.

	C_{10}		C_{12}		C_{14}		C_{16}	
$h\,k\,l$	$a=10.01_8$ Å $b=13.34_4$ Å $c=26.92_6$ Å $\beta=88.08°$		$a=10.02_3$ Å $b=13.34_9$ Å $c=30.21_9$ Å $\beta=87.96°$		$a=9.99_0$ Å $b=13.36_4$ Å $c=33.97_3$ Å $\beta=87.85°$		$a=10.00_0$ Å $b=13.36_0$ Å $c=37.70_0$ Å $\beta=88.00°$	
	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
0 0 1	26.808	26.908	30.152	30.201	33.940	33.949	37.700	37.685
0 0 2	13.466	13.455	15.121	15.100	17.057	16.976	19.095	18.838
0 0 3	8.977	8.970	10.089	10.066	11.355	11.317	12.693	12.560
0 0 4	6.746	6.728	7.559	7.550				
0 0 5	5.353	5.382	6.032	6.040	6.751	6.790		
0 0 6	4.492	4.485	5.009	5.033	5.663	5.658	6.307	6.280
1 1 0	8.051	8.009	8.017	8.012	7.994	7.990	8.010	8.003
1 1 1	7.747	7.733						
1 1 2	6.901	6.964	7.287	7.162				
0 2 0	6.740	6.672	6.685	6.675	6.629	6.682	6.654	6.680
0 2 2	5.986	5.977	6.045	6.105	6.183	6.217	6.307	6.296
1 2 0	5.561	5.552	5.532	5.554	5.547	5.553		
−1 2 1	5.365	5.418			5.441	5.462	5.469	5.479
1 2 2	5.184	5.166	5.269	5.246	5.302	5.311	5.376	5.355
2 0 0	4.998	5.006	5.009	5.008	4.980	4.991	4.995	4.997
2 0 1	4.926	4.952	4.950	4.969	4.951	4.965		
2 1 0	4.671	4.687						
−2 1 1	4.593	4.593						
2 1 2	4.493	4.470	4.509	4.521	4.563	4.549		
0 3 1	4.377	4.388	4.420	4.402	4.454	4.417	4.382	4.422
2 1 3	4.172	4.209						
1 2 5			4.121	4.129	4.349	4.343	4.493	4.513
2 0 4			4.241	4.244	4.373	4.375	4.468	4.479
2 1 4			4.040	4.044	4.180	4.158	4.250	4.247
1 3 1	4.024	4.027	4.040	4.038	4.096	4.096	4.062	4.050
2 2 0	3.988	4.004	4.010	4.006	4.003	3.999	4.011	4.001
2 2 2	3.870	3.866	3.893	3.900	3.922	3.919	3.936	3.936
−2 2 2	3.805	3.810	3.850	3.845				
2 2 3	3.690	3.694	3.744	3.759	3.798	3.806		
2 2 4			3.572	3.581	3.643	3.660		
2 3 0	3.295	3.325	3.321	3.326	3.329	3.324	3.323	3.325
2 3 1	3.295	3.309						
2 3 2	3.237	3.245	3.256	3.265	3.287	3.277	3.295	3.287
3 1 0	3.237	3.238	3.240	3.239	3.231	3.229	3.240	3.232
3 1 1	3.214	3.227						

molecules Z per each unit cell can be easily obtained by means of the linear dependence of the smectic periodicity d on the number n of carbon atoms in the alkyl chains [21]: $d=ZV_o/S+(ZV_{CH2}/S)n$, where $S=ab$ is the area of the base of the cell and V_{CH2} the known volume of one methylene group (28 Å^3 at 100°C) [22]. From the experimentally determined slope of the d vs. n straight line, the derived Z value is 2.1 suggesting that each cell contains two molecules. The area of the unit cell (133 Å^2) occupied by four melted aliphatic chains leads to a cross-sectional area of approximately 33 Å^2 available to each one. The area of the disordered alkyl chains in smectic liquid crystalline phases generally lies between 21 and 27 Å^3 [20]. It is therefore evident that there is enough lateral space in the paraffin layers for the aliphatic chains to interdigitate to some extent. This interdigitation can also explain the fact that the polar layers are correlated with each other, leading to a three-dimensional crystal-like structure as was also suggested for the tetragonal phase of quaternary dihydroxy alkylammonium derivatives [21].

On the other hand the X-ray patterns of the triaza derivatives recorded at temperatures above their main transition contain more than two equidistant reflections in the small angle region due to the smectic layering of the molecules, and one diffuse ring in the wide angle

region centred at 4.5 Å typical of the liquid-like conformation of the alkyl chains. The lamellar spacings vary linearly with the number n of methylene groups in the alkyl chains according to the equation d (Å) $= 7.9_{\pm 0.6} + 1.92_{\pm 0.05}\ n$ at 70°C (figure 2). The Y-intercept indicating the thickness of the polar sublayer is in very good agreement with the distance between the sulphate groups as estimated using HyperChem software (Hypercube, Inc) and that obtained from the crystallographic data of 1,5,9-triazadodecane N,N',N''-tritosylamide [23]. It is concluded therefore that the sulphate groups are positioned in the upper and lower surfaces of the polar sublayers in close contact to the protonated amino groups. As is widely accepted for amphiphilic-type molecules incorporating incompatible lipophilic and hydrophilic parts [22, 24], the smectic layers consist of alternating polar and apolar layers periodically stacking in space. In the present case, the polar parts are surrounded by three alkyl chains. This necessitates an alternating ordering of the polar moieties to allow an equal number of alkyl chains to be positioned above and below the hydrophilic sublayer, as shown schematically in figure 4. This requirement does not allow a regular packing of the triazadodecane cores that could lead to the formation of ordered smectic phases as observed for symmetric multi-polar cores such as the piperazinium [14] or tetraazacyclotetradecane cores.

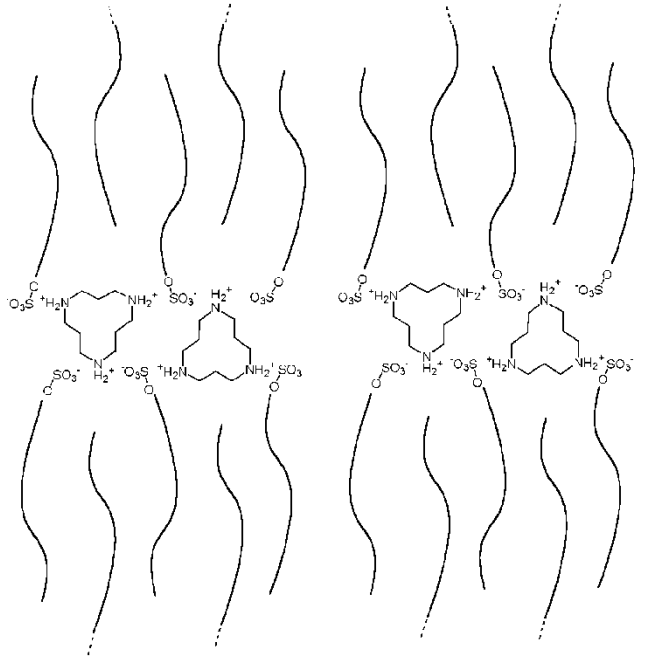

Figure 4. Schematic representation of the structure of triaza derivatives in the smectic phase. The molten alkyl chains are, to some extent, interdigitated.

4. Conclusions

The effect of multi-cationic polar groups on the thermotropic properties of amphiphilic molecules has been investigated for the case of tetraazacyclotetradecane and triazacyclododecane n-alkylsulphates. The tetraaza derivatives melt into a viscous, highly ordered lamellar phase with the alkyl chains in a disordered conformation and characterized by in-layer and inter-layer ordering. The triaza derivatives melt into a disordered smectic A phase which is attributed to the less symmetric polar group that hinders in-layer organization. Extensive hydrogen bonding between the NH_2^+ group and the oxygen atoms of the sulphate ion are present in the low temperature crystalline phases and also favour the formation of the highly ordered mesophase.

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