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Cubic and columnar thermotropic mesophases of potassium dialkylphosphate salts

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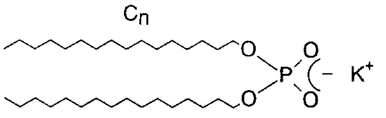
Long chain potassium dialkylphosphate salts, from dioctyl to dioctadecyl, were synthesized and their thermal stability was checked by thermogravimetry. Their thermotropic liquid crystalline behaviour was investigated using differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. Crystalline at room temperature, they were all found to exhibit upon heating a I*a*3*d* body-centred cubic phase followed by a columnar mesophase of hexagonal symmetry. Structures and structural parameters are discussed.

1. Introduction

It was found recently that, in addition to forming vesicles when dispersed in water [1–3], the alkali metal salts of dihexadecylphosphoric acid are perfectly capable of producing thermotropic liquid crystals when heated over the melting temperature of the crystals [4]. They thus fall into the category of what is sometimes described as amphotropic materials [5]. The lithium and sodium salts give rise specifically to columnar mesophases, while the potassium, rubidium, and caesium salts display a I*a*3*d* body-centred cubic phase as well, in the temperature range between the crystal and the columnar mesophase.

In the present endeavour, the potassium salts of a homologous series of dialkylphosphoric acids from dioctyl to dioctadecyl were synthesized, their thermal stability was evaluated by thermogravimetry, and their liquid crystalline behaviour investigated by polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction. As a function of increasing temperature, these compounds were all found to display a lamellar crystal phase at room temperature, then a I*a*3*d* body-centred cubic mesophase in the vicinity of 100°C, and finally a columnar mesophase of hexagonal symmetry at high temperatures. Special emphasis was laid in this work on the influence of the length of the alkyl chains on the structural parameters of the phases observed and on the phase transitions involved.



n = 8, 10, 12, 14, 16 and 18

2. Synthesis

The synthesis of the dialkylphosphate potassium salts was performed in two steps. First, the corresponding dialkylphosphoric acids were prepared as described previously [4]. Two equivalents of alkanol with one equivalent of pyridine dissolved in dry benzene were added dropwise with stirring at 0°C, to a dry benzene solution of freshly distilled phosphorus oxychloride ($POCl_3$). After heating under reflux for 5 h and cooling to room temperature, the mixture was washed exhaustively with dilute aqueous hydrochloric acid to remove pyridine. After evaporation of the organic layer, the residue was recrystallized twice from ethyl acetate. Purity was checked by elemental analysis. $C_{16}H_{35}PO_4$: calc. C 59·60, H 10·94; found C 59·56, H 10·98%. $C_{20}H_{43}PO_4$: calc. C 63·46, H 11·45; found C 63·61, H 11·46%. $C_{24}H_{51}PO_4$: calc. C 66·32, H 11·83; found C 66·50, H 11·96%. $C_{28}H_{59}PO_4$: calc. C 68·53, H 12·12; found C 68·54, H 12·23%.

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$C_{32}H_{67}PO_4$: calc. C 70·28, H 12·35; found C 70·30, H 12·41%. $C_{36}H_{75}PO_4$: calc. C 71·71, H 12·54; found C 71·29, H 12·59%.

In a second step, the dialkylphosphoric acids were neutralized with stoichiometric amounts of potassium hydroxide. The reaction was carried out in ethanol for the octadecyl, hexadecyl, and tetradecyl derivatives, and in acetone for the others. The final products were recrystallized twice from ethanol for octadecyl, hexadecyl, and tetradecyl, from a mixture of ethanol–acetone (1 : 1 v/v) for dodecyl, and from ethyl acetate for octyl and decyl. Purity was checked by elemental analysis. $C_{16}H_{34}PO_4K$: calc. C 53·30, H 9·50; found C 52·93, H 9·91%. $C_{20}H_{42}PO_4K$: calc. C 57·66, H 10·16; found C 56·83, H 10·56%. $C_{24}H_{50}PO_4K.H_2O$: calc. C 58·74, H 10·67; found C 58·95, H 10·79%. $C_{28}H_{58}PO_4K.H_2O$: calc. C 61·49, H 11·05; found C 61·26, H 11·09%. $C_{32}H_{66}PO_4K.H_2O$: calc. C 63·74, H 11·36; found C 64·51, H 11·58%. $C_{36}H_{74}PO_4K.H_2O$: calc. C 65·61, H 11·62; found C 65·79, 11·76%.

3. Thermal behaviour

The compounds synthesized were first studied by thermogravimetry (TA-TGA 2050 analyser). As found previously for the dihexadecyl salt [4], they were all reasonably stable at temperatures below 180°C. Isothermal experiments at 165°C showed that the samples withstood a 3 hour heating with weight losses smaller than 1%. On the other hand, separate experiments showed that the salts from dodecyl to octadecyl lose one molecule of water on heating in the temperature range from 70 to 100°C, in total agreement with elemental analysis; they also showed them to recover water rapidly on cooling to room temperature in the open air. The hydration difference of the longer with respect to the shorter alkyl chain salts does not affect the liquid crystal behaviour of the compounds, since liquid crystallinity appears at temperatures where hydrates no longer exist.

The thermotropic liquid crystal polymorphism of the salts was then investigated by differential scanning calorimetry (TA-DSC 10 calorimeter, heating and cooling rates of 10°C min^{-1}) and polarizing optical microscopy (Leitz-Wetzlar, Linkam TMS 91 hot stage). Visual observation showed that all the compounds undergo two successive phase transitions on heating above room temperature. At temperature T_c, they melt into an isotropic, rather viscous phase, which is a cubic mesophase as discussed later; at temperatures $T_d > T_c$, they transform into a birefingent, rather fluid phase exhibiting optical textures similar to those previously reported for the dihexadecylphosphate caesium salt in its columnar mesomorphic state (see figure 3 in [4]). This polymorphic behaviour, already observed in the particular case of the dihexadecylphosphate potassium salt [4], was then fully confirmed by DSC (see the table). Complete melting (above 200°C) into a true isotropic liquid could not be observed without thermal degradation. Upon cooling, both transitions took place reversibly, with a hysteresis of about 10 to 20°C. As shown in figure 1, the transition temperature from the crystal to the cubic mesophase increases with the number of carbon atoms in the alkyl chains, while that from the cubic to the columnar phase decreases monotonically. The stability range of the cubic mesophase therefore increases significantly when the length of the alkyl chains, and hence the lipophilic character of the molecules, decreases.

The enthalpy measured at the transition from the crystal to the cubic mesophase, when the alkyl chains fall into conformational disorder as is well known, increases linearly with the length of the alkyl chains (see the table). The slope of the corresponding straight line ($6{\cdot}95 \pm 0{\cdot}30\,\mathrm{kJ\,mol^{-1}}$, as deduced from a linear least square fit of the data for $n \geqslant 10$) indicates that the

Table. Phase transition temperatures T (onset) and enthalpies ΔH of the potassium dialkylphosphate salts, measured by differential scanning calorimetry: n is the number of carbon atoms in the alkyl chains; subscript indices c and d indicate crystal to cubic and cubic to columnar phase transitions, respectively.

n	T_c/°C	T_d/°C	ΔH_c/kJ mol^{-1}	ΔH_d/kJ mol^{-1}
8	37	81	33	3
10	53	178	55	2
12	67	163	71	2
14	75	143	87	2
16	82	132	98	2
18	86	116	111	2

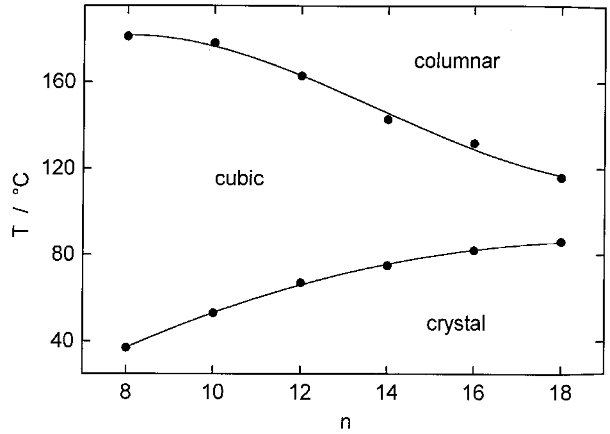

Figure 1. Phase transition temperatures of the potassium dialkylphosphate salts from crystal to cubic then to columnar, measured by differential scanning calorimetry, as a function of the number of carbon atoms in the alkyl chains.

molar enthalpy of melting increases by about 3·5 kJ per methylene unit, that is, by about 15% less than for *n*-alkanes (4·1 kJ, see in [6]). This is probably related to the fact that the enthalpy of the crystal is larger than normal, due to stereochemical constraints arising from the chain packing, as discussed below (also see [7]). The crystal to mesophase transition enthalpy for the dioctyl salt falls slightly below the straight line, probably due to a different molecular packing in the crystal state. As for the transition from cubic to columnar, which corresponds to a change in the spatial arrangement of the polar heads alone [4], this involves enthalpies which are small and practically independent of the chain length (see the table).

The thermotropic liquid crystal polymorphism of the salts was finally investigated by X-ray diffraction (Guinier focusing camera, CuK_{α_1} radiation, INEL CPS-120 curved position-sensitive detector, INSTEC hot stage). The thermotropic behaviour found by polarizing optical microscopy and differential scanning calorimetry was thus fully confirmed, the spacing of the first small angle Bragg reflection observed changing abruptly at exactly the same temperatures as those listed in the table.

4. Crystalline phase

The X-ray patterns of the crystalline phase, registered at temperatures below T_c (see the table), contain quite a few equidistant sharp reflections in the small angle region, characteristic of a lamellar arrangement of the molecules, together with several reflections in the wide angle region, indicative of a three-dimensional ordering. Virtually independent of temperature, the lamellar periods *d* measured from the small angle reflections depend strongly, and in a linear fashion, on the number of carbon atoms in the alkyl chains (figure 2). Very close to twice the length of the molecules in a fully extended, hair-pin conformation (folded back at the tetrahedral phosphorus atom), they suggest that the alkyl chains, standing upright in the crystalline lamellae, are arranged in double layers as shown in figure 3.

The slope of *d* versus *n* (2·81 ± 0·04 Å, as deduced from a linear least square fit of the data for $n \geq 10$) is larger than the usual lengthening (2·54 Å [8]) per CH_2–CH_2 unit of fully extended, all-*trans*-alkyl chains, implying that the alkyl chains in the crystal phase are longer than normal. As suggested by Kitaigorodskii in another connection [8], such a stretching is presumably due to geometrical factors; in all probability, the compact arrangement of the strongly interacting phosphate groups forces the alkyl chains to pack tighter and hence to become longer than normal through an enlargement of the C–C–C bond angles. The stretching of the alkyl chains of course makes the enthalpy of the crystal increase, just as observed in the present work (see above). As for the intercept of *d* versus *n* (6·15 ± 0·43 Å), which corresponds to the thickness of the potassium phosphate sub-layers in the lamellae, this value is comparable to the size of the phosphate groups themselves (see [9]).

It is finally worth noting that the lamellar thickness of the octyl compound lies below the *d* versus *n* straight line (see figure 2), suggesting a special lamellar structure for this particular compound, as revealed in another way by the visual aspect of the X-ray powder patterns in the wide angle region. The distinct structural behaviour for the octyl compound also shows in the smaller enthalpy change at the transition from the crystal to the cubic phase (see above).

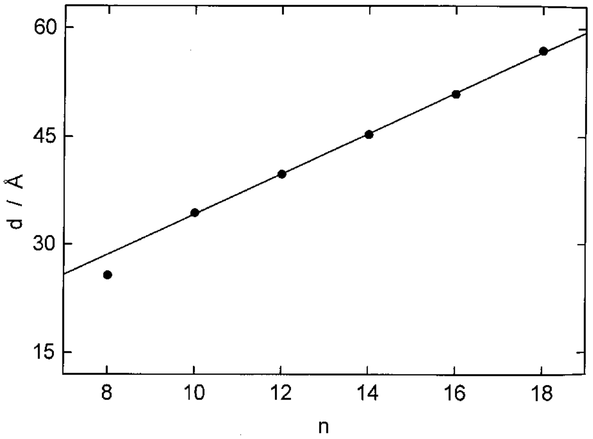

Figure 2. Variation of the lamellar period *d* of the crystal phases of the potassium dialkylphosphate salts at 25°C as a function of the number of carbon atoms *n* in the alkyl chains.

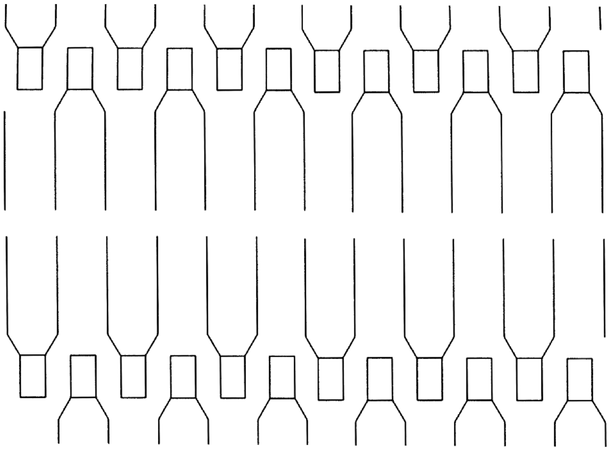

Figure 3. Schematic view of the crystal structure of the potassium dialkylphosphate salts. The alkyl chains and the potassium phosphate head groups are represented by straight lines and rectangles, respectively.

5. Cubic phase

The X-ray patterns of the optically isotropic phases, registered at temperatures between T_c and T_d (see the table), are identical in all respects to those described recently for the potassium, rubidium and caesium salts of dihexadecylphosphoric acid (see figure 4 in [4]). In addition to a broad band located in the wide angle region at about 4·7 Å and related to the alkyl chains in a disordered conformation, the patterns contain up to eight sharp reflections in the small angle region, with reciprocal spacings fitting the sequence $\sqrt{6}:\sqrt{8}:\sqrt{16}:\sqrt{20}:\sqrt{22}:\sqrt{24}:\sqrt{26}:\sqrt{38}$ ... and having relative intensities in perfect agreement with those given previously in the literature (table 2 in [4]). These patterns are characteristic of the well known $Ia3d$ body-centred cubic mesophase proposed some time ago by Luzzati and Spegt for the strontium alkanoates [10]. The structure involved consists of two interwoven but otherwise unconnected networks of 24 short columns, linked three by three in a coplanar fashion, and formed from the potassium phosphate groups of the molecules surrounded by the alkyl chains in a disordered conformation.

The cubic lattice parameter a, deduced from the small angle reflections (figure 4), depends very little on temperature. Its negative relative thermal expansion coefficient, determined by a linear least square fit of the experimental data, decreases steadily with increasing n (according to the equation: $10^4 \times (\partial a/\partial T)/a = 0{\cdot}79_{\pm 0{\cdot}55} - 0{\cdot}61_{\pm 0{\cdot}04} \times n$) from $-4{\cdot}1 \times 10^{-4}\,\mathrm{K}^{-1}$ for the octyl to $-10{\cdot}2 \times 10^{-4}\,\mathrm{K}^{-1}$ for the octadecyl derivative. As the molar volume of the material can only expand upon heating, $(\partial V/\partial T)/V \cong +7 \times 10^{-4}$†, the observed thermal contraction implies that the number N $(=a^3/V)$ of molecules per unit cell necessarily decreases, and all the more strongly as the chains become longer: its relative thermal expansion coefficient $(\partial N/\partial T)/N = 3 \times (\partial a/\partial T)/a - (\partial V/\partial T)/V$ goes from $-19 \times 10^{-4}\,\mathrm{K}^{-1}$ for the octyl to $-37 \times 10^{-4}\,\mathrm{K}^{-1}$ for the octadecyl derivative.

On the other hand, the lattice parameter increases markedly with the number n of carbon atoms in the alkyl chains. To all appearances (figure 5), the value grows in a linear fashion according to the equation: $a \cong 30{\cdot}6 + 3{\cdot}01n$ at 105°C (determined by a least square fit method). However, since the alkyl chains are in a liquid-like state, and so fill in the space among the columnar polar cores in a uniform and isotropic way, this linear dependence is probably devoid of any clear physical meaning and should therefore be considered purely coincidental.

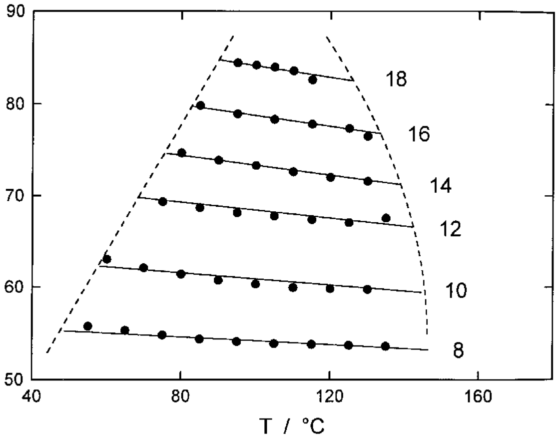

Figure 4. Temperature dependence of the unit cell parameter a of the cubic phases of the potassium dialkylphosphate salts. Numerals represent the number of carbon atoms in the alkyl chains. Dashed lines are the boundaries of the stability range of the cubic phase, as determined by DSC.

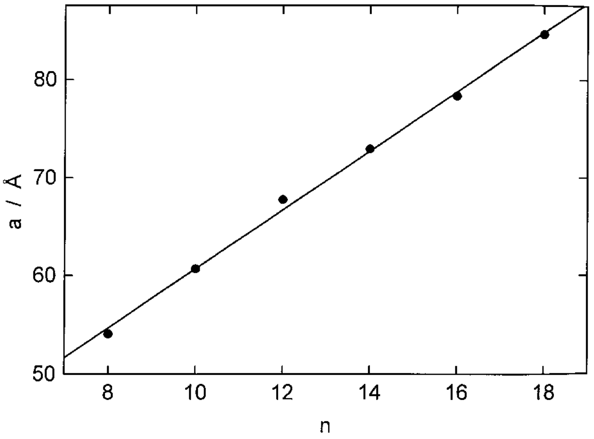

Figure 5. Variation of the unit cell edge length a of the cubic phases of the potassium dialkylphosphate salts at 105°C as a function of the number of carbon atoms n in the alkyl chains.

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†As is well known, the molar volume of a homologous series of compounds increases linearly with the number q of methylene groups in the molecules following the equation $V_q = V_0 + qV_{\mathrm{CH2}}$ where V_{CH2} is the molar volume of one methylene group and V_0 that of the rest of the molecules. Dilatometric studies of several dihexadecyl metal phosphates (to be published) show that the molar volume expands upon heating with a relative thermal expansion coefficient, $(\partial V/\partial T)/V$, of about $+7 \times 10^{-4}\,\mathrm{K}^{-1}$. Furthermore, they show that in the columnar state at 165°C the volumes of the sodium and rubidium salt molecules are 1078 and 1097 Å^3, respectively, allowing us to take for the dihexadecylphosphate potassium salt the intermediate value of 1088 Å^3. Likewise, in the cubic state at 105°C the volumes of the sodium and rubidium salt molecules are 1032 and 1044 Å^3, respectively, and that deduced for the potassium salt 1038 Å^3. It is then easy to calculate the molar volume for the whole series of dialkylphosphate potassium salts using the equation $V_n = V_{16} + 2(n - 16) \times V_{\mathrm{CH2}}$. The values of V_{CH2} as a function of temperature are obtained from [11].

As shown in figure 6, the number N of molecules per unit cell, as determined ($N = a^3/V$) from the experimental values of a and the estimated values of V, increases with n quite strongly, almost doubling from 269 for the octyl to 515 for the octadecyl derivative at 105°C. The reason is that N is closely related to the length of the columns ($L \approx a/\sqrt{8}$), and therefore to the cell parameter, which grows with the length of the alkyl chains. Putting things in a different way, the effect of the chain lengthening has repercussions directly on the volume a^3 ($=NV$) of the unit cell through the volume V of the individual molecules, and indirectly on the number N of molecules in the unit cell through the length of the columns. Corresponding to a stepwise lengthening of the columns by precisely one molecule per methylene group added to each alkyl chain, the n dependence of N (as calculated by a linear least square fit of the data in figure 6), $\partial N/\partial n \cong 24{\cdot}2 \pm 0{\cdot}8$ at 105°C, is quite disconcerting, for it conveys the suggestion that the columns, made of an integral number of molecules, are all identical with each other. Even if plausible from a strict point of view of crystal symmetry, this suggestion is, however, totally unreasonable here. Indeed, the number N of molecules determined experimentally is not by itself an integral multiple of the number (24) of columns per unit cell. And more importantly, N does not vary with temperature in a stepwise manner, but in a smooth and continuous manner as shown in figure 4. In addition, its n dependence is not the same at all temperatures ($\partial N/\partial n$ is 27 at 80°C and 21 at 150°C). As stated above, the temperature dependence of N is very important; it decreases from $\partial N/\partial T = -0{\cdot}51\ \mathrm{K}^{-1}$ for the octyl to $-1{\cdot}91\ \mathrm{K}^{-1}$ for the octadecyl derivative, implying an overall reduction in N over the whole temperature range of stability of the cubic phase by 73 and 59, respectively.

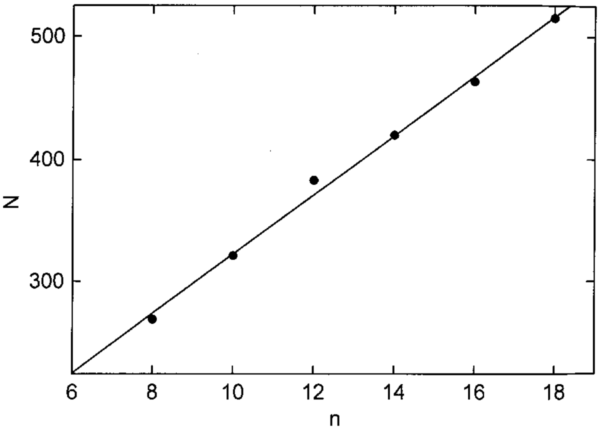

Figure 6. Variation of the number of molecules N per unit cell in the cubic structure at 105°C as a function of the number of carbon atoms n in the alkyl chains.

The conclusion from all this discussion is that, contrary to what is generally taken implicitly for granted, the columns are not at all identical with one another, but must in fact be polydisperse.

To describe the structure of the cubic phase in greater detail, it is of course necessary to specify how the potassium phosphate groups are arranged inside the columnar cores. Unfortunately, this information cannot be obtained in a straightforward way from the experimental data collected in the present work, because the confinement of the Bragg reflections to the very central part ($2\theta < 10$ deg) of the X-ray patterns† drastically reduces the resolution of the structure to some 10 Å, that is, far beyond the atomic scale. One must therefore be satisfied with such sketchy notions as the stacking period h of the polar groups along the columnar axes or the radius R of the polar cores of the columns.

To give an estimate of the intracolumnar stacking period h ($=24L/N$), one only has to know the average length L of the columns and the average number N of molecules per unit cell. But the trouble is that L is not available directly from experiment. Indeed, as pointed out by Luzzati and Spegt for the strontium soaps on the basis of crystallographic arguments [10], the columnar cores in the $Ia3d$ phase are not perfectly joined end to end, but separated by a short gap (of about 3 Å) that is void of polar groups. Consequently, their length is not equal to $a/\sqrt{8}$ as expected from crystal geometry, but reduced to $L = a/\sqrt{8} - \varepsilon$. Figure 7 shows how h depends upon n, as calculated from the experimental values of a and N for a set of selected gaps ranging from $\varepsilon = 0$ to 10 Å. If, contrary to all expectations, the columnar cores should nevertheless be joined without discontinuity ($\varepsilon = 0$), h would have to decrease quite strongly with increasing n, from 1·71 Å for the octyl to 1·38 Å for the octadecyl derivative. Such a behaviour would of course be questionable for two reasons. First, the variability of h would denote a certain looseness of the packing of the polar heads inside the columns, in open contradiction to earlier observations of the columnar phase of alkaline earth and copper soaps [6, 11] and of the $Ia3d$ cubic phase of strontium soaps [12]. (The stacking period of the polar heads in the columnar phase of strontium soaps, $h_{\mathrm{col}} = 1/0{\cdot}596 = 1{\cdot}678$ Å [12], was indeed found to be independent of the chain length. The corresponding

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†The strong attenuation of the Bragg reflections at $2\theta > 10$ deg is due partly to the thermal agitation of the potassium phosphate groups (especially as these are embedded in a liquid matrix of alkyl chains), but more likely to the static disorder of the soft cubic phase, that is, to the presence of numerous dislocations and elastic distortions, and also to the fluctuation of the length of the columns and of the number of molecules per unit cell.

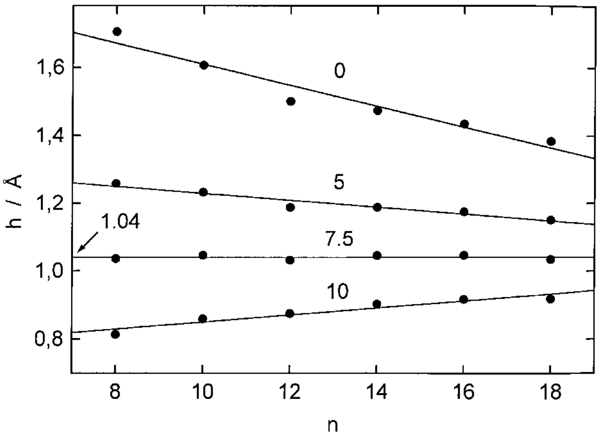

Figure 7. Variation of the intracolumnar stacking period h of the polar heads in the columns of the cubic phases of potassium dialkylphosphates, calculated at 105°C for a set of selected gaps round the columnar ends (indicated by numerals ranging from $\varepsilon = 0$ to 10 Å) as a function of the number of carbon atoms n in the alkyl chains.

period in the cubic phase, $h_{\mathrm{cub}} = 24V[(a/\sqrt{8}) - \varepsilon]/a^3$ (where $\varepsilon \cong 3$ Å [10]), may easily be deduced from published experimental data [12] by assuming that the molar volume V does not change significantly at the transition from cubic to columnar: $h_{\mathrm{col}}/h_{\mathrm{cub}} = a3/\{12 \times \sqrt{3}D^2[(a/\sqrt{8}) - \varepsilon]\} = 1{\cdot}00 \pm 0{\cdot}01$ (figure 8). It is thus found that the stacking period in the cubic phase is identical with that in the columnar state, and consequently independent of the chain length.) Secondly, the decay of h would indicate a steady growth of the linear density of the polar heads along the columns, a growth which is difficult to understand considering that the lateral space swept by the molten alkyl chains has normally a tendency to expand with n.

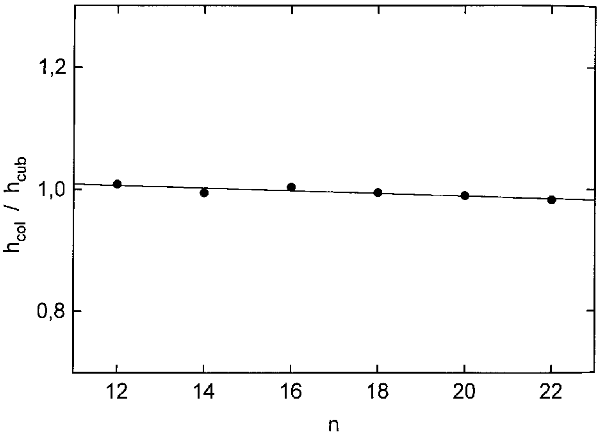

Figure 8. Variation of $h_{\mathrm{col}}/h_{\mathrm{cub}}$ of strontium alkanoates as a function of the number of methylene groups n in the alkyl chains.

In contrast, as soon as a short gap ($\varepsilon > 0$) is admitted to exist round the columnar ends, then the stacking period h ceases to depend strongly upon n. It even remains perfectly constant and is equal to $1{\cdot}04 \pm 0{\cdot}01$ Å, for a particular gap of 7·5 Å (figure 7), thus matching perfectly the behaviour (invariability of h) of the cubic phase of the strontium soaps. It is useful to remark that the very existence of a gap is quite plausible for at least two reasons. In the first place, unless the polar groups are by pure accident arranged in a specially appropriate fashion inside the columns, their regular packing can hardly propagate coherently through adjacent columns oriented at an angle—here, at 120 degrees as required by the I*a*3*d* cubic structure. As a result, columns can hardly fit together accurately and are by necessity disjointed. In the second place, the disordered alkyl chains are in great need of lateral space to be able to spread out round the tightly packed polar groups (see below an estimation of the molecular area of the alkyl chains at their anchoring point onto the polar cores) and so to develop properly a random conformation. Columns are hence broken into pieces and bound to stand at a distance to compensate for space deficiency along their axes, especially as they must, for symmetry reasons, come together three by three in a convergent configuration.

The value of 1·04 Å (see figure 7) found for the intracolumnar period h is much smaller than the size of the potassium phosphate groups [9], suggesting that these groups are not superposed in simple rows within the columns, but aggregated round the columnar axis in rather extended regions. Assuming for simplicity that the columnar cores are circular cylinders of radius R, and using the equation $V_0 = \pi R^2 h$, in which $V_0 \cong 139$ Å^3§ is the volume of one polar head at 105°C, one calculates their diameter to be about 13 Å, that is, about twice the size of the phosphate groups. In addition, one also calculates the molecular area of the alkyl chains at the surface of the polar cores: $S = 2\pi Rh/2 \cong 21{\cdot}2$ Å^2, which is smaller than that (23–25 Å^2) of disordered alkyl chains in thermotropic liquid crystals [11] and close to that (~ 19 Å^2) of fully stretched chains in a crystal. With a gap of 7·5 Å, one finally finds that the average length of the columns ($L = a/\sqrt{8} - \varepsilon = a/\sqrt{8} - 7{\cdot}5$) increases linearly with the lengthof the alkyl chains, from about 12 Å for the octyl to 22 Å for the octadecyl derivative at

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§With a volume of 1088 Å^3 at 165°C for the potassium dihexadecylphosphate molecules (see previous footnote †) and a volume of 29·34 Å^3 for a methylene group at 165°C [13], it is easy to calculate for the polar head of the molecules a volume $V_0 = 1088 - 32 \times 29{\cdot}34 \cong 149$ Å^3. Likewise, with a volume of 1038 Å^3 at 105°C for the potassium dihexadecyl phosphate molecules and a volume of 28·10 Å^3 for a methylene group at 105°C [13], the volume calculated for the polar head of the molecules is $V_0 = 1038 - 32 \times 28{\cdot}10 \cong 139$ Å^3.

105°C. Thus, the columnar cores are not as long as one might like to imagine, but quite short in fact, their length hardly exceeding their diameter.

6. Columnar phase

The X-ray patterns of the birefringent phases observed at temperatures above T_d (see the table) are typical of columnar liquid crystalline structures of hexagonal symmetry. They contain three to four sharp reflections in the small angle region with reciprocal Bragg spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, indicative of two-dimensional hexagonal lattices; they also contain a broad band in the wide angle region, at about 4·7 Å, related to the alkyl chains in a disordered conformation. The structure involved is similar to that described long ago for divalent metal alkanoates [14, 15] and more recently for the dihexadecylphosphate alkali metal salts [4]. The polar heads of the molecules are arranged in columns surrounded by the alkyl chains in a disordered conformation, oriented parallel to one another, and packed according to a two-dimensional hexagonal lattice.

The interaxial spacings D of the columns, measured from the small angle reflections (figure 9), depend very weakly, but significantly, on temperature. Their relative thermal expansion coefficient decreases with increasing n (according to the equation: $10^4(\partial D/\partial T)/D = 16{\cdot}4_{\pm 1\cdot 8} - 1{\cdot}27_{\pm 0\cdot 14} \times n$, as calculated by a linear least square fit of the data in figure 9), passing from positive (roughly $+6\times10^{-4}\,\mathrm{K}^{-1}$) for the octyl to negative (roughly $-6\times10^{-4}\,\mathrm{K}^{-1}$) for the octadecyl derivative. This thermal behaviour is at variance with earlier observations—in particular with observations on columnar phases of alkaline earth metal soaps [6] showing instead that the D spacings constantly increase with temperature, and in a like manner for all homologues, the volume expansion being achieved at constant linear density of the columns.

On the other hand, D increases strongly with the number n of carbon atoms in the alkyl chains. According to current literature (see for example [7]), the hexagonal unit cell area $\Sigma = (\sqrt{3}/2)\times D^2$ of columnar phases grows with n strictly in a linear fashion. The reason is that in a homologous series of compounds the stacking period h of the molecules inside the columns (supposed to be infinitely long and uniform along their axis) is kept constant, while the molar volume $V = \Sigma h$ increases linearly with n. In the present work, however, Σ versus n is slightly, but quite indisputably, curved upwards (figure 10), indicating that h is now changing with n. As shown in figure 11, the period h, calculated from the experimental values of Σ and the estimated values of V using the equation $V = \Sigma h$, indeed decreases appreciably with increasing n, going from 1·31 Å for the octyl to 1·21 Å for the octadecyl derivative. It is important to add immediately that h seems to depend appreciably on temperature as well. Its relative thermal expansion coefficient, roughly estimated using the equation $(\sqrt{3}/2)D^2h = V$, seems indeed to increase steadily with n, since the slope of D versus T declines with increasing n.

It would be tempting to interpret the n and T dependence of h as an indication of the 'molten state' of the potassium phosphate groups inside the columnar cores, because of some insufficiency of the attractive interactions of the molecules to compensate for thermal motions. However, as already discussed for the cubic phases, such an admission would be in sharp contradiction with previous results on metal soaps [6, 16] and

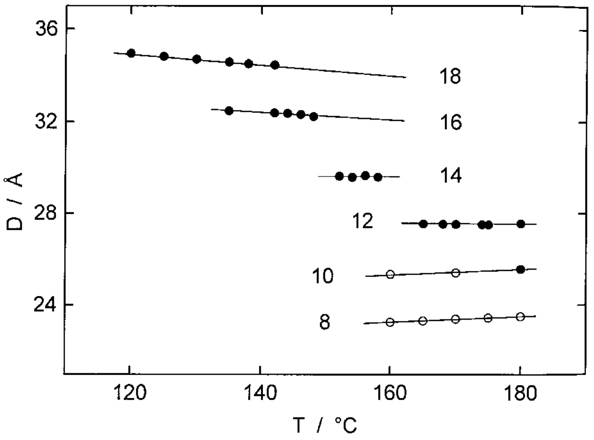

Figure 9. Variation of the hexagonal unit cell edge length D of the columnar phases of the potassium dialkylphosphate salts as a function of temperature. Numerals represent the number of carbon atoms in the alkyl chains. Solid and open circles represent data measured upon heating (above T_d) and cooling (below T_d) respectively.

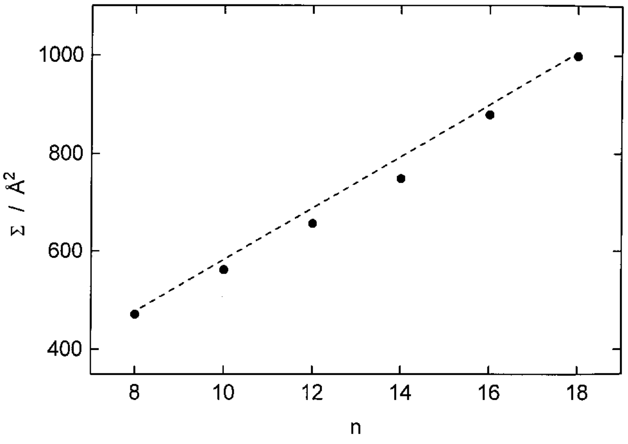

Figure 10. Variation of the hexagonal unit cell area Σ of the columnar phases of the potassium dialkylphosphate salts at 165°C as a function of the number of carbon atoms n in the alkyl chains.

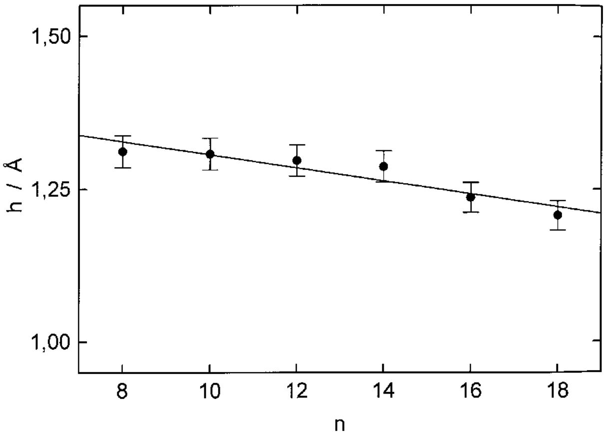

Figure 11. Variation of the intracolumnar stacking period h of the polar heads in the polar cores of the columnar phases of potassium dialkylphosphates, calculated at 165°C as a function of the number of carbon atoms n in the alkyl chains.

would better be abandoned. It seems definitely more reasonable to admit instead that the packing of the polar heads in the columnar phases does not vary and has the same linear density as in the cubic phases ($h_0 \cong 1{\cdot}04$ Å). With such a packing, which is denser than calculated above ($h_0 < 1{\cdot}21 < h < 1{\cdot}31$ Å), one is immediately led to conclude that the columns should not be infinitely long as commonly observed, but broken into short pieces† of length $L = \varepsilon h_0/(h - h_0)$, separated along their axis by a short gap ε.‡ (With gaps of the order of 5 Å, the columnar trunks should not exceed some 30 to 40 Å, and although longer than in the cubic phases, they should still remain rather short compared with their diameter.) The alignment of the columnar trunks on top of one another along the columnar axes is very likely assured by the van der Waals attractions of the polar cores which, due to the presence of the disordered alkyl chains, can come closer to one another along their axes than laterally ($\varepsilon < D - 2R$).

7. Conclusion

The present work shows clearly that the potassium dialkylphosphate salts produce well defined liquid crystals, namely Ia3d body-centred cubic, followed at higher temperatures by columnar liquid crystals of hexagonal symmetry, just as observed in another connection with strontium alkanoates [10, 12]. The phase diagram of a series of compounds from dioctyl to dioctadecyl was established by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction, showing the temperature range of the cubic mesophases to narrow down as a function of increasing length of the alkyl chains.

The structural parameters of the cubic and columnar mesophases have been determined by X-ray diffraction and discussed in detail. It was found that both phases consist essentially of the same structural elements, that is, of short columns formed by a dense and rigid core of polar potassium phosphate groups packed with a stacking period of 1·04 Å, surrounded by alkyl chains in a disordered conformation. The restricted length of the columns, of about 12 to 22 Å for the cubic and of no more than 30 to 40 Å for the columnar phases, was interpreted as due both to steric reasons (the disordered alkyl chains needing for development of a random conformation more space than is available at the surface of the polar cores) and to thermodynamic reasons (the interactions of the polar groups probably being insufficient to secure strong aggregation numbers). Quite unexpectedly, the aspect ratio of the polar columnar cores was found not to exceed unity by a great deal, ranging as a function of increasing alkyl chain length from 1 to 2 for the cubic, and around 2 to 3 for the columnar phases.

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† The disruption of the columns is very likely to be due to an incomplete aggregation of the molecules according to thermodynamics [17].

‡ The number of molecules per individual column may be calculated in two different but equivalent ways: either as L/h_0 if the molecules are taken to be densely packed with a period h_0 and confined to discrete columns of length L, or else as $(L + \varepsilon)/h$ if the molecules are taken to be less densely packed with a period $h > h_0$ and to cover along the columnar axis a length of $L + \varepsilon > L$. Clearly, $L/h_0 \equiv (L + \varepsilon)/h$; that is, $L = \varepsilon h_0/(h - h_0)$.

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