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# Thermotropic liquid crystal behaviour of alkaline-earth-metal dihexadecyl phosphate salts

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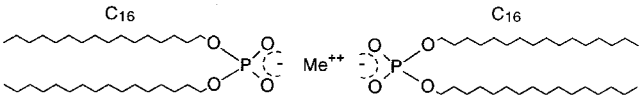
Alkaline-earth-metal dihexadecyl phosphate salts were synthesized, and their thermal stability was evaluated by thermogravimetry. Their thermotropic liquid crystal behaviour was investigated by differential scanning calorimetry, polarizing optical microscopy, dilatometry, and X-ray diffraction. On heating, the calcium, strontium, and barium salts exhibit columnar liquid crystal phases, whereas the less ionic beryllium and magnesium salts melt directly into isotropic liquids.

## 1. Introduction

It was recently shown that the alkali-metal dialkyl phosphate salts are able not only to form vesicles when dispersed in aqueous media [1–3], but also to produce thermotropic liquid crystals when heated above the melting temperature of the crystal [4, 5]. The potassium, rubidium, and caesium salts produce an $Ia\bar{3}d$ body-centred cubic phase followed at higher temperature by a columnar mesophase of hexagonal symmetry, while the lithium and sodium salts exhibit a columnar phase exclusively. Similar structures were also observed with certain alkaline-earth-metal and divalent transition-metal alkanoates: columnar with magnesium and cadmium [6, 7], cubic and columnar with strontium alkanoates [8, 9]. The nature of the metal seems therefore to affect the mesomorphic ordering of the long chain metal-containing amphiphilic salts.

As an extension of previous work, the present study deals with the thermotropic liquid crystal behaviour of the dihexadecyl phosphate salts of beryllium, magnesium, calcium, strontium, and barium (abbreviated to DHP-Me). The experimental techniques used were polarizing optical microscopy (POM), differential scanning calorimetry (DSC), dilatometry, and X-ray diffraction (XRD).



Me = Be, Mg, Ca, Sr, Ba

## 2. Synthesis

The synthesis was carried out by the interaction of sodium dihexadecyl phosphate [4, 5] in ethanol with stoichiometric amounts of alkaline-earth-metal chloride. Readily precipitating from the mixture as white powders, the salts were washed with ethanol and water and then recrystallized twice from a chloroform–ethanol (1 : 1 v/v) mixture. Purity was confirmed by elemental analysis. $C_{64}H_{132}P_2O_8Be$: calc. C 69.84, H 12.09; found C 69.80, H 12.24%. $C_{64}H_{132}P_2O_8Mg$: calc. C 68.88, H 11.92; found C 68.88, H 12.04%. $C_{64}H_{132}P_2O_8Ca$: calc. C 67.92, H 11.76; found C 67.88, H 11.84%. $C_{64}H_{132}P_2O_8Sr$: calc. C 65.20, H 11.30; found C 65.31, H 11.41%. $C_{64}H_{132}P_2O_8Ba$: calc. C 62.55, H 10.83; found C 62.28, H 10.73%.

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## 3. Thermal stability and polymorphism

In order to define their thermal stability range, the compounds synthesized were analysed by thermogravimetry (TA-TGA 2050 analyser, nitrogen flux, heating rate of 10°C $\mathrm{min}^{-1}$). As found previously for the corresponding alkali-metal salts [4, 5], the compounds proved reasonably stable when maintained at temperatures below 250°C over periods of time not exceeding two hours. In addition, and contrary to their alkali-metal counterparts, they proved non-hygroscopic.

The thermotropic liquid crystal behaviour of the salts was studied by POM (Leitz-Wetzlar, Linkam TMS 91 hot-stage), DSC (TA DSC 10 calorimeter, heating and cooling rates of 10°C $\mathrm{min}^{-1}$), and XRD (powder samples in Lindemann capillaries, Guinier focusing camera, $\mathrm{CuK}_{\alpha_1}$ radiation, INEL CPS-120 curved position-sensitive detector, INSTEC hot stage). Visual observation showed that, before degrading thermally near 250°C, the Ca, Sr, and Ba salts undergo a unique phase transition at temperatures in the range from 85 to 95°C, transforming from a crystalline solid into a birefringent viscous fluid. Because thermal degradation made it impossible to melt the samples into an isotropic liquid and proceed as usual by careful cooling from the isotropic melt, the optical textures of the fluid phases could not develop satisfactorily enough to permit an unambiguous characterization of the liquid crystalline phases observed. On the other hand, the Be and Mg salts proved to melt, at about 69 and 84°C, respectively, directly into an isotropic viscous fluid, transiently gaining some slight birefringence when sheared mechanically. As suggested below by XRD, the birefringent viscous fluids are columnar liquid crystals of hexagonal symmetry, while the isotropic ones are amorphous and contain clusters of randomly oriented columns (columnar cybotactic groups) much smaller than the wavelength of visible light. These transitions were fully confirmed by DSC (see the table).

## 4. Dilatometry

To obtain further insight into the thermotropic polymorphism of the compounds synthesized and, especially, to calculate the structural parameters of the phases encountered, the molar volume of the Mg salt was investigated by dilatometry in the temperature range from ambient to 150°C, well below the appearance of thermal degradation. The experiments involved a home-made computer-driven dilatometer using about 1 g of carefully degassed sample immersed in about 10 ml of mercury, with heating and cooling steps of 0.1°C every 2 min [10–12].

Table. Phase transition temperatures (onset) and enthalpies for the alkaline-earth-metal dihexadecyl phosphate salts measured by DSC upon heating.

| | $T$/°C | $\Delta H$/kJ $\mathrm{mol}^{-1}$ |
|---|---|---|
| DHP-Be | 69.0 | 98 |
| DHP-Mg | 84.0 | 156 |
| DHP-Ca | 86.3 | 126 |
| DHP-Sr | 91.8 | 107 |
| DHP-Ba | 93.6 | 146 |

In complete compliance with previous observations of liquid crystals [10, 12], the molar volume of DHP-Mg increases steadily with temperature in the stability range of each of the two phases observed and jumps suddenly at 84°C (at the same phase transition temperature as that detected by DSC, see the table) by roughly 80 $\mathrm{cm}^3\,\mathrm{mol}^{-1}$ corresponding to the melting of the alkyl chains (figure 1). Upon cooling, the volume decreases quite reversibly, the transition back to the crystal taking place as usual with a strong hysteresis. In the high temperature fluid phase, the volume varies perfectly linearly with temperature according to the equation $V = V_0\,(1 + \alpha T)$, where $V_0$ is the molar volume at 0°C and $\alpha$ the relative thermal expansion coefficient. A least squares linear fit of the experimental data leads to $V_0 = 1136\ \mathrm{cm}^3\,\mathrm{mol}^{-1}$, near the value found for the sodium and rubidium dihexadecyl phosphate salts [12], and to $\alpha = 7.64 \times 10^{-4}\,°\mathrm{C}^{-1}$, near the value generally measured for common liquids and liquid crystals [5, 13].

As is well known, the molar volume of alkyl compounds grows linearly with the number $q$ of methylene groups in the molecules, following the equation $V = V_\mathrm{p} + q \times V_{\mathrm{CH}_2}$, where $V_{\mathrm{CH}_2}$ is the molar volume of one methylene group and $V_\mathrm{p}$ that of one polar head group (increased by the excess volume of one methyl with regard to one methylene). With a molar volume of 1223 $\mathrm{cm}^3\,\mathrm{mol}^{-1}$ for DHP-Mg at 100°C, and

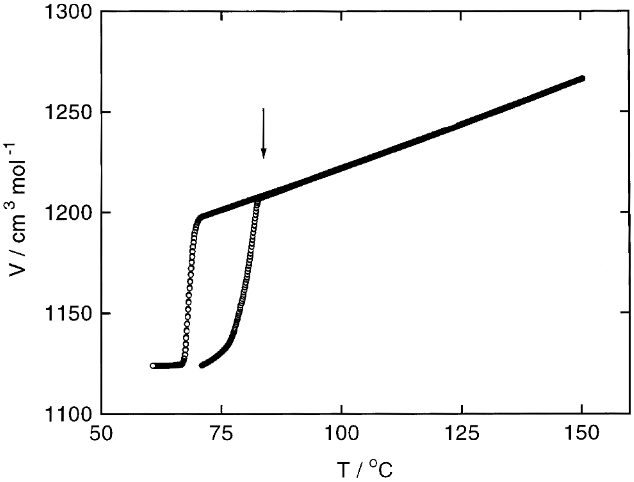

Figure 1. Variation of the molar volume of magnesium dihexadecyl phosphate as a function of increasing and decreasing temperature. The arrow indicates the phase transition detected by DSC.

$16.86\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ for the methylene groups at the same temperature [13], it is easy to calculate the molar volume of the polar head groups of the molecules. The value found, $144\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ ($239\,\mathrm{Å}^3$), is about twice that of the alkali-metal salts ($\sim 140\,\mathrm{Å}^3$) [5], which consist of only one phosphate group.

## 5. Low temperature solid phase

The X-ray patterns recorded at low temperature, below the phase transition detected by DSC, contain several equidistant sharp reflections in the small angle region, indicative of a lamellar arrangement of the molecules. The lamellar periods measured are 52.6, 47.5, 44.7, 44.5, and 44.1 Å for the Be, Mg, Ca, Sr, and Ba salts, respectively. Comparable to those observed with the corresponding alkali-metal salts (ranging from 48.0 to 51.1 Å [4, 5]), these values are close to twice the length of the molecules in a fully extended hairpin conformation (of about 25 Å as estimated by molecular modelling using Biosym®). They suggest that the alkyl chains are arranged in double layers, probably standing upright for Be while being tilted away from the layer normal for the others by about 25 to 30 degrees.

In the wide angle region, the X-ray patterns contain a small number of rather broad reflections, indicative of an ill-developed three-dimensional crystal arrangement of the molecules. For the Be derivative, the presence of a single reflection at 4.15 Å is consistent with a hexagonal packing of fully stretched alkyl chains, similar to that found for paraffins just below their melting temperature [14]. The cross-sectional area of the chains, $4.15^2 \times 2/\sqrt{3} = 19.9\,\mathrm{Å}^2$, is identical to that reported for paraffins in the rotator phase [14] or for the lyotropic smectic B phases of potassium soaps [15]. The range of the hexagonal in-layer ordering of the molecules, deduced from the width of the wide angle reflection, is of about 140 Å, as usually observed in smectic B phases [16]. For the Mg derivative, the presence of two rather sharp peaks at 4.57 and 3.76 Å is consistent with a centred rectangular arrangement of fully stretched alkyl chains with cell parameters $a = 7.52$ and $b = 5.76$ Å. The molecular area of the chains, $7.52 \times 5.76 \div 2 = 21.7\,\mathrm{Å}^2$, is larger than that of paraffins in an orthorhombic structure ($\sim 19\,\mathrm{Å}^2$ [14]), suggesting a tilt of about 29 degrees.

## 6. High temperature fluid phases

The X-ray patterns of the fluid, birefringent phases observed with the Ca, Sr, and Ba salts above the phase transition detected by DSC (see the table) are characteristic of a columnar structure. They contain three or four sharp small angle reflections with reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, indicative of a two dimensional hexagonal lattice. They also contain a diffuse band in the wide angle region at 4.55 Å, related to the alkyl chains in a disordered conformation. The structure involved is therefore similar to that described long ago for the alkaline-earth-metal alkanoates [6–9] and recently for the alkali-metal dialkyl phosphate salts [4, 5]. The polar heads of the molecules are superposed on top of one another in columns surrounded by the molten alkyl chains and assembled in a hexagonal fashion.

Figure 2(*a*) shows that the interaxial spacing of the columns, deduced from the small angle reflections, increases slightly as a function of temperature, with a relative thermal expansion coefficient $(\partial D/\partial T)/D$ ranging from 2 to $3.2 \times 10^{-4}\,\mathrm{K}^{-1}$. In accordance with

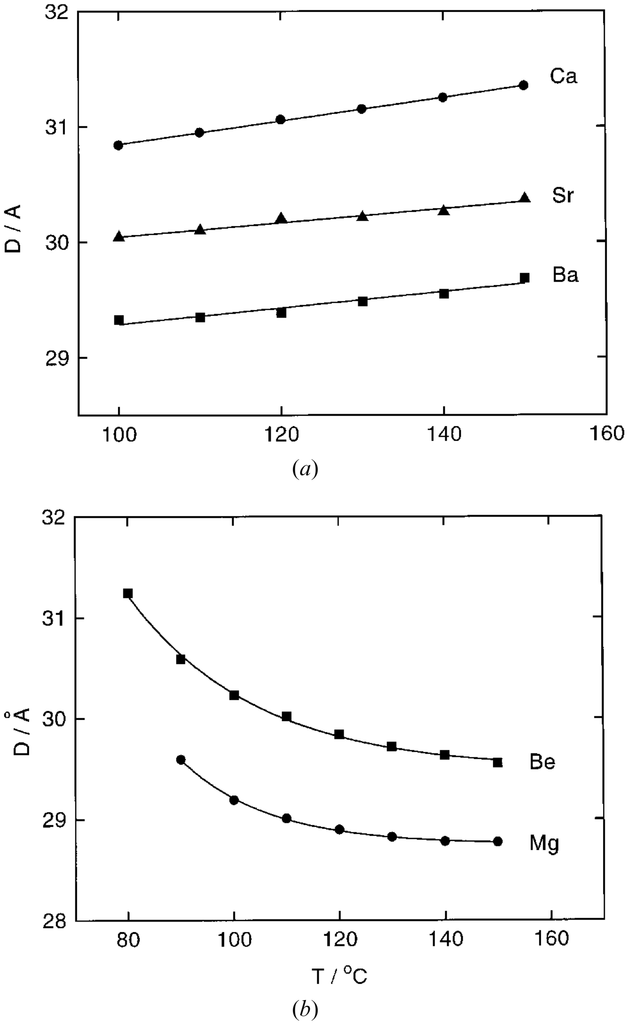

Figure 2. Temperature dependence of the interaxial distance of the columns (*a*) in the hexagonal columnar phases of calcium, strontium, barium, and (*b*) in the columnar cybotactic groups of beryllium and magnesium dihexadecyl phosphate.

earlier observations on alkaline-earth-metal soaps [6–8], this behaviour suggests that the volume expansion is achieved at constant linear density of the molecules along the columns. As for the absolute $D$ values measured for the different soaps, they decrease significantly when the ionic radius of the metal atoms increases. Knowing that the volume of the metal atoms is negligibly small as compared with the overall volume of the dihexadecyl phosphate salts, the molecular volume of all the alkaline-earth-metal salts may safely be taken to equal that measured dilatometrically for the Mg salt: $V = 2031$ Å$^3$ at 100°C. The intracolumnar stacking period of the polar groups, $h = 2V/\sqrt{3}D^2$, may then be easily calculated. About twice that found for potassium dialkyl phosphate salts (1.24 Å) [5], it increases from 2.47 Å for Ca to 2.60 for Sr to 2.73 Å for Ba. Moreover, with the reasonable assumption that the volume expansion coefficient for all the salts is approximately the same as that found for the Mg salt, the temperature dependence of $h$ may also be calculated (figure 3). Clearly, $h$ is independent of temperature suggesting that the packing of the polar heads inside the columnar cores is compact.

On the other hand, the X-ray patterns of the Be and Mg salts above the phase transition detected by DSC (see the table) contain three diffuse bands in the small angle region with reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}$, indicating an ill-developed columnar ordering. From the width at half-height of these bands, the range of the columnar ordering may be estimated as extending over only five repeating units. The high temperature isotropic phase of the Be and Mg salts appears therefore to correspond to the presence of columnar cybotactic groups in an amorphous liquid. Quite interestingly, the interaxial $D$ spacing of the columns inside the cybotactic groups decreases significantly with increasing temperature, figure 2 (*b*), more for Be than for Mg, while the calculated intracolumnar period $h$ is no longer constant, but increases considerably (figure 3). This behaviour may be attributed to the nature of the bonds between the metal atoms with the phosphate groups. As is well known [17], among all the alkaline-earth elements, beryllium has a unique chemical behaviour with a predominantly covalent chemistry, while magnesium has a chemistry intermediate between that of beryllium and the heavier elements, which are predominantly ionic in character and which form a closely allied series of salts. The polarization of anions by these metal atoms produces a degree of covalence, thus reducing the strength of the electrostatic attractions of polar heads inside the columns.

It is of interest to recall in this context the main characteristics of the structure of the short chained Mg and Ba diethyl phosphate salts, which were established some time ago by XRD on single crystals [18, 19]. In both cases, the metal atoms, surrounded and linked together by the phosphate groups, are piled up along the $c$ axis in a way prefiguring the columns formed in the columnar liquid crystalline phases described in the present work. In these crystal structures, the metal atoms are coordinated to the oxygen atoms of the phosphate groups following a geometry that depends on their nature; their stacking period is hence larger for Mg than for Be, as also observed in their dihexadecyl derivatives (figures 2 and 3).

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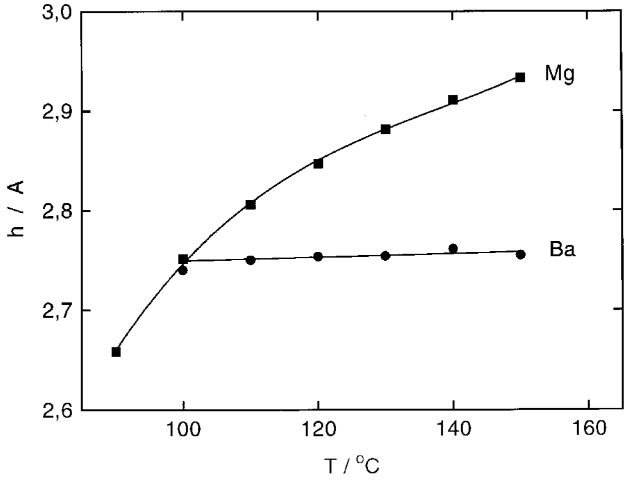

Figure 3. Temperature dependence of the stacking period $h$ of magnesium and barium dihexadecyl phosphate in the columnar phase.

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