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Dimitra Kardassi [a], Dimitris Tsiourvas [a], Constaninos M. Paleos [a], Benoit Heinrich [b] & Antoine Skoulios [a]

[a] Institute of Physical Chemistry, NCSR 'Demokritos', 15310 Aghia Paraskevi, Attiki, Greece

[b] Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue de Loess, 67037, Strasbourg, Cedex, France

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Dilatometric Studies of Liquid Crystalline Sodium and Rubidium Dihexadecylphosphate

DIMITRA KARDASSI[a], DIMITRIS TSIOURVAS[a], CONSTANINOS M. PALEOS[a], BENOIT HEINRICH[b] and ANTOINE SKOULIOS[b,*]

[a] *Institute of Physical Chemistry, NCSR 'Demokritos', 15310 Aghia Paraskevi, Attiki, Greece;*
[b] *Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue de Loess, 67037 Strasbourg Cedex, France*

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The thermotropic liquid crystal polymorphism of sodium and rubidium dihexadecylphosphates, previously investigated by polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction, was further investigated using dilatometry. Their molar volumes and thermal expansion coefficients in the cubic and columnar mesomorphic state were measured.

Keywords: Crystalline sodium; rubidium; dihexadecylphosphates; optical microscopy

INTRODUCTION

It was recently shown that the alkali-metal salts of the dihexadecylphosphoric acid, from lithium to caesium ($(n\text{-}C_{16}H_{33}O)_2PO_2Me$, show liquid crystalline behaviour when heated in the pure state at high temperature [1]. Studied by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction, they were found to exhibit a lamellar structure in the crystalline state at room temperature and a columnar structure of hexagonal symmetry in the liquid crystalline state at high temperature. The potassium, rubidium, and caesium salts were found to exhibit an additional Ia3d

*Corresponding author. Tel.: 33-88107158, Fax: 33-88107246.

body-centered cubic structure in the intermediate temperature range between the crystal and the columnar phase. In a detailed study of a homologous series of the potassium salts of dialkylphosphoric acid, from dioctyl to dioctadecyl, the structural parameters of the crystal, cubic and columnar phases were analyzed systematically as a function of temperature and of the length of the alkyl groups [2].

The present work using dilatometry, is intended to provide further information about the thermal behaviour of two such compounds, namely the sodium and rubidium dihexadecylphospates. Its specific goal is to provide a measure of their molar volumes both in the cubic and the columnar mesomorphic state, and to evaluate their thermal expansion co-efficient. Combined with data from X-ray diffraction, these parameters contribute, as reported previously in the literature [2], to a more thorough description of the structural arrangement of the molecules in the mesomorphic state.

EXPERIMENTAL

As reported previously [1], the sodium and rubidium salts considered in the present work were synthesized by neutralization of dihexadecylphosphoric acid with stoichiometric amounts of the corresponding metal hydroxides in ethanol. They were recrystallized at least twice from ethanol. Their purity was checked by elemental analysis. $C_{32}H_{66}PO_4Na$: calc. C 67.57, H 11.69; found C 67.44, H 11.78. $C_{32}H_{66}PO_4Rb.H_2O$: calc. C 56.19, H 10.56; found C 59.13, H 10.19. Checked by thermogravimetry (TA 2050 analyzer), their thermal stability was found quite satisfactory, provided heating is reasonably brief and temperature is maintained below 150°C.

The molar volumes of the compounds were measured as a function of temperature using dilatometry [4]. The dilatometer consisted of a cylindrical reservoir of about 10 cm^3, designed to contain about 1 g of sample together with mercury, surmounted by a long calibrated capillary tube about 0.6 mm in diameter. Temperature was fixed by immersion of the dilatometer in a silicon-oil bath. Driven by a computer [5], experiments allowed both for automatic acquisition of data and for control of temperature (within 0.03°C) with heating and cooling steps of 0.1°C every 2 minutes.

For the volume measurements to be meaningful, it is generally necessary to submit the samples to careful degassing (several heating and cooling cycles under vacuum from the crystalline to the liquid crystalline state) prior to filling the dilatometer with mercury. In the present work, this treatment turned out particularly troublesome to achieve successfully, owing to the

hygroscopicity of the samples and their limited thermal stability. Indeed, during the degassing process, the samples, particularly the rubidium compound, were found to liberate appreciable amounts of water, condensing visibly onto the internal walls of the dilatometer capillaries. To avoid thermal degradation, special care was therefore taken to hold the temperature below 150°C and to run the dilatometric experiments as fast as possible.

RESULTS AND DISCUSSIONS

To volume of both compounds was systematically investigated as a function of increasing, then decreasing temperature in the range from ambient up to 150°C. Figure 1 shows the first-order phase transition between the low-temperature crystal and the high temperature columnar liquid crystal of the sodium derivative (detected by differential scanning calorimetry at 74°C [1]). In complete compliance with previous observations of the thermal behavior of liquid crystals [4], the molar volume grows with temperature in the stability range of each one of the two phases observed and increases abruptly at the phase transition by some 21.60 cm^3, due essentially to the melting of the alkyl

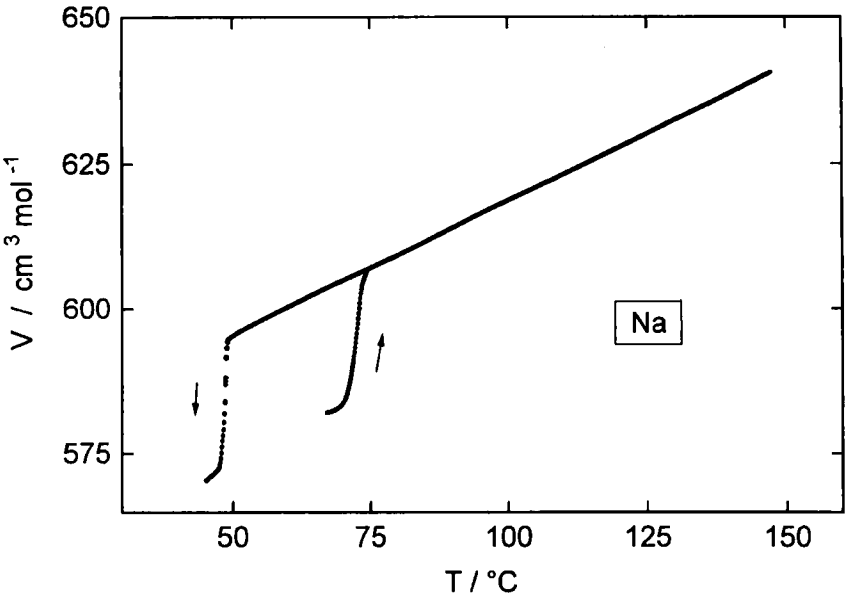

FIGURE 1 The molar volume of sodium dihexadecylphosphate as a function of increasing and decreasing temperature through the phase transition from the low-temperature crystal to the high-temperature columnar liquid crystal. Data are collected every 0.1°C.

chains. Upon cooling, the volume decreases quite reversibly in the columnar phase, and the crystal forms again as usual, with a strong hysteresis (of about 25°C under the cooling conditions of the experiment) due to nucleation.

In the columnar state, the molar volume varies perfectly linearly with temperature, according to equation: $V = V_0(1 + \alpha T)$, where V_0 is the molar volume extrapolated at 0°C and α the relative thermal expansion coefficient. A least-squares linear fit of the experimental data leads to a molar volume of $V_0 = 572.1 \pm 0.5\,\text{cm}^2\,\text{mol}^{-1}$ (corresponding to a specific volume of $1.14\,\text{cm}^3\,\text{g}^{-1}$ at 165°C) and to a relative thermal expansion coefficient $\alpha = 8.044 \times 10^{-4}\text{°C}^{-1}$, which is of quite the same magnitude as normally found with liquid crystals [6].

Measured at the transition temperature T_0. Data are collected every 0.1°C.

The temperature dependence of the molar volume of the rubidium was found generally similar to that of the sodium derivative. The volume showed indeed to grow with temperature continuously in the stability range of each phase observed and to jump markedly at the transition from the low-temperature crystal to the high-temperature liquid crystal, here a cubic mesophase [1]. However, the volume showed to undergo an additional jump upon further heating, corresponding to the first-order transformation of the cubic into a columnar mesophase [1]. As shown in Figure 2, this additional jump is rather small (only $3.4\,\text{cm}^3\,\text{mol}^{-1}$), just as expected for a transition between two mesomorphic phases both involving long alkyl chains in a molten state. A least-squares linear fit of the experimental data leads to a molar volume of $V_0 = 579.9 \pm 0.5\,\text{cm}^3\,\text{mol}^{-1}$ for the cubic and $V_0 = 583.3 \pm 0.5\,\text{cm}^3\,\text{mol}^{-1}$ for the columnar phase, and to a relative thermal expansion coefficient of $\alpha = 8.074 \times 10^{-4}\text{°C}^{-1}$ for both phases. It is a satisfaction to note that the volume excess of the rubidium with respect to the sodium compound in the columnar state ($11.2\,\text{cm}^3\,\text{mol}^{-1}$) agrees well with the difference in volume of the rubidium and sodium ions ($15.8\,\text{cm}^3\,\text{mol}^{-1}$, as deduced from their ionic radii: 1.47 and 0.97 Å, respectively [7]).

It is important to observe that the transition temperatures detected by dilatometry for the rubidium derivative were by several degrees lower than those measured by differential scanning calorimetry (92°C for the crystal to cubic, and 134°C for the cubic to columnar mesophase [1]). The reason is that the degassing of this particular compound, which was synthesized as a monohydrate, proved especially difficult to carry out efficiently, requiring repeated heating cycles to expel the solvation water exhaustively, and thus inevitably resulting in a slight thermal degradation of the material, also showing through an increased width of the temperature range of the phase transition (Fig. 2). It is equally important, however, to stress that, because

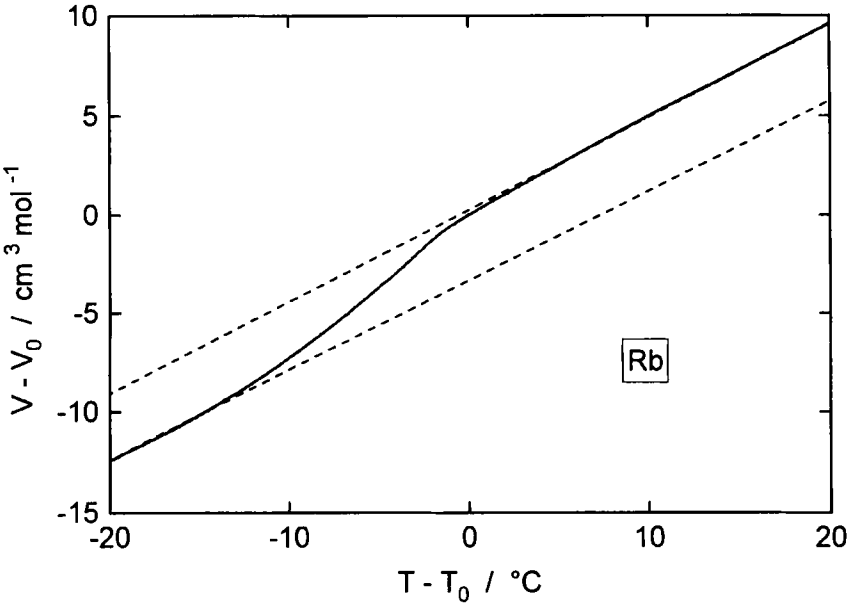

FIGURE 2 Variation of the molar volume V of rubidium dihexadecylphosphate as a function of increasing temperature close to the transition between the low-temperature cubic and the high-temperature columnar phase. V_0 is the volume measured at the transition temperature T_0. Data are collected every 0.1°C.

thermal degradation below 150°C is not expected to produce volatile by-products, the molar volume measured is not expected, as otherwise suggested by common experience in the field of liquid crystal dilatometry, to be significantly erroneous; and indeed the molar volumes of the sodium and rubidium derivatives are perfectly consistent with one another.

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