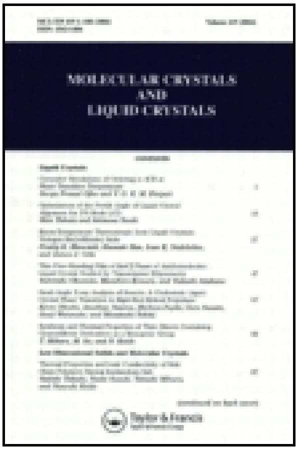

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Some Aspects of Amphotropic Behaviour of Homologous n-Alkane-1,2-Diols

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SOME ASPECTS OF AMPHOTROPIC BEHAVIOUR OF HOMOLOGOUS n-ALKANE-1,2-DIOLS

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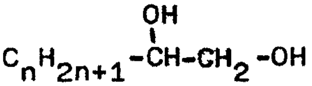
Abstract The phase behaviour of simple n-alkane-1,2-diols and their mixtures with water is reported. The addition of water stabilizes the liquid crystalline behaviour. The higher homologues show several transitions above the melting point in the water-saturated region. The structural behaviour of n-pentadecan-1,2-diol investigated by means of X-ray diffraction is described.

INTRODUCTION

Simple n-alkane-1,2-diols show both thermotropic and lyotropic liquid-crystalline behaviour [1], which is typical for amphotropic materials. From 2-n-alkyl-propane-1,3-diols it is known that they show a liquid-crystalline behaviour only after addition of water [2]. For instance, in a 2-n-hexadecyl-propane-1,3-diol/water mixture two phase transitions were found above the melting point, indicating the occurrence of a second liquid-crystalline phase. From the comparison of the phase behaviour of the analogous 1,2- and 1,3-diols the question arises of whether the n-alkane-1,2-diols with longer alkyl chains show a similar polymorphism. Therefore, we have synthesized and investigated additional members of this homologous series.

EXPERIMENTAL

The synthesis of the n-alkane-1,2-diols  $C_nH_{2n+1}-\overset{OH}{C}H-CH_2-OH$ has already been described [3]. A weighed quantity of the diol was mixed with excess water (50 wt.-%). The dispersions were deposited in DSC pans or sealed in capillaries.

The calorimetric measurements were performed using a Perkin-Elmer (Norwalk, CT) DSC-2 instrument. X-ray diffraction measurements were carried out with a powder diffractometer HZG 4 (VEB Präzisionsmechanik Freiberg, G.D.R.) using a transmission technique [4]. The repeat distance of lamellae d_L or the lattice constant of the hexagonal phase a_H were calculated from the long spacings. The short spacings characterize the physical state of the chains, and an area per molecule A_M is deducible after indexing.

On the base of texture observations the mesophases in the water-free samples were preliminaryly designated as S_A^+ and S_B^+. In the hydrated samples the nomenclature of the lyotropics is used (subgel L_ξ, gel L_β, liquid-crystalline phases L_α or H_α, crystal cr, isotropic phase is) [1,4].

RESULTS and DISCUSSION

The water-free compounds form an isotropic phase after melting. However, metastable liquid-crystalline phases can be observed on cooling the isotropic sample. In homologues with n = 6-8 the S_A^+- and S_B^+-phases were found, whereas the higher homologues show only the S_B^+-phase before recrystallization. With increasing chain length the crystallization is more hindered. No crystallization could be observed for the diol with n = 17

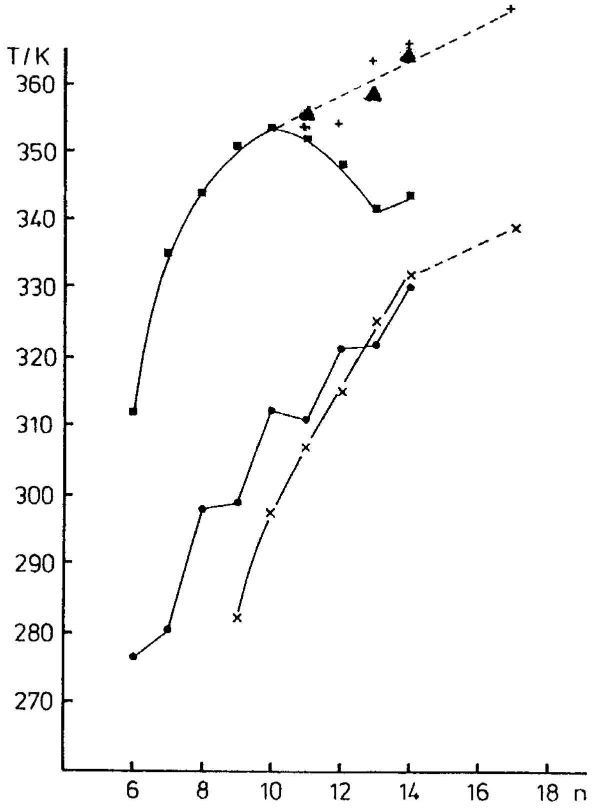


FIGURE 1 Transition temperatures of homologous n-alkane-1,2-diols in the water-saturated state (50 wt.-% water) in dependence on the chain length n.
● melting temperatures (cr - Lß or Lα); ▼ transition Lg - Lß; x transition Lß - Lα; ■ transition Lα - Hα or is; ▲ transition Hα - is (DSC); + transition Hα - is (microscopy).

in the measured temperature range.

The addition of water causes a remarkable stabilization of the mesophases in all cases investigated (Figure 1).

The melting temperatures show an even/odd alternation. The clearing temperatures rise with increas-

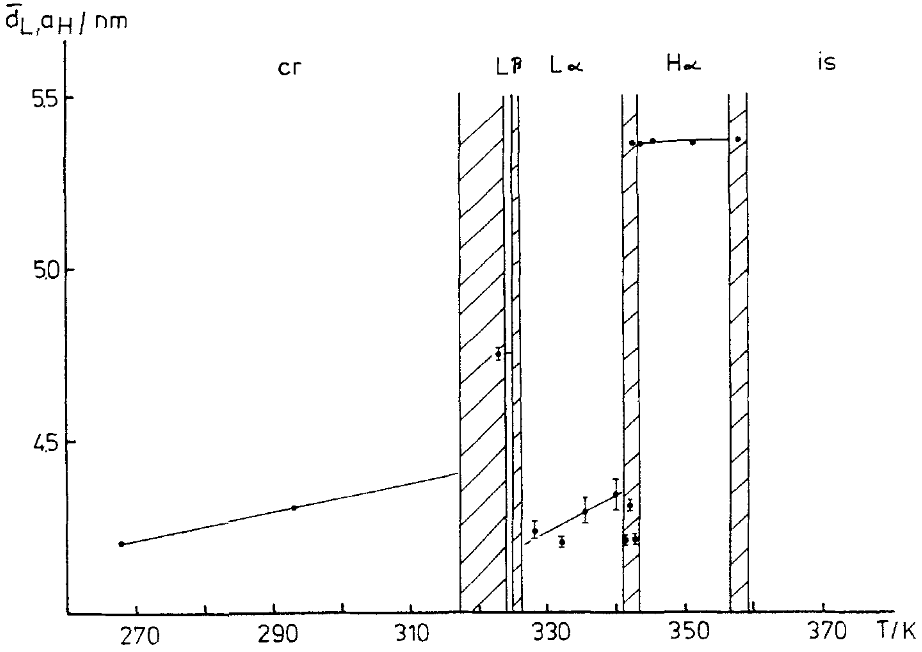


FIGURE 2 System: n-pentadecane-1,2-diol (n = 13)/ water (50 wt.-%). Temperature dependence of the repeat distance of lamellae d_L and lattice constant of the hexagonal phase a_H. Hatched area - reversible phase transition region. Phase notation: cr - crystalline phase; Lß - gel phase; Lα, Hα - liquid-crystalline phases; is - isotropic phase.

ing chain length. The diols with n = 11-12 show two and the compounds with n = 13-14 three phase transitions above the melting point. A monotropic transition occurs on cooling the homologues with n = 9-12.

To get more information about the polymorphism the phase structures of n-pentadecane-1,2-diol (n=13) were studied by means of X-ray diffraction in a 50 wt.-% water mixture. Below 322 K a crystalline phase was found characterized by a set of sharp peaks in the diffractometer trace. At 322 K the transition into the gel phase Lß with rigid chains occurs. The increase of the repeat distance indicates that simultaneously the hydration of the diol takes place. The value of d_L = 4.75 nm in comparison to the molecular length (2.15 nm) suggests an opposite arrangement of the chains in the bilayers of the gel phase. The area per molecule of $A_M = 0.217$ nm^2 is highly compared to values of aliphatic chains [5] (<0.2 nm^2). This finding expresses the competition in the lateral packing of the molecule between the voluminous diol group and the aliphatic chain.

The temperature region of the gel phase is very small. At 325 K the melting of the alkyl chains leads to a lamellar liquid-crystalline phase Lα. It is connected with a remarkable decrease of the repeat distance (vertical contraction) and a lateral dilatation: the A_M-value increases to $A_M = 0.24$ nm^2. In the Lα-phase only a slight temperature dependence of d_L can be observed. At 342 K a phase transition into a second liquid-crystalline phase Hα takes place. From the molecule shape of the 1,2-diols the existence of an inverse hexagonal phase can be deduced.

By means of the structural parameters d_L and A_M a bilayer unit can be defined. The comparison of the volume of the molecules determined by the procedure of KITAIGORODSKI [6,7] with that of the bilayer unit allows the calculation of a packing coefficient. In the gel phase a value of 60 % was estimated. Surprisingly after the melting of the chains the packing coefficient increases to 63.5 % in the Lα-phase. Then it decreases linearly to 58 % with increasing temperature. At this critical value the transition Lα - Hα occurs. Taking into consideration the above mentioned competition in the lateral packing of headgroups and chains the increase of the packing coefficient at the transition Lß - Lα is easy to understand: the molden chain occupies the bilayer unit better than a rigid chain.

From the results of the X-ray investigations the polymorphism of the whole homologous series can be described. **The diol with n = 13 is the first member with** a stable gel phase. The diols with n = 9-12 show only a metastable gel phase on cooling the sample. Starting from n = 10 the liquid-crystalline phase Lα is destabilized with increasing chain length n and an invers hexagonal phase Hα exists between the Lα- and the isotropic phases. In the homologues with n = 17 a Lα-phase was not observed. The crystallization of this compound is very slow. Instead of this a subgel phase Lç with orthorhombically packed chains appears on cooling the gel phase.

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