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SHORT COMMUNICATION

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Structural and calorimetric investigations on nonaqueous liquid crystals and gel phases in the binary system K-behenate/glycerol

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Abstract Two mixtures of the binary system K-behenate/glycerol, $x_{KC_{22}} = 0.30$ and 0.50 (x = mole fraction), have been investigated as a function of temperature using small- and wide-angle X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The binary phase diagram based on texture observations using polarizing optical microscopy was confirmed. XRD and DSC measurements provided concordant results with respect to the range of the phase regions in the phase diagram. Only differences between the DSC curves for rising and falling temperatures were detected. The recorded XRD and DSC data of the liquid crystals and gel phases observed are also in agreement with previously reported investigations on K-soap/glycerol. The C $\leftrightarrow$ G and G $\leftrightarrow$ L_α phase transitions correlate with a sharp shift in the *d* value of the first small-angle reflection. The G phase is characterized by a split of the first small-angle reflections. Also, the position and shape of the wide-angle reflections change and the peak intensity is reduced.

Key words Nonaqueous liquid crystals · Hexagonal and lamellar phase · Gel phase · X-ray diffraction · Calorimetry
Phase diagram

Introduction

We continue our structural investigations on gel structures and lyotropic mesophases of K-soap/glycerol (Gl) [1–5] with studies on K-behenate (KC_{22})/Gl. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) investigations were performed on samples with mole fractions $x_{KC_{22}} = 0.30$ and 0.50. The primary objective was the structural characterization of the crystalline phase, C, the gel phase, G, and the lamellar phase, L_α.

The preliminary phase diagram based on texture observations using polarizing microscopy [6] is shown in Fig. 1. At mole fractions $x_{KC_{22}} > 0.20$ the C $\leftrightarrow$ G $\leftrightarrow$ L_α phase sequence occurs (Fig. 1). For mole fractions $x_{KC_{22}} < 0.20$ the C $\leftrightarrow$ H_α $\leftrightarrow$ S phase sequence is found. Generally, the borders of the C/G and G/L_α phase regions in the phase diagram are shifted towards higher temperatures compared to the previously reported K-soap/Gl systems. This is due to the relatively long carbon–hydrogen chains of the KC_{22} molecules and the resulting higher relative amount of mass at a given mole fraction. Consequently, the L_α as well as the H_α phase exist at relatively low mole fractions. Details of the XRD measurements and data analysis were given in Refs [1, 2].

Results

Investigations of the KC_{22}/Gl system at the composition $x_{KC_{22}} = 0.30$

The X-ray diffractograms and the DSC curve for rising temperature are shown in Fig. 2a. The C $\leftrightarrow$ G phase transition occurs very gradually over a temperature range of about $\Delta T \approx 20K$ according to the diffractograms and DSC data. A pretransition is observed within the C phase at T = 338 K. The pretransition corre-

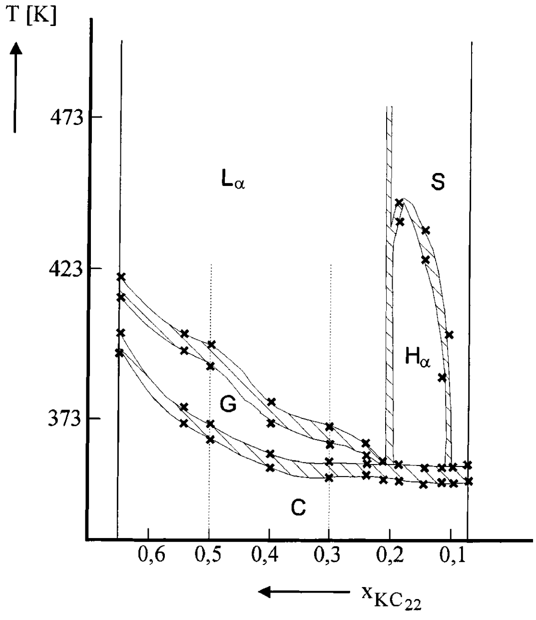

Fig. 1 Phase diagram of the K-behenate/glycerol binary system [6]. *Symbols*: *C* = crystalline phase, *G* = gel phase, H_α = hexagonal phase, chains fluid, L_α = lamellar phase, chains fluid, *S* = isotropic, micellar solution

sponds to the superimposition of two wide-angle peaks (Fig. 2a, curves 4, 5). In addition, the amorphous small-angle background increases. The *d* values of the first small-angle reflections with DSC curves at rising and falling temperatures are compared in Fig. 2b. The C ↔ G phase transition correlates with a shift in the *d* values of the first small-angle reflections of $\Delta d \approx +0.20$ nm (Fig. 2b). (The definition of the *d* value was given in Ref. [2]). Also, the characteristic split of the first small-angle reflections in the G phase is observed. The C ↔ G phase transition is more pronounced in the curve for falling temperature. The L_α phase shows small-angle reflections only up to the second order. This indicates a reduced molecular order of the lamellar structure. The average lamellar distance is 4.5 nm (Fig. 2b).

Investigations of the KC_{22}/Gl system at the composition $x_{KC_{22}} = 0.50$

As for the system described in the previous section, a C ↔ G ↔ L_α phase sequence occurs at this concentration. The wide-angle diffractograms and the DSC curve for rising temperature are displayed in Fig. 3a. The DSC curve reveals two weak pretransitions below the C ↔ G transition at 343 and 353 K. This again correlates with superimposed reflections in the wide-angle range (Fig. 3a, curves 2, 3). The elevation in the left shoulder of the reflection at $2\Theta = 19°$ disappears. The two reflections at $2\Theta = 26$ and 27° merge gradually into one reflection at $2\Theta = 27.5°$, which is also present within the G-phase.

The small-angle diffractograms and the DSC curve at rising temperature are shown in Fig. 4. The C ↔ G transition again correlates with a split of the small-angle 0 0 1 reflection and a shift in the *d* value of $\Delta d \approx +0.25$ nm. In addition, the phase transition is characterized by the distinct regrouping and intensity loss of the wide-angle reflections. The main C ↔ G phase transition influences the diffractogram more strongly than the pretransitions.

Noteworthy is the width of the DSC peak of about $\Delta T = 25$ K, corresponding to the G ↔ L_α phase transition. It cannot be explained by a potential thermodynamic nonequilibrium transition caused by the heating rate of $\Delta T/\Delta t = 2$ K/min (see also Ref. [4]). In fact, a G/L_α two-phase region has to be assumed. Within this two-phase region both first small-angle reflections have

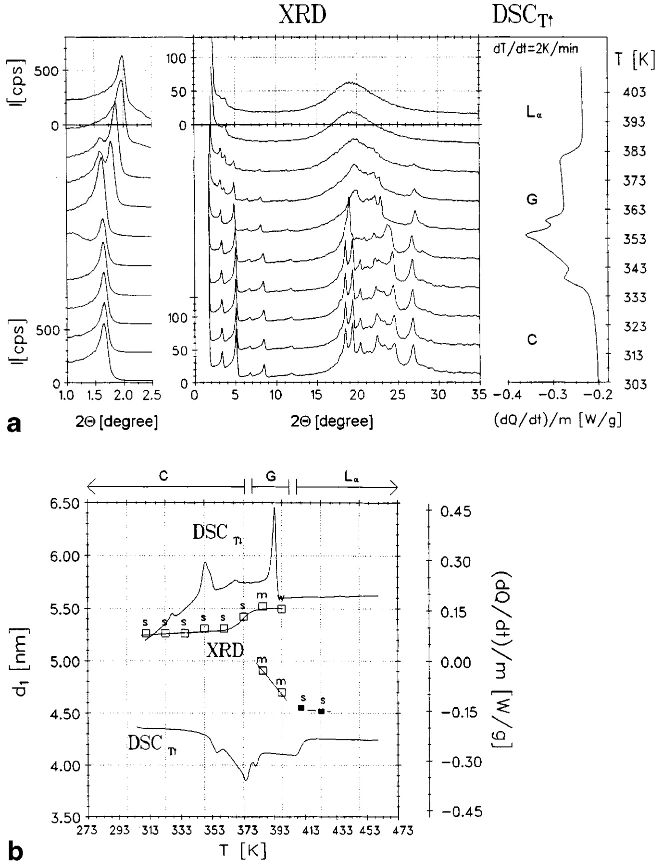

Fig. 2 **a** small- and wide-angle X-ray diffractograms (*XRD*) and differential scanning calorimetry (DSC) curve at rising temperature for K-behenate/glycerol at $x_{KC_{22}} = 0.30$. **b** *d* values of the first small-angle reflections and DSC curve at rising and falling temperatures for K-behenate/glycerol at $x_{KC_{22}} = 0.30$. *Symbols*: □ reflections of the C and G phases, ■ reflections of the L_α phase. Reflection intensity: *w* = weak, *m* = medium, *s* = strong

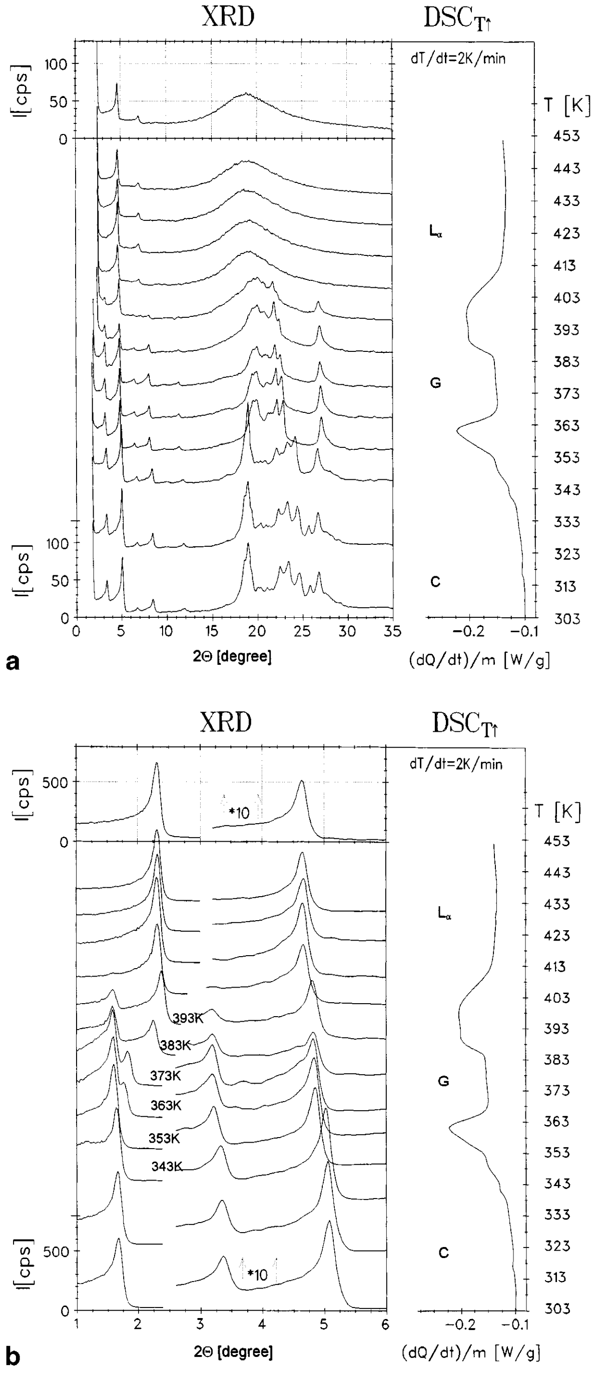

Fig. 3 **a** Wide-angle XRD and DSC curve at rising temperature for K-behenate/glycerol at $x_{KC_{22}} = 0.50$. **b** Small-angle XRD and DSC curve at rising temperature for K-behenate/glycerol at $x_{KC_{22}} = 0.50$

nearly the same intensity. Also, the wide-angle reflections show a reduced intensity of about 50% in this temperature range. It is also observed that the lamellar structure is already formed at T = 403 K as indicated by the completely amorphous wide-angle background. In the small-angle range only the reflections caused by the lamella are found. The molecular layers of the L_α phase have relatively high structural order as indicated by the intensity and sharpness of the small-angle 0 0 1 reflections (Fig. 3b). Up to three orders can be observed. This was expected due to the high chain length of the KC_{22} molecules.

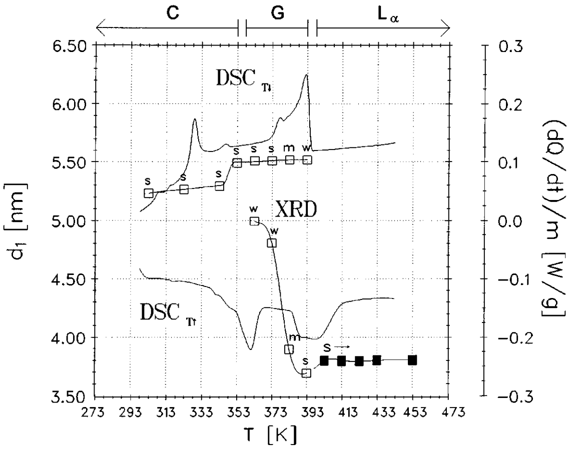

Fig. 4 *d* values of the first small-angle reflections and DSC curve at rising and falling temperatures for K-behenate/glycerol at $x_{KC_{22}} = 0.50$. *Symbols*: □ reflections of the C and G phases, ■ reflections of the L_α phase

In Fig. 4 the *d* values of the first small-angle reflections with DSC curves obtained for rising and falling temperatures are compared and confirm the previous interpretation. Significant differences between the DSC curves for rising and falling temperatures are noticed.

With the C ↔ G phase transition the characteristic split of the first small-angle reflection occurs and the *d* value of the second reflection decreases by $\Delta d = -1.3$ nm between T = 363 and 393 K. Within the lamellar phase the *d* values remain practically temperature-independent at $d = 3.8$ nm. A slight minimum is noticed at T = 393 K.

Conclusions

Two mixtures of the KC_{22}/Gl system were studied at mole fractions $x_{KC_{22}} = 0.30$ and 0.50 as a function of temperature. Small- and wide-angle XRD investigations and DSC measurements confirmed the binary phase diagram published before (Fig. 1) [6].

No discrepancies between the XRD and DSC measurements were found with respect to the range of the phase regions: however, differences between the DSC curves at rising and falling temperatures were detected [7].

For mixtures at the mole fraction $x_{KC_{22}} > 0.20$ the phase sequence C ↔ G ↔ L_α occurs, while for $x_{KC_{22}} < 0.20$ the phase sequence C ↔ H_α ↔ S is found.

The L_α phase originates from the G phase, while the H_α phase originates from the C phase. The structural order of the bilayers of the L_α phase improves with increasing surfactant concentration. The phase transitions C ↔ G and G ↔ L_α correlate with abrupt changes in the *d* values of the first small-angle reflections.

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