Colloid Polym Sci 278:90–95 (2000)

SHORT COMMUNICATION

H.-D. Dörfler
A. Hieke

Influence of the chain length of K-soaps on the phase diagram and structural parameters of nonaqueous liquid crystals and the gel phase in K-soap/glycerol binary systems*

Received: 9 August 1999
Accepted in revised form: 20 September 1999

*Dedicated to Professor Dr. h.c. G. Lagaly on occasion of his 60th birthday

H.-D. Dörfler (✉) · A. Hieke
TU Dresden, Institut für Physikalische
Chemie und Elektrochemie; Kolloidchemie
Mommsenstrasse 13, D-01062 Dresden
Germany

Abstract Analogously to the aqueous K-soap/water systems already examined, the five glycerol · (Gl)-containing systems KC_n/Gl ($n = 12$, 14, 16, 18, 22) also built up hexagonal (H_α), lamellar (L_α), isotropic micellar (S), gel-like (G) and crystalline phases (C). These phases were identified by texture observations with a polarizing microscope, by differential scanning calorimetry measurements and by X-ray diffraction investigations. The appertaining phase regions were plotted in the binary phase diagram. Binary Gl-containing K-soap systems have the following properties. The H_α phase is built up at low soap concentration. The L_α phase is formed at high soap concentrations. The temperature of the phase transition $H_\alpha \leftrightarrow S$ runs through a maximum. Increasing the chain lengths of the soaps shifts the formation of the H_α phase to lower soap concentration. A strong correlation between the chain length of K-soaps and the *d* values of L_α, H_α, G and C phases is found. Based on the comparison of the X-ray diffractograms of the G phase a structural model is proposed. The G phase consists of two groups of domains with two different dimensions.

Key words X-ray diffraction measurements · Nonaqueous liquid crystals · Gel phase · Structural parameters · K-soaps

Introduction

Our previously published investigations [1–6] dealt with the influence of concentration and temperature on the structural behaviour of the gel (G) phase and nonaqueous liquid crystals in K-soap/glycerol (Gl) binary systems. The investigation comprised small-angle and wide-angle X-ray diffraction measurements (XRD), differential scanning calorimetry measurements and polarized microscopy texture observations on selected concentrations of the binary systems K-laurate (KC_{12})/Gl [2], K-myristinate (KC_{14})/Gl [3], K-palmitate (KC_{16})/Gl [4], K-stearate (KC_{18})/Gl [5] and K-behenate (KC_{22})/Gl [6].

Preliminary phase diagrams based on texture observations [7] were used to select the concentrations for the XRD measurements; however, the older phase diagrams contained certain inconsistencies with respect to the appearance of different G and isotropic (I) (cubic) phases. Detailed XRD measurements revealed that the binary systems considered exhibit only one modification of the G phase. It was shown that the I phase, possibly a cubic phase, was in fact nonexistent. This led to a correction of preliminary phase diagrams [2–5]. Here, the structural parameters of all the binary systems are summarized with respect to the chain lengths of the K-soaps.

Results

Comparison of the K-soap/Gl phase diagrams

A survey of the polymorphic transitions observed in the five K-soap/Gl systems given in Table 1. The list has been arranged with respect to the concentration ranges

Table 1 Comparison of the polymorphism and phase behaviour of K-soap/glycerol systems as a function of the chain length of the soaps. Abbreviations: *C* = crystalline phase, L_α = lamellar phase, H_α = hexagonal phase, *G* = gel phase, *S* = isotropic, micellar solution

System	Concentration range (mol %)	Polymorphic transitions
Potassium laurate/glycerol	25–42	$\mathrm{C} \leftrightarrow \mathrm{H}_\alpha \leftrightarrow \mathrm{S}$
(KC_{12}/Gl)	43–63	$\mathrm{C} \leftrightarrow \mathrm{G} \leftrightarrow \mathrm{L}_\alpha$
Potassium myristinate/glycerol	19–27	$\mathrm{C} \leftrightarrow \mathrm{H}_\alpha \leftrightarrow \mathrm{S}$
(KC_{14}/Gl)	28–34	$\mathrm{C} \leftrightarrow \mathrm{G} \leftrightarrow \mathrm{H}_\alpha \leftrightarrow \mathrm{S}$
	35–65	$\mathrm{C} \leftrightarrow \mathrm{G} \leftrightarrow \mathrm{L}_\alpha$
Potassium palmitate/glycerol	17–25	$\mathrm{C} \leftrightarrow \mathrm{H}_\alpha \leftrightarrow \mathrm{S}$
(KC_{16}/Gl)	26–33	$\mathrm{C} \leftrightarrow \mathrm{G} \leftrightarrow \mathrm{H}_\alpha \leftrightarrow \mathrm{S}$
	34–65	$\mathrm{C} \leftrightarrow \mathrm{G} \leftrightarrow \mathrm{L}_\alpha$
Potassium stearate/glycerol	15–29	$\mathrm{C} \leftrightarrow \mathrm{G} \leftrightarrow \mathrm{H}_\alpha \leftrightarrow \mathrm{S}$
(KC_{18}/Gl)	30–65	$\mathrm{C} \leftrightarrow \mathrm{G} \leftrightarrow \mathrm{L}_\alpha$
Potassium behenate/glycerol	10–20	$\mathrm{C} \leftrightarrow \mathrm{H}_\alpha \leftrightarrow \mathrm{S}$
(KC_{22}/Gl)	21–65	$\mathrm{C} \leftrightarrow \mathrm{G} \leftrightarrow \mathrm{L}_\alpha$

of the different phase regions of the phase diagrams in the direction of rising temperatures.

Comparing the mesomorphic, G and C phases and the corresponding phase regions we conclude that the chain length of the homologous K-soaps (KC_{12}–KC_{22}) exerts a systematic influence.

The hexagonal (H_α) phase

As expected, the H_α phase was observed in regions of low soap concentrations. A comparison between the H_α phase regions of the phase diagrams demonstrates that both the concentration ranges and the minimum soap concentrations required for H_α-phase formation decrease with increasing length of the K-soaps, with minimum concentrations ranging from $x_{\mathrm{KC}_{12}} = 0.25$ for KC_{12} to $x_{\mathrm{KC}_{22}} = 0.1$ for KC_{22}. It is further noted that the phase-transition temperature rises with increasing chain length and the temperature range of the H_α phase becomes broader. This effect is caused by hydrophobic interaction between the alkyl chains and becomes stronger with longer chains and thus stabilizes the hexagonal structure over a wider temperature range. The temperature variation as a function of concentration of the phase transition runs through a maximum for all the systems described. These results agree with the structural investigations of McBain et al. [8] for K-soap/water systems.

The lamellar (L_α) phase

Samples rich in K-soap subjected to homogenization under high-temperature conditions decompose; therefore, only experiments with compositions below $x_{\mathrm{KC}_n} = 0.65$ are useful. Comparing the positions of the L_α-phase regions in the phase diagrams reveals that the temperature of the phase transition $\mathrm{L}_\alpha \leftrightarrow \mathrm{S}$ decreases with increasing chain length of the K-soaps: 620 K for KC_{12} and 583 K for KC_{22} [2–6]. This may be related to the melting points of the pure K-soaps, which fall with increasing chain length. Analogously to the H_α phases, the concentrations required for L_α-phase formation shift to lower soap concentrations with increasing chain length. Also the concentration range of the stable L_α phase is broadened. The temperature of the phase transition $\mathrm{G} \leftrightarrow \mathrm{L}_\alpha$ in all binary systems rises steadily with increasing K-soap concentration. Thus, higher K-soap concentrations require higher temperatures to form L_α phases.

The G phase

All five systems discussed here are characterized by the appearance of a G phase. In the KC_{14}/Gl, KC_{16}/Gl and KC_{18}/Gl systems the G phase is always the intermediate phase between the C phase and the lyotropic mesophase in the direction towards higher temperatures. Surprisingly, KC_{12}/Gl and KC_{22}/Gl do not form an intermediate G phase between the C phase and the H_α phase. In these two systems the C phase passes directly into the H_α phase. The G phase of these systems is built up only in concentration regions where the L_α phase also exists. Since the G phase does not produce the characteristic textures, the morphology of the polarizing microscope images does not show the typical features.

X-ray studies

Prior to the discussion of the results from the XRD measurements, it is necessary to remember the definition of the parameter "*d*". Since the complete structure determination of the lyotropic systems is practically impossible [2, 9], the available information is limited to the interpretation of *d* values and the changes of certain reflections. With the exception of the S phase at least one long-spacing periodicity exists that correlates to the chain length of the soap molecules. In the case of a C phase, the *d* value is identical to $d_{001} = (c^*)^{-1}$ and gives the perpendicular distance between the (001) planes. The *d* values enable a direct comparison between different systems and phases to be made. After transition into the G phase, the long-spacing reflection is split into two small-angle reflections. With the transition to H_α phases, cylindrical structures are formed; the crystallographic parameter *a* is the edge length of the hexagons. The small-angle reflection at the lowest angle corresponds to the perpendicular packing distance $d_{100} = a \sin(60°)$ of the layers formed by the cylinders. The *d* value of the L_α phases describes the distance of the molded [*a, b*] planes, the only periodicity of these one-dimensionally ordered systems.

Due to the broadening of the small-angle reflections (including instrumental broadening) the *d* values are only obtained with an error of about 0.05 nm. The instrumental broadening increases with decreasing diffraction angle. Consequently, higher-order reflections and reflections from molecules with shorter chain lengths are in general measures more precisely. Here, the averages of the first three orders of the *d* values are given. This also allows the analysis of temperature expansion coefficients.

The *d* values as a function of K-soap concentration x_{KC_n} at 303 K for the KC_{12}/GL, KC_{14}/Gl, KC_{16}/Gl, KC_{18}/Gl and KC_{22}/Gl systems are shown in Fig. 1. In addition, the length, *l*, of two stretched single K-soap molecules, based on a molecular modeling simulation, is indicated (=2*l*). All systems are in the C phase. With the exception of KC_{14} and KC_{22} a slight tendency of an increase in *d* with an increase in soap concentration may be noticed; however, this increase ($\Delta d \le 0.05$ nm) lies within the uncertainty of the measurement.

The *d* value is shown as a function of the number of carbon atoms at $x_{\mathrm{KC}_n} = 0.5$ in Fig. 1. Values are given at T = 303 K for the C phase and at T = 433 K for the L_α phase and the theoretical value for perfectly aligned K-soap molecules (=2*l*) is also given. The *d* values of the C phase rise with $\Delta d/\Delta n_c = 0.217$ nm/carbon atom, about 87% of the theoretical value of $\Delta d/\Delta n_c = 0.248$ nm/carbon atom for perpendicular soap molecules. Assuming stretched molecules, these values imply an inclination of $\delta \approx 67°$ with respect to the [*a, b*] plane; however, it cannot be assumed that the K-soap molecules have uniform orientation and are perfectly stretched.

The lower curve in Fig. 2 shows the *d* values for the L_α phase at T = 433 K. The increase is $\Delta d/\Delta n_c = 0.128$ nm/carbon atom. The relatively small value indicates fluid chains which reduce the effective length of the K-soap molecules.

The dependency of the *d* values on the number of carbon atoms is shown for all K-soap/Gl systems at $x_{\mathrm{KC}_n} = 0.30$ in Fig. 3. The parameters are given at T = 303 K for the C phase and at 383 K for the H_α phase and the theoretical value for perfectly aligned K-soap molecules is also given. In the C phase, the *d* values rise with $\Delta d/\Delta n_c = 0.222$ nm/carbon atom, within an error identical to the value found for $x_{\mathrm{KC}_n} = 0.50$. For the H_α phase a value of $\Delta d/\Delta n_c = 0.165$ nm/carbon atom is measured. It is reasonable to assume that, on average, the K-soap molecules are directed radially into the cylinders of the H_α phase. Consequently, the typical unit cell parameters are, at least for low concentrations, primarily determined by the chain length of the K-soaps, and their concentration has a minor influence.

The temperature dependence of the *d* values of the first small-angle reflections for all K-soap/Gl systems at $x_{\mathrm{KC}_n} = 0.50$ is illustrated in Fig. 4. The systems are in the C phase and the G phase; the transition temperature is marked as a dashed line in Fig. 4. Generally, there are no simple characteristics describing the behaviour of the

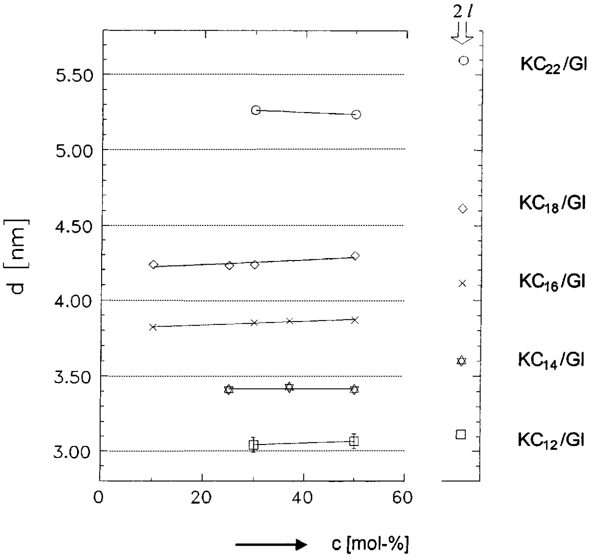


Fig. 1 *d* values of the first small-angle reflections of the K-soap/glycerol (Gl) binary systems as a function of concentration at T = 303 K for the crystalline (*C*) phase. Abbreviations: KC_{12} = K-laurate, KC_{14} = K-myristinate, KC_{16} = K-palmitite, KC_{18} = K-stearate, KC_{22} = K-behenate, 2*l* is the length of two stretched soap molecules in the bilayer; *c* is the mole percent of K-soap

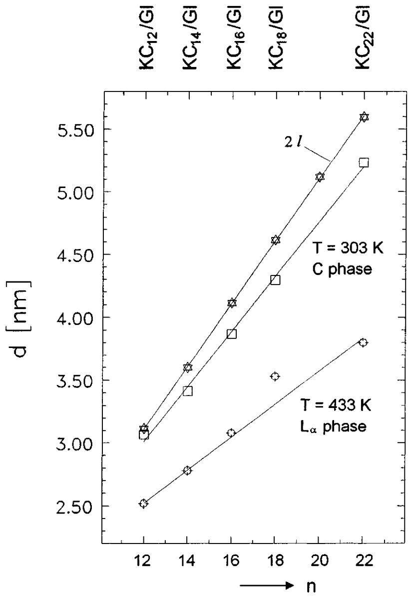


Fig. 2 *d* values of the first small-angle reflections of the K-soap/Gl binary systems as a function of chain length, *n* (total number of carbon atoms per soap molecule), at T = 303 K for the C phase and at T = 433 K for the lamellar (L_α) phase; all systems at $x_{\mathrm{KC}_n} = 0.50$

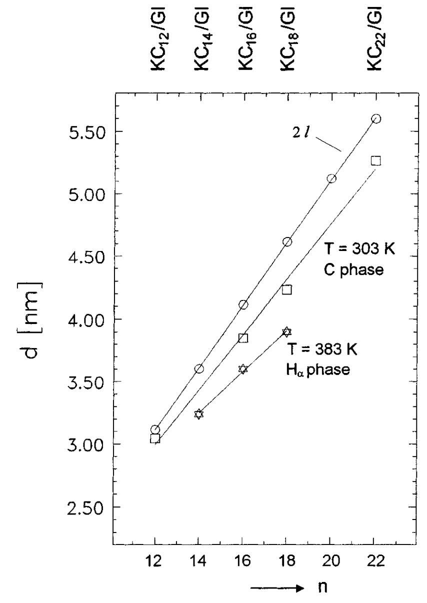


Fig. 3 *d* values of the first small-angle reflections of the K-soap/Gl binary systems as a function of chain length, *n* (total number of carbon atoms per soap molecule), at T = 303 K for the C phase and at T = 383 K for the hexagonal (H_α) phase; all systems at $x_{KC_n} = 0.30$

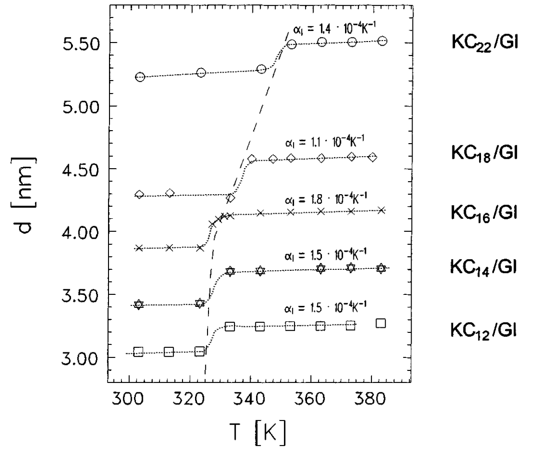


Fig. 4 *d* values of the first small-angle reflections of the K-soap/Gl binary systems as a function of temperature; all systems $x_{KC_n} = 0.50$, C and gel (*G*) phases. α is the linear thermal expansion coefficient

d values within the C phase and the G phase. The following relations are found:

- The abrupt increase in the *d* values during the phase transition C ↔ G is approximately $\Delta d = 0.2$–0.3 nm for all systems. The chain length of the soaps seems to have no influence. Consequently, the effect may be dominated by the influence of the Gl on the structure-forming process. The temperature of the phase transition C ↔ G increase with increasing chain length.
- Generally, the first small-angle reflections of the G phase are split. The *d* values of the new, second reflection decrease in a nonlinear fashion in a temperature interval of about 20 K with *d* ranging from −0.5 to −1.0 nm.
- The *d* values of the H_α phase decrease with rising temperature. This may be caused by increasingly fluid chains of the soap molecules which reduces the diameter of the cylinder in the H_α phase.
- The *d* values in the L_α phase for example the perpendicular distance of the lamellae, show different behavior. Systems with high soap concentrations ($x_{KC_n} = 0.50$) show an expansion with temperature at temperatures near the lower phase boundary but no measurable temperature dependence at higher temperatures. In addition, a slight minimum in the *d* values with rising temperatures is observed during the phase formation. In contrast, systems with low soap concentrations and which are closely located to H_α-phase regions show a negative dependence of the *d* values on temperature.

Model of the G-phase structure

All five systems discussed here and in Refs. [1–7] are characterized by the appearance of a G phase. In KC_{14}/Gl, KC_{16}/Gl and KC_{18}/Gl the G phase is always the intermediate phase between the C phase and the lyotropic mesomorphic phase in the direction of higher temperature; however, to our surprise, the systems KC_{12}/Gl and KC_{22}/Gl did not form an intermediate G phase between the C phase and the H_α phase. In these two systems the C phase passes directly into the H_α phase. The G phase of these systems form only at concentrations where the L_α phase also exists. Unfortunately the G phase does not produce characteristic textures, but information about the properties and the structure of G phase are obtained from XRD measurements.

Most challenging for evaluation of a structural model of the G phase is the splitting of the first small-angle reflections. Luzzati et al. [10] suggested that the molecules assume an interdigitated arrangement within the bilayer. A similar model with an undulating arrangement of soap molecules within the bilayer is shown in Fig. 5. Both models are not able to explain the splitting of the small-angle reflections. Due to the undulating arrangement of the soap molecules the crystallographic unit cell has to be extended in the direction of the *a*-axis. It must comprise two molecules in order to have the required translational symmetry; however, diffractograms computed for such unit cells show no splitting of the small-angle reflections [9]. Only a rapider decay of the intensity of higher-order reflections occurs compared to a nonundulating arrangement of the molecules. As the repetitive length, the *c*-axis, is maintained, the undulating arrangement of the molecules only influences the structure factor *F* [2]; however, the presence of an

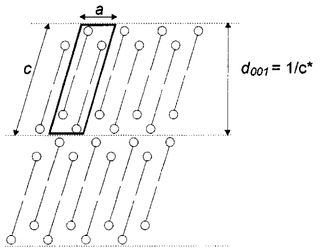


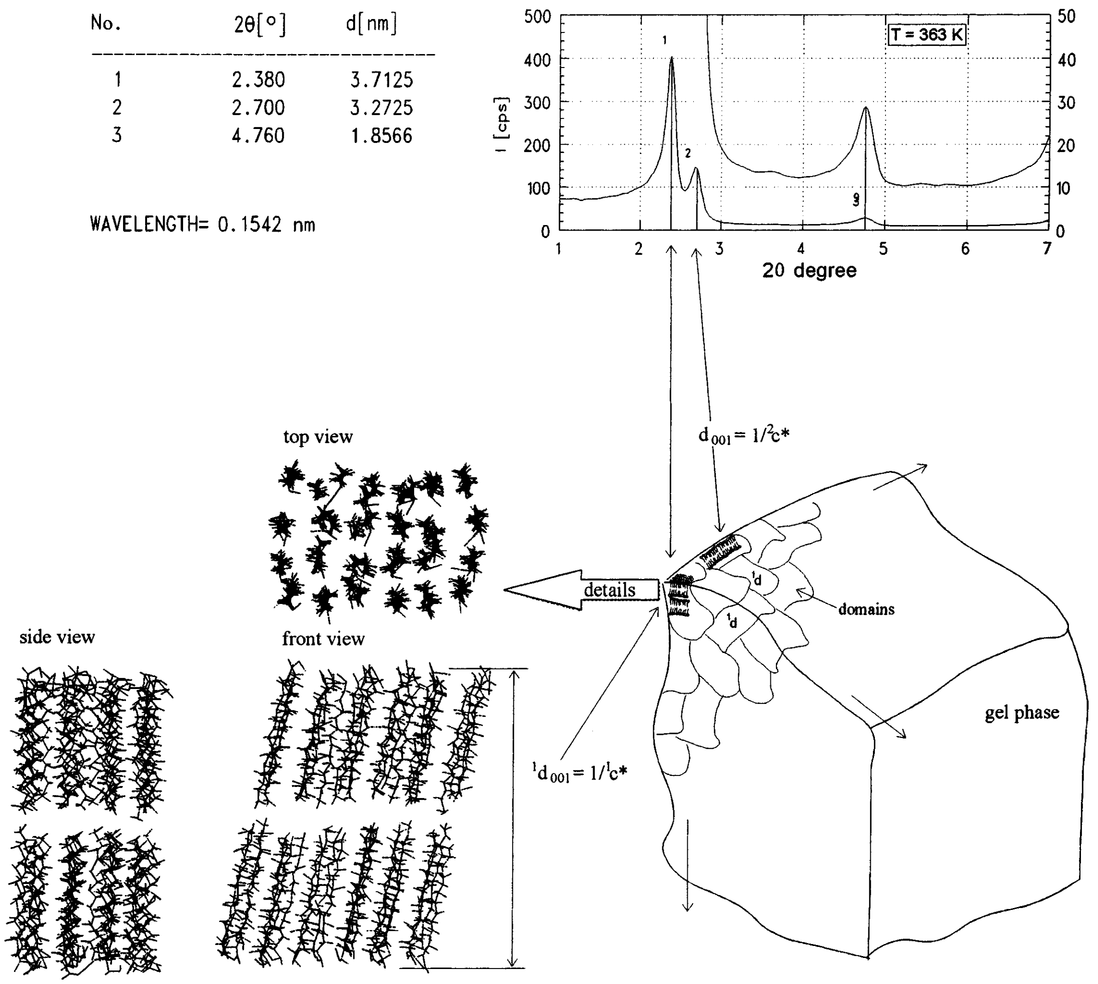
Fig. 5 Undulating arrangement of soap molecules in a bilayer. *a* and *c* are the unit cell parameters and $d_{001} = 1/c^*$ is the lattice plane distance

undulating arrangement can also not be completely excluded. Though experimentally very complicated, it could be detected by measuring the exact intensity decay of the higher-order small-angle reflections.

A theoretical possibility to explain the splitting of the small-angle reflections would be the deformation of the unit cell. A hypothetical cubic unit cell would yield small-angle reflections with *d* value ratios of $1{:}\sqrt{2}{:}\sqrt{3}{:}\sqrt{4}{:}\ldots$ A slight tilt or distortion of the cubic shape would lead to slightly different (0 0 1) and (0 1 0) lattice plane distances. This would be registered as a splitting of the small-angle reflections; however, the triclinic unit cell of the C and G structures has only one large lattice constant; hence the splitting cannot be explained in this way.

Probably, the most likely explanation is to assume that G phases consist of inhomogeneities in the form of two types of crystallographic domains. These domains probably contain approximately 10^3–10^5 soap molecules forming two bilayer structures with different spacings. The two types differ only in slightly different *c*-axis and consequently representative *d* values. With rising temperature the relative proportion of the two structures changes, causing the observable intensity change of the two small-angle reflections. In addition, a reduced crystallographic order within each domain is feasible. A simplified model of this structure is illustrated in Fig. 6.

Fig. 6 Model of the structure of the G phase. The observed splitting of the small-angle reflections results from the presence of two kinds of domains



No.	2θ[°]	d[nm]
1	2.380	3.7125
2	2.700	3.2725
3	4.760	1.8566

WAVELENGTH= 0.1542 nm

Comparison of the K-soap/Gl systems with K-soap/water systems

McBain and coworkers [8, 11] and Luzzati et al. [10] have carried out comprehensive studies of the phase behaviour of the Me-soap/water systems (Me = K, Na, etc.). The published phase diagrams result from texture observations by polarizing microscopy and from X-ray diffraction measurements. We found the following correspondences:

- A L_α phase and a H_α phase are observed.
- The H_α phase is built up at low K-soap concentrations.
- The L_α phase is observed at high K-soap concentrations.
- The temperature of the phase transition $H_\alpha \rightarrow S$ runs through a maximum.
- The higher the K-soap concentration, the higher the temperature of formation of the L_α phase.
- With increasing chain length, the minimum K-soap concentration required for forming the H_α phase shifts to lower K-soap concentrations.
- The temperature of the transition $L_\alpha \rightarrow S$ decreases with increasing chain length.

The following differences in the phase behavior of the aqueous and nonaqueous systems were observed:

- An optically isotropic (cubic phase, intermediate phase) is observed in all aqueous systems tested but not in the Gl containing systems.
- In aqueous systems the L_α phase extends from high to low K-soap concentrations, but in the Gl-containing systems the extends is in the opposite direction.
- The temperatures of formation of the H_α and L_α phases are lower in the Gl-containing systems than in the aqueous systems.
- With increasing chain length the maximum extension of the concentration region of the H_α phase decreases in Gl-containing systems but increases in aqueous systems.

This comparison demonstrates that there are more correspondences than differences between K-soap/water and K-soap/Gl systems. This result underlines the influence of the solvent on the formation of lyotropic mesophases: the dimension and position of the different regions in the phase diagrams can be manipulated by applying solvents of "waterlike" structure.

References

1. Hieke A, Dörfler HD (1999) Colloid Polym Sci 277:494
2. Hieke A, Dörfler HD (1999) Colloid Polym Sci 277:762–776
3. Hieke A, Dörfler HD (1999) Colloid Polym Sci 277:777–784
4. Hieke A, Dörfler HD (1999) Colloid Polym Sci 277:1104–1108
5. Hieke A, Dörfler HD (1999) Colloid Polym Sci 277:1109–1114
6. Hieke A, Dörfler HD (1999) Colloid Polym Sci 1220–1223
7. Dörfler HD Senst A (1993) Colloid Polym Sci 271:173
8. McBain JW, Vold RD, Frick M (1940) J Phys Chem 44:1013
9. Hieke A (1995) Thesis TU Dresden
10. Luzzati V, Mustacchi H, Skoulious A (1958) Discuss Faraday Soc 25:340
11. McBain JW, Lee WW (1943) Oil Soap (Chicago) 17:230