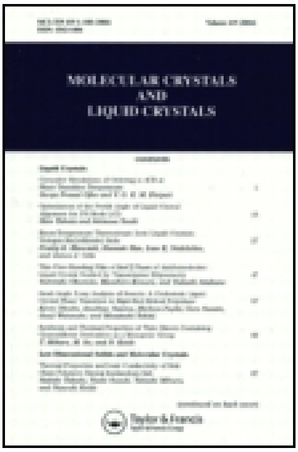

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Effect of Protic Solvents on the Formation of Lyotropic K-Myristinate Mesophases: Texture Observations and Binary Phase Diagrams

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Effect of Protic Solvents on the Formation of Lyotropic K-Myristinate Mesophases: Texture Observations and Binary Phase Diagrams*

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The phase diagrams of following binary soap systems (soap = K-myristinate = KC_{14}) were examined by polarization microscopy: system KC_{14}/glycerol (G), KC_{14}/ethylene glycol (E) and KC_{14}/butylene glycol (E). Comparing these three phase diagrams, we found alterations in types of phase diagrams that depends on the chemical structure of the solvent. The following polymorphism were observed: In the system KC_{14}/G: $C \leftrightarrow G \leftrightarrow H \leftrightarrow I \leftrightarrow L \leftrightarrow S$ (C = crystalline phase, G = gel phase, H = hexagonal phase, I = isotropic phase, L = lamellar phase, S = isotropic solution). In the system KC_{14}/E: $C \leftrightarrow G \leftrightarrow L \leftrightarrow S$ and in the system KC_{14}/B the same phase sequence: $C \leftrightarrow G \leftrightarrow L \leftrightarrow S$.

The differences in number, position, extension and sequence of occurring lyotropic mesophases are a function of the composition in the binary system and temperatures. The influence, which the solution medium exerts on the formation of structures in the binary systems, is distinct and pronounced.

Key words: *Lyotropic mesophases, phase diagrams, polymorphism, protic solvents, K-myristinate.*

INTRODUCTION

It is well known that lyotropic mesophases are mainly formed in multicomponent systems where the solvent or dispersion medium supports the formation of mesophases of amphiphilic compounds by favouring suitable structures. In particular a great number of binary systems of the type surfactant/water and ternary and quaternary systems have been systematically studied in the last 50 years which are mainly summarized in.[1–6] In all the binary systems water has been used as solvent or as second or essential component.

Of course the question arises what an influence other types of solvents, as for instance protic and aprotic liquids, will exert on the formation of lyotropic mesophases. In the literature we find only the very first attempts to get some information about this topic. B. Schwandner[7] tested a number of commercial surfactants in various non-aqueous solvents as for instance glycerol, ethylene glycol, and dimethyl sulfoxide. In order to get a survey of mesophase formation she examined contact samples using the so-called "penetration method" after Tiddy *et al.*[8] with the aid of a polarizing microscope. In the polar protic solvents glycerol and ethylene glycol, mainly lamellar and hexagonal

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* To the memory of Prof. Dr. Dr. h. C. Horst Sackmann.

phases have been detected. Though surfactants are less soluble in the aprotic solvent dimethyl sulfoxide than in such protic liquids as ethylene glycol and glycerol, the formation of lyotropic mesophases has been also observed in this solvent. In the aprotic solvent dimethyl formamide, however, no mesophase formation has been detected. This may be caused by the tendency of many surfactants to become instable and to decompose in dimethyl formamide.

On the other hand Friberg *et al.*[15–28] used glycerol and ethylene glycol in binary and ternary systems investigating phospholipids or surfactants to study the polymorphism and phase regions of the lyotropic mesophases extensively. Furthermore Lattes *et al.*[29–32] showed by X-ray studies and texture observation that surfactants in water substitutes as formamid and glycerol are able to form mesophases. The phase diagram of cetyltrimethylammonium bromide/formamide was determined and mesomorphic phases were observed which closely resembled those found in water. The comparison of the results from cetyltrimethylammonium bromide/formamide and cetyltrimethyl bromide/glycerol systems with the corresponding cetyltrimethyl bromide/water system showed the same phase sequence, but the existence regions of these phases hexagonal↔monoclinic↔ (close to a centered rectangular phase) ↔cubic ↔ lamellar are different and the structure parameters smaller.

The results of these preliminary examinations suggest that among polar solvents the protic ones are probably more appropriate for the formation of lyotropic mesophases than aprotic solvents. Perhaps aprotic solvents are not able to screen the head group charges with the aid of hydrogen bonds. This will influence the whole aggregation process.

Therefore the aim of our studies was to proof the influence of glycerol, ethylene glycol and butylene glycol on the phase formation in the three binary systems K-myristinate/ethylene glycol, K-myristinate/butylene glycol and K-myristinate/glycerol in order to determine preliminary phase diagrams by microscopic texture observation.

METHODS

Polarization Microscopy

We used a polarizing microscope of the type JENAPOL 30-0060 Carl Zeiss (Jena). With this microscope both orthoscopic and conoscopic observations could be performed. As generally known, sample preparation, thermal sample pretreatment, layer thickness of the samples in the flat glass cell and measuring temperature, all these parameters will exert an influence on texture.

On the basis of texture photographs birefringent lamellar and hexagonal phases can be clearly distinguished. But the isotropic cubic phase is optically isotropic and without any special texture, when tested with crossed polarizers, because birefringence does not occur in isotropic systems.

Sample Preparation

On the average we tested about 15 singular concentrations for each binary system. The singular concentrations varied in the ratios of K-myristinate to glycerol. Defined amounts of glycerol and K-myristinate were put into test tubes with standard taperground joints (length 4 cm) by weighing them with a microbalance. Afterward the test tubes were closed by taper-ground stoppers and in addition tightened by an adhesive plaster. Then the samples were cautiously heated by means of a powerful hot-air apparatus (type PHG 600 CE; Bosch, Bayreuth). When the substances or mixtures had begun to melt, they were completely homogenized by applying a shaking device (type VF 2, Fa. Jahnke and Kunkel, IKA Labortechnik) together with a hot-air-blower. Samples rich in K-myristinate were subjected to this procedure several times, because of the high melting points of the K-soaps that made homogenization rather difficult and only feasible at high temperatures. Due to these high melting points we extended our tests only up to K-myristinate concentrations of $c = 65$ mol-% or $c = 80$ mol-%.

Adjustment of Sample Temperature during Texture Observation

Texture examination was performed at temperatures between about T = 303–623 K. Heating was carried out by means of a Mettler-Thermosystem which consisted of the control device FP 80 HT and the heating stage FP 82 Hotstage. The measuring cell, which contained the flat capillary, was connected with the control device. Then a defined, suitable temperature program could be realized. It comprised the temperatures at the beginning and at the end, and further the speeds of heating and cooling. Generally we made 3 texture observations per sample.

Contact Samples

Contact samples have already proved to be a suitable and telling method for examining binary phase diagrams of thermotropic liquid crystals in regard to miscibility properties and phase diagram type determination. The so called “penetration method,” which Tiddy *et al.*[8] has applied for investigation of the textures of lyotropic mesophases, is a further development of this technique. The K-myristinate is put on the specimen slide and covered by a cover slip. Then a drop of solvent (glycerol etc.) is deposited on the border of the cover slip. Owing to adhesive forces acting between specimen slide, cover slip and solvent, the solvent is pulled from the border toward the inner parts, and in this way the surfactant is wetted. In the contact zone a concentration gradient between K-soap and glycerol is built up, since the surfactant concentration will, of course, be higher in direction of the sample centre. This concentration gradient belongs to definite concentration regions of the phase diagram. Consequently, the textures of the different phase of the binary system to be observed at constant temperature can be made visible. That means that we make cross sections at defined temperatures through the whole phase diagrams with the aid of these contact samples and their textures.

Materials

The K-myristinate were obtained by applying the methanolate method.[10,11] The product obtained in this way formed a white precipitate which was then subjected to a fourfold recrystallisation in absolute methanol. The subsequent drying was performed for 24 hours in a drying pistol over P_2O_5 at $T \approx 345$ K. The melting and the transition temperatures of the neat phase served as purity criteria.

Glycerol (Reachim 99.3%) was carefully distilled in vacuum (Kp = 453 K) before it was used. Ethylene glycol and butylene glycol were made by VEB Laborchemie, Apolda and VEB Chemische Werke Buna respectively. The glycols were dried in presence of Na_2SO_4 (p.a.) and gently distilled under vacuum.

RESULTS

Phase Diagram of the System Potassium Myristinate (KC_{14})/Glycerol (G)

According to the textures of the contact samples shown in Figure 1 the following phases exist in the binary system KC_{14}/G at a temperature of $T = 396$ K: the crystalline phase C, the lamellar phase L, the optically isotropic phase I, the hexagonal phase H and the isotropic solution S. At singular concentrations an additional phase, a gel phase G, is observed. The phase diagram presented by Figure 2 gives a survey of the results of texture observations at singular concentrations. The width of the heterogeneous two-phase regions indicated by hatched areas is, on the average, of about $\Delta T = 4 - 7$ K. Samples of K-myristinate concentrations below $c = 18$ mol-% formed no mesophases.

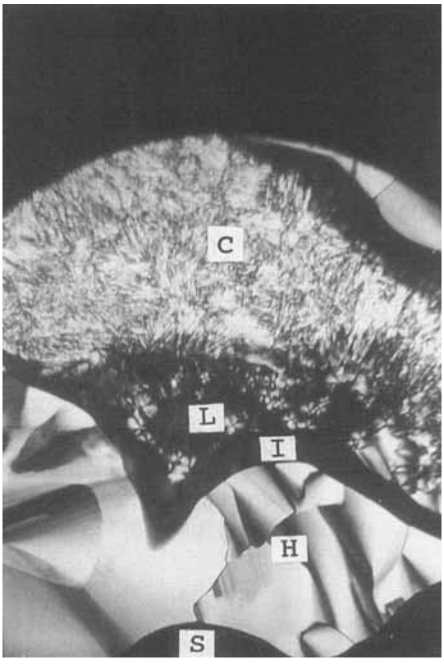

FIGURE 1 Textures of the binary system potassium myristinate/glycerol using the penetration method. Crossed polarizers; magnification: 100x; temperature: $T = 396$ K. The textures show the polymorphism: C↔L↔I↔H↔S. Abbreviations: C = crystalline phase; L = lamellar phase; I = isotropic phase; H = hexagonal phase; S = isotropic solution.

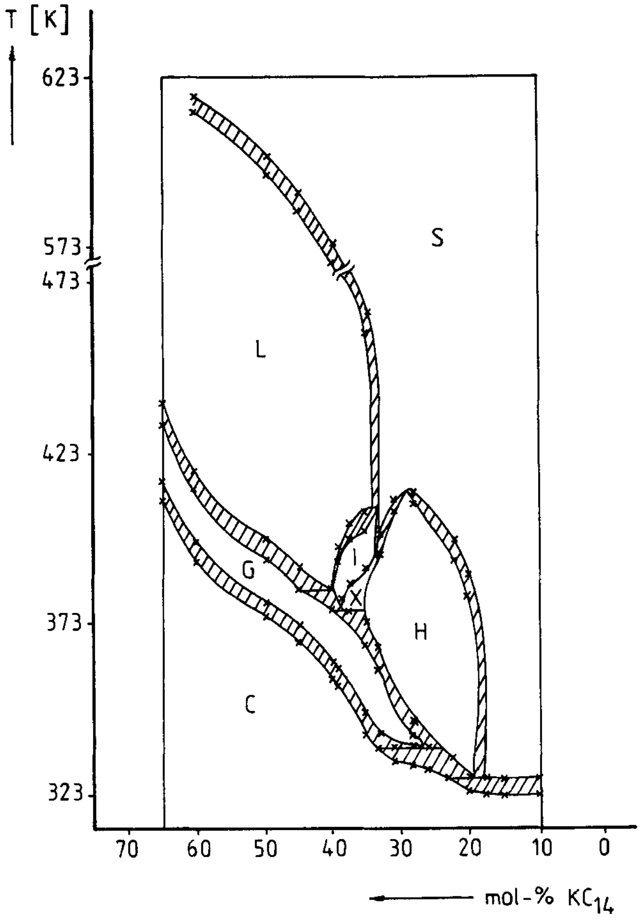

FIGURE 2 Phase diagram of the binary system potassium myristinate/glycerol. Concentration are given in mol-% KC_{14}. Phase notation: C = crystalline phase; G = gel phase; L = lamellar phase; H = hexagonal phase; I = isotropic phase; X = probably modified gel phase; S = isotropic solution.

On elevating the temperature their crystals melt and form an isotropic solution. The phase region of the H-phase extends between $c = 19 - 37$ mol-%. The lowest temperature, at which the formation of the hexagonal phase is possible, depends strongly on K-myristinate concentration. It rises steadily from $T = 328$ K to $T = 378$ K in the direction of increasing K-myristinate concentrations. Analogously to system KC_{12}/G^{12} the separating line between the phases H and S has a maximum. This maximum value is found at about $c_m = 30$ mol-% and $T_m = 413$ K. Above $T = 413$ K mixtures in this concentration range was formed only an isotropic solution.

At concentrations between $c = 27 - 65$ mol-% the crystalline phase C is succeeded by a gel phase G. The appertaining phase transition temperatures start at $T = 335$ K and increase continuously up to $T = 410$ K with increasing K-myristinate concentra-

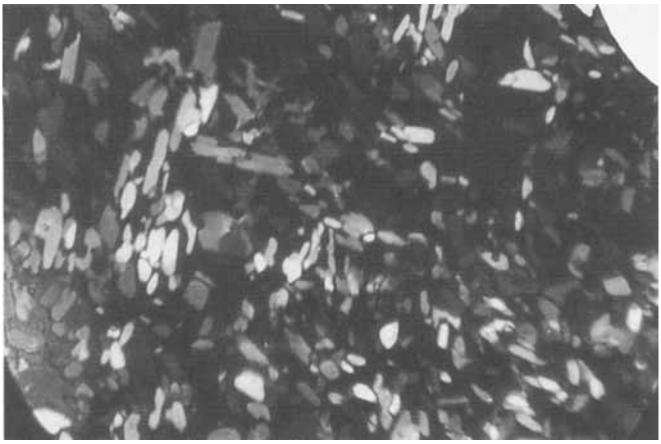

FIGURE 3 Picture of the heterogeneous two-phase region gel/isotropic phase X in the binary system potassium myristinate/glycerol. Crossed polarizers; magnification: 100x; temperature: $T = 386\,\mathrm{K}$; concentration: $c = 35\,\text{mol-}\%\ \mathrm{KC}_{14}$.

tion. The width of this gel phase region is around $\Delta T = 20\,\mathrm{K}$ over the whole concentration range. Characteristic textures are not formed, but up to K-myristinate concentrations of $c = 40\,\text{mol-}\%$, a flocculent gel region is observed, which changes into a curd-like structure at higher temperatures.

Figure 3 points out that an optically isotropic region, named I-phase (I = isotropic) is inserted between the phase regions of the L-phase and the H-phase at concentrations from $c = 34$–$39\,\text{mol-}\%$. It is possible that this region of the phase diagram is of cubic structure. But the question is still open and must be cleared up by additional X-ray diffraction measurements.

When we elevate the temperature in the concentration range $c = 34$–$39\,\text{mol-}\%$, the crystalline phase melts and turns into a gel phase. The adjoining phase region represents a heterogeneous two-phase region X where a coexistence of G- and I-phase is assumed. When the temperature is further elevated, the rests of the gel phase turn into the I-phase and the formation of the isotropic phase is finished. The photographs, taken by the polarizing microscope in Figure 4, illustrate this temperature-dependent process. Surprisingly slow melting of the "gel particles" is accompanied by an increase in number and size of dark regions until the polarizing microscope shows only one completely dark, optically isotropic area. In the phase diagram the optically isotropic phase occupies a mean temperature width of $\Delta T = 10\,\mathrm{K}$ with a maximum extension between $T = 388$–$403\,\mathrm{K}$.

When the temperature range of the optically isotropic phase is exceeded, spherulites, which characterize the lamellar phase, appear in polarized light. The L-phase has been identified by its fine mosaic texture (compare Figure 4). It exists within the concentration range from $c = 34\,\text{mol-}\%$ up to $c = 65\,\text{mol-}\%$. Between $c = 34$–$40\,\text{mol-}\%$ the temperature of the phase transition $\mathrm{L} \leftrightarrow \mathrm{S}$ drops from $T = 403\,\mathrm{K}$ to $T = 383\,\mathrm{K}$, while between $c = 40$–$65\,\text{mol-}\%$ this transition temperature increases steadily.

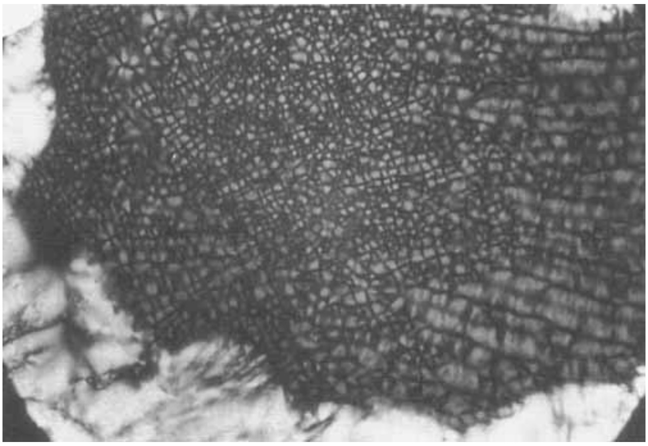

FIGURE 4 Fine mosaic texture of the lamellar phase in the binary system potassium myristinate/glycerol. Crossed polarizers; magnification 100 x; temperature: $T = 430\,K$; concentration: $c = 35$ mol-% KC_{14}.

Beyond this phase transition temperature the L-phase exists over a large concentration range, but it is not observed at temperatures above $T = 615\,K$. Here the region of the isotropic phase begins. In the system under discussion mosaic textures and "oily streaks" are the most frequent textures of the lamellar phase.

Summarizing the system KC_{14}/G can be characterized by polymorphism which are shown in Table I. But polarizing microscopy does not give answers to all questions. Thus it could not be decided, if the regions designated as X were in fact heterogeneous two-phase regions. For this reason additional calorimetric measurements are necessary. It must further be clarified by X-ray diffraction, whether the I-phase, which has been interpreted as an optically isotropic region, is actually of cubic structure.

TABLE I

Summary of the Polymorphic Transitions of the Binary K-Myristinate/Glycerol, K-Myristinate/Ethylene Glycol and K-Myristinate/Butylene Glycol Systems. Phase Notation: C = Crystalline Phase; L = Lamellar Phase; S = Isotropic Solution; I = Isotropic Phase; H = Hexagonal Phase. The Temperature of the Phase Transitions are Different from Another Because of the Special Properties of the Phases in the Single Systems. Abbreviations: G = Glycerol: E = Ethylene glycol; B = Butylene glycol

System	Concentration range (mol-%)	Polymorphic transitions
KC_{14}/G	19–27	C↔H↔S
	27–35	C↔G↔H↔S
	34–39	C↔G↔X↔I↔L↔S
	40–65	C↔G↔L↔S
KC_{14}/E	5–32	C↔G↔S
	35–80	C↔G↔L
KC_{14}/B	5–44	C↔G↔S
	47–80	C↔G↔L

Phase Diagram of the System Potassium Myristinate (KC_{14})/Ethylene Glycol (E)

Results obtained by the penetration method indicated the existence of a lamellar mesophase in this system. The photograph taken of the textures in Figure 5 at $T = 403$ K, suggest in direction of increasing soap concentration the phase sequence $C \leftrightarrow L \leftrightarrow S$. Due to the appearance of mosaic and spherulite textures, the existence of the lamellar mesophase L could be unequivocally proved.

The results of texture observation by polarization microscopy on singular mixtures of the system of KC_{14}/E are summarized in the phase diagram: Figure 6. Four phase regions are distinguished. On increasing the temperature the system passes through the following states: from $c = 5$ to 32 mol-%: $C \leftrightarrow G \leftrightarrow S$; from $c = 35$ to 80 mol-%: $C \leftrightarrow G \leftrightarrow L$.

As seen from the phase diagram, in this system again the crystalline phase C was also built up within the whole concentration range and changed into the gel phase G, when temperature was elevated. At concentration below $c = 14$ mol-% no gel phase G was formed and the crystalline phase C passed directly into the "melting region M" (two-phase region) and later on into the isotropic solution S, if temperature was increased. The phase transition from the gel phase G into the lamellar mesophase L occurred at concentrations below $c = 30$ mol-%, e.g., between $c = 14$ and 30 mol-%.

Phase Diagram of the System Potassium Myristinate (KC_{14})/Butylene Glycol (B)

The results of the texture observations, obtained by the penetration method, correspond with those of the KC_{14}/E system (see Figure 5). At increasing soap-concentra-

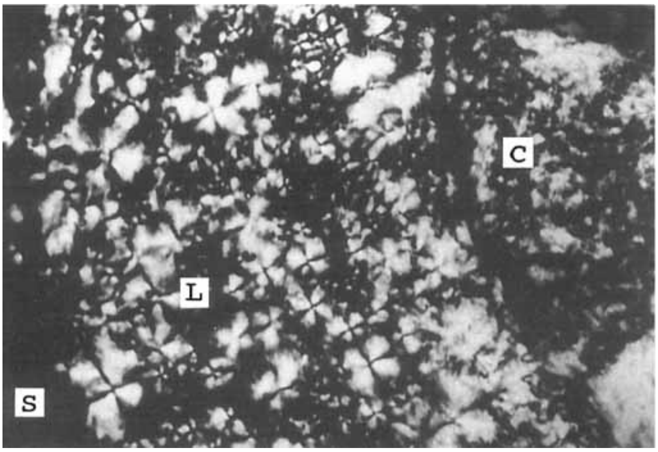

FIGURE 5 Texture of the binary system potassium myristinate/ethylene glycol using the penetration method. Crossed polarizers, magnification: 100 x; temperature: $T = 403$ K. The textures are showing the polymorphism $S \leftrightarrow L \leftrightarrow C$.

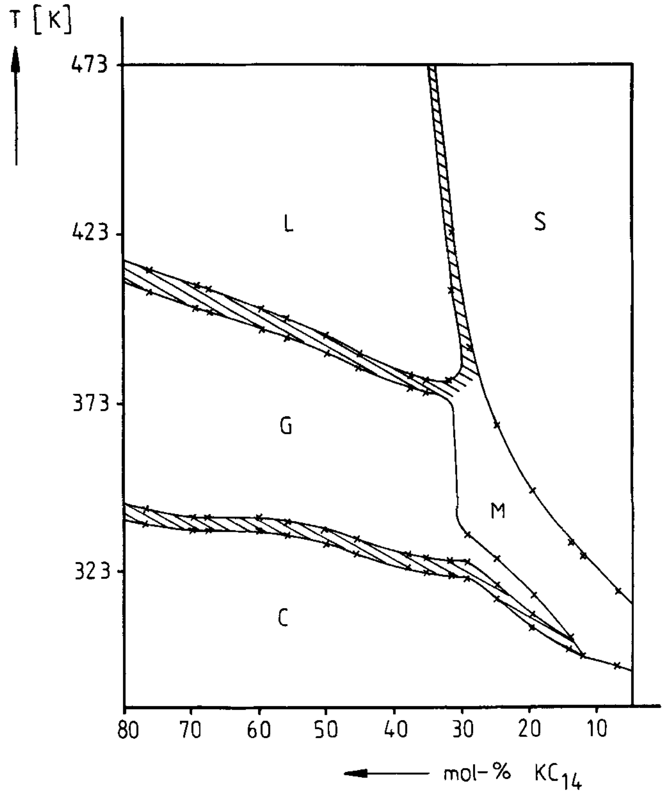

FIGURE 6 Phase diagram of the binary system potassium myristinate/ethylene glycol. Concentrations are given in mol-% KC_{14}. Phase notation: C = crystalline phase; G = gel phase; L = lamellar phase; S = isotropic solution; M = "melting region" (two-phase region).

tions and at temperatures of more than $T = 440$ K the following textures of polymorphic transitions were observed: C↔L↔S.

The results, obtained by the polarizing microscopic texture observation on singular mixtures of the system KC_{14}/B are represented in the phase diagram of Figure 7. Depending on the mixture composition and on temperature, 4 phases were fixed in the binary system. In the various ranges of concentration of the binary phase diagram the following polymorphism were found: from $c = 5$ to 44 mol-%: C↔G↔S; from $c = 47$ to 80 mol-%: C↔G↔L. Hence it follows that the type of the phase diagram for the system KC_{14}/B corresponds with that one for the system KC_{14}/E.

With increasing temperatures the crystalline phase C was followed by the gel phase G. Both phases exists over the whole concentration range of investigated concentration. At concentrations of less than $c = 42$ mol-% and with increasing temperatures, the "melting range M" occurred. In comparison with the KC_{16}/B system[10], it had a greater extension as regards the range of temperature. The lamellar phase L developed from the gel phase G from $c = 44$ mol-% and about $T \sim 440$ K. The transition from the lamellar phase L to the isotropic solution S was seen up to $T \sim 473$ K and only within the range

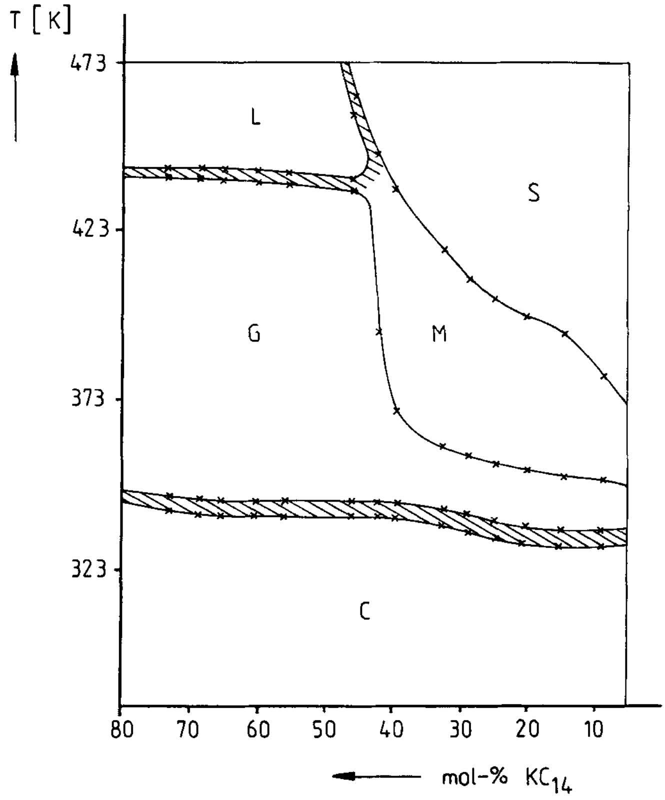

FIGURE 7 Phase diagram of the binary system potassium myristinate/butylene glycol. Concentration are given in mol-% KC_{14}. Phase notation: C = crystalline phase; G = gel phase; L = lamellar phase; S = isotropic solution; M = "melting region" (two-phase region).

of concentration between $c = 44$ and 47 mol-%. In mixtures of a composition of less than $c = 47$ mol-%, the lamellar phase turned out to be stable up to temperatures of about $T \sim 473$ K.

DISCUSSION AND CONCLUSION

A comparison of the three phase diagrams brings out that number and type of phases, location and extension of the phase regions and their succession in the phase diagram were dependent of the solvent type. In the binary system KC_{14}/G we found at concentrations rich in glycerol the phase sequences $C \leftrightarrow H \leftrightarrow S$ and $C \leftrightarrow G \leftrightarrow H \leftrightarrow S$. Than follows in the concentration range rich in K-soap the phase sequences $C \leftrightarrow G \leftrightarrow X \leftrightarrow I \leftrightarrow L \leftrightarrow S$ and $C \leftrightarrow G \leftrightarrow L \leftrightarrow S$. This means that probably two gel phases appeared and a isotropic I-phase occurred.

In the system KC_{14}/E we found the phase sequence $C \leftrightarrow G \leftrightarrow S$ in the concentration range rich in ethylene glycol. On the other hand in the concentration range rich in

K-soap we have pointed out the phase transitions C↔G↔L. The same type of phase transitions is typical for the system KC_{14}/B. Only the temperature and concentration ranges, in which the phases exist, are different. In Table I we have summarized the comparison of polymorphism and phase behavior for the three systems which we have discussed already.

It is useful to compare our phase diagrams with those of the K-soap/water systems published in the literature. McBain *et al.*[4,5] and Luzzati *et al.*[6] have carried out comprehensive studies of the phase behavior of soap/water systems. The diagrams published by these authors result from textures observations and X-ray diffraction measurements. By comparing the phase diagrams of the four systems KC_{12}/H_2O, KC_{14}/H_2O, KC_{16}/H_2O and KC_{18}/H_2O they have established the following phase sequence: S↔H↔L. The phase diagrams of these systems differ solely in the positions of the phase regions with respect to temperature and composition. In all these aqueous systems a gel phase has also been observed. Later on Luzzati *et al.*[6] have completed the phase diagrams of the systems K-soap/water by additional X-ray experiments. In each of the four systems they have detected a small concentration range of the cubic phase I inserted between the H- and the L-phase. This cubic phase is stable up to temperatures of about $T = 373$ K. At higher temperatures it changes into the isotropic solution S.

The results, which summarized in Table I together with the results discussed above, underline the influence exerted by the solvent type on the formation of lyotropic mesophases. This influence is of predominantly quantitative character, i.e. extensions and positions of regions in the phase diagrams can be manipulated by applying solvents of water-like structure.

In conclusion we can point out that the C-phase, G-phase and L-phase appeared in all of the observed systems. On the contrary, the H-phase and the I-phase were found only in the system KC_{14}/G and in the K-soap/water systems mentioned above.

As well in the waterless and in the water-containing systems the lamellar phase is observed at high K-soap concentrations. The temperature curve of the transition H↔S in the phase diagrams runs through a maximum. The temperatures of the formation of lamellar and hexagonal mesophases are smaller in the waterless systems than in aqueous systems. The higher the K-soap concentration, the higher the temperature of the formation of the lamellar phase.

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