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Lyotropic liquid-crystalline phase composed of aliphatic amino stearates and water

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Polarization microscopy, differential calorimetry D.S.C. and X-ray diffraction have been used to examine the lyotropic mesophases which occur in solutions of amino salts in water. The following systems were investigated: methylamino, *n*-propylamino, *n*-butylamino, isobutyl-amino and *n*-hexylamino stearates as one component of the system and water as the other. The types of lyotropic phase and the range in which they occur were determined as functions of concentration and temperature.

1. Introduction

The results known up to now show that ammonium [1–5] and alkali metal salts [6–11] of higher fatty acids with amphiphilic molecular structures form with water lyotropic mesophases. It is reasonable to expect that amino salts of higher fatty acids will also form lyotropic liquid crystals in combination with water. In this work we present results for binary liquid-crystalline phase systems formed from water and the stearates of selected amines: methylamine, *n*-propylamine, *n*-butylamine, isobutylamine and *n*-hexylamine. The purpose of this work was to establish the type and range of occurrence of the mesophase, as well as to find the dependence between mesophase formation and the structure of the amino stearates.

2. Experimental

The amino stearates were prepared by direct reaction of stearic acid and the corresponding amine, and were identified as amine salts with the formula $(C_{17}H_{35}COO)^{\ominus}RNH_3^{\oplus}$. The methods used to identify and determine the purity of these salts have been described previously [12].

Microscopic measurements were carried out using a Boetius microscope model PHMK 05 made by VEB Analytik Dresden, equipped with double polarizing filters. Measurements were made with the sample in capillaries flattened according to the method described by Doscher and Vold [13]. Calorimetric measurements were carried out with differential scanning calorimetry using a differential microcalorimeter Perkin-Elmer D.S.C.-1B. The heat of the phase transition was calculated by means of a gravimetric method.

X-ray studies were performed by diffraction and photographic methods. Diffractograms were recorded on Dyfraktograf URS-50 JM in the 2θ angular range from 1° to 30°, photographs were taken in the 2θ range from 2·5° to 30°. Each sample was studied three times:

(1) at room temperature;

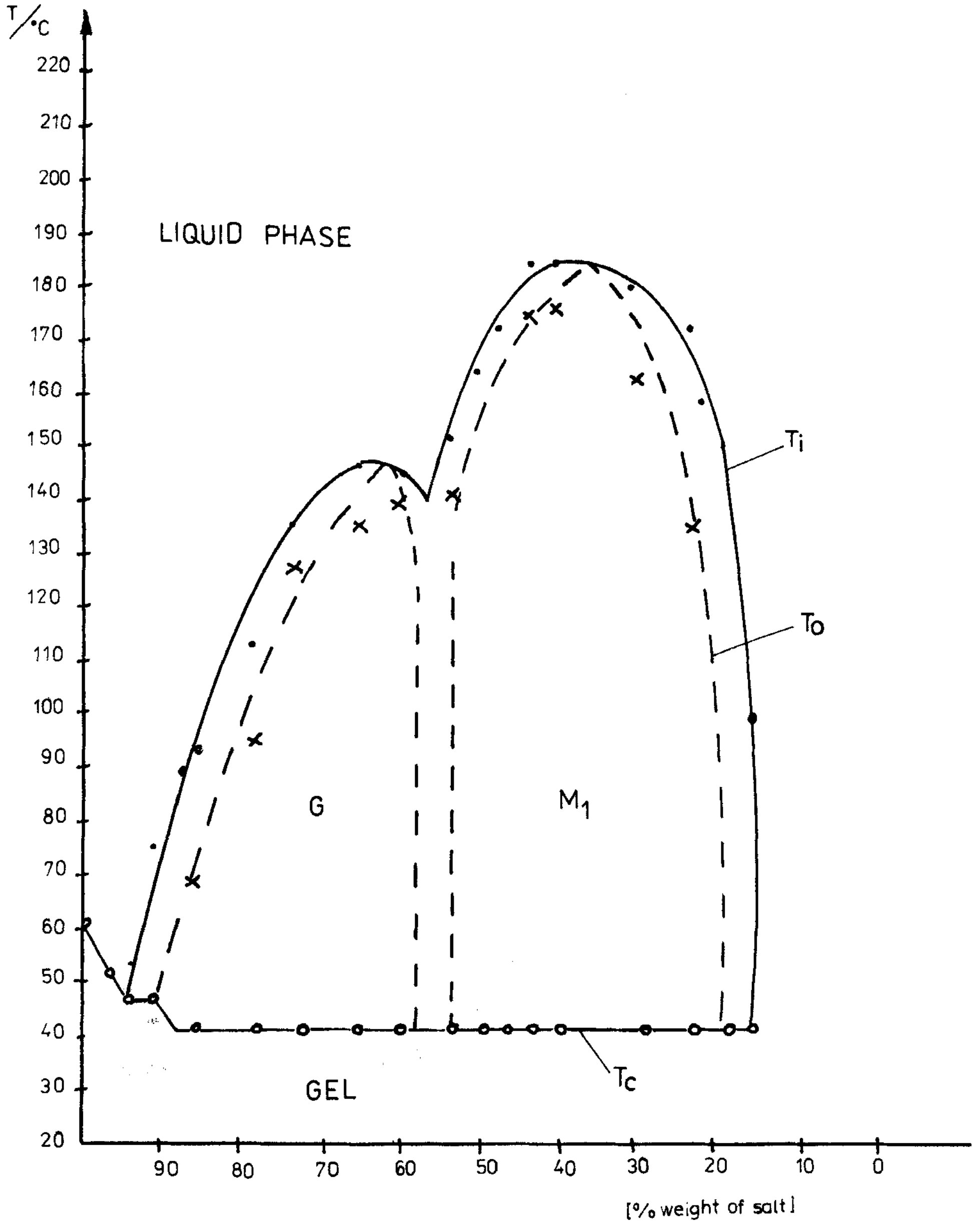

Figure 1. Phase diagram for the *n*-butylamino stearate–water system.

(2) above T_c the temperature characteristic of the phase transition from the solid phase to the liquid-crystalline phase; the range of these temperatures was from 55° to 70° C

(3) again at room temperature after cooling the sample.

Interplanar spacings, *d*, were calculated using Bragg's equation:

$$2d\sin\theta = n\lambda,$$

where $\lambda = 1{\cdot}54$ Å.

3. Results

The phase diagrams have been determined as a function of x, the percentage weight of the salt. Figure 1 shows the phase diagram for the n-butylamino stearate-water system. The remaining diagrams comprising 8 pages have been deposited with the British Library Lending Division; copies of this Supplementary Publication may be obtained from the British Library by using the procedure described at the end of this issue and quoting the number SUP 16508.

Below the T_c line (i.e. the Krafft temperatures) n-hexylamino stearate exists as a heterogeneous mixture often called a coagel; methyl, n-propyl, n-butyl and isobutylamino stearates form transparent or translucent gel phases which crystallize slowly.

The region of occurrence of lyotropic mesophases both neat and middle, occurs between the T_c and T_i lines. The region between the T_i line and the T_0 dashed line is the equilibrium region of two co-existing phases.

Analysis of changes in the melting point, T_m, of the pure compounds and the Krafft temperature, T_c, in the region independent of concentration, as a function of the amine carbon chain length and also the consideration of the system containing isobutylamino stearate leads to the relation presented graphically in figure 2. A similar variation is also shown by the maximum temperature of existence for the neat and middle phases. These values decrease with an increase in the length of the amine carbon chain for the systems studied.

The results of calorimetric studies listed in table 1 confirmed the visual observations concerning the phase transitions between the liquid-crystalline phase and the gel or coagel. The transition temperatures T_c of these were constant.

The changes of molar enthalpy, ΔH, at the phase transition to the lyotropic liquid-crystalline phase have also been calculated. The results obtained appeared to be characteristic for the type of transition given.

Interpretation of the results of X-ray studies (see table 2) in the 2θ angular range from 1° up to 30° confirmed the existence of a liquid-crystalline phase above temperature T_c (that is the T_c line). A single diffuse diffraction ring (a broad band for the diffraction method) with a maximum at $2\theta \approx 20°$ ($d = 4{\cdot}5$ Å) is present above the T_c line in the

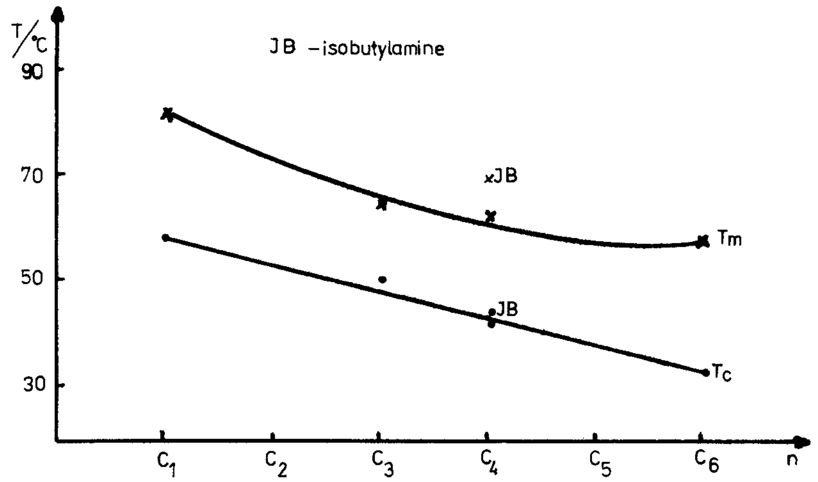

Figure 2. Change of the melting point, T_m, and the Krafft temperature, T_c, of the amino stearates studied as a function of the length of the amine carbon chain, n.

Table Table 1. Results of calorimetric measurements of binary systems of amino stearates with water.

Compound + water	wt % of the compound	Rate of heating/cooling/° min^{-1}	T_{CM}/°C	T_{CK}/°C		ΔH/kJ mol^{-1}	
				On heating	On cooling	On heating	On cooling
Methylamino stearate	70·7	4	57–58	58·7	57·7	15·9	15·7
n-Propylamino stearate	63·2	2	50–51	49·6	48·0	22·8	23·6
n-Butylamino stearate	64·2	4	41–42	42·5	41·0	11·5	11·8
Isobutylamino stearate	66·5	2	43–44	41·7	40·1	27·0	24·3
n-Hexylamino stearate	68·3		32–33				

T_{CM}, transition temperature to the lyotropic liquid-crystalline phase measured by means of microscopy; T_{CK}, transition temperature to the lyotropic liquid-crystalline phase measured by calorimetry; ΔH, molar enthalpy of transition to the lyotropic liquid-crystalline phase.

Table 2. Results of X-ray diffraction measurements for binary systems composed of amino stearates and water.

	Room temperature				$T > T_c$; 55–70°C				Room temperature after cooling the sample			
	X-ray diffraction method		Photographic method		X-ray diffraction method		Photographic method		X-ray diffraction method		Photographic method	
Compound + water	d/Å	I	d/Å	I	d/Å	I	d/Å	I	d/Å	I	d/Å	I
Methylamino stearate			17 D								17 s	
			4·8	5			4·5 D				4·8	1
			4·3	10							4·3	10
n-Propylamino stearate	4 s		4 s		4·5 D		4·5 D		4·1 s		4 s	
n-Butylamino stearate	4 s		4 s		4·5 D		4·5 D		4 s		4 s	
Isobutylamino stearate	4 s		4 s		4·5 D		4·5 D		4 s		4 s	
n-Hexylamino stearate	36·8 s	6			4·5 D				31·5 s	5		
	18·4 s	4			4				15·16 s	3		
	4·5 s	8							9·5 s	3		
	3·95 s	10							4·05 s	10		
	3·52 s	4							3·95 s	8		
									3·5 s	2		

T_c, transition temperature to lyotropic phase; d, interplanar spacings; s, sharp reflection; D, diffuse reflection; I relative intensity of streaks.

X-ray pictures of the liquid-crystalline phase, irrespective of the structure and concentration of the initial sample. All systems, except *n*-hexylamino stearate, studied at room temperature showed a narrow band characteristic of the gel phase. The *n*-hexylamino stearate–water system showed at room temperature several diffraction maxima corresponding to a polycrystalline structure observed also in visual studies, called a coagel.

4. Conclusions

The results of experimental studies presented here permit us to make the following conclusions.

(1) All the amino stearates studied form lyotropic liquid crystals in binary systems with water. The length and branching of the carbon chain of the amines have no influence on the course of the processes discussed.

(2) A neat phase occurs within the 90–50 wt % concentration range of stearates and a middle phase within the 50–20 wt % range for all the binary systems studied.

(3) Primary aliphatic amino stearates with a shorter carbon chain, i.e. C_1–C_4 both straight and branched, form with water a gel phase below the Krafft temperature (i.e. the T_c line). An increase of the amine carbon chain length causes the formation of a crystalline suspension, the so-called coagel, below this line.

(4) The melting points of pure amino stearates, the Krafft temperatures and the temperatures corresponding to the maximum existence of the neat and middle phases decrease with an increase of the amine carbon chain length. For the amine salts with a branched carbon chain (isobutylamine) the melting point and the Krafft temperature are higher than for the amine salt with a straight chain containing the same number of carbon atoms.

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