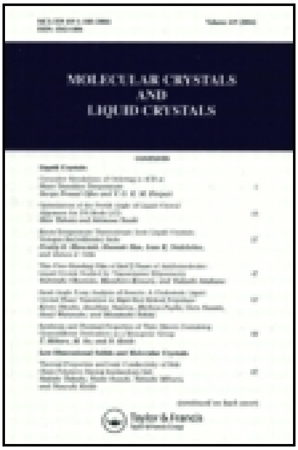

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THE LYOMESOPHASE FORMATION ZONE AND THE RHEOLOGICAL CHARACTERISTICS OF BINARY SODIUM ALKYLSULFATE AQUEOUS SYSTEMS

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Abstract A description is given of the concentration dependence of lyomesophase formation by even-numbered homologues of sodium alkylsulfate. The similarity of the data obtained by rheological investigations to those of lyotropic polymer systems is shown.

INTRODUCTION

The hydrophobic effect is one of the most important factors in the formation of supermolecular structures. With respect to micelle solutions of surface active substances, the influence of the hydrophobic fragment, anionic groupings and counter ion on critical micelle concentrations (CMC) has been studied sufficiently in detail. A definite quantitative interconnection between the hydrocarbon fragment length of the amphiphile molecule and CMC has been established.[1]

As for the dependence of the manifestation of lyotropic mesomorphism on the specific features of the structure of the hydrophobic fragment of molecules of surface active substances (SAS), this question remains insufficiently investigated.

A study of the lyotropic mesomorphism of sodium alkylsulfate was made to establish the interconnection between the length of the hydrocarbon radical of SAS and the zone of lyomesophase formation.

FINDINGS

An investigation of the lyomesomorphism of even-numbered homologues (C 10 - C 16) of sodium alkylsulfates has shown that the given substances have a number of common properties: double phase zones during transition from the micelle state and crystallohydrate to the mesophase, and the presence of hexagonal and lamellar phases. At the same time,

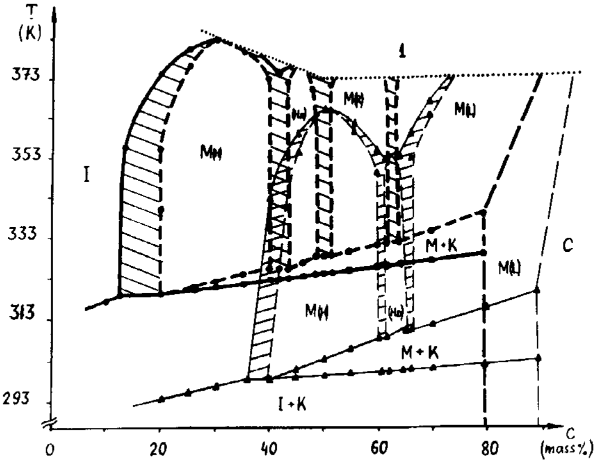

FIGURE 1 Phase diagrams of sodium alkylsulfate aqueous systems. ▲ -sodium dodecylsulfate ● -sodium hexadecylsulfate

I - isotropic solution, M - mesophase,
K - crystallohydrate, 1 - irreversible modification zone.

concrete concentrations, the temperatures of phase transitions, the number and type of intermediate phases and lyomesophase parameters are considerably dependent on the length of the alkyl chain (Fig.1).

In all the systems investigated there is a hexagonal phase, the transition to which is realised by homologue 10 at room temperature and 40 mass % of the amphiphile, and by homologues 12, 14 and 16 at increased temperatures and concentrations of 37, 25 and 20 mass % respectively. It is clear that, with the extension of the hydrocarbon zone in even-numbered homologues of sodium alkylsulfate, the concentrations of hexagonal phase formation (CHPF) shift to the area of lower concentrations and higher temperatures. Expressing CHPF in molar concentrations to the litre,

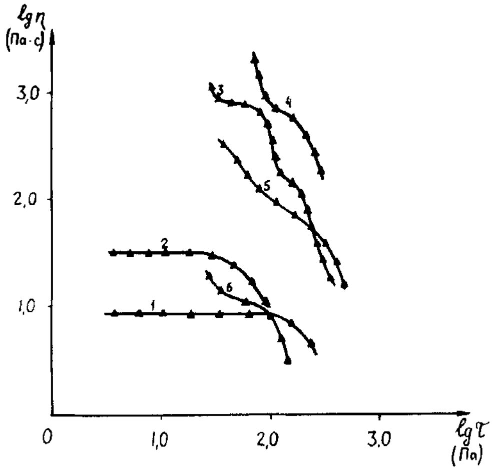

FIGURE 2 Flow curves of sodium tetradecylsulfate aqueous systems. T = 333 K.
Concentrations: 1 - 30 mass %, 2 - 40 mass %, 3 - 41 mass %, 4 - 42 mass %, 5 - 43 mass %, 6 - 45 mass %.

it may be calculated that with the shortening of the hydrocarbon chain by two ethyl groups, the importance of CHPF approximately doubles. Comparing these data with information available on concentrations of the mesophase transition of other amphiphiles, we established that the conformity we found is of a sufficiently general character. In any case, the homologues of sodium and potassium carboxilates studied previously also have the same conformity.

An X-ray analysis of the structural parameters of the hexagonal mesophase network (a) and the radii of micelle aggregates shows that the greater the values of "a", the lesser the value of CHPF. The computation of these data testifies that the type of micelle aggregate formation in hexagonal phases with increased concentrations also depends on the length of the hydrocarbon fragment in the molecule: with

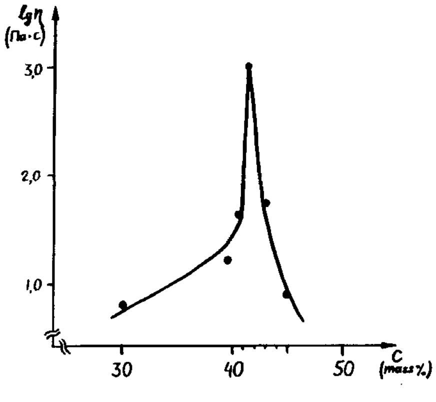

FIGURE 3 Concentration viscosity dependence of sodium tetradecylsulfate aqueous systems. Lgτ const=2,0 T const=333 K.

homologues 10 and 12 there is an increase in the micelle aggregate radii, while with homologues 14 and 16 there is a complex mechanism presupposing an increase in the radius in combination with a lengthening of the micelles.[2]

As seen from the findings of rheological investigations (Fig.2), the form of the flow curves in different temperature and concentration regions is close to that observed in high molecular lyomesophases.[3] An anomalous increase of shifting viscosity on the bounds of the phase transition is observed. Figure 3 shows the displacement of the rheologically determinable region of the mesophase in the direction of higher concentrations than those found in observations of the same system with a statical polarization microscope. A similar shift is also found in a number of cases in polymer lyomesophases. This similarity in the behaviour of systems may be explained by the fact that the dominating role of cooperative effects characteristic of lyotropic polymer is also typical of the lyomesophases of lyotropic SAS (surface active substances).

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