

CHARACTERIZATION OF LYOTROPIC LIQUID CRYSTALLINE PHASES BY  
TRANSMISSION-, AND SCANNING ELECTRON MICROSCOPY <sup>1</sup>

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**This paper is dedicated to Professor A. Bonefačić on the occasion  
of his 70<sup>th</sup> birthday**

The morphology of freshly prepared as well as of aged cadmium dodecylbenzene-sulphonate precipitates showed significant differences between the crystalline and liquid crystalline samples, as shown by transmission-, and scanning electron microscopy at room temperature. Since water evaporated from the samples during the investigation, the remaining material from the liquid crystalline phase gave data on the shape and size of the aggregates. It was shown that electron microscopy at room temperature gives useful information on the lyotropic liquid crystalline phases, presuming the physical parameters were compared with some other techniques, such as X-ray diffraction and light microscopy using crossed polarizers.

## 1. Introduction

Precipitation interactions between heavy metal ions and surfactants in aqueous solutions find their importance in many aspects of application, e.g., in environmental protec-

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tion of natural waters. The dynamics and the formation of crystalline solid, as well as of liquid crystalline phases, from the homogeneous solutions due to the reaction between dodecylbenzenesulphonic acid (HDBS) (that has been used in the industrial and in household detergents) and metal ions were investigated earlier [1-3]. It was shown that kinetics of both phases, crystalline and liquid crystalline, is different; indeed, it depends on the concentration relationship between the reacting components [4].

It is known that the surfactant molecules form amphiphilic aggregates, whose structures depend on surfactant concentration in the solution. The structures built by amphiphilic molecules in the presence of water are different from classical molecular crystals. The micelles of various shapes, liquid crystals, sponge phases, bicontinuous phases, vesicles, microemulsions, and crystalline solids were found in the binary surfactant/water systems, and in many-component systems [5-7]. Although Fournier [8] described recently the way in which focal conic units of lamellar phases assemble to give larger structures, these structures have already been understood by Sir W. Bragg [9]. Although the focal conic arrangements have been studied in smectic phases [8,9], the same structures can be applied to lamellar phases, while such textures have been found also in the viscous samples of lamellar phases separated from supernatant solutions.

In this work, the shape and size of both phases, crystalline and liquid crystalline, were investigated using transmission- (TEM) and scanning electron microscopy (SEM); in addition, the structural properties of phases were represented by X-ray diffraction patterns, and by textures from light microscope (LM) equipped with crossed polarizers. The results concerning liquid crystalline structure confirmed the recent investigation using light scattering technique [10]. The goals of the investigation represented here were to prove the possibility of EM identification of lyotropic liquid crystalline phases at room temperature, as well as to show the difference between liquid crystals and crystalline solid by using the EM techniques; in addition, we intended to emphasise the conformity of determination of the structures represented by EM observation with the results achieved with other techniques.

## 2. Experimental

The samples for TEM, Zeiss EM 10 A, and for SEM, Cambridge Stereoscan 600, were prepared by mixing solutions of cadmium nitrate and HDBS. All measurements were performed at room temperature.

Required concentrations for the formation of liquid crystals from solution were:  $[\text{Cd}(\text{NO}_3)_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{HDBS}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ , while those for the nucleation of crystals were equimolar, i.e., both reacting components amounted to  $[\text{Cd}(\text{NO}_3)_2] = [\text{HDBS}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ . The X-ray diffraction patterns of the heterogeneous systems were obtained using a standard Siemens X-ray diffractometer with a counter and Si-crystal monochromatized  $\text{CuK}\alpha$  radiation.

Identification of liquid crystalline phases and crystalline solids were performed on a Leitz Wetzlar light microscope (LM) with polarizing equipment. Samples were prepared by putting the colloidal suspension from a test tube between the objective and cover glass.

### 3. Results and discussion

The different appearance of crystalline and liquid crystalline phases is shown in SEM micrographs in Figs. 1a-b and 2a-b, respectively.

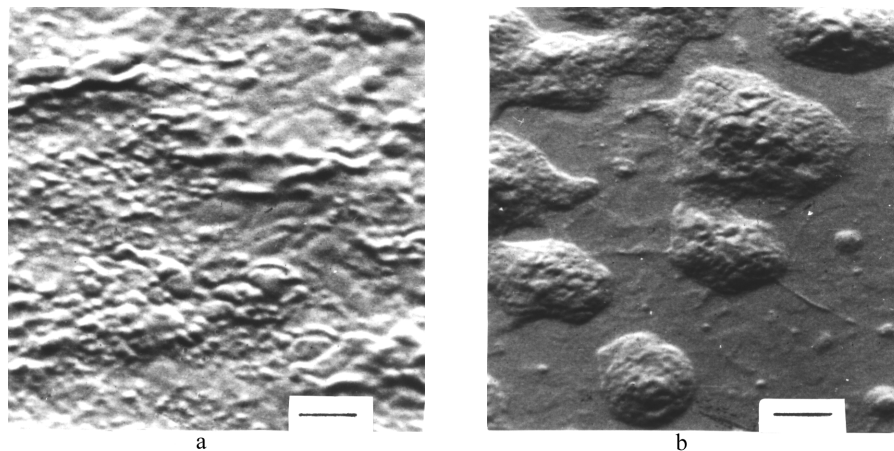


Fig. 1. SEM photomicrographs presenting the crystalline solid of  $\text{Cd}(\text{DBS})_2$ : a) one day after preparation of the sample, bar = 6  $\mu\text{m}$ ; b) sample aged two months. Bar = 9  $\mu\text{m}$ .

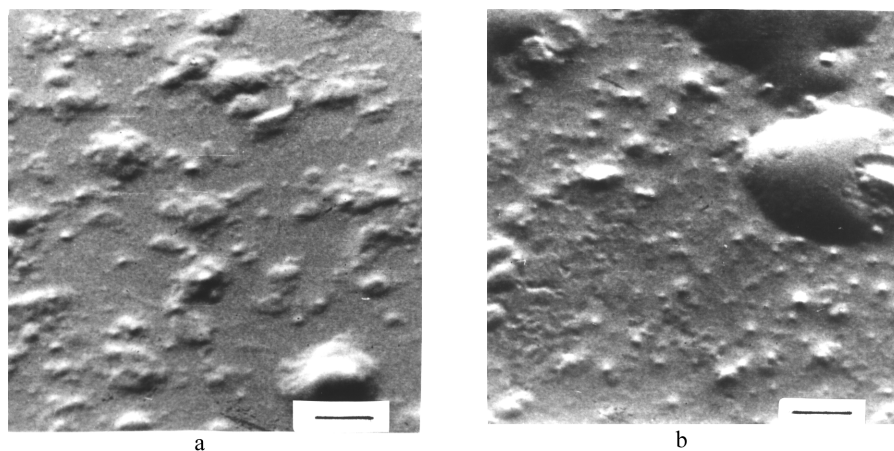


Fig. 2. SEM photomicrographs of the liquid crystalline phase of Cd-dodecylbenzenesulphonate: a) one day after preparation of the sample, Bar = 4  $\mu\text{m}$ ; b) sample aged two months. Bar = 6  $\mu\text{m}$ .

The samples were observed one day and two months after preparation. At the concentrations of HDBS and cadmium nitrate required for the formation of the crystalline phase, a great number of crystal nuclei from the solution form much faster than the liquid crystalline phase. After several months, all crystalline solid represented in Fig. 1b agglomerated into a compact phase of large clusters.

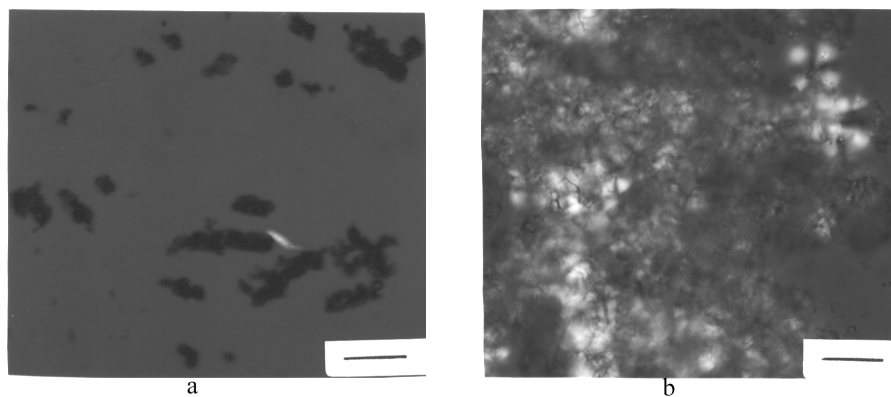


Fig. 3. Photomicrographs from polarization LM: a) crystals (dark), b) liquid crystals (exhibiting optical birefringence), one day after preparation of the Cd-dodecylbenzenesulphonate samples; crossed polarizers and  $\lambda$  plate. Bar = 140  $\mu\text{m}$ .

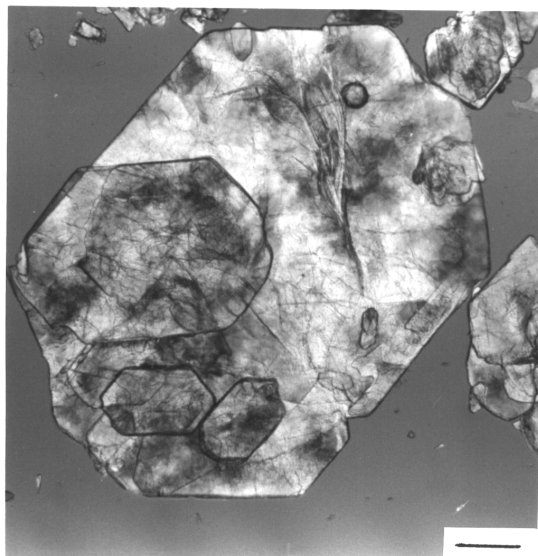


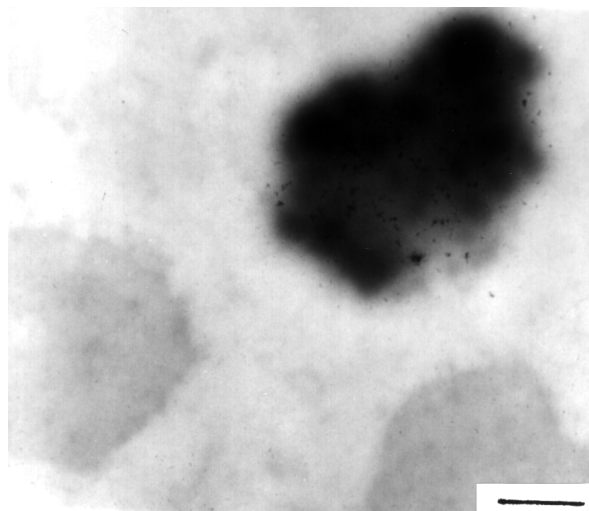
Fig. 4. Photomicrograph from polarization LM of NaDBS crystals showing birefringence under crossed polarizers and  $\lambda$  plate. Bar = 50  $\mu\text{m}$ .

An equilibrium regarding the size and the shape of the globular liquid crystalline particles is reached after one day, and the system does not change much within a period from one day until several months (Fig. 2a-b). The size of the liquid crystalline globular particles amounted to  $(472 \pm 84)$  nm after one day, and  $(661 \pm 160)$  nm two months after the preparation of the system. The particle sizes were estimated from 30 determinations. The

measured sizes of both, the aggregated and the "free" particles in a solution, are in good agreement with those measured earlier by dynamic light scattering [10].

The formation of lamellar phases, as followed by LM, is always exhibited by optical birefringence, as it is shown in Fig. 3b. This effect is not always observed for solid crystalline phase. In Fig. 3a, an example of a "dark" crystalline phase with no optical birefringence is represented. On the contrary, a well-ordered surfactant crystalline phase of other dodecylbenzenesulphonates can exhibit optical birefringence as it is shown in Fig. 4. The crystals show a hexagonal shape.

Corresponding TEM micrographs shown in Fig. 5 are less indicative, but the hexagonal contours of the crystallized sample are also shown.



*Fig. 5. TEM photomicrograph of the Cd(DBS)<sub>2</sub> crystals one day after the sample preparation. Bar = 0.7 μm.*

The liquid crystalline samples of other alkylbenzenesulphonate surfactants in electrolytic solutions also show birefringent textures as observed by using LM equipped with the crossed polarizers. Indeed, the characteristic textures, all of them belonging to the lamellar arrangement, can be seen in Figs. 6a-b. In Fig. 6a, the lamellar droplets in the solution (at the top), the fan shaped texture as formed of the chains of droplets (at the left side) and focal conics similar to the arrangement of a set of focal cones within a polygon obtained by crossed polarizers already by Sir W. Bragg [9] (in the middle), are represented for the Al-dodecylbenzenesulphonate sample. Much better example of the "polygon" focal conic arrangement is shown in Fig. 6b for the Ni-dodecylbenzenesulphonate sample.

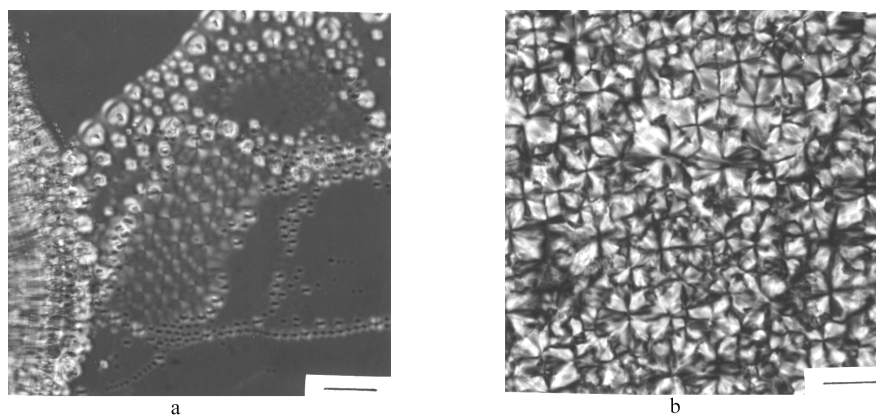
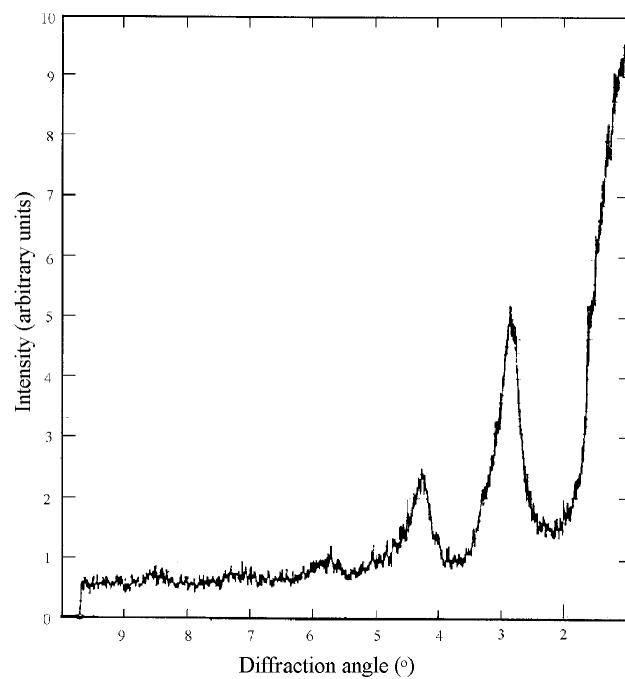


Fig. 6. Photomicrographs of the lamellar phases of the electrolyte/dodecylbenzenesulphonate systems from LM: a) aluminium, crossed polarizers and  $\lambda$  plate; b) nickel, crossed polarizers without  $\lambda$  plate. Bar = 50  $\mu\text{m}$ . Fig. 7. X-ray diffraction pattern of Cd-



dodecylbenzenesulphonate liquid crystalline phase. Y-axis: intensity in arbitrary units, X-axis: diffraction angle in degrees.

The arrangement of self-associating surfactant molecules was tested by determination of the X-ray diffraction patterns. The X-ray diffraction patterns contain several orders of sharp maxima at low angles which confirm that the liquid crystalline phase is lamellar, as it is seen in Fig. 7. In addition, it can be seen in Fig. 8 that crystalline solid showed also a lamellar arrangement.

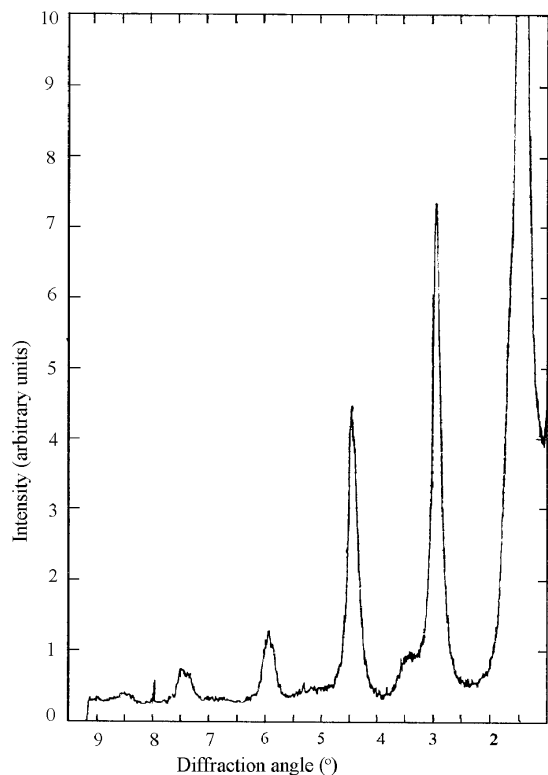


Fig. 8. X-ray diffraction pattern of Cd(DBS)<sub>2</sub> crystals. Y-axis: intensity in arbitrary units, X-axis: diffraction angle in degrees.

The interplanar distance for lamellar phase of Cd-dodecylbenzenesulphonate is found to be  $(3.14 \pm 0.06)$  nm, and for crystalline solid it is  $(3.07 \pm 0.06)$  nm. For comparison, the calculated length of the linear C<sub>12</sub>-isomer is 2.65 nm. It is quite understandable that the interplanar distance of a crystalline phase shows better agreement with the calculated value than the liquid crystalline phase does, since there is no hydration layer on the crystal surface, and only the constitutive water occurred to be within the surfactant bilayers.

The morphology of phases, as investigated using EM, has been improved with diffraction data and with the data obtained by polarization LM. For the future, it is planned to investigate the micro-morphology of phases by using EM selected area electron diffraction.

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## References

- 1) Težak, F. Strajnar, D. Šarčević, O. Milat and M. Stubičar, *Croat. Chem. Acta* **57** (1984) 93;
- 2) Težak, F. Strajnar, O. Milat and M. Stubičar, *Progr. Colloid and Polymer Sci.* **69** (1984) 100;
- 3) Težak, and S. Popović, *Croat. Chem Acta* **62** (1989) 861;
- 4) Težak, M. Martinis, S. Punčec, I. Fischer-Palković and F. Strajnar, *Liquid Crystals* **19** (1995) 159;
- 5) H. Hoffmann, C. Thunig, U. Munkert, H. W. Meyer and W. Richter, *Langmuir* **8** (1992) 2629;
- 6) J. Charvolin, *Progr. Colloid and Polimer Sci.* **81** (1990) 6;
- 7) K. A. Dawson, *Pure Appl. Chem.* **64** (1992) 1589;
- 8) J. B. Fournier and G. Durand, *J. Phys. II (France)* **1** (1991) 845;
- 9) W. Bragg, *Nature* **133** (1934) 445;
- 10) Težak, S. Punčec and M. Martinis, *Liquid Crystals* (in press).

#### KARAKTERIZACIJA LIOTROPNIH TEKUĆIH KRISTALA UPOTREBOM TRANSMISIJSKE I "SCANNING" ELEKTRONSKE MIKROSKOPIJE

Pri promatranju pomoću transmisijske i "scanning" elektronske mikroskopije, morfologija liotropnih tekućih kristala kadmium dodecilbenzensulfonata, kako svježe pripremljenog, tako i starenog uzorka, pokazuje značajne razlike u usporedbi s morfologijom kristalne faze. Budući da istraživanje uzrokuje isparavanje vode iz uzorka, obrisi zaostalog čvrstog materijala faze tekućih kristala mogu indicirati oblik i veličinu čestica. Pokazano je da elektronska mikroskopija pri sobnoj temperaturi može dati korisne informacije za istraživanje liotropnih tekućih kristala, ako se fizikalni parametri mogu potvrditi i drugim tehnikama, što je načinjeno istraživanjem difrakcije X-zračenja i svjetlosnom mikroskopijom uz ukrižene polari- zatore.