

CCA-1424

YU ISSN 0011-1643

UDC 541.123

Original Scientific Paper

Solid/Liquid Equilibria in Aqueous Systems of Dodecyl Benzene Sulphonate and Alkaline Earth Ions

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Received February 2, 1983

Solubility/precipitability boundaries and the morphology of solid phases were investigated and equilibria constants calculated for Mg, Ca, Sr, Ba — dodecyl benzene sulphonate salts. The experimental methods of tyndallometry, polarizing microscopy and X-ray diffraction gave consistent results. The measurements were performed at 293 K.

The solubility of $M(\text{DBS})_2$ salts decreased in the order $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$; pK^0_{sp} were calculated to be: (10.80 ± 0.07) for $\text{Mg}(\text{DBS})_2$, (10.48 ± 0.07) for $\text{Mg}(\text{DBS})_2$ (for DBS dimer), (11.23 ± 0.03) for $\text{Ca}(\text{DBS})_2$, (12.00 ± 0.08) for $\text{Sr}(\text{DBS})_2$, (12.4 ± 0.2) for $\text{Ba}(\text{DBS})_2$.

It is demonstrated that at least two precipitated phases can be obtained: a partially ordered phase, probably belonging to the smectic A liquid crystal, while the other phase appears to be a solid crystal.

INTRODUCTION

Precipitation features of detergents in aqueous solutions of electrolytes are interesting for colloid chemistry from a theoretical point of view, as well as for practical purposes. Dodecyl benzene sulphonates (DBS) have appeared recently as a component of household detergents, and therefore they are supposed to be present in waste water. This is already one excellent reason to attempt to learn more about them. However, in certain conditions DBS exhibits liquid crystalline properties,¹ and intermediate states and phase transitions between solids and liquids have now become of great interest for many reasons.^{2,3} It is also important to note that the liquid crystalline state is ubiquitous in investigations of ordered — disordered transitions and biological membrane structure.^{4,5} Although numerous substances exhibiting liquid crystalline behaviour were discovered

almost a hundred years ago, interest in them has grown recently.^{6,7} Optical and X-ray studies have been published on the mesomorphic behaviour of lyotropic liquid crystals.¹ A first attempt at a comparison between aqueous and nonaqueous lyotropic liquid crystals⁸ has been made and investigations of lamellar liquid crystal structure in mixed solvents⁹ have been performed.

A recent paper¹⁰ reported the isothermal ternary phase diagrams of sodium and calcium-surfactant systems determined by ²H NMR spectroscopy. Several review articles have been published on recent developments in the field of liquid crystals.^{1,2,3}

Not much work has been done yet on lyotropic liquid crystal phases. Many more investigations have been published on thermotropics than on lyotropics, but no data can be found in the literature on the formation of lyotropics in aqueous electrolyte solutions.

The aim of this work was to follow the precipitation phenomena of HDBS — M(NO₃)₂ aqueous solutions, to determine the solubility of the DBS⁻ — cation of alkaline earth salts, and to identify the structure and morphology of precipitates. It was convenient to follow the coacervation processes by optical and X-ray methods.

EXPERIMENTAL

Materials. All chemicals of p.a. grade were used as commercially distributed: Mg-, Ca-, Ba(NO₃)₂ (Kemika, Zagreb) and Sr(NO₃)₂ (Merck, Darmstadt); Mg(NO₃)₂ and Ca(NO₃)₂ were standardized by complexometric titrations with EDTA and Eryochrome Black T as indicator (A. Vogel, A Textbook of Quantitative Inorganic Analysis, Longman, London, Ed. III, 1961, pp. 434 and 436).

Dodecyl benzene sulphonate (DBS) is a commercially used detergent supplied by »Prva Iskra«, Barić, Beograd. It is a mixture of dodecyl benzene sulphonic acid 97–98%, sulphuric acid 1% and a nonsulphonized part 1.5–2%. The molar concentration of HDBS was calculated as a nominal value of a molecular mass of 326.5. The homogeneous solution was prepared by dissolving the commercial detergent in double distilled water.

The aggregation processes in HDBS aqueous solutions show the formation of dimers at 1.36×10^{-4} , of premicelles at 2.4×10^{-4} , and micelles at 1.7×10^{-3} mol dm⁻³ HDBS (Figure 1).

Methods. Precipitation systems were prepared by the method of mixing the reacting components described earlier.¹⁴

The samples for the light microscope were prepared by putting a drop between slide and cover under crossed polarizers.

The samples for X-ray diffraction examinations were prepared by depositing a film of aqueous sediment (about 1 mm thick) on a flat surface which served as the sample holder.

All experiments were performed at 293 K.

Techniques. Turbidity changes after mixing the reacting components were followed on Zeiss tyndallometer connected to a Pulfrich photometer. Critical dimerization concentration (c.d.c.) was determined using a Pye Unicam spectrophotometer UV SP 1800. Critical premicellization (c.p.c.) and critical micellization concentration (c.m.c.) were determined by using the light scattering method on a Virtis Brice Phoenix universal light scattering photometer, model DU 2000, and by the surface tension method. The results for c.m.c. were in accordance with the results of Lundlum.¹⁵

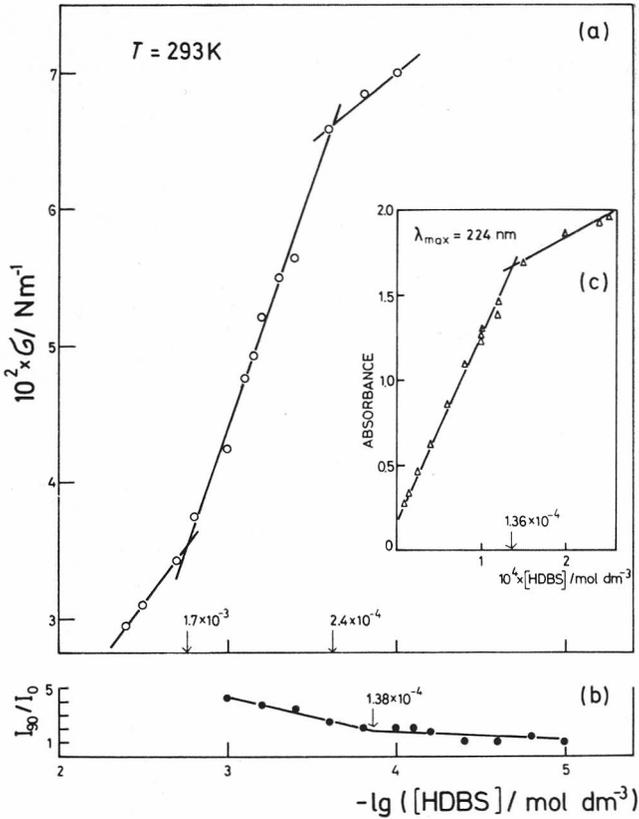


Figure 1. (a) Surface tension, (b) light scattering intensity, (c) absorbance, as a function of HDBS concentration. The arrows denote critical dimenzation, premicellization and micellization concentrations. It can be seen that the critical values measured by different instrumental methods are in good agreement

Optical micrographs were obtained by using a Leitz Wetzlar light microscope with polarizing equipment. The structural characterization of phases present at various concentrations of HDBS and $\text{Mg}(\text{NO}_3)_2$ in aqueous solution was performed using a standard Siemens X-ray diffractometer with counter and Si-crystal monochromatized Cu $K\alpha$ radiation.

The Composition of Aqueous Solutions. The interpretation of results presented in precipitation diagrams (PD) is based on the graphical method described by Kratochvil et al.¹⁶ For simple ionic solubility occurring only in the linear range of the solubility/precipitability boundary, the equilibrium can be described by the relation:



and by the solubility product:

$$K_{\text{sp}}^0 = a(\text{M}^{+2}) \cdot a^2(\text{DBS}^{-})$$

At low ionic strength the influence of activity coefficients can be neglected, and so far K_{sp}^0 calculated by using total concentrations of reacting components.^{17,18}

The equilibrium constants for associates — aquacomplexes indicated by segments in the PD parallel with abscissae,¹⁹ are assumed according to the following equilibrium:



with the equilibrium constant of the association process:

$$K_{\text{ass}}^0 = \frac{[\text{Mg}_N(\text{DBS})_{2N}]^0(\text{aq})}{[\text{Mg}^{+2}] \cdot [\text{DBS}^-]^2}$$

The approximation is made that at limiting conditions the total concentration of $\text{Mg}_N(\text{DBS})_{2N}$ is equal to the total concentration of HDBS because practically all HDBS is in the form of associates due to a high excess of $[\text{M}^{+2}]$. Therefore, if it is assumed that $N = 1$, the equilibrium constants of association can be calculated by using the equation:

$$K_{\text{ass}}^0 = \frac{[\text{HDBS}]}{K_{\text{sp}}^0}$$

The stability constants of the complex species in these systems can be conditionally calculated, but we consider it better not to apply these calculations, because the aggregation processes take place in a concentration region where complex ion equilibria can be assumed. It is the region above the c.m.c. where it is not possible to make a statement about mono- or polynuclear complexes.

RESULTS AND DISCUSSION

The general precipitation characteristics of HDBS — $\text{M}(\text{NO}_3)_2$ systems are presented in Figure 2. Tyndallometric curves taken 600, and 3600 seconds and 1 day after mixing the reacting components show regions: (I) complex solubility in high concentrations of HDBS, (II) precipitation, and (III) clear solution in a low concentration of HDBS. The arrows denote the so called »first clear« system used for construction of the PD and for further interpretation of equilibrium constants. In region (II) there is shown the appearance of two different kinds of sediment. The concentration between 4×10^{-5} and 10^{-3} mol dm^{-3} of HDBS is characterized by the formation of white a crystalline precipitate. The coacervation process takes place from 10^{-3} to 2×10^{-2} mol dm^{-3} of HDBS and exhibits a three phase oily substance, consisting of a water phase (as solvent), oil phase (concentrations of HDBS higher than c.m.c), and a liquid crystalline phase of $\text{Mg}(\text{DBS})_2$. The stoichiometry of species in the water phase at the solubility/precipitability limiting conditions (i.e. the number of ligands and the equilibrium constants) is calculated from the PD presented in Figure 3. The precipitation diagram was constructed from the set of tyndallometric measurements obtained with a constant concentration of one reacting component and a varying concentration of the other component.

It is obvious in Figure 3 that there are several characteristic concentration regions:

(A) region of very low turbid systems with the limiting condition for the formation of ionic associates — aquacomplexes of the assumed composition: $[\text{Mg}_N(\text{DBS})_{2N}]_{\text{aq}}^0$ with the precipitation/solubility boundary at 3×10^{-5} mol dm^{-3} of HDBS; K_{ass}^0 was calculated and is listed in Table I.

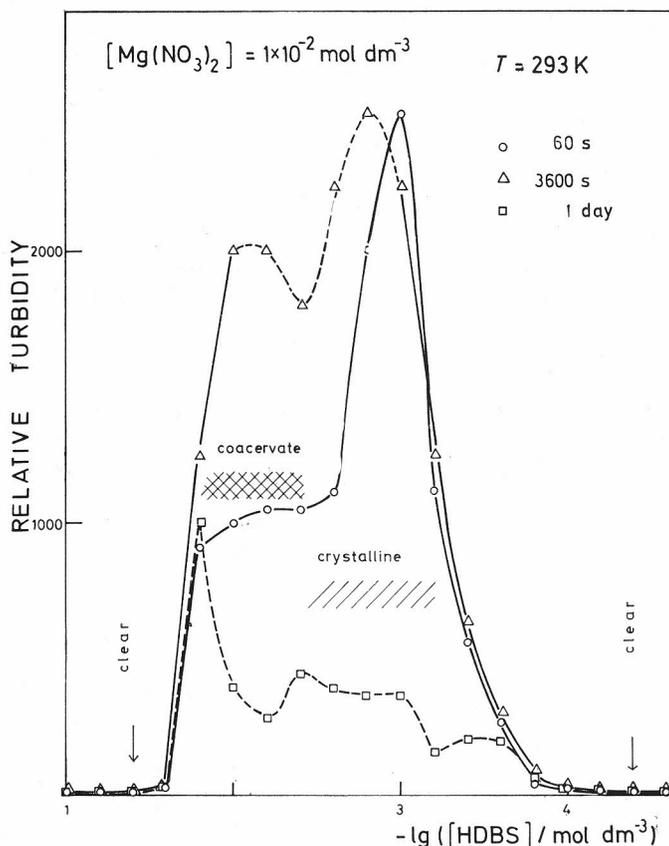


Figure 2. Variation of tyndallometric values with HDBS concentration at constant $\text{Mg}(\text{NO}_3)_2$ concentration showing maximum in light scattering, where the two kinds of sediment appear: coacervate and crystalline; the «first clear» systems corresponding to the turbidity of water are denoted by arrows

(B) region of coacervation showing three phases: water — liquid crystal. There is HDBS in excess and the c.m.c. is exceeded, while the concentration of $\text{Mg}(\text{NO}_3)_2$ is too small for the formation of such numerous crystal nuclei as in region (C); as a result there is a relatively large excess of DBS^- spreading as an oil phase at the water/crystal interface, and therefore ordering of $\text{Mg}(\text{DBS})_2$ crystals occurs as in a liquid crystalline phase. System I in the PD was chosen for X-ray diffraction measurements.

(C) is the region where the relationship between reacting ions is such that the fast formation of a great number of crystal nuclei is possible and a white crystalline precipitate is formed. Point II in the PD was used as the chosen system for X-ray diffraction investigation.

(D) region represent a very weak turbid system with limiting equilibria of the solubility products of $\text{Mg}(\text{DBS})_2$ ($\text{Mg}^{+2} + \text{DBS}^-$ monomer) and of

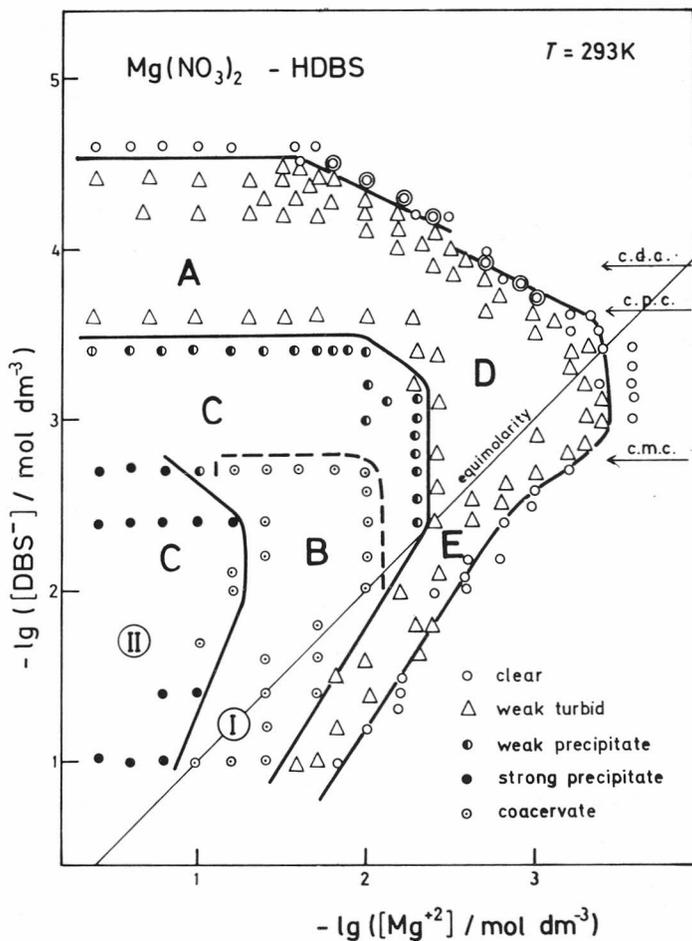
Figure 3. Precipitation diagram of $\text{Mg}(\text{NO}_3)_2$ — HDBS

TABLE I

Summary of Solubility/Precipitability Boundaries for DBS-alkaline Earth Ion Systems at 293 K

Cation	pK_{sp}^0	slope	coefficient of correlation	$\lg K_{ass}^0$	c.c.
Mg^{+2} (I)	(10.80 ± 0.07)	-0.457	-0.979	6.28	4×10^{-4}
Mg^{+2} (II)	(10.48 ± 0.07)	-0.559	-0.980		
Ca^{+2}	(11.23 ± 0.03)	-0.498	-0.999	6.71	4×10^{-5}
Sr^{+2}	(12.00 ± 0.08)	-0.489	-0.997	7.30	8×10^{-6}
Ba^{+2}	(12.4 ± 0.2)	-0.512	-0.982	7.48	2.5×10^{-6}

c.c. = critical concentration = $[\text{Mg}^{+2}]$ in mol dm^{-3} at which the boundary changes slope.

$\text{Mg}(\text{DBS})_2$ ($\text{Mg}^{+2} + (\text{DBS}^-)_2$ dimer). K_{sp}^0 values for Mg — DBS monomer or dimer, are listed in Table I. Their values are very close to each other. (E) region is characterized by the solubility/precipitation limit of complex ion formation. According to Kratochvil's method we can assume mono or polynuclear complexes $[\text{Mg}(\text{DBS})]_n$ where n can be $n = 1, 2, 3, \dots, n$. As DBS concentrations are above the c.m.c., we found that it would be very unreliable to count with definite type of species.

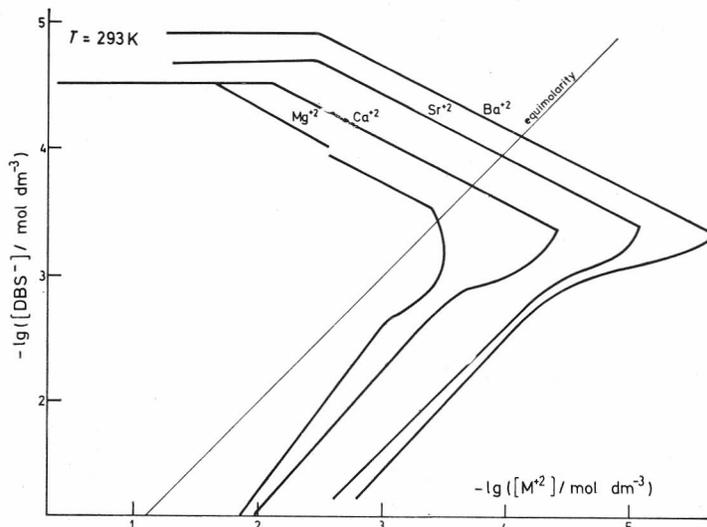


Figure 4. Countours of precipitation diagrams of $\text{M}(\text{NO}_3)_2$ — HDBS

Figure 4 presents the solubility/precipitability limits for Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} — DBS^- . The precipitation diagrams are very similar, and the solubilities decrease in the order: $\text{Ba} < \text{Sr} < \text{Ca} < \text{Mg}$. Generally in an excess of $\text{M}(\text{NO}_3)_2$ the formation of associates is the predominant process. The solubility product can be calculated in the equivalency region. In the presence of excess DBS^- , complex solubility is the predominant process above the c.m.c. The premicellization and the micellization concentrations strictly determine the conditions where two different processes play the predominant role: the formation of simple ions, the transition region between the c.p.c. and c.m.c., and the formation of complex ions above the c.m.c.

The precipitation diagrams for HDBS — alkaline earth nitrates are very similar to those obtained using sodium dodecyl sulphate as the

anionic component,¹⁷ and to those obtained with other alkylbenzene sulphonates.¹⁸

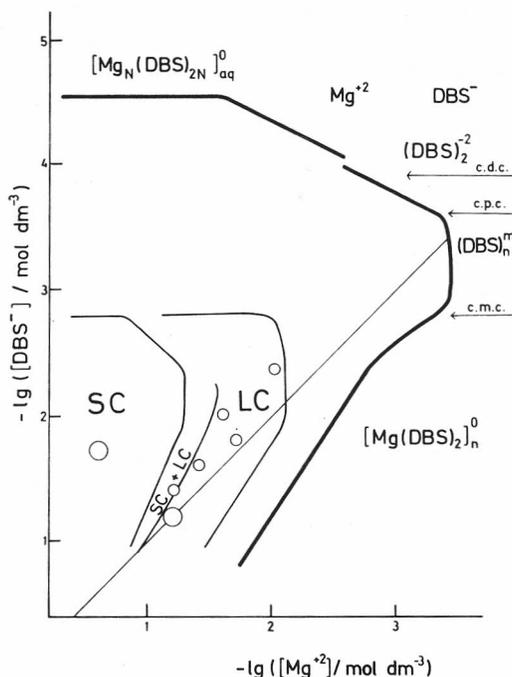


Figure 5. Solubility/precipitability boundary in the system $\text{Mg}(\text{NO}_3)_2$ — HDBS and the countours of precipitation regions of solid (SC), liquid (LC) crystalline phases and the transition region exhibiting mixed SC and LC phases. Smaller open circles denote samples chosen for investigation of optical textures, the larger open circles samples chosen for both optical textures and X-ray diffraction. The appearance of supposed predominant ionic species in solution are denoted

Microscopic studies. The morphology of solid phases in the system Mg^{+2} — DBS^- was investigated by microscopic studies using crossed polarizers, which exhibited the exciting properties of liquid crystals. It is obvious that the optical textures of the displayed ordered phases in the fluid state correspond to the stoichiometric relations in the PD. Thus we attempted to investigate the liquid crystalline state by using the X-ray diffraction method. The agreement with the results from optical microscopy was very good. Several systems were chosen from region B in the PD (denoted by open circles in Figure 5) for examination under polarized light in the optical microscope. There are three characteristic regions exhibited on the PD in solid/liquid equilibria: solid crystal formation (SC), transition region with solid and liquid crystal formation (SC + LC), and the coacervation region characterized by liquid crystal formation (LC), presented in Figure 5, as well as all ionic species that can be assumed to be present in bulk solution, depending on reacting ion concentrations. Crystallization characteristics of these three regions are well shown in micrographs in Figure 6.

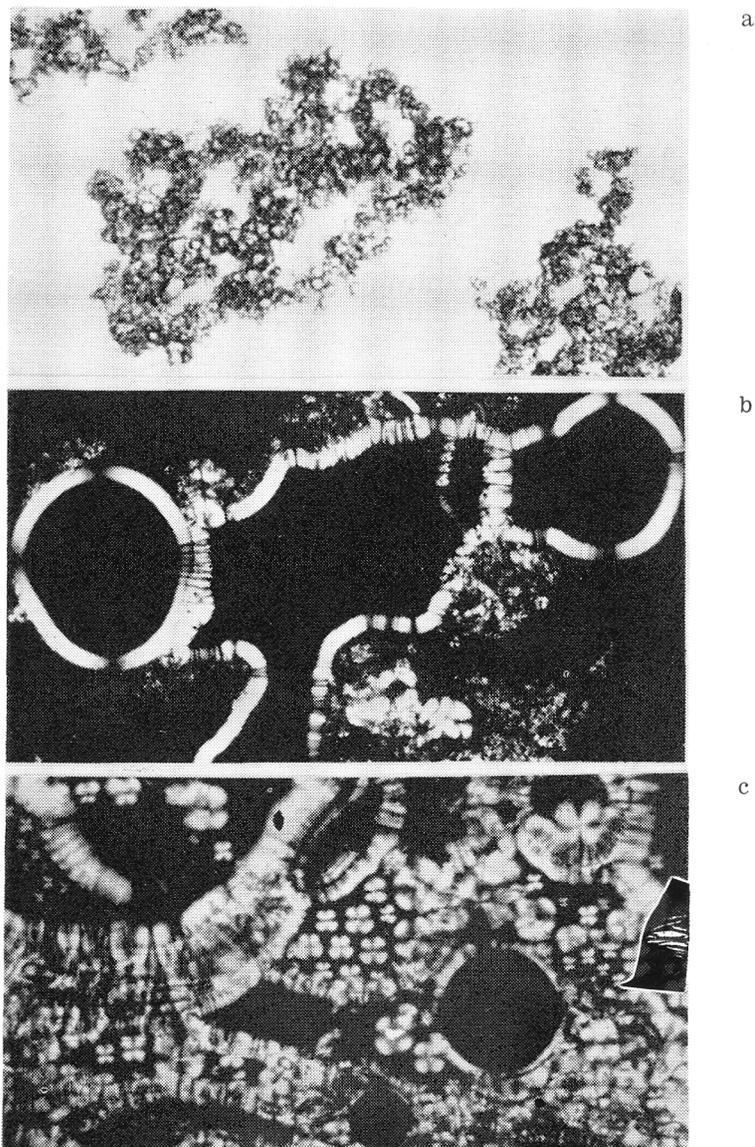


Figure 6. Micrographs of sediment from the different regions of Figure 5: (a) SC ($[\text{Mg}(\text{NO}_3)_2] = 2.5 \times 10^{-1}$, $[\text{HDBS}] = 2 \times 10^{-2}$) in nonpolarized light, and in polarized light (b) SC+LC ($[\text{Mg}(\text{NO}_3)_2] = 1.0 \times 10^{-1}$, $[\text{HDBS}] = 6.0 \times 10^{-2}$), and (c) LC ($[\text{Mg}(\text{NO}_3)_2] = 1.0 \times 10^{-2}$, $[\text{HDBS}] = 4.0 \times 10^{-3}$). Total magnification 205 x. All concns. in mol dm^{-3}

Figure 7 and 8 present the variety of structures which contain various formations: droplets, single chains or compositions of closely arranged chains, all of them showing the effect of optical birefringency. In figure 7 (c), taken in polarized light, several single and double chains can

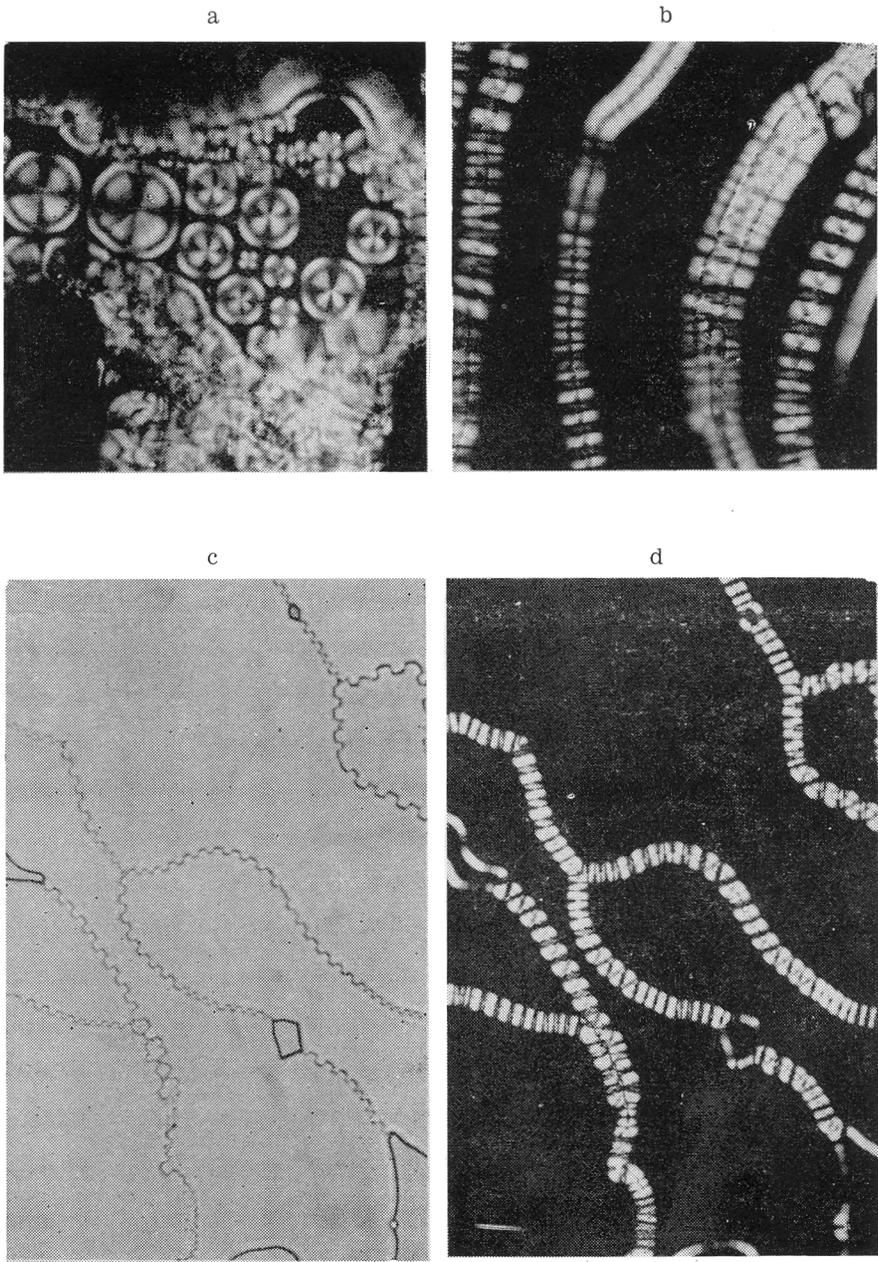


Figure 7. Micrographs of coacervates: (a) birefringent droplets ($[\text{Mg}(\text{NO}_3)_2] = 2.0 \times 10^{-2}$, $[\text{HDBS}] = 1.5 \times 10^{-2}$), polarized light, total magnification 180 x; (b) chains ($[\text{Mg}(\text{NO}_3)_2] = 2.0 \times 10^{-2}$, $[\text{HDBS}] = 1.5 \times 10^{-2}$), polarized light, total magnification 384 x; (c) and (d) chains of ordered droplets and spreading layers of HDBS between them in polarized and nonpolarized light, respectively ($[\text{Mg}(\text{NO}_3)_2] = 2.0 \times 10^{-2}$, $[\text{HDBS}] = 1.5 \times 10^{-2}$). Total magnification in (c) and (d) 154 x. All concens. in mol dm^{-3}

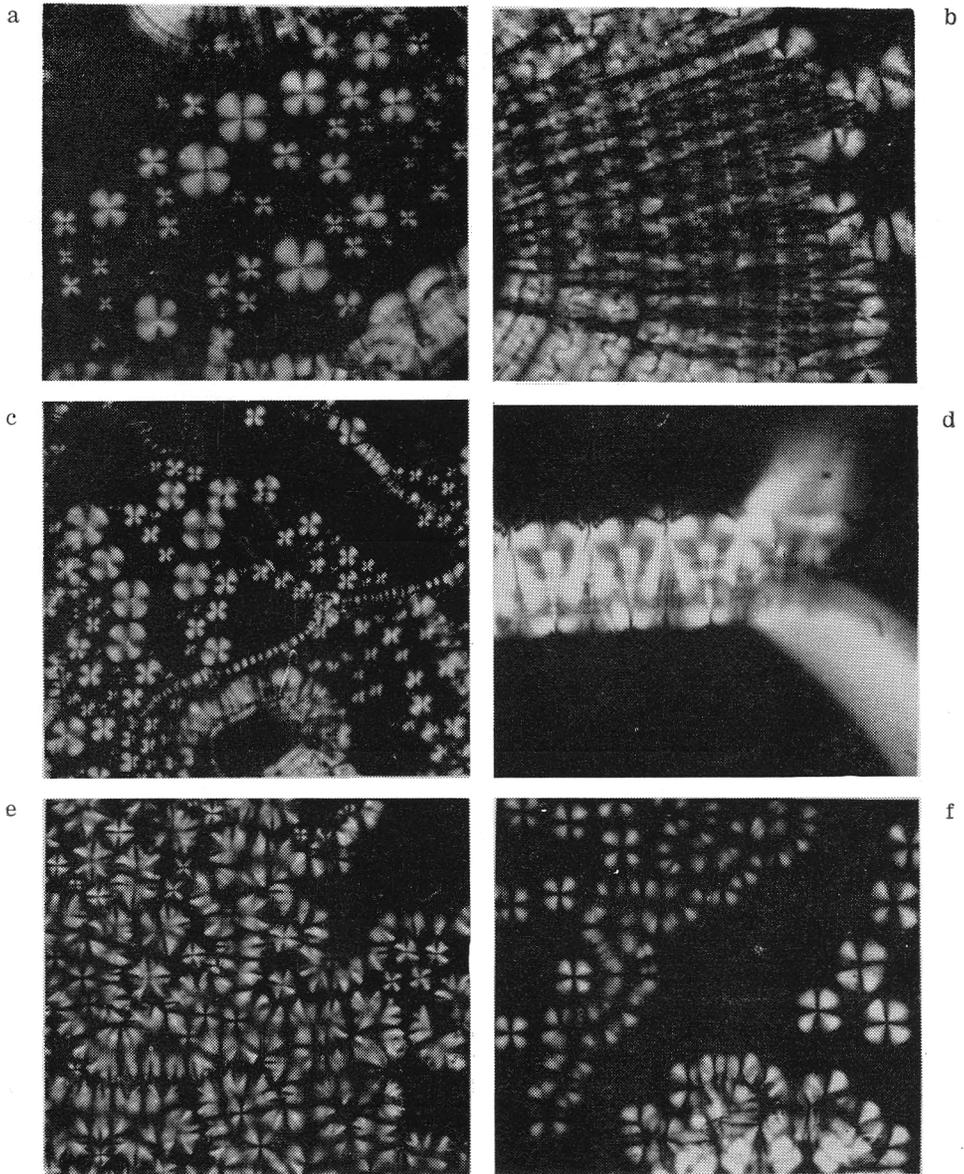


Figure 8. Micrographs of various optical textures showing birefringent formations:

- (a) $[\text{Mg}(\text{NO}_3)_2] = 6.0 \times 10^{-2}$, $[\text{HDBS}] = 6.0 \times 10^{-2}$,
- (b) $[\text{Mg}(\text{NO}_3)_2] = 6.0 \times 10^{-2}$, $[\text{HDBS}] = 4.0 \times 10^{-2}$,
- (c) $[\text{Mg}(\text{NO}_3)_2] = 4.0 \times 10^{-2}$, $[\text{HDBS}] = 4.0 \times 10^{-2}$,
- (d) $[\text{Mg}(\text{NO}_3)_2] = 4.0 \times 10^{-2}$, $[\text{HDBS}] = 2.5 \times 10^{-2}$,
- (e) $[\text{Mg}(\text{NO}_3)_2] = 2.5 \times 10^{-2}$, $[\text{HDBS}] = 1.0 \times 10^{-2}$,
- (f) $[\text{Mg}(\text{NO}_3)_2] = 2.0 \times 10^{-2}$, $[\text{HDBS}] = 1.5 \times 10^{-2}$.

Total magnification 384 x. All concns. in mol dm^{-3}

be seen, while in (d), taken in nonpolarized light, only outlines of liquid crystals within double chains, and the continued line of spread DBS monolayers between single chains can be observed. It is obvious that chains consist of single droplets, arranged in a special order. Figure 8 shows the variety of birefringent shapes of liquid crystals taken from the B region. It is especially interesting to follow the kinetics of formation of one double chain in part (d), where the time needed for ordering of droplets into chains is shorter than the exposure time, and we can only see the light traces.

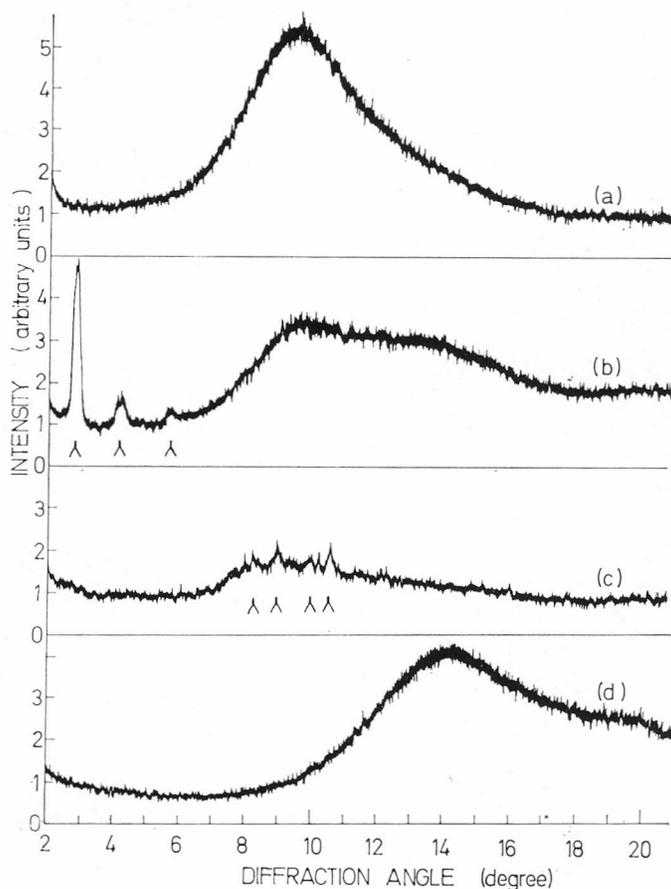


Figure 9. X-ray diffraction spectra obtained of:

- (a) HDBS as received from manufacturer;
- (b) oily substance precipitated in solution with $[\text{Mg}(\text{NO}_3)_2] = 6.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{HDBS}] = 6.0 \times 10^{-2} \text{ mol dm}^{-3}$;
- (c) white crystalline substance precipitated in solution with $[\text{Mg}(\text{NO}_3)_2] = 2.5 \times 10^{-1} \text{ mol dm}^{-3}$ and $[\text{HDBS}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$;
- (d) water.

Ordinate: X-ray diffraction intensity I in arbitrary units.
 Abscissae: Diffraction angle θ (in degrees).

X-ray studies. For the present structural study of the phases precipitated in water two representative samples were chosen. The first (sample I) was a dark yellow oily substance obtained as a precipitate from a solution containing 6×10^{-2} mol dm⁻³ of [Mg⁺²] and [DBS⁻]. The second (sample II) was a white flaky precipitate obtained from a solution containing 2.5×10^{-1} mol dm⁻³ [Mg⁺²] and 1.2×10^{-2} mol dm⁻³ [DBS⁻]. Parts of the recorded diffractograms for samples I and II are shown in Figure 9 (curves (b) and (c), respectively). The diffractograms obtained for pure DBS and pure water over the same angular range (curves (a) and (d), respectively) are also shown for comparison in Figure 9.

The dark yellow oily substance displayed three peaks in the small angle region, denoted by arrows in Figure 9. The corresponding interplanar spacings were calculated using the Bragg relation $d = \lambda / 2 \sin \vartheta$, where the wavelength is equal to $\lambda = 1.54 \text{ \AA}$ for CuK_α radiation and ϑ is the diffraction angle. Values of 15.55 Å, 10.39 Å, 7.82 Å were obtained for the three peaks. The wide diffuse »halos« at larger angles exhibited three maxima with corresponding d -values of about 4.7, 3.3, and 2.3 Å.

For the white flaky substance a quite different diffractogram was obtained (Figure 9c) with no peaks at lower angles, but a set of narrow peaks is discernable, just in the range of the weak diffuse halo on curve (b). The values of d -parameters corresponding to these peaks are approximately 5.30, 4.95, 4.46 and 4.22 Å. However, in the case of a much lower concentration of [DBS⁻] compared to that of [Mg⁺²], the white substance formed exhibits some degree of crystallinity shown by the appearance of several small peaks at larger angles (curve c).

These results indicate that the yellow oily phase has a liquid crystalline structure, probably of the smectic A type. The sequence of d -values reported here can be interpreted as one half, one third and one quarter of a single interplanar spacing $D = (31.2 \pm 0.1) \text{ \AA}$. This we can attribute to the smectic layer thickness. In addition, we suppose that the first diffuse halo arises from the high degree of disorder of molecules within each layer. The average first neighbour molecular distance in a plane estimated here with $d = 4.7 \text{ \AA}$ seems to be the same as for pure HDBS (Figure 9a), and is in agreement with that reported before.¹

It is surprising to note that the small-angle diffraction rings reported earlier¹ for pure HDBS are absent on curve (a). This fact might be connected with the influence of water in our sample or to different preparation procedures. In addition, the d -value reported here for the smectic layer thickness is about 20% higher than that reported for pure HDBS or NaDBS¹ and can probably be ascribed to the influence of the Mg⁺² ions. In future a more detailed study will be made of this point.

CONCLUSION

In conclusion we can stress the following: HDBS shows the formation of precipitates in aqueous solutions of alkaline earth nitrates. From the type of precipitation diagram it is obvious that, for a linear range in the equivalency region, the solubility product equilibrium can be stated according to the cation : anion relation of 1:2 (proved from the slope 0.5

for all alkaline earth). From the solubility/precipitability boundary parallel with the abscissae, the formation of ionic associates — aquacomplexes was found for an excess of electrolyte concentration. A complex solubility was found in the excess of HDBS when the c.m.c. was exceeded. The solubility decreases in the order $Mg > Ca > Sr > Ba$.

In the region of precipitation a white, flaky crystalline phase, as well as an oily coacervate, or mixed systems were observed above the c.m.c. of HDBS. It is demonstrated by X-ray and optical methods that for different concentrations of Mg^{+2} and DBS^- in water at least two precipitated phases can be obtained: a partially ordered phase as presented by diffractogram (b), probably a smectic A liquid crystal, while the other phase as presented by diffractogram (c) is totally ordered, and appears to be a solid crystalline material.

Acknowledgements. — The authors wish to thank Mrs. B. Kostanić-Cerovec and Mrs. B. Sem for technical assistance.

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SAŽETAK

Ravnoteže čvrsto/tekuće u vodenim sustavima dodecil benzen sulfonata i zemnoalkalijskih iona

Đ. Težak, F. Strajnar, O. Milat, M. Stubičar i D. Šarčević

Istražene su granice topljivosti/taloženja i morfologija čvrste faze, te izračunane konstante ravnoteže za [dodecilbenzen-sulfonate (DBS) soli — Mg, Ca, Sr i Ba]. Eksperimentalne metode raspršenja svjetla, polarizacijske mikroskopije i difrakcije X-zraka dale su konzistentne podatke. Mjerenja su vršena na 293 K. Topljivost soli $M(DBS)_2$ pada u nizu $Mg > Ca > Sr > Ba$; izračunate su ove vrijednosti pK_s^0 : $(10,80 \pm 0,07)$ za $Mg(DBS)_2$, $(10,48 \pm 0,07)$ za $Mg(DBS)_2$ (za DBS dimer), $(11,23 \pm 0,03)$ za $Ca(DBS)_2$, $(12,00 \pm 0,08)$ za $Sr(DBS)_2$, $(12,4 \pm 0,2)$ za $Ba(DBS)_2$.

Pokazano je da se u području taloženja dobivaju najmanje dvije faze, i to: djelomično uređena faza koja vjerojatno pripada tekućem kristalu (smektik A), a druga je faza čvrsta kristalinična.