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Structures and Textures of Crystalline Phases and Lyotropic Mesophases of Alkylbenzenesulfonates

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The molecular arrays in crystalline *n*-alkylbenzenesulfonates (C₈—C₁₂) were determined by X-ray diffraction and found to be lamellar bilayers with the basic lamellar thickness of 30.1—36.9 Å for single-tailed, and 22.25—30.0 Å for C₁₂ double-tailed surfactants, depending on the length of surfactant molecule. In the colloid dispersions of metal-dodecylbenzenesulfonates as well as in the systems of double-tailed C₁₂-isomers, microscopic investigations of liquid crystal textures showed the characteristic lyotropic nematic, lamellar, pseudo-isotropic and transient phases with batônments.

INTRODUCTION

Alkylbenzenesulfonates show the formation of different phases in water solutions, *i. e.* the crystalline phase and lyomesophases in colloidal dispersions.^{1,2} While the variety of features concerning thermotropics,³ has been described it is not the case with lyotropics, especially concerning their microscopic textures, which were first time discovered by R. Virchow⁴ and O. Lehmann,⁵ first presented in a paper by F. B. Rosewear,⁶ and later shown by some other authors.⁷⁻¹⁰ In the present paper some microscopic textures of nematic, lamellar and pseudo-isotropic lyomesophases in aqueous dispersions are presented. The investigations were performed in water solutions of dodecylbenzenesulfonic acid (HDBS), of metal salts of HDBS, as well as of sodium salts of octyl, nonyl, decyl, undecyl, dodecyl-benzenesulfonates (single- and double-tailed). The crystalline phases and mesophases were characterized by polarization microscopy and X-ray diffraction.

EXPERIMENTAL

Materials

Metal nitrates (magnesium, ferric) were of *p. a.* grade from Merck, Darmstadt; the water solutions were prepared using chemicals as commercially distributed and standardized complexometrically (A. Vogel, *A. Textbook of Quantitative Inorganic Analysis*, Longman, London, Ed. III, 1961). Highly pure sodium salts of *n*-alkylbenzenesulfonates (C₈BSNa, *x* = 8, 9, 10, 11, 12), and of 1-(4')dodecylbenzenesulfonate (1-(4')BSNa) and 1-(6')dodecylbenzenesulfonate (1-(6')BSNa) were obtained

by courtesy of Henkel Co. and Hüls Co., FRG. HDBS of *p. a.* grade was supplied by »Prva Iskra«, Barić-Beograd and used as commercially distributed (not isomerically pure), standardized potentiometrically with the standard NaOH solution.

All samples were prepared with doubly distilled water.

Techniques

Microscopic observations were made on a Leitz Wetzlar light microscope with polarizing equipment. The microscopic specimens were prepared by putting the dispersion system or pure salt (in the case of contact specimens) between the subject and cover glasses. Contact specimens were made by letting the water penetrate within dry salts or HDBS under the subject and cover glass. Dispersions of metal-dodecylbenzenesulfonates were prepared in advance by mixing the water solutions of reacting components.

The X-ray diffraction patterns were made on a standard Siemens diffractometer with a counter and Si-crystal monochromatized $\text{CuK}\alpha$ radiation. The interplanar spacings of sodium salts of *n*-alkylbenzenesulfonates and double-tailed 1-(4')- and 1-(6')-isomers were calculated from these data.

RESULTS AND DISCUSSION

Figure 1 presents the diffraction patterns of C_xBSNa dry crystals, containing many diffraction lines (at least 5 orders) and indicating three-dimensional crystalline substances of low symmetry. The planar lamellar ordering can be supposed in the basic lamellar bilayers. These crystal phases exhibit strong optical birefringence (see Figure 2.11 of crystals in water at room temperature). The crystals obtained by homogeneous precipitation by cooling the isotropic solution exhibit also high optical birefringence and quite reasonable monodispersion. The basic lamellar thickness changes with the number of CH_2 -groups as it is tabulated in Table I. The crystalline phases are the only form appearing in water at room temperature in the case of C_xBSNa . The phase diagrams will be published elsewhere.²

The systems of double-tailed surfactants (1-(4)- and 1-(6')dodecylbenzenesulfonates in water) show no crystalline phases at room temperature,² while the X-ray diffraction patterns (Figure 1) of the dry samples have shown quite a different behaviour. The appearance of two different phases with two interplanar spacings between bilayers has been recorded for both crystalline 1-(4')- and 1-(6') samples, presenting four orders of diffraction lines: 30.0 and 26.95 Å for 1-(4') sample and: 25.3 and 22.25 Å for 1-(6') sample. These data indicate: (i) the strictly defined crystal structures of lamellar ordering in the crystalline substances of low symmetry as it has been found for *n*-surfactants; it can be assumed that the two spacings present the crystalline phases with and without crystalline water within crystal structure; (ii) two possible states of water bound to the surfactants in crystal. This water cannot correspond to the lamellar — nonlamellar transition since the diffraction pattern in Figure 1 has been recorded of the same sample at room temperature. Two conclusions can be proposed: that there are two equilibrated phases in this sample, one with and the other without crystal water within the bilayers, or that these phases present different »smectic« phases (S_A and S_C from thermotropic classification) with no water within bilayers. Both phases exhibit the same structural symmetry, which can be supposed to be the lamellar bilayers. It is maintained in the paper by N. Casillas¹¹ that lamellar liquid crystal phase retain »bulklike« water between

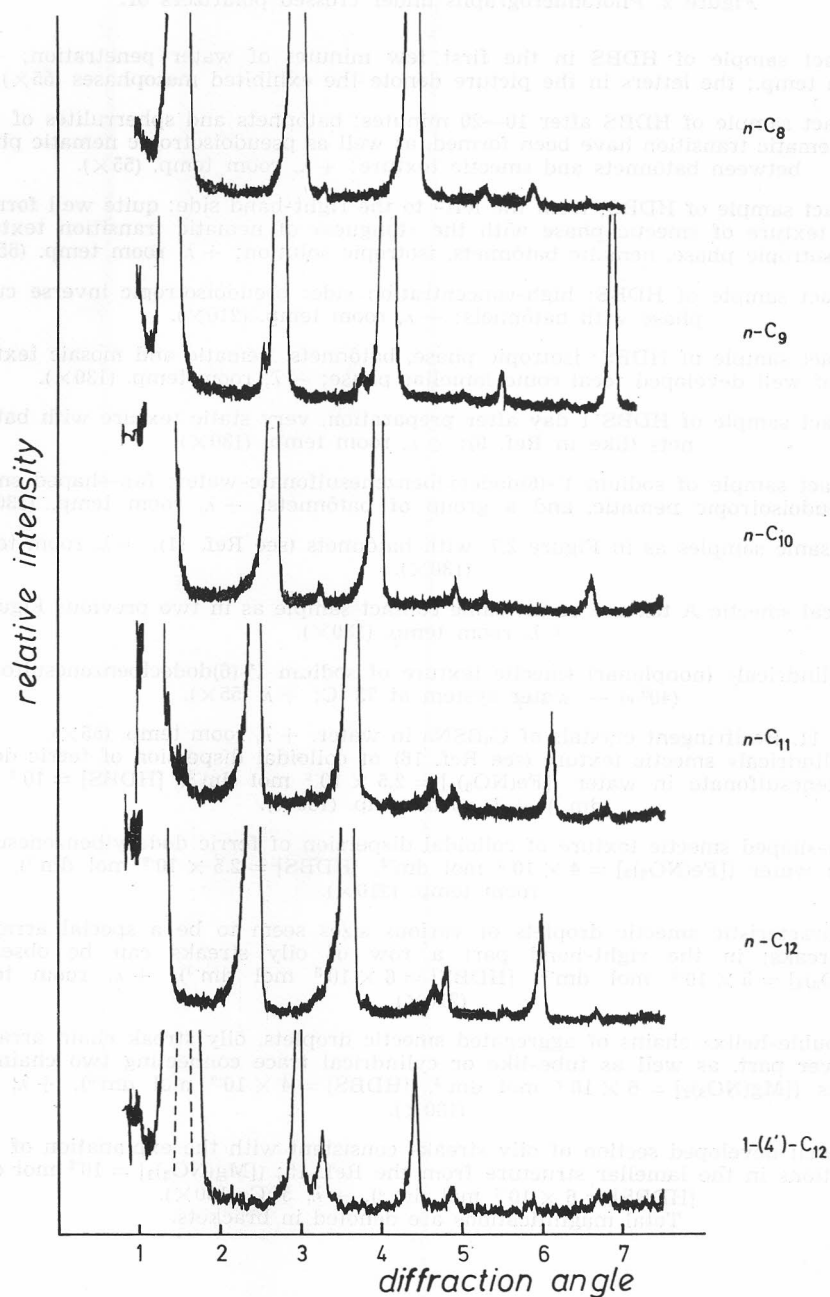
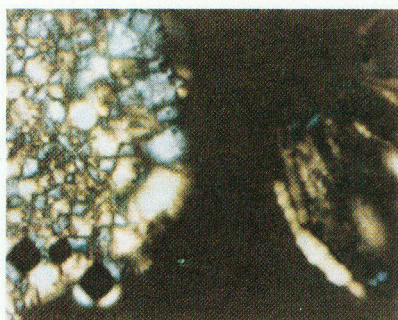
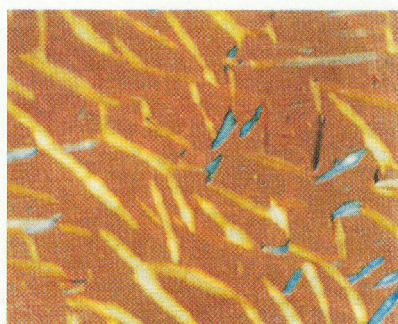
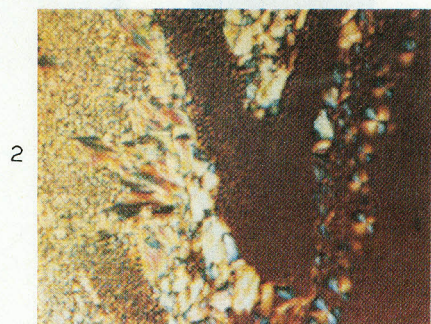
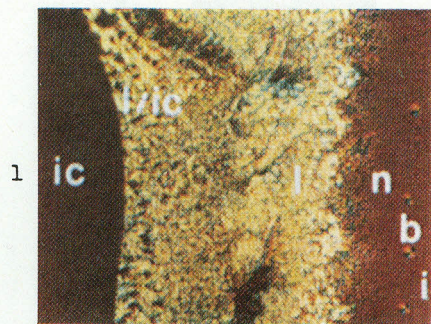


Figure 1. X-ray diffraction patterns of C_8 — C_{12} *n*-alkylbenzenesulfonates and 1-(4')-dodecylbenzenesulfonate. Diffraction angle in θ° .

Figure 2. Photomicrographs under crossed polarizers of:

1. Contact sample of HDBS in the first few minutes of water penetration; $+\lambda$, room temp.; the letters in the picture denote the exhibited mesophases (55 \times).
 2. Contact sample of HDBS after 10–20 minutes; batônnetts and spherrulites of isotropic/nematic transition have been formed, as well as pseudoisotropic nematic phase between batônnetts and smectic texture; $+\lambda$, room temp. (55 \times).
 3. Contact sample of HDBS; from the left- to the right-hand side: quite well formed mosaic texture of smectic phase with the »tongues« of nematic transition texture, pseudoisotropic phase, nematic batônnetts, isotropic solution; $+\lambda$, room temp. (55 \times).
 4. Contact sample of HDBS: high-concentration side: pseudoisotropic inverse cubic phase with batônnetts; $-\lambda$, room temp. (210 \times).
 5. Contact sample of HDBS: isotropic phase, batônnetts, nematic and mosaic texture of well developed focal conic lamellar phase; $-\lambda$, room temp. (130 \times).
 6. Contact sample of HDBS 1 day after preparation, very static texture with batônnetts (like in Ref. 9); $+\lambda$, room temp. (130 \times).
 7. Contact sample of sodium 1'-(6)dodecylbenzenesulfonate-water: fan-shaped smectic, pseudoisotropic nematic, and a group of batônnetts; $+\lambda$, room temp. (130 \times).
 8. The same samples as in Figure 2.7. with batônnetts (see Ref. 11); $+\lambda$, room temp. (130 \times).
 9. Typical smectic A texture of the same contact sample as in two previous Figures; $+\lambda$, room temp. (130 \times).
 10. »Cylindrical« (nonplanar) smectic texture of sodium 1'-(6)dodecylbenzenesulfonate (40%) — water system at 73 °C; $+\lambda$ (55 \times).
 11. Berifringent crystals of C_9BSNa in water, $+\lambda$, room temp. (55 \times).
 12. »Cylindrical« smectic texture (see Ref. 16) of colloidal dispersion of ferric dodecylbenzenesulfonate in water ($[Fe(NO_3)_3] = 2.5 \times 10^{-2}$ mol dm $^{-3}$, $[HDBS] = 10^{-2}$ mol dm $^{-3}$), $+\lambda$, room temp. (130 \times).
 13. Fan-shaped smectic texture of colloidal dispersion of ferric dodecylbenzenesulfonate in water ($[Fe(NO_3)_3] = 4 \times 10^{-3}$ mol dm $^{-3}$, $[HDBS] = 2.5 \times 10^{-2}$ mol dm $^{-3}$), $+\lambda$, room temp. (210 \times).
 14. Characteristic smectic droplets of various sizes seem to be a special array of oily streaks; in the right-hand part a row of oily streaks can be observed ($[Fe(NO_3)_3] = 5 \times 10^{-3}$ mol dm $^{-3}$, $[HDBS] = 6 \times 10^{-3}$ mol dm $^{-3}$), $+\lambda$, room temp. (210 \times).
 15. »Double-helix« chains of aggregated smectic droplets, oily streak chain array in the lower part, as well as tube-like or cylindrical trace connecting two chains of droplets ($[Mg(NO_3)_2] = 6 \times 10^{-2}$ mol dm $^{-3}$, $[HDBS] = 4 \times 10^{-2}$ mol dm $^{-3}$), $+\lambda$, 5 °C (130 \times).
 16. A well developed section of oily streaks consistent with the explanation of edge dislocations in the lamellar structure from the Ref. 15; ($[Mg(NO_3)_2] = 10^{-2}$ mol dm $^{-3}$, $[HDBS] = 6 \times 10^{-3}$ mol dm $^{-3}$), $+\lambda$, 5 °C (130 \times).
- Total magnifications are denoted in brackets.



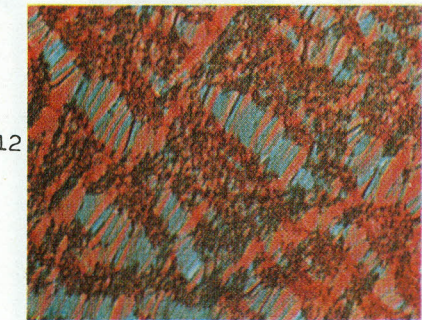
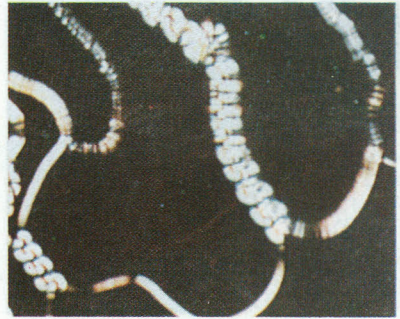
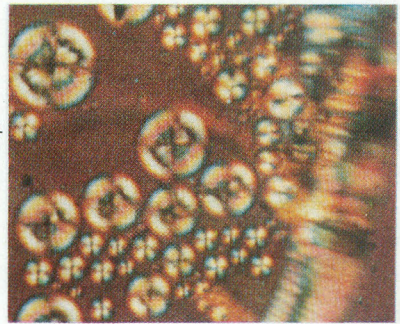
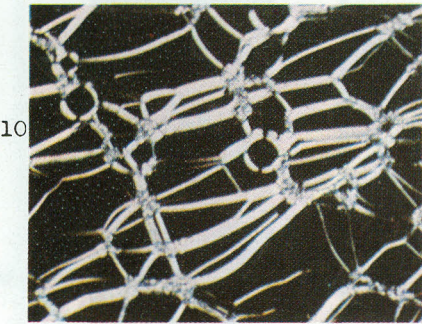
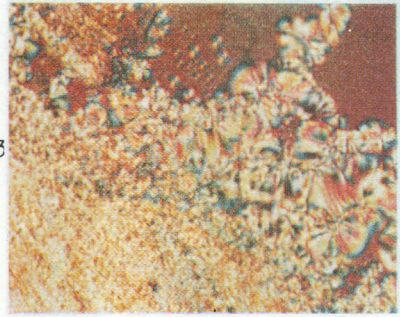
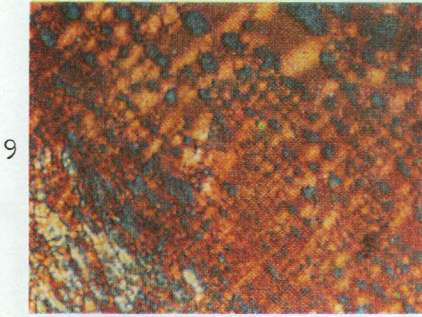


TABLE I

The basic lamellar spacings $D/\text{Å}$ of $n\text{-C}_x\text{BSNa}$, $1\text{-}(4')\text{-BSNa}$ and $1\text{-}(6')\text{-BSNa}$ crystalline phases

x		$D/\text{Å}$
8	$n\text{-C}$	30.1
9	$n\text{-C}$	32.5
10	$n\text{-C}$	33.5
11	$n\text{-C}$	36.5
12	$n\text{-C}$	36.9
12	1-(4')	30.0; 26.95
12	1-(6')	25.3; 22.25

the bilayers, that this water shows differences from the »bulk« water and the »interfacial« water close to bilayers. Consequently it can be assumed from the X-ray diffraction patterns in this paper that a certain amount of water has been retained in one of the crystal phases, and not in the other, and that the differences in spacings of the two equilibrated phases for the both 1-(4') and 1-(6') surfactants amount to 3.05 Å (obtained by subtraction of the two interplanar spacings for the same surfactant sample). As regards the differences in interplanar spacings, the values of 3–4 Å for metal-dodecylbenzenesulfonate liquid crystals and dried samples have been obtained in the paper.¹²

The contact sample of 1-(6')dodecylbenzenesulfonate with the increasing water concentration shown in Figure 2.7, as well as in Figure 2.8 in detail, exhibits the phase regions from the right- to the left-hand side: with bâtonnets (b), pseudo-isotropic = nematic (n) and lamellar (l) with fan-shaped texture. This particular nematic phase has been confirmed by microscopic and ²H-NMR measurements.² The textures with isotropic, pseudo-isotropic (nematic), lamellar, and transition phases with bâtonnets can be clearly distinguished in the contact samples of the above described double-tailed surfactant with water, as well as in HDBS with water. The bâtonnets, always appearing at the border-lines: isotropic — nematic — lamellar¹³ and in the pseudo-isotropic regions, can be considered as liquid monocrystals grown under supersaturation conditions within transient phase limits. Two pseudo-isotropic regions appeared in the following HDBS samples: (i) nematic in the low content of surfactant (disc-shaped micelles of the nematic phase are the precursors for the lamellar phase⁹); (ii) inverse cubic in the high content of surfactant. Characterization of the water penetration into the samples of HDBS (Figures 2.1–2.5) makes it possible to recognize a complete phase diagram by observing just the microscopic texture. Many phases with transient regions appeared in the micrographs in Figure 2, just as it had been explained by M. C. Holmes *et al.*¹⁰ The following phases can be seen in the HDBS samples in Figure 2.1 presented by the textures from the right- to the left-hand side: the isotropic solution (i) in the highest water content, the bâtonnets and nematic spherrulites (b) in the transient region between isotropic and pseudo-isotropic nematic (n) (the precursor for the lamellar phase), the mosaic lamellar phase (l), the transient lamellar — inverse cubic region, characterized by »diluted lamellar mosaic« (l/ic), and finally optically iso-

tropic inverse cubic phase (*ic*). The phases that developed 10–20 minutes after water penetration are presented in Figures 2.2–2.5.

The third group of textures, all of them lamellar, belongs to the systems containing HDBS and uni-, bi- or tri-valent metal ions.¹⁴ Several textures of lamellar phases in colloidal dispersions of metal-dodecylbenzenesulfonates in water are presented in Figures 2.12–2.16 as characteristic representatives. They exhibit a variety of anisotropic textures depending on the defects and dislocations of the planar or cylindrical array of molecular bilayers,³ including lamellar droplets, focal conics, mosaic, oily streaks, fan-shaped, myelinic forms, as well as aggregated droplets into a network of tubes, or double-chain string-like aggregates. These various lamellar textures, the main forms in alkylbenzenesulfonate lyotropics, indicate the structure explained by C. Williams and Y. Boulingand¹⁵ (References Nos. 10, 50 and 146 cited in the book of Demus³): disclinations in planar bilayers, and defects in non-planar smectic texture by C. E. Williams and M. Kléman¹⁶. W. J. Benton and C. A. Müller¹⁷ proposed the model of oily streaks, which can be related to the defects presented by the texture in Figure 2.16. Mosaic texture in a lamellar phase,⁹ similar to lamellar polyhydrate of Triton,¹⁸ was found only by »pure« HDBS — water samples (Figure 2.5), and none by metal dodecylbenzenesulfonates.

CONCLUSION

It can be summarized that, at room temperature, sodium salts of *n*-alkylbenzenesulfonates exhibit only the crystalline phases of low symmetry and bilayer array of molecules with one interplanar spacing corresponding to the length of surfactant molecule. They appeared as lamellar mesophases at elevated temperatures,² since 1-(4')- and 1-(6')-isomers (double tailed C₁₂ surfactants) exhibit nematic and lamellar lyomesophases at room temperature and at elevated temperatures. The appearance of two interplanar spacings by isomeric double tailed surfactants indicates the presence of two phases with lamellar ordering, *i. e.* two phases in equilibrium with or without crystalline water.

The dodecylbenzenesulfonic acid containing single- and double-tailed isomers exhibits nematic and lamellar as well as inverse cubic phases (in high contents of HDBS 85–98%).

The formation of lamellar liquid crystal arrangement occurs in colloid dispersions of metal dodecylbenzenesulfonates precipitated from aqueous solutions of metal nitrates and HDBS, showing a variety of microscopic textures. Disclinations in the lamellar phases of alkylbenzenesulfonates with or without metal ions seem to be different, since different characteristic textures have been found.

REFERENCES

1. Đ. Težak, M. Čolić, V. Hrust, S. Popović, S. Prgomet, and F. Strajnar, *Progr. Colloid and Polymer Sci.* **74** (1987) 87.
2. Đ. Težak *et al.* (to be published).
3. D. Demus and L. Richter, *Textures of Liquid Crystals*, VEB Deutscher Ver. für Grundstoffindustrie, Leipzig, 1978.
4. R. Virchow, *Virchows Archiv* **6** (1854) 571.
5. O. Lehmann, *Flüssige Kristalle*, Leipzig, 1904.

6. F. B. Rosevear, *J. Am. Oil. Chem. Soc.* **31** (1954) 628; F. B. Rosevear, *J. Soc. Cosmetic Chemists* **19** (1968) 581.
7. A. S. C. Lawrence, *Mol. Cryst. Liq. Cryst.* **7** (1969) 1.
8. A. Saupe, *J. Colloid Interface Sci.* **58** (1976) 583.
9. F. Ballet, Y. S. Leong, J. C. Wittmann, and F. Candau, *Mol. Cryst. Liq. Cryst.* **64** (Letters) (1981) 305.
10. M. C. Holmes, N. Boden, and K. Radley, *Mol. Cryst. Liq. Cryst.* **100** (1983) 93.
11. N. Cassilas, J. E. Puig, R. Olayo, T. J. Hart, and E. I. Franses, *Langmuir* **5** (1989) 384.
12. Đ. Težak, S. Popović, S. Heimer, and F. Strajnar, *Progr. Colloid and Polymer Sci.* **79** (1989) 293.
13. K. Radley and A. Saupe, *Mol. Cryst. Liq. Cryst.* **44** (1978) 227.
14. Đ. Težak, F. Strajnar, O. Milat, and M. Stubičar, *Progr. Colloid and Polymer Sci.* **69** (1984) 100.
15. C. Williams, Doctoral Thesis, Univ. Paris-Sud (Orsay), 1976 (after Ref. 3).
16. C. E. Williams and M. Kléman, *J. Physique Colloq.* **36** (1975) C1—315.
17. W. J. Benton and C. A. Müller, *Progr. Colloid and Polymer Sci.* **68** (1983) 71.
18. R. Heusch and F. Kopp, *Ber. Bunsenges. Phys. Chem.* **91** (1987) 806.

SAŽETAK

Strukture i teksture kristaličnih faza i liotropnih mezofaza alkilbenzensulfonata

Đurđica Težak i Stanko Popović

Mjerenjem difrakcije X-zraka nađeno je da su lamelarni dvosloji u kristaličnim fazama *n*-alkilbenzensulfonata (C₈—C₁₂) bazične lamelarne debljine 30,1—36,9 Å za jednolančane, i 22,25—30,0 Å za dvolančane surfaktante, ovisno o duljini alkilnog lanca. U koloidnim disperzijama metalnih alkilbenzensulfonata, kao i kod dvolančanih C₁₂-izomera, mikroskopska istraživanja pokazala su karakteristične faze liotropnih nematika, te lamelarnih, pseudo-izotropnih i prijelaznih faza s batônnetima.