

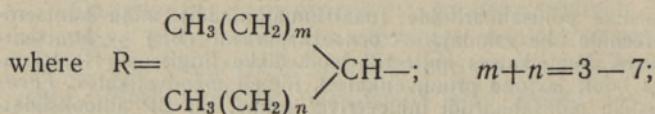
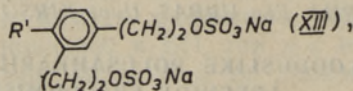
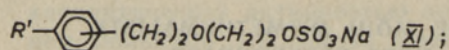
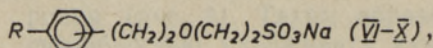
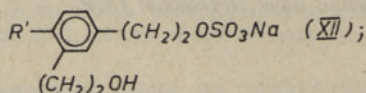
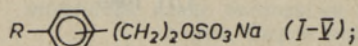
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J. JOERS, Helje URBEL

INFLUENCE OF STRUCTURAL ELEMENTS ON PHYSICO-CHEMICAL PROPERTIES OF SURFACE-ACTIVE DERIVATIVES OF ALKYLAROMATIC ALCOHOLS *

(Presented by O. Kirret)

The sulphoderivatives of alkylaromatic alcohols synthesized by us are novel surfactants. The surface-active derivatives of alkylphenylethanols and 1-alkyl-2,4-hydroxyethylbenzene are as follows: the sodium salts of sulphoesters of secondary alkyl-2-phenyl ethanol C_6-C_{10} (sulphates C_6-C_{10} , Table, I—V) [1, 2], sodium salts of secondary alkyl-2-phenylethoxyethane sulphoacids (isethionates C_6-C_{10} , VI—X) [3], sodium salt of sulphoester of the secondary octyl-2-phenylethoxy-ethanol (ethoxylate C_8 , XI), and sodium salts of sulphoesters of secondary 1-alkyl-2,4-hydroxyethyl benzenes (mono- and disulphate, XII, XIII) [4]:



$R'=R$, where $m+n=5$.

The above-mentioned compounds have been identified by sulphur and by infrared and proton magnetic resonance spectra. Every preparation is a mixture of isomers. The position of the benzene ring related to the alkyl chain has been determined already by a synthesis of alkyl benzenes which consist of a balanced mixture of isomers. According to the position of substitutes of the benzene ring, the alkylphenyl ethanol consist of *ortho*- and *para*-isomers; 1-alkyl-2,4-hydroxyethyl benzene includes 1,2,4-isomer only.

The sulphates C_6-C_{10} , ethoxylate C_8 and disulphate contain a considerable amount of sodium sulphate as a by-product. The by-product of isethionates C_6-C_{10} is 1,4-disulphoethoxyethane and those of mono-

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The physico-chemical properties of surface-active derivatives of alkylaromatic alcohols and lauryl sulphate

N of of com-	R	Solu- bility S_s mole/l	$d_4^{20} \cdot 10^3$, kg/m ³	τ CMC $\cdot 10^{-1}$ mole/l	Surface tension, $\sigma \cdot 10^{-3}$ (N/m) at CMC	Maximum surface excess concent- ration, $\Gamma_{\infty} \cdot 10^{-9}$ kmole/m ²	Area per molecule, $S_0 \cdot 10^{-2}$ nm ²	Diameter of adsorp- tion layer, $\delta \cdot 10^{-1}$ nm	Wetting angle θ (degrees) at CMC	Foam stability H_2/H_0 at CMC	Content of sulphur, %		Content of by- products, %	Formula
											experi- mental	theor- etical		
I	C ₆ H ₁₃	2.92	1.2870	13.80	29.3	6.40	26.0	15.3	45.0	0.87	12.34	10.4	16.0	C ₈ H ₁₇ NaO ₄ S
II	C ₇ H ₁₅	2.33	1.2691	5.37	26.5	5.71	29.1	14.5	56.5	0.54	11.94	9.95	15.8	C ₉ H ₁₉ NaO ₄ S
III	C ₈ H ₁₇	1.96	1.2345	4.57	25.5	5.76	28.8	15.7	46.0	0.96	11.37	9.53	14.1	C ₁₀ H ₂₁ NaO ₄ S
IV	C ₉ H ₁₉	1.66	1.2308	2.51	27.4	3.57	46.5	10.2	40.5	0.96	10.86	9.15	12.8	C ₁₁ H ₂₃ NaO ₄ S
V	C ₁₀ H ₂₁	1.43	1.2280	2.29	29.4	2.29	72.5	6.8	42.5	0.98	10.48	8.80	12.2	C ₁₂ H ₂₅ NaO ₄ S
VI	C ₆ H ₁₃	2.53	1.2706	9.55	30.3	6.89	24.1	18.2	42.5	0.87	10.5	9.53	7.5	C ₁₀ H ₂₁ NaO ₄ S
VII	C ₇ H ₁₅	1.51	1.2508	3.98	26.3	5.19	32.0	14.5	41.0	0.58	10.17	9.15	7.4	C ₁₁ H ₂₃ NaO ₄ S
VIII	C ₈ H ₁₇	1.34	1.2090	2.63	29.0	2.92	56.9	8.8	40.0	0.86	9.74	8.80	6.8	C ₁₂ H ₂₅ NaO ₄ S
IX	C ₉ H ₁₉	1.06	1.2033	1.82	30.2	2.65	62.8	8.3	49.0	0.90	9.56	8.47	7.3	C ₁₃ H ₂₇ NaO ₄ S
X	C ₁₀ H ₂₁	0.662	1.2002	1.58	26.6	2.00	83.1	6.5	44.5	0.94	9.62	8.17	9.8	C ₁₄ H ₂₉ NaO ₄ S
XI	C ₈ H ₁₇	1.74	1.2150	2.04	29.4	2.26	73.7	7.1	40.0	0.84	9.97	8.43	10.5	C ₁₂ H ₂₅ NaO ₅ S
XII	C ₈ H ₁₇	1.53	1.2172	0.98	27.8	1.54	107.9	5.2	55.0	0.73	9.71	8.43	26.3	C ₁₂ H ₂₅ NaO ₅ S
XIII	C ₈ H ₁₇	1.30	1.2265	7.80	32.5	4.07	40.8	16.0	56.4	0.91	12.14	11.19	8.4	C ₁₂ H ₂₅ Na ₂ O ₈ S
XIV	C ₁₂ H ₂₅	0.21	1.1591	6.08	38.6	4.19	39.7	10.4	58.0	0.95	11.09	11.12	—	C ₁₂ H ₂₅ NaO ₄ S

sulphate are disulphate and sodium sulphate. All the above-mentioned by-products increase the quantity of sulphur in surfactants as compared with the theoretical amount. Without inorganic by-products the preparations do not crystallize in ethanol and are poorly separated from organic impurities [5,6]. Comparing some preparations with examples not containing inorganic salts, it has been determined that the above-mentioned amount of by-products has no effect upon their physico-chemical properties.

The properties of water solutions of various surface-active derivatives of alkylaromatic alcohols described above have been investigated. The regularity of the alteration of physico-chemical properties depending on the length of the alkyl radical, their nature and the position of structural elements in the molecule have been determined. The phenylene ring, differently from well-known relative surfactants, is placed in the middle of the aliphatic chain. It is interesting how much that structural factor influences the physico-chemical properties of the compound.

The following physico-chemical parameters have been determined (Table):

1. Solubility (S) has been measured in distilled water at 20°C. Every preparation synthesized by us has a splendid water solubility; by increasing the number of carbon atoms, the solubility decreases as usual. In comparison with lauryl sulphate (XIV), the present compounds, and especially the sulphates, own a several times better solubility even when having a considerably higher molecule mass. The secondary alkyl sulphates (S — 1.2 mole/l), and also the structurally related dodecyl benzene sulphonates (S — 0.4 mole/l) subdue the present preparations [7].

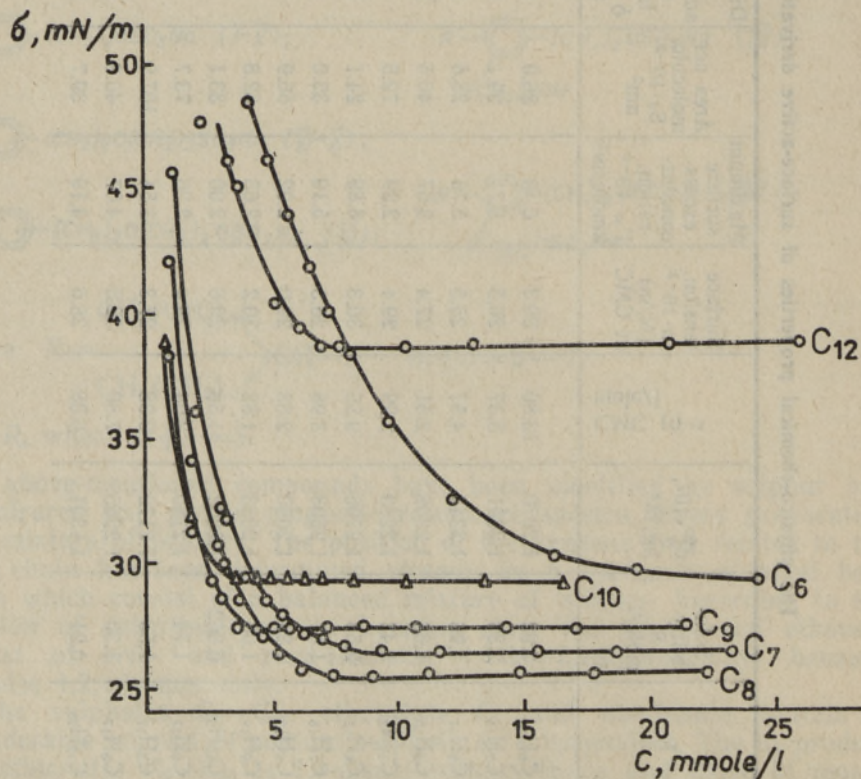


Fig. 1. Dependence of surface tension (σ) of sulphates C₆—C₁₀ and lauryl sulphate (C₁₂) upon the concentration of their solutions at 20°C.

2. Surface tension (σ) and the critical micelle concentration (CMC).

In studying the properties of surfactants in relation to their structure, the more characteristic parameters are surface tension and CMC. The static surface tension has been measured by the stalagmometrical method at 20°C (Figs 1—3). CMC has been determined by minima on the curves of surface tension, built up in a semi-logarithmic system of co-ordinates [8].

σ at CMC of the solution of sulphonates and isethionates C_6 — C_{10} , similarly to the well-known alkyl sulphates, decreases up to the intermediate homologues with a following increase in the last members. CMC decreases linearly by growing the number of carbon atoms in the alkyl chain, with the exception of the first members of the homologues series which, due to their insufficiently hydrophobic alkyl radical, have no classical properties of colloidal surfactants.

The transition of the homologues series of sulphates to isethionates is accompanied by an alteration of properties — the solubility and CMC decrease, σ at CMC alters to a lesser extent. Complementing the hydrocarbon chain of sulphates with an ether bond and approximating the benzene ring to the centre of the radical (sulphate C_{10} , V, and ethoxylate C_8 , XI) we achieve an increase in the solubility, which rises from 1.43 to 1.74 mole/l. Complementing the benzene ring of the sulphate C_8 (III) with the hydroxyethyl group (mono-sulphate, XII), we get a considerable decrease of CMC (from 4.57 to $0.98 \cdot 10^{-3}$ mole/l) and a certain increase of σ (from 25.5 to $27.8 \cdot 10^{-3}$ N/m). Comparing the mono-

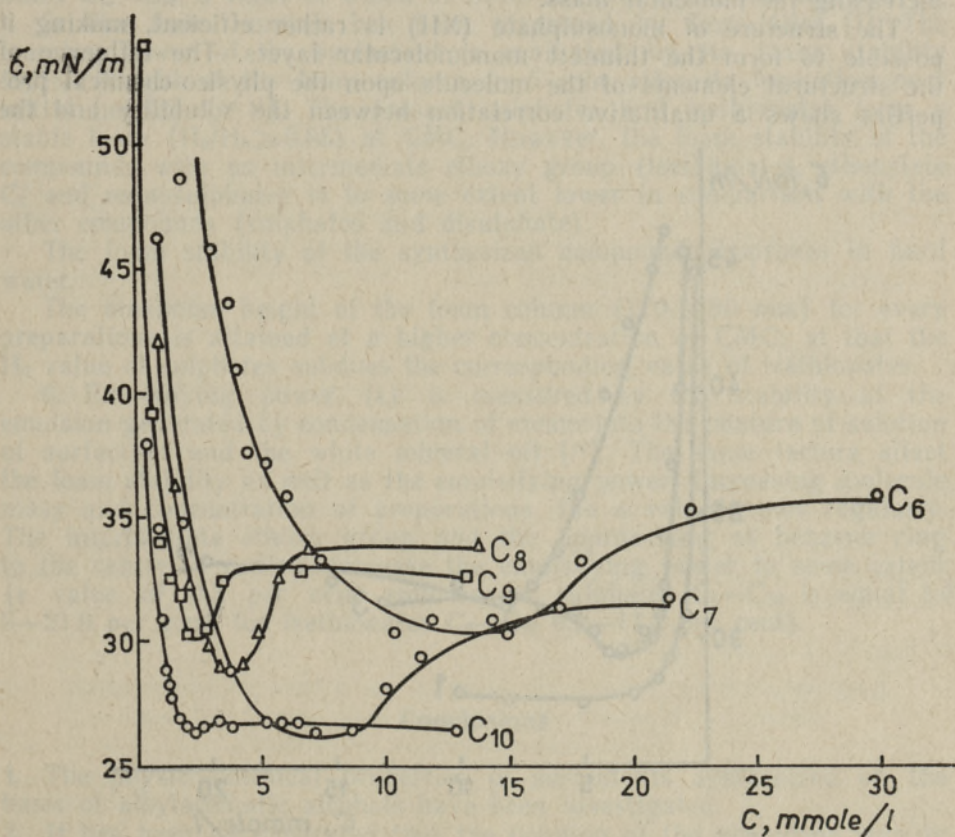


Fig. 2. Dependence of surface tension (σ) of isethionates C_6 — C_{10} upon the concentration of their solutions at 20° C.

sulphate (XII) with isethionate C_8 (VIII), one can see that the free alcoholic group decreases CMC more than twice, and σ decreases from 29.0 to $27.8 \cdot 10^{-3}$ N/m. These alterations are explained by an increase in the dimensions of the molecule and by an improvement of the hydrophilic-lipophilic balance (HLB). Disulphate, on the contrary, has a lower surface activity, nearing by its properties to lauryl sulphate. That can be explained by the presence of two sulphate groups, resulting in a displacement of the molecule HLB in the direction of the hydrophilic part. It is remarkable that by surface activity the sulphates subdue the isethionates, which attain CMC at a lower concentration. Of all the experimented preparations, the best surfactant is mono-sulphate, having the least CMC at a relatively low surface tension.

3. Maximum surface excess concentration Γ_∞ , molecular measurements — the diameter of the adsorption layer δ and the area per molecule S_0 in the adsorption layer — have been determined by curves of the surface tension, by means of the equations of Gibbs and Langmuir [9, 10]. The sufficient accuracy of the method used is confirmed by a coincidence of the experimental S_0 value of lauryl sulphate ($39.7 \cdot 10^{-2}$ nm²) with the values given in the relevant literature (39.0 and $37.8 \cdot 10^{-2}$ nm²) [11, 12].

The sharp increase in the S_0 value within the range of the homologues series, by passing over from isethionate C_7 to C_8 and from sulphate C_8 to C_9 , affirms the qualitative alteration in the structure of the surface layer. The values of δ and Γ_∞ decrease as a result of the reduction of the packing density of hydrophobic radicals in the surface layer by increasing the molecular mass.

The structure of monosulphate (XII) is rather efficient, making it possible to form the thinnest monomolecular layers. The influence of the structural elements of the molecule upon the physico-chemical properties shows a qualitative correlation between the solubility and the

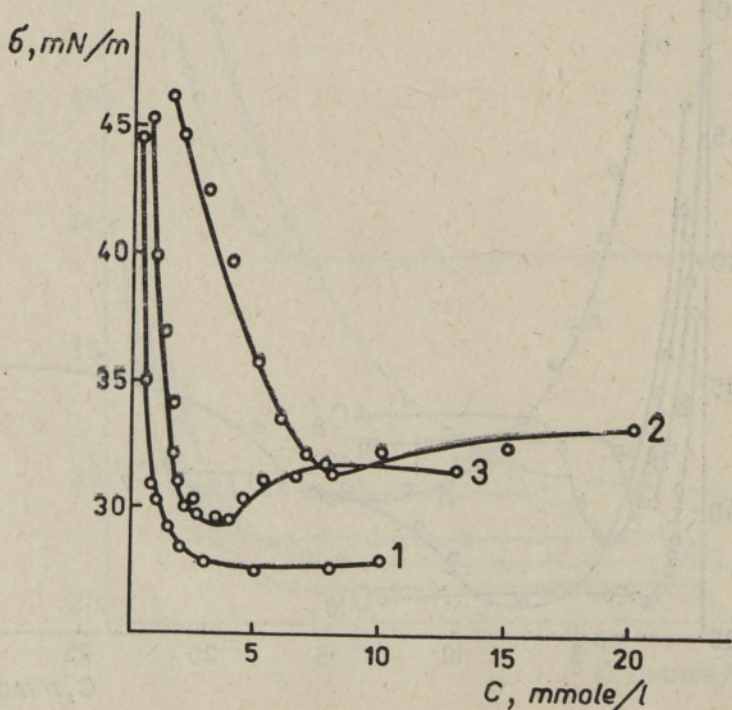


Fig. 3. Dependence of surface tension (σ) of monosulphate (1), disulphate (2) and ethoxylate C_8 (3) upon the concentration of their solutions at 20° C.

area per molecule in the adsorption layer. Substituting the sulphate group (ethoxylate C_8 , XI) with sulphonate (isethionate C_8 , VIII), the solubility and area per molecule are subjected to the same decrease by 23.0 and 22.8 per cent, accordingly.

4. The wetting power of the solutions is estimated by the wetting angle (θ) which is measured in the water solution of the surfactant against paraffin at 20°C [8].

As a rule, the extreme values of the wetting power are obtained before CMC. After CMC the surface tension and the wetting angle do not change. The lowest θ value (38—46 degrees) of the sulphates is attained at the concentration that is considerably higher than CMC (from 4 to $18 \cdot 10^{-3}$ mole/l). The lowest θ value of isethionates and ethoxylate C_8 can be found at CMC or at its significantly higher concentration. The value of the wetting angle, as well as the other properties of the surfactants, depend upon the structure of the molecule. The compounds having a phenylene ring in the middle of the alkyl chain and an intermediate ethoxy group or free hydroxyethylene group at suitable HLB, indicate a good wetting power.

For example, sulphate C_9 (IV), isethionates C_7 — C_8 (VII; VIII), ethoxylate C_8 (XI) and monosulphate (XII) own low θ values (38—40 degrees), nearing CMC or at its relatively low concentration. The sulphate and sulphonate groups have the same wetting power, the θ values of isethionate C_8 and ethoxylate C_8 being equal (40 degrees). By their wetting power, those compounds considerably surpass the sodium lauryl sulphate, and the more relative by structure sec. alkylbenzene sulphonates C_{12} — C_{18} , θ value of which at CMC is equal to 55—60 degrees.

5. The foam number has been measured by Ross-Miles [7]. The foaming power of the surfactant is evaluated by its foam stability H_5/H_0 (height of the foam column in 5 min after its formation over initial height) [13, 14]. The present sulphates and isethionates form a stable foam ($H_5/H_0 \geq 0.85$) at CMC. However, the foam stability of the compounds with an intermediate ethoxy group (isethionates, ethoxylate C_8 and monosulphate) is to some extent lower in comparison with the other compounds (sulphates and disulphate).

The foam stability of the synthesized compounds improves in hard water.

The maximum height of the foam column (170—190 mm) for every preparations is attained at a higher concentration of CMC; at that the H_0 value of sulphates subdues the corresponding value of isethionates.

6. Emulsifying power (ϵ) is measured by the stability of the emulsion generated by condensation of steam into the mixture of solution of surfactant and the white mineral oil [15]. The same factors affect the foam stability as well as the emulsifying power. Increasing molecule mass and concentration of preparations, the ϵ value grows regularly. The intermediate ethoxy group and the approaching of benzene ring to the centre of radical decrease the emulsifying power to some extent (ϵ value of 0.3 per cent solution of sulphates C_6 — C_{10} is equal to 9—21.9 per cent, for isethionates C_6 — C_{10} 9.0—17.0 per cent).

Conclusions

1. The physico-chemical properties of surfactants synthesized on the basis of alkylaromatic alcohols have been investigated.
2. It has been demonstrated that the position of the phenylene ring in the middle of the aliphatic chain increases solubility considerably, decreasing surface tension, CMC and the wetting angle of surfactant.

3. It has been determined that the position of the phenylene ring in the middle of aliphatic chain accompanied by an intermediate ether bond or free hydroxyethyl group, decreases surface excess concentration, increasing the wetting and the foaming power.

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STRUKTUURIELEMENTIDE MÕJUST ALKUULAROMAATSETE ALKOHOLIDE PINDAKTIIVSETE DERIVAATIDE FÜSIKALIS-KEEMILISTELE OMADUSTELE

On uuritud sek. alküül-2-fenüületanoolide naatriumisoolade, sek. alküül-2-fenüületüül-oksüetaansulfohapete naatriumisoolade ja sek. 1-alküül-2,4-hüdroksüetüülbenseenide sulfoestrite naatriumisoolade vesilahuste füüsikalise-keemiliste omaduste sõltuvust struktuurist. On määratud nende ainete lahustuvus, tihedus, pindpinevus, kriitiline mitsellimoodustamiskontsentratsioon, adsorptsioonikihi molekulaarparameetrid, määrgamis-, vahumoodustamis- ja emulgeerimisvõime.

Я. ИЙЕРС, Хелье УРБЕЛЬ

ВЛИЯНИЕ СТРУКТУРНЫХ ЭЛЕМЕНТОВ НА ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ПОВЕРХНОСТНО-АКТИВНЫХ ПРОИЗВОДНЫХ АЛКИЛАРОМАТИЧЕСКИХ СПИРТОВ

Исследована зависимость физико-химических свойств от структуры натриевых солей сульфозэфиров втор. алкил-2-фенилэтанолов, натриевых солей втор. алкил-2-фенилэтилоксизтансульфокислот и натриевых солей сульфозэфиров втор. 1-алкил-2,4-гидроксизтилбензолов. Установлены растворимость, плотность, поверхностное натяжение, критическая концентрация мицеллообразования, молекулярные параметры адсорбционного слоя, смачивающая, пенообразующая и эмульгирующая способности.