

Synthesis and Studies on Surface and Self-assembly Properties of Polyphenylsulfonates in Aqueous Solution. Part 1: Sodium 5'-Phenyl-1,1':3',1''-terphenyl-4-sulfonate

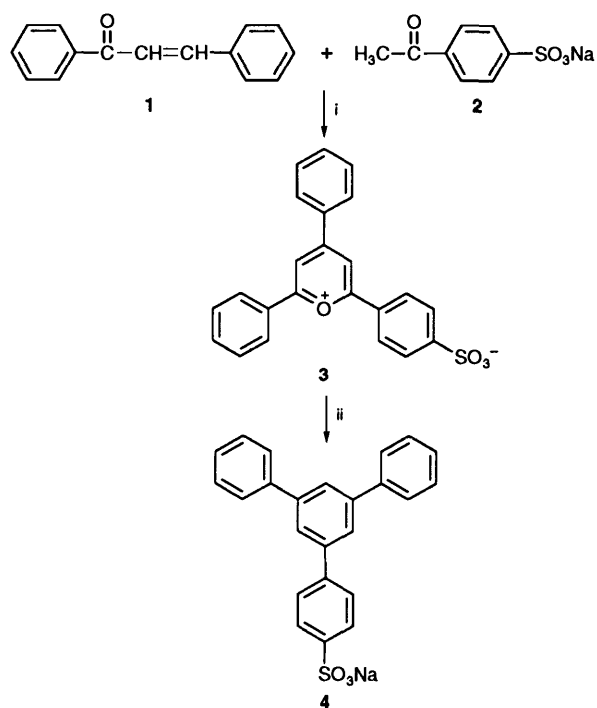
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The title compound represents an unexplored class of amphiphiles. Their hydrophobic moiety is solely aromatic and consists of an uncondensed polyphenyl system. Micellization of such amphiphiles in aqueous solutions should lead to assemblies with a unique structural feature in that the core of the micelle would consist of a non-rigid system of arenic hydrocarbons. Results of surface tension measurements, at 25 °C, of solutions of the studied salt suggest that association occurs already at the concentration of $ca. 1 \times 10^{-3} \text{ mol dm}^{-3}$ in pure water and $4 \times 10^{-5} \text{ mol dm}^{-3}$ in 0.02 mol dm^{-3} NaCl. The solubility of the salt in water increases exponentially with temperature. Results of vapour pressure osmometry obtained at 45 and 60 °C confirm extensive self-assembly processes in aqueous solutions of the salt.

There is abundant literature on solubility, surface activity and self-assembly properties of amphiphilic sulfonates in aqueous and nonaqueous solutions. Interest has been focused mainly on alkylsulfonates, alkylbenzenesulfonates, dialkylphthalenesulfonates, bis(2-ethylhexyl)sulfosuccinates and sulfobetaines.

The hydrophobic moieties of all these amphiphiles consist exclusively or mainly of long-chain aliphatic hydrocarbons. It seemed interesting to investigate the surface and colloidal properties of amphiphilic sulfonates with the hydrophobic moiety composed solely of a polyphenyl, uncondensed and non-rigid system. It is well known that the hydrophobic character of a phenylene group, as evaluated by comparison of the surface activity or critical micelle concentration (c.m.c.) of appropriate pairs of amphiphiles, corresponds to that of an aliphatic hydrocarbon chain composed of 4 ± 0.5 methylene groups. This aspect of fragmental hydrophobicity has been recently discussed by van Oss *et al.*¹ One might thus expect marked surface and self-assembly activity of sulfonated terphenyls and their phenyl-substituted derivatives in aqueous solutions. Amphiphiles of this type appear not to have been reported as yet. Micellization of such salts should lead to assemblies with a unique structural feature in that the core of the micelle would consist of arenic hydrocarbons. Sulfonation of polyphenyls is presumably an easy task. Problems may, however, arise upon attempting the separation of the mixture of monosulfonated isomers. We have thus decided to prepare a model salt, **4**, by adopting a two-step synthetic route, through a pyrylium salt, **3**, as shown on Scheme 1. The pyrylium salt was synthesized by condensing benzylideneacetophenone, **1**, with sodium *p*-acetylbenzenesulfonate, **2**, in the presence of perchloric acid, according to the general procedure given earlier.² It was then transformed into the salt **4**, hereafter referred to as SPhTS1, a derivative of symmetrical triphenylbenzene, by applying the procedure described by Zimmermann and Fischer.³

It is worth mentioning that the colloidal properties of sulfonic acids with a system of fused aromatic rings have been revealed already by Sandquist⁴ who has shown, through conductivity, diffusion and cryoscopic measurements, that phenanthrene-3-sulfonic acid and its 9-halogenoderivatives aggregate in aqueous solutions. These studies were later extended by Bolam and Hope.⁵ Another early report is from Norris⁶ who found that sodium anthraquinonesulfonate is more colloidal than sodium naphthalenesulfonates. There exists abundant literature on aggregational properties of anionic dyes, mainly in the form



Scheme 1

of sulfonates, reviewed by Burdett.⁷ The colloidal properties of drugs which have in their structure a fused system of aromatic rings or a non-rigid polyphenyl system with a methylene bridge have been reviewed by Attwood and Florence.⁸ Such drugs bear, apart from the aromatic system, an aliphatic chain linked to a hydrophilic functional group which, most frequently, is an amine group. In this paper we will refer mainly to single and double-tailed *p*-alkylbenzenesulfonates which have been studied very intensively during the last decade of years as model colloidal electrolytes. We treat the latter type of salts as aliphatic analogues of SPhTS1.

Experimental

Elemental and thermogravimetric analyses were performed by the Regional Laboratory of Physico-Chemical Analyses, Kraków. IR spectra were recorded with an IR 75 Specord

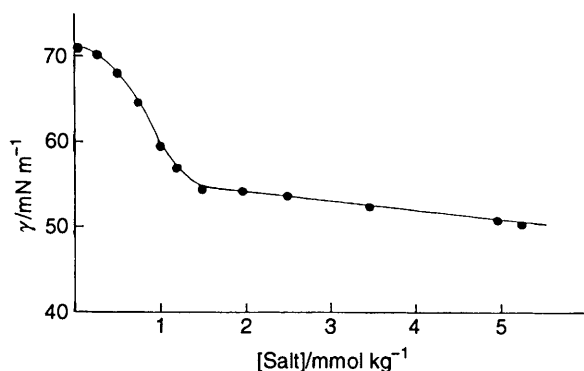


Fig. 1 Surface tension of aqueous solutions of SPhTS1 at 25 °C

(Zeiss, Jena) spectrometer as nujol mulls. UV spectra were recorded on a UV/VIS Specord (Zeiss, Jena) and a Shimadzu UV 2100 spectrometer. ¹H NMR spectra were taken at 100.0 MHz with a Tesla BSS67 A spectrometer using [²H₆] DMSO as solvent and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard. Vapour pressure osmometry measurements at 45 and 60 °C were carried out on a Knauer type osmometer. Sodium chloride of AR grade, dried at 250 °C for 2 h and sodium benzenesulfonate recrystallized three times from ethanol were used as reference solutes.

Solubility measurement. A suspension of SPhTS1 in aqueous solution was vigorously stirred for 2 h, the temperature being controlled to within ± 0.02 °C. An aliquot of the suspension was then withdrawn and filtered at the same temperature in a chamber equilibrated with vapours of the solvent. The absorption band in UV was used for determination of concentration of the filtrate after proper dilution. At higher temperatures the solubility was determined both spectrophotometrically and by weighing the residue left after evaporation of the solvent first under vacuum and then by heating at 120 °C.

Surface tension measurement. The drop weight method was used at 25 °C in a thermostat controlled to within ± 0.1 °C. The time duration for 1 drop was 2 to 3 min.

2,4-Diphenyl-6-(4-sulfophenyl)pyrylium Hydroxide. Inner Salt 3.—Sodium 4-acetylbenzenesulfonate **2** (Aldrich) (8.9 g, 40.0 mmol), benzylideneacetophenone **1** (16.6 g, 80.0 mmol) and perchloric acid (10 cm³, 70%) were heated at 100 °C for 2 h with constant stirring. Ethanol (200 cm³) was added to the hot oil and the mixture was heated at reflux for 30 min, then cooled to room temp. and the yellow precipitate filtered off and washed with hot ethanol (100 cm³). The pyrylium salt was purified first by refluxing in acetic acid (100 cm³), then by triturating with cold water (500 cm³) and finally by refluxing in acetone (200 cm³). The product was dried *in vacuo* over P₂O₅ and then air-conditioned. Repeated drying–air-conditioning indicated reversible formation of a hemihydrate as found by weighing and confirmed thermogravimetrically. Higher hydrates were formed when the salt was equilibrated with water vapour. Decomposition of the dry salt occurred at 365 °C. Yield 7.3 g (47%) (Found: C, 69.45; H, 4.1; S, 8.1. Calc. for C₂₃H₁₆O₄S·½H₂O: C, 69.51; H, 4.31; S, 8.07%; ν_{max}/cm⁻¹ 3600–3200, 1630, 1590, 1490, 1270–1190 and 1090; δ_H 9.20 (s, 2 H, pyrylium ring protons), 8.7–8.6 (m, 6 H, *o* to pyrylium ring) and 8.2–7.8 (m, 8 H).

Sodium 5'-Phenyl-1,1':3',1''-terphenyl-4-sulfonate 4.—Pyrylium salt **3** (6.6 g, 15 mmol) and anhydrous sodium acetate (3.7 g, 45 mmol) were refluxed in acetic anhydride (30 cm³) for 3 h with constant stirring, with occasional bubbling of argon through the mixture. The yellow suspension changed to a brown solution in the course of the reaction. The mixture was cooled to room

temp. and left overnight. The precipitate was separated and washed with ethyl acetate and diethyl ether. It was then crystallized from ethanol and propanol and finally twice from water. The salt formed a trihydrate when equilibrated with vapours of its aqueous solution saturated at 25 °C. Yield 2.7 g (35%). When stored at room temp. in air the salt underwent efflorescence to an extent dependent upon the humidity. Thermogravimetric analysis indicated that the water molecules were lost upon heating to 85 °C. The salt did not undergo decomposition at temperatures < 350 °C (Found: C, 60.9; H, 5.1. Calc. for C₂₄H₁₇SO₃Na·3H₂O: C, 62.33; H, 5.01%); the residue (consisting presumably of sodium carbonate) left in the furnace, amounting to 14.1% of the weight of the analyzed sample, accounts for the low content of C found. ν_{max}/cm⁻¹ 3650–3200, 1660–1620, 1590, 1570, 1210–1190 and 1030; δ_H 7.95–7.30 (m, 17 H, aromatic protons).

Results and Discussion

The UV absorption spectrum at room temp. of a 1.25 × 10⁻⁵ mol dm⁻³ aqueous solution of SPhTS1 shows a maximum at λ = 256.5 nm; ε = 5870 m² mol⁻¹, which does not change significantly within the concentration range of 1–50 × 10⁻⁵ mol dm⁻³. Sodium chloride strongly reduces the solubility of SPhTS1 as expected but has negligible influence on its spectrum.

The concentration dependence of the surface tension of aqueous solutions of SPhTS1 at 25 °C is shown in Fig. 1. A break in the slope of the plot is observed at a concentration of *ca.* 0.0015 mol dm⁻³. At higher concentrations, limited by solubility of SPhTS1, the decrease of the surface tension is not halted, as is the case for typical micellizing systems. A similar pattern of the γ vs. [salt] plot was observed for solutions of SPhTS1 in 0.02 mol dm⁻³ NaCl, the break being shifted to a concentration of *ca.* 1.5 × 10⁻⁴ mol dm⁻³.

We consider these breaks to be due either to a critical micellization concentration (c.m.c.) or to the onset of a stepwise, non-micellar association process leading initially to dimers and consequently to higher oligomers. The gradual decrease of surface tension with increase of concentration in the micellar region would indicate a high degree of ionization of small micelles. Although we were unable to trace in the available literature similar patterns of surface tension vs. concentration plots, some related results seem to support this view. Thus, *e.g.* a pre-micellar aggregation of the symmetrical double-tailed sodium 4-(1'-heptyloctyl)benzenesulfonate has been suggested recently by Mikulski *et al.*⁹ who found an abnormal course of the dependence of molar conductivity on the square root of concentration of the salt at 25, 35 and 45 °C. Characteristic bumps appeared on the plots at concentrations of *ca.* 1 × 10⁻⁴ mol dm⁻³. A large value of the micelle ionization degree amounting to 0.69 and a small aggregation number of 32 was determined by Lianos and Lang¹⁰ from the variation of conductance as a function of concentration of sodium 4-(1'-propylonyl)benzenesulfonate. In line with these results Zana *et al.*¹¹ found from conductivity measurements that the ionization degree of sodium 4-(1'-hexyloctyl)benzenesulfonate amounts to 0.71 ± 0.05 at 25 °C and to 0.78 ± 0.06 at 52 °C. The fluorescence quenching technique used by the authors yielded a value of 39 ± 4 for the aggregation number of the salt. Small angle neutron scattering measurements were carried out by Caponetti *et al.*¹² to demonstrate, among others, the difference between the degrees of dissociation (0.5 vs. 0.3) and aggregation number (44 vs. 89) for sodium 4-(1'-pentylheptyl)benzenesulfonate and for the isomeric 4-dodecylbenzenesulfonate respectively.

It is of some interest to note that the surface excess concentration, Γ, of SPhTS1, calculated using Gibb's adsorp-

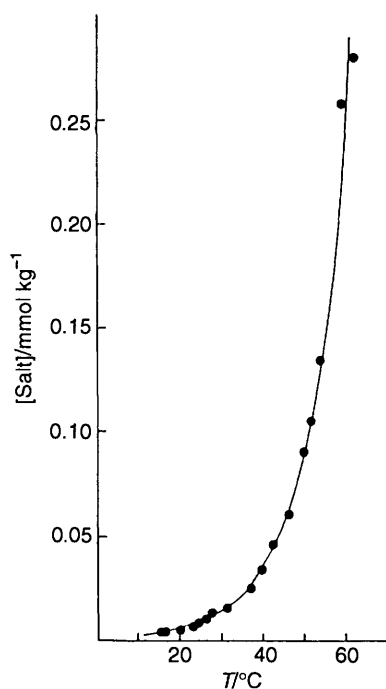


Fig. 2 Temperature dependence of solubility of SPhTS1 in water

tion equation $\Gamma = (C/nRT)/(d\gamma/dC)$, with $n = 2$ for solutions in pure water and $n = 1$ for solutions in 0.02 mol dm^{-3} NaCl, increase linearly with concentration up to the observed breaks and then decrease, almost symmetrically, at higher concentrations. The intersections of the two linear plots, corresponding to Γ_{\max} , occur at $C = 9.25 \times 10^{-4}$ and $4.2 \times 10^{-5} \text{ mol dm}^{-3}$ respectively. The minimum area, A_{\min} , for surfactant molecule at the air-aqueous solution interface, calculated from the relation $A_{\min} = 1/N_A \Gamma_{\max}$, where N_A is Avogadro's number, amounts to 0.46 and 0.23 nm^2 for solutions in pure water and in 0.02 mol dm^{-3} NaCl respectively. Surprisingly, these values are markedly lower, by comparison, than data reported for sodium dodecylbenzenesulfonate: 0.50 nm^2 (0.01 mol dm^{-3} NaCl; 25°C)¹³ and 0.45 nm^2 (estimated from Γ_{\max} , 0.1 mol dm^{-3} NaCl; 70°C).¹⁴ Waligóra *et al.*¹⁵ however, report a value of 0.29 nm^2 only (0.1 mol dm^{-3} NaCl; 25°C). It is worth noting that a bulky double-tailed substituent at the *para*-position in respect to the sulfonate group does not lead to an increase in the area occupied by the molecule at the interface. And thus, Lascaux *et al.*¹⁶ report a value of $0.45 \pm 0.03 \text{ nm}^2$ for a series six isomeric sodium hexadecylbenzenesulfonates ranging from 4-(1'-ethyltetradecyl)benzenesulfonate to 4-(1'-heptylnonyl)benzenesulfonate (9×10^{-4} – $7 \times 10^{-2} \text{ mol dm}^{-3}$ NaCl; 45°C). Introduction of two vicinal methyl substituents into the benzene ring of the surfactant leads to a marked increase in the surface area occupied by the molecule as shown by Varadaraj *et al.*¹⁷ for sodium 2,3-dimethyl-4-dodecylbenzenesulfonate (1.07 nm^2 at 65°C and 1.11 nm^2 at 75°C ; 0.1 mol dm^{-3} NaCl). However, when both methyl groups are situated *ortho* to the sulfonate group, the area per molecule appears to be unaffected by the substituents as shown by the data of Sivakumar¹⁸ for sodium 4-(1'-propyloctyl)-2,5-dimethylbenzenesulfonate (0.46 nm^2 , 43°C , 0.03 mol dm^{-3} NaCl). It thus appears that the molecules of SPhTS1 adsorbed at the air-water interface undergo strong interaction, presumably leading to tile-like stacking.

A cooperative process of aggregation of SPhTS1 in water is seen upon inspection of the solubility curve measured for the temperature range of 16 – 65°C (Fig. 2). At more elevated temperatures the saturated isotropic solutions were markedly viscous. The slope of the plot increases gradually with temperature and the solubility can be described by the relation:

$$\ln m = (0.095 \pm 0.001)T - 7.219 \pm 0.044 \quad (1)$$

where m denotes molality and T the temperature in degrees Celsius. Eqn (1) yields, for 20 and 60°C , values of $0.0049m$ and $0.224m$ respectively, which corresponds to a 45.7 fold increase in solubility. The data of Fabre and Kamenka¹⁹ for dodecylbenzenesulfonate indicate a 49 fold increase in solubility over this temperature range, the upper limit being well above the accepted Krafft point.¹ According to an early report of Tartar *et al.*²⁰ the solubility of the salt in this temperature range increases by a factor of 17.5 only. Gershman²¹ determined solubility-temperature curves for branched alkylbenzenesulfonates with a general formula sodium 4-(1'-methylalkyl)benzenesulfonate where the alkyl group contained 10 to 16 carbon atoms. The log m vs. temperature plots exhibited more or less distinct breaks which were assumed to correspond to c.m.c. at the Krafft points. The plots were linear in the pre- and post-micellar region. Micellization induced an enhanced solubility of the salts, the increase amounting to an order of magnitude over a range 2 – 5°C . A very low increase in solubility was reported by Franes *et al.*²² for the double-tailed sodium 4-(1'-heptylnonyl)benzenesulfonate. The solubilities amounted to $0.06 \text{ wt}\%$ at 25°C and $0.7 \text{ wt}\%$ at 90°C , which corresponds to a 11.7 fold increase over the broad temperature range. The surfactant forms a lamellar liquid crystalline phase upon hydration already at room temp. According to Magid *et al.*²³ this liquid crystalline phase is in equilibrium with a micellar state in the aqueous phase. A homologue of this salt, shorter by two methylene groups, namely sodium 4-(1'-hexyloctyl)benzenesulfonate, does not form a liquid crystalline phase. Its solubility in water is higher by an order of magnitude (0.5%) at room temp. and the clarification temperature increases nearly linearly with concentration.¹¹

It thus appears that the temperature dependence of solubility of alkylbenzenesulfonates and of SPhTS1 does not conform to the phase separation model which predicts a dramatic increase in solubility above the Krafft point. Well known examples of surfactants which fit to this model are the cationic hexadecyltrimethylammonium bromide with the transition point at 26.6°C ²⁴ and the anionic sodium dodecylsulfate for which Franes *et al.*²⁵ report a narrow temperature range of $28 \pm 1^\circ\text{C}$ above which the solubility of the surfactant in 0.6 mol dm^{-3} NaCl increases more than 500 -fold. Lack of a distinct transition point on the solubility curves was however observed on several other occasions and in this context Moroi and Matuura²⁶ suggest that since the Krafft point is not a single point but a diffuse temperature range it might be called the micelle temperature range (MTR) or a Krafft range. They argue that the observed phenomena of surfactant solutions can be explained by the mass action model for micelle formation. The MTR is thus a narrow temperature range over which the surfactant solubility of monomers becomes sufficiently high for monomers to start micellization. This aspect of solubility of alkylsulfates was also discussed by Gaboriaud, Charbit and Dorion.²⁷

Upon examining the temperature dependence of solubility of SPhTS1 presented on Fig. 2, one might be tempted to estimate a 'break' or MTR on the plot *e.g.* by drawing tangents to the slopes of the solubility *versus* temperature curve, and reading off their point of intersection. Such a procedure is, in this case, misleading since the apparent break depends strongly on the solubility scale adopted. It is worth noting that a mathematical analysis of the $m = A \exp^{kt}$ relation which describes the course of the plot on Fig. 1 ($A = \exp^{-0.077}$ and $k = 0.095$) shows that the maximum of the curvature of the m vs. T plot occurs at the temperature of 96.9°C ! The solubility at that temperature would amount to *ca.* $7m$ which corresponds to an $81 \text{ wt}\%$ solution with a composition of 1 mol of SPhTS1 and 7 mol of water.

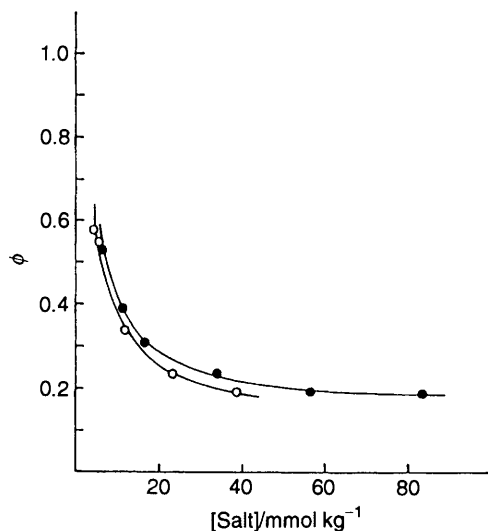


Fig. 3 Relative osmotic coefficients of SPPhTS1 in water at 45 (○) and 60 °C (●)

Extensive aggregation of SPPhTS1 already at concentrations of the order of $5 \times 10^{-3} m$, at the temperatures of 45 and 60 °C, is evidenced by the vapour phase osmometry results shown in Fig. 3 where ϕ is the relative osmotic coefficient *i.e.* it represents the ratio of response of the osmometer reading for SPPhTS1 and for NaCl of equal molalities. The osmometer readings for NaCl and sodium benzenesulfonate were the same within the experimental error of $\pm 5\%$ at the concentration range applied for SPPhTS1. It is the terphenyl group, in the *para* position with respect to the sulfonate group of the parent compound, which imparts to SPPhTS1 the strong tendency to aggregate in aqueous solutions. The present results do not allow speculation about the size of the aggregates and their polydispersity, but they show, however that terphenyl sulfonates may serve as model surfactants for comparative studies of colloidal properties of classical micelles with a polymethylene core and of those with an interior composed of polyphenylene groups.

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