Synthesis and studies on surface and self-assembly properties of polyphenylsulfonates in aqueous solution. Part 2.[1] Sodium 2'-methyl-5'-phenyl-1,1':3',1"-terphenyl-4-sulfonate

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A study of the effect of introduction of a methyl group into the central benzene ring of the symmetrical triphenylbenzene sulfonate on its aggregation behaviour in aqueous solutions has been carried out. The solubility of the sodium salt in water is enhanced and its saturated solution at 25 °C is in equilibrium with a lamellar liquid crystalline phase. The onset of aggregation of the salt was revealed by surface tension measurements. Conductivity data suggest that dimerization precedes the formation of higher oligomeric species. Extensive self-assembly processes have been confirmed by vapour pressure osmometry.

Association of surface active colloidal electrolytes in aqueous solutions occurs due to the hydrophobic interactions of their hydrocarbon moieties.[2] Typically, the hydrophobic part of such electrolytes consists of a single long aliphatic chain usually called the 'tail'.[3] Recently we have described an amphiphilic surfactant namely, sodium 5'-phenyl-1,1':3',1"-terphenyl-4-sulfonate (SPhTS), whose hydrocarbon moiety is solely aromatic being composed of the symmetrical triphenylbenzene ring system. Results of vapour pressure osmometry have shown that the salt undergoes extensive aggregation in aqueous solutions at 45 and 60 °C. However, a Krafft point, which is characteristic for single-chain amphiphiles could not be revealed on the solubility curve for SPhTS in water. It was found that the solubility increases exponentially over the temperature range of 15 to 65 °C. The onset of self-assembly seems to occur at the concentration of *ca.* 0.0015 mol dm^{-3} as judged from the break on the surface tension isotherm at 25 °C.[1] Extensive conductivity measurements of aqueous solutions of SPhTS carried out at 25, 32.5 and 40 °C and of the acid (SPhTH) at 25 °C also revealed breaks on the conductivity *vs.* molality plots at concentrations close to that found on the surface tension isotherm.[4] Plots of equivalent conductivity *vs.* square root of molality for SPhTS exhibited undulations in the vicinity of the concentrations where onset of association was assumed and it was suggested that such anomalous behaviour was due to the existence of dimers at concentrations well below the operational critical micelle concentration (cmc).

It appears that SPhTS, with the non-rigid, uncondensed triphenylbenzene ring system, does not associate in a mode characteristic for single-chain aliphatic electrolytes. A co-operative multi-step stacking process seems rather to operate in aqueous solutions of this salt. Its solubility at room temperature is, however, too low to enable broad investigations of its colloidal properties. The present work was undertaken with the aim of elaborating a related sodium polyphenylsulfonate whose solubility would be markedly enhanced. It was assumed that introduction of an inert substituent to the triphenylbenzene ring system, *e.g.* of a methyl group, would lower the crystallinity of the salt of interest which should lead to a decrease in the melting point and hence to an increase of its solubility.[5] Accordingly, the mps of the parent 1,3,5-triphenylbenzene and 1,3,5-triphenyl-2-methylbenzene are 173 and 135 °C, respectively.[6] Synthesis of the appropriate sulfonate with the methyl group at the central benzene ring in the triphenylbenzene system was carried out by adapting the general synthetic route described by Zimmerman and Fisher.[6] The reaction is illustrated in Scheme 1. The salt under study will be abbreviated as SMePhTS.

$(C_2H_5CO)_2O/C_2H_5COONa$ $|-CO_2, -C_2H_5COOH$

Scheme 1
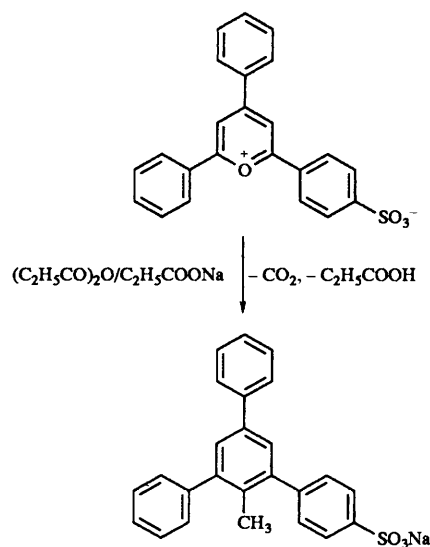
Experimental

Thermogravimetrical analyses were performed on a Derivatograph-C (MOM-Budapest).

IR spectra were recorded on a Bruker IFS48 spectrometer as KBr pellets. UV spectra were recorded on a UV/VIS Specord (Zeiss Jena) and a UV H.P. 8452A spectrometer. ^1H NMR spectra were taken at 500 MHz with a Bruker AMX500 spectrometer using D_2O as solvent and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal standard. Vapour pressure osmometry and surface tension measurements were carried out as described previously.[1] Conductivity measurements were performed at 25 ± 0.1 °C using a Radelkis type OK-102/1 meter. The cell constant was determined using KCl solutions. Aqueous solutions were equilibrated with atmospheric carbon dioxide and corrections were made for solvent conductivity. The molality changes were performed by step-wise additions of fixed amounts of water to the concentrated solution of SMePhTS. Equilibrium conductivity values were obtained within 5 mins. The solubility of SMePhTS in water was determined as follows: a portion of the aqueous suspension, equilibrated for several days at 25 ± 0.05 °C was withdrawn, filtered through a 0.22 mμ millipore filter, weighed, properly diluted and analysed spectrophotometrically in the UV region.

Sodium 2'-methyl-5'-phenyl-1,1':3',1''-terphenyl-4-sulfonate

The pyrylium salt[1] (see Scheme 1) (3.2 g, 8 mmol) and well powdered, anhydrous sodium propionate (2.3 g, 24 mmol) were gently refluxed in propionic anhydride (15 cm^3) for 3 h with constant stirring. The yellow suspension underwent gradual dissolution accompanied by evolution of carbon dioxide. The mixture was then cooled to room temperature, left overnight and the solidified material was triturated several times with diethyl ether and dried in air. Ethanol (40 cm^3) was added to the crude product and the mixture was refluxed for 10 min. After cooling the precipitate was separated and washed with a small amount of cold ethanol. The product was recrystallized twice from aq. NaCl and then from ethanol (96%). The salt was dried in air then heated at 120 °C to constant weight and kept over P$_2$O$_5$: yield 1.33 g (39.4%). SMePhTS forms an ill-defined hydrate when kept under ambient conditions. For the present purposes the salt was recrystallized additionally from propanol and from ethanol.

Thermogravimetric analysis indicated that the water molecules were lost at 83.7 °C (9.6% by weight). Decomposition of the salt occurred at 331 °C. ν_{max}/cm^{-1} 3449v br (OH), 3042 (CH), 1598, 1567, 1496 (aromatic rings) and 1191v str (SO$_3^-$); δ_H 1.35 (s, 3 H, CH$_3$), 6.51–6.70 (m, 14 H, protons at peripheral aromatic rings) and 7.57 (s, 2 H, protons at the central aromatic ring).

Results and discussion

The UV adsorption spectra at room temperature of a 2.00 × 10^{-5} mol dm^{-3} aqueous solution of SMePhTS has a maximum at 248 nm; $\varepsilon = 2235$ m^2 mol^{-1}. The corresponding values for SPhTs are 256.6 nm and 5870 m^2 mol^{-1}. The blue shifted maximum and the reduced value of ε is an indication of steric hindrance and an increased departure from coplanarity of the phenyl groups in the terphenyl ring system due to the presence of a 2'-methyl group. This observation is in accord with differences found upon comparison of spectra for biphenyl[7] and sym-triphenylbenzene,[6] respectively.

The fact that the peripheral phenyl rings are more strongly twisted out of plane of the central ring which carries a methyl substituent leads, as expected, to a decrease in crystallinity of the salt which is manifested in the fact that the SMePhTS crystals swell in water at room temperature and undergo transformation into a lamellar liquid crystal phase as judged from polarized-light microscopy observations. This phase is in equilibrium with an isotropic micellar phase whose molality amounts to 0.026 m† at 25 °C. By comparison, the molality of SPhTS in a saturated aqueous solution at that temperature equals 0.0079 m. It should be noted that the 'instantaneous' solubility of SMePhTS in water at 25 °C is higher than the equilibrium value here reported. A slightly opalescent solution is formed upon dissolution of the salt and, when kept overnight a second phase separates out presumably due to some ordering processes occurring in the solution. It is worth noting that the effect of introduction of a methyl group into the central benzene ring of SPhTS on the solubility of the salt in water, although marked, is not so dramatic as observed in the case of the tetramethyl- and ethyltrimethyl-ammonium bromides where the difference in their solubilities in chloroform is 77-fold.[8]

The general pattern of the concentration dependence of the surface tension of aqueous solutions of SMePhTS is similar to that found for SPhTS,[1] i.e. a further slight decrease of surface tension is observed with growth of concentration of the amphiphile above a distinct break indicating the onset of aggregation. The break occurs at a concentration of 1.0 mmol dm^{-3} which is lower by a factor of about 1.5 when compared with the corresponding value found for SPhTS. Note that a
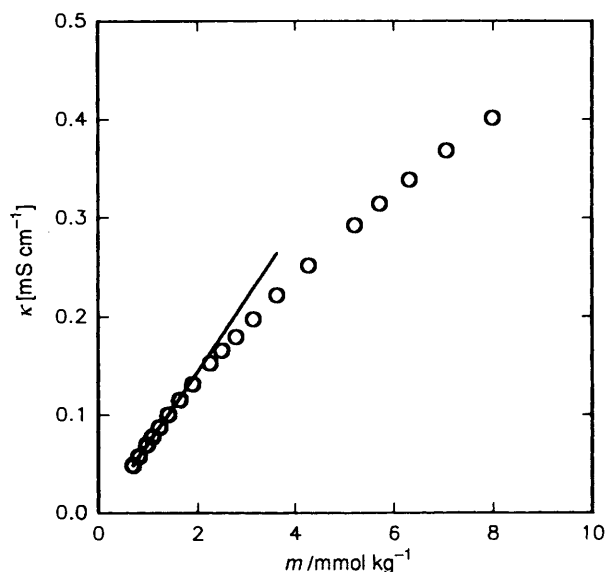
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† 1 m = 1 mol kg^{-1}

Fig. 1   Specific conductivity vs. molality of SMePhTS

factor of 2 is generally found for cmc values of homologous single-chain amphiphiles differing by one methylene group. It appears that the methyl group in SMePhTS is partly shielded by the phenyl groups leading thus to a decrease in the strength of hydrophobic interactions.

The pC_{20} and the cmc/pC_{20} values for SMePhTS amount to 3.0 and 1, respectively. pC_{20} is the negative logarithm of the concentration at which a surface tension of 52 mN m^{-1} is reached[9] and the operational cmc is taken here to be equal to the concentration at which the break on the surface tension isotherm is observed. The low value of the cmc/C_{20} ratio indicates that SMePhTS has a stronger tendency to aggregate than to adsorb at the solution–air interface.

Aggregation of SMePhTS in aqueous solutions has been confirmed by conductometry. The specific conductivity vs. molality curve for SMePhTS is shown in Fig. 1. A departure from linearity occurs at 1.56 mmol kg^{-1} and corresponds to the break at 1.0 mmol dm^{-1} observed on the surface tension isotherm. At higher molalities the plot on Fig. 1 appears to be slightly concave. Conductometry appears to be less sensitive to the onset of aggregation than the surface tension probe. Indeed for SPhTS the break on the conductivity vs. molality plot was found at 1.98 mmol kg^{-1}.[4] The corresponding break on the surface tension isotherm amounted to 1.50 mmol dm^{-3}.[1] A reason for this finding will be given below. The ratio of the slopes of the linear fragments in the conductivity plots has been frequently treated as a measure of the degree of counter-ion binding to the micelles. Prior to such interpretations one should, however, examine the shape of the equivalent conductivity vs. square root of molality plots. Such a plot for SMePhTs is shown in Fig. 2. It is immediately apparent that the conductance behaviour of the salt is anomalous. The equivalent conductivity actually increases in the low concentration range instead of assuming a negative Onsager slope. A similar observation was made in the case of SPhTS at 25, 32.5 and 40 °C and of the corresponding acid, SPhTH, at 25 °C.[4] The anomaly occurs in the vicinity of the operational cmc corresponding to the breaks found on the surface tension and conductivity isotherms.

Positive deviations from the Onsager slopes, although not so profound as in the case of the polyphenylsulfonates have been observed on several occasions. Early findings of this type were reviewed by Mukerjee et al.[10] who thoroughly discussed the conductivity behaviour of sodium dodecylsulfate (SDS) and ascribed the observed deviations to dimerization of the amphiphile. It is worth noting that their observations have
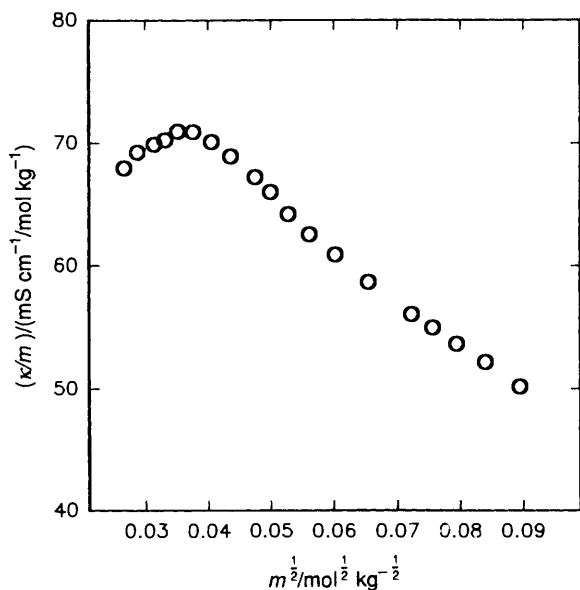
Fig. 2 Equivalent conductivity *vs.* square root of molality of SMePhTS

salt far beyond dimerization. Within the experimental error v.p.o. results for the low concentration range were comparable with those obtained for the parent SPhTS.[1]

The tendency to form lamellar structures exhibited by SMePhTS once again shows resemblance to the behaviour of double-tailed benzene sulfonates which are well known to form lyotropic lamellar liquid-crystalline phases.[14–16] It seems interesting to note that according to the model of Israelachvili et al.,[17] packing of molecules into a lamellar array may be facilitated by an increase in the v/al ratio. Here v would be the volume of the triphenylbenzene moiety, l its length and a the area of the sulfonate group. The volume occupied by the polyphenyl system can be augmented by the increase in the dihedral angle between the planes of the phenyl rings. Qualitative considerations suggest that in the present case this effect was achieved by the steric hindrance of the methyl group at the central benzene ring. In conclusion it may be stated that a small substituent properly situated in the terphenyl ring system dramatically influences the colloidal properties of polyphenylsulfonates.

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neither been confirmed nor denied by later numerous conductivity studies on SDS.[11] Quite recently Mikulski et al.[12] found that the symmetrical double-tailed sodium 4-(1'-heptyloctyl)benzenesulfonate exhibited characteristic undulations on the equivalent conductivity *vs.* square root of concentration plot and ascribed them to premicellar aggregation. This type of salt seems to be an aliphatic analogue of SPhTS, both amphiphiles having the sulfonic group attached to a benzene ring, the double-tailed aliphatic group at the *para* position being substituted by a terphenyl group. The tendency to form dimers appears to increase with the number of π electronic bonds in the hydrophobic moiety. The presence of an aromatic ring system is not, however, a prerequisite for this phenomenon since Boyd[13] has shown that sodium hexacyanoheptatrienide undergoes reversible dimerization in aqueous solution. The effect of dimerization of the salt was so marked that its equivalent conductivity in water plotted against square root of concentration increased almost linearly throughout the whole concentration range studied. The anomalous behaviour of polyphenylsulfonates occurs at too narrow concentration ranges to undertake attempts to estimate their dimerization constants. Formation of dimers of the studied amphiphiles may explain the observation that the breaks on the conductivity *vs.* concentration plots were systematically found at higher concentrations than those read out from surface tension isotherms. In the latter case the breaks indicate the detectable onset of formation of dimers which presumably are not surface active although their contribution to conductivity is still high. The breaks on the conductivity isotherms seem to be closer to the onset of formation of micellar systems. The enhanced solubility of SMePhTS enabled the extension of the range of concentration for vapour pressure osmometry studies at 45 °C up to 0.12 mol kg^{-1} where the relative association coefficient dropped down to 0.16 indicating extensive aggregation of the