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Effect of sodium salicylate on the solution properties of sodium dodecyl sulphate

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Summary

The effect of sodium salicylate at low and high concentration levels on some solution properties of sodium dodecyl sulphate (SDS), namely critical micelle temperature (CMT), critical micelle concentration (CMC) and micellar solubilisation, was investigated. Sodium salicylate (SS) exerts a dual effect on these properties depending on the concentration. Relatively low salicylate concentrations result in an increase in CMT, lowering of CMC and enhancement of dye solubilization, probably due to decreased monomer solubility and micellization at lower surfactant concentration. Within the higher concentration range, where the hydrotropic activity of salicylate is displayed, the effect of SS on the above properties is reversed. Increased surfactant solubility and interference with micelle formation account for the results obtained. The effect of SS on the properties of anionic surfactants at a given salicylate concentration may be considered as a consequence of the electrolytic and hydrotropic properties of sodium salicylate.

Introduction

Hydrotropic agents are finding increasingly widespread applications in pharmaceutical formulation as solubilizers and co-solubilizers (Kariss and Newmark, 1964; Woolfson et al., 1986; Darwish et al., 1989; El-Khordagui, 1991), enhancers of drug absorption from different sites (Nishihata et al., 1981, 1983; Osborne, 1988), in the formulation of detergent products and rinse aids (Cox and Friberg, 1981; Otten and Nestor, 1986) and the extractive separation of close boiling point substances (Gaikar and Sharma, 1986). This makes the understanding of the hydrotropic action and the potential interactions of hydrotropes with various systems of practical value.

Hydrotropic agents have been reported to undergo self-aggregation in aqueous solution to form non-covalent molecular assemblies, although the cooperativity of association is much less than that encountered in surfactant systems (Friberg and Rydhag, 1970; Desnoyers et al., 1973; Badwan et al., 1983; Balasubramanian et al., 1989). Aggregate formation appears to occur at a minimum concentration characteristic of each agent and to

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be of relevance to the marked increase in the solubilization capacity of hydrotropic solutions (Badwan et al., 1983; Balasubramanian et al., 1989) and reduction in solvent polarity (Saleh et al., 1986a,b; Balasubramanian et al., 1989). Such changes in the solution properties of hydrotropic agents with concentration may have important implications for systems involving association structures such as surfactants.

Previous investigations of hydrotrope-surfactant systems showed that sodium salicylate (SS) interacts at relatively low concentration with cationic surfactants, inducing a considerable extent of viscoelasticity in solution and the formation of enormously elongated giant micelles (Wan, 1967; Rao et al., 1987; Shikata et al., 1987). A hydrotrope of non-traditional structure, Diacid, was demonstrated to destabilize the lamellar liquid crystalline phases obtained in aqueous dispersions of detergents, thus enhancing the solubility of lipophiles (Cox and Friberg, 1981; Friberg et al., 1986). Further, SS and related benzoate salts were reported to raise the cloud point of the nonionic surfactant Triton X-100 (Valaulikar et al., 1991).

The objective of the present work was to investigate the effect of the hydrotropic agent, SS, over a wide concentration range on the solution properties of a traditional anionic surfactant, sodium dodecyl sulphate (SDS).

Materials and Methods

SDS (BDH Chemicals, Poole, U.K., especially purified grade, min. 99.0%), SS and sodium benzoate (SB) (Riedel-De Haën, Seelze-Hannover, Germany) and Sudan III dye (Prolabo, Rhône-Poulenc, France) were used in the study.

Effect of SS and SB on the critical micelle temperature (CMT) of SDS

SDS was dissolved in SS or SB solutions of the required concentrations to obtain a 3.45×10^{-2} M (1% w/v) solution of the surfactant. The test solutions were kept at 4°C for 2 h to allow the formation of the hydrated SDS solid phase. There was no sign of phase separation when solutions of the benzoate salts were refrigerated. The CMT values were then determined as the midpoint of a narrow temperature range over which the solid phase of SDS dissolves on slow warming (0.5°C/min) with continuous agitation using a magnetic stirrer. The results presented are the averages of five determinations.

Surface tension measurements

The effect of SS (0.02–3.00 M) on the critical micelle concentration (CMC) of SDS was investigated at 26°C using a Wilhelmy balance type tentiometer (Schneider Electronic Tentiometer with automatic calibration, Prolabo, France). A fixed volume of SDS solutions either in water or in SS solutions was used for all measurements. Water was glass-redistilled from alkaline $KMnO_4$. The platinum blade used was cleaned by thorough rinsing and heating to incandescence in a flame between measurements. The data presented are the averages of at least six determinations using a fresh sample per three measurements. All precautions were taken to keep the glassware used meticulously clean and the solution surface undisturbed during measurement.

Solubilization study

The effect of SS at two concentration levels (0.3 and 3.0 M) on the solubilisation of the water-insoluble dye, Sudan III, by SDS was determined at 26°C. After an equilibration period of 72 h, samples were filtered using 0.45 μm Millipore discs, suitably diluted with 0.1 N NaOH and the absorbance determined at 507 nm using a Unicam SP 1800 spectrophotometer.

Results and Discussion

As the temperature of micellar solutions of anionic surfactants is raised slightly above the Krafft point, the temperature at which solid hydrated surfactant and micelles are in equilibrium with monomers (Shinoda and Hutchinson, 1962), the monomer solubility increases, and to restore the solid-monomer equilibrium, the hydrated solid goes into solution as monomers which associate to form micelles (Mazer et al., 1976). The tem-

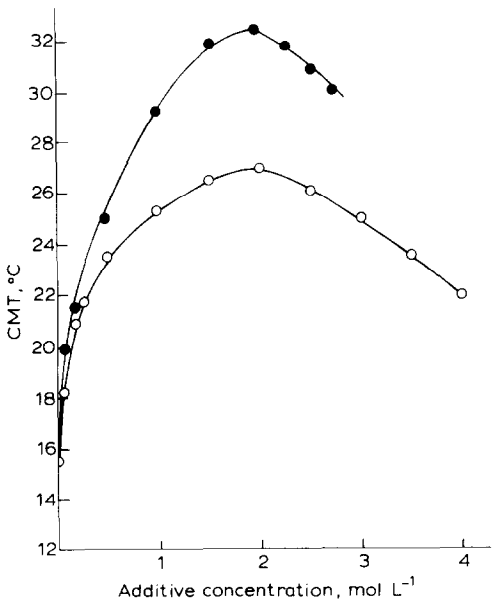

Fig. 1. Effect of (○) sodium salicylate and (●) sodium benzoate on the CMT of sodium dodecyl sulphate.

perature at which the hydrated solid surfactant dissolves completely is referred to as the critical micelle temperature (CMT). The CMT of anionic surfactants was reported to be independent of the surfactant concentration and to increase on addition of electrolytes, since it is affected by the monomer solubility and the CMC of the surfactant (Nakayama and Shinoda, 1967; Mazer et al., 1976). In the present study, the effect of SS as a particular type of electrolyte on the CMT of SDS was investigated. Further, location of the CMT phase boundary of SDS-SS systems was considered a preliminary to ensure physical stability of test solutions used for subsequent experiments.

The results in Fig. 1 show that the CMT of SDS increased as a function of SS concentration up to 2 M, the incremental increase in CMT being greater over the concentration range 0–1 M. This was followed by a decrease at higher salicylate concentrations. The initial increase in CMT at relatively low SS concentrations may be accounted for by a reduction in monomer solubility brought about by suppression of the ionic atmosphere around the polar head groups of SDS. This effect is similar to that exerted by NaCl on the CMT of anionic surfactants (Nakayama and Shinoda, 1967; Mazer et al., 1976). At the higher SS concentration range, where the salicylate concentration exceeds the

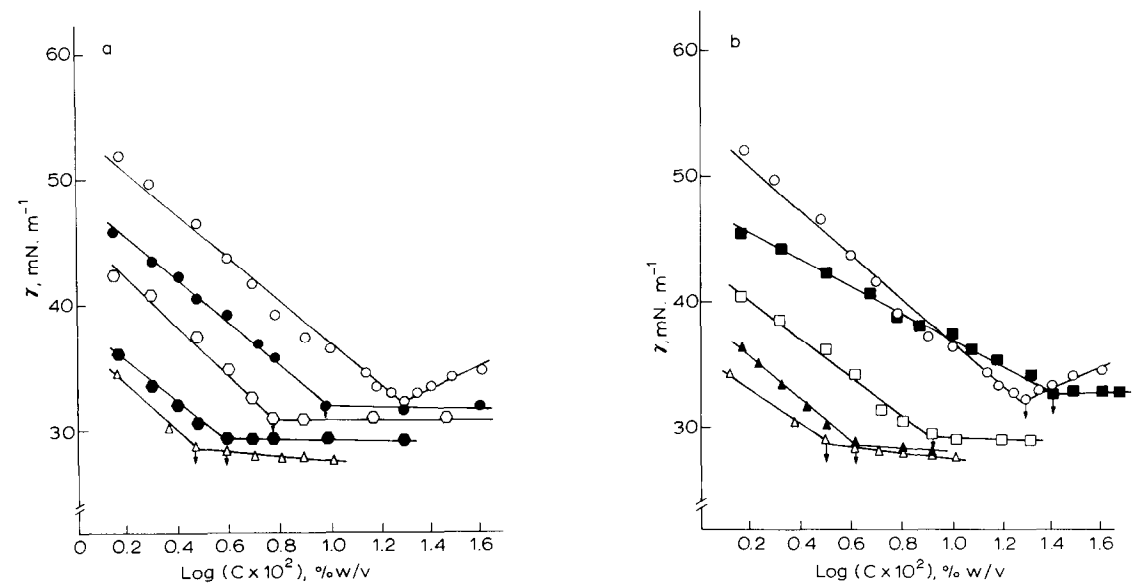

Fig. 2. Effect of SS concentration on the surface tension of SDS solutions at 26°C. Panel a: (○) no SS, (●) 0.02 M, (⬡) 0.05 M, (⬢) 0.2 M and (△) 0.5 M SS; panel b: (○) no SS, (△) 0.5 M, (▲) 1 M, (□) 1.6 M and (■) 3 M SS.

aggregation or minimum hydrotrope concentration, approx. 0.8 M (Badwan et al., 1983; Balasubramanian et al., 1989), the hydrotropic activity of salicylate comes into play and appears to oppose the electrolytic effect of SS exerted at lower concentrations, resulting in increased monomer solubility. However, the inflection of the SS effect occurred at an SS concentration higher than that of aggregation (approx. 0.8 M). This indicates the importance of the role played by the counterion (Na^+) in systems involving charged species. Accordingly, the pattern of change of the CMT of SDS as a function of SS concentration may be regarded as the resultant of the effects of SS both as an electrolyte and as a hydrotropic agent. This view was supported by the effect of a weaker hydrotrope, SB (Darwish et al., 1989), on the CMT of SDS (Fig. 1). Although a similar phase behaviour was maintained, the temperature boundary between the hydrated solid and the micellar phases of SDS was markedly higher.

The effect of SS on the surface activity of SDS in aqueous solutions at 26°C is shown in Fig. 2a and b. The plots of surface tension vs log SDS concentration indicate a marked decrease in the CMC of SDS with increasing SS concentration, the CMC reaching a minimum at 0.5 M SS. This was followed by an incremental increase at higher SS concentrations. Variation in the CMC of SDS as a function of SS concentration is shown in Fig. 3. Changes in the CMC of surfactants, the maximum concentration of molecular dispersion, provide a measure of the balance of forces causing the formation of micelles (Schick et al., 1962). The initial decrease in CMC observed at lower SS concentrations can be attributed to the electrostatic effect of SS. Release of the common counterion (Na^+) results in increased adsorption of the surfactant monomer at the air-solution interface and enhanced micellization in the bulk of the solution. Such effects of electrolytes on the properties of ionic surfactants are well established (Attwood and Florence, 1983). However, the CMC-decreasing effect of SS was less compared to that of NaCl and sodium acetate included for comparison, though SS exhibits some surface activity (Saleh and York, 1978; Balasubramanian et al., 1989). For instance, at 0.2 M con-

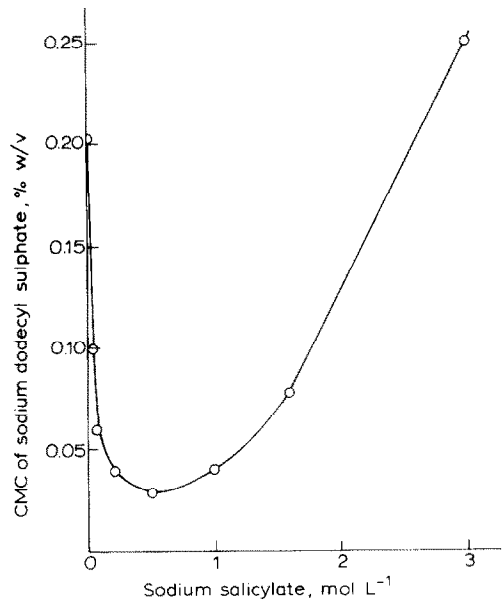

Fig. 3. CMC of SDS as a function of SS concentration at 26°C.

centration of the added salts, the ratio of the values of CMC in the presence and absence of additives, CMC/CMC_0, was 0.186 and 0.113 for SS and either NaCl or sodium acetate, respectively. This is probably due to the structural and solute-solvent interactions in solutions of hydroxybenzoates (Desnoyers et al., 1973) in addition to the hydrotropic activity of SS, although much weaker at lower salicylate concentrations.

The gradual increase in the CMC of SDS at salicylate concentrations beyond 0.5 M (Fig. 2b) appears to be the result of the electrostatic effect of SS and its hydrotropic activity, i.e., increased solubilizing capacity and reduction in solvent polarity, which become increasingly pronounced at SS concentrations above approx. 0.8 M (Badwan et al., 1983; Balasubramanian et al., 1989). This may salt-in the monomer and weaken hydrophobic bonding between the surfactant molecules, thus interfering with micelle formation. As shown in Fig. 2b, the CMC of SDS at 3 M SS exceeded CMC_0 in pure water, indicating the predominance of the hydrotropic effect of salicylate. SS has also been reported to interfere with the self-association properties of different systems, such as methylcellulose and methylene blue (Touitou

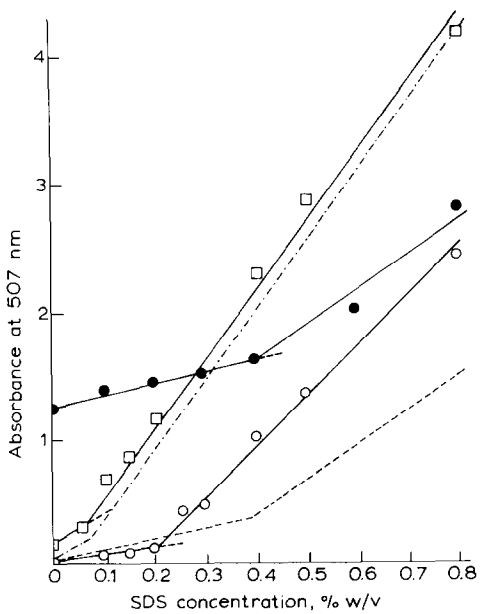

Fig. 4. Solubilization of Sudan III by SDS at 26°C (○) in the absence of SS and presence of (□) 0.3 M and (●) 3 M SS. Net solubilizing effect of SDS at (·–·–·) 0.3 M and (- - - - -) 3.0 M SS.

and Donbrow, 1982; Touitou and Fisher, 1986). The dual effect of SS on the CMC of SDS strongly implies that the relative contribution of the salicylate anion becomes increasingly pronounced compared to that of the counterion at salicylate concentrations higher than the minimum hydrotrope concentration and outweighs the latter at fairly high SS concentrations.

Dye solubilization studies have been carried out to probe micelle structure as well as the CMC (Attwood and Florence, 1983; Sudbeck et al., 1991). In the present study, the effect of SS on the solubilization of the hydrophobic dye, Sudan III, by SDS was investigated in order to gain insight into changes in the micellar properties of SDS brought about by SS. The effect of SS has been assessed at two concentration levels (0.3 and 3.0 M) and at 26°C, a temperature higher than the CMT of the SDS–SS solutions used. The solubility diagrams in Fig. 4 show that at the pre-aggregation SS concentration, 0.3 M, a concentration at which the dye solubility is limited, micellar solubilization of the dye was markedly enhanced and set in at a lower SDS concentration (approx. 0.05%) compared to approx. 0.2% in the absence of SS. Normally, an increase in micellar core solubilization is a consequence of increased micelle size and aggregation number (Rosen, 1978; Weers, 1990). Enhancement of dye solubilization and displacement of the apparent CMC of SDS to a lower concentration imply changes in the micellar properties of SDS similar to those exerted by inorganic electrolytes (Attwood and Florence, 1983). On the other hand, at the post-aggregation SS concentration (3.0 M), the net solubilizing effect of SDS appears to be much reduced with a shift of the apparent CMC to a higher SDS concentration (approx. 0.4%). This indicates interference with micelle formation, probably attributed to increased solubility of the surfactant monomer at high SS concentration. These findings lend support to the interpretation of the CMT and surface tension data.

In conclusion, the anionic hydrotropic agent, SS, exerts a concentration-dependent effect on the solution properties of SDS. The normal electrolytic effect exerted at relatively low salicylate concentrations is opposed at higher concentrations by the hydrotropic action of SS, interfering with the molecular association of the surfactant. As many hydrotropic agents are compounds of pharmaceutical, biochemical and industrial interest, their interactions with surfactants and other systems involving association structures may be of relevance to biological systems and the formulation of products combining both types of agents.

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