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## Interactions in phenol-sodium dodecyl sulphate-water systems

Changes in environment resulting from micelle formation and solubilization can be followed by observing chemical shifts in the nuclear-magnetic-resonance spectra of the components. We have used nmr spectroscopy to study interactions between phenol, water and the surfactant sodium dodecyl sulphate.

Spectra were obtained in  $D_2O:H_2O$  (60:40) at  $35^\circ$  using a Perkin-Elmer R-12 high resolution spectrometer. Chemical shifts were determined by locking to tetramethylsilane as an external standard and expanding the field to 50 or 100 Hz per chart width; the accuracy of the shifts is within about  $\pm 0.2$  Hz. Corrections for diamagnetic susceptibilities were made where necessary.

A change of medium from a polarizing to a more inert environment (such as the hydrocarbon environment of a micelle of the surfactant) may cause a considerable high-field shift (Eriksson & Gillberg, 1966). Fig. 1a shows the high-field shift for the phenol ring protons with increasing surfactant concentration. As this concentration increases, the ratio of micellar phenol to free phenol increases. Since the observed chemical shift is the weighted average of the free and solubilized peak positions this gives rise to a high-field shift.

Extrapolation of the phenolic proton shifts to zero chemical shift gives an intercept

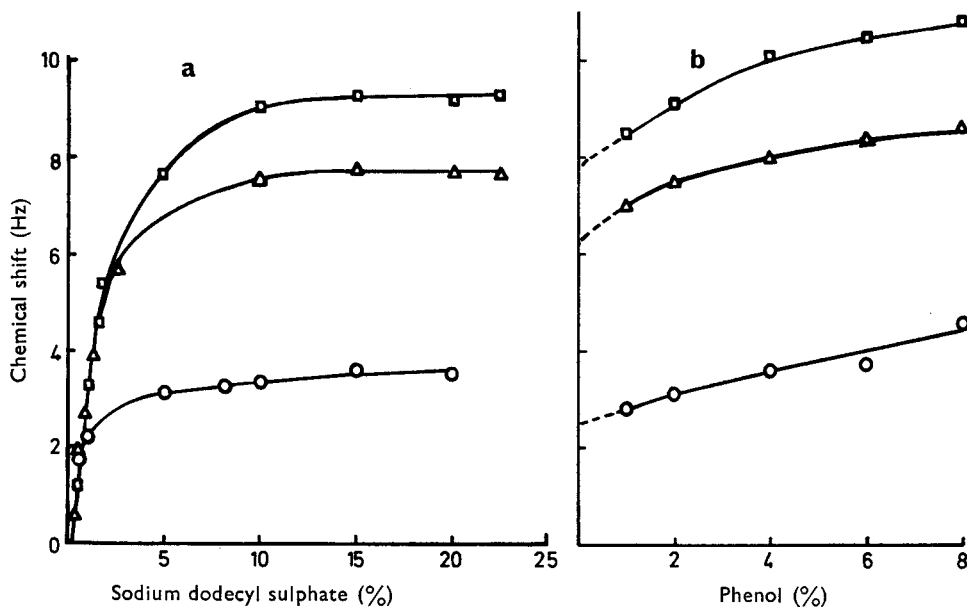


FIG. 1. Chemical shifts of ring protons of phenol: (a) 2% phenol in the presence of varying concentrations of sodium dodecyl sulphate (measured with respect to the peak positions of 2% phenol in water), (b) varying concentrations of phenol in the presence of 10% sodium dodecyl sulphate (measured with respect to the corresponding positions in water).  $\square$  *meta* protons;  $\triangle$  *para* protons;  $\circ$  *ortho* protons.

at about 0.15% which represents the critical micelle concentration for the surfactant in the presence of 2% phenol at 35°.

The greater high-field shift of the *meta* and *para* protons with respect to the *ortho* protons indicates a greater change in the environment of the former. This could be explained in terms of palisade solubilization of the phenol, with the hydroxyl group directed towards the outside of the micelle.

Fig. 1b shows the high-field shift of the phenol ring protons with increasing phenol concentration in the presence of 10% of the surfactant. Extrapolating to infinite dilution (zero phenol concentration) gives the total shift in terms of shift due to the diamagnetic anisotropic shielding of the aromatic rings and the shift due to the change from an aqueous to a hydrocarbon medium. The high-field shift due to the diamagnetic anisotropy of the aromatic rings indicates that the planes of the rings are randomly arranged and are not stacked or layered on top of one another.

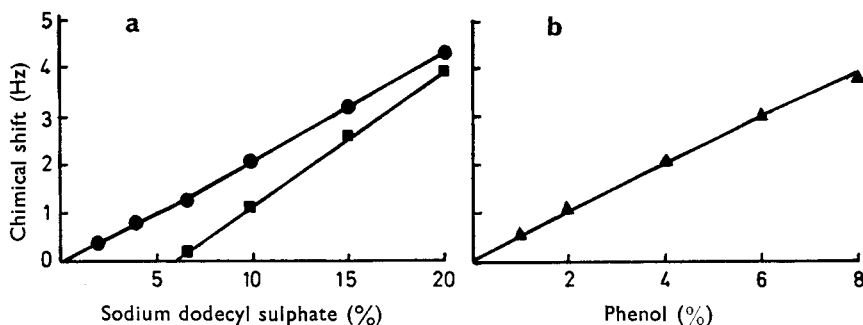


FIG. 2. Chemical shifts of water protons in the presence of (a) ● varying concentrations of sodium dodecyl sulphate (measured with respect to water). ■ 2% phenol and varying concentrations of sodium dodecyl sulphate (measured with respect to water containing 2% of phenol). (b) ▲ Varying concentrations of phenol (corrected for shift contributions by the phenolic hydroxyl protons and susceptibility changes).

It is interesting to note the high-field shift of the water protons in the presence of surfactant (Fig. 2a). This effect was first observed by Clifford & Pethica (1964) and is attributed to disturbance of the water structure by the surfactant. Hydration of the ions tends to oppose this shift and the observed effect is the net result of the two opposing shifts (Pople, Schneider & Bernstein, 1959). The presence of phenol reduces this shift and none is observed until the surfactant concentration reaches about 6%. It is suggested that phenol also disrupts water structure, so that no high-field shift is observed until sufficient surfactant is present to remove most of the phenol to the micellar pseudophase. This postulate is supported by (a) the marked high-field shift of water protons in the presence of increasing concentrations of phenol (Fig. 2b), only about half of which can be attributed to the diamagnetic anisotropic shielding of the aromatic rings, and (b) by the decrease in the water-peak shift (from 1.6 to 1.1 to 0.5) with increase in phenol concentration (from 1 to 4 to 8% w/v) at constant (10%) surfactant concentration.

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October 26, 1970

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