

Short Communication

A study of hydrotropic salts, cyclohexanol and water systems

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Several mechanisms have been proposed to explain the phenomenon of hydro-tropy, first introduced by Neuberg (1916). Winsor (1950) concluded that hydro-tropy and solubilization are essentially similar phenomena. Further, a recent study of the physical properties of hydrotropic salt solutions indicated molecular aggregation at a critical concentration of the salt (Badwan et al., 1980). Hence, it was thought of value to compare the behaviour of hydrotropic salts to that of surface-active agents in ternary systems. For further understanding of the phase diagrams obtained, the effect of hydrotropic salts on the near infrared spectrum of water was investigated.

Phase diagrams for the systems: water, cyclohexanol and sodium benzoate, sodium salicylate or sodium lauryl sulphate were determined at 22°C. The maximum concentration of the third component was 25% w/w (the - - - - - line in Fig. 1).

The effect of sodium benzoate, sodium salicylate and sodium chloride on the near infrared spectrum of water was determined using a Carl Zeiss DMR 21 spectropho-tometer. Absorption spectra over the range 1.4–1.7 μm were obtained using 1-mm path-length cells. The effect of the hydrotropic salt concentration on the stretching vibration of the O–H bond of water and the stretching vibration of the C–H bond of the hydrotropic salt was determined.

The phase diagrams for the 3 systems under study are shown in Fig. 1. Hydro-tropic salt systems and the sodium lauryl sulphate system show two-layer areas of different shapes. The maximum height of the two-layer area being toward water in hydrotropic salts systems and toward cyclohexanol in the sodium lauryl sulphate system. Phase equilibria in Fig. 1 tend to indicate that the hydrotropic salts used solubilize water in cyclohexanol while sodium lauryl sulphate expectantly does the opposite. In the latter system, relatively low concentrations of sodium lauryl sulphate

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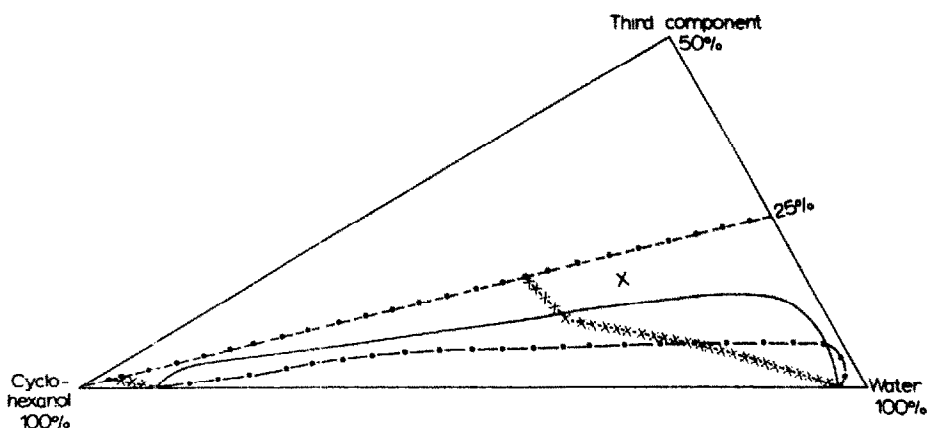


Fig. 1. Phase diagrams for cyclohexanol-water systems containing sodium benzoate (—), sodium salicylate (---) and sodium lauryl sulphate (x—x).

result in a decreased miscibility of water in cyclohexanol. Diluting a selected one-layer hydrotropic salt system x (Fig. 1) with cyclohexanol would not show phase separation while diluting the same system with water would definitely result in two-layer formation.

The phase diagrams (Fig. 1) also show that the solubilizing effect of sodium

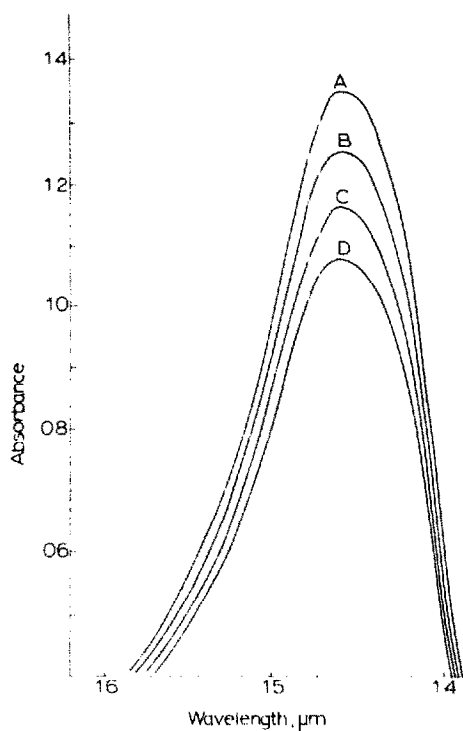


Fig. 2. Effect of sodium benzoate concentration w/w on the characteristics of the O-H stretching band of water. A: pure water; B: 10%; C: 20%; and D: 33%.

TABLE I

O-H AND C-H STRETCHING BAND CHARACTERISTICS FOR SODIUM BENZOATE, SODIUM SALICYLATE AND SODIUM CHLORIDE SOLUTIONS

nm	% Sodium benzoate			% Sodium salicylate		% Sodium chloride
	0	10	20	10	20	30
V_m	1456	1458	1460	1458	1460	1445
$W_{1/2}$	128	131	133	129	130	108
$V_{m'}$	-	1668	1670	1666	1669	-

salicylate is greater than that of sodium benzoate pointing out the important role played by the OH group in the salicylate ion.

From the phase diagrams it could be concluded that hydrotropy is different from micellar solubilization. The increased solubility of water in cyclohexanol in the presence of hydrotropic salts might imply that these salts affect the structure of water in favour of a more hydrophobic mode. Changes in the water-water interaction may be reflected in changes in the characteristics of the O-H stretching band of water in the near-infrared region (Klotz, 1965). Hence, the effect of hydrotropic salts on the characteristics of this band (wavelength of maximum absorption, V_m and the

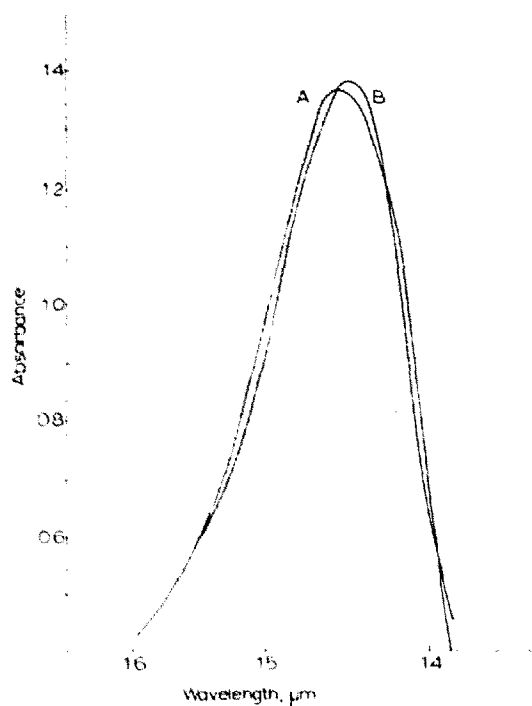


Fig. 3. Effect of sodium chloride on the characteristics of the O-H stretching band of water. A: pure water; B: 30% w/w NaCl.

bandwidth at mid-height, $W_{1/2}$) was investigated.

Increasing the concentration of sodium benzoate results in a shift of V_m to higher values and an increase in $W_{1/2}$ (Fig. 2). Sodium salicylate exerts similar effects (Table 1). Such changes may suggest a higher degree of water structuring (Klotz, 1965) indicating that hydrotropic salts are structure makers. This view is supported by the opposite effect produced by a non-hydrotropic sodium salt, sodium chloride (Fig. 3 and Table 1), the addition of which breaks down the structure of the solvent (Frank, 1965).

Further, the C-H stretching band of the hydrotropic salts under study is also affected by the hydrotrope concentration. A shift in the wavelength of maximum absorption, V_m , of the C-H stretching band of sodium benzoate to high values as a function of the salt concentration can be observed (Fig. 4). A similar effect is exerted by sodium salicylate (Table 1). This may indicate that the water in the vicinity of the C-H bond becomes less polar, i.e. more structured.

The C-H band of sodium benzoate solution in Fig. 4 also shows a distinct isosbestic point which suggests an equilibrium between two or more discrete species each making a distinct contribution to the absorption band. The water involved in the hydration of the hydrotropic salt molecules may hence be considered to give rise

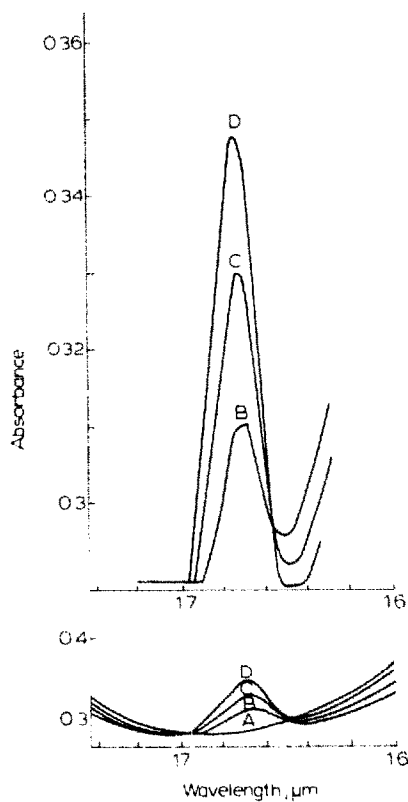


Fig. 4. Shift in the wavelength of maximum absorption of the C-H stretching band of sodium benzoate as a function of the salt concentration w/w. A: pure water; B: 10%; C: 20%; and D: 33%.

to absorptions which are different from those of water in the pure liquid (Armishaw and James, 1976).

In conclusion, solubilization by hydrotropy is different from micellar solubilization. The solubilization of water in organic solvents by hydrotropic salts may be explained by the effect of these salts on the structure of water as indicated by near infrared studies. A more detailed study of the behaviour of hydrotropic salts in organic solvent-water systems is undertaken at present in our laboratory.

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