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SHORT COMMUNICATION

A temperature dependent micellar change

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AS part of a broader programme of investigation of problems of emuslification, the variation of critical micelle concentration with temperature for aqueous solutions of dodecylpyridinium bromide (DPB) has been studied (Adderson & Taylor, 1964) and thermodynamic quantities have been calculated on the basis of the phase change model of micellisation (see e.g. Matijevic & Pethica, 1958; Shinoda & Hutchinson, 1962). In this way variations with temperature, of the entropy change and heat capacity change resulting from micelle formation have been interpreted as indicating a change in the nature of the micelles at about 55° (Adderson & Taylor, 1964). To test this hypothesis, other properties of the solutions have been studied.

EXPERIMENTAL

The surfactants were prepared and purified as described previously (Adderson & Taylor, 1964). The solubilisation of Waxoline Yellow IS* by 0·02 molal solution of DPB has been studied from 25–70°. The solution of DPB was placed in a sealed spectrophotometric cell with an excess of the dye twice recrystallised from benzene. The cell was kept at constant temperature in a Unicam S.P.500 spectrophotometer and the absorption of the solution at 485 mμ measured against (*a*) water, (*b*) a similar solution saturated with dye at 25° as reference. The results obtained for (*a*) are shown graphically in Fig. 1 (a), those for (*b*) were qualitatively the same, showing two straight lines intersecting at about 55°.

The CMC of DPB had previously been obtained by the conductivity method (Adderson & Taylor, 1964). The slope of the conductivity *versus* concentration curve for solutions (*a*) below the CMC (*b*) above the CMC have now been calculated at each temperature of measurement.

The solubilisation of Waxoline Yellow IS by 0·01 molar tetradecylpyridinium bromide (TPB) was studied in the same way as for DPB. The slopes of the conductivity *versus* concentration curves for TPB were obtained in the same way as those for DPB.

DISCUSSION

Figs 1 (a) and 2 (b) show a sharp break in the curve at about 55°. By contrast Figs 1 (c), 2 (c) and 2 (d) are almost linear.

The sharp change in the solubilising power of DPB solution at about 55° is consistent with the suggested change in the nature of the micelle from a gel-like to a liquid state (Adderson & Taylor, 1964). A change in

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* α-Benzeneazo-β-naphthol (C.I. 12,055).

the structure of a phase is likely to be accompanied by a change in its solvent powers. The absence of a break in the curve for TPB and the presence of a break for DPB when measured against the dye solution as reference, indicates that the effect observed with DPB is a property of DPB solution and not of the dye.

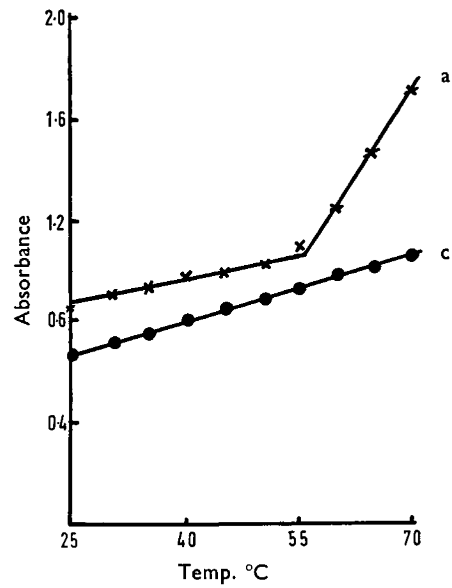

FIG. 1. Solubilisation of Waxoline Yellow IS. ×, 0·02M dodecylpyridinium bromide. ●, 0·01M tetradecylpyridinium bromide.

Again a break in the conductivity slope curve 2 (b), absent in 2 (a), 2 (c) and 2 (d) indicates a change in the micelles of DPB at about 55°. The slope of the conductivity versus concentration curve for a surfactant solution at concentrations above the CMC is a function in part of the mobility of the micelle. Evans (1956) derived the following equation (modified here for DPB):

$$1000S_2 = p^2(1000S_1 - \Lambda_{Br^-})/n^{4/3} + p\,\Lambda_{Br^-}/n$$

where S_2 is the slope of the specific conductivity against concentration curve above the CMC, S_1 the slope below the CMC, p the micellar charge and n the number of DPB ions in the micelle. To obtain this expression Evans eliminated the micelle mobility by assuming the micelle to be spherical and introducing Stokes' law. He was then able to calculate p and n. However the mobility of an ion in a unit field depends on its charge, shape and size, and a change in the slope of the conductivity plot may result as much from change of shape as from change of size and charge. For this reason no attempt is made to calculate size and charge until further information has been obtained about micelle shape. Fig. 2 does indicate a change in the mobility of the DPB micelles at about 55° additional

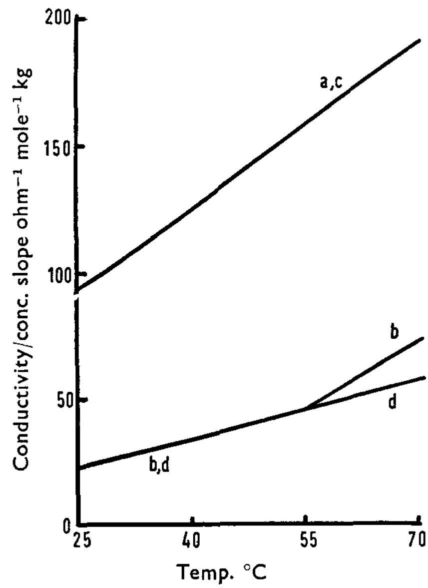

FIG. 2. Variation with temperature of slope of curve of conductivity *v*. concentration. (a) and (c) dodecylpyridinium bromide and tetradecylpyridinium bromide below CMC. (b) and (d) same above CMC.

to that normally expected from a change in temperature; this change moreover is not shown by the single ions. The results again are consistent with a change in the nature of the micelle, a change not shown by TPB.

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The paper was presented by MR. ADDERSON.