Ionic effects on the cloud temperatures of aqueous non-ionic surfactants

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Aqueous micellar non-ionic surfactant solutions exhibit a cloud point temperature, T_c, at which the solution becomes turbid and ultimately separates into two phases. At temperatures near to T_c these surfactants have the useful properties of increased equilibrium solubilization capacity and increased rates of solubilization. These properties are important in design of pharmaceutical delivery systems and studies of digestive processes in animals.

The underlying mechanism of the clouding phenomenon, for surfactants containing polyoxyethylene chains is thought to entail dehydration of the ether oxygen atoms with increasing temperature (Corkhill et al 1966). This leads either to formation of very large micelles or to secondary aggregation of micelles. This process is influenced by the presence of added electrolytes, whose effects on T_c, solubilization, micelle size and other properties have been subjects of several studies (Maclay 1956; Schick 1962; Popescu & Ana 1973; Schott & Han 1975, 1976; McDonald & Richardson 1981). In general, T_c is linearly dependent upon electrolyte concentration or ionic strength with small hydrated ions having the largest effects. In this communication it is suggested that the main effect of the electrolyte is to change the free volume of the solvent. Some preliminary T_c measurements of aqueous micellar solutions of Triton X-100 (iso-octylphenoxypolyethoxyethanol containing 9·3 moles of ethylene oxide, BDH Ltd) or octaoxyethylene n-dodecyl ether, $C_{12}E_8$, (Nikko Ltd, Japan) are presented. Comparison of the Triton X-100 values with those of Maclay (1956) showed good agreement and the values for both systems were reproducible to ±0·2 °C.

The experimental data have been treated using the approach proposed by Hey et al (1976) to describe the cloud point behaviour of polyvinylmethylether and the helix-coil transition temperature of ribonuclease in the presence of added electrolyte. The transfer of dissolved ethylene oxide segments to an aggregated state was described as a phase transition in terms of changes in the partial molal internal energy ($\bar{U}$), volume ($\bar{V}$) and entropy ($\bar{S}$) of the segments. The change in T_c, δT_c, brought about at pressure P by the addition of m moles of salt kg^{-1} solvent was related to $\delta\Delta\bar{U}$, the change brought about on $\Delta\bar{U}$ by the presence of ions, as follows:

$$\delta T_c/m = \frac{\delta\Delta\bar{U} - P\,(V_{salt} - \bar{V}_{salt})}{\Delta\bar{S}}$$

where V_{salt} is the molal van der Waals' volume, $\bar{V}_{salt}$ is the partial molal volume and m is the molality of the salt. Here the following assumptions were made: (a) $\Delta\bar{S}$ remains unchanged; (b) the temperature dependence of the partial molal quantities in the range T_c to $T_c \pm \delta T_c$ can be neglected; (c) T_c is solely determined by the salt effect; (d) the ethylene oxide chains utilize voids in the solvent; (e) the electrolyte solutions are dilute, so that changes in $\Delta\bar{U}$ are due to weak ion binding to sites on dissolved ethylene oxide segments leading to a situation where $\delta\Delta\bar{U}$ would depend linearly on m.

Linear T_c against m plots were found in the range 0–1·0 M in agreement with the observations of Maclay (1956) and Schick (1962). Fig. 1 shows plots of $\delta T_c/m$ against $(V_{salt} - \bar{V}_{salt})$ constructed from the slopes (strictly the initial slopes) of the T_c - m plots for Triton X-100 and $C_{12}E_8$ respectively in the presence of three series of halides. Ionic radii (Pauling 1952) were used to calculate the V_{salt} values and $\bar{V}_{salt}$ at infinite dilution were taken from the compilation of Millero (1971). These plots are linear in accord with the treatment of Hey et al (1976) justifying the assumption of a constant $\Delta\bar{S}$ process. Observation of parallel lines, one for each series of anions with a common cation, implies that $\delta\Delta\bar{V}$ is determined by both cation and anion whereas $\delta\Delta\bar{U}$ depends only on the cation. Thus the intercepts of the lines on the $\delta T_c/m$ axis reflect the tendency for cation binding in the order $Ca^{2+} > Li^+ > Na^+$. The positive values of $\Delta\bar{S}$ and $\delta\Delta\bar{V}$ are consistent with the aggregated state, resulting from a dehydration process leading to decreased hydrogen bonding, being favoured by increasing temperature.

The behaviour of these surfactants, which have moderately long polyethylene oxide chains, resembles closely that found for polyvinylmethylether (Hey et al 1976), while the same general trends were observed in the polyethylene oxide system (Boucher & Hines 1978) although the fit was regarded as only rough. However, marked anion binding was found in this system and the proposed treatment would not be expected to fit so well because of the assumption of weak ion binding. The data also indicate that the same mechanism applies to all cations studied, unlike solutions of similar surfactants in the presence of high concentrations of added electrolyte investigated by Schott & Han (1975, 1976) who found it necessary to invoke a classification of cation behaviour in terms of those being able to complex to ether oxygen atoms such as Ca^{2+} and Li^+ and those having no tendency to bind such as Na^+. However, it is likely that

$\delta T_c/m(^\circ C\ molal^{-1})$

+20

●CaI$_2$

+10   ■LiI
  LiI
NaI▲
NaI

0   ■LiBr
  ●CaBr$_2$

  LiBr■LiCl
NaBr

-10

NaBr

  ▲NaCl
  ●CaCl$_2$
-20   LiCl

  NaCl

-30

-40   ▲NaF

  -10   0   +10

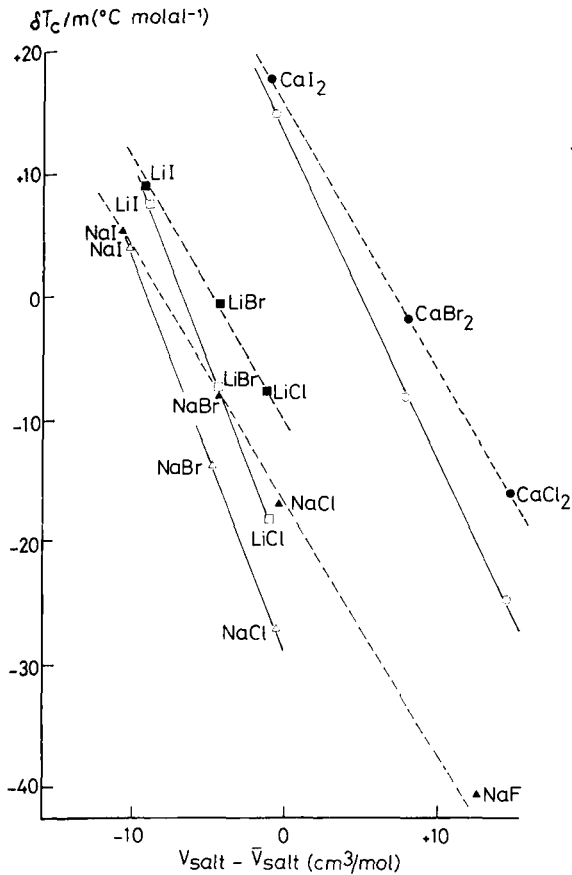$\overline{V}_{salt} - \overline{V}_{salt}\ (cm^3/mol)$

FIG. 1. Salt effects on T_c of aqueous solutions of Triton X-100 (2% w/v)—open symbols: and $C_{12}E_8$ (1% w/v) —filled symbols.

the structure of the solvent is completely dominated by the solute at such high salt concentrations; the above treatment implies that the water structure is substantially unperturbed.

Fig. 1 shows that the entropy change, $\Delta \bar{S}$, is smaller in the case of the Triton X-100 micelles. This results from the presence of a benzene ring in the hydrophobe of this surfactant in such a position that a greater solvent penetration of the micelle/solution interface may be expected with an associated greater tendency to be salted in by electrolyte. Further work is required to confirm this and to study the influence of the nature of the hydrophobic chain, especially units adjacent to the hydrophilic moiety, on the tendency to dehydrate.

In conclusion, the data presented here appears to support the speculation of Hey et al (1976) that this interpretation may be useful in separating solvent effects from ion-binding effects for a wide range of solubility phenomena in the presence of ions. The results indicate that the approach may be fruitful in assessing the role of surfactant molecular structure in the clouding process, and the large range of temperatures over which this treatment applies raises more fundamental implications in the consideration of water structure itself.

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