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STUDIES ON KRAFFT POINT SOLUBILITY IN SURFACTANT SOLUTIONS

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ABSTRACT

The thermal transitions from dispersed solid state to micellar solutions were studied for ionic surfactants in binary and pseudobinary aqueous surfactant systems. Particular attention was focused on the region close to the Krafft point, T_k. The experimental results are interpreted in thermodynamic terms by adopting a phase separation model for micelle formation.

INTRODUCTION

Most physico-chemical properties of ionic surfactants in aqueous solutions show a very complex dependence on the composition, ionic strength of the medium, and/or intensive variables. For instance, the progressive addition of surfactant to its diluted aqueous solutions gives rise to the formation of micelles, dynamic aggregates containing 20 to 100 surfactant molecules, or ions, above the so-called Critical Micellar Concentration, CMC [1].

Another interesting property is the unusual temperature-dependence of surfactant solubility. For ionic monodispersed amphiphiles, in particular, this is below the CMC, but a sudden increase in solubility is observed when micelles begin to form, suggesting that the monomer solubility determines the total solubility at temperatures $T<T_k$, followed by the micellar solubility when the CMC is reached and $T>T_k$.

Micelle formation has been rationalized on thermodynamic grounds by adopting a (pseudo) phase separation [2] or a mass action [13] approach. Both models have their advantages and consequences.

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This paper describes systematic studies on the surfactant solubility trend in binary and pseudo-binary aqueous surfactant solutions and offers a cogent thermodynamic analysis of the experimental findings in agreement with the approach of Hall and Pethica [4]. Attention was concentrated on perfluorinated surfactants, because of the noticeable interest they have recently attained. Comparison was made with a hydrocarbon surfactant to clarify the observed trend.

EXPERIMENTAL

Materials

Perfluorononanoic acid, HPFN, from Riedel, was used as received, since its melting point is very close to the previous literature data [5]. Its purity is appreciably high, because no surface active impurities could be detected by surface tension versus log C plots close to the CMC. Details on the preparation and purification of its sodium salt, NaPFN, have been reported elsewhere [6].

Cetyltrimethylammonium bromide, CTAB, from Fluka, was purified by dissolution in hot ethyl alcohol, precipitated by addition of cold acetone and dried under vacuum at 90 °C for one day.

NaBr, from Fluka, was vacuum dried at 150 °C for two days. Water was bidistilled, deionized and degassed. The other solvents were of analytical purity.

The solutions were prepared by weight and left overnight at 4 °C in flasks closed with glass stoppers to avoid the adsorption of carbon dioxide.

Methods

Electrical conductance was measured with an Amel conductivity meter, in a cell thermostated to ±0.02 °C. To avoid thermal gradients readings were taken at least twenty minutes after thermal equilibrium was reached in the measuring cell. Individual readings (microSiemens) were accurate to ±2%.

Densities, ρ, were measured with Johnston-Adams pyknometers in a water circulating bath, controlled within ±0.01 °C. Their temperature dependence was taken relative to that of the solvent. The accuracy of individual ρ values is within 1×10^{-5} g cm^{-3}.

Surface tension was measured with a Du Noüy ring tensiometer (Cambridge Instr.). Its measuring vessel was thermostated to 0.1 °C by circulating water. The accuracy of the surface tension data is better than 0.4 dyn cm^{-1}.

Turbidity was measured in a home-built apparatus, consisting of a mono-

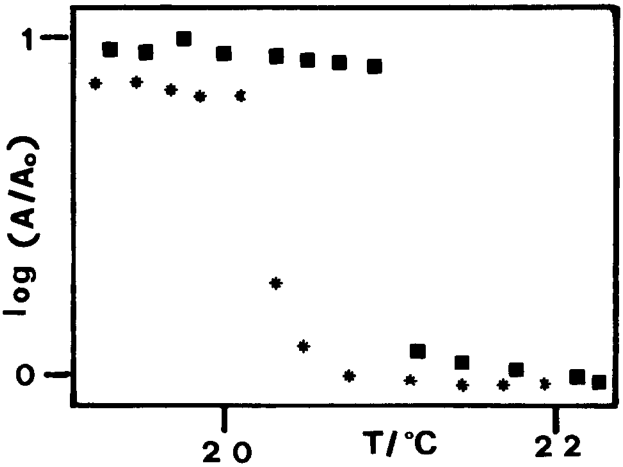

Fig. 1. Relative turbidity (Absorbance solution/Absorbance solvent) as a function of the temperature for 7.2×10^{-3} (*) and 1.12×10^{-2} (■) mol Kg^{-1} NaPFN solutions.

chromatic light source and a photoresistor in a thermoregulable copper cell. The photoresistance was connected to an ohm-meter. In most instances, the accuracy of the clearing point temperatures is better than 0.2 °C. A few selected turbidity versus temperature plots are shown in Fig. 1.

RESULTS

The equilibria between coexisting phases were studied for the following binary systems

A) H_2O-HPFN
B) H_2O-NaPFN
C) H_2O-CTAB

Some pseudo-binary systems containing CTAB and fixed amounts of NaBr in water, or NaPFN in wter-NaBr solutions, were also considered to determine the dependence of Krafft point temperatures, T_k, (i.e. the lower limit of the liquid line dispersed solid-micellar solution) on the ionic strength of the medium. Partial phase diagrams, (see Fig. 2), for regions close to the CMC were constructed from the electrical conductance, turbidity and density findings. Despite some scattering on the individual transition temperatures, the T_k's are accurate to within 0.2 °C. A selected set of T_k's is given in Table 1.

TABLE 1

T_k's at the CMC, for ionic surfactant solutions with or without added NaBr.

Surfactant	T_k/°C	molality of added NaBr
NaPFN	19.6	-
HPFN	43.8	-
CTAB	26.6	-
CTAB	27.0	0.05
CTAB	30.3	0.15
CTAB	34.6	0.50
NaPFN	21.4	0.075

The volumetric properties of NaPFN are reported in Table 2: they indicate that the volume change on fusion and micellization, $\Delta_{f,m}V_m$, is nearly twice that of the formation of micelles, $\Delta_{mcl}V_m$.

The partial phase diagram of the system H_2O-NaPFN is illustrated in Fig. 2. Our results indicate that metastable micellar solutions can exist at $T<T_k$, in agreement with previous studies on similar systems [7] and our own more general suggestions [8]. Only values obtained on increasing the temperature are reported in the phase diagram and in Table 1 since large thermal hysteresis can occur. For instance, a 0.021 mol Kg^{-1} CTAB aqueous solution (concentration approximately twenty times higher than the CMC) can be cooled to ten degrees below T_k without precipitation. Even two weeks later no precipitation was observed, in agreement with recent findings on the kinetics of gel-coagel phase transitions [9].

TABLE 2

Volumetric properties of solid, molecularly dispersed and micellar NaPFN extrapolated to the Krafft temperature, 19.6 °C. Values for the molecular and micellar solutions, respectively, were calculated from $\Phi_{V,exp} = CMC\,\Phi_{V,mon} + (C - CMC)\,\Phi_{V,mcl}$, where $\Phi_{V,exp}$ is the measured apparent molar volume and C is the surfactant molality.

State	V_m/ $cm^3\ mol^{-1}$
Solid	306
Molecularly dispersed	318
Micellar	336

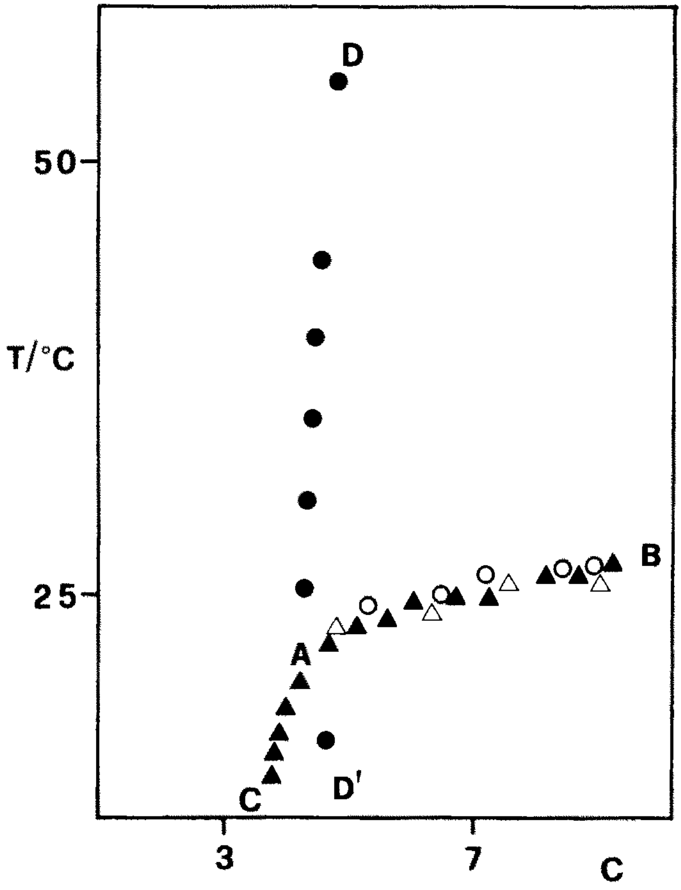

Fig. 2. Partial phase diagram of the system H_2O-NaPFN, obtained from the electrical conductance (▲), density (o) and turbidity (Δ) findings. The DAD' line (full circles) is the CMC versus temperature curve, the CA and AB lines indicate the surfactant monomer and the micellar solubility curves, respectively. Concentrations are in millimolality.

DISCUSSION

If we accept current ideas underlying the phase separation approach to micelle formation [2], the Krafft point is to be regarded as a triple point at which monodispersed surfactant ions and counterions coexist with a micellar and a solid surfactant phase. If not properly considered, this approach poses severe methodological problems, since the definition of micelles as a separate phase is difficult to reconcile with intuitive ideas on micellar solutions, particularly of ionic ones.

Hartley showed that, if micelles are considered as a separate phase [10], the intensive properties of these systems are univocally determined at a fixed temperature [11]. If micelles are considered as a reaction product of surfactant and solvent, the number of components perhaps becomes three if, and only if, micelles are considered as a separate phase [4,12]. This approach should allow us to perform a thermodynamic analysis of data according to the theory of phase equilibria. Let us apply it to systems containing water, surfactant and a neutral electrolyte with an ion in common with the surfactant species. At the Krafft point, the chemical potentials for each compound in molecular, solid and micellar phases will be univocally determined. For the surface active agent

$$d\mu = S\,dT + V\,dP - \Sigma_h(\partial\mu/\partial X_i)_{T,P,X_j}\,dX_i \tag{1}$$

where the terms S and V refer to the partial molar entropy and volume of the surfactant in the solid, micellar or non-micellar form and X_i is the surfactant mole fraction in each phase. The other symbols have their usual meaning. The summation is extended over h components. Combination of eqn. (1) with Gibbs-Duhem equation for the species in solid form gives

$$\begin{aligned} 0 &= \Sigma_h X_s(S_n - S_s)dT + \Sigma_h X_s(V_n - V_s)dP + \\ &+ \Sigma_h \Sigma_{i=2} X_s\,(\partial\mu_s/\partial C_{i,n})_{T,P,C_{j,n}}\,dC_{i,n} \end{aligned} \tag{2}$$

where the terms containing dT and dP contributions indicate the variations in partial molar entropies and volumes respectively, associated with the dissolution of the species from solid (subscript s) to micellar or non-micellar (subscript n) form.

At the Krafft point $C_n = \mathrm{CMC}$ and the equations linking the Krafft point variations with composition and/or ionic strength can be obtained from eqn. (2) by eliding dC terms.

We used eqns. (1) and (2) in a tentative prediction of the variation of Krafft temperatures with the ionic strength of the medium. For CTAB aqueous solutions, the computed values are 27.6, 29.5, and 32.3 °C at 0.05, 0.15 and 0.50 NaBr mol Kg^{-1} respectively, which can be compared with the experimental findings in Table 1. The agreement is satisfactorily good. Small discrepancies are to be ascribed to the fact that we supposed ln CMC to be linearly dependent on the ionic strength of the medium and neglected the variations on counterion binding consequent to the addition of NaBr. The approximation is perhaps consistent with Mukerjee *et al.* [13] phenomenological expression, which states that

$$\ln \mathrm{CMC} = A - \beta \ln a_{\mathrm{counterion}} \tag{3}$$

where β is the counterion binding constant.

The molar volume of the solid and the apparent molar volumes of NaPFN, (Table 2), indicate that the volume change upon fusion and dissolution in micellar form is about 30 $\mathrm{cm^3\ mol^{-1}}$, while that due to micelle formation is slightly lower than 20 $\mathrm{cm^3\ mol^{-1}}$. Both variations are in agreement with findings for similar systems [14]. The effect of applied pressure on Krafft points can be evaluated from the molar volumes in different phases from

$$(\partial \ln X_m/\partial P)_T = (V_m - V_s)/RT \tag{4}$$

where X is the mole fraction of surfactant in micellar form (subscript m) and other symbols are as before. Typical values for the process are $1.2\times10^{-3}\ \mathrm{atm^{-1}}$ for NaPFN and $8\times10^{-4}\ \mathrm{atm^{-1}}$ for CTAB respectively. Those are comparable with available literature data [14].

Individual Krafft points lie on a liquid line representing the coexistence of the micellar and solid surfactant phases. It is thus possible to determine the enthalpy of fusion associated with the above process from

$$\ln (X_2/X_2) = (2-\beta)\ \frac{\Delta_{f,\mathrm{mcl}}H}{R}\ \frac{T_{f,2}-T_{f,1}}{T_{f,2}T_{f,1}} \tag{5}$$

where X_i indicates the mole fraction of the component in micellar form at $T_{f,i}$ and $\Delta_{f,\mathrm{mcl}}H$ is the enthalpy of fusion and dissolution of the amphiphile in micellar form. The other symbols are as before. The term (2-β) accounts for the micelle ionization degree, which is supposed to be nearly independent of temperature. The (2-β) values for NaPFN and CTAB are 1.45 and 1.30 respectively, according to usual counterion binding constants for these compounds [6], while the value for the acid was close to 1.55, according to e.m.f. studies.

Raw $\Delta_{f,\mathrm{mcl}}$ values from eqn. (5) are 20.1, 18.2 and 12.5 kcal $\mathrm{mol^{-1}}$ for NaPFN, HPFN and CTAB respectively. Since the enthalpic contribution due to the solid surfactant fusion is only a part of $\Delta_{f,\mathrm{mcl}}H$, we can obtain ΔH_f^0 by subtracting the contribution due to micelle formation. We can obtain the latter quantity according to

$$\Delta H^0_{\mathrm{mcl}} = -RT^2(2-\beta)(\partial \ln \mathrm{CMC}/\partial T)_P \tag{6}$$

As regards NaPFN, careful analysis of previous experimental data indicates that ΔH^{o}_{mcl} is close to 2.5+3.0 kcal mol^{-1}, for temperatures very close to T_k [14-16] and makes only a minor contribution to the overall enthalpic effect calculated from eqn. (5). Similar conclusions can be drawn for CTAB.

Previous experiments on ionic surface active agents indicate that ΔH^{o}_{mcl} is a temperature-dependent quantity and can be either positive or negative [17]. It is hard thus to ascertain whether the phenomena observed holds to be true for most systems or is peculiar to the systems under test.

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