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POLYMER-SURFACTANT INTERACTIONS

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Abstract

Aqueous solutions containing poly(vinyl-pyrrolidone) and sodium caprylate, or poly(vinyl-pyrrolidone) and tetraethylammonium perfluorooctanesulfonate, respectively, have been investigated by volumetric, ionic conductivity and surface tension methods. The presence of an interaction region has been determined from conductivity and surface tension. The width of such a region depends on the amount of polymer in the mixture, temperature, surfactant content and added electrolyte (NaCl). The observed behaviour was explained in terms of the combined effects played by the alkyl-chain hydophobicity, polar head group(s) and counter-ions.

An approximate solution to a mass action model for the binding of surfactants onto polymers has been introduced. It allows determining the width of the interaction region as a function of polymer mass percent in the mixture.

Keywords: conductivity, interactions, phase diagrams, polymers, surface tension, surfactants

Introduction

Polymer-surfactant systems are the subject of significant research interest [1–3]. Papers dealing with experimental investigation [4–5] and theoretical modelling [6] in the field have been recently reported. Studies presented so far concern water-soluble homo-polymers, for instance poly-(ethylene oxide), PEO, or poly-(vinyl pyrrolidone), PVP, and surfactants such as sodium dodecylsulfate, SDS [7–8]. Not much is known on the interactions occurring between the above homo-polymers and anionic, or cationic, short-chain surfactants.

Polymer-surfactant interactions are controlled by a balance between hydrophobic and electrostatic interactions and are modulated by temperature and ionic strength. The role of the above effects in the stabilisation of polymer-surfactant systems is not easy to quantify. That's why the combination of experimental investigation and theoretical modelling are important.

To shed light on this subject, some physico-chemical properties of the systems were investigated: (I) PVP and sodium caprylate, SCAP, in water; (II) PVP and sodium caprylate in 1 molal aqueous NaCl; and, (III) PVP and tetraethylammonium perfluorooctanesulfonate, TEAPFOSS, in water.

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Experimental results relative to the above systems are presented. Information on the occurrence of polymer-surfactant interactions was inferred from surface tension and ionic conductivity experiments. An approximate solution to the mass action model for polymer-surfactant interactions [9] is used to account for the observed behaviour.

Experimental

Materials

Sodium caprylate, SCAP, and tetraethyl-ammonium perfluorooctanesulfonate, TEAPFOSS, nominal purity higher than 98%, were from Sigma Aldrich. The surfactant purification was performed by foaming [10]. According to surface tension, the purified products do not show the presence of surface-active impurities.

Poly(vinyl-pyrrolidone), viscosity averaged molecular mass, $<M_w>$, of 28 KD, (Aldrich), was used. Its aqueous solutions were dialysed, to remove salts and low-molecular mass impurities.

Methods

Surface properties

A Kruss K10T unit, thermostatted by circulating water, measured the surface tension, τ (in mN m^{-1}) [11]. The platinum Du Noüy ring was roasted, washed in HCl and cleaned with doubly distilled water. Surface tension values were obtained from five independent determinations with an accuracy of ±0.3 mN m^{-1}. The data were analysed according to

$$d\tau = -\Gamma_2[2RT\,\mathrm{dln}a_2] \approx -\Gamma_2[2RT\,\mathrm{dln}m_2] \qquad (1)$$

where T is the Kelvin temperature, Γ_2 the surface excess concentration, R the gas constant and m_2 the surfactant molality.

The occurrence of polymer-surfactant interactions has been inferred in two changes in slope in the surface tension *vs.* $\ln m_2$ plots, Fig. 1A. On thermodynamic grounds, the critical association concentration (*cac*) and the critical micellar concentration (cmc^*) are the points at which $\partial^3\tau/\partial(\ln m_2)^3 = 0$ [12]. The accuracy on *cac* and cmc^* values obtained from surface tension is to ±3%.

Volumetric properties

The density, ρ (in g cm^{-3}), was measured by an Anton Paar DMA 60 vibrating tube densimeter [13]. The apparent, $\Phi_{V,2}$, and partial, V_2, molal volumes, (cm^3 mol^{-1}), were obtained by

$$\Phi_{V,2} = MW/\rho - 10^3(\rho-\rho°)/\rho\rho° m_2 \qquad (2)$$

$$V_2 = \partial(m_2\Phi_{V,2})/\partial m_2 \qquad (2')$$

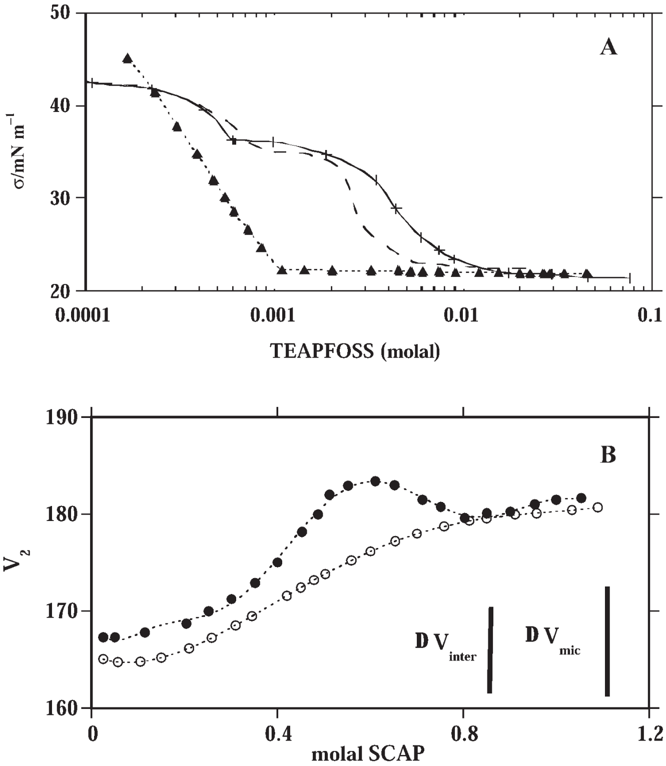

Fig. 1 A – Surface tension, τ, in mN m^{-1}, *vs.* tetraethylammonium perfluorooctanesulfonate molality, TEAPFOSS, at 25°C. Triangles refer to aqueous solution, points to 0.1 and crosses to 0.3 PVP mass% aqueous solutions
B – Partial molal volume, V_2 (cm^3 mol^{-1}) of sodium caprylate in water, empty symbols, and in 1 mass% PVP, full symbols, as a function of surfactant molality, molal SCAP, at 25°C

where *MW* is the surfactant molal mass. In Fig. 1B the partial molal volume of sodium caprylate is reported as a function of m_2. It is not possible to determine the *cac* and *cmc** values from the above plot. Data in Fig. 1B give the volume change due to the molecular association features.

Electrical conductance

An Amel unit, model 730 measured electrical conductance, κ (S). The measuring cell was thermostated by circulating oil. An F25 precision thermometer (Automatic System Laboratories) measured the temperature with an accuracy of ±0.003°C.

In presence of polymer-surfactant interactions, electrical conductance data as a function of the surfactant content (keeping the PVP content fixed) show the occurrence of two changes in slope at the *cac* and *cmc** values, respectively [14]. The accuracy on such concentration thresholds is between 2 and 3%.

Results

Volumetric properties

In Fig. 1B is reported the behaviour observed in the H_2O–PVP–SCAP system as a function of surfactant molality. V_2 values are quite different from those measured in the binary H_2O–SCAP system. The volume change associated to micelle formation was evaluated as indicated in previous studies [15]. The volume change associated to polymer-surfactant interactions, ΔV_{inter}, is lower than ΔV_{mic}. It is not possible to evaluate *cac* and *cmc** values from volumetric properties.

Because of the very low *cac* and *cmc** values (below, or close to the millimolal range), the volumetric investigation of H_2O–PVP–TEAPFOSS system is subject to a large uncertainty. Estimates indicate ΔV_{mic} values close to 14 cm^3 mol^{-1} and ΔV_{inter} slightly above 10 cm^3 mol^{-1}. It must be pointed out that available volumetric data on polymer-surfactant systems indicate $\Delta V_{inter}<\Delta V_{mic}$ [16].

Electrical conductance

The $\kappa(m)$ curves show the presence of two well-defined changes in slope, associated to the onset of polymer-surfactant interactions (at the *cac*) and to micelle formation (at the *cmc**), respectively [14]. The former quantity indicates the saturation concentration of the surfactant in molecular form, in presence of the polymer. The *cmc**, conversely, is the concentration at which the polymer binding-sites become saturated and free micelles begin to form.

Surface properties

The surface tension of aqueous surfactant systems shows changes in slope around the *cmc*. In presence of polymer two such changes are observed, at *cac* and at *cmc**, respectively. The distance between the above points, Fig. 1A, is roughly proportional to the amount of polymer in the mixture. On thermodynamic grounds the *cac* and *cmc** values are points at which $\partial^3\tau/(\partial \ln m_2)^3=0$ [17].

Phase diagrams

Depending on added PVP, an intermediate region separates the molecular from the micellar region [18,19]. In ternary, or pseudo-binary, phase diagrams three portions of the solution region can be distinguished. They are: 1. the molecular solution (below the *cac*), 2. the polymer-surfactant interaction region, and, 3. the micellar one (above the *cmc**), respectively.

The above behaviour may be put in evidence by drawing the pseudo-binary phase diagrams reported in Figs 2A, 2B and 3. In all cases, *cmc** is proportional to the polymer content in the mixture, whereas *cac* is much less dependent on PVP content. The width of the interaction region decreases on increasing T and ionic strength. The width of the normalised (with respect to the *cmc*) interaction region is lower in caprylate than in TEAPFOSS.

Discussion

The interactions of surfactants with PVP occur in both sodium caprylate and TEAPFOSS systems, irrespective of the nature and properties of the amphiphilic molecules. The polymer-surfactant interaction regions are drawn in Figs 2A, 2B and 3.

In the case of sodium caprylate, hydrophobic interactions between the surfactant alkyl chain and the non-polar portions of PVP may occur. Because of the molecular properties of TEAPFOSS (having a hydrocarbon incompatible fluoro-methylene chains) no hydrophobic interactions with PVP are expected. Indeed, polymer-surfactant interactions occur also in this system and contributions different from the hydrophobic ones must be considered.

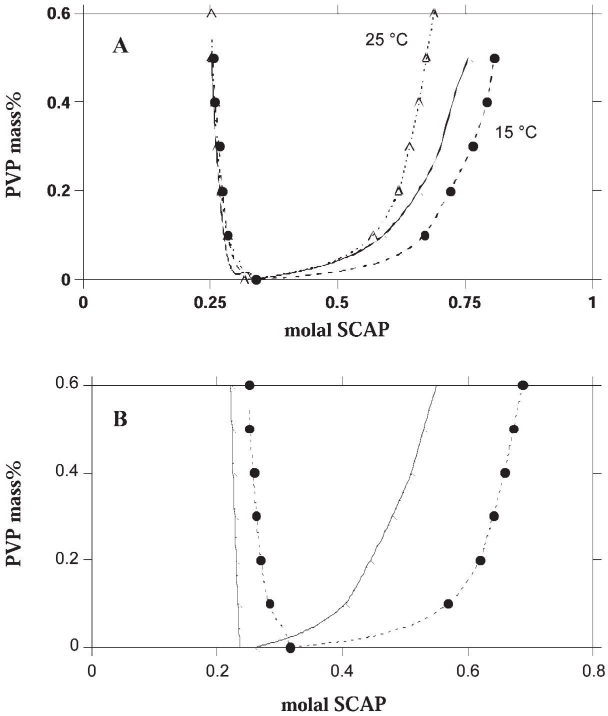

Fig. 2 A – Plot of the *cac* and *cmc** lines in a pseudo-binary diagram, reporting the PVP mass% as a function of SCAP molality. Data refer to 15 (full circles), 20 (points) and 25°C (triangles). B – Effect of 1 molal NaCl on polymer-surfactant interactions for the (water–1 molal NaCl)–PVP–SCAP system, points, compared to that in water, full symbols, at 25°C

Partly responsible for the observed phase behaviour are ion-dipole interactions between PVP and charged micelles. The Gibbs energy of transfer of aggregates from bulk water to a non-specified polymer binding-site is another possible contribution. Terms due to the polymer must be considered, too.

Information on enthalpic and entropic contributions controlling polymer-surfactant interactions may be obtained from the temperature dependence of the (cmc^*/cac) ratio, which is a Gibbs energy of transfer term. In the case of sodium caprylate, the entropy of transfer regularly increases with the amount of polymer in the medium [20, 21].

As a consequence of polymer-surfactant interactions, changes in the spontaneous curvature of polymer-bound micelles occur. This hypothesis finds support from fluorescence studies, indicating that the aggregation numbers of polymer-bound micelles are lower than the free ones [22].

Attempts to quantify the observed phase behaviour on thermodynamic grounds are not an easy task. The chemical potential of micellar surfactant, in fact, is due to:

– the Gibbs energy of transfer of alkyl chains from water to a hydrocarbon liquid;

– the difference between bulk hydrocarbons and the micellar core (due to the chain packing into micelles);

– the Gibbs energy of formation of an interface separating the micelle core from the bulk;

– steric contributions, and

– electrostatic ones.

As can be seen from the aforementioned list, the number of contributions to the surfactant chemical potential is high. In presence of polymer-surfactant interactions, each of the above contributions splits in two terms, due to free and polymer-bound micelles, respectively. The interfacial term due to polymer-bound micelles, for instance, is significantly different from that of free ones [23]. That's why it is very difficult to evaluate the surfactant chemical potential in the above systems.

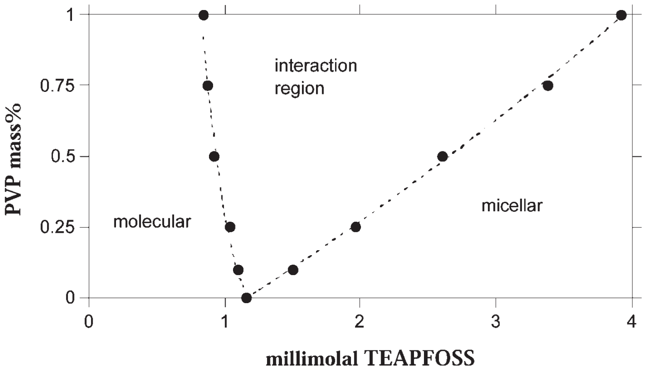

Fig. 3 The *cac* and cmc^* lines in a diagram reporting the PVP mass% as a function of the TEAPFOSS millimolality, at 25°C

In absence of statistical mechanics models, we use an approach based on a mass action approach to micelle formation. In this context the surfactant content, X_{tot}, is expressed as [9]

$$X_{tot}=X_1+MX_M+Nn_bX_P[X_N/1+X_N] \tag{3}$$

where M is the aggregation number of free micelles, N that of polymer-bound ones and X_1 the mole fraction of molecular surfactant. X_M and X_N are the mole fraction of free and polymer-bound micelles, respectively, X_P the polymer mole fraction in the medium and n_b the number of polymer binding-sites. When X_N<<1, the term $Nn_bX_P[X_N/1+X_N]$ approximates to $Nn_bX_PX_N$.

The equilibrium values of X_M and X_N, respectively, can be expressed by

$$X_N=X_1^N\exp^{(-N(\Delta\mu^o_{int}/KT))} \tag{4}$$

$$X_M=X_1^M\exp^{(-M(\Delta\mu^o_{mic}/KT))} \tag{4'}$$

where $\Delta\mu°$ terms are the changes in the chemical potential associated to the formation of free or polymer-bound micelles, respectively. The optimal aggregation numbers are given by the equations $(\partial\Delta\mu^o_{int}/\partial N)=0$ and $(\partial\Delta\mu^o_{mic}/\partial M)=0$, respectively.

Let us define *cac* and *cmc** curves as power-law equations of X_P, according to

$$cmc^*=X_{cmc}+aX_P+bX_p^2+cX_p^3+\ldots \tag{5}$$

$$cac=X_1=X_{cmc}+AX_P+BX_p^2+CX_p^3+\ldots \tag{5'}$$

where a, b, c, A, B, C are proper constants. When X_P is low, Eqs (5) and (5') may be linearised, without loss of accuracy. Keeping X_{tot} fixed and assuming that X_P is moderate, the differential form of Eq. (3) may be written as

$$(\partial X_{tot}/\partial X_P)=0=(\partial X_1/\partial X_P)+M(\partial X_M/\partial X_P)+Nn_b(\partial(X_PX_N)/\partial X_P) \tag{6}$$

Because of the mass action constraint, M, N and n_b terms do not depend on polymer and surfactant content. As can be seen in Fig. 4, $(\partial X_1/\partial X_P)$ and $(\partial X_M/\partial X_P)$ are the

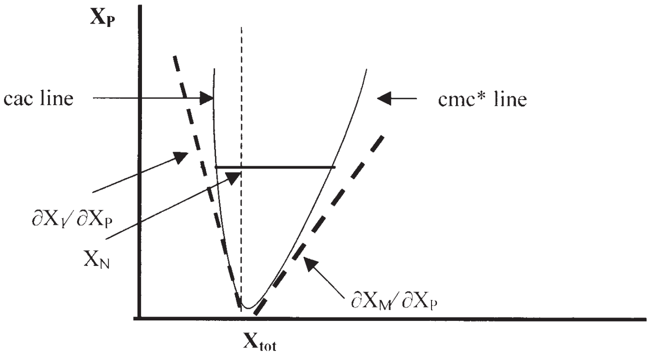

Fig. 4 Scheme indicating how to relate the quantities X_1, X_P, X_M and X_N each other. The figure was drawn according to Eqs (6) and (7)

tangents to *cac* and *cmc** curves. In the dilute regime (when Eqs (5) and (5’) may be linearised), the relations linking X_N to other quantities imply the approximate equality

$$X_N \approx [(\partial X_1/\partial X_P)^2 + (\partial X_M/\partial X_P)^2 - 2X_P^2]^{1/2} \tag{7}$$

where $(\partial X_1/\partial X_P) \approx A$, and $(\partial X_M/\partial X_P) \approx a$. The better the approximation is, the lower the polymer content is. [N.B. For thermodynamic consistency, the limit of Eq. (7) as X_P approaches 0 should be considered]. Accordingly, the links between quantities of interest can be obtained from the above approximation.

Equilibrium models have been extensively used to account for polymer-surfactant interactions [6, 9, 22, 23]. The approximation presented here holds in dilute regimes. Equation (7), in fact, relates the width of the interaction region to the polymer and the surfactant nature, i.e. the affinity between the components can be evaluated. It can be demonstrated, too, that the affinity is proportional to the width of the interaction region.

The present approximation indicates the occurrence of some differences between the water–PVP–SCAP and the water–PVP–TEAPFOSS systems. In the former case, a progressive growth of polymer-bound micelles can be inferred from the phase diagrams. This hypothesis finds support from the fact that T and ionic strength decrease the width of the interaction region. In the water–PVP–TEAPFOSS system, conversely, the unfavourable interactions between the rigid CF_2 chains and PVP do not allow polymer-bound micelles to grow in size.

Conclusions

The aim of this study was to get information on polymer-surfactant interactions in presence of short chain surfactants. Experimental findings indicate that a combination of hydrophobic and electrostatic effects gives rise to the behaviour observed in these systems. Both *cac* and *cmc** values are sensitive to temperature, ionic strength and polymer content in the solvent medium.

The approximate solution to the mass action model for polymer-surfactant interactions indicates that the width of the interaction region is controlled by the affinity between surfactant and polymer.

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