

I.B.Ivanov, L. Grigorov, T. Kolarov, "Influence of Neutral Salts on the Properties of Adsorbed and Foam Films of Polyoxyethylene Surfactants" "Proceedings of the International Conference on Colloid and Surface Science", ed. E.Wolfram, Vol. 2, p.169, Akademiai Kiado, Budapest, (1975).

INTRODUCTION

The stabilization of lyophobic colloids by polymers and surfactants with long macromolecular chains has been the subject of intensive investigations (e.g. [1-7]) for the last few years. The theoretical explanation of the effects observed was given mainly by Meier [5] and Hesselink, Vrij and Overbeek [7]. It can be assumed that the factors stabilizing the colloid particles should be responsible also for the stability of foam films formed from solutions of similar surfactants.

It is the purpose of our report to check this concept through investigating some thermodynamic properties of adsorbed and foam films of polyoxyethylene surfactants. The measurements of the contact angle between foam film and bulk liquid combined with measurements of the bulk liquid surface tension allow the calculation of the films' thermodynamic parameters.

EXPERIMENTAL

The surfactant used was monodisperse polyoxyethylene lauryl ether with 18 oxyethylene groups $/C_{12}(EO)_{18}/$ prepa-

red in prof. Lange's laboratory. Sodium chloride was analytical grade applied after heat treatment at 500° C. Double distilled water was used in preparing the solutions. The technique of foam film formation was the same as described previously, e.g. [12]. Contact angles were measured by the topographic method [8] through an extrapolation to zero film thickness [10]. The surface tension of the solutions was determined by the Wilhelmy method using a scratched glass plate [11]. The experiments were carried out at $20 \pm 0,2^\circ \text{ C}$.

RESULTS AND DISCUSSION

Surface tension measurements. Fig. 1. gives the surface tension (σ^l) - surfactant concentration (C_s) results for $C_{12}(\text{EO})_{18}$ in KCl solutions (the electrolyte concentrations in mol/lit are denoted on the left hand side of the figure). From the slopes and intersections of these curves the values of the area per molecule A_0 and the standard free energy of adsorption $\Delta\mu_s^\circ$ can be evaluated [16]. The results for A_0 (open symbols) and $-\Delta\mu_s^\circ$ (closed symbols) as a function of electrolyte concentration C_e are shown on fig. 2.

Gibbs adsorption isotherm for the system under consideration has the form

$$d\sigma^l = -\Gamma_s^l d\mu_s - \Gamma_e^l d\mu_e \quad (1)$$

where Γ^l is adsorption, μ - chemical potential and the subscripts "s" and "e" denote respectively surfactant and electrolyte. The estimation shows that the last term in eq. (1) is negligible. Therefore, if σ^l is constant for a number of solutions, then μ_s is constant also i.e. $(d\mu_s)_{\sigma^l} = 0$ and we can put down

$$\frac{d \ln \gamma_s}{d C_s} = - \left(\frac{\partial \ln c_s}{\partial C_e} \right)_{\sigma^l} \quad (2)$$

where γ_s is the activity coefficient. When C_s is smaller than C_e the activity coefficient γ_s depends only on

The values of surfactant and electrolyte concentrations corresponding to constant surface tension are taken from the curves on fig. 1 and the dependence of the surfactant's activity coefficient on the electrolyte concentration C_e (fig. 3) is deduced. The slope of this curve gives the salting out coefficient. Fig. 3 indicates that the salting out becomes considerable at 1,3 mol/lit and does not increase after 2,0 mol/lit. The inflection point is at about 1,6 mol/lit. The same characteristic points can be seen (see fig. 2) from the dependences of $\Delta\mu_0^s$ and Λ_0 on the electrolyte concentration: maxima at 1,6 mol/lit and no alternation after 2,0 mol/lit. The fact that the absolute value of the adsorption free energy as well as the area per molecule are increasing with electrolyte concentration suggests that the polyoxyethylene chain is gradually emerging onto the surface and partially lies flat on it. The following decrease of Λ_0 and $-\Delta\mu_0^s$ at higher electrolyte concentrations is probably related to the steric hindrance between the adsorbed surfactant molecules on the surface which makes the polyoxyethylene chains plunge back into the solution. A similar hypothesis was earlier put forward by Kretzschmar [13] for another case.

Contact angle measurements. From the contact angles measured the film tension Δ is calculated according to the formula [9,10]:

$$\Delta = 2\sigma^l \cos \theta_0 \quad (3)$$

where θ_0 is the contact angle. It is convenient to introduce [14] the excess film tension

$$\bar{\Delta} = 2\sigma^l - \Delta \quad (4)$$

The dependence of $\bar{\Delta}$ on the electrolyte concentration at constant surfactant concentration ($5 \cdot 10^{-4}$ mol/lit) is shown on fig. 4. For the time being we are not a position to do any interpretation of the $\bar{\Delta}$ changes at electrolyte concentrations higher than 2,0 mol/lit since in this region the

surfactant concentration used is above the critical micelles concentration. Up to 1,3 mol/lit salting out is insignificant (see fig. 3) and $\bar{\Delta}$ does not depend on the electrolyte concentration. The remaining part of the curve on fig. 4 can be explained on the basis of Hesselink, Vrij, Overbeek theory [7]. They have shown that the repulsion caused by the macromolecules is mainly due to two effects i. osmotic effect, which is predominant at larger thicknesses and ii. volume restriction effect, which becomes important at smaller thicknesses. The increase of $\bar{\Delta}$ between 1,3 and 1,6 mol/lit can be related to the osmotic effect. Since with the augmentation of the salt concentration the solvent becomes worse [15], the osmotic effect decreases and the excess film tension increases. At concentrations higher than 1,6 mol/lit the film becomes thinner and the volume restriction becomes significant. This leads to an increase of the repulsion, which results in a decrease of the excess film tension.

Gibbs-Duhem equation for the excess film tension at constant temperature can be written down [10] in the form.

$$d\bar{\Delta} = (\Gamma_s - 2\Gamma_s^l) d\mu_s + (\Gamma_e - 2\Gamma_e^l) d\mu_e \quad (5)$$

where Γ_s and Γ_e are respectively the surfactant and electrolyte adsorptions in the film as a whole. The small term due to the disjoining pressure is neglected. Let us suppose that in our case the electrolyte term is small also. Combining eqs (1) and (5), both without electrolyte terms, we get the equation

$$\frac{d\bar{\Delta}}{d\sigma^l} = \frac{2\Gamma_s^l - \Gamma_s}{\Gamma_s^l} \quad (6)$$

Therefore, the adsorption relative change $(2\Gamma_s^l - \Gamma_s) / \Gamma_s^l$ in the film with respect to its value on the bulk surface can be calculated from the dependence of the excess film tension on the bulk surface tension. This dependence is

shown on fig. 5. It can be seen that up to 1,3 mol/lit there is no any adsorption change (no salting out). Between 1,3 and 1,6 mol/lit the adsorption in the film is higher than at the bulk surface. This is due to the increased attraction of polyoxyethylene chains of opposite monolayers, which hinders the chains to emerge onto the film surfaces. Between 1,6 and 2,0 mol/lit the adsorption in the film is less than at the bulk surface. This is due to the volume restriction effect which hinders the polyoxyethylene chains to plunge back. The relative change of adsorption is very small in both concentration ranges (about 0,1 %) so that it cannot be detected by any direct measurements, e.g. by radiotracer measurements [17].

Although the above interpretations are only qualitative, they seem to be correct since identical considerations apply equally well to different effects, such as the adsorption data, the dependence of the excess film tension on the electrolyte concentration and the change of the relative adsorption. This conclusion is supported by the fact that the characteristic points for different properties lie always at one and the same electrolyte concentration. Experiments with other neutral salts (NaCl, KBr, K_2SO_4) give similar results. Some uncertainty in our treatment remains however about the relative adsorption range 1,6 - 2,0 mol/lit since there, the neglected electrolyte term in Gibbs-Duhem equation (5) can, at least in principle, be significant. There exists some possibility that the effects observed in the above region of electrolyte concentrations might be due also to attraction between desolvated polyoxyethylene chains. The experiments carried out at present will check these hypotheses.

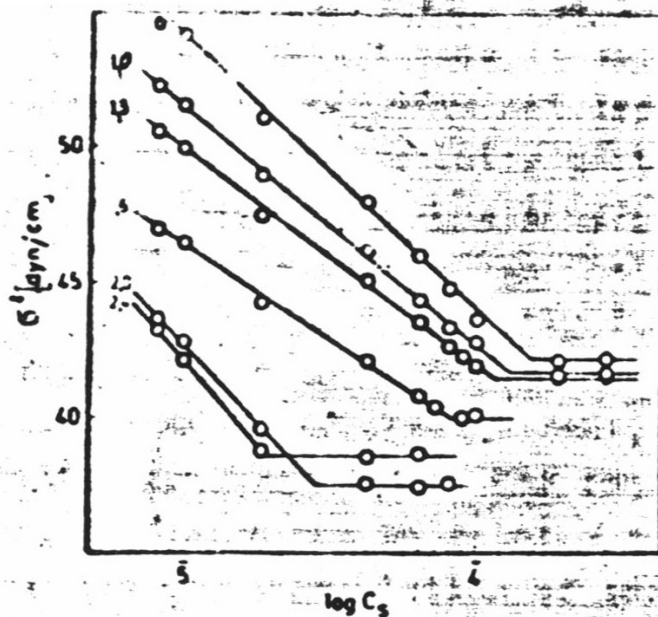


Fig. 1. Surface tension σ^s of $C_{12}(EO)_{18}$ on surfactant concentration C_s curves at KCl concentrations denoted on the left hand side of the figure in mol/l:.

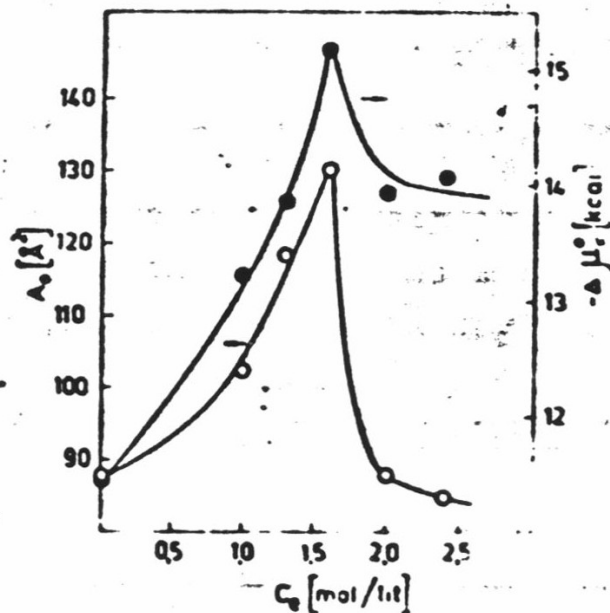


Fig. 2. Area per molecule A_0 (open symbols) and standart free energy of adsorption $\Delta\mu_s^\circ$ (closed symbols) of $C_{12}(EO)_{18}$ as a function of KCl concentration C_e .

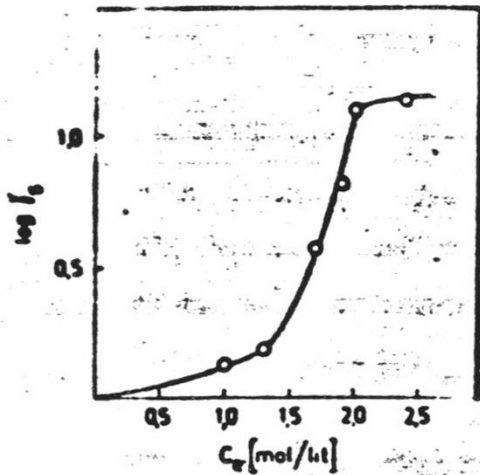


Fig. 3. Activity coefficient f_{\pm} of $C_{12}(EO)_{18}$ as a function of KCl concentration C_e .

Fig. 4. Dependence of the excess film tension $\bar{\Delta}$ on the KCl concentration C_e .

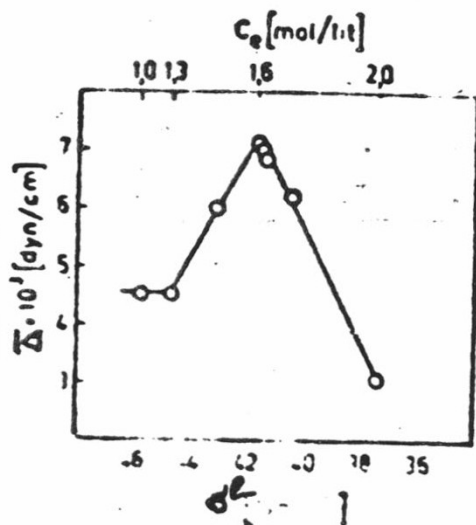
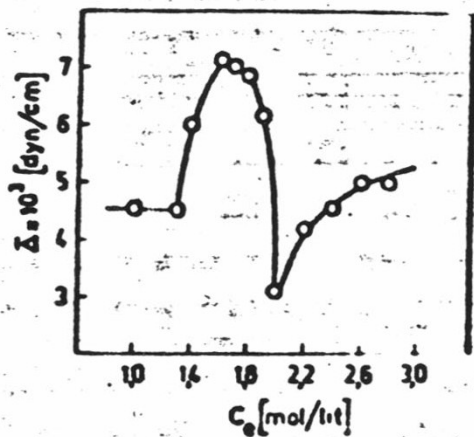


Fig. 5. Dependence of the excess film tension $\bar{\Delta}$ on the bulk surface tension σ' of $C_{12}(EO)_{18}$.

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