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ON THE MECHANISM OF ADSORPTION OF A CATIONIC SURFACTANT ON QUARTZ

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Abstract: Experimental data on surface charge of quartz in dependence on concentration of CTAB solution and pH were obtained using capillary electrokinetic method. The results are compared with the developed theory of the Langmuir-type adsorption that takes into account adsorption both on charged and noncharged surface centers. Computer optimization procedure results in adsorption potential values -15 kT and -11 kT, respectively. A ratio between surface concentrations of the centers was also estimated.

INTRODUCTION

Mechanism of cetyltrimetylammonium bromide (CTAB) adsorption from aqueous solutions on quartz is not yet fully understood. At present, there are two models describing this process: monolayer and two-layer. First layer is formed from CTA^+-ions electrostatically adsorbed on dissociated OH-groups on quartz surface. The second layer is suggested to form due to hydrophobic interaction after completion of the monolayer [1-4]. We have performed an attempt to develop a theory that takes into account adsorption of a cationic surfactant simultaneously on two types of surface sites, namely charged and noncharged ones [5].

RESULTS AND DISCUSSION

For calculation of adsorption isotherms, two models of the Langmuir-type adsorption were used: 1) model of parallel

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monolayer adsorption on two different types of surface centers, charged and noncharged; ii) model of consecutive adsorption when adsorption of a second layer occurs on electrostatically pre—adsorbed cations, forming some kind of hemimicelles. The developed theory gives dependencies of surface charge σ, formed as a result of adsorption, on concentration of surfactant solution C_s. In both cases, the surface charge is equal

$$\sigma/\sigma_o = 1 - (\tau_1 + m\tau_2) \tag{1}$$

where σ_o is the initial surface charge of a quartz surface at $C_s = 0$, $\tau_1 = N_1/N_c$ and $\tau_2 = N_2/N_c$ are the degree of coverage of charged and noncharged centers, respectively. The value of m is equal in the first case to N_n/N_c and in the second case N_2/N_c, where N_n and N_c are surface concentrations of noncharged and charged sites, and N_2 is the surface concentration of adsorbed ions in the second layer.

Consideration of rates of adsorption and desorption in the state of dynamic equilibrium results in the following equations for the monolayer and two-layer models:

$$\sigma/\sigma_o = 1 - [K_1C/(1 + K_1C)] - [m\,K_2C/(1 + K_2C)] \tag{2}$$

$$\sigma/\sigma_o = (1 - m\,K_1K_2C^2)/[1 + K_1C(1 + K_2C)] \tag{3}$$

Here $K_1 = \exp(-\Phi_1/kT)$, $K_2 = \exp(-\Phi_2/kT)$ and $C = C_s/c_o$, where $c_o = 55.5$ M is the limiting concentration of water molecules, Φ_1 and Φ_2 are the potentials of specific adsorption on charged and noncharged sites, respectively.

Derived equations (2) and (3) contain three unknown parameters, namely Φ_1, Φ_2 and m. They were determined using computer optimization procedure when comparing the theory with experimental data. Experimental dependencies of surface charge on concentration of CTAB aqueous solutions were determined using the method of capillary electrokinetics [6,7], when solution is pumped through a thin (r = 5 to 10 µm) single quartz capillary. The values of the surface charge were calculated from Gouy and Helmholtz-Smoluchowski equations measuring streaming potentials and streaming currents.

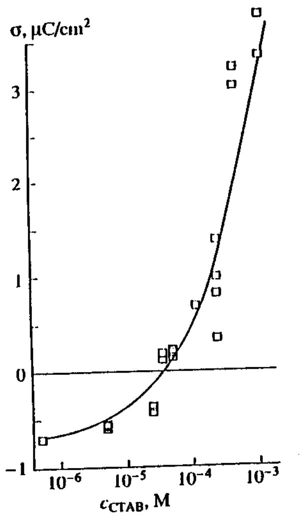

Fig.1 Experimental values of surface charge σ (points) and calculated ones using equations (2) and (3) (solid curve) in dependence of CTAB concentration.

Fig.1 shows the result of comparison of experimental data with theory in the case when σ_0 at pH 6.5 was equal to - 0.7 μC/cm^2. Experimental data are shown by points, whereas solid curve was calculated using equations (2) and (3). No marked difference between monolayer and two-layer models is seen. Both the models give nearly the same values of parameters: $\Phi_1 = -15$ kT, $\Phi_2 = -11$ kT and $m = 8$. The same values of parameters were calculated also in the the cases of higher (at pH 9.5) and lower (at pH 5) initial surface charges σ_0.

Comparison of experimental data with two theoretical models of adsorption shows that both give the similar results. This may be explained supposing that potentials of adsorption Φ_2 are nearly the same for noncharged quartz sites and for the pre adsorbed surfactant molecules. This results in a mixed mechanism when surfactant may adsorb simultaneously on noncharged centers and on pre adsorbed molecules forming the second layer. Mechanism of mixed adsorption demands further progress in the theory.

Developed models of cationic surfactant adsorption explain the effect of charge reversal and observed dependencies of contact angles on surfactant concentration [8].

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