ON THE ROLE OF ADSORPTION KINETICS IN THE PHENOMENA OF WETTING DUST PARTICLES BY DROPS OF SURFACTANT SOLUTIONS

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Abstract

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ON THE ROLE OF ADSORPTION KINETICS IN THE PHENOMENA OF WETTING DUST PARTICLES BY DROPS OF SURFACTANT SOLUTIONS

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In studying the dust-collecting action of sprayed aqueous solutions of surfactants of the semicolloidal type—for example, wetting agents DB and OP-10—we established significant differences in their dust-collecting capacity, despite the closeness of their chemical composition and molecular structure ([1]). These differences were also retained in solutions having practically identical, maximally reduced static surface tension (down to 30–35 erg/cm^2).

In contrast to solutions of molecularly soluble surfactants—organic acids, alcohols, etc., in which adsorption equilibrium is established in fractions of a second ([2])—in colloidal-micellar solutions of soap-like wetting agents, a considerable time is required to attain the adsorption equilibrium corresponding to the static values of surface tension ([3]).

Meanwhile, the capture of dust particles by drops of water takes place under kinetic conditions of their brief collision (contact), which in some cases leads to the entrainment of dust particles by drops, while in others it does not give this result because of the dynamic detachment of drops from the dust particles ([4]). Since the probability of capturing a particle as a result of its wetting by the solution increases as its surface tension at the moment of collision decreases, it is obvious that the efficiency of dust collection will depend to a considerable extent on the degree to which, by this moment, an adsorption layer has had time to form and, consequently, on how much by this moment the dynamic value of the surface tension (σ_d) will have been lowered, i.e., how closely it approaches the static value (σ_s), corresponding to the equilibrium state of the surface layer of a drop of solution at the given concentration.

It follows from this that the lowering of the static surface tension of surfactant solutions does not characterize their true wetting properties under real conditions of dust collection: σ_d may vary from values close to the surface tension of pure water (σ_0) down to the lowest value, σ_s.

Obviously, these differences, caused by the peculiarities of the properties of solutions of colloidal wetting agents, could be revealed by investigating their

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surface activity at different lifetimes of the solution–air interface (τ), which under dust-collection conditions can vary over wide limits. Therefore, in view of the possibilities of ordinary methods of measurement, we studied σ_d of the solutions by the drop-counting method at $\tau = 2$ sec and σ_s by the hanging-drop method ([5]) at $\tau = 2$ min, which in our cases always corresponded to the attainment of adsorption equilibrium.

It is evident from Fig. 1 that in solutions of DB and aerosol OT the kinetics of establishment of adsorption equilibrium manifests itself relatively rapidly, and both isotherms—of dynamic and static surface tension, $\sigma_d(C)$ and $\sigma_s(C)$—rapidly approaching one another with increasing concentration, practically coincide at a certain value of it. For DB this value corresponds to 0.08–0.1%, and for aerosol OT to 0.22–0.25%, which agrees with the value of the critical micelle concentration (CMC) known from the literature[6]. It is known that at this point and at higher concentrations

Fig. 1. Isotherms of dynamic (σ_d) and static (σ_s) surface tension of solutions of the wetting agents DB and aerosol OT.
1 $-\sigma_d$ at $\tau = 2$ sec.; **2** $-\sigma_s$ at $\tau =$ min.

the formation of an equilibrium (saturated) adsorption layer is achieved practically in a very short time, certainly much less than tenths of a second[7]. Thus, determination of the CMC by joint measurements of σ_d and σ_s as a function of the concentration at which they practically coincide may be regarded as a new method for estimating this quantity.

A different regularity in the course of the isotherms is found for the wetting agent OP-10 (Fig. 2). In this case the difference between σ_d and σ_s is large and, what is especially significant, does not disappear even in solutions of higher concentrations (up to 4%), two orders of magnitude greater than the concentration at which a constant value $\sigma_s \sim 30$ erg/cm^2 is reached. This is precisely what indicates the low rate of formation of adsorption layers in solutions of this type of surface-active substance, as a result of which, at short lifetimes of the solution–air interface, sufficiently low values of σ_d are not attained at any concentrations. The reason for this is that the indicated wetting agents, unlike DB and aerosol OT, are a molecular mixture of components of different molecular weight (with hydrocarbon chains of different length and structure), as a result of which micelle formation in their solutions

occurs gradually, over a broad range of concentrations ([8]). This also determines the retarded kinetics of formation of their adsorption layers and the low effectiveness of their dust-collecting action.

Fig. 2. Isotherms of dynamic (σ_d) and static (σ_s) surface tension of solutions of the wetting agent OP-10. 1—σ_d at $\tau = 2$ sec.; 2—σ_s at $\tau = 2$ min.

Figure 2: Fig. 2. Isotherms of dynamic (σ_d) and static (σ_s) surface tension of solutions of the wetting agent OP-10. 1—σ_d at $\tau = 2$ sec.; 2—σ_s at $\tau = 2$ min.

In solutions of wetting agents in which micelle formation occurs at a definite point of convergence of the isotherms $\sigma_d(C)$ and $\sigma_s(C)$, corresponding to the CMC, when $\sigma_d - \sigma_s \approx 0$, the effectiveness of collisions of dust particles with drops of the solution under kinetic conditions will be greatest.

Fig. 2. Isotherms of dynamic (σ_d) and static (σ_s) surface tension of solutions of the wetting agent OP-10. 1—σ_d at $\tau = 2$ sec.; 2—σ_s at $\tau = 2$ min.

The dependence of the comparative effectiveness of the action of additions of surface-active substances (1), relative to water (E), on the difference $\sigma_d - \sigma_s$ is given in Fig. 3, from which it is seen that the wetting agents DB and OT aerosol do indeed possess the greatest effectiveness. The dependence of E on $\sigma_d - \sigma_s$ is meaningful only at practically identical and sufficiently low σ_s. In general, it could be assumed that the dependence of E on σ_d or on $\sigma_0 - \sigma_d$ should be characterized for different surface-active substances by a single universal curve. However, this is not the case, since the dust-collecting action is determined, in addition, by the specific nature of the surface of the dust particles, manifested in their interaction with drops of the solution. Indeed, we have shown ([4]) that, when surface-active substances whose polar groups can be chemically fixed on a solid surface are used as additions to water, the dust-collecting ability of water is not increased ($E > 1$), but, on the contrary, is decreased ($E - 1 < 0$, see curve 6).

This, evidently, can be explained by hydrophobization of the dust particles (quartz in the case of amines, apatite in the case of fatty acids) as a result of bimolecular

migration of surface-active molecules from the surface of the solution droplet to the solid dust particle.

This effect is not observed, and the dust-capturing capacity increases normally both on dusts that are not capable of chemisorptive hydrophobization and on any dust at elevated concentrations of any surface-active substances with a sufficiently low value of σ_d—such aqueous solutions wet any hydrophobic surfaces, which also explains the transition of curve 6 into the wetting region.

Fig. 3. Dependence of the effectiveness of the action of wetting agents on quartz dust (E) on $\Delta\sigma = \sigma_d - \sigma_s$.
1—wetting agent DB, 2—aerosol OT, 3—refined alkylarylsulfonate, 4—wetting agent OP-10, 5—sulfonol, 6—dodecylamine acetate.

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REFERENCES CITED

1. A. B. Taubman, S. A. Nikitina, DAN, 110, No. 4 (1956).

2. C. S. Addison, *J. Chem. Soc.*, 1944, 477.

3. A. Schwartz, D. Perry, *Surface-Active Agents*, IL, 1953.

4. A. B. Taubman, S. A. Nikitina, DAN, 110, No. 5 (1956).

5. M. M. Kusakov, N. M. Lyubman, A. Yu. Koshevnik, *Proceedings of the Petroleum Institute, Academy of Sciences of the USSR*, 2, 53 (1952).

6. A. P. Brady, D. I. Salley, *J. Am. Chem. Soc.*, 70, 914 (1948).

7. N. K. Adam, H. L. Shute, *Trans. Farad. Soc.*, 34, 758 (1938); G. C. Nutting, F. A. Long, N. B. Harkins, *J. Am. Chem. Soc.*, 62, 1496 (1940); 63, 84 (1941).

8. L. M. Kushner, W. D. Hubbard, *J. Phys. Chem.*, 58, No. 12, 1163 (1954).

Note: Figure translations are in progress. See original paper for figures.