PHYSICAL CHEMISTRY

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

L. M. LEVITSKII, S. A. NIKITINA, A. B. TAUBMAN

MICELLE FORMATION IN SOLUTIONS OF SURFACTANTS AND KINETIC WETTING

(Presented by Academician P. A. Rebinder on 13 XI 1962)

The process of micelle formation in aqueous solutions of synthetic soap-like surfactants (SAS), accompanied by a sharp change in many properties of these solutions at the critical concentration of micelle formation (^1), is connected, as we have shown, with the kinetics of formation of adsorption layers of these SAS, manifested in a considerable discrepancy between the surface tension of solutions (σ), measured under dynamic conditions (σ_d), and at adsorption equilibrium (σ_s).

Investigation of this dependence made it possible to establish that, in addition to the usual value of the critical concentration $(C_k)_1$, another value–$(C_k)_2$–is detected in solutions by generally accepted methods; together with the first it lies in a relatively narrow interval of concentrations of dilute solutions, in which the micelle-formation process takes place, beginning at $C = (C_k)_1$ and ending at $(C_k)_2$ (^2). Subsequently, qualitative indications of the existence of a second micelle-formation point were obtained in studying the solubilization of a dye in solutions of nonionic SAS (^3).

At the same time we showed that a characteristic feature of the position of the point $(C_k)_2$ on the concentration axis (C) is the coalescence at this concentration of the isotherms of static and dynamic surface tension, which indicates that, at solution concentrations $C > (C_k)_2$, the rate of formation of adsorption layers becomes practically independent of the duration of existence of the interface. At the same time, another important characteristic of SAS solutions–their wetting ability–had not in general been connected with the state (molecular or micellar) of the solution and, thus, the question of whether this property changes at the critical concentrations $(C_k)_1$ and $(C_k)_2$ remained open.

Therefore, in the present work the ability of SAS solutions to effect kinetic wetting during impregnation of porous bodies was investigated, since in this case, owing to adsorption of the SAS on the highly developed surface of the solid, a large concentration deficit arises in the boundary layers of the solution, causing a slowing of the kinetics of formation of the adsorption layer and of the rate of establishment of equilibrium between it and the bulk of the solution (^4). Obviously, it is precisely under such conditions that the influence of micelle formation may be revealed in wetting phenomena.

Figure 1

Figure 1: Figure 1

The wetting ability of the solutions was evaluated by determining the duration of impregnation until immersion into the bulk of the liquid (solution) of a sample of standard cotton fabric hydrophobized with organic substances (ˆ5), or of a membrane collodion ultrafilter, hydrophobic by nature (ˆ6). The use of such filters (the least dense filters No. 6 are most suitable for this), owing to the high uniformity of their structure, ensures

provides good reproducibility of the measurement results. A convenient modification of this procedure may be measurement of the time required for a filter to become saturated when a drop of solution is applied to it. A drop of volume 0.001 ml, applied from a micropipette to the filter, retains its visible diameter during absorption ($d \sim 2$ mm), while the wetting zone is 5-6 mm. The saturation time is recorded from the disappearance of the clearly visible meniscus of the drop; for example, for a 0.05% solution of the wetting agent DB on filter no. 6, about 23–25 sec is required. One filter of 30 mm diameter makes it possible in this way to carry out more than 10 separate measurements. It was established that both variants of the method give coincident data. The objects of study (Table 1) were Aerosol OT (sodium dioctyl sulfosuccinate) and nonionic polyoxyethylene ethers of alkylphenols—DB, OP-10, and the analogous ethers of butylphenol TB-15 and TB-25*.

Fig. 1. Dependence of the contact angle of wetting $(1, 2)$ and the saturation time of fabric $(3, 4)$ on the concentration of surfactant solution.
$1, 3$ –Aerosol OT; $2, 4$ –sulfonol

How sharply the influence of adsorption kinetics on wetting may manifest itself is shown in Fig. 1. As can be seen, under static conditions the wetting action on the paraffin surface, expressed by the curve of dependence of the contact angle of wetting on surfactant concentration, $\theta = f(C)$, practically coincides for Aerosol OT and sulfonol (curves 1 and 2), whereas when porous systems (fabric or filter) are saturated, exceptionally sharp differences in the wetting properties of Aerosol OT—a highly effective wetting agent—and sulfonol, which has a relatively weak wetting action, are fully manifested on the wetting isotherms $\tau_m = f(C)$ (curves 3 and 4).

At the same time, with a sufficiently large number of experimental points it was possible to establish that the course of the curves $\tau_m = f(C)$ is nonmonotonic, and in the region of the usually investigated concentrations of dilute solutions ($C \ll 1\%$) they show two breaks, which are especially clearly visible if the curves are plotted on a logarithmic scale, as was done in Fig. 2. It follows from Fig. 2 that, for each surfactant, this dependence is expressed by a straight line consisting of three sections, each of which is somewhat shifted along the ordinate axis relative to the preceding one. These shifts evidently characterize the degree of increase in the wettability of the solid surface caused by a change in the bulk

Table 1

Surface-active substances*	Critical micelle-formation concentrations, measured by methods of surface tension $(C_k)_1$	Critical micelle-formation concentrations, measured by methods of surface tension $(C_k)_2$	Critical micelle-formation concentrations, measured by methods of wetting upon saturation of fabric or filter $(C_k)_1$	Critical micelle-formation concentrations, measured by methods of wetting upon saturation of fabric or filter $(C_k)_2$
Aerosol OT	0.119	0.231	0.110	0.225
DB**	0.026	0.085	0.021	0.085
OP-10	0.035	0.162	0.035	0.166
TB-15*	0.010	0.028	0.015	0.025
TB-25	0.019	0.043	0.022	0.068

* For the structure of the preparations studied, see (7,3).
** It should be noted that each of the investigated nonionic surfactants, by the conditions of synthesis, is not an individual compound but a more or less broad mixture of homologs, as a consequence of which the accuracy of estimating the value of C_k proves to be reduced in comparison with ionic compounds.

* Preparations of the TB series were synthesized and used as wetting agents by P. I. Ermilov(3), to whom the authors express their gratitude for providing samples of these preparations for the study.

properties of solutions at definite concentrations. If these concentrations are compared with the values of the critical micelle-formation concentrations measured by us earlier and in the present study, it is easy to conclude that the indicated changes in wetting ability are associated with the process of micelle formation and are fixed at two concentration points coinciding with the values $(C_k)_1$ and $(C_k)_2$.

Indeed, from Table 1 it is seen that the values $(C_k)_1$ and $(C_k)_2$, determined by the wetting (impregnation) method, are in good agreement with the data obtained by us from surface-tension isotherms and, consequently, with the results of applying other methods for this purpose (nephelometry, spectrophotometry, etc.) (2,7).

Fig. 2. Wetting isotherms of hydrophobized fabric by surfactant solutions. 1—TB-15; 2—DB; 3—aerosol OT; 4—OP-10

Figure 2: Fig. 2. Wetting isotherms of hydrophobized fabric by surfactant solutions. 1—TB-15; 2—DB; 3—aerosol OT; 4—OP-10

Obviously, the greater the number of experimental points on the wetting isotherm, the more rigorously the positions of the break points of the straight lines can be fixed; therefore, measurements of this kind of kinetic wetting may be regarded as a method for determining the critical concentrations of micelle formation.

Fig. 2. Wetting isotherms of hydrophobized fabric by solutions of surfactants. 1—TB-15; 2—DB; 3—aerosol OT; 4—OP-10

Fig. 2 also shows that, in accordance with data obtained earlier by us, measurements of kinetic wetting lead to a correct assessment of the effectiveness of the action of synthetic wetting agents and make it possible to establish its relation to their molecular structure. Obviously, the preparation TB-15 has a hydrophobic-hydrophilic balance close to the optimum and is therefore an effective wetting agent ([3]). This applies to an even greater degree to aerosol OT, for which, unlike all the other surfactants investigated, a straight line without breaks was obtained, since practically instantaneous immersion of the fabric or filter specimen took place already at $C = (C_k)_1$. All this agrees with the generally accepted proposition that a branched molecular structure favors the manifestation of high wetting properties in surfactants.

Thus, in the present work it has been shown for the first time that micelle formation affects the kinetic wetting action of surfactant solutions, which is evidently connected with the slow kinetics of formation not only of adsorption layers, but also of micelles in the bulk of the solution.

It is important to note that there are no grounds for believing, as some authors do ([3]), that at $C \geq (C_k)_2$ a change in the shape of the micelles occurs, since both points $(C_k)_1$ and $(C_k)_2$ lie close to one another in one region of low concentrations (Table 1), in which only spherical micelles, postulated by Hartley ([8]), exist. For the intermediate concentration region between these points, in which the micelle-formation process proceeds, the only characteristic feature is the presence in the solutions of unequal numbers of micelles, the smallest at $C = (C_k)_1$ and the largest at $C = (C_k)_2$, so that the final equilibrium distribution of different kinds of structural units (molecules (ions), micelles), both in the bulk of micellar solutions and between the bulk and the adsorption layers, is established not at $C = (C_k)_1$, as was assumed earlier, but at $C = (C_k)_2$, beyond which the distri-

remains unchanged over a broad concentration range, up to the appearance in the solution of another type of micelle *.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
13 XI 1962

REFERENCES

1. W. C. Preston, J. Phys. Coll. Chem., **52**, 84 (1948).

2. A. B. Taubman, S. A. Nikitina, DAN, **135**, No. 5, 1179 (1960).

3. P. I. Ermilov, Scientific Notes of the Yaroslavl Technological Institute, **6**, 53 (1961).

4. S. A. Nikitina, A. B. Taubman, DAN, **116**, No. 1, 113 (1957).

5. *Unified Methods for the Analysis and Evaluation of Detergents*, All-Union Scientific-Research Institute of the Fat Industry, 1958, Leningrad, p. 65.

6. V. M. Tets, *Sanitary Microbiology*, Moscow, 1958, p. 85.

7. A. B. Taubman, V. V. Konstantinova, A. S. Kryukova, *Chemistry and Technology of Fuels and Oils*, No. 3, 61 (1960).

8. G. Hartley, *Paraffin-chain salts*, Paris, 1936.

9. R. Mattoon, R. Stearns, W. Harkins, J. Chem. Phys., **15**, 209 (1947); W. Harkins, J. Chem. Phys., **16**, 156 (1948).

---

* One may note, for example, that for potassium laurate and myristate $C_k = 0.024$ and 0.006 M, respectively, whereas X-ray data, which are the principal evidence for the existence of large micelles of nonspherical shape, indicate the formation of such structures in solutions only at $C \geqslant 0.24$ M, i.e., about 6% (9).

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