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Abstract

Full Text

Physical Chemistry

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On a New Way of Experimentally Investigating the Desorption of Surface-Active Substances from Liquid Phase Boundaries

(Presented by Academician P. A. Rehbinder, 30 I 1965)

For investigating the kinetics of formation of adsorption layers at liquid/gas and liquid/liquid boundaries, we have applied methods of measuring surface tension from the dimensions of a stationary bubble or drop (the sessile-bubble method) ⁽¹⁾. Subsequently, an attempt was made to study the possibility of desorption of a substance from a surface adsorption layer by replacing the solution under investigation around the bubble (drop) with a pure solvent under static conditions (without mechanical disturbance of the adsorption layer and, correspondingly, of the bubble or drop).

The experiments carried out confirmed the correctness of such an approach and, on the other hand, showed that only the sessile-bubble (drop) method provides a real possibility of studying desorption under static conditions in the case of liquid phase boundaries. The experiment was carried out as follows. Into a special thermostated optical cell, provided with a device for passing liquid under constant hydrostatic pressure, the solution under investigation of a surface-active substance is poured, in which a sessile gas bubble is formed. Then, in the usual manner, the change in surface tension is recorded (photography followed by measurements of the parameters of the bubble contour and calculation of the surface tension from the corresponding tables). After this, upon expiration of a specified time for formation of the surface layer, a pure solvent is pumped sufficiently slowly through the cell (approximately 3 l in 20 min), until the dissolved substance has been completely removed from the volume.

During the process of "washing" and after its completion, the surface tension is continuously recorded. After completion of this stage of the experiment, a new bubble is formed, so to speak, in the washing substrate, and the surface tension of this substrate is again recorded.

With the aid of this procedure we succeeded in visually demonstrating the desorption of surface-active molecules from the adsorption layer at the boundary with gas. As an example, we give typical results for sodium oleate: in addition to the curve of surface tension characterizing the desorption process (an increase in surface tension from 33.3 erg/cm² for a 0.01% solution at 20° and pH 11.0

to 72.0 erg/cm²), the surface tension of the liquid under investigation after replacement of the solution by flowing water at the same pH (72.0 erg/cm²) and the surface tension of the washing substrate (72.5 erg/cm²) are very close to the value of the surface tension of pure water under analogous conditions.

On the other hand, we have for the first time experimentally shown the irreversibility of adsorption of macromolecular surface-active substances at the liquid/gas boundary, using polyvinyl alcohol as an example. The adsorption layer that had formed (surface tension 63.0 erg/cm² ...).

(for a 0.3% solution) shows no signs of desorption after replacement of the solution by pure water even after a long time has elapsed (the surface tension did not change after 20 hours), whereas the surface tension of the washing substrate is much higher (72.5 erg/cm²) and corresponds to the surface tension of pure water. This clearly shows that polyvinyl alcohol molecules cannot spontaneously, at least over a long time, leave the adsorption layer. It should be noted that the question of reversibility and irreversibility of the adsorption of polymer molecules has been considered theoretically (²).

Moreover, with the aid of the proposed approach it is possible to consider the question of the equilibrium nature of adsorption at liquid phase boundaries, since it permits an approach to the state of adsorption equilibrium under changes in the concentration in the solution from two sides.

In addition to the study of desorption and the problems associated with it, the proposed method opens up broad possibilities for investigating, under static conditions, various kinds of interactions in adsorption layers, making it possible to carry out stepwise measurements at one and the same undisturbed phase boundary (bubble or drop).

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