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Abstract

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ON THE INFLUENCE OF MONOLAYERS OF SOLUBLE AND INSOLUBLE SURFACE-ACTIVE SUBSTANCES ON THE DISSIPATION OF ENERGY OF STATIONARY SURFACE WAVES

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Here we present the results of measurements of energy dissipation in cylindrical stationary surface waves on aqueous solutions of caproic and capric acids, in comparison with the dissipation on pure water. The results are compared with the relative dissipation caused by insoluble monolayers of myristic acid.

As a measure of relative dissipation the quantity

$$\bar{a} = \frac{(z/\xi)}{(z/\xi)_0} - 1, \qquad (1)$$

is adopted, where z is the amplitude of oscillation of the vessel, and ξ is the amplitude of the surface wave (1). The method used in this work was described earlier (^{1}). The data presented here are more accurate owing to the use of a more stable sound generator (this applies in particular to the data (1) on the dependence of the resonance frequency $\nu_{\max}$, at constant surface wavelength λ, on the concentration of the solutions, which should be regarded as approximate).

The surface tensions σ were calculated from the formula

$$\nu_{\max}^2 = 2\pi\sigma/\rho\lambda^3 + g/2\pi\lambda, \qquad (2)$$

where $\nu_{\max}$ is the resonance frequency at constant wave number, or λ, for all measurements, g is the acceleration of gravity, and ρ is the density. All measurements were carried out at 20°, at $\lambda = 0.38$ cm, in a vessel of the same dimensions as in (1), and at amplitudes $\xi \ll \lambda$ ($\xi \approx 30\,\mu$).

Fig. 1. 0.07 M aqueous solutions of caproic acid $C_5H_{11}COOH$. The curve of the dependence $\bar{a}(C)$ is drawn through the experimental values A. Experimental

Figure 2

Figure 1: Figure 2

Figure 3

Figure 2: Figure 3

values of $\Delta\sigma$: , —our data, —calculated by formula (2), —by the ring method; —data of Dervishian (2); —data of Shishkovsky (3).

The results of the measurements are given in Figs. 1-3 in the form of curves $\bar{a}(C)$, $\Delta\sigma(C)$ ($\Delta\sigma = \sigma_0 - \sigma$, where σ_0 is the surface tension of water and σ that of the solution), or $\bar{a}(F)$ and $\Delta\sigma(F)$, where C is the volume concentration and F is the area per molecule in the insoluble monolayer.

The decreases in surface tension calculated by formula (2) for aqueous solutions of caproic acid (Fig. 1) agree well with Dervishian' s data (2) and with our measurements by the ring method.

Fig. 2. 0.07 M aqueous solutions of capric acid $C_9H_{19}COOH$. Curve **1** for the dependence $\bar{a}(C)$ is drawn through the experimental values **A**. For the dependence $\Delta\sigma(C)$: **B**, **V** are our data, **B** calculated by formula (2), **V** obtained by us by the ring method; **G**—data of Deryagin[2]; curve **2**—according to Frumkin' s data[7].

Fig. 3. Monolayers of myristic acid on 0.01 N HCl. For the dependence $\bar{a}(F)$, curve **1** is drawn through the experimental points **A**. The dependence $\Delta\sigma(F)$ is represented by Adam' s curves[4,2,3] and by our data (**B**), calculated by formula (2).

The deviations of Shishkovsky' s values[3], shown in the same figure, are probably due to the fact that the acid he used was not sufficiently pure, as is mentioned in his work.

Comparatively good agreement of the $\Delta\sigma$ values was obtained also for myristic acid (Fig. 3) with Adam' s data[4]: the $\Delta\sigma(F)$ curves measured on surface balances are close to the values calculated by formula (2). The scatter of our data is explained by the fact that the monolayer was applied in the form of a $2.07 \cdot 10^{-4}\,M$ solution in chloroform to a relatively small cuvette area (about 10 cm^2). Although an "Agla" syringe with a volume-reading accuracy of $2 \cdot 10^{-4}$ ml was used, the error due to evaporation is significant.

No agreement is observed for capric acid (Fig. 2). In this case, however, the data obtained by different methods and by different authors differ considerably from one another.

The curves $\bar{a}(C)$ have the same form as those obtained earlier[1]. A characteristic feature is the sharply expressed dissipation maximum in the case of capric acid (Fig. 2), which corresponds to the same maximum in the case of caprylic acid[1]. The fact that this maximum appears for higher homologues at extremely low bulk concentrations gave grounds to suppose that it is not caused by the mechanism of change in the boundary conditions of the flow—the Marangoni-Gibbs type effect. The explanation of the maximum on the dissipation curve in the latter case is based on the assumption that, at higher bulk concentrations, the gradients of surface concentration that impede the flow on the surface are compensated by an increased supply of substance to the surface from the bulk by diffusion[5,6], as a result of which, after the rise of the curves, their decline is observed. It is easy to calculate that, at

at volume concentrations of the order of 10^{-5} M and at frequencies of the order of 100 Hz (capric acid), the exchange with the solution is extremely small.

The decisive factor for excluding effects of this type is the result obtained with the practically insoluble monolayers of myristic acid, for which the same maximum is observed (Fig. 3), although compensation from the bulk is excluded here.

It may therefore be assumed that the well-reproducible dissipation observed by us—at least its highest values in the region of the maxima—is not caused by a change in the flow regime, but reflects, possibly, the actual dissipation of energy in the adsorption layer. It is interesting to note that the dissipation peak for a myristic-acid monolayer occurs with compact packing of the layer by lying molecules ($F \simeq 45$ Å^2), precisely where the transition to a "liquid-expanded" monolayer begins. Approximate calculations (because of the unreliability of the data on $\Delta\sigma$) show that for capric acid as well the maximum most probably lies at packing of the same type.

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