Physical Chemistry

1963

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Figure 1

Figure 1: Figure 1

Abstract

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Physical Chemistry

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On the Influence of Organic Acids on Boundary Friction and Adhesion of Solids in Hydrocarbon Liquids

(Presented by Academician P. A. Rebinder, 25 VI 1963)

Organic acids are widely used as surface-active substances for reducing coagulation and frictional interaction (1). However, the mechanism of this effect cannot be considered clarified even qualitatively. Although Hardy (2) found a linear dependence of the coefficient of friction of surfaces lubricated with pure fatty acids on their molecular weight up to stearic acid, Bowden (3) confirmed this dependence only for the lower members of the homologous series. Experiments on the influence of organic acids on the lubricating ability of oils, structure formation, and the stability of dispersed systems likewise do not lead to unambiguous conclusions about the role of the structure of the molecules of the surface-active substance, which in many cases is explained by the uncertainty of the thickness and state of the boundary layer of liquid (4).

For the purpose of studying the protective action of organic acids (mainly fatty acids) dissolved in hydrocarbon liquids under more definite conditions, we used the method described earlier (5,6), which makes it possible to measure the resistance to thinning and shear σ_τ of a thin (0.02—2.00 μ) layer of liquid separating mirror-polished, plane-parallel (in the experiments described, steel) disks, with simultaneous measurement and regulation of the contact pressure σ_n and of the thickness h of this layer (error $+0.01$ μ). Measures were taken to eliminate dust and foreign surface-active substances. The experiments were carried out at $20 \pm 2^\circ$. The narrow naphthene-paraffin fraction of oil MS-20, isolated by the chromatographic method, is denoted by us as NPF; deeply refined (white) cable oil S-110 of paraffin base, as KM.

Fig. 1. Thickness of the residual layer and properties of boundary layers of solutions of fatty acids.
$1, 5 - \sigma_n$; $2, 3, 4 - \sigma_\tau$; $6, 7, 8 - f_{\mathrm{st}}$.
$1, 2, 7$–0.05% $C_{17}H_{35}COOH$ in isooctane;

Fig. 2

Figure 2: Fig. 2

$3, 6$—0.05% $C_5H_{11}COOH$ in isooctane;
$4, 5, 8$—0.01% $C_{15}H_{31}COOH$ in NPF.

The resistance to thinning and shear of polymolecular boundary layers of solutions of fatty acids rapidly increases as their thickness decreases (Fig. 1), in first approximation according to a power law.* At constant values of h^*_{min} σ_{p} is 1.5-3 orders of magnitude greater than σ_τ. As h_{min} decreases within the range 0.2-0.02 μ, σ_{p} and σ_τ increase almost symbatically. Accordingly, the coefficient of static friction under polymolecular lubrication with solutions of fatty acids lies within the range from 0.002 to 0.06 and depends little on the thickness of the boundary layer.

If the shear is completely localized in the boundary layer, then it is sufficient for it to consist of 10-15 layers of fatty-acid molecules to reduce the coefficient of friction to 0.01 and below. Such layers reduce the static adhesion forces of contacting flat surfaces to a value below the sensitivity limit of the method (< 5 g/cm^2). The low value of the coefficient of friction in the polymolecular boundary layer of fatty acids may also serve as an additional factor in the stabilization of disperse systems protected by such surface-active substances, since particles colliding at an angle to the straight line connecting their centers will slide relative to one another without approaching to within the range of effective action of van der Waals attraction.

Fig. 2. Dependence of the coefficient of static boundary friction of contacting surfaces and of the resistance to shear of boundary layers on the length of the hydrocarbon chain of fatty acids. Solid curves $\sigma_\tau = \psi(C_n)$, dashed curves $f = \psi(C_n)$: $1, 7$—0.1% in isooctane; 2—0.05% in benzene; $3, 4, 5$-$8, 10$—0.1% in NPF; 9—0.5% in benzene; 6—0.1% in KM; $1, 5, 6, 7$—$\sigma_{\text{p}} = 4$ kg/cm^2; $2, 9$—$\sigma_{\text{p}} = 0.2$ kg/cm^2; 3—$\sigma_{\text{p}} = 2$ kg/cm^2; $4, 10$—$\sigma_{\text{p}} = 6$ kg/cm^2; 8—$\sigma_{\text{p}} = 22$ kg/cm^2.

The resistance to thinning and shear of the boundary layers of the solutions studied is determined by the length of the hydrocarbon chain of the fatty acids and by the properties of the solvents. It was shown ([5,6]) that $h_{\text{min}} = K_1 + K_2 C_n$, where C_n is the number of carbon atoms in the hydrocarbon chain of the acid, and K_1 and K_2 are constants, the first of which is equal to h_{min} of the solvent, while the second depends on the structure of its molecules. The resistance to shear at low contact pressures is also described by a linear dependence (Fig. 2): $\sigma_\tau = K_3 - K_4 C_n$. The constant K_3 increases with increasing contact pressure, i.e., with decreasing h_{min}, and at $\sigma_{\text{p}} = \text{const}$ it is the inverse function of h_{min} of the solvent; the constant K_4 depends on the composition of the solvent (in

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* In contrast to boundary layers of electrolyte solutions, for which the dependence of σ_n on h obeys an exponential law ([8]).

aromatic and naphthenic hydrocarbons it is smaller than in paraffinic ones) and, to a lesser extent, on the contact pressure.

When the contact pressures exceed 6-10 kg/cm^2, the linear dependence over the entire range of C_n is violated (curve 10, Fig. 2). In solutions of lower fatty acids at these loads the thickness of the boundary layer becomes so small that the resistance to shear is determined not only by the properties of the polymolecular layers, but also by the resistance to shear in the bimolecular adsorption layer, and at still higher pressures by the adhesive-mechanical interaction of protrusions of the surface microrelief. In all probability, the deviation of the linear dependence of the coefficient of friction on the molecular weight of the lubricant, discovered by Bowden, is explained by the fact that the spherical slider he used created a high contact pressure and not all lubricants ensured localization of shear only in the polymolecular boundary layer.

* h_{min} is the thickness of the boundary layer at which its resistance to thinning is equal to the contact pressure ([7]).

The values of the coefficients of static boundary friction during lubrication with solutions of fatty acids in low-molecular-weight hydrocarbons, as well as the shear resistance, are an inverse linear function of the length of the hydrocarbon radical of the acids (curves 1 and 9 in Fig. 2). The constant K increases with increasing contact pressure and depends on the nature of the solvent (for a solution in benzene it is higher than for solutions in isooctane). The applicability of Hardy' s rule (linearity of the function $f = \psi(C_n)$) to solutions of fatty acids in lower hydrocarbons indicates a similarity in the structure of the boundary layers of the individual acids and of their solutions.

When the molecular weight of the linear solvent molecules, or more precisely their length, exceeds the corresponding value for the acid molecules, Hardy' s rule is not obeyed for solutions (curves 4, 5, and 8 in Fig. 2). This is explained by the fact that h_{min} is determined not only by the acids but also by the solvent, and the molecules of the latter can appreciably increase σ_τ (Table 1).

In order to separate the effect of fatty acids on the values of σ_τ and h_{min}, the shear resistance of their boundary layers was measured at a constant, controlled value of the external pressure, h ($h < h_{\text{min}}$). It turned out (Fig. 3) that shear does not depend on the length of the fatty-acid molecules, but is determined in the first approximation by the value of h, and in the second by the composition of the solvent. Consequently, the effect of the structure of organic acids introduced into hydrocarbon liquids to increase their antifriction action is manifested directly in an increase in the resistance to thinning of the boundary layer, which at a given contact pressure leads to a decrease in the shear resistance owing to removal of the sliding plane from the surface of the solid.

Fig. 3. Shear resistance of the boundary layers of fatty-acid solutions and the length of their hydrocarbon chain at $h_{\text{min}} = \text{const}$.
1—0.05% in benzene; 2—0.1% in isooctane; 3, 4, 5—0.1% in NPF; 1, 2, 4—$h_{\text{min}} = 0.10\,\mu$; 5—$h_{\text{min}} = 0.06\,\mu$; 3—$h_{\text{min}} = 0.13\,\mu$.

Table 1

Effect of the solvent on the properties of the residual boundary layer of 0.05% solutions of stearic acid, $h_{\text{min}} = 0.06\,\mu$

Solvent	σ_{p}, kg/cm^2	σ_{τ}, kg/cm^2
Benzene	3.0	0.021
Hexane	3.8	–
Isooctane	4.0	0.035
Dodecane	5.2	0.052
NPF	22.0	0.217

The kinetics of separation of plane-parallel disks divided by a boundary layer of solutions of surface-active substances does not obey the laws of hydrodynamics of a viscous liquid. According to the Stefan–Reynolds equation, the separation time of such disks t should be inversely proportional to h^2 (7). In reality, in hydrocarbon solutions of fatty acids the separation time t is considerably smaller (and the approach time larger) than t , calculated from the value of h_{min}. For example, in the case of a 0.1% solution of stearic acid in isooctane ($h_{\text{min}} = 0.14\,\mu$, disk $r = 0.9$ cm) $t = 4.05$ sec, $t = 362$ sec. The phenomenon noted is explained by the preservation of the wedging pressure accumulated during the approach of the disks (7). This pressure is not compensated with time (or decreases very slowly) as a result of the static resistance to shear of the boundary layers of fatty-acid solutions in narrow flat gaps.

Although h_{min} increases with increasing length of the hydrocarbon radical of the fatty acid (5), t also increases in the homologous series (Fig. 4). The wedging pressure P_r, calculated from the relation, changes correspondingly,

$$P_r S = F \quad - F \quad = \frac{3\pi\eta r^4}{4t \; h_{\text{min}}^2}.$$

The calculated value of P_r is lower than the true value, since $\eta_{\text{bulk}} < \eta_{\text{boundary}}$.

Direct X-ray methods have shown that fatty acids in water–benzene solutions (^{9}) and on a metal surface (^{10}) form layers in which the molecules are oriented parallel to one another and approximately perpendicular to the phase surface. According to (^{11}), on a metal surface in viscous oils fatty acids are capable of retaining such an orientation in layers up to $0.9\,\mu$ thick. Our experimental data are well explained if it is assumed that such a molecular structure is also formed by solutions in hydrocarbon liquids, with solvent molecules distributed between the molecules of the surface-active substance. The constancy of σ_τ for various fatty acids at $h_{\text{min}} = \text{const}$ confirms that shear in the polymolecular layer occurs along the terminal CH_3 groups.

Figure 4

Figure 3: Figure 4

Fig. 4. Separation time (t_{sep}) of plane-parallel disks and the thickness of the residual layer ($h_{\min}$), calculated (effective) wedging pressure (P_r), for 0.1% solutions of fatty acids in isooctane, as a function of the length of the hydrocarbon radical of the acid (number of carbon atoms–C_n):
1—P_r; 2—$h_{\min}$; 3—t_{sep}

The linear structure of the molecules and the associated ability to create a layered supramolecular structure are apparently the principal reason for the protective action of polymolecular layers of adsorbed fatty acids. Disruption of the linear structure of acid molecules and an increase in their isodiametric character lead to weakening of the boundary layer (Table 2). For the formation of a monomolecular adsorbed layer, the energy of interaction of the acid with the metal plays an important role; however, as is evident from comparison of the resistance to thinning of solutions of fatty acids with that of more active chloro-fluoro derivatives and benzoic acid (Table 2), in a polymolecular layer an increase in the activity of the acid does not increase the strength of this layer. The difference between carboxylic acids and thiocarboxylic acids close to them (Table 2) can be explained by the fact that the former, owing to hydrogen bonds, form dimers in solutions, which approximately doubles the effective length of the molecules.

Table 2

Magnitude of boundary layers $h_{\min}$ of 0.025% solutions of organic acids (in microns)

Acid	$\sigma_p = 0.2$ kg/cm^2	$\sigma_p = 2.0$ kg/cm^2	Acid	$\sigma_p = 0.6$ kg/cm^2	$\sigma_p = 2.0$ kg/cm^2
Stearic	0.11	0.08	Enanthic	0.08	0.06
Oleic	0.10	0.07	2 Cl-4-enanthic	0.06	0.05
Phenylstearic	0.15	0.13	Benzoic	0.07	0.04
Sebacic	0.05	0.03	Thioenanthic	0.04	0.03

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Received
30 V 1963

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