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Abstract

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THE INFLUENCE OF THE RADIUS OF CATIONS ON THE PROPERTIES OF BOUNDARY LAYERS OF ELECTROLYTE SOLUTIONS IN PLANE GAPS BETWEEN QUARTZ SURFACES

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The application of a sensitive method for measuring the kinetics of adhesion and detachment of mirror-polished plane-parallel disks ([1], [2]) showed that thin boundary layers of solutions of surface-active substances and electrolytes in gaps between solid bodies offer static resistance to thinning and possess an increased viscosity in comparison with the bulk viscosity ([2], [3]). In connection with the role of electrolytes in the coagulation interaction of particles of a disperse system, the influence of the concentration and radius of cations on the properties, recorded by the above-mentioned method, of boundary layers of solutions of chloride salts of alkali and alkaline-earth metals in gaps between negatively charged quartz disks immersed in these solutions was investigated. As is known, the radius of ions determines their position in the lyotropic series ([4]). The following were measured: 1) the thickness of the boundary layer h_{gr}, equal to one half of the thickness of the gap between approaching disks at which the hydrodynamic law of outflow of a viscous liquid—the Stefan-Reynolds equation—begins to be violated; 2) the ratio of the boundary viscosity, measured from the rate of detachment of the disks, to the bulk viscosity η_0/η; 3) the thickness of the residual layer, equal to one half of the layer of solution not squeezed out of the gap between the disks by a specified load (up to 8 kg/cm^2) during the time of determination (from 3 to 9 hours); 4) the resistance to thinning of the residual layer, the index of which is

$$\bar{E}_{\sigma_{\mathrm{p}}' - \sigma_{\mathrm{p}}''} = \frac{h_{\min}' \left(\sigma_{\mathrm{p}}'' - \sigma_{\mathrm{p}}'\right)}{h_{\min}' - h_{\min}''},$$

where $h_{\min}'$ and $h_{\min}''$ are the thicknesses of the residual layers at specific loads σ_{p}' and σ_{p}''; 5) the dimensionless coefficient of boundary thickening

$$\psi = \frac{t_{\mathrm{ot}} \cdot \sigma_{\mathrm{ot}}}{\eta},$$

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

where t_{ot} is the time of detachment of one disk from the other at the normal detaching stress σ_{ot}; 6) the disjoining pressure (^{5}, ^{6}), corresponding to the equilibrium part of the residual layer. It was shown (^{3}) that the thickness of the residual layer of an electrolyte solution under alternating loading and unloading is partly reversible. It was assumed that the specific load compressing the equilibrium part of the residual layer is equal to the disjoining pressure.

The thickness of the boundary layer of the investigated solutions does not exceed 0.35 μ and decreases with increasing load. h_{gr} of solutions of divalent ions is substantially smaller than that of monovalent ions. For cations of the same valence, the thickness of the boundary layer increases as their radius decreases, i.e., as the hydration of the ions increases (see Table 1). This latter dependence is more clearly expressed for monovalent cations than for divalent ones, which is explained by the more considerable change in the radius of the ions and, correspondingly, in hydration in the series Li^+—Cs^+ than in the series Mg^{2+}—Ba^{2+}. With increasing temperature, h_{gr} decreases, and at 60° the difference between the ions falls below the sensitivity limit of the method ($\pm 0.01\ \mu$). Pri-

the increase in viscosity in the boundary layer depends on the thickness of the latter (^{1,2}). Integral values of η_0/η, measured by separating the disks after their contact for 10-60 min at contact pressures of 0.2-2.0 kg/cm^2, increase with increasing solution concentration, but when the latter reaches 5-10 mg-equiv/l, further change in it has little effect.

At a constant low solution concentration, an increase in the cation radius causes a decrease in the boundary viscosity, which qualitatively corresponds to the change in the electroviscous effect as a function of the electrokinetic potential. Thus, at 20°, after contact of the disks for 30 min under a pressure of 1 kg/cm^2, η_0/η for 0.01 N solutions of LiCl, NaCl, KCl, and RbCl is respectively 4.6, 4.2, 3.3, and 3.0.

Fig. 1. Effect of temperature on the coefficient of boundary thickening of electrolyte solutions in the gap between quartz surfaces. $t_p = 30$ min, $\sigma_p = 1$ kg/cm^2, $\sigma_{\text{sep}} = 0.08$ kg/cm^2.
1—NaCl—100 mg-equiv/l; 2—CaCl_2—10 mg-equiv/l; 3—NaCl 10 mg-equiv/l; 4—LiCl 10 mg-equiv/l; 5—NaCl—1 mg-equiv/l; 6—H_2O.

Fig. 2. Dependence of the thickness of the residual layer of 0.01 N electrolyte solutions on cation radius and load.
1—monovalent cations, $\sigma_p = 0.2$ kg/cm^2;
2—same, $\sigma_p = 1$ kg/cm^2;
3—same, $\sigma_p = 2.0$ kg/cm^2;
4—divalent cations, $\sigma_p = 0.2$ kg/cm^2;

5—same, $\sigma_p = 2.0$ kg/cm^2;
6—monovalent cations, $\sigma_p = 1$ kg/cm^2
(curves 1—5—at 20°, curve 6—at 60°).

An increase in temperature has a nonuniform effect on η_0/η. In the peripheral part of the boundary layer the increase in boundary viscosity decreases faster than the bulk viscosity, and η_0/η decreases; for example, for a $0.005\,N$ NaCl solution in the gap between disks equal to $0.23\,\mu$, it decreases from 2.1 to 1.0 between 20 and 80°. At a gap thickness close to $2h_{\min}$, this ratio either depends little on temperature or, more often, increases with it (for a $0.01\,N$ LiCl solution in a gap $0.04\,\mu$ greater than $2h_{\min}$, when the temperature changes from 20 to 90°, it increases almost twofold). The latter, as has already been noted for mineral oils ([2]), indicates a higher activation energy of flow and temperature coefficient of viscosity in the boundary layer than in the bulk of the liquid. Integral values of η_0/η, measured after a specified time of contact of the disks, also increase with rising temperature: from 20 to 80°, after 45 min of contact, for $0.005\,N$ KCl solutions, by a factor of 2.9, which is explained both by the distinctive temperature coefficient of viscosity of the boundary layer and by the decrease in the residual gap between the disks (see below, and also ([2, 3])).

The coefficient of boundary thickening, measured after contact of the disks for 10 min or more, is very sensitive to electrolytes. As is seen from Fig. 1, in aqueous solutions between quartz it increases with increasing temperature, concentration, valence, and cation radius.

The value of ψ may increase owing to thickening of the boundary layer, as in the case of previously studied solutions of fatty acids in mineral oils ([1,12]), and owing to a decrease in the gap between the disks. From the Stefan–Reynolds equation it follows that ψ is a function of the geometric factor and, at a constant disk radius, is inversely proportional to the square of the gap. Since the boundary viscosity decreases with increasing cation radius and, at solution concentrations above 10 mg-equiv/l, practically does not change, their influence on ψ cannot be regarded as a consequence of boundary thickening. On the other hand, it is known that these factors, as well as an increase in valence, lead to compression of the diffuse layer of ions ([4,10]). Finally, it seems improbable that the viscosity of the boundary layer increases with increasing temperature; therefore there is every reason to believe that the increase in ψ shown in Fig. 1 is caused by a decrease in the gap between the disks and, in the systems studied, may serve as an indicator of the latter.

The thickness of the residual layer of electrolyte solutions decreases with increasing temperature. At small loads and a temperature of 20°, increasing the concentration at first leads, in deep-purified water, to an increase in $h_{\min}$ from a value below the sensitivity limit of the method to 0.1—$0.3\,\mu$, and subsequently (above 7—10 mg-equiv/l) has no effect on this value. In the case of loads not exceeding 1—2 kg/cm^2, $h_{\min}$ decreases with increasing cation radius and, especially, with decreasing hydration (Fig. 2). At higher loads the influence of hydration becomes insignificant, and the relation between $h_{\min}$ and the cation radius r_k approaches a simple dependence of the form: $h_{\min} = k_1 - k_2 r_k$, where k_1 is a constant that decreases with increasing ion valence, temperature, and load and with decreasing solution concentration below 10 mg-equiv/l; k_2 is a constant close to zero at high loads. The smaller thickness of the residual layer of solutions of divalent cations than that of solutions of monovalent cations agrees with the ratio of the thicknesses of the diffuse layers of the first and second ions.

Table 1

Effect of cation radius, solution concentration, and temperature on h_{r} (μ)
at a normal pressure of 1 kg/cm^2

Temperature, °C	Solution concentration, mg-equiv/l	LiCl	NaCl	KCl	RbCl	MgCl$_2$	CaCl$_2$	BaCl$_2$
20	10	0.27	0.16	0.12	0.11	0.14	0.10	0.09
40	1	0.11	0.08	0.06	–	–	0.06	0.07
40	10	0.13	0.09	0.08	0.07	0.08	0.07	0.07
40	100	0.15	0.12	0.10	–	–	0.12	0.09
60	1	0.05	0.04	0.04	–	–	0.04	0.03
60	10	0.08	0.07	0.06	0.06	0.06	0.05	0.06

As was to be expected, the disjoining pressure of the solutions studied increases as the distance between the solid bodies decreases (Fig. 3). It also increases with decreasing cation radius and upon transition from divalent ions to monovalent ones. In the case of small gaps the differences between ions apparently become smoothed out; however, it is not excluded that the latter also depends on a decrease in the sensitivity of the method.

The influence of cation radius is clearly manifested in the resistance to thinning of residual layers (Fig. 4). It is interesting that an increase in the radius of monovalent cations causes an increase in $\overline{E}_{\sigma'_{\mathrm{p}}-\sigma''_{\mathrm{p}}}$, whereas it leads to a decrease in disjoining pressure. An increase in load and, correspondingly, a decrease in the thickness of the residual layer leads to an increase in its resistance to thinning (Table 2).

Many of the regularities described can be interpreted on the basis of

Table 2

Resistance to thinning of residual layers of 0.01 N electrolyte solutions at 20°

Electrolytes	σ_{p} 0.2–2.0 kg/cm^2: h'_{min}	σ_{p} 0.2–2.0 kg/cm^2: $\overline{E}$, kg/cm^2	σ_{p} 1.0–4.0 kg/cm^2: h'_{min}	σ_{p} 1.0–4.0 kg/cm^2: $\overline{E}$, kg/cm^2	σ_{p} 2.0–4.0 kg/cm^2: h'_{min}	σ_{p} 2.0–4.0 kg/cm^2: $\overline{E}$, kg/cm^2
LiCl	0.24	3.6	0.20	4.6	0.11	5.5
NaCl	0.13	5.8	0.12	6.0	0.09	6.7
KCl	0.12	7.7	0.10	9.0	0.08	10.6
$CaCl_2$	0.08	4.1	0.07	8.4	0.06	9.6
$BaCl_2$	0.08	4.0	0.06	9.7	0.04	17.0

modern concepts of the structure and thickness of diffuse layers and of their interaction; however, in order to explain the influence of the ion radius, especially such as Li^+ and Na^+, it is also necessary to invoke the concept of ion hydration. The binding energy of ions with water molecules lying outside the first sphere of the hydration shell constitutes an insignificant part of the total hydration energy (11). It is therefore not surprising that, at low contact pressures, hydration of ions in boundary layers can substantially affect the properties of these layers, whereas at relatively high pressures its role is small.

Fig. 3. Wedging pressure of electrolyte solutions in flat gaps between quartz surfaces at 20° (h_r is half the equilibrium gap).
1 –LiCl –10 mg-eq/l;
2 –NaCl –10 mg-eq/l;
3 –KCl –10 mg-eq/l;
4 –NaCl –1 mg-eq/l;
5 –$CaCl_2$ –10 mg-eq/l.

Fig. 4. Dependence of the resistance to thinning of the residual layer of electrolyte solutions on the cation radius (temperature 20°).
1 –dependence on the radius of monovalent cations (concentration 10 mg-eq/l),
2 –the same for divalent cations,
3 –dependence on the concentration of the LiCl solution.

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