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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# ON THE MECHANISMS OF ACTION OF NEUTRAL ELECTROLYTES ON THE BOND BETWEEN PARTICLES IN A COAGULATION STRUCTURE

*(Presented by Academician P. A. Rehbinder, December 8, 1959)*

The development of the theory of coagulation structure formation has broadened the concept of coagulation interaction between particles of disperse systems. If in the past this type of interaction was considered characteristic only of dilute colloidal solutions, it is now known that it also plays a very substantial role in forming the properties of concentrated and polydisperse suspensions, pastes, and sediments ([1,2]). Correspondingly, the question of the mechanism of the action of electrolytes on the coagulation bond between particles has broadened. In the present work, dimensional modeling ([3]) was used to investigate the influence of electrolytes on the elementary act of particle interaction: the thickness and resistance to thinning of boundary layers of electrolyte solutions in the gap between mirror-polished, plane-parallel round quartz disks immersed in these solutions were measured according to the method of ([4]), and the friction of spherical surfaces of negatively charged quartz and positively charged ruby in the same solutions was measured according to the method of ([5]). In the apparatus with disks, the distance between the surfaces could be measured within the range from 3-5 to 0.02 $\mu$ (experimental error $\pm 0.01\,\mu$), with contact pressure from 0.04 to 10 kg/cm$^2$; in the tribometer, direct contact of conjugate surfaces is realized with contact pressure from 50 to 550 kg/mm$^2$.

It follows from works ([3,6]) that electrolytes increase the kinetic resistance of thin layers of water to the approach of disks and impart to these layers static (equilibrium and nonequilibrium) resistance, leading to the preservation in the gap between quartz disks of a residual (non-squeezed-out) layer of solution (thickness $h_{\min}$). The influence of electrolytes on the kinetic resistance to the approach of particles apparently does not attain a large magnitude, since the boundary viscosity in the peripheral part of the boundary layer is increased by ions by more than a factor of 5 ([3]), and the transition to the residual layer is abrupt.

**Table 1**

Kinetic bond of plane-parallel quartz disks (diameter 12 mm) in electrolyte solutions after contact for 30 min under a load of 4 kg/cm$^2$ (pull-off force 0.08

kg/cm$^2$)

| Electrolytes | Solution concentration, mg-eq/L | Pull-off time, sec. | Electrolytes | Solution concentration, mg-eq/L | Pull-off time, sec. |
|---|---|---|---|---|---|
| LiCl | 10 | 2.9 | $MgCl_2$ | 10 | 14.7 |
| NaCl | 1 | 3.7 | $CaCl_2$ | 10 | 15.5 |
| NaCl | 10 | 4.3 | $BaCl_2$ | 5 | 30.0 |
| NaCl | 1000 | 9.3 | $BaCl_2$ | 10 | 34.0 |
| KCl | 10 | 13.0 | $AlCl_3$ | 10 | 43.0 |
| RbCl | 10 | 14.1 | $Th(NO_3)_4$ | 10 | 45.4 |

On the other hand, the kinetic bond ($^3$) of flat particles, expressed by the time of their detachment, depends substantially on the composition of the solution surrounding them (Table 1). The limiting viscosity has a known influence on this effect, but more important is that the composition of the solution determines the thickness of the residual layer (Table 2), and consequently also the gap between the surfaces, which is established under a given, not excessively high, contact pressure. It should be noted that the kinetic bond depends not only on the distance between the surfaces, but also on the shape of the gap; therefore the influence of electrolytes on the detachment time of convex particles should be substantially smaller than that of flat ones.

**Table 2**

Thickness of the residual layer in $0.01N$ electrolyte solutions and its resistance to thinning in the gap between quartz disks

| Electrolytes | $h_{\text{min}}$ (μ) at contact pressure (kg/cm$^2$) | $h_{\text{min}}$ (μ) at contact pressure (kg/cm$^2$) | $h_{\text{min}}$ (μ) at contact pressure (kg/cm$^2$) | $\bar{E}$ (kg/cm$^2$) in the pressure interval | $\bar{E}$ (kg/cm$^2$) in the pressure interval |
|---|---|---|---|---|---|
| Electrolytes | 0.2 | 2.0 | 4.0 | 0.2–2.0 | 2.0–4.0 |
| LiCl | 0.25 | 0.11 | 0.06 | 3.3 | 5.5 |
| NaCl | 0.14 | 0.09 | 0.05 | 5.0 | 6.7 |
| KCl | 0.12 | 0.08 | 0.04 | 7.7 | 10.6 |
| RbCl | 0.11 | 0.08 | – | 7.2 | – |
| $CaCl_2$ | 0.08 | 0.06 | 0.04 | 4.1 | 9.6 |
| $AlCl_3$ | 0.08 | 0.05 | 0.03 | 6.2 | 12.0 |
| $Th(NO_3)_4$ | 0.07 | 0.03 | 0.03 | 6.0 | 18.0 |

Fig. 1

Figure 1: Fig. 1

The thickness of the residual layer is determined by the concentration of the solution (Fig. 1), by the number of charges of the counterions and their radius (Table 2). With an increase in contact pressure and, correspondingly, a decrease in the distance between the surfaces, the role of the ionic radius decreases; and at high solution concentrations the influence of the number of ionic charges also decreases. The curves $h_{\min} = f(C)$ are inverse to the curves of the dependence of the coefficients of static friction and adhesion of microscopic particles on the concentration of electrolyte solutions (7). The resistance to thinning of the residual layer is determined above all by its thickness; therefore, in the selected load interval (up to 6–8 kg/cm$^2$), in solutions that form thinner residual layers at a given pressure, the index of this resistance $\bar{E}$ is in most cases higher. As the concentration of the solution increases to 5–10 mg-eq/l, $\bar{E}$ increases, but subsequently it hardly changes.

**Fig. 1.** Influence of concentration (in g-eq/l) on the thickness of the residual layer of solution in the gap between quartz surfaces at a contact pressure of 0.2 kg/cm$^2$. 1 –$BaCl_2$; 2 –KCl; 3 –NaCl.

Qualitative consideration of the data obtained leads to the conclusion that the gap between quartz surfaces in electrolyte solutions is associated with the thickness of the diffuse layer of adsorbed ions and with the interaction of these layers. Proceeding from the Gouy–Chapman double-layer theory, B. V. Deryagin (8) and A. N. Frumkin (9) obtained equations describing the repulsion of flat diffuse layers. For the case in which the surface potential is much smaller than $RT/F$, these equations coincide. Expressing $\chi$ (the index of the thickness of the ionic atmosphere according to Debye–Hückel) in terms of $KZ\sqrt{C}$, where $K$ is a constant, $Z$ is the number of charges of the ion of the diffuse layer, and $C$ is the concentration of the solution, the equation may be rewritten in the following form, convenient for checking by the method of alignment: $F_r = KZ^2Ce^{-hKZ\sqrt{C}}$, where $F$ is the repulsive force of the conjugated diffuse layers, and $h$ is the distance between the surfaces.

The agreement of the experimental data (points in Fig. 2) with the theoretical dependence shows that in electrolyte solutions with concentrations up to 8–10 mg-eq/l the ions prevent the surfaces from approaching to the distance of the effective action of van der Waals forces, owing to the electrostatic repulsion of the diffuse layers. In more concentrated–

concentrated solutions, and also at relatively large distances between the surfaces, of the order of the thickness of the boundary layer, a nonelectrostatic factor of interaction must operate.* Since in these cases

**Fig. 2.** Verification, by the method of rectification, of the applicability of the equation for the repulsive force of interacting diffuse layers of adsorbed ions. **1,**

**2** –$F_r = f(z, C)$. **1** –at $h_{\min} = 0.06 \pm 0.01\,\mu$, **2** –at $h_{\min} = 0.04 \pm 0.01\,\mu$; **3** –$F_r = f(C_{\mathrm{KCl}})$ (the numbers on the curve are the values of $C$ in mg-eq/l). **4, 5, 6** –$F_r = f(h)$. **4** –at $\chi = 1.5$ mg-eq per 1 l of $CaCl_2$, **5** –at $\chi = 2.5$ mg-eq per 1 l of KCl, **6** –at $\chi = 1$ mg-eq per 1 l of NaCl

the predominant importance belongs to the radius of the ions (at least within the range of mono- and divalent cations ([6])); it is most probable that this factor is the outer ([10]) or secondary ([11]) hydration of the ions.

**Fig. 3.** Coefficient of friction ($f$) and wear of ruby in electrolyte solutions of different composition and concentration as a function of the microhardness ($H$) of ruby in these solutions. **1** –static friction; **2** –wear (friction for 10 min.); **3** –kinetic friction

The high contact pressures, which in our tribometric experiments approach the microhardness of the minerals investigated, overcome the repulsive force of adsorbed ions, but the influence of electrolytes on the interaction of the surfaces of these minerals does not cease. As is seen from Table 3, the change in friction as a function of the composition of the solution does not correspond to the expression given above for the repulsive force of diffuse layers, and the coefficient of friction is determined by the number of charges of anions and cations, which indicates a mechanism of ion action not associated with the surface charge.

The specific action of electrolytes at high contact pressures is connected with their influence on the surface of minerals. It was shown ([12]) that in solutions of neutral electrolytes the microhardness of ruby and quartz decreases (one of the manifestations of the adsorption-induced decrease in the strength of solids ([13])). The friction (and wear) of ruby, and in individual groups of solutions also of quartz, increases with decreasing microhardness, independently, to a first approximation, of the composition of the ions and the concentration of the solution (Fig. 3),

* It is quite possible that the development of the theory of interaction of diffuse layers on the basis of more modern ideas about their structure than those proposed by Gouy will expand the range of applicability of the mechanism of electrostatic repulsion; however, there is no reason to suppose that it will become universal.

Table 3

Coefficient of friction of ruby and quartz in 0.001 N solutions of neutral electrolytes
(contact pressure: ruby 530, quartz 108 kg/mm$^2$; preliminary interaction of the minerals with the solutions: 1 hour).

| Electrolytes | Static friction, ruby | Static friction, quartz | Kinetic friction, ruby | Kinetic friction, quartz | Electrolytes | Static friction, ruby | Static friction, quartz | Kinetic friction, ruby | Kinetic friction, quartz |
|---|---|---|---|---|---|---|---|---|---|
| LiCl | 0.105 | 0.440 | 0.150 | 0.320 | $K_2SO_4$ | 0.110 | 0.490 | 0.170 | 0.370 |
| KCl | 0.097 | 0.465 | 0.160 | 0.330 | $K_3Fe(CN)_6$ | 0.114 | 0.550 | 0.200 | 0.375 |
| $AlCl_3$ | 0.112 | 0.420 | 0.220 | 0.330 | $K_4Fe(CN)_6$ | 0.113 | 0.605 | 0.210 | 0.390 |
| $Th(NO_3)_4$ | 0.114 | 0.350 | 0.225 | 0.350 | | | | | |

which is explained by an increase in the true contact area with "plasticization" of the surface. If, in this case, the specific force of molecular interaction does not decrease (which in the present case is very probable), then the electrolytes increase the total force of molecular interaction.

The effective manifestation of the mechanisms considered for the action of electrolytes on the bond between particles (and macroscopic bodies) in solutions is determined by the distance between the surfaces.

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## CITED LITERATURE

[1] P. A. Rehbinder, *Reports of the Conference on the Viscosity of Liquids and Colloidal Solutions*, Publishing House of the Academy of Sciences of the USSR, 1, 1941, p. 361; *Koll. zhurn.*, 20, 527 (1958). [2] G. Freundlich, *Thixotropy*, IL, 1939; G. I. Fuks, *Koll. zhurn.*, 12, 228 (1950). [3] G. I. Fuks, *Proceedings of the 3rd All-Union Conference on Colloid Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1956, p. 301; *Koll. zhurn.*, 20, 748 (1958). [4] G. I. Fuks, *Zav. lab.*, 21, No. 12, 1445 (1955). [5] G. I. Fuks, ibid., 22, No. 5, 594 (1956). [6] G. I. Fuks, N. I. Kaverina, *DAN*, 121, 332 (1958). [7] G. I. Fuks, V. M. Klyuchnikov, E. V. Ivanova, *DAN*, 65, 307 (1949). [8] B. V. Deryagin, *Izv. AN SSSR, ser. khim.*, No. 5, 1153 (1937). [9] A. N. Frumkin, A. V. Gorodetskaya, *Acta Physicochimica URSS*, 9, 327 (1938). [10] O. Ya. Samoilov, *Structure of Aqueous Electrolyte Solutions and Hydration of Ions*, Publishing House of the Academy of Sciences of the USSR, 1957. [11] D. Bockris, *Some Problems of Modern Electrochemistry*, IL, 1958. [12] G. I. Fuks, *Koll. zhurn.*, 22, No. 2 (1960). [13] P. A. Rehbinder, *Zs. Phys.*, 72, 191 (1931); *Physicochemical Mechanics*, Moscow, 1958.

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