# PHYSICAL CHEMISTRY

1963

SovietRxiv

Figure 1

Figure 1: Figure 1

## Abstract

## Full Text

# PHYSICAL CHEMISTRY

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# ON THE INFLUENCE OF NEUTRAL ELECTROLYTES ON COAGULATION INTERACTIONS IN A SUSPENSION OF GLASS SPHERES

*(Presented by Academician P. A. Rebinder on 19 VI 1963)*

Direct determination of the dependence of the structure and mechanical properties of disperse systems on the interaction forces of the particles of the disperse phase is difficult because of the heterogeneity of the system and the lability of the particles, which can be modified by the same factors as the structure of the system as a whole. More unambiguous results can be obtained on model systems ($^1$).

In the present work the coagulation interaction (coagulation bond) was investigated in a model system consisting of 50-60% by weight (compaction by sedimentation) glass spheres of diameter 30 $\mu$ in bidistilled water and in solutions of neutral electrolytes. The spheres were obtained by melting dispersed particles of chemical glass No. 23 in a stream of hot air by the method ($^2$), followed by repeated fractionation to isolate nearly monodisperse particles (checked under a microscope). The limiting shear stress of the suspension ($^{3,4}$), measured with a cone plastometer of increased sensitivity ($^5$), served as an indicator of coagulation structure formation.

**Fig. 1.** Influence of the concentration of electrolyte solutions ($C$) on the limiting shear stress ($\theta$) of a 50% suspension.

The qualitative effect of the concentration of electrolyte solution on the limiting shear stress $\theta$ (Fig. 1) is the same as on the adhesion force of microscopic particles ($^6$). At first, as the adsorption layer is filled with potential-determining ions—which ends at very low concentrations (the small specific surface of the particles)—$\theta$ decreases. Subsequently, with increasing concentration, the double layer of adsorbed ions is compressed and, accordingly, the bond strength of the particles increases and $\theta$ rises. The decrease in the limiting shear stress

Figure 2

Figure 2: Figure 2

at high concentrations is, in all probability, explained by modification of the glass surface. After prolonged residence in concentrated solutions the spheres become covered with a matte film. Colloid-chemical transformations of the surface of glass in strong salt solutions were noted by A. A. Grebenshchikov and by many subsequent authors ([7]). Thus, in the concentrated suspensions studied, depending on the composition of the dispersion medium, two mechanisms of change in the coagulation interaction may appear: an electrostatic one, due to interaction of diffuse

**Fig. 2.** Test of the applicability of the Derjaguin-Frumkin equation by the leveling method for calculating $\theta$. Dependence of $F_r = k_n/\theta$ on ion valency (3) and electrolyte concentration: NaCl (2), CsCl (1).

layers, and a physicochemical one, leading to a change in the structure and mechanical properties of the particle surfaces.

The electrostatic character of the interaction of particles in solutions whose concentration corresponds to the second segment of the curves in Fig. 1 is confirmed by the agreement of the value of $\theta$ with the equation of B. V. Deryagin (8) and A. N. Frumkin (9), derived for the mutual repulsive forces of two like diffuse layers. After an insignificant transformation this equation can be written in the following form, convenient for experimental verification by the method of comparison:

$$F_r = kZ^2Ce^{-hkZ\sqrt{C}},$$

where $F_r$ is the repulsive force, $k$ is a constant, $Z$ is the valence of the ions of the diffuse layer, $C$ is the concentration of the solution, and $h$ is the thickness of the diffuse layer.

If

$$\theta = \frac{k_n}{F_r},$$

then

$$\theta = \frac{k_n}{kZ^2Ce^{-hkZ\sqrt{C}}}.$$

As is seen from Fig. 2, this dependence is obeyed with sufficient accuracy both for the valence of the counterions and for the concentration of the solution. The adopted method of investigation did not allow the third variable—$h$—to be

Fig. 3. Effect of ion radius on the concentration of maximum "stabilization" $C_s$ (2) and $\theta$ (1) at $C = 1 \cdot 10^{-2}$ g-equiv/l

Figure 3: Fig. 3. Effect of ion radius on the concentration of maximum "stabilization" $C_s$ (2) and $\theta$ (1) at $C = 1 \cdot 10^{-2}$ g-equiv/l

changed, but in the preceding work (10) it was shown that the dependence of the repulsive force of interacting diffuse layers on the gap thickness between flat particles obeys the Deryagin–Frumkin equation. Consequently, the limiting shear stress of concentrated suspensions of monodisperse spherical particles in electrolyte solutions of low concentration is inversely proportional to the repulsive force of the particles, and its magnitude can be calculated from the parameters of the composition of the diffuse layer of adsorbed ions.

**Table 1**

**Effect of temperature on the limiting shear stress of a 50% suspension in LiCl and CsCl solutions**

| Solution | Concentration of solution, g-equiv/l | Temperature, °C | Temperature, °C |
|---|---|---|---|
| Solution | Concentration of solution, g-equiv/l | 20 | 70 |
| LiCl | $5 \cdot 10^{-4}$ | 1.49 | 1.15 |
| LiCl | $1 \cdot 10^{-3}$ | 1.49 | 1.25 |
| LiCl | $1 \cdot 10^{-2}$ | 1.29 | 1.46 |
| CsCl | $5 \cdot 10^{-4}$ | 1.22 | 1.16 |
| CsCl | $1 \cdot 10^{-3}$ | 1.25 | 1.24 |
| CsCl | $1 \cdot 10^{-2}$ | 1.47 | 1.50 |

**Fig. 3.** Effect of ion radius on the concentration of maximum "stabilization" $C_s$ (2) and $\theta$ (1) at $C = 1 \cdot 10^{-2}$ g-equiv/l.

The ion radius also has a certain secondary effect on $\theta$, or more precisely, their hydration. This is more noticeable for monovalent ions (Fig. 3). It is interesting that with decreasing hydration not only does $\theta$ increase, but the concentration of the solution at which the curve $\theta = f(C)$ reaches its minimum value also increases, i.e., the concentration of maximum "stabilization" $C_s$ of the system increases. In other words, hydration of the ions of the diffuse layer supplements the wedging effect of electrostatic interaction.

The range of variation of the limiting shear stress upon changing the composition of the solution is smaller than the variation of the adhesion force of particles according to (6) and of sticking of plane-parallel disks according to (11). This is explained by the fact that in our suspensions, owing to the small radius of curvature of the spheres and the absence of Brownian motion, high contact pressures develop. In the upper layer of the suspension it exceeds 100 kg/cm$^2$ (calculated according to Hertz) and increases with approach to the bottom of the vessel. The diffuse layer is additionally compressed by the mechanical action. With a further increase in pressure (centrifugation of the suspension), the effect of the valence of the ions and of their concentration is leveled out (Fig. 4). Evidently, contact pressures of the order of 30 kg/mm$^2$ exceed the wedging pressure of the diffuse layers, and the electrostatic factor of the interaction ceases to determine the value of $\theta$. This may

can be used to measure the total electrostatic wedging pressure of adsorbed ions.

Within the range from 20 to 80° (the investigated range), $\theta$ depends little on temperature. Only a slight decrease of this quantity is observed in the case of dilute solutions, and its increase in more concentrated ones (Table 1). As was to be expected ($^{11}$), at elevated temperature the influence of the ion radius and the hydration effect associated with it disappears.

For the suspensions studied, the number of coagulation bonds per unit area is known (from the packing density and particle size). The experimental values of $\theta$ can be compared with those calculated from the adhesion force $F_a$, measured by (6) for the same particles in solutions of identical composition and at the same contact pressure. It was shown ($^6$) that in a homogeneous suspension of monodisperse particles, even spherical ones, the adhesion force of individual particles is not the same (owing to the nonuniformity of their surface and the dependence of $F_a$ on $h$); therefore the calculation of $\theta$ was carried out using the minimum and mean values of the adhesion force obtained from the distribution curve of $F_a$.

**Table 2**

Experimental and calculated from the adhesion force of individual particles ($^6$) values of the limiting shear stress of 50% suspensions (contact pressure 112 kg/cm$^2$)

| Solution | Concentration, mg-equiv/l | $\theta_{\text{exper.}}$, g/cm$^2$ | $\theta_{\text{calc.}}$, g/cm$^2$, $F_a$ min. | $\theta_{\text{calc.}}$, g/cm$^2$, $F_a$ mean |
|---|---|---|---|---|
| LiCl | 1.0 | 1.49 | 0.69 | 10.2 |
| KCl | 0.1 | 1.51 | 0.70 | 11.9 |
| KCl | 1.0 | 1.22 | 0.51 | 8.9 |
| $BaCl_2$ | 1.0 | 1.42 | 0.63 | 9.8 |
| $BaCl_2$ | 10.0 | 1.93 | 1.31 | 17.2 |
| $Th(NO_3)_4$ | 1.0 | 2.54 | 1.49 | 23.4 |

As can be seen from the data of Table 2, the values of $\theta$ and $F_a$ change sympathetically with changes in the composition of the dispersion medium. The experimental values of $\theta$ lie between those calculated from the minimum adhesion medium. This shows that shear in the suspension is realized mainly through rupture of the weakest bonds, but is not localized in one plane and, possibly, is accompanied by rotation of the particles.

**Fig. 4.** Influence of contact pressure on the dependence of the suspension $\theta$ on the composition of electrolyte solutions. Contact pressure: 1—112 kg/cm$^2$; 2, 3 —2000 kg/cm$^2$; 4, 5—3000 kg/cm$^2$; NaCl (1, 3, 5); $AlCl_3$ (2, 4); LiCl (5); CsCl (5); $BaCl_2$ (4); $Th(NO_3)_4$ (5)

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Received
30 V 1963

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