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Abstract

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INVESTIGATION OF CHANGES IN ION TRANSFERENCE NUMBERS AND OF THE SUSPENSION EFFECT IN LIQUID SUSPENSOID DIAPHRAGMS

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Changes in the transference numbers of ions in various capillary systems, both with a rigid skeleton and powder systems made up of separate particles in contact with one another, have been observed and studied by many investigators (1). This phenomenon can be explained by the existence of a double electric ionic layer at the phase boundary and by the participation of the ions entering it in the transfer of current through the capillary system. A similar phenomenon was observed for solutions of high-molecular compounds and, in particular, A. I. Yurzhenko (2) showed for gelatin that the transference numbers of the chlorine ion in gelatin remain practically constant, regardless of whether the gelatin is in the form of a jelly or a sol (in the molten state). The latter indicates that the changes in transference numbers may not be affected substantially by how the structure present in the solution is created —by mobile particles (large molecules in the case of gelatin) or by an immobile continuous skeleton. It follows from this that in suspensions of irreversible colloids (suspensoids) a change in the transference numbers of ions may also occur in the case of a stable suspension of considerable concentration. The space between the particles may likewise be regarded as a system of pores, albeit a mobile one.

[Figure 1 and Figure 2 visible on page]

Fig. 1. Change in transference numbers in suspensions of quartz and bentonite as a function of the amount of disperse phase. *I*-*IV*—quartz, particle size: *I*—6-10 μ, *II*—3-6 μ; *III*—1-3 μ: *IV*—< 1 μ; *V*—bentonite

Fig. 2. Structural viscosity and transference numbers for a bentonite suspension as a function of the amount of disperse phase. *I*—Pt: (P—pressure in millimeters of water column, t—time in seconds); *II*—Δn_{Cl}

The suspension effect, discovered and first investigated by Wiegner and Pallmann (3), attracted the attention of many investigators, especially in recent

Figure 3

Figure 1: Figure 3

years (^{4}-^{9}). The essence of this phenomenon consists in the fact that

The pH of a suspension and of the ultrafiltrate or centrifugate separated from it are, in the general case, not the same. The difference in pH values increases with increasing suspension concentration, and the direction of this change depends on the sign of the charge of the particles of the solid phase. When the particles have a negative charge, the pH of the suspension is lower than that of the ultrafiltrate; for a positive charge the opposite result is obtained. Although there are various points of view regarding the nature of this phenomenon, most authors invoke Donnan equilibrium to explain the observed facts, by means of which the main results of measurements can be explained quite satisfactorily. Ennie, Nielsen, Coleman, and others (^{5}) express another point of view in explaining the cause of the suspension effect; they see the cause of the suspension effect in the large diffusion potential that arises when measuring ion activity (in particular pH) at the boundary where the KCl salt bridge joins the suspension.

Overbeek (^{10}) compares the Donnan emf and the suspension effect and speaks of their identity. He comes to the conclusion that the experimentally measured Donnan potential is composed of the potential difference between the suspension and the solution, i.e., the membrane potential, and two diffusion potentials, and that the classical equation for the Donnan emf is erroneous if the mobilities of the counterions depend on the suspended particles. This error probably exists in those cases where the particles have a considerable charge.

Fig. 3. Effect of the concentration of suspensions of bentonite and quartz on the magnitude of the suspension effect (a_{H}): **I**—for a bentonite suspension; **II** —for a bentonite centrifugate; **III**—for quartz suspensions (< 1 μ); **IV**—for a quartz centrifugate.

The present work had as its purpose the elucidation of the dependence of the change in ion transference numbers through liquid suspensoid diaphragms on the amount of disperse phase in the suspension and on the degree of dispersity of its constituent particles, and then the finding of a relation between changes in ion transference numbers and the observed values of suspension effects. Bentonite from the Oglavlinskoe deposit and quartz powder, classified by elutriation into a number of fractions, were selected as the objects of study. The results of experiments on ion transference numbers* in suspensions of bentonite and quartz in 0.01 N KCl solutions are presented in Fig. 1.

It is evident from Fig. 1 that, with increasing concentration of the disperse phase, a decrease in the transference numbers of the Cl ion in the suspension is observed, i.e., in other words, an increase in the transference number of the cation K^+, which is consistent with the negative sign of the charge of these particles.

An increase in the dispersity of the particles also leads to a decrease in the transference numbers of the Cl ion. A bentonite suspension, having particles finer than the quartz fractions, and a φ-potential of the same order as that of quartz, gave a considerably larger effect of change in transference numbers.

To elucidate the influence of structure formation in the suspension on the chan ···the transfer numbers were measured, determinations of the structural viscosity were carried out, the results of which for bentonite are shown in Fig. 2. The course of the curves shows that in this case the structure is not the determining factor in the change of the transfer numbers of the Cl-ion, since otherwise the course of the curves would be identical.

Table 1

Suspension effect for quartz suspensions of different particle size

Disperse phase, %	pH of suspensions	pH of centrifugate
Particles smaller than 1 μ	**Particles smaller than 1 μ**	**Particles smaller than 1 μ**
1.2	5.80	5.80
2.3	5.70	5.80
8.8	–	5.80
19.7	–	5.80
26.0	5.56	5.80
40.0	5.44	5.80
Particles 1-3 μ	**Particles 1-3 μ**	**Particles 1-3 μ**
2.1	5.48	5.46
8.3	5.38	5.48
20.0	–	5.46
32.0	5.24	5.46
Particles 3-6 μ	**Particles 3-6 μ**	**Particles 3-6 μ**
27.0	5.32	5.36
34.5	–	5.36
67.0	5.30	–
Particles 6-10 μ	**Particles 6-10 μ**	**Particles 6-10 μ**
61.0	5.76	5.76

Figure 3 gives data from measurements of the activity of H-ions a_H with a glass electrode in suspensions and centrifugates of bentonite and quartz (the fraction with particle size less than 1μ). For quartz and bentonite a rectilinear

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* Measurements of the transference numbers of the Cl ion were carried out analytically by the method used in a number of works at the Department of Colloid Chemistry of Leningrad State University ([1]), in a device of somewhat modified design, adapted for measuring the effect in liquid media.

dependence is observed in the increase of the H-ion activity of the suspension with increasing percentage of the disperse phase, as had previously been noted by other authors.

Data on the influence on the suspension effect of the concentration of the disperse phase and of particle size are given in Table 1.

As can be seen from the table, for the quartz fraction with particle diameter 3-6 μ there is almost no suspension effect even at a disperse-phase concentration of 67%, whereas for quartz with particle diameter < 1 μ, at a concentration of 40%, this effect amounts to about 0.4 pH.

Thus, the data presented show that fine suspensions of the suspensoid type can considerably change the ion transfer numbers, and this change, increasing with concentration, is directly related to the suspension effect.

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REFERENCES CITED

1. *Collected volume. Electrokinetic Properties of Capillary Systems.* Publishing House of the Academy of Sciences of the USSR, 1956, p. 130.
2. A. I. Yurzhenko, *Bull. All-Union Chem. Soc. named after D. I. Mendeleev*, No. 8-9 (1951).
3. G. Wiegner, *Koll. Zs.*, **51**, 49 (1930); H. Pallman, *Kolloidchem. Beih.*, **30**, 334 (1930).
4. A. I. Rabinovich, P. S. Vasil' ev, T. V. Gotovskaya, *DAN*, **3**, 109 (1935).
5. H. Jenny, *Science*, **112**, 164 (1950).
6. C. E. Marshall, *Science*, **113**, 43 (1951).
7. E. Erikson, *Science*, **113**, 418 (1951).
8. K. J. Mysels, *Science*, **114**, 424 (1951).
9. C. E. Marshall, *Science*, **115**, 361 (1952).
10. J. Th. G. Overbeek, *J. Coll. Sci.*, **8**, No. 6 (1953).

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