A. A. Baran, D. N. Strazhesko, Yu. M. Glazman, B. V. Eremenko

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Abstract

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A. A. Baran, D. N. Strazhesko, Yu. M. Glazman, B. V. Eremenko

ON THE DENSITY OF COVERAGE OF THE SURFACE OF THE DISPERSE PHASE OF LYOPHOBIC SOLS BY POTENTIAL-DETERMINING IONS

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An analysis of the enormous body of factual material relating to the problem of the stability of colloidal systems leads to the conclusion that the adsorption factor is of great importance in the mechanism of coagulation of lyophobic sols by electrolytes ([1]). The numerous data available in the literature on ion sorption during coagulation are, however, of little use for theoretical treatment, since most of them were obtained by indirect methods and therefore are not sufficiently reliable (for details see ([2], [3])). Moreover, because the magnitude of the sorption surface was unknown, as a rule the sorption was calculated per unit mass of the disperse phase, which also considerably devalues the measurement results. Meanwhile, reliable quantitative data on the sorption of counterions are of very great interest. If it is assumed that in the critical state of a sol the ion exchange in the outer shell of the electrical double layer is practically completed or, at any rate, close to completion ([4]), then the corresponding quantities, referred to unit area, may characterize a very important parameter of the colloidal system: the density of electric charges on the surface of the disperse phase. The present investigation was undertaken in order to make such an estimate.

For this purpose, the total uptake of counterions during coagulation of hydrophobic sols of arsenic sulfide (with concentration $C = 8$ mmol/l), antimony ($C = 6$ mmol/l) and ($C = 8.6$ mmol/l), silver iodide ($C = 10$ mmol/l), and manganese dioxide ($C = 15.6$ mmol/l) was determined by a direct radiometric method.

At the same time, the surface area of the disperse phase in the indicated systems was measured from the limiting value of monomolecular adsorption of methylene blue by the coagulates of these colloidal solutions.

The sulfide sols were obtained by passing hydrogen sulfide, respectively, through solutions of As_2O_3 ([5]), $K(SbO)C_4H_4O_6$ ([6]), and $Hg(CN_2)$ ([7]); the manganese dioxide sol was obtained by reduction of potassium permanganate with hydrogen peroxide ([2]); the silver iodide sol was obtained by the interaction of silver nitrate and potassium iodide ([8], [2]).

The sorption of the cations Rb^{+}, Ca^{2+}, and Y^{3+}, labeled with the radioactive isotopes Rb^{86}, Ca^{45}, and Y^{91}, was determined at the critical concentrations of electrolytes (coagulation was observed after one hour) from the radioactivity of the precipitates of the disperse phase ([2], [3]). The adsorption of methylene blue was measured on coagulates obtained under the same conditions; these were first washed 2-3 times with demineralized water ($\chi \sim 1.0 \cdot 10^{-6}\ \Omega^{-1} \cdot cm^{-1}$) and then centrifuged. In calculating the specific surface area (Table 1), we assumed, in accordance with ([9], [10]), that 1 mg of methylene blue covers, as a monomolecular layer, an area equal to 1 m^2.* The numerical values given in Table 1 indicate a satisfactory–

* This relation was obtained by the authors ([9]) on the assumption that methylene-blue molecules have a spherical form. In fact, they have the form of a parallelepiped with dimensions $16 \times 8 \times 4$ Å ([11]). If these data are taken into account, coverage of an area of 1 m^2 by 1 mg of methylene blue approximately corresponds to orientation of its molecule with the lateral face 16×4 Å toward the hydrophobic surface.

in satisfactory agreement with the results of determining the surface area of the precipitates by BET (from low-temperature adsorption of krypton) and with the method used in the present work.

The measured sorption values of various counterions made it possible to calculate the number of potential-determining ions adsorbed, in the critical state of the colloidal system, per unit surface area of the dispersed phase (Table 2). These data were obtained on the assumption that, at coagulating concentrations of electrolytes, ion-exchange absorption of counterions had already reached its limit. It should, however, be noted that the density of electric charges on the surface of the dispersed phase is, generally speaking, not constant–in particular, it depends on the content of the potential-determining electrolyte in the intermicellar solution. In different sols, fluctuations of this quantity are very different. Thus, the concentration of J^{-} ions has relatively little effect on the sorption of Nd^{3+} cations by colloidal particles of silver iodide ([13]). At the same time, removal of dissolved hydrogen sulfide from a mercuric sulfide sol (the concentration of H_2S decreased approximately from 10 to 0.05 mmol/l) was accompanied in our experiments by a very substantial decrease in the sorption of Ca^{2+} ions–from 3.2 to 0.5 μmol/g. A colloidal solution of manganese dioxide behaves similarly in this respect: even during short-term dialysis the content of potential-determining OH^{-} ions in it decreases by two orders of magnitude, and this leads to a rather substantial decrease in the cation-absorption capacity –approximately fourfold. The results of our determinations of sorption values refer to sols that contained sharply different amounts of potential-determining ions. Colloidal solutions of arsenic and antimony sulfides were prepared with a minimal excess of hydrogen sulfide in them, whereas the mercuric sulfide sol, on the contrary, was practically saturated with H_2S. The silver iodide sol contained J^{-} ions at a fairly considerable concentration (10^{-3} g-ion/l), and the colloidal solution of manganese dioxide was subjected to dialysis before the experiments.

Table 1.

Specific surface area of precipitates of the substance of the dispersed phase, m^2/g

Sol	Freshly precipitated coagulate (from adsorption of methylene blue)	Coagulate dried in vacuum at room temperature (from adsorption of methylene blue)	Coagulate dried in vacuum at room temperature (by BET)
Sb_2S_3	88	87	85
As_2S_3	126	–	–
HgS	16	12	13
AgJ	11.5	–	12 (12)
MnO_2	36	–	–

The data given in Table 2 indicate that the density of electric charges on the surface of colloidal particles of arsenic and antimony sulfides is at least twice as high as the degree of coverage of the dispersed phase by potential-determining ions in mercuric sulfide and silver iodide sols; moreover, taking into account what was said above, this difference may increase still further. At the same time, it follows from the results of our experiments that the considerations on this question found in the literature ([14]), although correct in general outline, are, quantitatively, undoubtedly greatly exaggerated.

We attempted to estimate the part of the surface of the dispersed phase that, in the critical state of the colloidal system, is occupied by adsorbed potential-determining ions. For the ions J^-, SH^-, and OH^-, which determine

Table 2

Charge density on the surface of the disperse phase of lyophobic sols

Ion coagulant	Coagulating concentration, mmol/l	Counterion sorption value, μg-mol/g	Counterion sorption value, μg-mol/m^2	Adsorbed potential-determining ions, 10^{-17}/m^2	Area occupied by potential-determining ions in 1 g of coagulant, m^2	Area occupied by potential-determining ions in 1 g of coagulant, % of coagulant surface (mean values)
Sol As_2S_3						
$^*Rb^+$	58.2	103.1	0.82	4.9	30.7	
$^*Ca^{2+}$	0.67	51.2	0.41	4.8	30.9	24.8
$^*Y^{3+}$	0.065	35.6	0.28	5.1	32.3	
Sol Sb_2S_3						
$^*Rb^+$	37.4	72.3	0.82	5.0	–	
$^*Ca^{2+}$	0.59	36.4	0.41	5.0	–	–
$^*Y^{3+}$	0.11	24.7	0.28	5.1	–	
Sol HgS						
$^*Rb^+$	42	6.1	0.38	2.3	0.46	
$^*Ca^{2+}$	1.05	3.2	0.20	2.4	0.48	2.9
Sol AgJ						
$^*Rb^+$	131	4.4	0.38	2.3	0.39_5	
$^*Ca^{2+}$	1.86	1.9	0.16_5	2.0	0.34	3.3
$^*Y^{3+}$	0.35	1.5	0.13	2.4	0.40	
Sol MnO_2						
$^*Rb^+$	31.3	705	19.6	$1.2 \cdot 10^2$	31.2	
$^*Ca^{2+}$	0.90	364	10.1	$1.2 \cdot 10^2$	32.2	93.2
$^*Y^{3+}$	0.57	280	7.8	$1.4 \cdot 10^2$	37.2	

Respectively, for the potential of the particles of AgJ, HgS, and MnO_2, the values of the radii 2.18 (J^-), 2.00 (SH^-), and 1.53 Å (OH^-) were adopted ([15]). As for the ions $AsOS^-$ and $AsS_2{}^-$, which play the role of potential-determining ions in the sol As_2S_3 ([6]), there is no information on their dimensions in the literature. Their dimensions can be estimated either by summing the covalent

radii of As, O, and S under the assumption (by analogy with O—As—O) that the valence angle O—As—S is approximately 100°, or from the molar volume of HAsOS, if for the specific gravity the probable value ~ 3 is adopted. In both cases, an almost identical value, ~ 4 Å, is obtained. The results of such approximate calculations are given in Table 2; they show that the fraction of the surface of colloidal particles occupied by potential-determining ions is, in general, small. The only exception is the manganese dioxide sol, for which the data obtained are precisely the least reliable, since there is reason to believe that the value of the specific surface area of the coagulate measured by us in this case (because of its comparatively high hydrophilicity and tendency toward rapid aging) is clearly underestimated.

Despite the fact that the adsorbed potential-determining ions are located on the surface of the disperse phase relatively far from one another, counterions of different valence are always—and even in HgS and AgJ sols, where the potential-determining ions occupy only about 3% of the area—absorbed in equivalent amounts. It is possible that the ions,

potential-determining ions, and counterions are adsorbed at different active centers (cf. (16)).

L. V. Pisarzhevsky Institute of Physical Chemistry
Academy of Sciences of the Ukrainian SSR

Kiev Technological Institute
of Light Industry

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