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Abstract

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RADIOMETRIC STUDY OF THE SORPTION OF COUNTERIONS DURING COAGULATION OF ARSENIC AND ANTIMONY SULFIDE SOLS BY MIXTURES OF ELECTROLYTES

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A critical examination of extensive experimental material leads to the conclusion that the adsorption factor plays an important role in the mechanism of coagulation of lyophobic sols both by individual electrolytes and by their mixtures (⁀1). Theoretically, it has indeed been shown that certain regularities in the coagulating action of electrolyte mixtures can be explained on the basis of ideas of purely concentration coagulation of highly charged sols, i.e., proceeding from the assumption that the particle potential remains sufficiently high even in the critical state of the system (⁀2). On the other hand, if one takes into account the decrease in the potential of colloidal particles in the process of coagulation and admits that it is lowered so strongly as a result of adsorption of counterions that Derjaguin' s stability criterion for weakly charged sols becomes applicable (⁀3), then it is possible to substantiate theoretically, if not all, then in any case very many of the regularities encountered experimentally in the coagulation of lyophobic sols by mixtures of electrolytes (⁀4). The experimental data are covered still more fully by calculations carried out very recently, in which the possibility of any values of the critical potential is taken into account (⁀5).

As is known, ideas concerning mutual suppression of the adsorption of counterions have repeatedly been invoked to explain the phenomenon of ionic antagonism, very widespread in the coagulation of sols by mixtures of electrolytes (^{6}-8). The experimental basis for these ideas, however, is extremely scanty: the literature contains information on the suppression of adsorption of only a few counterions at one or two concentrations of the competing ion (⁀7, ⁀9, ⁀10). Moreover, most investigators limited themselves to the study of positive antagonism, leaving aside the adsorption behavior of coagulating ions under additivity and synergism.

We decided to measure the sorption of counterions during coagulation of typical lyophobic negatively charged hydrosols of As_2S_3 and Sb_2S_3 by electrolyte mixtures over a wide range of concentration ratios of the components of the mixture and under different regularities of coagulating action; the sorption values were determined by the direct radiometric method, which had proved satisfactory in our previous work (⁀11).

Sols of arsenic and antimony sulfides were prepared, as usual, from arsenic oxide and, respectively, potassium antimonyl tartrate (⁀11). The coagulating electrolytes used were $\overset{*}{\mathrm{Rb}}\mathrm{Cl}$, $\overset{*}{\mathrm{Ca}}\mathrm{Cl_2}$ (or $\mathrm{Ca(\overset{*}{N}O_3)_2}$), $\overset{*}{\mathrm{Sr}}\mathrm{Cl_2}$, and $\mathrm{Y(\overset{*}{N}O_3)_3}$, labeled with the radioactive isotopes $\mathrm{Rb^{86}}$, $\mathrm{Ca^{45}}$, $\mathrm{Sr^{89}}$, and $\mathrm{Y^{91}}$. The radiochemical purity of the preparations used was carefully monitored (for details see (⁀11)). The coagulation thresholds were determined visually one hour after adding to the sol a previously prepared mixture of electrolytes (⁀6). Adsorption measurements were carried out at the critical concentrations of the added electrolyte mixtures according to the procedure described ···

reported earlier (^{11}). For each pair of electrolytes, two series of experiments were set up simultaneously. In one series coagulation was carried out with mixtures of electrolytes labeled with one of the two cations; in the other, exactly the same amounts of mixtures were added to the sols, but labeled with the second counterion. The total sorption of coagulating ions was found by summing the separately determined uptake values for the individual labeled cations. For brevity, Table 1 gives data for only one of the two sols studied, since analogous results were obtained for the other.

Table 1a

Sorption of $^*\mathrm{Ca^{2+}}$ and $^*\mathrm{Rb}$ ions (in μg-eq per 1 g of the dispersed phase) during coagulation of $\mathrm{As_2S_3}$ sol with mixtures $^*\mathrm{CaCl_2}$—$^*\mathrm{RbCl}$. [RbCl] = 500 mmol/l, [$\mathrm{CaCl_2}$] = 9.15 mmol/l; coagulation threshold: RbCl—58.7 mmol/l; $\mathrm{CaCl_2}$—0.61 mmol/l

$^*\mathrm{CaCl_2}, \mathrm{RbCl}$	$^*\mathrm{Ca^{2+}}$	$^*\mathrm{Rb^+}$	$^*\mathrm{Ca^{2+}} + {}^*\mathrm{Rb^+}$
10 : 0	108.6	–	108.6
9 : 1	98.4	9.2	107.6
8 : 2	96.8	20.9	117.7
7 : 3	79.4	34.8	114.2
6 : 4	70.0	46.5	116.5
5 : 5	58.6	58.4	117.0
4 : 6	40.6	65.5	106.1
3 : 7	23.0	83.3	106.3
2 : 8	15.8	91.2	107.0
1 : 9	9.4	98.9	108.3
0 : 10	–	109.5	109.5

Table 1b

Sorption of $^*Ca^{2+}$ and $^*Sr^{2+}$ ions (in μg-eq per 1 g of the dispersed phase) during coagulation of Sb_2S_3 sol with mixtures $^*CaCl_2$—$^*SrCl_2$ $[CaCl_2] = 9.15$ mmol/l; $[SrCl_2] = 9.15$ mmol/l; coagulation threshold: $CaCl_2$—1.02 mmol/l; $SrCl_2$—1.02 mmol/l

$^*CaCl_2, SrCl_2$	$^*Ca^{2+}$	$^*Sr^{2+}$	$^*Ca^{2+} + {}^*Sr^{2+}$
10 : 0	72.4	–	72.4
9 : 1	65.7	7.5	72.4
8 : 2	56.6	14.2	70.8
7 : 3	49.9	21.8	71.7
6 : 4	45.2	29.4	74.6
5 : 5	37.0	37.6	74.6
4 : 6	28.8	45.2	74.0
3 : 7	20.7	51.1	71.8
2 : 8	15.3	58.2	73.5
1 : 9	6.8	65.9	72.7
0 : 10	–	74.2	74.2

Table 1c

Sorption of $^*Ca^{2+}$ and $^*Y^{3+}$ ions (in μg-eq per 1 g of the dispersed phase) during coagulation of As_2S_3 sol with mixtures $^*Ca(NO_3)_2$—$^*Y(NO_3)_3$. $[Ca(NO_3)_2] = 4.87$ mmol/l; $[Y(NO_3)_3] = 1.28$ mmol/l; coagulation threshold: $Ca(NO_3)_2$—0.59 mmol/l; $Y(NO_3)_3$—0.058 mmol/l

$^*Ca(NO_3)_2, Y(NO_3)_3$	$^*Ca^{2+}$	$^*Y^{3+}$	$^*Ca^{2+} + {}^*Y^{3+}$
10 : 0	109.3	–	109.0
9 : 1	77.6	30.0	107.6
8 : 2	58.3	51.8	110.1
7 : 3	41.2	66.9	108.1
6 : 4	27.8	89.7	117.5
5 : 5	20.6	92.4	113.0
4 : 6	16.8	93.6	110.4
3 : 7	10.0	97.8	107.8
2 : 8	6.4	103.8	110.2
1 : 9	2.8	108.0	110.8
0 : 10	–	110.1	110.1

The character of the regularities observed in the coagulation of As_2S_3 and Sb_2S_3 sols by different combinations of electrolytes was as follows: when mixtures of $CaCl_2$—RbCl were added, a clearly expressed antagonism occurred; in the case of $CaCl_2$–$SrCl_2$, the action of the ions was additive; and upon joint addition of $Ca(NO_3)_2$ and $Y(NO_3)_3$, a distinct synergism was observed.

In considering the results of the adsorption experiments, attention is first drawn to the equivalent character of the uptake of counterions of different valence during coagulation of the sols by individual electrolytes (Table 1). This fact is of interest in the light of the well-known and, in essence, still unfinished discussion in the colloid-chemical literature concerning the equivalence of adsorption of coagulating ions ([12–14]). It is especially noteworthy, however, that regardless of the regularity in the coagulation of As_2S_3 and Sb_2S_3 sols by one or another mixture of electrolytes, the total sorption of both counterions remains constant—within the limits of measurement error, estimated at about 5%—over the entire region of the coagulating-action curve (see the last columns of Tables 1a, b, c). Thus, the equivalence of counterion sorption is maintained when not only individual electrolytes but also their mixtures are added to the indicated sols (cf. also [10]).

In conclusion, it should be noted that mutual suppression of counterion sorption was observed in our experiments during coagulation of As_2S_3 and Sb_2S_3 sols by any of the electrolyte pairs investigated, i.e., not only in ionic antagonism (Table 1a), but also in the additive action of ions (Table 1b) and in synergism (Table 1c). This shows that it is necessary to make a clear distinction between the experimentally measured value of the total uptake of counterions and their adsorption in the strict sense of the word. Obviously, only the latter determines the decrease in the effective potential of the colloidal particles, on which the coagulation of the sol precisely depends.

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REFERENCES

1. V. M. Barboi, Yu. M. Glazman, I. M. Dykman, *Kolloid. zhurn.*, **24**, 382 (1962); V. M. Barboi, Yu. M. Glazman, *Kolloid. zhurn.*, **25**, 282 (1963); V. M. Barboi, *Kolloid. zhurn.*, **25**, 385 (1963).
2. Yu. M. Glazman, I. M. Dykman, *Kolloid. zhurn.*, **18**, 13 (1956); Yu. M. Glazman, I. M. Dykman, E. A. Streltsova, *Kolloid. zhurn.*, **20**, 149 (1958).
3. B. V. Deryagin, *Kolloid. zhurn.*, **7**, 285 (1941); B. V. Derjaguin, *Trans. Farad. Soc.*, **36**, 730 (1940).

4. V. M. Barboi, Yu. M. Glazman, I. M. Dykman, *Kolloid. zhurn.*, **23**, 376, 381 (1961).

5. V. M. Barboi, *Kolloid. zhurn.*, **26**, 3 (1964).

6. H. Freundlich, H. Rape, *Zs. phys. Chem.*, **86**, 458 (1914).

7. H. V. Weiser, *J. Phys. Chem.*, **23**, 665 (1921); **28**, 232 (1924); **29**, 955 (1925); **30**, 20 (1926).

8. T. R. Bolam, J. J. L. Mulr, *J. Chem. Soc.*, 1933, 1022.

9. S. Ghosh, N. R. Dhar, *Koll. Zs.*, **41**, 223 (1927).

10. M. Herak, M. Mirnik, *Croat. Chem. acta*, **34**, 153 (1962).

11. Yu. M. Glazman, D. N. Strazhesko, *DAN*, **75**, 411 (1950); Yu. M. Glazman, D. N. Strazhesko, B. E. Tartakovskaya, *Kolloid. zhurn.*, **15**, 161 (1953); Yu. M. Glazman, D. N. Strazhesko, N. A. Bisikalova, *ZhNKh*, **3**, 115 (1958); A. A. Baran, Yu. M. Glazman, D. N. Strazhesko, *Kolloid. zhurn.*, **26**, 278 (1964).

12. H. Freundlich, *Koll. Zs.*, **1**, 321 (1907); *Zs. phys. Chem.*, **73**, 385 (1910); H. Freundlich, K. Joachimsohn, G. Ettisch, *Zs. phys. Chem.*, **141A**, 249 (1929).

13. A. I. Rabinovich, in: *Coagulation of Colloids*, collected volume, 1936, p. 169.

14. E. I. V. Ferwey, *Usp. khim.*, **10**, 1194 (1935).

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