On the Stability of Colloidal Solutions.

Part V.

The Effect of similarly charged Ions as a Factor in Electrolyte Antagonism in the Coagulation of Sols and the Mechanism of Stabilisation.

BY

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In several previous papers (Sen and Mehrotra, *Zeit. anorg. Chem.*, 1925, *142*, 345 ; Sen, *J. Phys. Chem.*, 1925, *29*, 517 ; *Zeit. anorg. Chem.*, 1925, *149*, 139) the antagonistic effect of electrolytes on the coagulation of sols has been investigated and some general conclusions have been reached.

It should be stated here that in explaining the so-called cationic antagonism in the cases studied by him, Weiser (*J. Phys. Chem.*, 1924, *28*, 232) advanced the view that the antagonistic action of two cations is only observed when they have greatly different precipitating powers. This mistake was undoubtedly due to the fact that he never used suitable mixtures of univalent cations as the coagulating ions. A similar fact was also simultaneously observed by Mukherjee and Ghosh (this *Journal*, 1924, *1*, 213) who suggested that a slight adsorption of anions would explain the observed antagonism of the several pairs of electrolytes. Similarly in the case of positively charged sols, the writer has shown the existence of antagonistic effects of suitable mixture of salts. In the present paper the earlier experiments with copper ferrocyanide sol have been extended with mixtures of univalent cations as the coagulating ions and an interesting effect of the influence of dilution of the

sol on the antagonistic action of salt pairs has been pointed out. The method of experimentation with the sols has been the same as described in previous papers.

TABLE I.

Sol—Copper ferrocyanide : *Electrolytes*—$K_2C_2O_4 + NaCl$.

$N/2$ $K_2C_2O_4$ taken in c.c.	$N/2$ NaCl reqd. for coagulation.		Difference.
	Observed.	Calculated.	
0	1·35	...	...
0·2	1·50	1·246	0·254
0·5	1·55	1·091	0·459
0·8	1·40	0·885	0·515
1·0	1·30	0·831	0·469
1·5	0·95	0·572	0·378
2·0	0·60	0·312	0·288
2·6	0·0	...	...

TABLE II.

Sol—Copper ferrocyanide : *Electrolytes*—Potassium tartrate + NaCl.

$N/2$ Potassium tartrate taken in c.c.	$N/2$ NaCl reqd. for coagulation.		Difference.
	Observed.	Calculated.	
0	1·35	...	...
0·2	1·45	1·19	0·26
0·5	1·35	0·95	0·40
0·8	1·05	0·71	0·34
1·0	0·85	0·55	0·30
1·3	0·50	0·31	0·19
1·7	0·0	...	...

TABLE III.

Sol—Copper ferrocyanide: *Electrolytes*—$Na_2C_2O_4 + KCl$.

| $N/3$ $Na_2C_2O_4$ taken in c.c. | $N/2 \cdot 20$ KCl reqd. for coagulation. | | Difference. |
	Observed.	Calculated.	
0·0	1·3	...	...
0·5	1·6	1·134	0·466
1·0	1·55	0·967	0·583
1·5	1·30	0·801	0·499
2·0	1·10	0·634	0·466
2·5	0·80	0·468	0·332
3·9	0·0	...	...

These results at first sight might indicate that the antagonism is between sodium and potassium ions, but the following results will show that the antagonistic behaviour is really due to the effect of the anions (*cf.* Mukherjee and Gh ;h, *loc. cit.*).

TABLE IV.

Sol—Copper ferrocyanide: *Electrolytes*—Potassium tartrate + KCl

| $N/2$ Potassium tartrate taken in c.c. | $N/2 \cdot 02$ KCl reqd. for coagulation. | | Difference. |
	Observed	Calculated	
0·0	1·3	...	...
0·2	1·3	1·15	0·15
0·5	1·0	0·92	0·08
0·8	0·75	0·69	0·06
1·0	0·60	0·54	0·06
1·3	0·35	0·31	0·04
1·7	0·0	...	...

TABLE V.

Sol—Copper ferrocyanide: *Electrolytes*—$K_2C_2O_4 + KCl$

$N/2$ $K_2C_2O_4$ taken in c.c.	$N/2 \cdot 02$ KCl reqd. for coagulation.		Difference.
	Observed.	Calculated.	
0·0	1·3	...	...
0·1	1·5	1·25	0·25
0·2	1·6	1·20	0·40
0·3	1·65	1·15	0·50
0·4	1·63	1·10	0·53
0·5	1·55	1·05	0·50
0·6	1·46	1·00	0·46
0·8	1·30	0·90	0·40
1·0	1·15	0·80	0·35
1·2	0·98	0·70	0·28
1·8	0·55	0·40	0·15
2·0	0·40	0·30	0·10
2·2	0·28	0·20	0·08
2·4	0·13	0·10	0·03
2·6	0·0	...	...

It may be observed that the antagonistic action is slightly more pronounced when the coagulating ions are different. This is probably due to the fact that the introduction of the same ion depresses the ionisation of stabilising electrolytes, potassium oxalate and tartrate. It seems probable that the stabilising effect is due to the oxalate and tartrate ions which is supported by the fact that these acids have not such a great effect as the corresponding salts, though the effect of hydrogen ion

has also to be remembered. These results thus show that the antagonistic effect of some salt pairs is due to the presence of anions. In a previous paper (*J. Phys. Chem.*, 1925, *29*, 517) it was shown that ferrocyanide, ferricyanide, oxalate, tartrate, etc., ions have considerable peptising effect on copper ferrocyanide sol and the difference in the precipitating values of these salts from that of potassium chloride is mainly due to this fact. It has now been observed that mixtures containing potassium chloride and either potassium ferrocyanide or oxalate or citrate or potassium tartrate show an antagonistic behaviour with copper ferrocyanide sol. Further, potassium oxalate has a higher precipitation value than potassium tartrate on copper ferrocyanide sol which points to the fact that the oxalate ion has a greater effect than the tartrate ion. Quite parallel to this, potassium oxalate and potassium chloride mixture shows a much greater antagonistic effect than a mixture of potassium chloride and potassium tartrate. These results, therefore, establish the fact that the presence of similarly charged ions can produce antagonistic effects in the case of mixtures of salts having the same coagulating ion.

In carrying these coagulation experiments, it has been found that the concentration of the sol has a great effect on the observed antagonistic action of mixtures of electrolytes. It is well known that several colloids like arsenious sulphide require higher concentrations of univalent electrolytes of the type KCl for coagulation when diluted than when concentrated, and an explanation was given on the assumption that similarly charged ion has a greater effect on a diluted sol than on a concentrated sol. If this be the case, then the antagonistic action of a pair of electrolyte, say KCl and $BaCl_2$, would be more pronounced on a diluted sol of arsenious sulphide than on a concentrated sol. The following data

show that this anticipation has been realised (*cf. Zeit. anorg. Chem.*, 1925, *149*, 139).

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TABLE VI.

Sol—Arsenious sulphide: *Electrolytes*—KCl + BaCl$_2$

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$M/2$ KCl taken in c.c.	Difference in the observed and calculated values of BaCl$_2$ $M/200$ reqd. for coagulation.	
	Original sol 3·4 gm./litre.	¼ diluted sol.
0·3	0·76	0·86
0·5	0·90	1·0
0·8	0·89	0·96
1·0	0·70	0·80
1·2	0·51	0·64

As to the mechanism of the stabilising effect of the similarly charged ion, it is apparent that the stability reaches a maximum and then decreases with the gradual addition of the stabilising electrolyte.

If we assume that for small additions of the stabilising electrolyte the preferential adsorption of similarly charged ion increases proportionately, then the log curve for the amount of electrolyte added and the difference between the observed and the calculated values of the coagulating electrolyte which gives a measure of the stability of the, colloid system, should be a straight line. This happens to be the case with such electrolytes as FeCl$_3$+KCl, Al(NO)$_3$ + KCl, etc., on a positively charged sol of ferric hydroxide, as has been pointed out by Ghosh and Dhar (*J. Phys. Chem.*, 1925, *29*, 659) who have also shown some limitations of this reasoning in a later paper

(private communication).   Unfortunately, however, a cor-
rect idea of these curves cannot be obtained unless a large
number of points are taken on both sides of the maxi-
mum.   No suitable experimental data for this are obtain-
able in the literature, though some can be obtained
by interpolation.   For this reason a large number of data
have been obtained with the mixture $K_2C_2O_4 + KCl$
and given in Table V.   In the following table, data
on the coagulation of arsenious sulphide sol are also
tabulated.

TABLE VII.

Sol—Arsenious sulphide : *Electrolytes*—$NaCl + CaCl_2$

$M/2$ NaCl taken in c.c.	Difference in the observed and calculated values of $CaCl_2$ $M/200$ reqd. for coagulation.
0·1	0·26
0·2	0·49
0·3	0·67
0·4	0·79
0·5	0·86
0·6	0·89
0·7	0·90
0·8	0·88
0·9	0·83
1·0	0·72
1·1	0·66
1·2	0·56
1·3	0·48
1·4	0·39

The log curves of the results given in Tables V and VII are plotted in the following figure. It will be observed
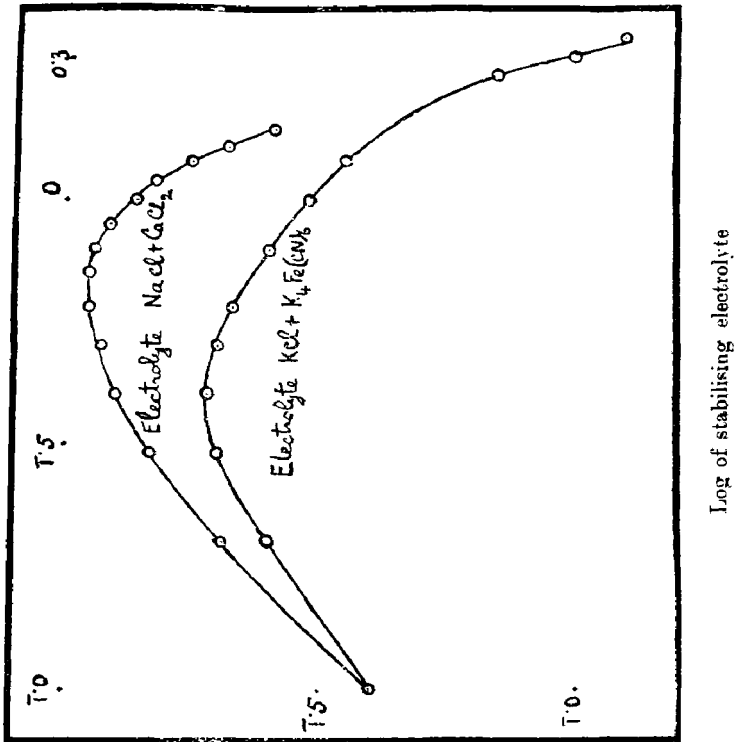
Log of difference

that the first three points in the curve for the mixture $K_2C_2O_4 + KCl$ can be represented by a straight line. After the maxim um point, however, the relations are no longer simple owing to the fact that the adsorption of the *same* charged ion does not increase proportionately any more with the addition of the stabilising electrolyte. On the other hand the adsorption of the coagulating ion may be assumed to be proportional to the amount of the stabilising electrolyte at the end of the curve, and consequently

the last few points give an approximate straight line. In the case of the mixture $NaCl + CaCl_2$ it will be apparent that the phenomena is more complicated and this is certainly due to the fact that the preferential adsorption of Cl′ by arsenious sulphide sol is never so marked as is observed in the case of say, adsorption of $Fe^{...}$ ion by ferric hydroxide sol. For this reason it cannot be assumed that the increase in the amount of adsorption of Cl′ ions by arsenious sulphide is connected with the amount of KCl added in such a simple manner as is the case of adsorption of the same charged ions by ferric hydroxide sol as estimated from the data of Freundlich and Wosnessensky. (*Kolloid Zeit.*, 1923, *33*, 222 ; *cf.* Ghosh and Dhar, *loc. cit.*). Consequently it seems that in the study of antagonistic action of electrolytes much importance cannot be given to these logarithmic interpretations of the experimental data for the reasons given above (*cf.* Clowes, *J. Phys. Chem.*, 1916, *20*, 407) and also because of the fact that the so-called exponential equations do not give us any real knowledge about the true mechanism of the process (Fischer, *Trans. Faraday Soc.*, 1922, *17*, 305).

Summary.

(1)   It has been shown that mixtures of potassium oxalate and potassium chloride, and potassium tartrate and potassium chloride show antagonistic behaviour in the coagulation of copper ferrocyanide sol. Similar effects are also observed with mixtures of potassium chloride and potassium citrate, ferrocyanide, etc.

(2)   It has been observed that mixtures containing the same stabilising ion but different univalent coagulating ions show a greater antagonistic behaviour than mixtures containing the same coagulating ion. This may be due to

the depression of ionisation of the stabilising electrolyte by the addition of a same ion of the electrolyte.

(3)   It has been pointed out that the antagonistic effect of two electrolytes is more pronounced with a diluted sol than with a concentrated sol of arsenious sulphide.   A similar effect will probably be obtained with other sols which behave in dilution experiments like arsenious sulphide.

(4)   The mechanism of stabilisation in presence of two electrolytes is briefly discussed.

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