

Chemistry. — "*The Stability of Suspensoids under Influence of Electrolyte Mixtures.*" By Prof. H. R. KRUYT and P. C. VAN DER WILLIGEN.

(Communicated at the meeting of December 19, 1925).

On the influence of electrolyte mixtures on the limiting value of colloids there already exists an old investigation by LINDER and PICTON¹⁾ and another by FREUNDLICH and PAPE²⁾. Nevertheless it is only of late years that more attention has been devoted to this problem, in the hope of finding an explanation for the so-called ion-antagonisms, which play an important part in the biological sciences. It is particularly FREUNDLICH and SCHOLZ³⁾, WEISER⁴⁾, MUKHERJEE⁵⁾, GHOSH and DHAR⁶⁾, and SEN⁷⁾ who have occupied themselves with this problem. All these authors have especially tried to find an explanation of the phenomena found by them from considerations derived from the theory of adsorption. The differences in ion adsorption would govern the electrical phenomena and these again the conditions of stability in the colloids. It seems, however, preferable to us, to make direct investigations on the connection between the influence of electrolytes on the electric charge and that on the stability, leaving the cause of the change in the electric charge for the present an open question.

For some years researches have been going on in this laboratory on the influence of *two* electrolytes, which simultaneously make their influence felt on capillary-electric phenomena. From this point of view we examined both the potentials of flow in glass and cataphoretic phenomena of oil-emulsions. In due time we hope to publish a detailed account of these investigations, which have already been partly concluded. In this communication we only wish to draw attention to some researches on the limiting value of electrolyte mixtures in suspensoid sols, while in some cases at the same time the cataphoresis of these sols has been measured.

FREUNDLICH and PAPE's researches have shown that in the As_2S_3 sol the limiting values for potassium and sodium were perfectly additive, whereas in electrolytes which had cations of different charge or adsorbability,

1) Journ. Chem. Soc. 67, 67 (1895).

2) Z. Physik. Chem. 86, 458 (1914).

3) Koll. Beih. 14, 267 (1922).

4) Journ. Phys. Chem. 25, 665 (1921) and 28, 232 (1924).

5) Journ. Indian Chem. Soc. 1, 213 (1924).

6) Journ. Phys. Chem. 29, 435 and 659 (1925).

7) Z. Anorg. Chem. 149, 139 (1925). Journ. Phys. Chem. 29, 517 (1925).

the limiting values lay on the whole below the additive value. FREUNDLICH and SCHOLZ (loc. cit.) have found on the other hand that in the same sol Li and Mg exert such an influence that the joint value is situated above that of the components; in a certain sense the term of antagonism might be applied here. In his *Kapillarchemie*¹⁾ FREUNDLICH suggests a connection between the hydration of these sols and the said phenomenon.

In this investigation we have started from the assumption that every electrolyte which increases the charge, must necessarily increase the limiting value of a second electrolyte. For, the higher the charge, the further we are from the critical potential and the more of this second electrolyte must be added to reach the latter. Increase of the electric charge is in general to be expected in negatively charged colloids, when a salt is added with an anion that is polyvalent or strongly adsorbable. Thus ELLIS²⁾ found that the OH-ion increased the charge of oil-emulsions, POWIS³⁾, that the same might be said of $K_4Fe(CN)_6$, KRUYT and VAN ARKEL⁴⁾ finding a similar influence of the OH-ion in Se-sols. Finally one of us has found that the charging of a glass-capillary by added salts is a pretty general phenomenon⁵⁾, the result of which was recently confirmed by FREUNDLICH and ETTISCH⁶⁾.

We have now examined the limiting value of different sols. The results for the As_2S_3 -sol, the HgS-sol, and the Se-sol are recorded in the subjoined tables. In every column in these tables the quantity of salt is indicated as percentage of the limiting value of this salt in case the other is not present; between brackets this quantity is given in millimols per litre.

The experiments were carried out as follows: 10 cc. of sol were shaken, while 1 cc. of the first electrolyte was added, then 5 cc. of the second electrolyte in varying concentration; the total volume in the coagulation glass was, therefore, always 16 cc. The result was examined after a night's standing (16 hours).

When the addition of the two electrolytes took place at the same time, the same results were obtained.

The results of table 1 corroborate those of earlier investigators. It is seen that the addition of LiCl to the As_2S_3 -sol requires more $MgCl_2$ than in the pure sol. This is, therefore, the phenomenon to which the name of *antagonistic* action is given.

The same result is shown by tables 2 and 3 for the HgS-sol, and also by tables 4 and 5 though less pronounced. It appears, therefore, very clearly here that polyvalent anions have a stabilizing influence on the action. In a very peculiar way this finds also expression as follows:

1) H. FREUNDLICH, *Kapillarchemie* (Leipzig 1922), p. 635.

2) Z. Physik. Chem. **80**, 597 (1912).

3) Z. Physik. Chem. **89**, 91 (1915).

4) Rec. Trav. Chim. **40**, 170 (1921).

5) H. R. KRUYT, These Proc. **17**, 615 (1914); **19**, 1021 (1917); Koll. Z. **22**, 81 (1918).

6) Z. Physik. Chem. **116**, 401 (1925).

TABLE 1.
As₂S₃-sol

Li Cl	Mg Cl ₂
0 (0)	100 (0.8)
25 (24)	138 (1.1)
50 (48)	156 (1.25)
72 (69)	180 (1.45)
100 (96)	0 (0)

TABLE 2.
HgS-sol

$\frac{K_4 Fe(CN)_6}{4}$	Mg Cl ₂
0 (0)	100 (1.0)
12.5 (10)	180 (1.8)
20 (15)	190 (1.9)
25 (20)	200 (2.0)
44 (35)	230 (2.3)
62 (50)	60 (0.6)
100 (80)	0 (0)

TABLE 3.
HgS-sol

$\frac{K_3 Fe(CN)_6}{3}$	Mg Cl ₂
0 (0)	100 (1.0)
33 (10)	130 (1.3)
66 (20)	60 (0.6)
100 (30)	0 (0)

TABLE 4.
HgS-sol

$\frac{K_2 SO_4}{2}$	Mg Cl ₂
0 (0)	100 (1.0)
16 (5)	110 (1.1)
33 (10)	120 (1.2)
100 (30)	0 (0)

TABLE 5.
HgS-sol

K Cl	Mg Cl ₂
0 (0)	100 (1.0)
16 (5)	110 (1.1)
33 (10)	120 (1.2)
100 (30)	0 (0)

If a HgS-sol is left standing for some days, it sinks down, and soon the sol cannot be restored through shaking. If, however, 10 m. mol. of K₄Fe(CN)₆ have been added, the sol can be restored simply by shaking even after a month.

In table 6 measurements are recorded of the cataphoretic velocity of the HgS-sol by means of the apparatus of BURTON. It is seen from fig. 1 how well these measurements agree with the results of the preceding tables. In fact the ferro cyanide of potassium gives a large increase of the charge, KCl a small increase corresponding to the nature of the antagonistic actions found. MgCl₂ immediately decreases the charge.

In the tables 7, 8, 9, and 10 coagulation values are given for the selenium sol. Here antagonism is again clearly seen with the ferro cyanide of potassium, the effect is weaker with K₂SO₄, and fails to appear with KCl, just as with potassium acetate, the same thing being found for sodium picrate and benzoate.

It was known to us from the investigations of KRUYT and VAN ARKEL that KOH increases the charge of the selenium sol. To our astonishment table 11 showed us that nevertheless this substance did not raise the limiting

TABLE 6.
 Cataphoretic velocity of the HgS-sol in the same dilution as in the flaking experiments.
 The velocity ν in microns per Volt per second.

Concentration	Cataphoretic velocity
sol + 10 m.mol $\frac{K_4Fe(CN)_6}{4}$	3.5 μ
sol + 20 " "	3.8 μ
sol + 35 " "	3.2 μ
sol + 50 " "	2.2 μ
sol + 5 m.mol KCl	3.2 μ
sol + 10 " "	3.2 μ
sol + 20 " "	2.2 μ
sol + 0.6 m.mol MgCl ₂	1.2 μ

value of MgCl₂. Quite conformable to the expectation, however, table 12 does yield the expected effect for the combination KOH and BaCl₂.

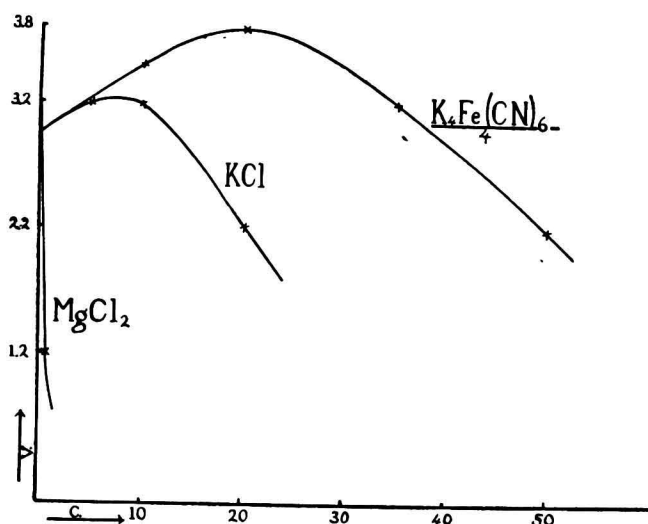


Fig. 1.

In table 13 we finally give measurements of the cataphoretic velocity in this sol; the measurements have been made according to the ultra-microscopic method of KRUYT and VAN ARKEL. Again, quite in accordance with what precedes, there appears to be increase of the charge in the case of potassium ferro cyanide and KOH.

We cannot satisfactorily account for the deviating behaviour of MgCl_2 . Something remarkable strikes us, however, in table 11, viz. that KOH in the smaller concentration does not change the limiting value of MgCl_2 , but

TABLE 7.
Se-sol

$\frac{\text{K}_4\text{Fe}(\text{CN})_6}{4}$	Mg Cl_2
0 (0)	100 (3.0)
8 (5)	112 (3.4)
16 (10)	116 (3.5)
25 (15)	122 (3.7)
33 (20)	122 (3.7)
50 (30)	100 (3.0)
100 (60)	0 (0)

TABLE 8.
Se-sol

$\frac{\text{K}_2\text{SO}_4}{2}$	Mg Cl_2
0 (0)	100 (3.0)
7.5 (3)	100 (3.0)
15 (5)	103 (3.1)
100 (40)	0 (0)

TABLE 9.
Se-sol

K Cl	Mg Cl_2
0 (0)	100 (3.0)
3 (1.25)	100 (3.0)
5 (2)	100 (3.0)
13 (5)	97 (2.9)
26 (10)	90 (2.7)
53 (20)	60 (1.8)
100 (38)	0 (0)

TABLE 10.
Se-sol

K acetaat	Mg Cl_2
0 (0)	100 (3.0)
6 (2.5)	100 (3.0)
12.5 (5)	100 (3.0)
25 (10)	80 (2.5)
37.5 (15)	66 (2.0)
100 (40)	0 (0)

that between 3 and 5 m. mol. it causes it to fall to a very low value. As this phenomenon is entirely wanting for BaCl_2 (table 12), a specific behaviour of the Mg -ion must play a part here.

We have further extended our investigation over the sols of the precious metals. Already FREUNDLICH and SCHOLZ had found in the Au -sol that no antagonistic phenomena appear there. We can confirm this (also for Pt and Ag) save for a remark to be made presently about the potassium ferrocyanides, but we have also been struck by another very remarkable fact. It is generally supposed that the hydroxyl-ion increases the stability of negatively charged sols. This supposition is confirmed by a value given by

TABLE 11.
Se-sol

KOH	Mg Cl ₂
0 (0)	100 (3.0)
1.2 (1)	100 (3.0)
2.5 (2)	100 (3.0)
3.7 (3)	97 (2.9)
5 (4)	30 (0.9)
6 (5)	3 (0.1)
12.5 (10)	<0.3 (<0.01)
25 (20)	<0.3 (<0.01)
100 (80)	0 (0)

TABLE 12.
Se-sol

KOH	Ba Cl ₂
0 (0)	100 (2.1)
3.7 (3)	120 (2.5)
6 (5)	175 (3.7)
12.5 (10)	192 (4.0)
25 (20)	165 (3.5)
55 (45)	100 (2.1)
100 (80)	0 (0)

TABLE 13.

Cataphoretic velocity of the Se-sol in the same dilution as in the flaking-experiments.
Velocity ν in microns per Volt per second.

Concentration	Cataphoretic velocity	Concentration	Cataphoretic velocity
sol only	5.6 μ	sol only	5.6 μ
sol + 3 m.mol KOH	5.9 μ	sol + 5 m. mol $\frac{K_4 Fe(CN)_6}{4}$	6.0 μ
sol + 5 " "	6.1 μ	sol + 10 " "	6.4 μ
sol only	5.6 μ	sol only	5.6 μ
sol + 2 m.mol KCl	5.5 μ	sol + 2.5 m.mol Na benzoate	5.5 μ
sol + 5 " "	5.4 μ	sol + 5 " "	5.4 μ
sol + 10 " "	5.1 μ	sol only	5.6 μ
sol + 20 " "	4.7 μ	sol + 1.2 m. mol BaCl ₂	3.0 μ

FREUNDLICH ¹⁾ for the platinum sol, the limiting value of which for Na OH would be 130 m. mol, whereas that for NaCl is only $2\frac{1}{2}$. Remarkably enough the corresponding value for the gold-sol is not to be found in the literature. To our astonishment we found as limiting value observed after 16 hours 26 m. mol. for KCl, 20 m. mol. for KOH in a gold-sol prepared by electric dispersion. In a silver-sol, prepared likewise by dispersion, which

¹⁾ Z. Physik. Chem. **44**, 152 (1903).

happened to give the same limiting value of 26 m.mol. for KCl, we also found again 20 m. mol. for KOH, while a repetition on the platinum-sol makes us doubt somewhat whether a value as we have described just now, may

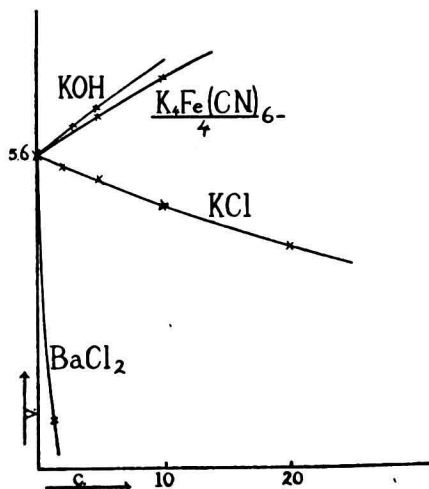


Fig. 2.

after all be assigned to FREUNDLICH's value for this sol. The limiting value which is found, depends in general somewhat on the interval that elapses between the addition of the electrolyte and the observation of the sol, but it now appeared that especially in the case of KOH this period is of the greatest influence. After one night's standing we found a limiting value of 140 m. mol., but when the estimation was made after two days' standing the flocculation concentration had shifted towards a value of about 20 m. mol., the limiting value for the neutral salts being by no means dependent on the time in the same degree.

Besides KOH appears not only to be inadequate to call forth antagonistic actions, but on the contrary it has a sensibilizing effect both on $MgCl_2$ and on $BaCl_2$. These experiences lead to the utter rejection of any supposition such as the charge of the sols of precious metals being attributed to absorbed hydroxyl ions. We get more the impression that the double layer in these sols is built up by complex compounds of the metals, and that alkaline surroundings have a very injurious influence on the structure of this double layer, at least that after a short time this double layer is destroyed¹⁾.

Investigations with ferrocyanide and ferricyanide on these precious metal sols have shown us this: for the gold-sol every estimation is exceedingly difficult after five minutes, because the colour of these salt-solutions hampers the observation of the change of colour in a high degree, a chemical interaction between sol and electrolyte very soon setting in, in consequence of which a colourless solution remains. Nevertheless, on a rough examination

¹⁾ See WO. PAULI'S papers of the last months in Koll. Beih. (Note added to the proofs).

of the colour, we got the impression that after all an antagonistic action of potassium ferro-cyanide and $MgCl_2$ does take place.

Summarizing we come to the conclusion that the cause of the so-called antagonistic flocculation effect is in general brought about by salts which increase the electric charge of the colloid. Undoubtedly polyvalence or good adsorbability of the ion of the same sign acts as a rule in this direction, but specific influences differing from sol to sol with respect to the same electrolyte make themselves felt here.

In connection with the investigations to which we alluded already above, we shall soon return to this subject.

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