

**Chemistry.** — *On the mutual influence of potential determining and non-potential determining ions in sols.* By H. R. KRUYT and MARGA KLOMPÉ.

(Communicated at the meeting of September 28, 1940.)

The facts discussed in this communication became manifest in an elaborate investigation on the connection between flocculation value and sol concentration. We hope in course of time to make detailed communications on this subject. The facts mentioned in this publication form an additional complication of the main theme, but are significant for their own sake and on account of other, related, phenomena, for which reason we wish here to consider them separately.

In our investigation we started from a negatively charged AgI-sol. In order, however, to avoid certain complications we made use of a so-called reprecipitation sol. The preparation is as follows: under ice-cooling the sol is made in the usual way from KI and  $\text{AgNO}_3$ , and without dialysis at once precipitated with an excess of  $\text{AgNO}_3$ . Immediately after this the precipitate is decanted 10 times with ice water, after which, under rapid stirring and ice-cooling, it is reprecipitated with 40 m. Mol KI final concentration. Then follows electrodialysis which subjects the sol to intense purification<sup>1)</sup>. The rapid mode of working and the strong cooling prevent excessive recrystallisation of the AgI-particles. Thus the surface remains active, which makes reprecipitation to 90 % possible. The sol is then brought to the pI required. The control of the pI was done in the way described in H. DE BRUYN's thesis<sup>2)</sup>. We propose later to give a detailed discussion of the other properties of reprecipitation sols and their difference from the normal ones. We know that such a sol consists of AgI-particles, having I-ions as charging ions, with  $\text{H}^+$  ions as counter ions. We worked with a sol of pI 4, one of pI 5 and one of pI 6. For the present we shall restrict ourselves to the results obtained with the sol of about pI 5.

Various dilutions were made of that sol, but by adding KI we made sure that all of them had the same pI as the original sol.

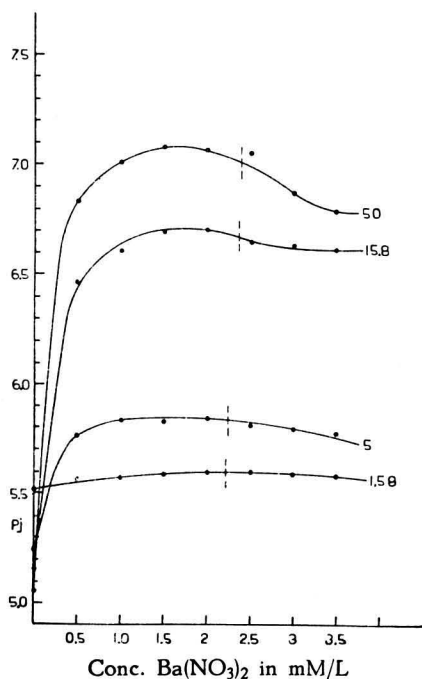
Of such a series of dilutions we next determined flocculation concentrations for non-potential determining ions, for  $\text{KNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{La}(\text{NO}_3)_3$ . We here restrict ourselves to one salt, viz.  $\text{Ba}(\text{NO}_3)_2$ . As it soon appeared that the pI of the sol was changed by the addition of an indifferent electrolyte, we carefully checked the dependence of pI on the  $\text{Ba}(\text{NO}_3)_2$  concentration. The subjoined figure and table represent the results.

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<sup>1)</sup> H. DE BRUYN and S. A. TROELSTRA, Koll. Z. 84, 192 (1938).

<sup>2)</sup> H. DE BRUYN, Diss. Utrecht 1938.

The pI values are set out as ordinates, the barium salt concentrations



as abscissae. Each of the curves applies to a sol of the AgI concentration indicated near the line, namely in m Mols/L (final concentration, i.e. after the addition of the electrolyte). The pI is here increased by two factors, namely the dilution with electrolyte and the influence of the salt. In order to eliminate in the figure the first factor, the initial points of the curves do not represent the pI of the pure sol, but the pI after dilution with water 1 : 1. We see that this influence of the dilution is strongest as the sol is more diluted. The concentrated sol, with the greatest surface can more easily yield an aftermath of I-ions, so there the pI will change least. See our subsequent considerations.

So for the undiluted sol with AgI 50 m Mol/L we find that the pI has increased by two units. In the more diluted sols we find the same phenomenon, but less marked, as the sol is more diluted.

Final conc. Ba(NO <sub>3</sub> ) <sub>2</sub> in m Mols/L	pI sol R I 50 m Mols AgI/L	pI sol R II 5.8 m Mols AgI/L	pI sol R III 5 m Mols AgI/L	pI sol R IV 1.58 m Mols AgI/L
pure sol	4.98	4.93	4.96	5.10
sol + H <sub>2</sub> O 1 : 1	5.05	5.16	5.24	5.41
0.5	6.84	6.46	5.77	5.56
1	7.01	6.61	5.83 <sup>5</sup>	5.57
1.5	7.07	6.69	5.83	5.59
2	7.06	6.70	5.84	5.60
2.5	7.05	6.64	5.81 <sup>5</sup>	5.60
3	6.86 <sup>5</sup>	6.63	5.80	5.59
3.5	6.79	6.60	5.78	5.58
flocculation value in m Mols/L	2.35	2.32	2.26	2.20

Experiences and considerations of the last few years in this laboratory<sup>1)</sup> account for this phenomenon, which is so astonishing at first sight. We shall consider the condition of the sol before the addition of the indifferent electrolyte. There is at the periphery of the AgI-particle an electric double layer, the potential leap  $\Delta\varepsilon$  of which is given in the relation of Nernst:

$$\Delta\varepsilon = -k \log [I^-] = k \times pI.$$

When an indifferent electrolyte is added, the double layer is compressed according to the theory of Gouy-Smoluchowski-Stern. The capacity of the double layer consequently decreases, and in the case of the charge remaining unchanged, the potential difference also decreases, but according to the relation of Nernst mentioned above, it is determined entirely by the pI. In order to maintain the connection the charge of the surface must be increased at the expense of I-ions from the intermicellary liquid. Now theoretically there are two possibilities:

1. There are so many I-ions in the liquid that the needed increase of the charge in the wall scarcely affects the pI. In this case potential difference and pI before and after the addition of the electrolyte are the same.

2. There are not enough I-ions in the intermicellary liquid, so that the removal effects a considerable change in the pI. In this case a number of I-ions will move to the surface — and hence from the liquid — until a new pI value has been formed and a corresponding  $\Delta\varepsilon$ , according to the formula of Nernst. The first case will be promoted by two circumstances: many I-ions in the intermicellary liquid, i.e. a sol of low pI, or little colloid surface, i.e. a low sol concentration.

In a sol of 50 m Mol/L and pI 5 neither the one, nor the other is the case. So the addition of the indifferent electrolyte, and with it the change in the capacity of the double layer, will cause a considerable increase of the pI of the sol. As the sol concentration decreases the phenomenon will become less manifest, just as is shown in our figure. The second conclusion too was confirmed by further investigation. When one starts from a sol of pI 4 the phenomenon is less evident.

This shows the difficulty of treating the connection between sol concentration and flocculation concentration. For even when the initial pI values are the same in all dilutions, the final pI values will differ after the addition of the flocculating electrolytes.

For the rest it is also interesting to note the localisation in our figure of the flocculation concentration. They are marked by a dotted line on each curve. It is seen that the pI shift is practically completed long before the flocculation value is reached.

After these results had been found with the negative sol, Dr. I. KUBAL

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<sup>1)</sup> Especially H. DE BRUYN, Diss. I.c. Cf. H. R. KRUYT and H. DE BRUYN, *Z. physik. Chem.* A **186**, 282 (1940).

((Prague) in the previous academic year made similar investigations in this laboratory with the positive sol. These too will be fully discussed later. We will now only state that essentially he obtained the same results, although circumstances are much more unfavourable in that case: it should be borne in mind that the solubility product of AgI is  $10^{-16}$  so the neutral point is at pI 8 (pAg 8) and the point of zero charge at pI 10 (pAg 6). A sol of pAg 4 still proves insufficiently stable, so one has to work with pAg 3.8. Even in the highest attainable sol concentration the pAg shift on the addition of an indifferent electrolyte is comparatively slight, though it considerably passed the experimental error, so that maxima were obtained which were lower but evidently similar to those in our figure.

These investigations draw the attention to the fact that one should be extremely careful in interpreting the distinction — perfectly justified in itself — between potential determining and non-potential determining electrolytes (called indifferent in the above). For the latter do indeed (though indirectly) change the potential leap, especially in a sol with a low concentration of potential determining electrolyte (high pI in negative, high pAg in positive sols respectively) and a large development of colloid surface (high sol concentration).

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