

Chemistry. — *Cataphoretic measurements and the theory of the critical potential.* By H. R. KRUYT and D. R. BRIGGS ¹).

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Stability of a lyophobic colloid system, which is the inverse function of the rate at which flocculation takes place, is governed by the electric charge on the surface of the colloid particle. HARDY (*Z. physik. Chem.* **33**, 385 (1900)) considered that flocculation would not take place until the potential had been lowered to zero, i.e., that even the smallest charge on the particle was sufficient to render it stable. POWIS (*Z. physik. Chem.* **89**, 186, (1915)) working with oil droplets in water found, however, that flocculation occurred when the cataphoretic velocity had yet a value considerably higher than zero and that flocculation was brought about by that concentration of electrolyte which was just sufficient to reduce the cataphoretic velocity to this value, the potential corresponding to which he named "the critical potential". He was able to repeat these results with the As_2S_3 sol (*J. Chem. Soc.* **109**, 734 (1916)) with the exception that, in this case, salts of monovalent cations brought about preprecipitation at a concentration of the salt for which the cataphoretic velocity was found to be still very much higher than that velocity which was "critical" for the polyvalent cation salts and indeed almost as high as that exhibited by the original sol. FREUNDLICH & ZEH (*Z. f. physik. Chem.* **114**, 65 (1925)), KRUYT, ROODVOETS & VAN DER WILLIGEN (*Colloid Symp.* **4**, 304 (1926)), KRUYT and VAN DER WILLIGEN (*Z. physik. Chem.* **130**, 170 (1927)) and MUKHERJEE (*Nature*, **122**, 960 (1928)) among others, have had the same experience, that is, the salts of the alkali metals (and of hydrogen) cause precipitation of the colloids at concentrations for which the cataphoretic velocity of the particles is sometimes as high as or even higher than of the original sol.

However, it has been assumed that the potential across the double layer is always proportional to the cataphoretic velocity. The at present accepted equation designating this relationship is a modification of the Lamb-Helmholtz equation and is

$$\zeta = \frac{6\pi\eta}{D} u$$

where ζ = electrokinetic potential
 u = cataphoretic velocity
 η = viscosity of medium
 D = dielectric constant.

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Following work by FÜRTH (Physik. Zeitschr. **25**, 676 (1924)) and PECHHOLD (Ann. d. Physik. **83**, 427 (1927)) on the variation of the dielectric constant of solutions of electrolytes, in which it was shown that the dielectric constant shows first a small decrease followed by a sharp increase as the concentration of electrolyte is increased, KRUYT and VAN DER WILLIGEN (Z. Physik. Chem. **130**, 170 (1927)) ascribed the exceptional behavior of these alkali cation salts to their influence on this factor in the high concentrations needed to bring about flocculation. It is evident from the above equation that if D were increased in value with increase in concentration of the salt, the cataphoretic velocity (u) could remain constant or even increase while ζ at the same time decreased. If, then, the ζ potential on the particle is counted the stabilising influence, its being lowered to the critical value could still be postulated even though the migration velocity remained high, by a corresponding increase in the dielectric constant. It is to be pointed out that this large increase in D is required to occur only in the interfacial region and that the corresponding value for the bulk of the solution does not need to change to a corresponding degree. Adsorption on the surface of the sol particle could account for a marked increase in concentration of electrolyte in that region needed to account for the larger change in D in that vicinity.

It seems, then, that the exceptional behavior of the monovalent cation salts is due to the fact that relatively high concentrations of these salts are necessary to bring about flocculation and that, at these higher concentrations there is introduced a secondary effect which causes anomalous values to be ascribed to the electrokinetic potential at the flocculation concentrations. The object of the present investigation was to find if POWIS' theory holds when only small concentrations of those monovalent cations which are very highly adsorbed and which bring about flocculation in concentrations of comparable molality to those required for polyvalent cation salts. Such salts are those of strychnine and new fuchsin.

Experimental.

The method used for measuring the cataphoretic velocity of the sols was a modified U -tube method developed by KRUYT and VAN DER WILLIGEN (Koll. Zeitschr. **44**, 22, (1928)) in which a four electrode cell is employed, the two inner electrodes being placed at a known distance apart in the two arms of the U -tube and kept at a definite difference of potential throughout the experiment. The liquid used above the sol in all cases was the ultrafiltrate of the sol with or without the electrolyte as the case might be. The electrolyte was added to the sol before ultrafiltration so that the ultrafiltrate might be truly that of the sample of sol being worked with. Ultrafiltration was accomplished in a manner adapted from the method of Bechold-Intlohn (Z. f. angew. Chem. **37**, 494 (1924)) and adequately described in the paper by KRUYT and VAN DER WILLIGEN.

A thin collodion membrane supported by a porous porcelain cup acted as the filter and allowed a fairly rapid filtration to be accomplished.

VAN DER WILLIGEN found that the rate of migration of the rising interface between the sol and its ultrafiltrate was proportional to the fall in potential per unit length in the column of ultrafiltrate, while the falling interface advanced at a rate proportional to the fall in potential per unit length in the column of sol, that is, each interface, for a given potential drop between the inner electrodes, advanced at a rate which was directly proportional to the specific resistance of the medium into which it advanced. He gave, as the average velocity (u) of migration

$$u = \frac{w_1 h_1 + w_2 h_2}{ZE}$$

where w_1 and w_2 are the observed distances moved by the rising and falling interfaces, respectively; h_1 and h_2 , the average length of ultrafiltrate and of sol, respectively, lying between the inner electrodes across which is maintained the constant potential drop E during the time Z of the observation.

This relation seems to hold very well with a sol in which no settling effect is observable after it has been run into the U -tube. Such is the case with the As_2S_3 -sol but not with the other sols used in these experiments. What this settling is due to is not exactly known but it seems to be a contraction of the sol which continues at an ever decreasing rate for some time after the sol is slowly let into the U -tube under the clear overlying solution (u -filtrate). If the sol is placed into the U -tube with no clear liquid above it, no settling occurs. The effect seems most noticeable when the number of particles is least. With the gold sol and the selenium sol, both of which show it, the difference between the specific conductivity of the sol and of its ultrafiltrate was found to be so small (Table I), that no difference would have been noticed between the migration rates of the two interfaces had not the settling effect been present. Since the settling occurred at the same rate in each arm of the U -tube, it was necessary only to take the average, distance moved as $\frac{1}{2}$ the sum in the calculation of u

$$u = \frac{\frac{1}{2}(w_1 + w_2)H}{ZE}$$

where H represents the length between the two inner electrodes across which the potential difference E is kept constant for time Z and w_1 and w_2 are the distances moved by the rising and falling interfaces respectively, during the time Z .

The flocculation values used in this research were those obtained when 2 cc. of electrolyte solution was added uniformly from a pipette to 10 cc. of the sol contained in a precipitation tube, the resulting solution uniformly mixed by rotational shaking before setting aside to be again shaken 24 hours later and finally observed after another $\frac{1}{2}$ hour. The flocculation

value was taken as that concentration of electrolyte which, through the above process, just gave a perfectly clear liquid above the coagulum. The selenium sol was very slow to settle after disturbance so that the flocculation values observed with it were those after 24 hours without further shaking. With the gold sol it is of interest to note that this flocculation value does not coincide with the change in colour from red to blue but requires a higher concentration of electrolyte.

In preparing the sol for the cataphoretic measurements the stock sol was always increased in volume by 20 %, the added liquid being pure water in cases where measurements on the pure sol were to be carried out, or an electrolyte solution of sufficient concentration to give the resulting sol the required concentration for the experiment. The electrolyte solution was always added to the sol in a manner as nearly as possible the same as that when adding it to determine the flocculation value. In both cases the percentage increase in volume due to added liquid was the same.

When the flocculation value had been obtained for a salt, the cataphoretic velocity was found for from 4 to 6 concentrations of this electrolyte, these concentrations usually being equally spaced between zero concentration and 90 % of the flocculation concentration. In this manner the trend of the curve could be found and extrapolation to the flocculation concentration made with a fair degree of accuracy. Cataphoretic measurements were carried out at 20° C. \pm 1° C., in a water bath. The usual potential difference maintained between the two inner electrodes was 18 Volts; this was lower in cases where the electrolyte content was high enough to allow sufficient current to pass to cause heating of the liquid in the *U*-tube, in which cases as low as 10 Volts was the potential maintained.

The As_2S_3 sol was prepared in the common way (See e.g. KRUYT and V. D. SPEK (Koll. Z. 25, 1, (1919)). 3 Grams of As_2O_3 were dissolved in 500 cc. distilled water at the boiling temperature, this solution being then added, drop by drop, to 200 cc. of distilled water which was kept saturated with washed H_2S gas the entire time during which the As_2O_3 solution was being added. When the reaction was complete the excess H_2S gas was removed by bubbling through the sol hydrogen gas which had previously been washed consecutively through alkaline KMnO_4 , HgCl_2 , NaOH solutions and water. The sol was kept until a short time before use at the concentration at which it was prepared but was diluted with four volumes of distilled water before the measurements were carried out with it. The diluted sol thus contained approximately 1.06 grams of As_2S_3 per liter.

The selenium sol was prepared according to directions modified from those given by KRUYT and VAN ARKEL (Koll. Z., 32, 29 (1923)) by bringing to the boiling temperature 550 cc. of doubly distilled water to which had been added 30 cc. of a 1.2 molar solution of hydrazine hydrate, then adding quickly 25 cc. of a 0.1 molar solution of SeO_2 , and finally

after the sol had reached a salmon yellow colour, 5 cc. more of the same solution were added. The containing flask was then removed from the flame. To this solution should be added $2\frac{1}{2}$ liters of water but experiment showed this resulting sol to contain too much electrolyte for our purpose. To free the sol from this electrolyte it was found possible to ultrafilter the sol prepared as above until nearly all electrolyte was removed (as its specific conductivity, Table I, clearly shows) and then adding water until the sol reached about the density of colour that it would have shown had the water been added before the electrolyte was removed. This purification by ultrafiltration, which is essentially a rapid dialysis is not successful with all sols but so long as the selenium sol was not freed entirely from liquid it could be again successfully dispersed by shaking in a fresh volume of water. This sol contained approximately 0.05 gram of selenium per liter. The particles of selenium sol were fairly large when viewed in the ultra-microscope but the sol was stable.

For some reason, probably because of the relatively large size of the particles, this washed selenium sol was found very difficult with which to obtain consistent results and the values are more erratic than are those obtained with the other sols.

The red gold sol was that of TEMMINCK GROLL (Chem. Weekblad 13, 617 (1916)) prepared by using H_2O_2 as the reducing agent. 330 cc. of the sol was prepared at a time, it being found impossible to prepare larger volumes successfully. To make 330 cc. of sol, 25 cc. of 3 % H_2O_2 were added to 250 cc. of doubly distilled water and to this was added, a drop at a time with constant and vigorous shaking, 30 cc. of a 0.066 % $NaAuCl_4$ solution, followed by 2 cc. of 0.1 N NaOH, then 20 cc. of the 0.066 % $NaAuCl_4$ solution and finally 3 cc. of 0.1 N NaOH. Each quantity thusly prepared was allowed to stand, with occasional shaking, for 30 minutes before it was added to the stock sol. Under the ultra-microscope this sol showed the characteristic green particles of a red gold sol. It contained 0.06 grams of gold per liter and was about 0.0015 normal in alkali which was probably present as Na_2CO_3 and $NaHCO_3$. It did not cause phenolphthalein to turn pink.

TABLE I.

Specific conductivities of the sols, diluted with the $\frac{1}{5}$ vol. of distilled water, and of their ultrafiltrates.

Sol	κ (for sol) $\times 10^6$	κ (for U-filtrate) $\times 10^6$	Ratio $\frac{\kappa_{uF}}{\kappa_{sol}}$
As_2S_3	37.50	16.20	0.451
Se	3.31	3.14	0.949
Au	188.00	185.00	0.984

TABLE II.

The flocculation values and the initial and critical cataphoretic velocities of the various sols with the electrolytes used.

	As ₂ S ₃ sol		Se sol		Au sol	
	Flocculation value millimols per liter	Cataph. veloc. μ /volt. sec.	Floc. value m. mol per liter	Cataph. veloc. μ /volt. sec.	Floc. value m. mol per liter	Cataph. veloc. μ /volt. sec.
Initial value	—	4.6	—	3.4	—	3.9
Strychnine NO ₃	0.098	1.7	0.018	2.3	0.41	2.15
New fuchsin Cl	0.117	1.7	—	—	—	—
BaCl ₂	0.60	1.65	2.85	2.0	0.47	2.15
AlCl ₃	0.042	1.55	0.0018	2.0	0.0043	2.1
KCl	60.0	3.4	16.6	2.2	24.0	3.65

Results and discussion.

The accompanying graphs show very clearly in every case that the monovalent cations which are highly adsorbed and cause flocculation at low concentrations, reduce the cataphoretic migration velocity uniformly to approximately the same value at the concentration of total precipitation as that which is characteristic of the polyvalent ions at their corresponding concentrations. Table II gives the flocculation concentrations for these salts and the approximate extrapolated value for the migration velocity at these concentrations together with the migration velocity for the original sol.

There are several things about these curves which are not entirely clear. It is difficult at present to explain why BaCl₂ should uniformly give a curve in which the cataphoretic velocity is reduced very quickly to a value very near to that shown at the concentration of complete precipitation, after which the curve is nearly flat for more than half its length on the concentration axis. There is indication that the flocculation value decreases with time. For example, with the Se sol the flocculation value after the sol had stood with the salt in it for 6 days was found to have changed to the neighbourhood of 1.35 millimols per liter instead of 2.85 millimols per liter as indicated at the end of 24 hours. This form of curve is general for BaCl₂ and may repay a closer examination. There is no reason to expect that it should differ markedly from that shown by AlCl₃ or the highly adsorbed monovalent cation salt. Another unexpected result was that shown by AlCl₃ with the gold sol. There is a probable explanation for this however, and that lies in the fact that there was a very small concentration of alkali present in the gold sol. This alkali promptly reacted

with the $AlCl_3$ to form $Al(OH)_3$ and thus removed the Al^{+++} ion from the solution. The $Al(OH)_3$ particles were probably carrying only a very slight positive charge because of the presence of the remaining alkali in the sol. Not until most of this alkali was removed by the added $AlCl_3$ was it possible for the Al^{+++} ions to remain in the solution and therefore

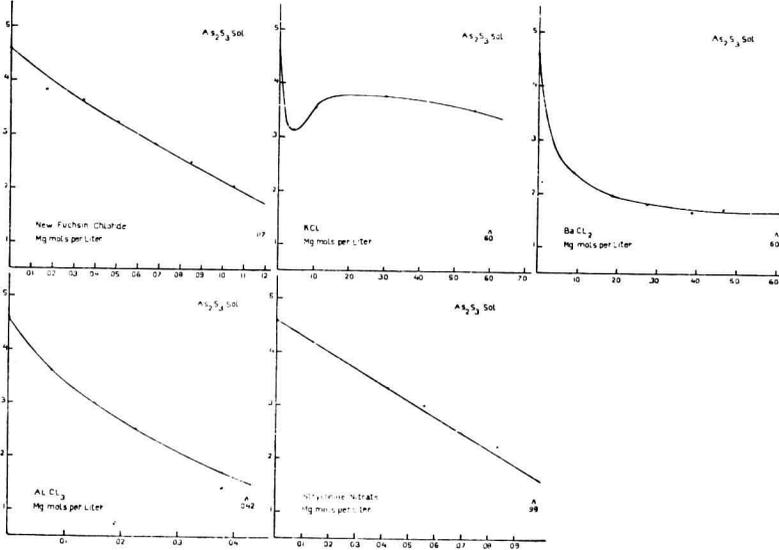


Fig. 1.

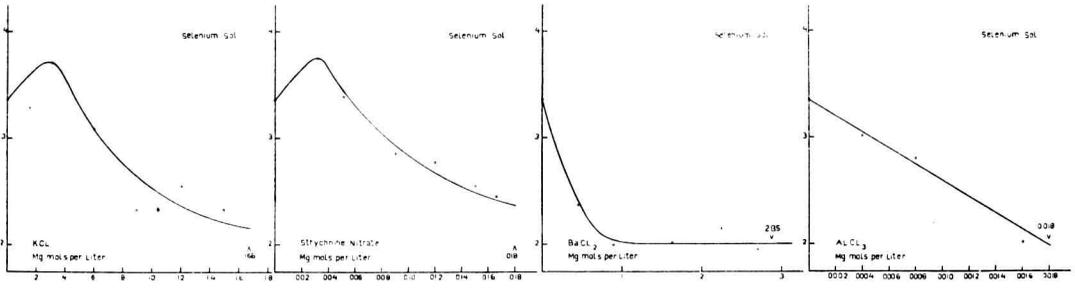


Fig. 2.

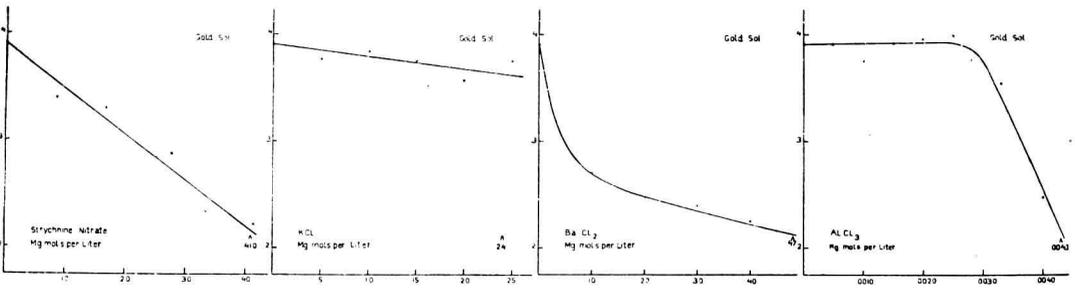


Fig. 3.

be adsorbed by the gold sol to reduce its ζ potential, whereupon only a very small amount of Al^{+++} ions sufficed to precipitate the sol. It is interesting that so long as no reduction of the cataphoretic velocity (up to 0.0025 millimols $AlCl_3$ per liter) was found, the gold sol retained its original red colour but at 0.0028 millimols per liter the sol had already turned blue though total precipitation after 24 hours occurred at a much higher concentration (0.0043 millimols per liter). In the case of the Se-sol, too, where the electrolyte content of the sol itself was very low, it is interesting that KCl reduced the cataphoretic velocity to a value near that of the other electrolytes at the flocculation concentration.

There are, indeed, a good many more unanswered questions arising from these results than there are those which have found an answer. However, the real object of the research, namely to find if the POWIS' rule holds for monovalent cation electrolytes when these can cause precipitation at concentrations of the same order as those required for polyvalent cation salts, has been successfully answered in the affirmative without a doubt. We can safely say that when flocculation can be brought about in low concentrations of electrolytes the migration velocity is always reduced to the same value when precipitation occurs.

One of us (D. R. B.) will publish presently an extended paper in which more data will be given and in which details will be fully discussed.

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