

Chemistry. — *The action of electrolytes on hydrophobic colloids.* By
H. R. KRUYT.

(Communicated at the meeting of April 27, 1935).

The problem of the action of electrolytes on hydrophobic colloids belongs to the very oldest in colloid chemistry. The effects of addition of electrolytes, such as flocculation and peptisation, were already known to GRAHAM; SCHULTZE¹⁾ and LINDER and PICTON²⁾ collected a large quantity of facts by their researches; HARDY³⁾ produced the key to the problem when stating that the action of the electrolytes is closely connected with the electrical behaviour of the colloids, and FREUNDLICH⁴⁾ tried to explain the mechanism of the electrolyte function in his adsorption theory. His opinion that peptisation is caused by adsorption of charging ions, flocculation by adsorption of discharging ions has proved untenable in this form, not the least by FREUNDLICH's own researches⁵⁾, after rendering excellent services for twenty years as work hypothesis.

The fact that a potential difference arises between the wall of a colloid particle and the surroundings has to be ascribed to unequal distribution of the potential-determinative ion. VERWEY⁶⁾ has excellently worked out this idea for the silver iodide sol. *AgI* in pure water displays a solubility, characterized by the solubility product 10^{-16} . The particles prove to be negatively charged. The distribution of the *J*-ions is consequently thus that more *J*-ions attach to the particle than remain in the solution. Not until the concentration of the iodine ions by addition of silver ions has been reduced from 10^{-8} to 10^{-10} , the iso-electric point is reached.

Potential-determinative are, of course, the particle's own ions. Moreover, it appeared that isomorphous ions are similarly distributed over the particle and the surroundings⁷⁾, which is conceivable from the conceptions formed by MUKHERJEE⁸⁾ and FAJANS⁹⁾ concerning the double layer on crystalline particles.

¹⁾ H. SCHULTZE, *J. pr. Ch.* (2) **25**, 431 (1882).

²⁾ LINDER and PICTON, *J. chem. Soc. London* **61**, 137 (1892).

³⁾ W. HARDY, *Z. physik. Chem.* **33**, 385 (1900).

⁴⁾ H. FREUNDLICH, *Kapillarchemie* 1. Aufl. 1909.

⁵⁾ H. FREUNDLICH, K. JOACHIMSOHN and G. ETTISCH, *Z. physik. Chem.* **141**, 249 (1929).

⁶⁾ E. J. W. VERWEY and H. R. KRUYT, *Z. physik. Chem.* **167**, 137, 149 and 312 (1933); E. J. W. VERWEY, *Thesis Utrecht* 1934; *Rec. Trav. Chim.* **53**, 933 (1934).

⁷⁾ H. R. KRUYT and P. C. VAN DER WILLIGEN, *Z. physik. Chem.* **139**, 53 (1928); H. R. KRUYT and H. A. CYSOUW, *Ibid.* **172**, 49 and 56 (1935).

⁸⁾ I. MUKHERJEE, *Trans. Faraday Soc.* **16 A**, 103 (1920).

⁹⁾ K. FAJANS and K. VON BECKENZATH, *Z. physik. Chem.* **97**, 478 (1921).

The potential difference, caused by unequal distribution of the potential-determinative ions, is little or not influenced by other, non-potential-determinative ions. Nevertheless these ions have a considerable influence on the structure of the double layer, that is on the distribution in space of the counterions. Whereas, consequently, the potential ε_F ¹⁾ is determined by potential-determinative ions, the ζ potential which, as is wellknown, depends strongly on the distribution in space of the counterions is indeed influenced by other ions, not belonging to the particle. In fig. 1 this has been expressed schematically. The potential is indicated as ordinate, the

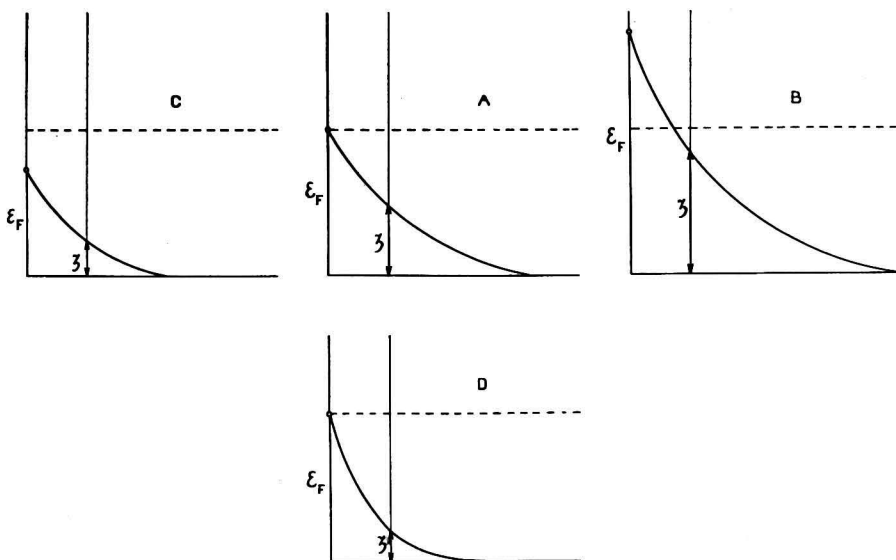


Fig.1.

distance from the wall as abscissa. If the initial condition of the sol is represented by fig. A, alterations may be made in it by increasing or lowering the concentration of the potential-determinative ions.

In fig. B it is supposed that ε_F is increased and in fig. C that it is decreased. Consequently the ζ potential is increased in B, decreased in C. On addition of a neutral electrolyte ε_F remains unaltered (fig. D) but, owing to the "pressure" of the added counterions, the course of the potential is steeper and consequently ζ in the case of fig. D decreased.

The change of ε_F , as the result of unequal distribution of a potential-determinative ion, is controlled by NERNST's formula :

$$\varepsilon_F = \frac{RT}{zF} \ln \frac{c_1}{c_2}$$

Here z represents the valency of the ion, c_2 the concentration of the

¹⁾ See for the meaning of this notation : L. W. JANSSEN, Thesis Utrecht 1933.

potential-determinative ion in the solution, and c_1 that on the wall of the particle. The latter magnitude consequently has the character of the "Lösungstension" of the wall for the potential-determinative ion. If c_2 is altered, the following equation is applicable:

$$d\epsilon_F = K d \ln c_2.$$

VERWEY (l.c.) tested and confirmed the correctness of this conclusion.

The change of distribution in space of the ions has been calculated by GOUY¹⁾ on the ground of the electrostatic attraction of the wall on the ions. STERN²⁾ besides traced the influence of the adsorption of the wall on these ions. HANS MÜLLER³⁾ and L. W. JANSSEN⁴⁾ worked out these theories further.

Summarizing we can say that the ζ potential, of such great importance for the stability of the hydrophobic colloids, consequently is influenced by

two factors, viz. by changes in ϵ_F at a practically constant course of the charge in space and by alteration of the charge in space at a constant total potential between wall and surroundings.

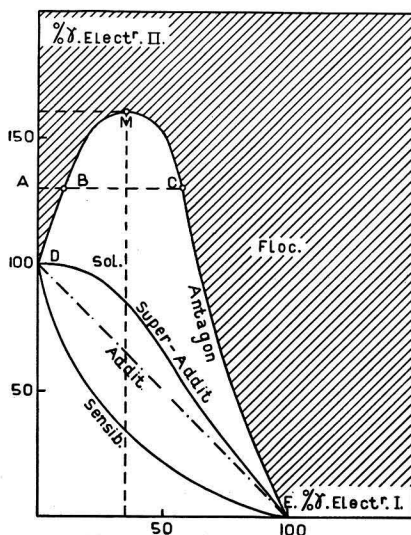


Fig. 2.

value for the electrolyte A , and γ_B that for the electrolyte B . Independently of their absolute value these two magnitudes are marked as 100%.

Four possibilities may now be imagined and are indeed practically found. In the first place an additive course, represented by a straight line; further *sensibilisation* is spoken of in case the flocculation values for the mixtures lie below the straight line, *superadditivity* if they lie above it, while we shall use the word *antagonism* exclusively in case the super additivity is so large that the flocculation curve ascends from γ_A .

1) G. GOUY, J. physique (4) 9, 457 (1910).

2) O. STERN, Z. Elektrochem. 30, 508 (1924).

3) H. MÜLLER, Koll. Beih. 26, 257 (1928).

4) L. W. JANSSEN, Thesis Utrecht 1933.

In a recently published dissertation C. F. VESTER¹⁾ first collected the numerous examples existing in this field and in particular paid attention

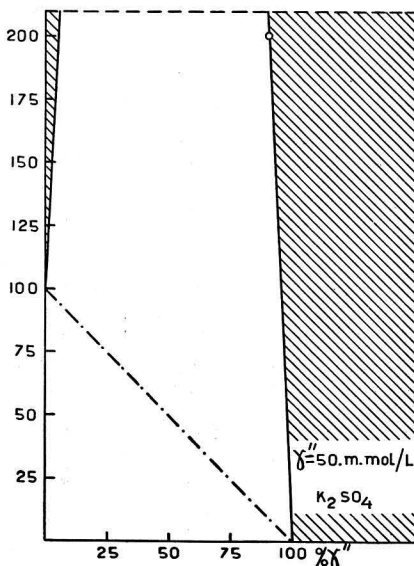
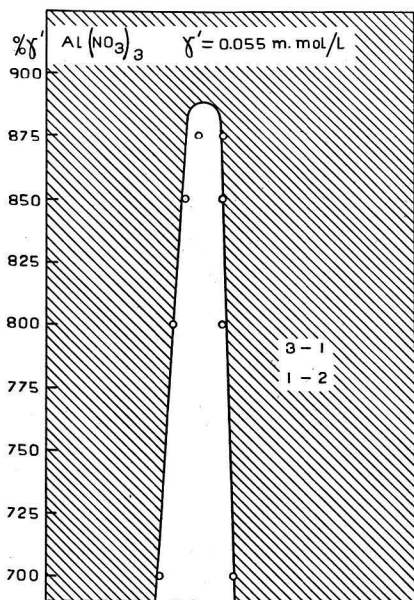


Fig. 3.

others, especially by that of the SO_4 -ions; this activity is calculated with the aid of the formula :

$${}^{10}\log f = -h_T z^2 \frac{\sqrt{I}}{1 + a_{gT} \sqrt{I}}$$

¹⁾ C. F. VESTER, Thesis Utrecht 1935.

to the most striking and at first sight always astounding fact of the antagonism. Meanwhile, after what has been remarked before, it is hardly necessary to say that a sharp distinction should be made here whether one of the electrolytes contains a potential-determinative ion or not. If such is the case, the antagonism is at once conceivable: for, if the electrolyte *B* contains a potential-determinative ion, ϵ_F rises on its addition, consequently also ζ , and more will be needed of the electrolyte *A* to attain the same critical flocculation potential. Vester, therefore, has correctly left aside all cases in which a potential-determinative ion occurred as a priori conceivable, but tried to account for the fact that also in combinations of non-potential-determinative ions antagonism may yet occur. How very pronounced such an antagonism may be, is for example apparent from fig. 3, which applies to the AgJ sol; the electrolyte *A* is $\text{Al}(\text{NO}_3)_3$, the electrolyte *B* K_2SO_4 . It is to be seen that the maximum of the antagonistic curve lies at 890% of the initial value for $\text{Al}(\text{NO}_3)_3$.

The explanation of this peculiar antagonistic curve becomes for the greater part clear, if the activity of the ions is considered. The activity of the Al-ions is namely strongly decreased by the presence of the

where

$$g_T = \sqrt{\frac{4\pi N e^2}{D k T}} \cdot 10^{-3} \quad h_T = \frac{1}{2.303} \cdot \frac{e^2 \rho_T}{2 D k T}$$

a the average distance at which the centres of two ions may approach each other,

z the valency of the ion, the activity of which is calculated.

Γ the totalized ionic concentrations $\sum c_i z_i$ for all ions present.

In the table below the activity is given of the different ions for the combination $\text{Al}(\text{NO}_3)_3 + \text{K}_2\text{SO}_4$. In the first and second column the concentrations of the components are given along the antagonistic curve, represented in fig. 3, which curve consequently contains the very pronounced maximum.

Conc. in m. mol./L		Activ. in m. gr. ion/L		Activ. in m. gr. ion/L	
$\text{Al}(\text{NO}_3)_3$	K_2SO_4	Al^{+++}	NO_3^-	K^+	SO_4^{--}
0.055	0	0.046	0.162	0.	0.
0.165	5.	0.044	0.428	8.6	2.8
0.358	20.	0.027	0.807	30.0	6.4
0.385	21.5	0.027	0.858	31.9	6.5
0.44	25.	0.024	0.958	36.3	6.9
0.468	27.5	0.023	1.003	39.3	7.2
0.481	27.5	0.023	1.032	39.3	7.2
0.481	35.	0.016	0.989	48.0	7.7
0.468	35.	0.016	0.962	48.0	7.9
0.440	35.	0.015	0.905	48.0	7.7
0.330	40.	0.009	0.648	53.5	8.0
0.138	45.	0.003	0.270	58.9	8.3
0.110	45.	0.001	0.217	58.9	8.3
0.	50.	0.	0.	64.1	8.4

In the third column the corresponding activity of the Al-ions is given, and similarly in the columns 4, 5 and 6 that for the other ions. It is now at once conspicuous that in column 3 *no maximum value occurs*, but that the activity of the Al-ions gradually decreases from 0.046 m.gr. ion/L to 0. At the value for the maximum in the concentration curve (0.481 m.Mol $\text{Al}(\text{NO}_3)_3$ per L) the activity of these ions is only half (0,023) of that at the original boundary value of $\text{Al}(\text{NO}_3)_3$, (0,046, belonging to the

concentration 0.055 m.Mol per L). In the maximum, consequently, the concentration is nine times as high, but the activity is only half of that at the original boundary value. That is brought about by the high concentration of the other salt and especially by that of its bivalent anion. It is remarkable that at the maximum the activity of the *K*-ions present is also about half of the activity at the original boundary value for K_2SO_4 (39 and 64 m.gr.ion/L. respectively). If, therefore, the flocculation curve is considered, expressed *not* in concentrations but in activities, the maximum disappears and the additivity curve is approached. Thus there is every reason to ascribe the large deviation with respect to the additivity line in the first instance to the influence exerted by the salts on each other's activity and only in the second instance to their influence on the double layer on the colloid wall.

The combination $Th(NO_3)_3 + Na_2SO_4$ is also calculated in this way. In this system a region of reversal of the charge also occurs (so-called irregular series). The results corroborate our speculations satisfactorily¹⁾.

The large amount of facts, collected by VESTER, relating to the influence of two electrolytes on the negative AgJ sol, led to the conclusion that it is essential for the occurrence of antagonism that the counterions differ in valency (that consequently the flocculation concentration of the *B*-component is considerably higher than that of the *A*-component). Further, the antagonism is the more pronounced as the anion of the *B*-component has a higher valency. These two conditions can now be explained by their influence on the ionic concentration: the high concentration of the mono-, bi-, or trivalent anion considerably lowers the activity of the polyvalent cation; consequently the concentration of this counterion has to be considerably increased in order to keep up flocculation in the presence of the second salt.

Summary.

1. When discussing the action of electrolytes on a sol, we have to distinguish between ions that are potential-determinative and those that are not (VERWEY); ζ changes in consequence of either ϵ alteration or a change in the distribution in space of the counterions (GOUY).

2. In so-called ion-antagonisms the cases in which a potential-determinative ion occurs form a group, the mechanism of which is a priori conceivable.

3. The cases of antagonism with non-potential-determinative ions prove to be dependent on very definite conditions with respect to the valency of the participating ions.

4. These cases are for the greater part explained by the influence exerted by the ions on each other's activity, especially by the influence of

¹⁾ See for particulars the cited dissertation of C. F. VESTER.

the anion of the second electrolyte on the activity of the (most strongly flocculating) cation of the first.

5. As an example the case has been calculated of the flocculation of the negatively charged AgJ sol, flocculated by $\text{Al}(\text{NO}_3)_3$ and K_2SO_4 . The antagonistic effect of the K_2SO_4 causes an almost ninefold concentration of the Al-ion. Nevertheless the activity of the Al-ions decreases along the flocculation curve (VESTER).

Utrecht, April 1935.

van 't Hoff Laboratory.

Medicine. — *Ueber die Reaktion der Augenmuskeln auf zwei gleichzeitig zugeführte vestibuläre Reize, zugleich ein Beitrag zur Frage der labyrinthären Genese des Dunkelnystagmus.* Von J. LE HEUX und A. DE KLEYN.

(Communicated at the meeting of April 27, 1935).

Die Entdeckung von RAUDNITZ¹⁾, dass junge Hunde im Dunkeln Augenzittern bekommen, hat besonders an Bedeutung gewonnen nachdem OHM²⁾, wohl der beste Kenner des Augenzitterns der Bergleute, feststellen konnte „dass der bei jungen Hunden durch Dunkelheit hervorgerufene Nystagmus in Bezug auf Ablauf, Ausschlag und Dauer der Zuckung, den Einfluss von Ruhe und Bewegung mit dem Augenzittern der Bergleute vollkommen übereinstimmt“. OHM hat sofort erkannt, dass sich durch die Entdeckung von RAUDNITZ die Möglichkeit ergibt, nähere experimentelle Untersuchungen auszuführen und auf diese Weise die rätselhafte Genese des Augenzitterns der Bergleute mehr oder weniger zu lösen.

Im Anfang meinte OHM aus eigenen Versuchen schliessen zu können, dass nach doppelseitiger Labyrinthexstirpation der Dunkelnystagmus bei Hunden verschwindet und der labyrinthäre Ursprung des Dunkelzitterns damit experimentell bewiesen sei.

Wie so oft, hat sich auch hier herausgestellt, dass man mit Schlüssen aus derartigen negativen Versuchsergebnissen sehr vorsichtig sein muss. Wie aus den Protokollen von OHM hervorgeht, war nach doppelseitiger Labyrinthexstirpation das Allgemeinbefinden seiner Versuchstiere schlecht und dieses war wahrscheinlich die Ursache des Verschwindens des Dunkelnystagmus nach dem Eingriff.

In einer Versuchsreihe, welche später im pharmakologischen Institut in Utrecht mit VERSTEEGH³⁾ ausgeführt wurde, konnte gezeigt werden, dass bei gutem Allgemeinbefinden der Tiere:

1) RAUDNITZ, R.: Vers. d. Ges. f. Kinderh. Karlsbad 1902.

2) OHM J.: Das Augenzittern der Bergleute und Verwandtes. Berlin, Springer 1916.

3) DE KLEYN A. und VERSTEEGH C.: Graefe's Archiv. 101, 1920, 228.