

the p_n curve is to be raised can be shown from the fact that at $p_n = 3$ ($a_n^+ = 1 \times 10^{-3} N$), $a_{K^+} = 0$ and at about $p_n = 4$ ($a_n^+ = 1 \times 10^{-4} N$), the $a_{K^+} \cong 0.5 \times 10^{-4} N$ as observed from the curves; consequently with the disappearance of 9×10^{-4} equivalents of H^+ ions we are getting only 0.5×10^{-4} equivalent of K^+ ions in the intermicellar solution. For the neutralisation of any acidic suspension, weak or strong, the concentration of the cation of the added base will always exceed or at least be approximately equal to the H^+ ions disappearing from the solution, and this can only happen by raising the p_n curve as a whole.

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AN ANALYSIS OF THE NEUTRALISATION CURVES OF THE COLLOIDAL ACIDS. PART IV

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The features of the conductometric titration curves of the colloidal acids have been discussed with reference to our previous theoretical findings on the features of the potentiometric titration curves. The changes such titration curves undergo, when a diacidic base is used for titrating the colloidal acid instead of a monoacidic base, have been brought out. An attempt has also been made to show the extent of agreement between our method of calculation and some published experimental informations on the neutralisation of colloidal AgI sols with hydrogen as the counter-ions.

Conductometric Titration Curves.—The nature of the potentiometric titration curves of the colloidal acids has already been analysed in detail (Gupta, this *Journal*, 1956, **33**, 587; 1957, **34**, 63). The assumptions involved in the deduction of the equations representing potentiometric titration curves of particular shapes necessarily and simultaneously fix up conductometric titration curves of definite and corresponding patterns. It has been assumed that only the free ions and the colloidal particles are the carriers of electricity and the adsorbed ions do not contribute to the conductivity under normal field strength used in the conductivity measurements. Under such circumstances, the expected nature of the specific conductivity-concentration curves will be exhibited by curves A' , B' and C' , corresponding to potentiometric curves A , B and C in Fig. 1., and by A' and B' to those corresponding to A and B in Fig. 2, respectively. A brief description of the theoretical curves shown in Figs. 1 and 2 is given below.

FIG. 1

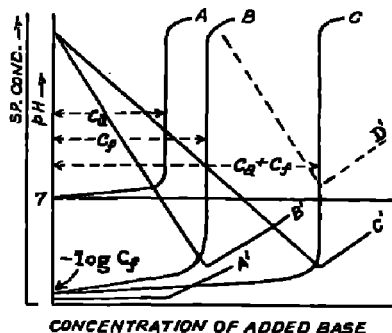
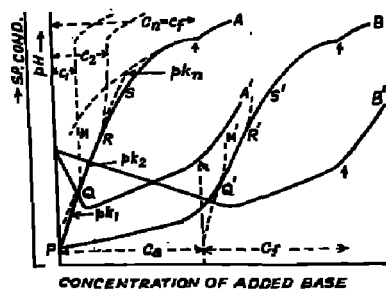


FIG. 2



Curve B in Fig. 1 presupposes that the active groups on the surface of the colloidal acids are strongly ionisable and wholly intermicellar, *i.e.*, there is no ion adsorption (cf. Fig. 1, Part I, *loc. cit.*). This condition implies a behaviour almost identical with that obtained from any soluble strong acid, the initial p_H corresponding to the total acidity present in the suspension. The monovalent alkali metal ions simply replace the free H^+ ions and, consequently, the expected nature of the conductivity curve (curve B') is identical with that obtained in the neutralisation curve of any strong acid.

Curve C in Fig. 1 shows the potentiometric neutralisation curve of colloidal acids with strongly ionisable groups with ion-adsorbing properties, *i.e.*, the active groups are partly micellar and partly intermicellar. As the adsorbed ions do not contribute to the conductivity, the neutralising branch of the specific conductivity curve becomes flatter as in C' in Fig. 1. If it is supposed that the intermicellar acidity in C is equal to the total acidity present in B, then the curves will start from the same point and the total drop in the conductivity in C' will be the same as occurs in B'. This means that the drop in B' has simply been spread out in C'. The end-point indicates neutralisation of both micellar and intermicellar acidities and the subsequent slope is identical with what is obtained when alkali is added to neutral salt solutions.

Curve A in Fig. 1 shows the neutralisation of an imaginary colloidal suspension where the active groups are wholly micellar. The intermicellar H^+ -ion concentration is due simply to the dissociation of water molecules. Thus, the p_H curve starts from 7. The initial conductivity in A' is therefore negligibly small, *i.e.*, equivalent to that present in the conductivity water. The addition of alkali does not raise the conductivity significantly until the end-point is reached because the competition due to small concentration of H^+ ions in the intermicellar solution is evidently very weak in this stretch, and most of the added cations of the base are exchanged for H^+ ions and adsorbed in the micellar positions. When the neutralisation of the micellar acidity is complete, the curve rises up as when alkali is added to pure water.

Curve D' in Fig. 1 shows what the specific conductivity curve would have been if the acidity in C were wholly intermicellar, *i.e.*, in that case both the branches of D' would be parallel to B' with the height of the point of intersection of the two branches

slightly raised due to higher concentration of the cations in the intermicellar solution and of the colloid anionic constituents on the surface of the colloidal particles (cf. Kruyt, "Colloid Science", Vol. I, 1952, p, 239, Fig. 25).

Curve A in Fig. 2 is due to the neutralisation of a colloidal suspension with wholly intermicellar but weakly ionisable functional groups. In this case there is no ion adsorption. The corresponding specific conductivity curve (curve A') shows a small initial drop, characteristic of a weak acid, a flat run due to buffering action of the neutralisation curve and finally another bend, signifying end of the neutralisation, the final slope corresponding to the alkali line. These curves therefore consist of three segments.

Curve B in Fig. 2 shows the neutralisation of colloidal acids with weakly ionisable groups and with built-in micellar acidity, *i. e.*, with ion-adsorbing capacities. As in C' in Fig. 1, here also the small initial drop spreads out in B' due to simultaneous ion adsorption. The rest of the curve B' is identical with that of curve A'. An experimental verification of this type of curve was published in the case of a clay sol (Sol C) in Part II (*loc. cit.*).

A comparison between curve C' in Fig. 1 and curve B' in Fig. 2 shows that there is an extra buffering portion between the two extreme branches in the latter curve, due to the weak acid buffering in the corresponding potentiometric curve. Theoretically, by gradually diminishing the extent of buffering, C' in Fig. 1 can be obtained from B in Fig. 2. The middle stretch of curve B' in Fig. 2 in that case will reduce to the point of intersection of the two branches in curve C' in Fig. 1. The smaller the buffering, the smaller is the length of the middle portion of the specific conductivity curve. This can be seen from the alkali-titration curves of the three AgI sols with hydrogen as counter-ions (De Bruyn and Overbeek, *Kolloid Z.*, 1938, 84, 186, Figs. 2a, 2b and 7). This also shows that the method of preparation of the colloidal acids has also a large say on their performances.

Neutralisation Curves with Alkaline Earth Hydroxides

The expression for the Donnan equilibrium between micellar and intermicellar solutions in the case of bivalent cations of the titrating base, say Ba^{2+} , may be represented by

$$\sqrt{\frac{(a_{Ba^{2+}})_I}{(a_{H^+})_I}} = \sqrt{\frac{(a_{Ba^{2+}})_a}{(a_{H^+})_a}}$$

by analogy, because it is difficult to deduce an equation for the bivalent ions by rigorous calculations considering each aggregate unlike what obtains in the case of monovalent ions. The above equation is, however, sufficiently exact if the micellar acidity is considered as a whole as one unit. Substitution from the electroneutrality relationships in the above equation gives corresponding relationships as were obtained in the case of alkali metal ions (Part I, *loc. cit.*).

In the case of the titration of a colloidal acid, where the functional groups are strongly ionisable with ion-adsorbing capacities, corresponding to case C, (a), in Part I (*loc. cit.*), and to the potentiometric curve C in Fig. 1, remembering,

$$(a_{H^+})_I = x, \quad z(a_{B_2^{2+}})_I = C_I + \frac{K_w}{x} - x, \quad z(a_{Na^+})_a = b - C_I = \frac{K_w}{x} + x$$

and

$$(a_{H^+})_a = C_a - b + C_I + (K_w/x) - x$$

one gets by substitution in the Donnan relationship and simplification

$$b = C_a - \frac{x \sqrt{4C_a(C_I + \frac{K_w}{x} - x) + x^2 - x^2}}{2(C_I + \frac{K_w}{x} - x)} + C_I + \frac{K_w}{x} - x \quad \dots (1)$$

where $z(a_{Na^+})_a$ is given by the first two terms and $z(a_{B_2^{2+}})_I$ by the last three terms of the right hand side of the above equation. The corresponding relation for the monoacidic bases, say NaOH, already deduced (Part I, *loc. cit.*), is

$$b = C_a - \frac{x \cdot C_a}{C_I + \frac{K_w}{x}} + C_I + \frac{K_w}{x} - x \quad \dots \quad \dots (2)$$

where $(a_{Na^+})_a$ and $(a_{Na^+})_I$ are given respectively by the first two terms and the last three terms of the right hand side of equation (2). As usual, the specific conductivities (κ) in the two cases are given by

$$\kappa = \frac{U_{H^+}(a_{H^+})_I + 2U_{B_2^{2+}}(a_{B_2^{2+}})_I + V_{OH^-}(a_{OH^-})_I + V_{Na^+}(2a_{Na^+} + a_{H^+} - a_{OH^-})_I}{1000}$$

and

$$\kappa = \frac{U_{H^+}(a_{H^+})_I + 2U_{Na^+}(a_{Na^+})_I + V_{OH^-}(a_{OH^-})_I + V_{Na^+}(2a_{Na^+} + a_{H^+} - a_{OH^-})_I}{1000}$$

where the symbols have their usual significances.

A concrete numerical example will help to clear the position. The values in the following example have been chosen in such a way that the results approach the experimental curves of Van Os, reported by Kruyt ("Colloid Science", Vol. I, 1952, p. 179, Figs. 42 and 43), as closely as possible. Supposing in a colloidal acid suspension with strongly ionisable groups, we have the values: $C_I = 1.3 \times 10^{-4}N$, $C_a = 7.4 \times 10^{-4}N$, and $K_w = 10^{-14}$ then the total colloidal acidity becomes $C_I + C_a = 8.7 \times 10^{-4}N$. The following limiting values of the equivalent conductivities at 18° have been assumed for the different ionic species: $U_{H^+} = 315.2$, $U_{Na^+} = 43.16$, $U_{B_2^{2+}} = 55$ and $V_{OH^-} = 173.8 \text{ ohms}^{-1}\text{cm}^2$, together with an arbitrary value of 20 $\text{ohms}^{-1}\text{cm}^2$ for V_{Na^+} , i.e., for the charge on the intracellular surface of the colloidal particles. Assuming any value of 'x', i.e., $(a_{H^+})_I$, the corresponding values of 'b', $(a_{Na^+})_I$, $(a_{Na^+})_a$, $(a_{B_2^{2+}})_I$, $(a_{B_2^{2+}})_a$, $(a_{OH^-})_I$ and κ can be calculated by evaluating the terms of the equations (1) and (2). The results are shown in Tables I and II. The theoretical potentiometric curves ($b-p_H$) and conductometric curves ($b-\kappa$) are shown in Fig. 3.

TABLE I

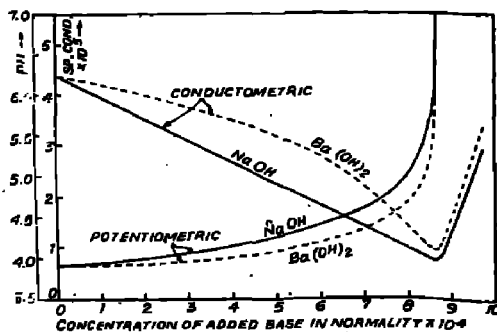
p_H	3.886	4.0	4.5	5.0	6.0	8.0	9.0	10.0	
$(a_{H^+})_f \times 10^4$	1.3	1.0	0.316	0.1	0.01	(negligible.)			
$(a_{OH^-})_f \times 10^4$	(negligible)						0.01	0.1	1.0
$(a_{Na^+})_f \times 10^4$	0.0	0.3	0.984	1.2	1.29	1.31	1.4	2.3	
$(a_{Ba^{2+}})_f \times 10^4$	0.0	1.707	5.6	6.83	7.343	7.4	7.4	7.4	
$b \times 10^4$	0.0	2.007	6.584	8.03	8.633	8.71	8.8	9.7	
$\kappa \times 10^5$	4.35	3.51	1.68	1.09	0.85	0.84	1.03	2.99	

TABLE II

p_H	3.886	4.0	4.5	5.0	6.0	8.0	9.0	10.0	
$(a_{H^+})_f \times 10^4$	1.3	1.0	0.316	0.1	0.01	(negligible.)			
$2(a_{OH^-})_f \times 10^4$	(negligible)						0.01	0.1	1.0
$2(a_{Na^+})_f \times 10^4$	0.0	0.3	0.984	1.2	1.29	1.31	1.4	2.3	
$2(a_{Ba^{2+}})_f \times 10^4$	0.0	3.827	6.582	7.156	7.38	7.4	7.4	7.4	
$b \times 10^4$	0.0	4.127	7.566	8.356	8.67	8.71	8.8	9.7	
$\kappa \times 10^5$	4.35	3.57	1.8	1.24	1.00	1.00	1.20	3.26	

The shape of the curves bears a striking resemblance to the potentiometric and conductometric titration curves with caustic alkali, obtained by De Bruyn and Overbeek (*loc. cit.*, cf. Fig. 7), in the case of an AgI sol with hydrogen as the counterions and specially to the specific conductivity curves with NaOH and Ba(OH)₂, obtained by Van Os (*loc. cit.*), for the same sol. The small weak acid-buffering in the above mentioned potentiometric titration curve of De Bruyn and Overbeek suggests that the acid colloidal AgI sols, though fairly strong, are not comparable to mineral acids in the dissociating powers of their intermicellar acidic groups, *i. e.*, H-I (Ag-I) on the surface of the AgI lattice of the colloidal particles, in this case. Consequently, instead of a sharp point signifying the end of neutralisation in the specific conductivity curve, a very small middle flat portion has been obtained in their experiments, as well as in those of Van Os.

FIG. 3



The Ba(OH)₂ curve of Van Os shows a greater amount of drop in specific conductivity at the end-point than that obtained with NaOH. This has been possible because

the Ba^{2+} ions in the intermicellar solution have an aggregating effect on colloidal suspensions which produce a slight diminution in the value of C_t and increase in the value of C_a by a corresponding amount towards the end-point. This happens with gradual accumulation of Ba^{2+} ions in the intermicellar solution, *i.e.*, with increase of $(a_{\text{Ba}^{2+}})_t$. The same thing was also observed in the case of the potentiometric titration with $\text{Ba}(\text{OH})_2$ of a clay sol, C_1 , to which we have already referred in Part II (*loc. cit.*). Changes in the state of aggregation during $(a_{\text{Ba}^{2+}})$ titration can produce large changes in the features of the titration curves, which we shall have occasion to deal with in detail, in our future communications.

Incidentally, the conductometric titration curves of a sulphur sol with H^+ ions as the counter-ions, described by Pauli (*J. Coll. Sci.*, 1947, 2, 33), which have the same features as the AgI hydrosols, may be analysed analogously.

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