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Studies on the Electrophoretic Velocity of Colloidal Particles by the Moving Boundary Method. Part IV. Critical Study of the Influence of Dialysis on the Electrophoretic Velocity of $Fe(OH)_3$ Sol and the Peak Point of the ζ-C Curve in the Aspect of Charge Density and Ionic Strength

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During the determination of electrophoretic velocity of $Fe(OH)_3$ sol at different stages of dialysis, a gradual increase is at first observed up to a certain stage of dialysis, followed by a decrease after attainment of the peak point. The specific conductance of the sol, proportional to the concentration of the residual electrolyte at different stages of dialysis, when plotted against the electrophoretic velocity, which is proportional to the zeta-potential, provides a characteristic peak point. This observation has been explained by deriving a relation connecting the electrophoretic velocity, U, the ionic strength, $\frac{1}{2}\Sigma cz^2$, and the charge on the colloidal particles. The concentration of the electrolyte in the colloidal system at the peak point has been suggested as corresponding to the critical stability concentration 'a' of the, sol, reported earlier in Bhattacharya's equation[5].

Kruyt[1], Freundlich and Rona[2]. and Elisafoff[3] studied the effect of adding increasing amounts of different electrolytes on the streaming potentials of glass capillaries and Powis[4] measured the electrophoretic velocity of oil-water emulsion particles in aqueous solutions. It was observed by them that ζ-potential at first increased to a maximum and then decreased on further addition of the electrolyte. Freundlich and Rona[2] and Elisafoff[3] further observed that the nature and valency of cations, such as heavy metals and basic dyes, showed a more remarkable effect on the increase of ζ-potential as the concentration of the added electrolyte was increased. They explained such observations on the basis of selective adsorption of the cations and anions. Since electrophoretic velocity, U, is directly proportional to the ζ-potential according to the equation:

$$U = E\epsilon\zeta/4\pi\eta$$

our studies have been based on U-sp. conductance curves, which are analogous to the ζ-C curves, studied by the foregoing authors.

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1. *Kolloid Z,* 1918, **22**, 81.
2. *Sitzungsber. Preuss. Akad. Wiss.,* 1920, **20**, 307.
3. *Z. physikal. Chem.,* 1912, **79**, 385.
4. *Ibid.,* 1915, **89**, 91.
5. Kumar *et al., J. Colloid Sci.,* 1955, **10**, 551.

Our results on the variation of the electrophoretic velocity of $Fe(OH)_3$ sol at different stages of dialysis under constant current conditions are reported herein. The technique employed was the moving boundary method, using the equiconducting solutions of lithium chloride as the supernatant liquid for obtaining greater sharpness in the descending boundary, as communicated earlier[6].

On certain assumptions it has been possible to explain our observations by deriving the relation:

$$U = \frac{E\sigma}{\eta}\sqrt{\frac{1000DRT}{16\pi e^2 N^2 \frac{1}{2}\Sigma cz^2}}$$

where U = electrophoretic velocity, σ = charge density, e = electronic charge, E = the field strength, η = the viscosity of the medium, N = the Avogadro number, D = dielectric constant, and $\frac{1}{2}\Sigma cz^2$ is the ionic strength.

The value of 'a' at the peak point has been determined both graphically and potentiometrically, but it has been found to be a very small quantity.

EXPERIMENTAL

The electrophoretic velocity was determined under a constant current by the procedure described earlier[7].

Coagulation of the sol was studied by two methods: (*i*) photoelectric and (*ii*) electrophoretic. In the former, the variation of light extinction with time, produced by a certain quantity of the electrolyte, was measured in a Gallenkamp photoelectric colorimeter. The time of coagulation at the same stage of aggregation of particles was determined by plotting Φ-t curves for different concentrations of the electrolyte added, as communicated earlier[8]. In the electrophoretic method, the movement of the boundary in Burton's U-tube ceased after a certain period by adding variable quantities of electrolyte to the sol. The time interval for the zero velocity was noted. Equiconducting solution of lithium chloride was taken as the supernatant liquid.

The sol was gradually freed of excess of the electrolyte by dialysis till the peak point in ζ-C curves was obtained. At this stage of dialysis, the concentration of chloride ions (counter ions) was determined potentiometrically with the help of a concentration cell of Ag/AgCl electrode[9]. Bhattacharya's equation[10], connecting the electrolyte concentration and time of coagulation, was also verified although 'a' was so small a quantity.

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[6] Bhatnagar and Bhattacharya, this *Journal*, 1959, **36**, 23.

[7] *Idem*, *Kolloid Z.*, 1960, **170**, 29.

[8] *J. Colloid Sci.*, 1956, **11**, 124.

[9] Mukherjee *et al.*, this *Journal*, 1931, **7**, 33.

[10] Kumar *et al.*, this *Journal*, 1962, **39**, 361.

*TABLE I

Cataphoretic velocity and sp. conductance at diff. stages of dialysis.

Supernatant liquid = equiconducting LiCl son. Descending buoundary, sharp.

Dialysed for.	Sp. conduc. (mhos).	Velocity of descending boundary (cm/sec/unit pot. grad).	Cl^- conc. at peak (mM/litre).
7 days	1.56×10^{-4}	41×10^{-5}	
9	0.87	52	
10	0.72	55	
11	0.65	63	6.8
12	0.59	54	
13	0.55	50	
16	0.50	45	

* Vide Fig. 1.

TABLE II

Coagulation of the sol with KCl (*by photoelectric colorimeter*).

a = 6.8 mM/litre.

Conc. of the electrolyte C (mM/litre).	$1/C$.	Time of coagulation (t).	$1/t$.	$(1/C)-a$.	Conc. of the electrolyte C (mM/litre).	$1/C$.	Time of coagulation (t).	$1/t$.	$(1/C)-a$.
A. Sol dialysed for 7 days. $\Phi=45$. (Fig 2, curve *i*).					B. Sol dialysed for 9 days. $\Phi=45$. (Fig 2, curve *ii*).				
280	0.0035	10 min.	0.100	0.0036	300	0.0033	9.0 min.	0.111	0.0033
260	0.0038	15	0.066	0.0039	280	0.0035	17.5	0.057	0.0036
240	0.0041	24	0.041	0.0042	260	0.0038	27.0	0.037	0.0039
220	0.0045	40	0.025	0.0046	240	0.0041	44.0	0.022	0.0042
200	0.0050	62	0.016	0.0051	220	0.0045	66.5	0.015	0.0045
180	0.0055	94	0.010	0.0057					
C. Sol dialysed for 10 days. $\Phi=40$. (Fig. 2, curve *iii*).					D. Sol. dialysed for 11 days. $\Phi=38$. (Fig. 2, curve *iv*).				
70	0.0142	1.5	0.666	0.015	47.5	0.0210	17.5	0.057	0.0245
65	0.0153	3.5	0.285	0.017	45.0	0.0222	31.0	0.032	0.0261
60	0.0166	9.0	0.111	0.018	42.5	0.0235	47.5	0.021	0.0280
55	0.0181	14.0	0.071	0.020	40.0	0.0250	65.0	0.015	0.0301
50	0.0200	20.0	0.050	0.023					
E. Sol dialysed for 12days. $\Phi=35$. (Fig. 2, curve *v*).									
40.0	0.0250	8.50	0.117	0.0302					
37.5	0.0266	12.25	0.081	0.0325					
35.0	0.0285	25.00	0.040	0.0355					
32.5	0.0307	33.50	0.029	0.0388					
32.0	0.0312	46.00	0.021	0.0430					

Φ denotes coagulation stage expressed in transmission.

TABLE III

Coagulation of the sol with electrolytes (dialysed for 13 days).
$a = 6\text{-}8\,\mathrm{m}M/\mathrm{litre}$.

*C.	1/C.	t.	1/t.	(1/C)—a.	*C.	1/C.	t.	1/t.	(1/C)—a.
A. With $BaCl_2$. $\Phi=28$. (Fig. 3, curve a).					B. With $AlCl_3$. $\Phi= 24$. (Fig. 3a, curve b).				
37.5	0.0266	4.5 min.	0.222	0.0325	250	0.0040	2.5 min.	0.400	0.0041
35.0	0.0285	7.5	0.133	0.0355	240	0.0041	6.0	0.160	0.0042
32.5	0.0307	13.0	0.076	0.0388	230	0.0043	11.0	0.090	0.0044
30.0	0.0333	19.0	0.052	0.0430	220	0.0045	16.5	0.060	0.0046
27.5	0.0363	26.5	0.037	0.0483	210	0.0047	21.0	0.047	0.0049

TABLE IV

Coagulation of $Fe(OH)_3$ *sol with electrolytes (electrophoretic method).*
$a = 6.24\ \mathrm{m}M/\mathrm{litre}$.

*C.	1/C.	**t.	1/t.	(1/C)—a.	*C.	1/C.	**t.	1/t.	(1/C)—a.
A. With KCl (Fig 4, curve A).					B. With $BaCl_2$ (Fig. 4, curve B).				
96	0.0104	58min.	0.017	0.0112	20.00	0.0500	37.0min.	0.027	0.072
80	0.0125	64	0.015	0.0136	18.65	0.0536	55.0	0.020	0.080
64	0.0156	73	0.013	0.0174	17.30	0.0577	63.0	0.015	0.(9)
48	0.0208	89	0.011	0.0242	15.95	0.0620	75.0	0.013	0.103
C. With $AlCl_3$ (Fig. 4, curve C).									
20	0.0500	40	0.025	0.072					
19	0.0526	52	0.019	0.078					
18	0.0555	63	0.015	0.084					
17	0.0588	74	0.013	0.092					

*C expressed in m*M*/litre.

**t denotes time of coagulation for zero electrophoretic velocity.

DISCUSSION

It will be seen (Table I and Fig. 1) that the value of U or ζ-potential gradually increases to a maximum at different stages of dialysis from A to B and the potential falls from B to C (Fig. 1). The U–sp. conductance curves are similar to the $\zeta \cdot C$ curves of Freundlich and Rona[2] and others[3]. The peak of the curve has been found to appear in the case of many sols and hence it suggests a very significant characteristic of the state of the sol where du/dk (where k stands for the sp. conductance of the sol) or $d\zeta/dc$ becomes equal to zero. This can therefore be interpreted as the state of equilibrium between the charge of the sol particles and the concentration of the counter ions in the ionic environment required for the stability of the sol and hence can be ***assumed*** to be connected with critical stability concentration 'a' of the electrolyte for the sol in Bhattacharya's equation[5].

$$C = a + (m \times 1/t)/(n + 1/t) \quad \text{or} \quad (1/C) - a = (nt/m) + 1/m.$$

Theoretical support to this equation was offered by Ghosh[11].

The electrophoretic velocity, U, according to Helmholtz and Smoluckhowski[12] is given by

$$U = \frac{E\epsilon\zeta}{4\pi\eta} \tag{i}$$

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[11] This *Journal*, 1958, **35**, 67.

[12] *Bull. Akad. Sci., Cacoview*, 1903, 182.

where ϵ is the dielectric constant, ζ, the zeta-potential, E, the field strength, and η, the viscosity of the medium. It is also known that the charge density

$$\sigma = \frac{\epsilon\zeta K}{4\pi} \qquad \text{(ii)}$$

$$\text{where } K = 1/d = \sqrt{\frac{8\pi E^2N^2\Sigma cz^2}{1000DRT}} \qquad \text{(iii)}$$

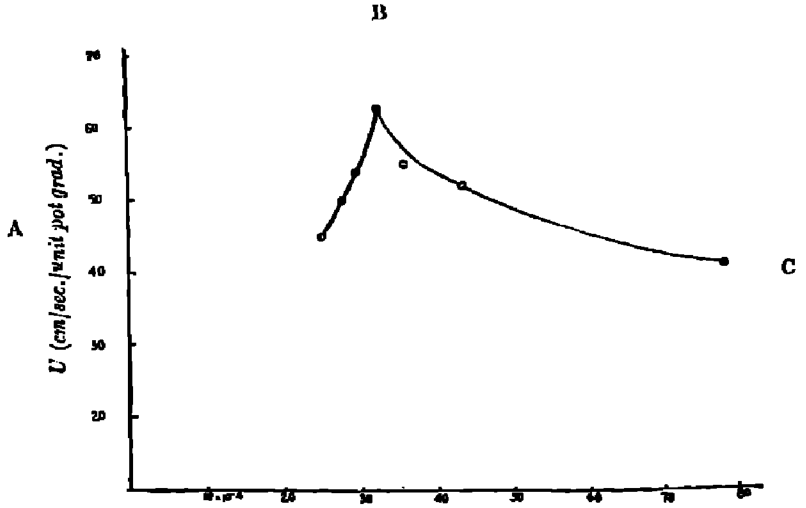

FIG. 1. Descending boundary.

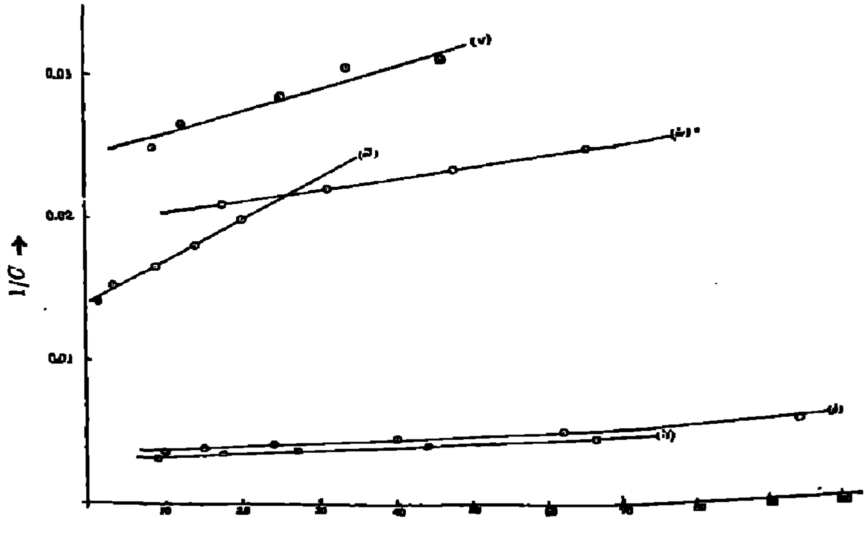

FIG. 2. Coagulation with KCl at diff. stages of dialysis.

according to Debye and Hückel, d being the thickness of the double layer, and other symbols having the usual significance (*vide supra*). Assuming the analogy between the colloidal particles and charged ions moving in the ionic environment, we may connect equations (*i*) (*ii*) and (*iii*) to derive the relation between the electrophoretic velocity U and ionic strength (*vide supra*).

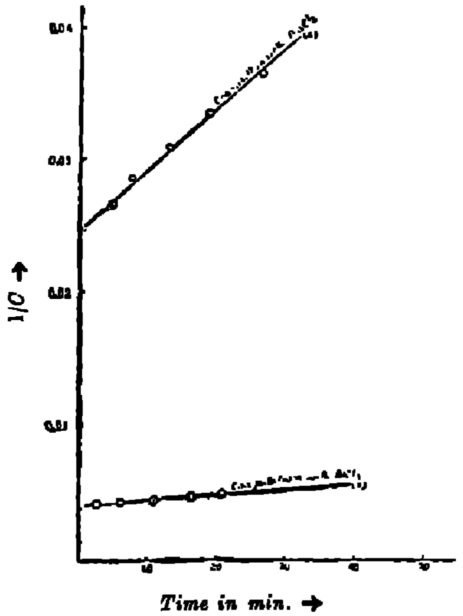

FIG. 3. Coagulation with $BaCl_2$ and $AlCl_3$.

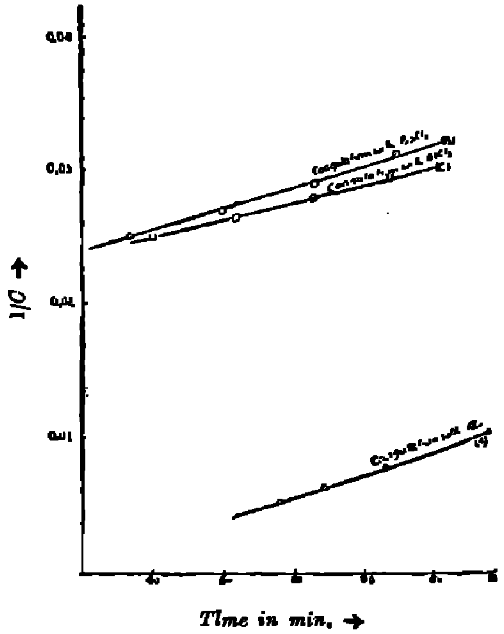

FIG. 3a. Coagulation with KCl, $BaCl_2$, and $AlCl_3$.

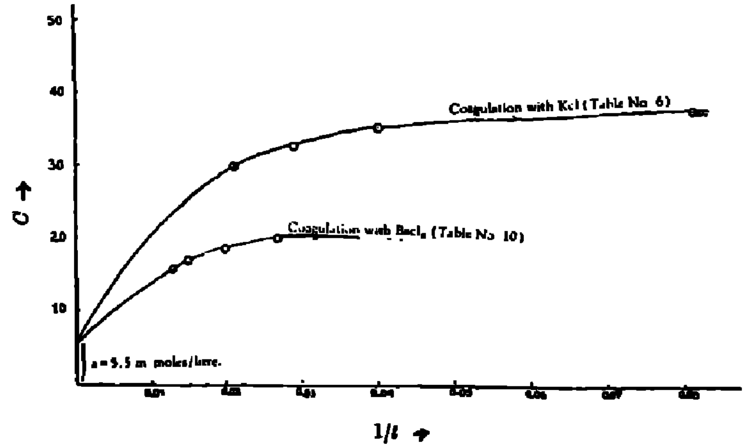

FIG. 4. Coaguiation with KCl by photoelectric method.

If the field strength E (under constant current), η, the visosity of the medium, and σ are assumed to remain constant, it directly follows that U is inversely proportional to the ionic strength. Under such conditions, the portion AB of the curve can be explained till the limiting equilibrium between the charge on the colloidal particles and its counter ions in the ionic environment of the double layer is reached at the peak of the curve. Further lowering of concentration of the electrolyte by dialysis may disturb this equilibrium and lower the charge density. After this stage U depends on σ, magnitude of which is in the decreasing order. Hence U or ζ gradually falls after the peak point and the sol tends to become less stable. If these assumptions are admissible, the concentration at the peak point may be visualised to correspond to the critical stability concentration 'a' of Bhattacharya's equation, where $(1/C)-a$ is linear with t, but when the value of 'a' becomes very small due to continued dialysis, 'a' can be neglected, when $1/C$ vs. t should be linear. This has been actually observed. Further work is in progress.

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