

Studies on the Electrophoretic Velocity of Colloidal Particles by the Moving Boundary Method. Part V. Influence of Dialysis on the Electrophoretic Velocity of $\text{Fe}(\text{OH})_3$ and Sb_2S_3 Sols in the Aspect of Thermodynamic Potential of the System and ζ -Potential

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The effect of decreasing electrolyte concentration during dialysis on the electrophoretic velocity of lyophobic sols has been studied. The increase in electrophoretic velocity up to a certain stage of dialysis has been attributed to the inverse relation between the electrophoretic velocity and ionic strength. The peak point observed in ζ - C curves is interpreted to denote the stable stage of the sol in equilibrium with a critical amount of the electrolyte. At the peak point du/dc or $d\zeta/dc$ is zero, which is the criterion for a maximum as well as for the equilibrium between the charge on the colloidal particles and the counter ions in the double layer. The rise and fall of electrophoretic velocity during dialysis have been explained by the concept of the thickness of the double layer and the thermodynamic and ζ -potentials.

The dependence of electrokinetic phenomenon on the concentration and nature of electrolyte is not yet perfectly understood, because the ζ -potential seems to be a function of the nature and concentration of ions in the mobile double layer and the Nernst potential difference between the solid and liquid phases is influenced by adsorption of ions. The Nernst potential, ϵ , which is the potential difference over the whole double layer, depends on the activity of the potential-determining ion, such as Ag^+ for silver particles, as happens in the case of electrode potentials. The double layer in the colloidal solutions may be considered analogous to the ionic atmosphere where a distribution equilibrium is set up, which is very much influenced by increasing or decreasing the concentration of electrolytes, thus varying the ζ -potential or the electrophoretic velocity of colloidal particles. In our studies on the electrophoretic velocity of $\text{Fe}(\text{OH})_3$ and Sb_2S_3 sols at different stages of dialysis, it has been observed that the electrophoretic velocity or the ζ -potential at first increases to a maximum and then decreases by continued dialysis. Krulyt¹, Freundlich and Rona², and v. Elissafoff³ explained that the electrophoretic behaviour showing a maximum was due to the adsorbability and valency of the anions, such as OH^- and $\text{Fe}(\text{CN})_6^{4-}$, in the systems, which they investigated. A more convincing explanation of this behaviour of sols seems to be possible if we consider the combined role of the changes in the thickness of the double layer and the thermodynamic potential of the system as the concentration of the electrolyte varies in the course of dialysis.

In this communication, the variations of the electrophoretic velocity or ζ -potential during dialysis of $\text{Fe}(\text{OH})_3$ and Sb_2S_3 sols have been explained by the concept of the thickness of the double layer and thermodynamic and ζ -potentials.

1. *Kolloid Z.*, 1916, 22, 81.
2. *Sitzungsber. Preuss. Akad. Wiss.*, 1920, 20, 397.
3. *Z. physikal. Chem.*, 1912, 79, 385.

EXPERIMENTAL

The electrophoretic velocity was determined under constant current by a procedure described earlier⁴. Equiconducting solutions of LiCl, NaCl, and BaCl₂ were taken as the supernatant liquid for Fe(OH)₃ sol and of CH₃COOH, HCl, and H₂SO₄ for Sb₂S₃ sol to form the boundary layer in Burton's U-tube⁵.

TABLE I

Cataphoretic velocity and sp. conductance at diff. stages of dialysis of Fe(OH)₃ sol with equiconducting supernatant liquid.

Dialysed for. (days)	Sp. conduc. (mhos)	*Velocity of descending boundary.	ζ-Potential.	*Velocity of descending boundary.	ζ-Potential.	*Velocity of descending boundary.	ζ-Potential
A. LiCl (Fig. 1, curve II).			B. NaCl (Fig 1, curve I).		C. BaCl ₂ (Fig 1, curve III).		
7	1.80 × 10 ⁻⁴	31 × 10 ⁻⁵	0.037 V	36 × 10 ⁻⁵	0.043V	19 × 10 ⁻⁵	0.022 V
10	1.18	36	0.043	43	0.051	23	0.027
12	0.82	51	0.061	58	0.069	30	0.035
13	0.69	40	0.047	50	0.059	26	0.031
15	0.59	33	0.038	38	0.045	22	0.026

TABLE II

Cataphoretic velocity and sp. conductance at diff. stages of dialysis of Sb₂S₃ sol with equiconducting supernatant liquid.

Dialysed for. (days)	Sp. conduc. (mhos)	*Velocity of descending boundary.	ζ-Potential.	*Velocity of descending boundary.	ζ-Potential.	*Velocity of descending boundary.	ζ-Potential.
A. Acetic acid (Fig. 2, curve II).		B. HCl (Fig 2, curve III).		C. H ₂ SO ₄ (Fig. 2, curve I).			
3	5.00 × 10 ⁻⁴	25 × 10 ⁻⁵	0.035V	23 × 10 ⁻⁵	0.027V	32 × 10 ⁻⁵	0.038 V
5	3.80	32	0.038	30	0.035	40	0.047
7	2.25	48	0.057	48	0.057	60	0.071
8	2.00	41	0.049	39	0.046	47	0.057
9	1.70	38	0.045	34	0.040	40	0.047

*Expressed in cm/sec./potential gradient

DISCUSSION

According to our observations (Tables I and II), the electrophoretic velocity or ζ-potential of Fe(OH)₃ and Sb₂S₃ sols is gradually increased to a maximum (vide Fig. 1 and 2) and then it falls as the electrolyte concentration is decreased by continued dialysis.

4. Bhatnagar and Bhattacharya, *Kolloid Z.*, 1960, 170, 29.

5. Mukherjee *et al.*, this *Journal*, 1938, 13, 372.

The appearance of the peak suggests a state of equilibrium with a critical amount of electrolyte in the bulk of the solution for the stability of the sol. Hence if the concentration of the electrolyte in the bulk falls below this limiting value by continued dialysis, this equilibrium will be disturbed to decrease the stability of the sol. According to the prevailing view, a schematic representation of the dependence of the ζ -potential on the thickness of the double layer and the Nernst potential will elucidate the variations in the electrophoretic velocity or ζ -potential observed during dialysis.

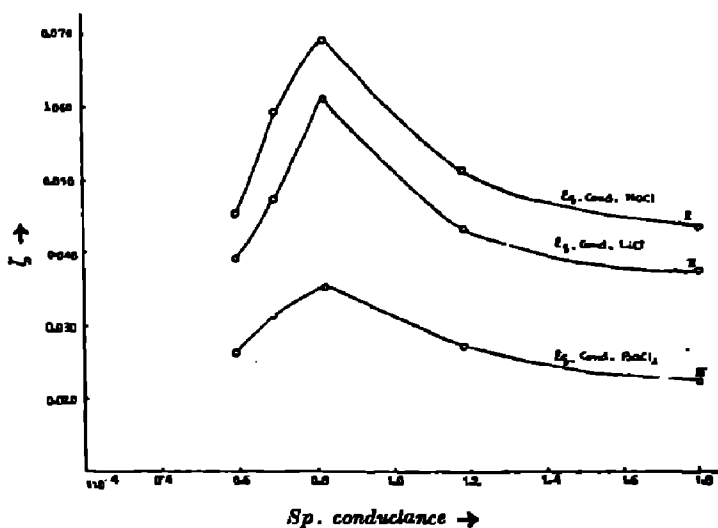


FIG. 1. Variation of ζ -potential during dialysis of $\text{Fe}(\text{OH})_3$ sol.

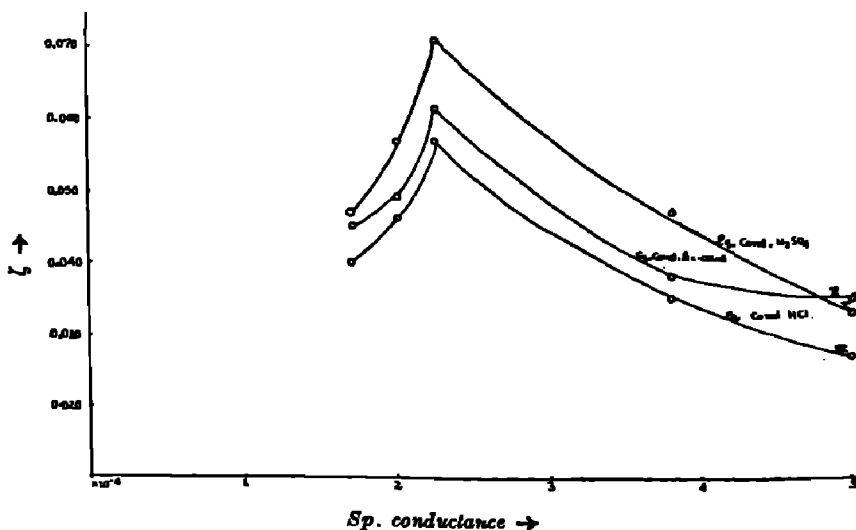


FIG. 2. Variation of ζ -potential during dialysis of Sb_2S_3 sol.

If ϵ_1 , the potential at A, is assumed to be the Nernst potential of the solid surface, ϵ_2 , the potential at the boundary limit, and ϵ_3 , of the diffused double layer at B, it readily follows from Fig. 3 that

$$\zeta\text{-Potential} = (\epsilon_1 - \epsilon_2) - \{(\epsilon_1 - \epsilon_2) - \epsilon_3\}.$$



FIG. 3

High electrolyte content
(a)

Low electrolyte content
at peak pt. (b)

After limiting equil. tending
towards instability (c)

In the colloid system ($\epsilon_1 - \epsilon_2$) is assumed to remain fixed with a certain limit of electrolyte concentration⁶, while the thickness of the double layer and the potential ϵ_3 at B simultaneously decrease as the electrolyte concentration increases. The ζ -potential therefore decreases at high concentrations of the electrolyte and increases at low concentrations to a certain limit, as is shown by the peak point in the ζ - C curve. Any further loss of electrolyte by dialysis will disturb the equilibrium of the diffused double layer and a new condition of equilibrium will be set up for the less stable sol after the peak point. Since the concentration of the electrolyte in the colloidal system will have been considerably reduced due to continued dialysis after the peak point, the thickness of the double layer will be wider and ϵ_3 may also reduce to provide a lower ζ -potential for the new condition of equilibrium, as is shown in Fig. 3 (c). Our observations on the changes in the electrophoretic velocity of $\text{Fe}(\text{OH})_3$ and Sb_2S_3 sols during dialysis are in agreement with the assumptions made in regard to the potentials discussed above. By applying the same assumptions, it may be possible to explain the observations of the workers¹⁻³ already cited, who had studied the effect of gradually increasing the amount of electrolyte on the ζ -potential of oil-water emulsion and streaming potential of the glass-water system by a process, which was the reverse of dialysis.

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6. Kravt, "Colloid Science", Vol I, 1952, p. 79.