

Variation of the Electrical Charge of Colloidal Particles

Part V. Effect of the Manner of Preparation of Arsenious Sulphide Sol on the Cataphoretic Speed in Presence of Electrolytes.

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The manner of variation of the cataphoretic speed of particles of this sol with different concentrations of the same electrolyte depends on the method of preparation or the dilution (Mukherjee and Choudhury, *J. Indian Chem. Soc.*, 1925, 2, 296 ; Mukherjee, Roychoudhury and Bhattacharyya, *ibid.*, 1928, 5, 735). Two different types of curves have been met with; in one the cataphoretic speed continually decreases with the concentration of the electrolyte (Mukherjee and Choudhury, *loc. cit.*, ; Mukherjee, Choudhury and Roychoudhury, *ibid.*, 1927, 4, 493 ; Freundlich and Zeh, *Z. phys. Chem.*, 1925, 114, 84) and in the other there is a fall in the cataphoretic speed at low concentrations of the electrolyte but an increase at higher concentrations (Mukherjee, Roychoudhury and Bhattacharyya, *loc. cit.* also Kruyt and Willigen, *Z. physikal Chem.*, 1927, 130, 17). It has also been observed that on dilution, a sol with a lower initial charge shows a rapid increase in the charge at lower concentrations of potassium chloride. These observations are of interest in relation to the properties of the primarily adsorbed ions including their valencies and the adsorption of the ions present in the solution (Mukherjee, *Trans. Faraday Soc.*, 1921, 16, 103). The concentration of hydrogen sulphide, of hydrogen ions and of arsenious oxide are expected to have an important effect on the relative amounts of sulphide and hydrosulphide ions on the surface. S. N. Mukherjee (*Kolloid Z.*, 1930, 53, 159) has shown that on the addition of arsenious oxide the cataphoretic speed of arsenious sulphide sol diminishes. One can visualise the possibility that when added in very small quantities it may increase the charge as the hydrogen ion concentration would be lowered and a larger proportion of sulphidions is present. This would happen when the amount of free sulphidions and hydrosulphidions adsorbed on the

surface is not sufficiently decreased owing to the diminished equilibrium concentration of hydrogen sulphide in the solution which is a necessary consequence of the addition of arsenious oxide. This expected rise has been observed using an amount of arsenious oxide (equivalent to a concentration of 0.0001N) lower than that used by S. N. Mukherjee (*loc. cit.*).

In the light of the theoretical consideration advanced in previous papers (*loc. cit.*) a difference in the relative adsorbabilities of the cation and anion should produce a difference in the slopes of the curves (see in particular Mukherjee, Roychoudhury and Bhattacharyya, *loc. cit.*). The electrical adsorption of two univalent cations by a primarily adsorbed divalent anion is of interest as showing the effect of the diameter of the ions.

EXPERIMENTAL.

The sol prepared as previously described was kept wrapped with black paper in a dark place.

The salts used were all of Merck's reagent quality twice recrystallised. The temperature of the thermostat was $35^{\circ} + 0.1^{\circ}$.

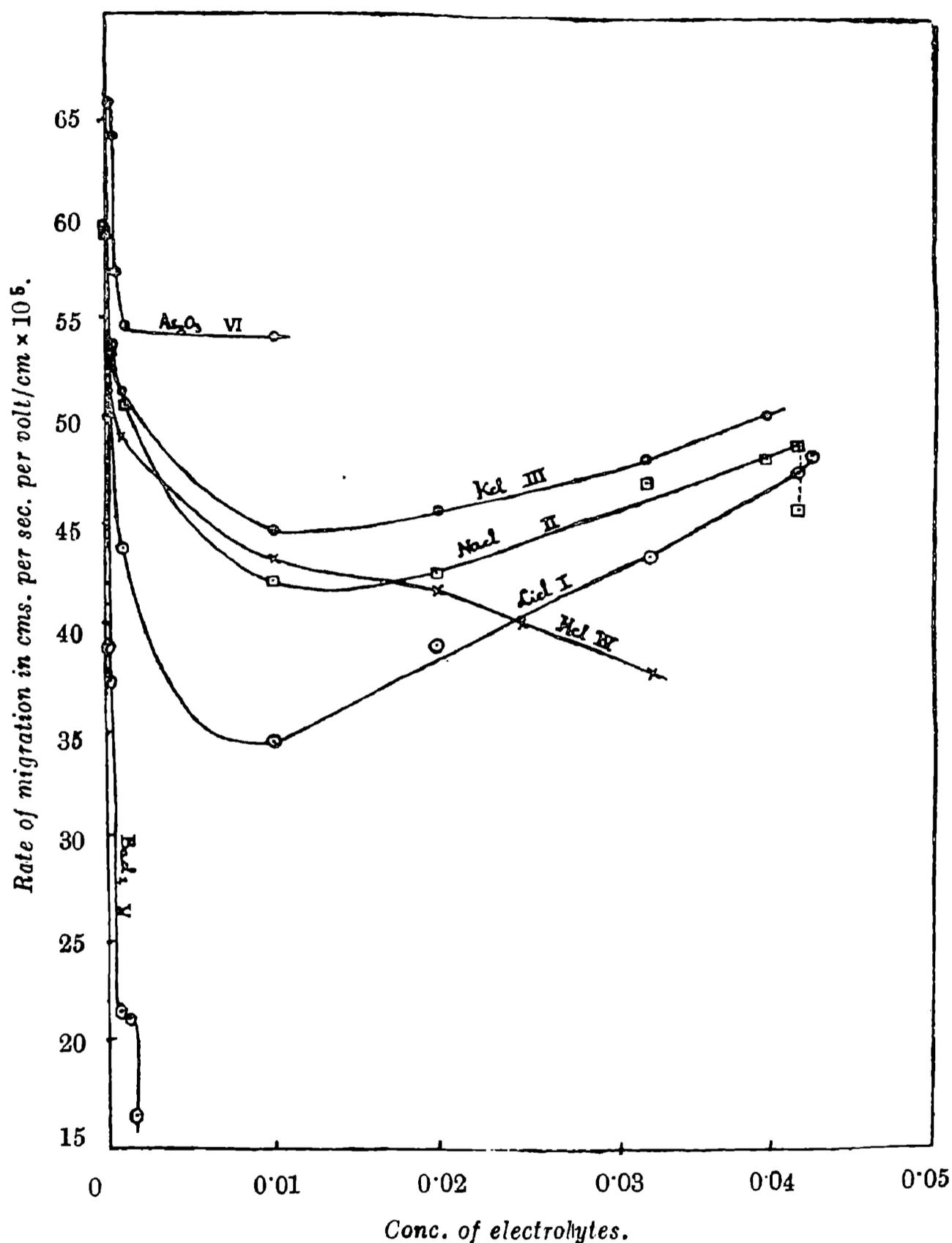
Corrections for viscosity were neglected as they were within the limits of the error. In view of the errors possible at low concentrations some of the data are given below to show the accuracy and to show how far the observed speed is independent of the direction of motion (Mukherjee, *Kolloid Z.*, 1932, **58**, 155).

TABLE I.

Rate of migration in cms. per sec. per volt/cm $\times 10^5$.

Electrolyte conc.	Direct.	Reverse.	Mean.
0	58.33 } 60.56 }	59.48 } 58.91 }	59.34
LiCl 0.0002 N	53.95 } 54.61 }	54.29 } 52.78 }	53.92
NaCl 0.0002	53.12	53.94	53.5
KCl 0.0002	53.62	52.10	52.86
HCl 0.0002	52.14	50.84	51.5
BaCl ₂ 0.0001	40.00	38.39	39.19
As ₂ O ₃ 0.0001	67.74	64.12	65.9

The cataphoretic speeds are shown in the Figure. Duplicate experiments were performed in most cases.



DISCUSSION.

The Influence of Arsenious Oxide.

1. While the diminution of the cataphoretic speed on addition of arsenious oxide is in keeping with its sensitising effect at all concentrations so far investigated (S. N. Mukherjee, *loc. cit.*) against coagulation by electrolytes, the increase observed here shows that higher

cataphoretic speed does not always confer a greater stability against coagulation by electrolytes. Reference may be made in this connection to the greater rate of diminution of the positive charge of a ferric oxide sol on the addition of potassium chloride when the initial cataphoretic speed is higher (Mukherjee, Roychoudhury and Biswas, *J. Indian Chem.Soc.*, 1931, 8, 373).

2. On account of the strong affinity of sulphidions for hydrogen ions only a small proportion of the total free negative charge of the surface is present in the form of primarily adsorbed sulphidion. On the addition of arsenious oxide the equilibrium concentration of hydrogen sulphide as also the amount of it that is adsorbed on the surface decreases. It is possible, however, that at one stage though there is a smaller total number of sulphide and hydrogen sulphide ions on the surface, the density of the charge will be greater on account of a greater proportion of sulphidions which carry two units of charge. The observed rise indicates that the limits within which this rise takes place are very small.

The Influence of Alkali Chlorides.

1. A comparison of the curves in the figure with those previously observed with this sol (*loc. cit.*) show that both hydrochloric acid and barium chloride uniformly decrease the cataphoretic speed. But the rate of decrease in the present case is definitely greater. The existence of a greater proportion of divalent sulphide ions will increase the electric adsorption and the greater slope of these curves is in agreement with the theory. But the uniformly lower value of the cataphoretic speeds which shows that the capacity of the three alkali chlorides to diminish the negative charge is in the order $\text{Li}^\circ > \text{Na}^\circ > \text{K}^\circ$ is contrary to previous observations as also the order of coagulating concentrations of these electrolytes. A difference is also noticed in the slopes of the ascending and descending portions of the curves. If the greater slope of the portions of the curves where the cataphoretic speed steadily diminishes be referred to the adsorption of cations then the adsorbability of these three cations appears to be in order $\text{Li}^\circ > \text{Na}^\circ > \text{K}^\circ$. On the other hand after reaching the minimum which, it may be noted, is reached at about the same chlorine ion concentration, the cataphoretic speed increases more rapidly in the case of lithium and the positive (increasing cataphoretic speed) slopes are also in the order $\text{Li}^\circ > \text{Na}^\circ > \text{K}^\circ$.

The assumed stronger adsorption of lithium ions cannot account for this order. If the increase in the negative charge be attributed to the adsorption of chlorine ions, then two explanations of this difference in the positive slope are possible: either (i) that the lower negative charge facilitates a stronger adsorption of the anion (chloridion) or (ii) that the adsorption of the cations is in the order $K^{\circ} > Na^{\circ} > Li^{\circ}$. The former explanation is in conformity with the observation that a lower initial cataphoretic speed favours a rise in the negative charge as shown by an increased cataphoretic speed on the addition of potassium chloride. If this explanation is true it is not necessary to assume that there is a reversal in the order of adsorption of the cations in the ascending portion of the curves. There is, however, one fact which seems to contradict the order of adsorption: $Li^{\circ} > Na^{\circ} > K^{\circ}$. This is that at 0.0002N the cataphoretic speeds indicate the order of adsorption $K^{\circ} > Na^{\circ} > Li^{\circ}$ as shown by the following respective values of the speeds: 52.86, 53.52, 53.92.

2. On theoretical grounds it is difficult to understand why the relative orders of adsorption of the cations will be different in different portions of the curves. Assuming that the order of adsorption of the cation is $Li^{\circ} > Na^{\circ} > K^{\circ}$ two difficulties are met with: of this, one has been referred to just now and consists in the cataphoretic speeds at 0.0002N salt concentration and the other is the slope of ascending portion which is uniformly greater for lithium and decreases in the order $Li^{\circ} > Na^{\circ} > K^{\circ}$ up to the coagulating concentration. If the lower negative charges were the cause of the difference in the slopes, as suggested in the previous paragraph then the slope should decrease as the negative charge increases. The curves do not support this conclusion. The other possible explanation is that the order of adsorption of the cation is really $K^{\circ} > Na^{\circ} > Li^{\circ}$ as observed with this sol prepared in a different way. The apparently opposite order of adsorbability is to be attributed to the fact that there is a large proportion of divalent sulphidion on the surface and that the simultaneous electrical adsorption of two univalent cations by a divalent anion depends also on the repulsion between the univalent cations. The ions are assumed to be electrically adsorbed in a *hydrated* condition and the diameters of the hydrated ions are assumed to be in the order, $Li^{\circ} > Na^{\circ} > K^{\circ}$ which conforms with the mobilities. The simultaneous electrical adsorption of two lithium ions will be easier but that of two potassium ions more difficult on account of

the smaller diameters of the potassium ions. With the result that at the smallest concentration where only one cation is adsorbed by a divalent ion, the order of cation adsorption should be $K^{\circ} > Na^{\circ} > Li^{\circ}$ as is shown to be the case at 0.0002N. When the adsorption of two cations become more and more in operation there is a change in the apparent adsorption order $Li^{\circ} > Na^{\circ} > K^{\circ}$. This persists till the greater adsorption of the chlorine ions asserts itself at the higher chlorine ion concentration at about 0.01N. The surface is now mostly covered by univalent anion 'complexes' and the usual order $K^{\circ} > Na^{\circ} > Li^{\circ}$ is reflected in the positive (increasing negative charge) slopes which is greater for the more weakly adsorbed cation. This explanation also enables us to understand the regular diminution of the speed observed in other sols and the usual order of cation effect on the speed, *viz.*, $K^{\circ} > Na^{\circ} > Li^{\circ}$. In the usual method of preparation, the sol is saturated with hydrogen sulphide which is driven with a current of hydrogen whereas in the other group of sols excess of arsenious oxide is ensured. The two groups of sols probably differ in that in the former the anions are mostly univalent and that in the second there is a considerable proportion of divalent anions.

3. The order $Li^{\circ} > Na^{\circ} > K^{\circ}$ is known and the adsorption of these ions in a dehydrated condition would explain such an order from the point of view of the electrical adsorption. Only further experiments can decide between these alternatives.