A COMPARISON OF THE ELECTROPHORETIC VELOCITIES OF CELLOPHANE AND COLLODION SUSPENSIONS WITH ELECTROOSMOTIC VELOCITIES THROUGH MEMBRANES OF THE SAME MATERIALS

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This paper is a report of the electrophoretic velocities of cellophane and collodion suspensions in $ThCl_4$ solutions of various concentrations, and of the electroosmotic velocities of the same solutions through cellophane and collodion membranes.

EXPERIMENTAL

Cellophane.—For the electrophoresis determinations a colloidal suspension of cellophane was prepared by soaking cellophane (previously washed free of glycerin and dried) in a mixture of about equal parts of acetone and ether for several days, putting a few cubic centimeters of this mixture into 100 cc. of water and aerating to remove the acetone and ether. On two occasions out of several trials satisfactory suspensions were obtained; they remained stable for several weeks. We regret that we are unable to specify the factors responsible for the success or failure of this procedure. This suspension was examined in a Northrop-Kunitz cell of predetermined cross-section and the current measured. It varied from 1×10^{-6} amp. in water to 5×10^{-3} in 4×10^{-2} M $ThCl_4$. The specific resistance of each solution was determined in the usual way and the volts per centimeter across the cell calculated as IR, as suggested by Abramson (1929). Zeta was calculated in millivolts as, zeta $= \frac{14 \times \text{micra/sec.}}{\text{volts/cm.}}$. The results are shown in Fig. 1, where zeta in millivolts is plotted against the negative logarithm of the molar concentration of $ThCl_4$. The isoelectric point is between 3 and 4×10^{-6} M.

The electroosmotic isoelectric point was then determined on intact cellophane membranes. A side arm was sealed to a tube of 2.5 cm. bore and 6 cm. length and a capillary of 1 mm. bore fitted to the side arm. A cellophane sheet was tied over one end of the large tube and sealed tight with collodion. The upper end of the tube was fitted with a rubber stopper and sealed with beeswax-rosin cement. This stopper was perforated by a tightly fitting tube forming an agar-KCl bridge.

The bridge passed to a large calomel-saturated KCl electrode; its lower end just above the membrane was turned up. The cell was filled with the solution under investigation and dipped into a beaker containing the same solution, the circuit being completed by an agar bridge in the beaker and another calomel electrode.

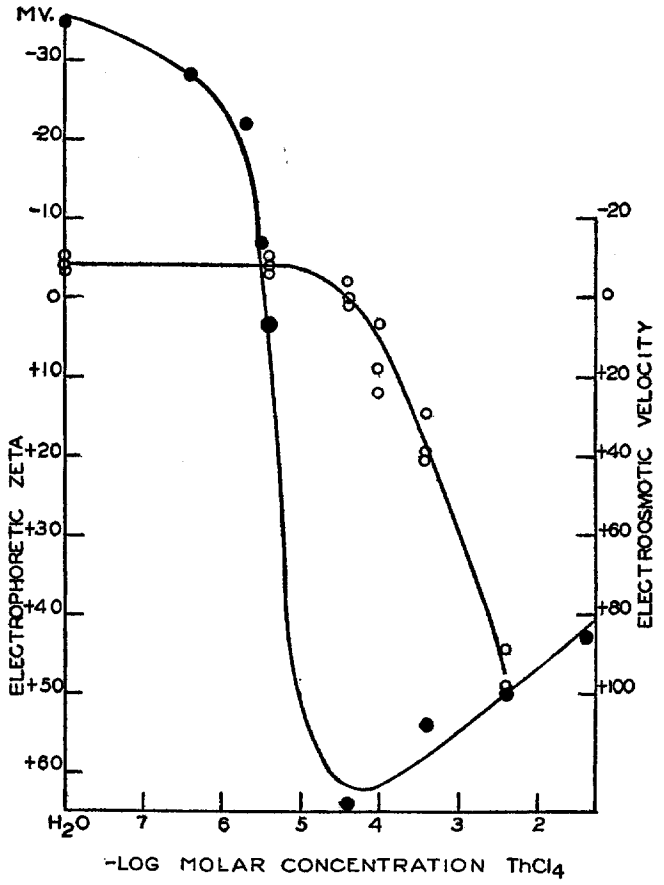

FIG. 1. Electrophoretic zeta potentials in millivolts of a cellophane suspension ●, and electroosmotic velocity in arbitrary units of three cellophane membranes O, as a function of the $ThCl_4$ concentration.

The movement of the meniscus in the nearly horizontal capillary side arm was observed with a microscope. 100 volts were applied at the electrodes. The current through the cell was always measured. Platinum electrodes were used at first but with these the current was not the same on reversal of polarity; with

calomel electrodes it was unchanged although it rose slowly with time, due, presumably, to the diffusion of KCl from the agar bridges. Higher concentrations than 4×10^{-3} M $ThCl_4$ could not be investigated because of the heating effect of the larger currents. The average of several readings with each direction of current was taken. The results on three membranes, with rate of electroosmotic transport expressed in arbitrary units, are given in Fig. 1.

Absolute values of zeta by the electroosmotic method can be given only if the E.M.F. across the membrane is known. This must be only a small fraction, in our experiments, of the 100 volts at the electrodes. We have attempted to determine this by determining the resistance of cellophane membranes in an apparatus of the type described by Green, Weech, and Michaelis (1929) and multiplying by the current. We have not yet succeeded, however, in measuring these resistances with consistent enough results to justify a statement as to the E.M.F. across the membranes. It appears probable that the membrane resistances are so low as not to be measurable with much accuracy. It is improbable that the E.M.F. across the membrane remains a constant fraction of the applied E.M.F. in the various solutions, since the ratio of surface to bulk conductivity must be high and since the diffusion of KCl introduces an inconstant error. Therefore, the zeta-concentration curve may not be of the same shape as the electroosmotic transport-concentration curve. Nevertheless, since the percentile changes undergone by zeta are beyond question much greater than those of E.M.F. across the membrane, the transport-concentration curve probably does not greatly differ qualitatively from the zeta-concentration curve. In any event, the isoelectric point to electroosmosis is accurately located at 4×10^{-5} M $ThCl_4$, a concentration about 10 times as great as the isoelectric point to electrophoresis. The advantage of comparing two processes, as electroosmosis and electrophoresis, by a comparison of their isoelectric points rather than by an evaluation of zeta at values other than zero, is that common to all null point methods.

It was thought that this difference in the electrophoretic and electroosmotic isoelectric points on cellophane might be due to inability of the thorium ion to penetrate into the small pores of the cellophane membranes in a reasonable time. That this is not the explanation was shown by the experimental findings that (1) membranes allowed to soak for many days in a concentration of 1×10^{-5} M $ThCl_4$ were still charged as in water, (2) actively filtering this solution through a membrane for several hours under pressure did not reverse the sign of charge on the membrane, and (3) even more striking, three membranes whose sign of charge had been reversed with a strong thorium solution (1×10^{-3} M) and whose pores must therefore have contained sufficient thorium to bring about reversal, very quickly showed a negative zeta potential when placed in 1×10^{-5} M $ThCl_4$.

The possibility was then considered that the cellophane suspension used in the electrophoresis study was simply a more soluble fraction of the cellophane membrane, with somewhat different chemical properties from those of the untreated membrane. The experiments were therefore repeated on collodion since with this

material suspensions could be obtained which were certainly of the same composition as the membrane.

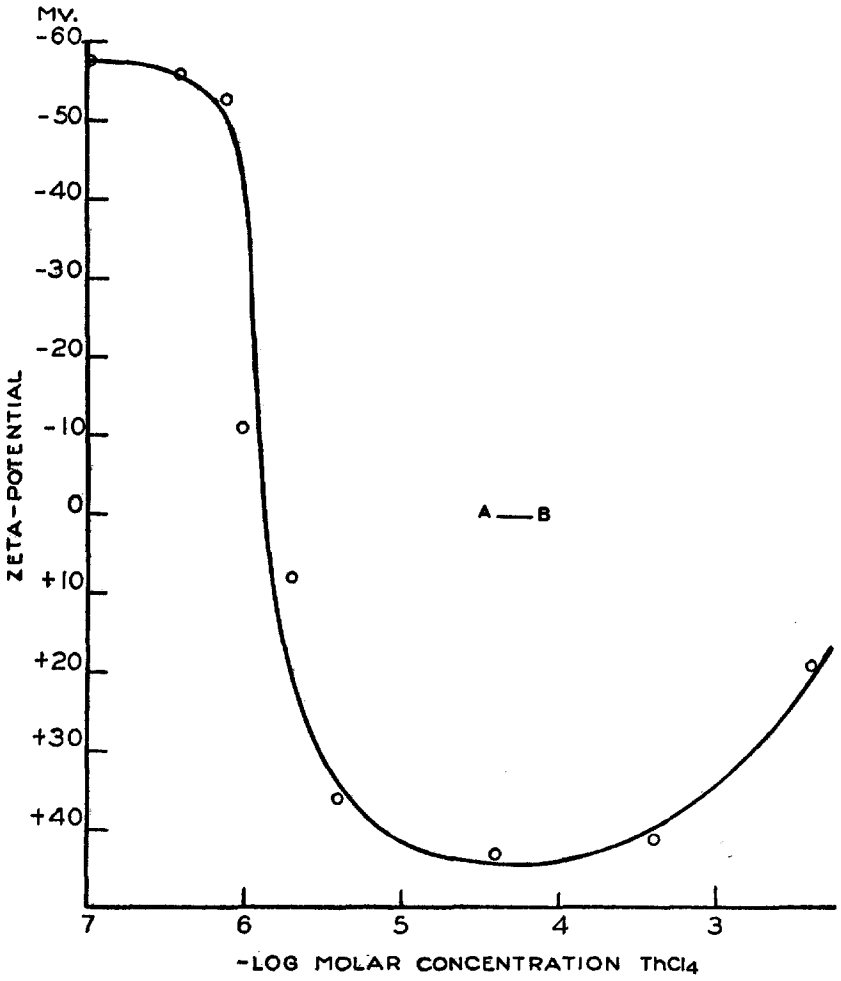

FIG. 2. Electrophoretic zeta potentials in millivolts of a collodion suspension as a function of $ThCl_4$ concentration. *A–B* represents the isoelectric zone for electroosmosis in five collodion membranes.

Collodion.—Collodion membranes of varying pore size were prepared by the method described by Bjerrum and Manegold (1927). The electroosmotic experiments on the collodion membranes were carried out exactly as with cellophane.

Since the membranes differed in permeability (estimated average pore diameter of most permeable membrane between 2 and 3 times that of least permeable) the electroosmotic velocities varied greatly at concentrations other than isoelectric, but the curves for all five membranes crossed the isoelectric point at concentrations between 4 and 6 $\times$ 10^{-5} M $ThCl_4$.

Microscopic collodion suspensions for electrophoretic measurements were prepared from the same stock collodion solution used for the preparation of the membranes. One part of this solution was diluted with ten parts of the solvent (alcohol and ether). Distilled water was then added slowly, with shaking, until a milky suspension was obtained. The ether and most of the alcohol were then removed by aeration. 1 cc. of this stock suspension was added to 250 cc. of the various thorium solutions under investigation. It should be mentioned that this procedure is not always successful in producing suspensions of the desired particle size (1 to 5μ); often the particles clumped rather rapidly. But in about a dozen trials, two suitable suspensions were obtained; these were kept in the ice box and used as a stock suspension for all future electrophoretic determinations.

The electrophoretic zeta-potential curve and the electroosmotic isoelectric zone are shown in Fig. 2. Here again the isoelectric concentration (between 1 and 2 $\times$ 10^{-6} M $ThCl_4$) for the particles is very much less than that found for the membranes (4 to 6 $\times$ 10^{-5} M $ThCl_4$).

DISCUSSION

That the difference in the isoelectric point of cellophane and collodion particles as compared with membranes of the same material is due to the small size of the membrane pores is indicated by the fact that in very large capillaries (300 μ radius) of pyrex glass, or on a flat glass surface, the same concentration of $ThCl_4$ (as well as $AlCl_3$ and $FeCl_3$) which is isoelectric for electroosmosis is also isoelectric for electrophoresis with pyrex particles (Monaghan, White, and Urban (1935)).

The behavior of the membranes is probably to be attributed to the influence of the small pores in preventing complete development of the electrical double layers. According to McBain and Kistler (1928), the largest pores in cellophane 600 membranes are of the order of magnitude of 2–3 $\times$ 10^{-7} cm. in radius. Let us now consider the probable thickness of the diffuse double layer (for a recent discussion see Müller, 1933). The thickness of the double layer decreases with increasing concentration, the decrease being faster the higher the valency of the ions, according to the expression $\lambda = \frac{4.32 \times 10^{-8} \text{ cm.}}{\sqrt{\Sigma z_i^2 \gamma_i}}$ where

λ = double layer thickness, γ_i = concentration in micromols per liter of ions of the 'ith' type, z_i = valence of ions of the 'ith' type. This expression holds with a fair degree of accuracy only when $z\zeta \lessapprox 25$ mv.

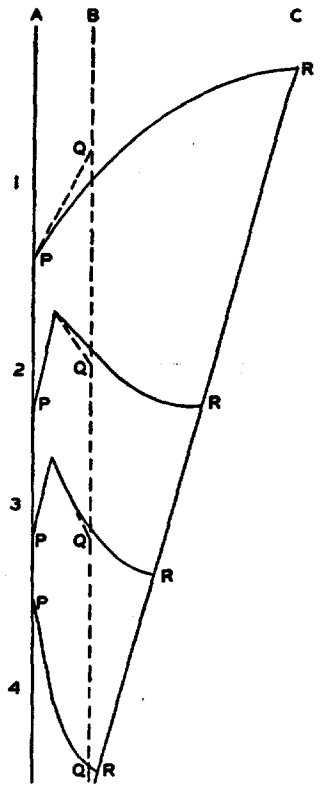

FIG. 3. Schematic representation of potential-distance curves in various concentrations of $ThCl_4$. A = solid wall; B = radius of pore in cellophane 600 membranes; C = outer limit of diffuse double layer around a cellophane particle. The potential difference PQ = electroosmotic zeta potential of cellophane membranes; PR = electrophoretic zeta potential of cellophane particles. Curve 1 represents conditions in water; Curve 2 in 3×10^{-6} M $ThCl_4$; Curve 3 in 4×10^{-5} M $ThCl_4$; Curve 4 in 4×10^{-3} M $ThCl_4$.

However, in the absence of data which would permit a more nearly rigorous evaluation of λ we may employ this expression to obtain a rough approximation. The calculation yields a double layer thickness

of 5.6×10^{-6} cm. at the electrophoretic thorium isoelectric concentration (3×10^{-6} M $ThCl_4$). This figure may be several hundred per cent from the true value; nevertheless it seems certain that the double layer thickness at this concentration is much greater than the radius of the membrane pores[1] and consequently that the double layer will be very much compressed in the membrane pores. It follows from the condenser equation $\zeta = \frac{4 \pi \sigma \lambda}{D}$ that, charge density, σ, remaining the same, ζ is directly proportional to the distance between the plates. A schematic representation of the probable course of the potential-distance curves as the thorium concentration is increased is given in Fig. 3 (see also Monaghan, White, and Urban (1935)). In water (Curve 1) where the double layer is normally quite diffuse, the zeta potential in the small-pored membrane will be greatly reduced from the normal value because of the necessarily compressed state of the diffuse layer. In 3×10^{-6} M $ThCl_4$, which is isoelectric for the particles, the membrane (electroosmotic) zeta potential has the same sign as in water (Curve 2). In 4×10^{-5} M $ThCl_4$ (Curve 3) the membrane is isoelectric, while the sign of electrophoretic zeta is reversed. In stronger solutions, 4×10^{-3} M $ThCl_4$, where the double layer thickness approaches the pore radius, the potential of the membrane will approach that of the particles, both being of reversed sign (Curve 4).

SUMMARY

It is demonstrated that the isoelectric concentration of $ThCl_4$ is much greater for electroosmosis in small-pored membranes (cellophane, collodion) than for electrophoresis of particles of the same material. An explanation for the difference is advanced, based on the influence of the small pores in preventing complete development of the electrical double layer.

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[1] Particularly since this value of λ designates mean double layer thickness and not the distance from the wall to the outer limit of the layer.

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