

ELECTRICAL FACTORS INFLUENCING THE RATE OF
FILTRATION OF AQUEOUS ELECTROLYTE SOLUTIONS
THROUGH CELLOPHANE MEMBRANES*

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Various observers have reported changes in filtration rate of aqueous electrolyte solutions through membranes with changes in concentration, independent of viscosity (Brukner, 1926; Manegold and Hofmann, 1930 *a, b*, 1931; Duclaux and Errera, 1924, 1926). In general the addition of an electrolyte increased the rate of filtration above that of water. Erbe (1932) failed to find any effect of KCl on membrane permeability.

Two types of explanation of the increased impermeability in the presence of electrolytes have been offered. The first is that of Duclaux and Errera, that the lower rates with water and very dilute solutions are due to an electroosmotic back-transport with stream potential as the driving voltage, which is diminished with increase in conductivity. This same concept has been applied to flow through capillary tubes (Abramson, 1931; Bull, 1932; see, however, Reichardt, 1933 for a discussion of the inadequacy of Bull's application of this concept to the effect of electroosmotic back-transport on stream potentials) and, with diffusion potentials substituted for stream potentials, to abnormal osmosis (Bartell, 1914, 1923; Freundlich, 1916; Loeb, 1922; Söllner, 1930; Grollman and Söllner, 1932).

The second is that of Brukner and Manegold and Hofmann, that the changes in permeability are due to changes in the thickness of a layer of oriented water dipoles held on the pore walls by electrical forces. For evidence that adsorbed water layers exist see Kolkmeijer

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and Favejee, 1933; Liepatoff, 1926; Nutting, 1927; Boswell and Dilworth, 1925; Dumanski, 1933, and for evidence that the development of such layers is a function of the electrokinetic potential see Buzagh, 1930; Zocher and Jacobsohn, 1929; Pauli, 1929.

It occurred to us that the question of the influence of electrical factors on filtration rates could best be studied by comparing the filtration rate of a solution in which these factors are absent, *i.e.* at the isoelectric point, with those of solutions where they are present. Since both effects discussed above decrease permeability, a maximum filtration rate at the isoelectric condition is predicted. Our experimental findings confirm this prediction.

Determination of Filtration Rates.—The cellophane "600" membranes were soaked in the solution to be filtered for 24 hours previous to the filtration. The membrane (diameter of filtering surface 7.0 cm.) was put into a porcelain filtering apparatus of the type illustrated by Jander and Zakowski (1929). The membrane was supported on each side by a perforated porcelain disc in direct contact. A large rubber stopper was sealed into the top by beeswax-rosin cement; a vertical glass tube was tightly fitted into a hole in this stopper. Pressure applied to the compartment below the membrane was read with a mercury or water manometer and the filtration rate determined by reading with a horizontally mounted microscope fitted with a micrometer ocular the rate of rise of the meniscus in the tube. The whole apparatus was immersed in an electrically controlled water bath at $25^{\circ} \pm 0.01$. The pressure (25 mm. Hg) was applied when the apparatus was first put into the bath and readings begun after 2 hours. With thorium solutions of concentration $m/50$ or less, any further change in rate with time was so slow as not to exceed, within the period of observation (approximately a half hour), the limits of experimental error. With more concentrated thorium solutions ($m/10$), the filtration rate slowly decreased over a period of several hours. This falling off with time is undoubtedly due to a mechanical blocking of the membrane, caused by the adsorption of colloidal thorium hydroxide onto the pore walls. Repeated determinations on a given membrane showed a maximum fluctuation of ± 1.5 per cent and an average of ± 1 per cent. A given membrane was used for a series in the various solutions. The rate with water remains constant after repeated determinations. The absolute values for the filtration rates with water on three membranes are 1.51, 1.48, and 1.09×10^{-8} cc./sec./cm.²/cm. H₂O. The first two figures are on membranes cut from the same piece of new cellophane; the last was on a sample cut from the same piece a few months later. Whether this decrease in permeability with age of the dry and unused membrane is a consistent occurrence we cannot say. These values may be compared with the figure of 5.6×10^{-9} (McBain and Kistler (1928), Table I) on cellophane 600, and with

the figure of 5.5×10^{-9} (Manegold and Viets (1931), Table I) for a sample of "Einmachecellophan" which was 0.006 cm. thick; McBain and Kistler found cellophane 600 to be 0.0098 cm. thick.

The procedure followed has been to determine on a given membrane the filtration rate of water; then of the various thorium chloride solutions and finally of water. The water rates at the beginning and end of a series were the same. This has been carried through for three membranes; the results are shown in Fig. 1. The percentage deviation in filtration rate from that of water (indicated by the horizontal line) is plotted against the negative logarithm of the molar concentration of ThCl_4 . The rate is seen to reach a maximum at a concentration of $4 \times$

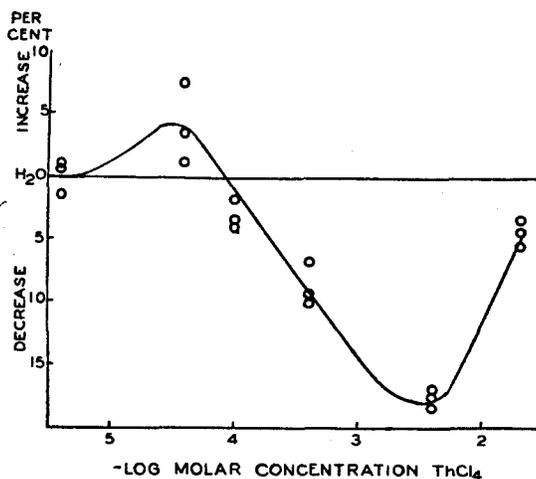


FIG. 1. Filtration rate through cellophane as a function of concentration, ThCl_4 , \circ .

10^{-5} M and then to fall off, becoming from 15 to 20 per cent less than the water rate in a concentration of 4×10^{-3} M ThCl_4 . Further increase in the thorium concentration results in an increase in filtration rate.¹

¹ This fact, that in 2×10^{-2} M ThCl_4 the filtration rate is considerably faster than in 4×10^{-3} M ThCl_4 , demonstrates conclusively that the changes in filtration rate with varying thorium concentration, up to a concentration of 2×10^{-2} M, are not due to mechanical blocking of the membrane by colloidal thorium hydroxide. If this blocking effect were an important factor, the filtration rate with 2×10^{-2} M would be less than with 4×10^{-3} M. As has been stated previously, however, in solutions more concentrated than 2×10^{-2} M ThCl_4 , a sufficient amount of the colloidal material is present to cause a noticeable blocking; hence filtration values for more concentrated solutions cannot be obtained.

Correlation of Changes in Filtration Rate with Zeta Potential.—The zeta potential of cellophane as a function of thorium concentration is discussed in the accompanying paper of this series. It was demonstrated that, while the absolute magnitude of the zeta potential cannot be determined on cellophane membranes, nevertheless the isoelectric point could be accurately located at a concentration of approximately 4×10^{-5} M ThCl₄. Also, the curve of electroosmotic velocity as a function of thorium concentration obtained with cellophane membranes (see Fig. 1 of the accompanying paper) indicates that the zeta potential of reversed sign obtained in 4×10^{-3} thorium chloride is much greater than the potential in water. The thorium filtration curve of Fig. 1 shows a maximum at 4×10^{-5} M ThCl₄, the concentration at which the membranes are isoelectric. As zeta of reversed sign increases (as indicated by the electroosmosis-concentration curve) the filtration rate falls until in 4×10^{-3} M it is about 22 per cent lower than at isoelectric. The increase in filtration rate as one passes from 4×10^{-3} to 2×10^{-2} M ThCl₄ is presumably correlated with a beginning return of zeta toward zero (irregular series) which has been repeatedly demonstrated at high thorium concentrations; we have not carried out electroosmotic observations with 2×10^{-2} M ThCl₄. It may be pointed out that the experiments with the stronger thorium solutions are the first to show a decrease in filtration rate below that for water on adding electrolytes, other than those explicable by mechanical plugging. This is as expected, since the mono and bivalent cations employed by other workers could not reverse zeta. The filtration rate is thus an inverse function of zeta, being diminished by an increase of zeta.

The question as to which is the more important of the two possible mechanisms, postulated earlier in the paper, by which electrokinetic factors might influence filtration rate is not decisively answered by this work. As regards the electroosmotic back-transport set up by stream potential, it would seem that, even with an increasing zeta as one passes the isoelectric point, the increased conductivity would so diminish stream potentials that this effect would diminish and filtration rate return toward the maximum. If, on the other hand, changes in effective pore diameter due to variations in the rigidity or viscosity of an adsorbed water layer and determined by zeta are the predominant factor, a continued diminution of filtration rate would be expected so

long as zeta is increasing. The fact that the latter occurs might be taken as presumptive evidence that the wall layer effect is of more importance than the stream potential-electroosmotic effect. However, since the ratio of the conductivity in the membrane with a concentrated solution to that with a dilute solution is probably much less than the ratio of the respective bulk conductivities, one cannot be sure how much the stream potential with the more concentrated solutions is decreased, and in the absence of this knowledge a decision as to the more important of the two factors cannot be made.

The experimental findings on filtration rate reported here agree rather well, except at one concentration, with those reported some time ago by Urban and White (1932). The present work was done under better experimental conditions and, where discrepancy exists, the present results are believed more reliable.

During the progress of this work Reichardt's paper appeared, in which is developed an equation for calculating the amount of electroosmotic "blocking" due to stream potential. The equation is

$$\psi = \frac{2A^2 d \lambda_0}{Br\lambda},$$

where ψ is the ratio of the volume back-transported electroosmotically to the volume pressed through by hydrostatic pressure, A and B are functions of $\frac{d}{r}$, where d is thickness of double layer and r is pore radius, λ_0 is the von Smoluchowski (electroosmotic) component of surface conductivity per unit cross-section of pore, and λ is total specific conductivity in the pore. Where ψ is 1, no filtration will occur, where ψ is 0, Poiseuille's law is obeyed. We hoped to apply our experimental findings to this equation to see if the observed departures from normal filtration agreed with those predicted by the equation but the evaluation of several of the factors in the equation is so uncertain as to render such an attempt at present premature.

In conclusion, some experiments testing a finding of Lepeschkin's may be mentioned. Lepeschkin (1933) reported that when filtration rate is plotted against filtration pressure a straight line is obtained which cuts the X (pressure) axis to the right of the origin. This X intercept, the pressure below which no filtration takes place, was termed

the membrane resistance. We have carried out a number of determinations of filtration rate as a function of pressure. In the earlier experiments results similar to those of Lepeschkin were obtained, shown as the broken lines in Fig. 2. It was soon found, however, that this was due to insufficient time for the membrane to come to equilibrium. If the rate at a high pressure was determined and the pressure lowered for another determination, several hours were required for the rate to

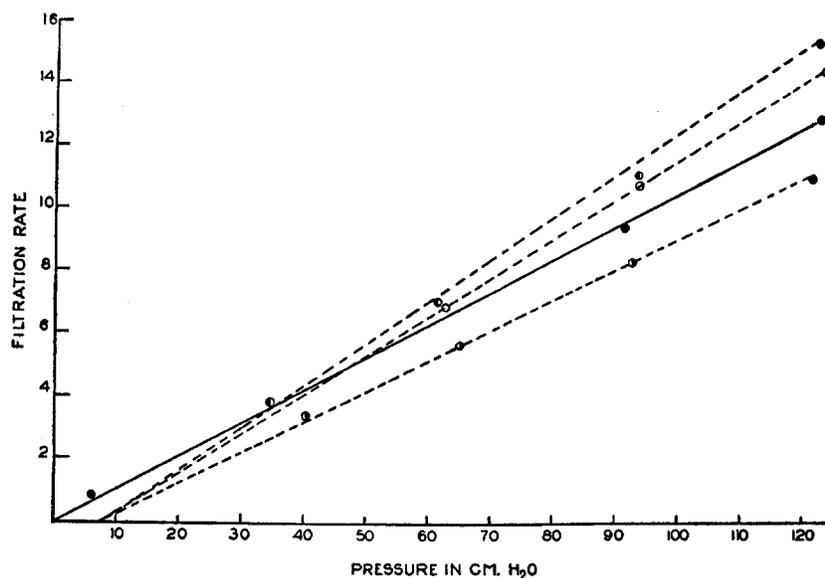


FIG. 2. Filtration rate in arbitrary units of ThCl_4 solutions through cellophane as a function of pressure. ○, water; ◐, 4×10^{-5} M ThCl_4 (isoelectric); ●, 4×10^{-3} M ThCl_4 ; ○, 4×10^{-3} M ThCl_4 (pressure equilibrium attained).

become constant. At the lower pressures it was necessary to leave the pressure on overnight to achieve constant conditions. When these precautions are observed the curve is a straight line passing through the origin; a typical result is shown as the full line of Fig. 2. We therefore believe that Lepeschkin's membrane resistance is an artifact.

SUMMARY

The mechanisms by which electrokinetic factors might influence the filtration rate of aqueous electrolyte solutions through membranes are discussed. The filtration rate of a thorium chloride solution in which

the membrane is isoelectric is compared with those of other solutions. The maximum filtration rate is found at the isoelectric concentration, the rate falling as the electrokinetic potential increases.

The results demonstrate an inverse relation between the electrokinetic potential and the filtration rate but do not permit the evaluation with any great exactitude of the respective rôles played by the two proposed mechanisms, namely, a stream potential-electroosmotic back-transport and a variation in effective pore diameter due to an orientation of water dipoles determined by electrical factors.

Evidence is presented that Lepeschkin's membrane resistance is an artifact.

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