

A NOTE ON THE OBSTRUCTIVE OR TORTUOSITY FACTOR IN PAPER ELECTROPHORESIS

J. T. EDWARD

Chemistry Department, McGill University, Montreal (Canada)

KUNKEL AND TISELIUS¹, in a classical study of paper electrophoresis, found the mobilities of ions in moist paper to be given by their mobilities in free solution multiplied by a "correction factor", which for reasons given below we have termed the "obstructive factor" ρ^2 . On the basis of an admittedly oversimplified model for the filter paper soaked with solution, they considered that

$$\rho = l/l' \quad (1)$$

where l and l' are the lengths of paths available to the ions in free solution and in moist paper respectively (see below). In this communication it is shown that, assuming this model, a more rigorous and detailed treatment leads to the relation

$$\rho = (l/l')^2 \quad (2)$$

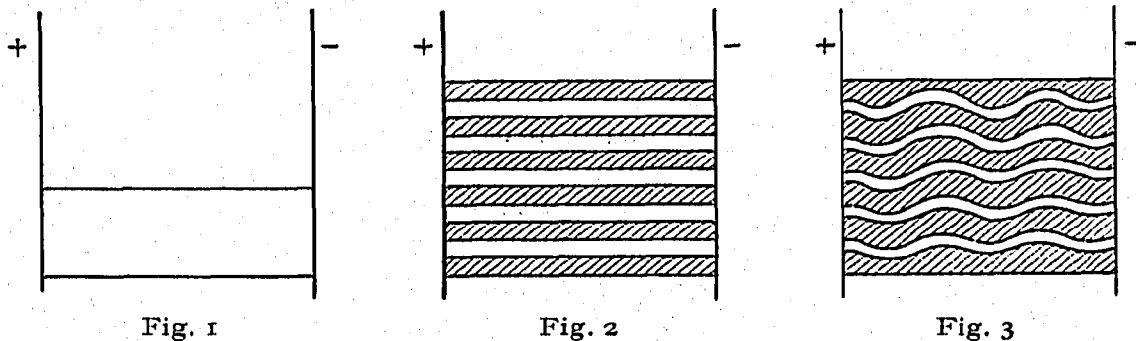


Fig. 1

Fig. 2

Fig. 3

Fig. 1. Solution between electrodes.

Fig. 2. Solution dispersed in a non-conducting solid (diagonal shading) in straight channels between the electrodes.

Fig. 3. Solution dispersed in a non-conducting solid in sinuous channels between the electrodes.

We consider a column of solution (Fig. 1), of specific conductance k , cross-sectional area A , and volume V , between electrodes a distance l apart. The conductance K of this solution is given by

$$K = \frac{kA}{l} = \frac{kV}{l^2} \quad (3)$$

This volume of solution is now dispersed in a fixed volume V_p of non-conducting solid between electrodes remaining a distance l apart (Figs. 2 and 3). The conductance K' of the solid + dispersed solution will depend on its geometry. In Fig. 2 the solution is contained in n channels, each of uniform cross-section A/n , volume V/n , and conductance kV/nl^2 . Hence $K' = K$. We now envisage a process in which, while V and V_p remain constant, the channels are lengthened to l' but still run through the block of

solid without intersecting with each other (Fig. 3). (This represents the model of KUNKEL AND TISELIUS for the solution held in the porous filter paper.) Since the volume in each channel remains V/n , the cross-sectional area must decrease to $(A/n)(l/l') = A'n$, A' being the total effective cross-sectional area of the solution in the n channels. The conductance in each channel is now kA'/nl' , and the total conductance K' will be less than K and given by

$$K' = \frac{kA'}{l'} = \frac{kV}{l'^2} \quad (4)$$

Since ρ has been defined² by

$$\rho = K'/K \quad (5a)$$

$$= K'l^2/kV \quad (5b)$$

it follows from equations 3 and 4 that for the model depicted in Fig. 3

$$\rho = (l/l')^2 \quad (6)$$

KUNKEL AND TISELIUS considered l' to equal $R'Ak$, where $R' = 1/K'$. However, from equation (4) it follows that

$$l' = R'A'k = R'Ak(l/l') \quad (7)$$

Hence the "correction factors" which they determined for various filter papers, defined by

$$\text{"Correction factor"} = \frac{l}{R'Ak} \quad (8)$$

will for the model of Fig. 3 equal $(l/l')^2$ and not l/l' as they supposed.

It should be noted that the obstructive factor as defined in equation (5b) is identical with the "correction factor" as defined in equation (8), and is operationally defined. Hence it does not depend on the conceptual model adopted for the filter paper-solution system. The actual model represented in Fig. 3 is highly artificial; ρ may be decreased further by having channels of length l' but of varying cross-sectional area; by reversible adsorption of the ions by the paper, etc. Consequently, it seems preferable to designate this factor by the non-committal term "obstructive factor", rather than by more specific terms such as "correction factor for added migration path length".

The mobility (velocity in unit potential gradient) u of an ion in free solution (Fig. 1) is defined by the equation

$$u = \frac{dl}{tE} \quad (9)$$

where d is the distance travelled by the ion in time t in a potential gradient E/l (*i.e.* E is the potential difference between the electrodes). The actual mobility of the ion will be unchanged in the system of Fig. 3, but the apparent distance d_p that it will travel in the same time with a potential difference E between the electrodes is given by

$$d_p = d(l/l')^2 = d\rho \quad (10)$$

This is because (a) the true potential gradient in the channels of Fig. 3 is E/l' , E/l representing the macroscopic or *apparent* potential gradient, and (b) the macroscopic distance d_p travelled by the ion is less than the actual distance in the winding channel by a factor l/l' (see KUNKEL AND TISELIUS¹ for the detailed argument). Then if we

define the "mobility in paper" u_p of an ion by its apparent velocity (d_p/l) when the apparent potential gradient along the paper (E/l) is unity, *i.e.*,

$$u_p = \frac{d_p l}{t E} \quad (11)$$

it follows from equation (9) and (10) that

$$\rho = u_p / u \quad (12)$$

While this equation has been derived on the basis of the simple model of Fig. 3, it can be shown to hold generally for solutions having non-conducting solids dispersed through them. The conductance K of the column of solution of Fig. 1 depends on the number and mobilities $u_1, u_2, u_3 \dots$ of the ions between the electrodes. For solutions of completely ionized substances the changed conductance K' produced by adding to the solution non-conducting liquid or solid (the distance l between the electrodes remaining unchanged) can only be due to the changed mobilities of the constituent ions, specific interactions between the ions and diluent being excluded. Hence

$$\rho = \frac{K'}{K} = \frac{u_{p1} + u_{p2} + u_{p3} + \dots}{u_1 + u_2 + u_3 + \dots} \quad (13)$$

If, as assumed by KUNKEL AND TISELIUS, the mobilities of all ions are affected equally by the dispersed solid, then

$$\rho = \frac{u_{p1}}{u_1} = \frac{u_{p2}}{u_2} = \frac{u_{p3}}{u_3} = \dots \quad (14)$$

which is identical with equation (12).

SUMMARY

On the basis of the model of KUNKEL AND TISELIUS, the factor by which the mobilities of ions are reduced when the solutions containing them are absorbed by filter paper is shown to be proportional to $(l/l')^2$, where l and l' are the lengths of the paths followed by the ions in free solution and in moist paper respectively.

REFERENCES

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