115. *Electrical Conductance of Particles of Ion-exchange Resin.*

By J. R. Parrish.

The relation between the conductivity of a resin, the conductivity of a column filled with the resin and a solution, and the conductivity of the solution has been determined experimentally. A theoretical equation which was in partial agreement with the experimental results has been modified empirically to represent the results more accurately.

The self-diffusion coefficient of the counter-ion in an ion-exchange resin can be calculated from the Nernst–Einstein equation. Thus the rates of exchange of different resins can be compared if their conductivities are known. If the electro-osmotic contribution to the conductivity is neglected, the calculated diffusion coefficients will not be exact, and extreme accuracy in the measurement of conductivity will not be required.

Granular resins have been avoided in accurate studies of conductance because of experimental difficulties and the lack of a method of proved validity for the calculation of the conductivity of the resin from the measured conductivities of the column and the solution. Kitchener[1] has listed the disadvantages of granular resins in the measurement of conductance. Helfferich[2] has given a bibliography of the theories developed for the conductivity of a system of two phases, but he considered that most of these theories would not be applicable to beds of ion-exchange resin. Heyman and O'Donnell[3] were the first to measure the conductivity of a column of granular resin, but they did not calculate the conductivity of the resin itself. Jenckel and von Lillin[4] used equation 1 of son Frey[5] to calculate the conductivity of a granular chelating resin. The variation of the conductivity of a column of spherical particles of ion-exchange resin with the conductivity of the surrounding solution has been expressed by means of an empirical equation.[6] However, the conductivity of the resin itself varies with the concentration of the solution, and this variation was calculated from certain assumptions. Even when no correction was made, the equation could be made to fit the experimental results by a suitable adjustment of the arbitrary parameters. Therefore this equation cannot be expected to give an accurate value for the conductivity of the resin from the values measured for the column and the solution. Being empirical, the equation does not relate the packing density of the column to its conductivity.

The packing density of equal spheres attains a reproducible value of 0·64 when allowance is made for peripheral effects and when the spheres are properly tapped down.[7] Spherical particles of ion-exchange resin behave similarly when the variation in size is small, and there are few irregular fragments.[8] For particles of irregular shape, the corresponding value is 0·54. Thus, if a suitable sample of resin is available, a packing density of 0·64 or 0·54 can be obtained in the conductivity cell. Otherwise the packing density of each sample must be determined.

The conductivities of resin, column, and solution for different concentrations of the solution and for different packing densities have now been measured.

Experimental

Apparatus.—The cell was constructed of soda-glass, and the resin was supported on a sintered-glass plate (porosity no. 1) which had been cemented in position (Fig. 1). The platinised platinum

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[1] Kitchener in Bockris, "Modern Aspects of Electrochemistry," Butterworths Scientific Publns., London, 1959, No. 2, p. 87.

[2] Helfferich, "Ionenaustauscher," Verlag Chemie, Weinheim, 1959, Vol. I, p. 423.

[3] Heyman and O'Donnell, *J. Colloid Sci.*, 1949, **4**, 405.

[4] Jenckel and von Lillin, *Kolloid Z.*, 1956, **146**, 159.

[5] son Frey, *Z. Elektrochem.*, 1932, **38**, 260.

[6] Sauer, Southwick, Spiegler, and Wyllie, *Ind. Eng. Chem.*, 1955, **47**, 2187; Spiegler, Yoest, and Wyllie, *Discuss. Faraday Soc.*, 1956, **21**, 174.

[7] Scott, *Nature*, 1960, **188**, 908.

[8] Parrish, *Nature*, 1961, **190**, 800.

electrodes were fused into the walls of the cell, so that the current passed across the column of resin. The cell was filled to a mark with the resin. This mark was high enough above the electrodes to allow for the bending of the current lines, but was as low as possible to minimise the pressure exerted by the resin at the depth of the electrodes. This design avoided the inconvenience and inaccuracy of a movable electrode, and it allowed a solution to be passed rapidly through the column.

The conductivity of the solution was measured as it passed through a second cell connected to the outlet of the first. The cells were immersed in liquid paraffin in a thermostat bath. The measuring apparatus was a WTW conductivity meter, type LBR, which allowed for the correction of phase angle, and operated at either 50 or 3000 cycles per sec.

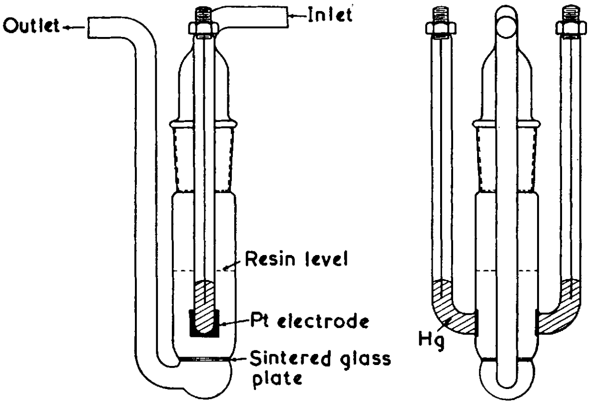

FIG. 1. The conductivity cell.

Measurements.—Before measurements were made, the cell was placed on an electromagnetic vibrator for 5 min. to ensure that dense random packing of the resin had been obtained. If necessary, the height of the resin was adjusted to the mark, and the vibrating was repeated. The height of the solution above the resin did not affect the measurements, but it was kept as constant as possible.

Solutions of hydrochloric acid or sodium chloride were used with anion-exchange resins in the chloride form and with cation-exchange resins in the hydrogen or sodium form respectively, so that no ion-exchange occurred. The strength of the solution was adjusted until the column and the solution had the same conductivity. At this point the resin necessarily had the same conductivity as the solution. The solution was then rapidly replaced by a solution of different conductivity, and the conductivity of the column was measured as soon as it became constant. When fairly large beads of a highly cross-linked resin were used, diffusion of electrolyte into or out of the resin was slow compared with the rate of replacement of the solution and, even if some diffusion had occurred, the conductivity of the resin would have been affected only slightly.

In this way, the conductivity of the resin, κ_r, the conductivity of the column, κ_1, and the conductivity of the solution, κ_s, could all be measured. For $\kappa_r > \kappa_s$ the ratio $\kappa_1\ \kappa_r$ was plotted against κ_s/κ_1 (Fig. 2). Two resins of the same packing density but of different cross-linking (16% and 8% of divinylbenzene) and of different conductivity gave points lying on the same curve except for the last points, which were determined when conductivity water flowed through the column. Here the conductance of one or both of the resins may have changed owing to the diffusion of electrolyte out of the particles. Since the other points fell on the same curve, it follows that the conductance of the resins did not change appreciably during the measurements. Resins of high swelling and/or low concentrations of fixed ions were not suitable for these measurements, but the results that have been obtained should apply to all resins. For $\kappa_s > \kappa_r$, the ratio κ_r/κ_1 was plotted against κ_1/κ_s (Fig. 3).

Precautions.—Air bubbles are often formed within the bed of resin. To remove them, the resin was stirred and then allowed to settle under vibration.

When the resin was bathed in distilled water, the conductance of the column varied with the flow rate of the water. This effect was more pronounced when fine particles were used, and it was apparently caused by the pressure drop within the bed. The conductance decreased on cessation of the flow, and its return to a constant value was hastened when the cell was tapped. The conductance could be increased by a similar amount when the pressure on the resin was increased by means of a perforated plunger. Readings were taken at zero flow rate after the cell had been tapped or vibrated to ensure a constant pressure.

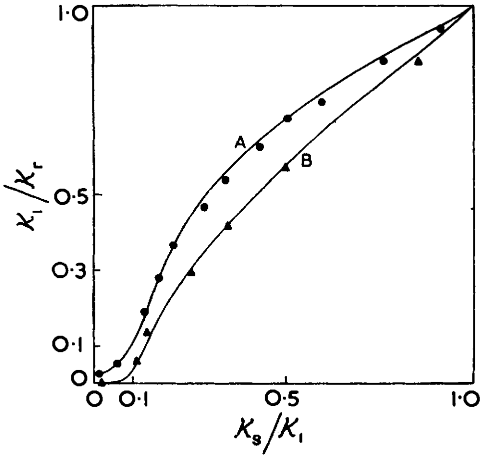

FIG. 2. $\kappa_r > \kappa_s$. Curve A represents equation (V) when $v = 0{\cdot}64$. The circles are experimental results when $v = 0{\cdot}64$. Curve B represents equation (V) when $v = 0{\cdot}54$. The triangles are experimental results when $v = 0{\cdot}54$.

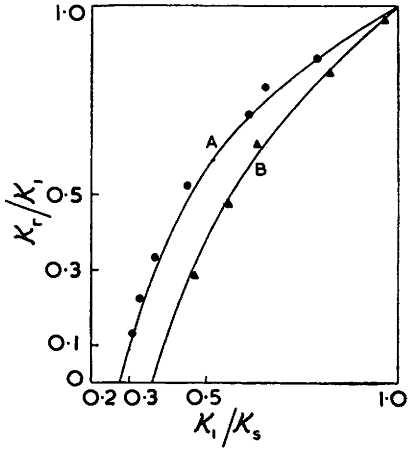

FIG. 3. $\kappa_s > \kappa_r$. As Fig. 2, but here the curves represent equation (II) as well as equation (V).

DISCUSSION

A useful comparison of equations designed to represent the conductivity (or permittivity etc.) of a system of two phases in terms of the conductivities and relative volumes of the phases has been made by Brown.[9] Clerk Maxwell's formula is the best approximation which is independent of the geometry of the particles. The equations of Bruggeman [10] and of Böttcher [11] for beds of spheres are attempts to improve on Maxwell's formula.

The applicability of various equations to a bed of resin was compared by evaluation of the ratio κ_1/κ_s for the case where the resin is an insulator. The reciprocal of this ratio is the " formation resistivity factor " of Archie.[12] Experimental values obtained by Wyllie and Gregory [13] for beds of porosity 0·25—0·56 were reported to be in agreement with Slawinski's formula [14] for spheres in perfect contact. Equation I of son Frey [5] is also in agreement with experiment. Thus experiments with beads of polystyrene in this laboratory gave an average value of 0·275 for κ_1/κ_s when the packing density was 0·60(4). This is in agreement with the results of Wyllie and Gregory, but son Frey's results give an interpolated value of 0·265. Slawinski's formula gives 0·278 and son Frey's equation I gives 0·270.

Equation I of son Frey was derived for aggregates in which both phases are continuous. The same author derived two other equations for aggregates in which one of the phases exists in isolated pockets. Since the isolated phase could be either the better or the worse

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[9] Brown, *J. Chem. Phys.*, 1955, **23**, 1514.
[10] Bruggeman, *Ann. Physique*, 1935, **24**, 636.
[11] Böttcher, " Theory of Electric Polarization," Elsevier, Amsterdam, 1952.
[12] Archie, *Amer. Inst. Min. Met. Engineers*, 1942, **146**, 54.
[13] Wyllie and Gregory, *Amer. Inst. Min. Met. Engineers*, 1953, **198**, 103.
[14] Slawinski, *J. Chim. phys.*, 1926, **23**, 710.

conductor, two equations were given, but these can be shown to represent the same relation. (In the original publication the last lines of equations II and III contain misprints.) The experimental values obtained on ion-exchange resins (Fig. 3) were in better agreement with equation II than with equation I,

$$\kappa_1/\kappa_s = \tfrac{1}{2}\left(\frac{1 - v^{\frac{2}{3}}\beta}{1 - v^{\frac{2}{3}}\beta + v\beta} + \frac{1 - \beta + v^{\frac{1}{3}}\beta - v\beta}{1 - \beta + v^{\frac{1}{3}}\beta}\right), \qquad \text{(II)}$$

where $\beta = (\kappa_s - \kappa_r)/\kappa_s$.

The difference between these two equations is 10% at a packing density, v, of 0·60, and 15% at v = 0·66. The polystyrene beads, unlike the ion-exchange resins, were difficult to wet and to pack under aqueous solutions. These effects might have caused experimental errors. Maxwell's expression, which was intended to apply only to isolated spheres, gives values which differ from those of equation II only in the third decimal place. Other equations were not in agreement with the experimental results, and Baron's equation as quoted by Helfferich [2] is the same as that of Bruggeman.[10]

The experimental results when $\kappa_r > \kappa_s$ (Fig. 2) were in serious disagreement with son Frey's equation I over the whole range. They were then compared with son Frey's equation III:

$$\kappa_1/\kappa_s = \tfrac{1}{2}\left(\frac{1 - \alpha + v^{\frac{2}{3}}\alpha}{1 - \alpha + v^{\frac{2}{3}}\alpha - v\alpha} + \frac{1 - v^{\frac{1}{3}}\alpha + v\alpha}{1 - v^{\frac{1}{3}}\alpha}\right), \qquad \text{(III)}$$

where $\alpha = (\kappa_r - \kappa_s)/\kappa_r$.

For v = 0·64 there was agreement when the value of α lay between 0 and 0·5. For values of α between 0·5 and 1·0, the theoretical line deviated from the experimental.

A Modified Equation.—The discrepancy is caused partly by the fact that the beads of resin are not completely isolated from each other; *i.e.*, the contact resistance between the beads is large but finite. Spiegler, Wyllie, and their co-workers [6] expressed that portion of the conductivity of the column which is independent of the conductivity of the solution as $b\kappa_r$, where b was found to be about 0·01. The empirical equation of these authors can be written in the form

$$\kappa_1/\kappa_s = 0{\cdot}63\gamma + 0{\cdot}01\gamma d/(1 - \gamma e) + 0{\cdot}34, \qquad \text{(IV)}$$

where $\gamma = \kappa_r/(e\kappa_r + d\kappa_s)$, and $d = 1 - e = 0{\cdot}95$.

The plot of κ_s/κ_1 against κ_1/κ_r obtained from this equation was compared with the experimental results obtained in this work for a similar resin. Agreement was poor over much of the range of κ_s/κ_1, but at low values of this ratio, where the term $b\kappa_r$ becomes important, agreement was good.

Equation III was improved by the addition of the term $b\kappa_r$, but the results were still inaccurate for values of κ_s/κ_1 between 0·05 and 0·50. This inaccuracy was caused by the failure, at low values of κ_s/κ_1, of one of the assumptions made in the derivation of equation III. It did not appear necessary or profitable to consider special effects, such as double-layer conductance and variations of κ_r within a single particle, which might obtain in beds of ion-exchange resin. An equation correct over the whole range was obtained by a modification of son Frey's calculation.

Consider the bed of resin to be represented by a cubic element of unit dimensions (Fig. 4). The resin itself is represented by a rectangular prism of cross-section a and length d. The packing density, v, is equal to ad. The conductance between the front and the back face of the cube is calculated on the assumptions of son Frey.[5] If the top and side of the inner prism are equipotential planes, then

$$\kappa_1/\kappa_s = (1 - d\alpha + ad\alpha)/(1 - d\alpha).$$

If it is assumed that the back of the prism is an equipotential plane, then

$$\kappa_1/\kappa_s = (1 - \alpha + \alpha a)/(1 - \alpha + \alpha a - ad\alpha).$$

These expressions represent limits, and their arithmetical mean is taken as the most likely value of κ_l/κ_s.

To allow for electrical contact between the particles we assume that a fraction of the total current goes through the particles alone, and that this fraction can be represented by

$$b\kappa_r = b\kappa_s/(1 - \alpha).$$

Here b does not represent an extra volume of resin. These expressions are combined to give

$$\kappa_l/\kappa_s = \tfrac{1}{2}\left(\frac{1 - d\alpha + ad\alpha}{1 - d\alpha} + \frac{1 - \alpha + a\alpha}{1 - \alpha + a\alpha - ad\alpha}\right)(1 - b) + \frac{b}{1 - \alpha} \qquad \text{(V)}$$

where $ad = v$, and $\kappa_l/\kappa_r = \kappa_l(1 - \alpha)/\kappa_s$.

The values of b and of the ratio $\sqrt{a}/d$ have to be found empirically. The value of b can be expected to depend on the pressure between the particles, on their compressibility, and on the packing density. It appears to be independent of the size of the particles within the limits 0·11—1·1 mm. in diameter. For spherical particles of resin of low swelling and of packing density 0·64, a value of 0·020 was found. For a crushed resin of packing density 0·54, the value was 0·002—0·004. It was difficult to measure b accurately.

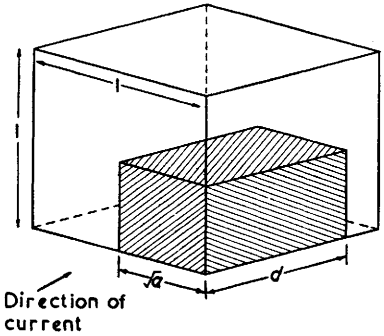

FIG. 4. The cubic element.

The ratio $\sqrt{a}/d$ is unity for only part of the range of α. It may be regarded as a shape factor which varies with α and with v. The following empirical relation was found to give good results (it has been checked at packing densities of 0·54, 0·59, and 0·64):

$$\sqrt{a}/d = 1 - 0{\cdot}9(0{\cdot}718 - v)\alpha^6.$$

When $\kappa_s > \kappa_r$, $\sqrt{a}/d$ is unity, and the term $b\kappa_r$ can be neglected. Equation V then reduces to equation II.

Conductivities of resins.

(κ is in ohm^{-1} cm.$^{-1}$ and refers to the resin itself.)

Resin	v	Ambient solution	100κ at 25°	Resin	v	Ambient solution	100κ at 25°
AG 50–X16 H ...	0·64	N-HCl	9·8	IR–120 Na	0·59	0·1N-NaCl	2·60
,, ...	,,	0·1N-HCl	9·5	,, ...	,,	0·01N	2·05
,, ...	,,	0·01N-HCl	9·7	IR–100 H	0·54	N-HCl	4·88
AG 50–X16 Na ...	0·64	0·1N-NaCl	0·88	,, ...	,,	0·1N	5·31
,, ...	,,	0·01N-NaCl	0·88	,, ...	,,	0·01N	4·81
IR–120 H	0·59	N-HCl	21·5	IR–100 Na	0·54	0·1N-NaCl	1·01
,, ...	,,	0·1N-HCl	20·2	,, ...	,,	0·01N	1·02
,, ...	,,	0·01N-HCl	18·6				

The conductivity of resins can now be calculated from the conductivities of the columns and of the solutions. Some typical values are given in the Table. It might be possible to derive an equation on a fundamental basis to replace this empirical relation, but the matter will not be pursued in this laboratory.

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