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The Electrical Conductivity of Packed Beds Containing Macroporous Cation Exchanger

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The Electrical Conductivity of Packed Beds Containing Macroporous Cation Exchanger

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SUMMARY

The electrical conductivity of packed beds containing macro-
porous Duolite C-25 polystyrene sulfonate cation exchanger equili-
brated with aqueous solutions of a single electrolyte (NaCl or HCl)
has been measured over a range of electrolyte concentrations. The
results are interpreted in terms of a two-phase model for the resin
particle involving (1) the resin matrix, with the conventional proper-
ties of polystyrene sulfonate cation exchanger, and (2) a macropore
dispersed phase which is assumed to have the same conductance as
the solution outside the particle. The resin particle conductivity
is calculated from the Bruggeman equation using measured bed and
interstitial solution conductivities. The external void fraction is
assumed to be 0.36. Applying the Bruggeman equation to the two-
phase model, the resin matrix conductivity can be calculated from
the previously calculated resin particle conductivities and the solu-
tion phase conductivities. A nearly constant resin matrix conduc-
tivity (which seems realistic for the electrolyte concentrations
studied) is calculated for a macropore volume fraction of approxi-
mately 0.15. The experimental value of about 0.10 is in good
agreement.

INTRODUCTION

Knowledge of the electrical conductivity of packed beds containing ion exchangers in contact with solutions of electrolytes is of interest as a means of ascertaining the mobilities of ions in the exchanger phase [1], especially when applied to the separation method known as electrochromatography [2]. Meredith and Tobias [3] have reviewed in depth the general problem of conduction in heterogeneous mixtures, while Kitchener [4], Sigodina et al. [5], and Helfferich [6] have summarized the more specific problem of conductivity involving ion exchangers. Experimental studies of the conductivity of packed beds containing ion exchangers are relatively few in number [1, 7-9].

In this work we have studied the electrical conductivity of the macroporous cation exchanger Duolite C-25 (produced by Diamond-Shamrock Corp.) [10, 11]. Macroporous exchangers differ from the conventional microporous resins such as Dowex 50, Amberlite IR-120, or Duolite C-20 only in that the resin is prepared with a certain volume-fraction of relatively open, unconnected channels [12].

EXPERIMENTAL

The cation exchanger used was macroporous cross-linked polystyrene sulfonate, Duolite C-25 in sodium form, purchased from Diamond-Shamrock Corp., Redwood City, Calif. This resin was wet-sieved, and the fraction that passed by a No. 20 U.S. Standard screen and was retained on a No. 28 screen was collected. The sodium-form resin used in conductivity runs was prepared by eluting the incoming resin with three cycles of 2 N HCl (reagent grade), distilled H_2O 1 N NaCl (reagent grade), and distilled water. Hydrogen-form Duolite C-25 was prepared in the same manner, but an extra treatment of 2 N HCl and distilled water was added. A small fraction of unsulfonated beads was removed by flotation. Titration of hydrogen ion eluted by NaCl form known weights of the hydrogen-form resin gave a cation-exchange capacity of 4.3 meq/g dry resin. The water content of the sodium form was 1.20 g/g dry resin.

Conductivity measurements were made using the following components: a Jones conductivity bridge (Leeds and Northrup Co.), an audio-frequency oscillator (Hewlett-Packard Co.), an oscilloscope null detector (Tektronix, Inc.), and two glass conductivity cells (one for measurements of solution conductivities, and one—shown in Fig. 1—for measurements on packed beds). A constant-temperature bath maintained the temperature within ±0.3°C. The packed beds were tapped during filling, and solution of the desired concentration was eluted over the packed bed until the resistance of the bed reached a constant value. A small excess of resin (of which the
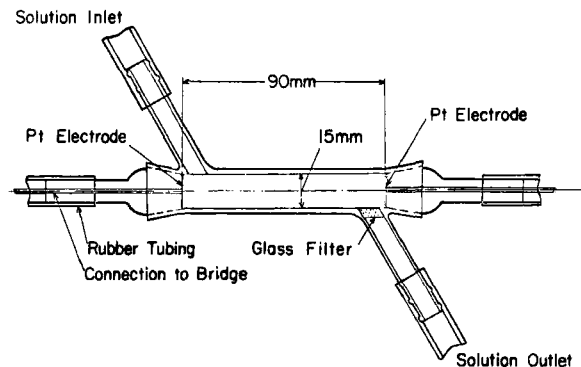
Solution Inlet

90mm

Pt Electrode

15mm

Pt Electrode

Pt Electrode

Rubber Tubing   Glass Filter
Connection to Bridge

Solution Outlet

Fig. 1. Conductivity cell used for packed beds.

exact amount was shown to have no measurable effect) was always kept in the upper inlet of the cell.

RESULTS AND DISCUSSION

Experimental Data

For mixtures of Na-form Duolite C-25 with NaCl solution, the interstitial concentration of NaCl was varied from 0.005 to 1.00 N; for the system of H-form Duolite C-25 with aqueous HCl, the concentrations of the latter ranged from 0.001 to 0.50 N. The cell constants of the two cells were determined using 0.01 N KCl. By use of the relation $\kappa = C/R$, the specific conductivities $\kappa(\Omega^{-1}/cm^{-1})$ of the various electrolyte solutions and the packed beds were calculated, where C is the cell constant (cm^{-1}), and R is the measured resistance (Ω) of the mixture.

Data for the sodium system (at 30 and 40°C) and for the hydrogen system (at 30°C) are plotted in Fig. 2. The point at which the bed and the interstitial solution have the same conductivity is termed the isoconductance point; at this one point the conductivities of resin and solution are equal.

The ratio of the specific conductivity (measured at the isoconductance point) of hydrogen-form resin to that of sodium-form resin is seen to be only about half the ratio of the ionic equivalent conductances of H^+ to that of Na^+ in aqueous solution. Spiegler and Coryell [1] postulated that an ion-exchange resin equilibrated with dilute aqueous solution conducts in part by a site-to-site transfer mechanism; such a mechanism appears quite probable for the Duolite C-25 matrix, which has a cross-linking of about 5.5% and an internal concentration of exchange sites greater than 2 M. Another
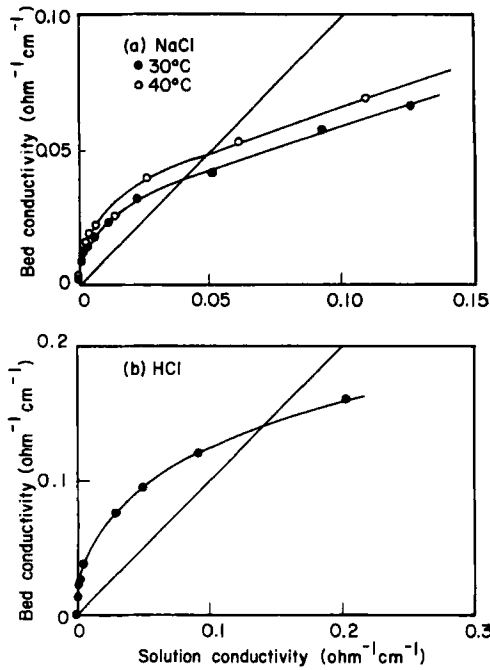
Fig. 2. Specific conductivity of packed bed containing Duolite C-25, plotted against specific conductivity of interstitial solution equilibrated with the packed bed. (a) Sodium-form contacted with solutions of NaCl at 30 and 40°C; (b) hydrogen-form contacted with solutions of HCl at 30°C.

difference between aqueous-solution and resin conductivities arises through the difference in the structure of water in the two phases. The isoconductance value is the most valid parameter for describing the electrical conductivity of the ion-exchanger matrix over a wide low-value range of interstitial-solution concentrations, provided that (1) there is no appreciable Donnan uptake of electrolyte by the resin, (2) no changes in resin structure occur when the interstitial-solution concentration is changed, and (3) there are only two phases present, an interstitial-solution phase and a homogeneous resin phase containing the cross-linked solfonated resin with its imbibed water.

Effect of Single-Phase Conductances

The properties of a heterogeneous mixture are not just simple sums of the corresponding properties of the individual phases,

weighted according to the volume-fraction occupied by each phase. For example, a dielectric constant of over 200 was measured for a resin-distilled water system, but this apparently high value was shown to arise naturally from the heterogeneous nature of the bed [13].

The theoretical treatment of the electrical or thermal conductivity of heterogeneous mixtures is not yet completely solved. The review by Meredith and Tobias [3] discusses the conditions for which various equations were derived. Packed beds of ion exchanges present special difficulties due to contact between conducting beads (so that a given bead does not have an environment of spherical symmetry about it). One must therefore choose from among the equations developed for dilute suspensions and assume the equation chosen applies to packed beds, or else use a more specific model for conductivity in packed beds of ion exchangers. Both approaches are attempted, taking into account the macroporous structure of Duolite C-25.

The Bruggeman equation [14] and the related equation due to Meredith and Tobias [3] are derived for geometric conditions moderately like those for a packed bed of spherical ion-exchanger particles. Parrish [9] found that an equation due to Son Frey, intended to apply to two-phase mixtures for which one phase occurs in isolated pockets, fit his results better than a second equation derived for two continuous phases by Son Frey. Since several equations fit experimental results moderately well, only the Bruggeman and Meredith-Tobias equations are applied. The aim here is mainly to present a simple and practical method for analyzing the conductivity of ion-exchanger packed beds. In particular, the sodium form of Duolite C-25 was chosen to illustrate the application of the method to the more complex macroporous exchanger.

For a packed bed of spherical particles of nearly uniform diameter, the volume-fraction occupied by the interstitial solution (the void-fraction) is in the range of 0.36-0.39 [15, 16]. A fairly accurate value of the void-fraction is required, since it is the dominant parameter in the theoretical equations which relate the conductivities of the two individual phases to the conductivity of the packed bed. For macroporous beads the situation is even more complicated, since the volume-fraction occupied by the macropores must also be known.

We adopt the notation: κ_b = the specific conductivity of the packed bed (containing wet resin beads plus interstitial solution or water); κ = the specific conductivity of the continuous, interstitial-solution phase; $\bar{\kappa}_p$ = the specific conductivity of the discontinuous, resin-particle phase; and f = the fraction of the bed volume occupied by the resin particle (the packing fraction). The equation derived originally by Bruggeman, and later by Baron [3] using a different

approach, is

$$\frac{\kappa_b - \bar{\kappa}_p}{(\kappa_b/\kappa)^{1/3}(\kappa - \bar{\kappa}_p)} = 1 - f$$

As pointed out by Helfferich [6], this equation is not applicable when the interstitial solution conductivity is very low. Meredith and Tobias [3], noting that this equation is more suited to packed beds than the better known Maxwell relation, derived a new equation which should serve as a convenient interpolation formula between Maxwell's and Bruggeman's equations. The Meredith-Tobias equation for spherical particles

$$\frac{\kappa_b}{\kappa} = \frac{[2(\bar{\kappa}_p + 2\kappa) + 2f(\bar{\kappa}_p - \kappa)][(2 - f)(\bar{\kappa}_p + 2\kappa) + 2f(\bar{\kappa}_p - \kappa)]}{[2(\bar{\kappa}_p + 2\kappa) - f(\bar{\kappa}_p - \kappa)][(2 - f)(\bar{\kappa}_p + 2\kappa) - f(\bar{\kappa}_p - \kappa)]}$$

served as a useful check on the Bruggeman equation.

The experimental values for the conductivity of the interstitial solution and of the packed bed, with $f = 0.64$ (the upper limit), were used to compute the conductivity of the resin-particle phase by use of the Bruggeman equation. These calculations did not take the macropores into account, as shown by the calculated increase in particle conductivity with increase in the interstitial solution concentration. This gradual increase is expected, since (1) even at low interstitial-solution concentrations the macropores should reach an electrolyte concentration level roughly equal to that external to the bead, (2) at higher interstitial-solution concentrations, 0.1 M and greater, the Donnan uptake of electrolyte becomes important, and (3) the resin begins to contract when equilibrated with interstitial concentrations above 0.1 M (which may result in a higher resin-matrix conductivity by bringing the exchange sites closer together). For dilute solutions, the macropore effect should predominate, since the Donnan uptake was shown by Sauer and co-workers [8] to involve only a slight correction, at least until the interstitial-solution conductivity is greater than the isoconductance value.

When the Bruggeman equation with $f = 0.58$ was used in conjunction with the data of Sauer et al. [8] for a microporous resin (Amberlite IR-120), the particle conductivity was constant for a wide range of interstitial concentrations and began to increase only at external concentrations above 0.1 M. These calculations lend support to our present treatment of the macroporous particle.

The Macropores

The equation of Fricke [17], discussed in detail by Meredith and Tobias [3], should be applied if the pores are most nearly approxi-

mated by an array of randomly oriented, ellipsoidal regions dispersed in the continuous resin matrix. Because of lack of exact knowledge of the pore structure, such an elaborate treatment is not justified, and a simpler approach is used. The macroporous structure is achieved [10] by prepolymerizing styrene monomer to a given viscosity and then copolymerizing the prepolymer with 5.5% by weight divinylbenzene (DVB). Any linear polymer which is trapped in the cross-linked structure is washed out either before or after sulfonation to produce a porous matrix.

Our view of the macropore phase within the bead is the reverse of that for the packed bed. Effectively the resin particle consists of a discontinuous (dispersed) macropore phase, with the hydrated resin matrix as the continuous phase. The macropores are assumed to have the same specific conductivity κ as the interstitial solution. The macropore volume-fraction relative to the total particle is denoted by χ and the specific conductivity of the wet resin matrix is denoted by $\bar{\kappa}_r$.

The Bruggeman equation can now be applied to the heterogeneous resin particle, written in the form

$$\frac{\bar{\kappa}_p - \kappa}{(\bar{\kappa}_p/\bar{\kappa}_r)^{1/3}(\bar{\kappa}_r - \kappa)} = 1 - \chi$$

If a reasonable value for χ can be measured or estimated, $\bar{\kappa}_r$ can be calculated.

Approximate values of χ were found in several ways:

(1) As a rather sensitive estimation method, the value of χ for which $\bar{\kappa}_r$ remains most nearly constant was calculated from Bruggeman's equation. If the macropores are properly accounted for, $\bar{\kappa}_r$ should be constant for the electrolyte concentrations studied. For each of the three systems a value of χ between 0.1 and 0.2 gave the most constant calculated values for $\bar{\kappa}_r$. The average values of $\bar{\kappa}_r$ were almost equal to the respective isoconductance points.

(2) Packed beds were equilibrated with solutions of NaCl, the NaCl was eluted with $NaNO_3$, and the eluted Cl^- was titrated. Assuming that the external void-fraction is 0.36 and that all additional Cl^- uptake occurs in the macropores, an average value of about 0.1 for χ was determined.

(3) Resin was equilibrated with solutions of NaCl, the external solution was centrifuged off, the beads were eluted with $NaNO_3$, and the liberated Cl^- was titrated. Values of χ slightly less than 0.1 were obtained.

(4) The densities and water contents of conventional microporous Duolite C-20 (from Diamond-Shamrock Corp.) and of Duolite C-25 were compared. If the larger water content of Duolite C-25 is attributed entirely to macropores, χ is slightly greater than 0.1. The

agreement between the calculated value using method (1) and the other three values adequately supports our choice of phases.

Another Model for the Resin Bed

Rather than resort to equations developed for hetergeneous mixtures, we can also analyze conductivity data in terms of the equivalent-conductor model for porous plugs, first proposed by Wyllie and Southwick [18] and applied by Spiegler and co-workers to packed beds of ion exchangers [8, 13, 19]. The bed is assumed to have three paths of electrical conductance in parallel. These three elements consist of (1) matrix and solution in series with each other, (2) a continuous matrix path (which accounts for contact between beads, a point not accounted for in the dispersion theories), and (3) a path exclusively through interstitial solution. Conductivity through macropores would be included in elements (1) and (3).

The porous-plug model involves three adjustable parameters, and can be expressed [8] by

$$\kappa_b = \frac{a\kappa\bar{\kappa}_r}{d\kappa + (1-d)\bar{\kappa}_r} + b\bar{\kappa}_r + (1-a-b)\kappa$$

where a, b, and d are the parameters. Data for the sodium form of Duolite C-25 best fit the above equation (assuming that $\bar{\kappa}_r$ equals 0.038) with the values $a = 0.64, b = 0.02$, and $d = 0.90$. This set agrees well with sets reported by Spiegler for other cationic exchangers [19].

Additional Aspects

Two other aspects of conductivity in macroporous resins are of interest. It has been established that the Nernst-Einstein relationship is applicable to ion-exchanger systems [1, 6]. If the specific conductivity of the matrix is known, the self-diffusion coefficient $\bar{D}_r$ ($cm^2 sec^{-1}$) of, for example, the sodium ion in the sodium-form matrix can be calculated from the relation

$$\bar{D}_r = \frac{10^3 RT\bar{\kappa}_r t}{F \bar{c}_r}$$

where R is the gas constant (watt sec $°K^{-1}$ $mole^{-1}$), T the absolute temperature ($°K$), t the transference number of the ion in the matrix, $\bar{c}_r$ the equivalent concentration of the ion in the matrix (meq ml^{-1}), and F the Faraday constant (coulombs eq^{-1}). At low interstitial concentrations where Donnan uptake is negligible, only the sodium ion can migrate relative to the matrix; the transference number is unity [1]. Assuming the pore volume-fraction is 0.15, we find that

$\bar{D}_r \approx 2.5 \times 10^{-6}$ cm^{2}sec^{-1} at 30°C. Such a value is in general agreement with the results of studies on other exchangers [5].

The temperature dependence of the conductivity of the sodium-form Duolite C-25 can be assessed by an Arrhenius-type equation:

$$\frac{d\ln\bar{\kappa}_r}{dT} \approx \frac{\Delta H\ddagger}{RT^2}$$

where $\Delta H\ddagger$ is the enthalpy of activation (cal eq^{-1}) for conductance through the matrix. Provided that $\Delta H\ddagger$ is constant over the small temperature range studied, we find $\Delta H\ddagger \approx 2$ kcal eq^{-1}.

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