N_{Sc} = Schmidt number, $\mu/\rho\mathfrak{D}$
N_{Sh} = Sherwood number, $k'D/\mathfrak{D}$
N_{St} = Stanton number, $h/c_p u\rho$
P = pressure, lb./sq.ft.
$\bar{u}$ = mean velocity, ft./hr.

Greek Letters

α = thermal diffusivity, $k/c_p\rho$, sq. ft./hr.
θ = mean residence time, hr.
μ = viscosity, lb./(ft.)(hr.)
ρ = density, lb./cu.ft.

Subscripts

a = arithmetic mean
M = logarithmic mean
T = terminal value

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The Composition Dependence of Effective Diffusivities for Electrolyte Penetration in Ion Exchange Resins

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During a recent analysis of a particle diffusion controlled ion exclusion process (1) in the system Dowex 50Wx8(Na^+ form)–water–sodium chloride–glycerol, literature values for the effective resin phase diffusivities of sodium chloride and glycerol (*4*) in this system were used to calculate theoretical column effluent curves. Because the resulting theoretical curves were in considerable disagreement with experimental effluent curves, a short experimental study was performed to check the reported diffusivities (in particular, sodium chloride). New sodium chloride diffusivity values, which gave excellent agreement between the theoretical and experimental sodium chloride effluent curves, were obtained. The purpose of this note is to present these new values, to explain the discrepancy between these new values and those reported earlier, and to indicate a method by which the new data may be correlated.

METHOD FOR MEASURING RESIN PHASE SODIUM CHLORIDE DIFFUSIVITIES

Effective resin phase diffusivities for sodium chloride were measured by the same technique used in the earlier study (*4*) with one important difference, which will be mentioned later. Briefly, the method involves saturating a bed of resin with a sodium chloride-glycerol–water solution of known composition, eluting the bed with a sodium chloride-free solution for a definite interval of time, extracting the sodium chloride remaining in the resin with water, and titrating the extract with standard silver nitrate solution to determine the total sodium chloride content. This procedure is repeated (using the same saturating solution) for several different elution times and a plot of the amount of sodium chloride remaining in the resin vs. elution time is prepared. By matching this plot with the following theoretical result, we obtain the sodium chloride diffusivity

$$\rho_i/\rho_i^\circ = (6/\pi^2) \sum_{m=1}^{\infty} (1/m^2) \exp\left(-m^2\pi^2 D_i\, t/R^2\right) \qquad (1)$$

The entire series of runs may be repeated for different saturating solution compositions to give information regarding the variation of the sodium chloride diffusivity with composition.

Inherent in the familiar theoretical Equation (1) are a number of assumptions: (a) pressure diffusion (associated with swelling and shrinking) may be neglected, (b) forced diffusion (for example due to electrical gradients) need not be considered explicitly, (c) the mass average velocity of the resin phase is zero, (d) the sodium chloride concentration over all particle surfaces is zero for $t > 0$, (e) there occurs no coupling between the sodium chloride diffusion flux and other diffusion fluxes, and (f) D_i is constant throughout the elution period. Assumption (b) is known (*2*) to be reasonably good for electrolyte diffusion in ion exchange resins where the coion concentration is considerably smaller than the counterion concentration, as in the present case. Assumptions (a), (c), (d), and (e) are probably reasonable, but have not yet been thoroughly checked. With regard to the last assumption, it is to be expected that the D_i may be strongly dependent on the composition of the internal solution of the resin phase, primarily through the dependence of the D_i on the viscosity of the internal solution, that is, through Nernst-Einstein effects (electrical effects, though present, do not lead to strong composition dependence).

PREVIOUS STUDIES

The resin phase sodium chloride and glycerol diffusivities reported in the literature (*4*) reflect the neglect of the above mentioned composition dependence. In this previous work, saturating

Table 1. Conditions and Results of the Investigation of the Variation of Resin Phase Sodium Chloride Diffusivity with Internal Solution Viscosity

Temperature: 25 ± 1°C. for all runs
Resin particle diameter range: 0.0297 to 0.0350 cm. (wet screening)
(diameter of 0.0324 used for calculations)
Resin bed volume range: 6 to 20 cc.
Elution flow rates: 50 to 70 (gal.)(min.)/sq. ft. empty bed cross section
Analysis for sodium chloride: titration with standard silver nitrate solution

	Saturating solution		Eluting	Internal		
Run series	wt. % sodium chloride	wt. % glycerol	solution, wt. % glycerol	solution viscosity, centipoise	Experimental sodium chloride, D_i sq. cm./sec. $\times 10^6$	$D_i \mu$ (sq. cm.) (centipoise)/ sec. $\times 10^6$
1	10.0	0	0	0.894	1.31 ± 0.08	1.17 ± 0.07
2	10.0	15.0	19.4	1.257	0.97 ± 0.06	1.21 ± 0.08
3	10.0	30.0	36.8	1.932	0.64 ± 0.04	1.24 ± 0.08
4	10.0	45.0	53.0	3.578	0.33 ± 0.02	1.18 ± 0.07

solutions containing as much as 25 wt. % glycerol were used, while all elutions were performed with distilled water. This procedure leads to a substantial decrease in the internal solution viscosity and to a corresponding increase in D_i during elution of the resin. In this study the invalid application of Equation (1) to the data implied, however, that the diffusivities of sodium chloride and glycerol were essentially independent of the composition of the saturating solutions. The explanation for this behavior seems to be that the curve-matching technique mentioned above relies primarily on the data for reasonably large times (the effect of the value of D_i on the log-log plot of Equation (1) is only readily apparent to the eye in the region of fairly large t). Since in this time region the internal solution is always reasonably dilute, then the matching procedure will necessarily result in D_i values which are reasonably constant and which are essentially equivalent to the D_i for dilute solution, regardless of the initial composition of the resin phase.

PRESENT EXPERIMENTAL WORK

If the Nernst-Einstein relationship, $D_i \mu$ = constant (at constant temperature), adequately characterizes the dependence of resin phase diffusivities on internal solution viscosity, then the experimental determination of diffusivities through matching of experimental data to Equation (1) will require the maintenance of time-invariant internal solution viscosity. On this basis a short experimental study was carried out in which the diffusivity of sodium chloride in Dowex 50Wx8 (Na^+ form) was measured under conditions of nearly constant internal solution viscosity. The one significant difference in procedure from that of the previous investigation was that, after saturating the resin bed with a sodium chloride–glycerol–water solution of a given composition, the bed was eluted, not with pure water, but with a water–glycerol solution with a composition designed to maintain a nearly constant internal solution viscosity during the elution period. The proper compositions of the eluting solutions were determined with the equilibria of Shurts and White (3) as follows. Given a saturating solution of, for example, 10% sodium chloride and 30% glycerol by weight, the equilibrium composition of the internal solution can be calculated from the equilibria

$$Y_S = 0.0286X_S + 1.408X_S^2 + 1.102X_S^2X_G \qquad (2)$$

$$Y_G = 0.5687\,X_G + 0.4472\,X_G^2 + 2.30\,X_G X_S - 1.13\,X_G^2\,X_S \qquad (3)$$

For $X_S = 0.1$ and $X_G = 0.3$, it is found that $Y_S = 0.0202$ and $Y_G = 0.2697$. Because of the low sodium chloride content of the internal solution, we may evaluate the viscosity of the internal solution by assuming the internal solution to be essentially a 27% glycerol solution. Since during the elution process $X_S \to 0$, then $Y_G \to 0.5687X_G + 0.4472\,X_G^2$. Thus, to maintain a nearly constant internal solution viscosity, the eluting solution must have a composition determined by the relationship $0.5687\,X_G + 0.4472\,X_G^2 = 0.2697$. From this it is determined that the eluting solution should be a 36.8% glycerol solution. (Since the diffusivity of sodium chloride in the resin is larger than that for glycerol, there will be a small variation of the internal solution viscosity during the elution. For the purposes of this study we assume that these deviations can be neglected.)

RESULTS

Table 1 summarizes the operating conditions and results of the experimental study. It may be noted that four different combinations of saturating and eluting solutions were used to cover a relatively wide range of viscosity. For each pair of saturating and eluting solutions, runs were made for five different elution times, usually 15, 30, 60, 90, and 120 sec. This yielded enough data to permit determination of the diffusivities sodium chloride to within 10%, using the curve-matching technique described earlier. It should be mentioned that the value of the sodium chloride diffusivity for dilute solution (no glycerol in either the saturating or eluting solution) agrees within the experimental accuracy with the dilute solution value of approximately 1.4 x 10^{-6} sq. cm./sec. obtained by the previous investigators. Also shown in Table 1 are calculated values of the product $D_i\mu$, the constancy of which (within the accuracy of the study) implies that the Nernst-Einstein relationship holds for the resin phase.

CONCLUSION

On the basis of limited data, it has been shown that the Nernst-Einstein relation has some promise as a means of estimating the dependence of resin phase diffusivities on the viscosity of the internal solution of the resin phase.

ACKNOWLEDGMENT

The author wishes to acknowledge the many helpful comments of Professor E. N. Lightfoot relative to this work, and to acknowledge the financial assistance of Union Carbide Corporation throughout the duration of the study.

NOTATION

D_i = diffusivity of species i, sq. cm./sec.
R = resin particle radius, cm.
t = time, sec.
X_i = weight fraction of species i in solution external to resin phase, dimensionless
Y_i = weight fraction of species i in internal solution of resin phase, dimensionless
μ = viscosity, g./(cm.)(sec.)
ρ_i = mass density of species i in multicomponent system, g./cc.
ρ_i^0 = mass density of species i in multicomponent system at zero time, g./cc.

Subscripts

i = arbitrary specie
S = sodium chloride
G = glycerol

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