

Solid Phase Transport of Glycerol and Sodium Chloride in Resin

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Diffusivities and equilibrium absorption of sodium chloride and glycerol in cation exchange resin Dowex-50 were determined by making a two-constant fit of experimental data to a diffusion model. The variables studied were: resin cross linkage—2% to 12% divinylbenzene, temperature—25° to 80°C, concentrations in the equilibrating solution, resin particle size, flow rate of the eluting distilled water. Diffusivities increase with decrease in cross linkage and with increase in temperature. The ratio of the diffusivities of sodium chloride or glycerol in the resin to that in water is between 0.2 and 0.35 for 2% DVB and between 0.025 and 0.1 for 12% DVB. Diffusivities were found to be independent of the third, fourth, and fifth variables. The amounts of solutes absorbed at equilibrium also increased with a decrease in cross linkage and an increase in temperature.

Most chemical reaction and separation systems involve the transport of one or more components in a solid phase. In processes such as solid catalyzed reactions the effect of solid phase transport may be negligible, although it is often difficult to identify it in the analysis of rate data. In other processes, such as ion exchange, the effect of solid phase transport may be large. In ion exclusion processes particularly the resistance to transport in the solid phase probably predominates in determining the effectiveness of separation.

The present investigation undertakes to determine the transport resistance which affects the separation of glycerol and sodium chloride through the use of a typical ion exchange resin, the sulfonated cross-linked polystyrene marketed as Dowex-50. The data have been evaluated on the basis of a diffusion mechanism.

EXPERIMENTAL

The experimental plan of this investigation was to determine the quantity of a given component which was extracted into water during a measured period of time from a known quantity of resin containing a definite, though unknown, amount of the component at time zero. These data were then fitted to the unsteady state diffusion equation written for a spherical particle on the assumption of a constant diffusivity with other appropriate assumptions

and boundary conditions, the result of the fitting process being values of diffusivities over a range of temperatures and concentration levels. The conditions of the experimental work were such that the transport resistance of the liquid phase was negligible.

MATERIALS USED

The resin used in this study was Dowex-50W, a sulfonated polystyrene resin cross linked with divinylbenzene. The degree of cross linking of the polystyrene chains is controlled by the amount of divinylbenzene used in the manufacture of the resin. In this study resin with 2, 4, 8, and 12% divinylbenzene was used. Dowex-50 is hard, tough, and usually in the form of spherical beads. When immersed in water or any other solvent it swells. The swollen resin is a gel. It may be considered as a homogeneous phase distinct from the external solution. The sodium form of the resin was used. The resin supplied by the manufacturer was treated repeatedly with concentrated sodium chloride solution and then washed with distilled water until free of chloride ion.

Batches of 20-to 50-mesh and 50-to 100-mesh resins were wet screened, and the resin particles caught by the wires of the screen were collected. These carefully sized

resin beads were dried at constant temperature of 20°C. and a constant humidity of 50%. Broken particles were rejected.

The diameter of the treated particles was measured under a microscope, and a mean diameter was calculated from measurements on 50 to 100 particles. The dimensions of the particles are presented in Table 1.

METHODS OF ANALYSIS

Sodium chloride and glycerol contents of the solutions analyzed were in the order of 10 to 1,000 p.p.m. Sodium chloride content was obtained by determining the concentration of sodium ions with a flame photometer. Glycerol was analyzed by oxidation with periodic acid and determining the excess periodate (7, 11).

EXPERIMENTAL PROCEDURE

For each resin and each particle size studied fifteen baskets made from stainless steel wire screen were filled with a weighed amount (1 g.) of the resin. The resin particles were spherical and uniform in size. Figure 1 shows a typical basket.

These baskets were immersed for about 12 hr. in a solution containing sodium chloride and glycerol in order to bring the resin to equilibrium with the surrounding solution.

Each basket was placed in a rubber conduit, and distilled water was pumped at high velocities through the assembly as indicated in Figure 2. During this time sodium chloride and glycerol transferred out of the resin particles and were carried away by the stream of the distilled water. Owing to high flow rate of the distilled water the equilibrating solution from the

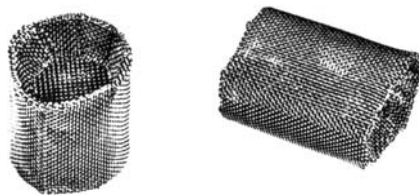


Fig. 1. A typical basket containing 1 g. of Dowex-50. (Size: 1 in. by 3/4 in. diameter.)

TABLE 1. SIZE OF RESIN PARTICLES USED
Diameter of the particles
in distilled water

Average	Range of 95% of particles	Sample size
0.6083 mm.	± 0.0315 mm.	129 particles
0.45 mm.	± 0.03 mm.	47 particles
0.965 mm.	± 0.04 mm.	50 particles
0.691 mm.	± 0.03 mm.	50 particles
0.706 mm.	± 0.03 mm.	50 particles

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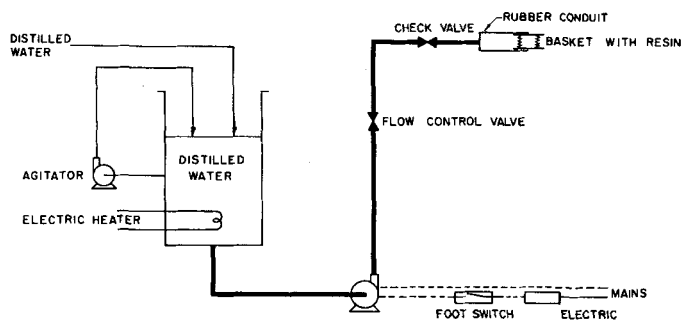


Fig. 2. Sketch of equipment used for diffusion study.

interstices between the particles was removed in a fraction of a second.

The process was interrupted suddenly by pulling the basket out of the conduit without discontinuing the flow. A synchronized electric timer recorded the time for which each basket was subjected to the stream of eluting distilled water.

The amounts of materials retained by the resin particles after elution with distilled water described above were determined by extracting them from the resin in 100 cc. of distilled water and analyzing the solution thus obtained. The actual extracting was carried out in three stages with about 30 cc. of distilled water for 10 min. for each stage. Further extraction showed that more than 99.7% of the material was extracted from the resin. The experimental conditions were such that during elution the film of the liquid adjacent to the resin particles has negligibly small concentration; consequently no special techniques are required for separating this film, and it does not produce any significant error in determining the amounts of materials retained by the resin particles after elution.

Data from an experimental run described above gave a table indicating the milligrams of sodium chloride and glycerol left in the resin when subjected to eluting distilled water for different periods of time.

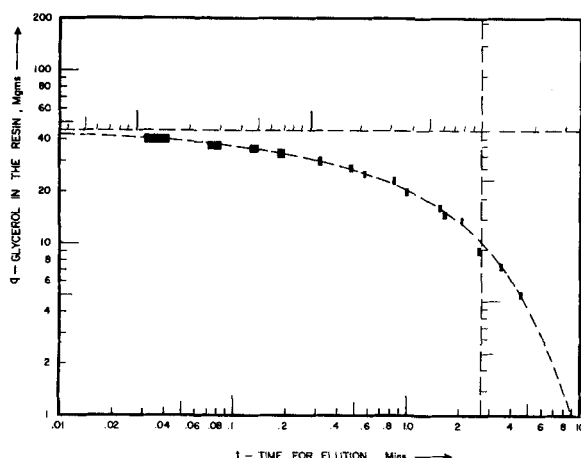


Fig. 3. Data and curve fitting for a typical run (7 to 11). Dotted lines give the dimensionless axes and the diffusion curve of the master plot that is superimposed on the data. The rectangle for each data point is determined by the accuracy of the measurements. At the origin of the master plot $q^* = 45$ mg. and $t^* = 2.7$ min.

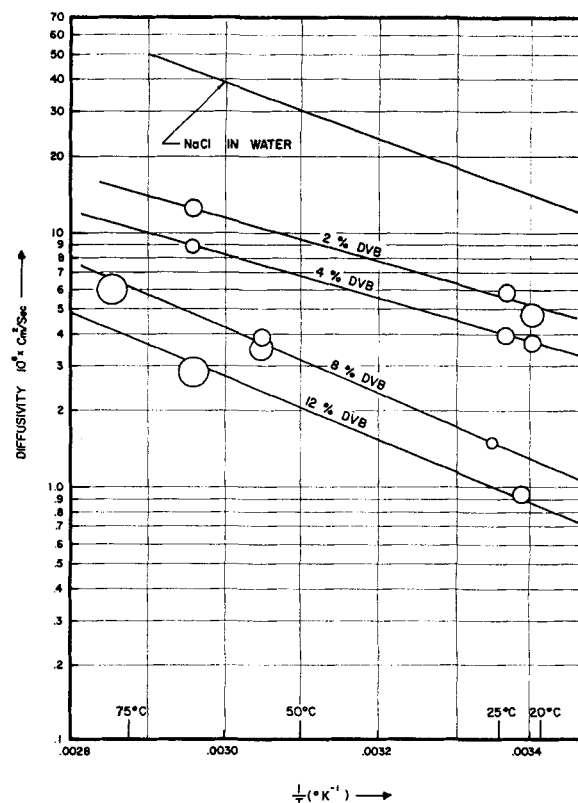


Fig. 4. Diffusivity of sodium chloride in Dowex-50. (Equilibrating solution 30% glycerol, 5% sodium chloride by weight.)

Table 2 shows the data obtained from a typical experimental run.

CALCULATION OF DIFFUSIVITIES

The amount of sodium chloride and glycerol remaining in the ion exchange resin at the time t depends on the amount that was present in equilibrium with the saturating solution at time zero and the resistance to the transfer of the materials from the resin to the eluting stream of water.

Equation (1) gives this relationship with a diffusion model and Fick's law assumed:

$$\frac{q}{q_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{n^2 \pi^2 D t}{R^2}} \quad (1)$$

The derivation of Equation (1) is readily available in the literature (1, 2, 3, 6). It is obtained by solving a partial differential equation representing a material balance for a unit element of volume within a resin particle. In the derivation it is also assumed that the resin particles are perfect spheres of equal and constant size, there is radial symmetry within each particle, the diffusivity is a constant, the concentration of the solute within the resin is uniform at the start of the elution process, and the concentration of the solute at the surface of the resin particles is zero at all times.

Generally fifteen to twenty points of data for q vs. t are obtained for each run. These are fitted to the above equation to obtain the values of the unknown parameters q_0 and D . The method of curve fitting used to obtain these parameters is described in the following section.

METHOD OF SUPERPOSITIONING

In Equation (1) q/q_0 is a unique function of the variable Dt/R^2 . Nu-

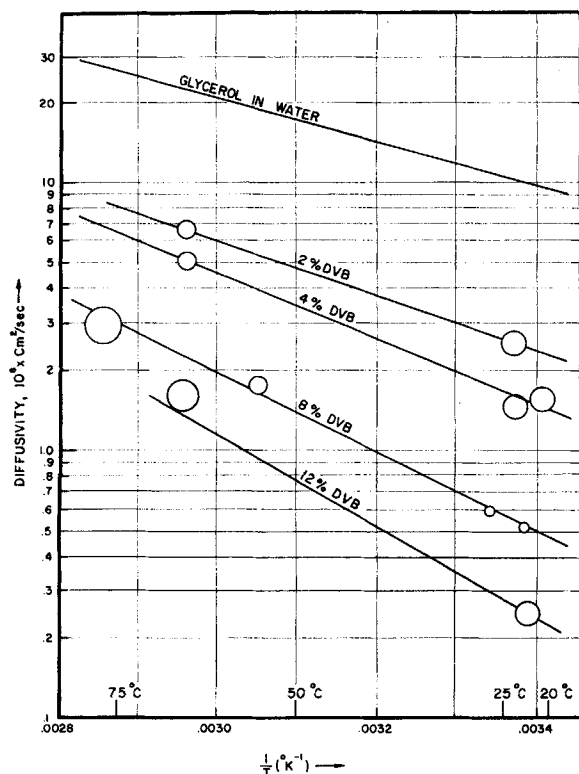


Fig. 5. Diffusivity of glycerol in Dowex-50. (Equilibrating solution 30% glycerol, 5% sodium chloride by weight.)

merical values of this function are available at several places in the literature (8, 12). A table of values, computed with the help of a digital computer and reported by Reichenberg (5), was used in this research. From this table a master curve was drawn by plotting the values of q/q_0 vs. $\pi^2 Dt/R^2$ on a logarithmic scale. For different values of the parameters q_0 , R , and D a curve of q vs. t would be obtained from the master plot by multiplying the ordinate by $1/q_0$ and the abscissas $\pi^2 D/R^2$. Since the multiplication by a constant is equivalent to a fixed displacement on a logarithmic scale, a plot of q vs. t on the same logarithmic scale as the master curve described above would have exactly the same shape as the master curve and would be displaced laterally along the two coordinate axes by the amounts $\log 1/q_0$ and $\log \pi^2 D/R^2$ respectively.

Hence in order to make a two-constant fit of the data of q vs. t the data are plotted on a logarithmic paper. A master plot of q/q_0 vs. $\pi^2 Dt/R^2$ is made on a transparent logarithmic paper on the same scale as the data. Now the master plot is moved horizontally and vertically, without any rotation at all, over the plot of the data until a good fit is obtained. When such a fit is obtained, the point on the master plot with the coordinates $q/q_0 = 1$ and $\pi^2 Dt/R^2 = 1$ coincides with some point, say (q^*, t^*) , on the paper on which the data is plotted. The co-

TABLE 2. DATA FROM A TYPICAL RUN

Run number: 7 to 11
Temperature: $(26.0 \pm 0.2)^\circ\text{C}$.
Cross linkage of the resin: 8% divinyl benzene
Weight of resin each basket: 1 g. (air dry) at 50% relative humidity and 25°C .
Resin saturation time: 16 hr.
Saturation solution: 9.80 wt. % sodium chloride and 9.49 wt. % glycerol

Time for elution, min.	Total amount of solutes, mg. glycerol	Remain- ing in the resin, mg. sodium chloride
0.037	39.8	
0.078	36.4	8.8
0.133	35.6	7.94
0.190	33.2	6.24
0.320	30.0	5.91
0.475	27.15	5.19
0.573	25.07	4.08
0.847	23.15	3.56
1.003	20.4	2.98
1.010	20.4	2.63
1.545	15.92	1.90
1.645	14.68	1.48
2.060	13.6	1.062
2.598	8.95	0.48
3.465	7.34	0.30
4.497	4.955	0.125
0	45.2*	11.7*

* The amounts of glycerol and sodium chloride at the zero elution time are included here only for comparison. They are not part of the data but are obtained from the correlation of the data in accordance with the method described in the next section.

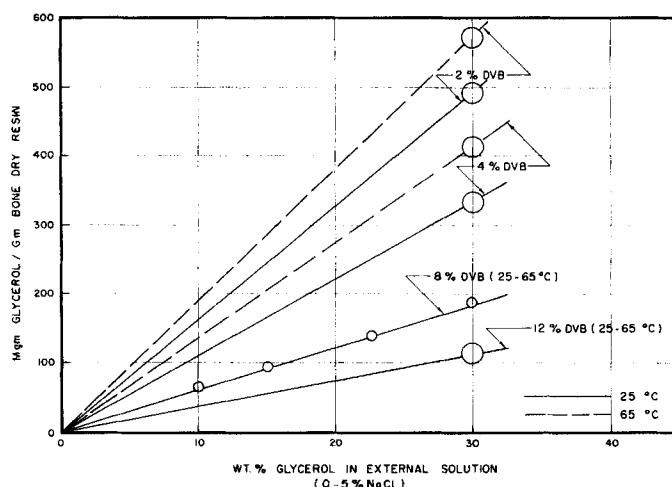


Fig. 6. Equilibrium data for glycerol in Dowex-50 (sodium form).

ordinates of this point q^* and t^* are read. Then the constants of the fit are obtained simply from the relations

$$q_0 = q^*$$

$$R^2/D\pi^2 = t^*$$

Figure 3 shows data from a typical run, plotted on the logarithmic scale and fitted by the method described here. As can be seen the range of q/q_0 covered by the data is from 0.9 to 0.05; that is the diffusion equation is fitted to a very wide range of the elution process. The range of values of time for the elution period for all data was generally 2 sec. to 10 min.

RELIABILITY OF THE METHOD OF SUPERPOSITIONING

To get some information about the reliability of the method of superpositioning a run of thirty-five data points was taken, and the data were plotted on three logarithmic papers; the first had the eighteen odd numbered data points of the run, the second had seventeen even numbered data points, and the third had all the thirty-five data points. All the three sets of data were fitted by ten different individuals by superpositioning a master plot, and the values of q^* and t^* were obtained. The values obtained in all the three fits agreed with each other to $\pm 5\%$.

RESULTS

Table 3 shows the diffusivities of sodium chloride and glycerol in Dowex-50 with 8% divinyl benzene at 25°C . obtained by fitting the data to diffusion model. As can be seen from the table the same values of diffusivities are obtained for different concentrations of equilibrating solutions, different resin sizes, and different flow rates of the eluting distilled water, justifying the use of the diffusion

model and the boundary conditions answered in the derivation of Equation (1). Runs made with different amounts of resin in the baskets and radically different shapes of the baskets also gave the same values of diffusivities.

Figures 4 and 5 show the diffusivities of sodium chloride and glycerol in wet Dowex-50 as a function of temperature and the cross linkage of the resins (expressed as per cent divinylbenzene content). For comparison the diffusivities of glycerol (15) and sodium chloride (13) in water are also shown on the figures. For the temperature range of 25° to 80°C. the ratio of the diffusivities of sodium chloride or glycerol in the resin to those in water is between 0.2 and 0.35 for 2% divinylbenzene and between 0.025 and 0.1 for 12% divinylbenzene.

Resins containing 2, 4, 8, and 12% divinylbenzene were used in the study. As the cross linking (per cent divinylbenzene) increases, the diffusivities decrease.

Diffusivities increase with increased temperatures. For resin with 8% divinylbenzene a plot of the logarithms of diffusivities vs. the reciprocals of the absolute temperatures gave straight lines for the experiments at 25°, 55°, and 78°C. For other cross linkages only two temperatures were investigated, 25° and 65°C., and the straight lines were drawn on the log *D* vs. 1/*T* plot as mentioned above.

Figures 6 and 7 show the equilibrium data obtained in this study. The limited range of concentrations covered was chosen from the range of concentrations encountered in industrial separations of glycerol and sodium chloride. The ordinates in Figures 6 and 7 are milligrams of glycerol and sodium chloride in 1 g. of bone dry resin, since these values are obtained directly from the data for each run

TABLE 3. DIFFUSIVITIES OF SODIUM CHLORIDE AND GLYCEROL IN DOWEX-50W X 8% DVB AT 25°C.

In general the diameter of the resin particles was 0.608 mm., the weight of the resin in each basket was 1.000 g., and the superficial velocity of eluting water was 150 cm./sec. except in the cases noted below the table.

	Conc. of equilbm. solution		Diffusivity of the resin	
	wt. % NaCl	wt. % Glycl	cm./sec. × 10 ⁶ NaCl	Glycerol
Diffusivity of sodium chloride as a function of concentrations	2	0	1.25 ± 0.2	
	5	0	1.5 ± 0.2	
	10	0	1.4 ± 0.2	
	10	10	1.45 ± 0.2	
	15	5	1.3 ± 0.2	
Diffusivity of glycerol as a function of concentrations	2	2		0.57 ± 0.05
	0	10		0.50 ± 0.05
	2	25		0.54 ± 0.05
	10	10		0.57 ± 0.05
	15	5		0.50 ± 0.05
Diffusivities as a function of particle size	10	10	1.45 ± 0.2	0.57 ± 0.05
	10	10	1.45 ± 0.2	†
	10	10	1.4 ± 0.2	0.55 ± 0.07†
Diffusivities as a function of flow rates	10	10	1.45 ± 0.2	0.57 ± 0.05
	10	10	1.4 ± 0.2	0.55 ± 0.05*
Diffusivities as a function of the weight of the resin sample	10	10	1.45 ± 0.2	0.57 ± 0.05
	10	10	1.4 ± 0.2	0.55 ± 0.05††
	10	10	1.4 ± 0.2	0.53 ± 0.05**

† The diameter of the resin particles was 0.450 mm.

* The superficial velocity of the eluting water was 30 cm./sec.

†† The weight of resin in each basket was 0.500 g.

** The weight of resin in each basket was 2.000 g.

and they are independent of the swelling and shrinking of the resin and the volume changes accompanying the same.

The amounts of sodium chloride and glycerol absorbed by the resin at equilibrium increases with decreased divinylbenzene cross linkage. Temperature produces, comparatively, a small effect on the equilibrium values. For higher percentages of divinylbenzene in the resin the effect of temperature on the equilibrium absorption is smaller

than that for lower percentages of divinylbenzene.

DISCUSSION

The experimental setup and the conditions were so devised as to render quite reasonable the assumptions involved in the derivation of Equation (1), such as uniform spherical particles, constant initial and surface concentrations, etc. A very high flow rate of eluting distilled water was required to rapidly replace the concentrated equilibrating solution from the interstices of the resin particles. Otherwise for small values of time (2 to 15 sec.) large errors would be introduced in the data in two ways. Since the total amounts of solutes eluted from the resin are of the order of 10 to 100 mg., even a small amount of equilibrating solution present in the liquid film adhering to the resin would produce a large error in the final measurement of the amount of solutes present in the resin. At the start of the elution process the resin would not be subjected to the condition of zero concentration of the solute at the interface, and a time lag would be introduced which in its turn would result in a lower value of diffusivity on fitting the data. The actual flow rate used in this research gave a superficial velocity of 150 cm./sec. through the resin bed. At this flow

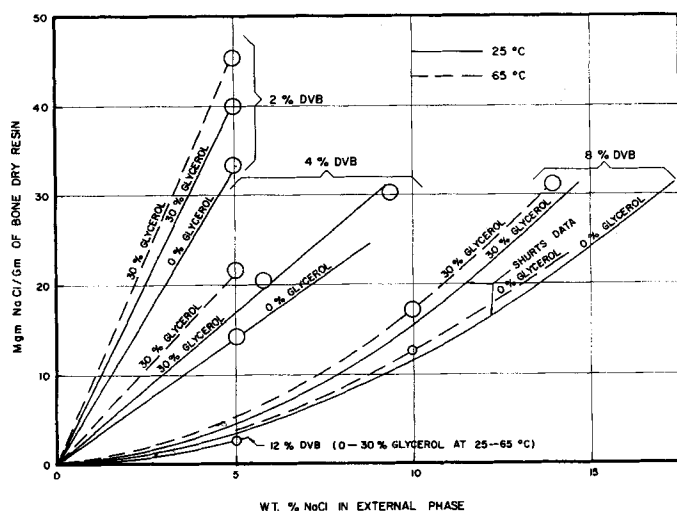


Fig. 7. Equilibrium data for sodium chloride in Dowex-50 (sodium form).

TABLE 4. EQUILIBRIUM ABSORPTION OF SODIUM CHLORIDE AND GLYCEROL IN DOWEX-50 WITH 8% DVB AT 25°C.

Concentrations of the solutes in aqueous phase		Milligrams of solute per gram of air dry resin				
		Glycerol		Sodium chloride		
wt. % Glycerol	wt. % NaCl	From curve fitting of data in this study	Calculated from Shurts correlation (9, 10)	From curve fitting of data in this study	Calculated from Shurts correlation (9, 10)	Reported by Whitcombe (14)
26.6	1.859	130	120			
4.85	15.0	25	24.7	22.5	24.4	28.1
1.91	2.3	7.5	7.5	1.0	0.86	9.9
9.66	9.94	45	45.7	11.0	10.0	11.5
9.54	0	38	37.4			
0	2.02			0.8	0.716	0.82
0	4.95			3.7	2.9	3.32
0	10.01			11.0	9.25	11.6

rate more than 99.5% of the equilibrating solution was displaced from the interstices of glass beads of the same size in less than a second. The flow rate was more than adequate to make the mass transfer resistance through the liquid film negligible and to carry away the eluted solutes so that their concentration in the bulk of the liquid phase during elution stayed at less than a part per million.

The derivation of Equation (1) assumes that the diameter of the resin particles and diffusivity are constant. Experimental evidence shows that for the range of concentrations studied in this research these are reasonable assumptions for the resin with 8% divinylbenzene (note Table 3). The effect of varying concentrations was not studied for other cross linkages. It is possible that for the resins with smaller degrees of cross linkage the diffusivities may be functions of the concentrations, since these resins swell and shrink more with changes in concentrations. The change in diameter of resin with 8% divinylbenzene is less than 4% with the changes in concentrations in the range of 0 to 15% sodium chloride and 0 to 25% glycerol (9, 10). In all calculations in this research the values of the diameter of the resin particles in distilled water were used. When a resin shrinks with change in concentrations, the diffusivity is likely to be reduced. Also the path for diffusion gets smaller. In a sense, these two effects are compensating.

For one cross linkage of the resin, 8% divinylbenzene, and one temperature, 25°C., it is possible to compare the equilibrium amounts of sodium chloride and glycerol obtained in this study with the values reported by Shurts and White (9, 10) and Whitcombe, Banchemo, and White (14). Table 4 shows that there is a fairly good agreement. This is interesting since the data of the other researchers

were taken under static conditions of equilibrium, whereas the values in this thesis have been obtained from fitting unsteady state rate data.

The values of diffusivities obtained in this research are essentially empirical constants obtained by fitting data to the diffusion model. Since sodium chloride is ionized, diffusion of sodium chloride as such is accomplished by the simultaneous diffusion of sodium ions and chloride ions. In accordance with the theory of electrolytic diffusion in ion exchanges (4, 5), the driving force for the diffusion consists of the concentration gradients and the electrical potential gradients caused by the difference in diffusivities of chloride ions and sodium ions. The net flux of the two ions however is the same in order to assure electroneutrality. Experimental data measuring the net flux may then be correlated as in this research to give an apparent value of diffusivity for sodium chloride molecules.

In general, concentration dependence of the apparent diffusivity of an electrolyte may be expected. The fact that in the present research the diffusivity of sodium chloride was independent of concentration indicates that either the diffusivities of the sodium and the chloride ions are about equal or that the experimental conditions are such that the diffusion of either one or the other ion is the rate controlling mechanism. In the present case of elution measurements the theory of electrolytic diffusion mentioned above leads one to expect that the rate would be controlled by the diffusion of the so-called co-ion in the resin, namely the chloride ion in the present investigation.

NOTATION

c = concentration of the solute at a distance r from the center of the resin sphere and at time t (g. or g.-moles/cc.)

D = molar concentration of (diffusing solute diffusing ion) within a resin particle (g.-moles/cc.)
 e = 2.7183
 n = variable of summation for a series of terms
 r = distance from the center of the resin sphere (cm.)
 R = the radius of the resin spheres (cm.)
 q = the total amount of sodium chloride or glycerol left in the resin at time t (g. or g.-moles)
 q_0 = total equilibrium amount of sodium chloride or glycerol present in the resin before the elution, that is at time t equal to zero (g. or g.-moles)
 t = time (sec.)
 ∂ = partial differential operator
 π = 3.1416
 Σ = summation

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