

Ion Exclusion Equilibria in the System Glycerol–sodium Chloride–water–Dowex-50

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Ion exclusion is an operation in which an ion exchange resin is used to separate an electrolyte from a nonelectrolyte in a polar solvent. An ion exchange resin tends to absorb a nonelectrolyte and to exclude an electrolyte. This is described quantitatively by the equilibrium distribution of the electrolyte, the nonelectrolyte, and the solvent between the resin phase and the liquid phase surrounding the resin.

As no ternary distribution data applicable to ion exclusion are available, and only a few binary data have been published, a principal purpose of this investigation was to determine the distribution data for a typical system: glycerol–sodium chloride–water–Dowex-50.

EXPERIMENTAL PROCEDURE

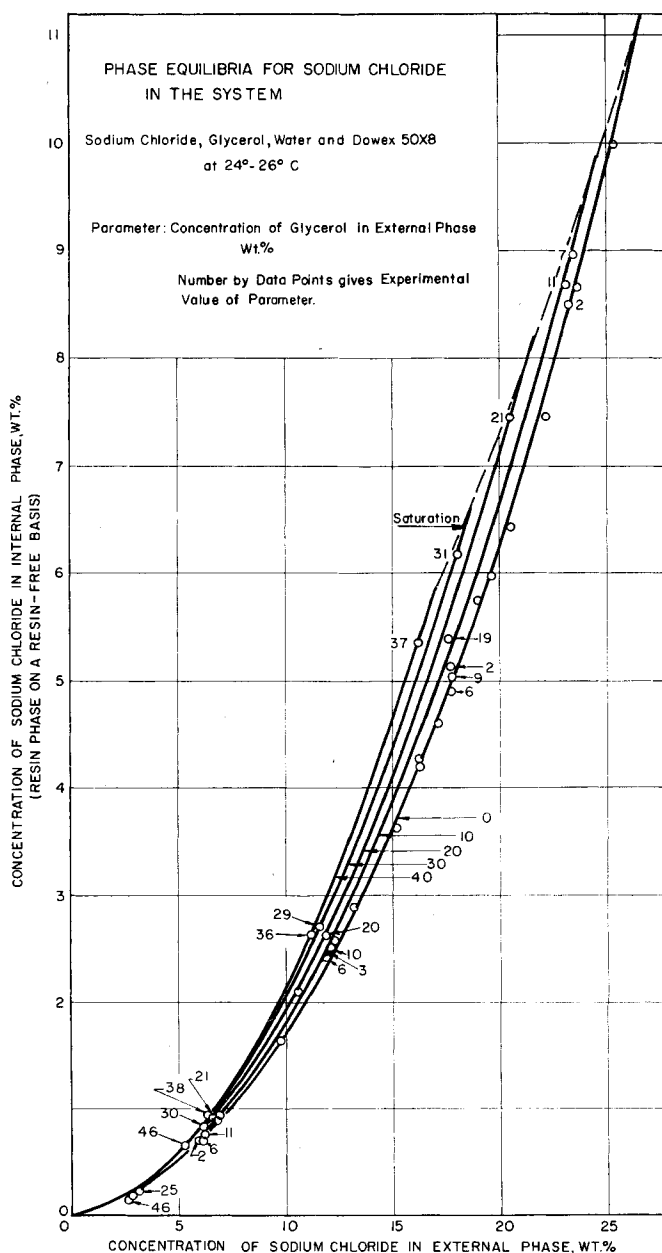
Material-balance Technique

The material-balance technique¹ is one of several methods of determining the composition of the resin phase. It depends upon the determination of the volume and composition of the external solution, which is in equilibrium with resin. Once the volume and composition of the external solution at equilibrium are known, the composition of the resin phase at equilibrium may be calculated by difference, provided the initial quantities of all the components have been measured. This may be clarified by considering the following volume balance,

$$V_R' + V_S' = V_R'' + V_S'' + \Delta V_T \quad (1)$$

Fig. 1. →

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Of these five quantities, all but V_s'' , the final solution volume, can be measured directly and accurately. The initial volumes of the resin and solution can be determined from their weight and density. The final volume of the resin is a function of the initial weight of air-dry resin and the composition of the final external solution. It can be accurately determined by swelling measurements conducted independently of equilibrium experiments. Likewise the correction to additive volumes ΔV_T can be correlated as a function of the composition of the external solution by independent measurements. Once the final solution volume V_s'' has been calculated, the weight of every component in both phases may be determined by difference.

Methods of Analysis

It was necessary to analyze accurately for sodium chloride and glycerol in aqueous solutions, as errors were magnified when differences were taken in the material-balance equations. A combination of density measurements and titration for the chloride ion was developed for this purpose.

The densities of ternary mixtures in the system sodium chloride-glycerol-water were determined by a careful pycnometer technique to a precision of ± 0.00003 g./ml. The compositions of binary mixtures of sodium chloride-water and glycerol-water were determined from density data. The sodium chloride content of dilute solutions was determined by a Beckman Flame Photometer and spectrophotometer, both of which could be read to several parts per million. They were calibrated by diluting standard salt solutions the concentration of which had been determined by density. The sodium chloride content of the ternary solutions was determined by Fajan's method of analysis (14).

The glycerol concentration in ternary mixtures was determined from the sodium chloride titrations and the density data. The precision of the ternary analysis was calculated to be ± 0.02 wt. % for sodium chloride and ± 0.04 wt. % for glycerol.

The resin contained 17.79 ± 0.10 wt. % water and had a density of 1.4673 g./ml. in the sodium form. It had an equivalent weight, milliequivalents/gram, of 5.00 ± 0.06 in the hydrogen form.

The initial volume of the air-dry resin was calculated from its initial weight and density, determined by the displacement of xylene. The decrease in the total volume of both resin and solution phases caused by the equilibration ΔV_T was measured in a pycnometer, the results of these measurements being shown in Figure 1.

The increase in volume of the air-dry resin caused by equilibration with various final concentrations of sodium chloride and glycerol solutions was measured by observing with Barker's technique (1) the swelling of resin beads under a microscope. [Each diameter ratio at a given concentration required at least twenty observations on ten beads to give a precision for D/D_0 of ± 0.0004 . The results of the swelling measurements are shown in Figure 2 and the data are available elsewhere (11)].

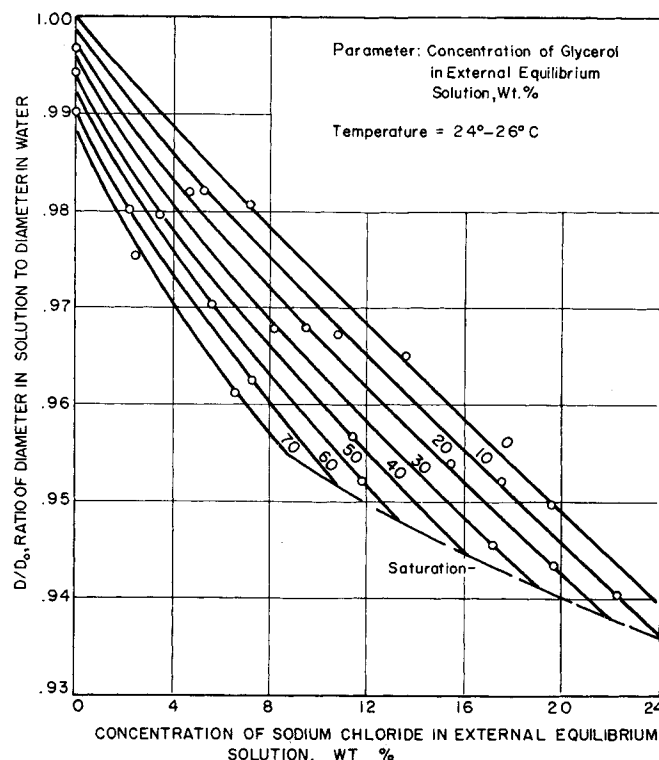


Fig. 2. Swelling of the resin.

Distribution Data

A weighed quantity of air-dry resin of known composition was equilibrated with a weighed quantity of a solution containing a known concentration of sodium chloride and glycerol. A portion of the equilibrium solution phase was analyzed to determine the sodium chloride and glycerol concentrations. These data enable accurate material-balance calculations to be made to determine the resin-phase composition. The experimental results are shown in Figures 3 and 4 and in Tables 1 and 2.

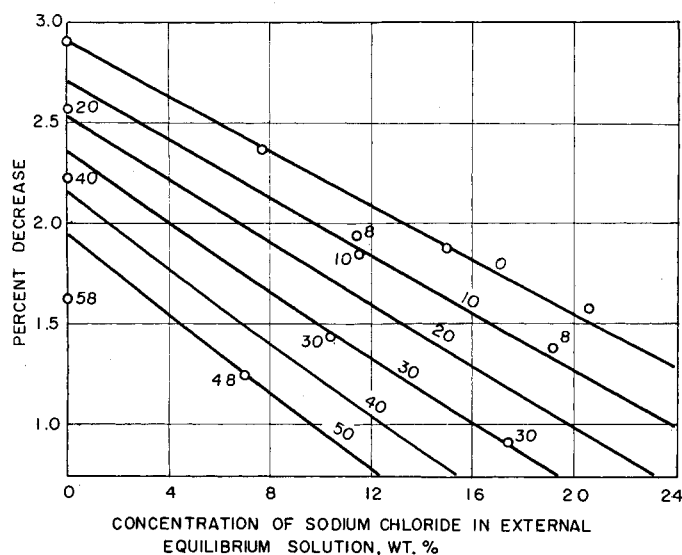
The data were correlated by the method of least squares to give the curves of Figures 3 and 4. Salt is seen to have a pronounced effect upon the distribution of glycerol, but the effect of glycerol upon salt is considerably less. The distribution coefficient Y/X for salt varies between 0.03 and 0.40 and that for glycerol between 0.6 and 1.3. The difference between their distribution coefficients makes their separation possible by ion exclusion, and the strong influence of the salt upon the glycerol is beneficial to this separation.

The sodium chloride distribution data were correlated with a standard residual error of ± 0.07 weight % and the glycerol data with an error of ± 0.15 weight %. It is enlightening to study the experimental errors which will cause deviations of the aforementioned magnitude. Table 3 summarizes the most important experimental errors. The controlling error in both cases appears to be the analysis of the external phase. The swelling error is probably next in importance. Table 3 serves as a minimum standard that must be met to take equilibrium data of the same precision when a 40-g. sample of resin is used.

TABLE 1. PHASE EQUILIBRIA DATA FOR BINARY EXTERNAL SOLUTIONS

Resin: Dowex-50, DVB content = 8.7, sodium form
 Temperature: 24° to 26°C .
 Notation: X_s , X_g concentration of sodium chloride or glycerol in the external phase, respectively, weight per cent. Y_s , Y_g concentration of sodium chloride or glycerol in the internal phase, respectively, weight per cent. The internal phase is defined as the solution in the resin phase on a resin-free basis.

Sodium chloride-water		Glycerol-water	
X_s	Y_s	X_g	Y_g
6.74	0.91	17.94	11.68
9.79	1.64	32.50	22.87
12.35	2.55	52.62	42.50
15.27	3.61	72.11	65.88
17.17	4.60	84.25	82.88
20.54	6.43		
23.10	8.16	12.41	7.71
		22.18	14.70
6.95	0.93	32.70	23.22
10.58	2.10	43.12	32.85
13.20	2.88	49.55	39.28
15.96	4.03	62.45	53.81
19.01	5.72	74.38	68.81
19.70	5.95	88.63	84.85
22.15	7.45		
23.63	8.64	2.24	1.52
		6.73	4.42
16.28	4.17		
16.25	4.27		
2.82	0.18		



terms were added to a correlating equation by trial and error until the deviations of the points showed no bias when plotted against the variables. The results of this process, which is reported in detail elsewhere (10), were for glycerol

$$\begin{aligned}
Y_G = & 0.5687X_G + 0.004472X_G^2 \\
& + 0.023023X_GX_S \\
& - 0.000113X_G^2X_S \\
& + 0.000661X_G^{0.5}X_S^2 \quad (2)
\end{aligned}$$

Standard residual error = 0.149

TABLE 2. PHASE EQUILIBRIA DATA FOR
TERNARY EXTERNAL SOLUTIONS

Resin: Dowex-50, DVB content = 8.7, sodium form

Temperature: 24° to 26°C.

System: Sodium chloride-glycerol-water-Dowex-50

Notation: X_S , X_G concentration of sodium chloride or glycerol in the external phase, respectively, weight per cent

Y_s , Y_G concentration of sodium chloride or glycerol in the internal phase, respectively, weight per cent. The internal phase is defined as the solution in the resin phase on a resin-free basis.

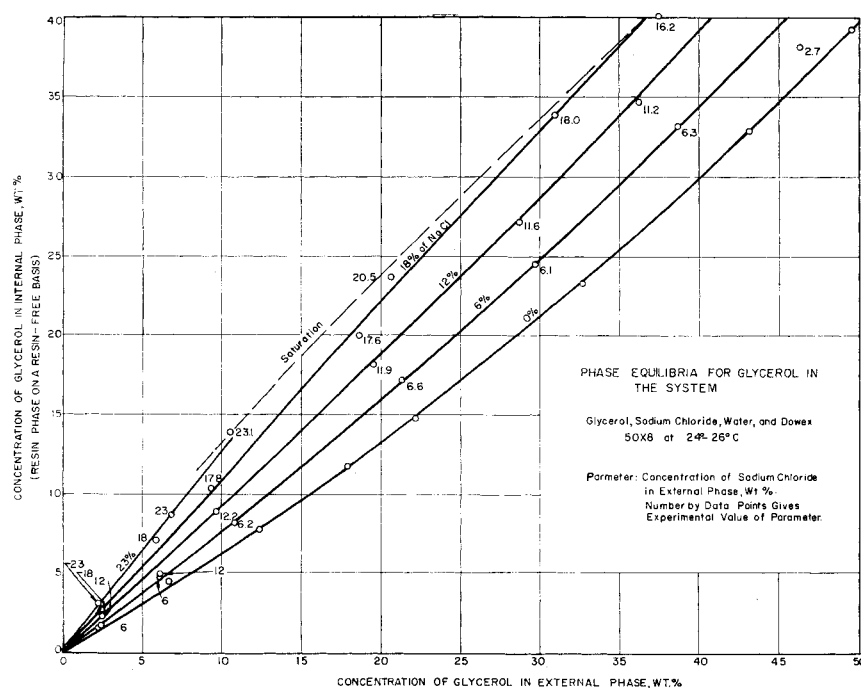


Fig. 4.

External phase		Internal phase	
X_S	X_G	Y_S	Y_G
6.21	10.81	0.75	8.17
11.19	36.16	2.62	34.73
16.21	37.45	5.34	40.13
17.79	9.38	5.01	10.32
6.15	29.78	0.83	24.46
11.61	28.69	2.70	27.08
11.86	19.59	2.61	18.02
17.63	18.65	5.38	19.94
12.20	9.70	2.51	8.92
6.59	21.35	0.91	17.05
6.32	38.63	0.95	33.19
18.03	30.93	6.17	33.82
12.11	2.58	2.50	2.27
23.23	2.33	8.50	3.02
5.98	2.49	0.72	1.72
17.77	2.54	5.12	2.61
23.44	6.85	8.95	8.64
23.09	10.51	8.68	13.90
6.13	6.18	0.69	4.70
11.93	6.15	2.41	4.90
17.77	5.90	4.88	7.02
3.18	25.27	0.21	19.14
2.70	46.32	0.16	38.17
20.49	20.63	7.45	23.61
5.31	45.76	0.65	40.49

CORRELATION OF THE DATA

It was impractical to make equilibrium determinations at a constant concentration parameter. Thus the data require that a family of curves be fitted to the points. The precision of the data seemed to justify developing suitable equations rather than drawing curves interpolated by eye through the points. A method reported by Ezekiel (4) was used in which

The following errors will cause the residual error of correlation.

Residual error of correlation
Weight of component in resin phase
Analysis of component in external phase
Swelling ratio, D/D_0
Total volume change
Moisture content of reagent

Sodium chloride	Glycerol
±0.07 wt. %	±0.15 wt. %
14 mg.	30 mg.
0.02 wt. %	0.04 wt. %
0.0007	0.0007
0.2 vol. %	0.2 vol. %
0.05 wt. % H ₂ O	0.05 wt. % H ₂ O

For sodium chloride

$$Y_s = 0.0286X_s + 0.01408X_s^2 + 0.0001102X_sX_g^2 \quad (3)$$

Standard residual error = 0.066

Where

X_g, X_s = weight per cent in external phase of glycerol and sodium chloride respectively

Y_g, Y_s = weight per cent in resin phase on a resin-free basis of glycerol and sodium chloride respectively

DISCUSSION

The equilibrium data of Figures 3 and 4 indicate that glycerol is absorbed by resin in preference to sodium chloride when a solution of glycerol-sodium chloride-water is equilibrated with resin. Thus resin can be used as a fractionation medium for separating glycerol from sodium chloride. The analysis of the performance of a continuous ion exclusion column using the equilibrium data of this investigation will be the subject of a future paper.

It has been shown previously (5, 6, 13) that the basic equation for ion exclusion is

$$RT \ln a_{i,e}^* = RT \ln a_{i,r}^* + P_r \bar{V}_{i,r} \quad (4)$$

The glycerol-water binary is especially suited for the study of activity coefficients in the resin phase. Equation (4) may be so arranged that the only unknown variable is $a_{g,r}^*$, the activity of glycerol in the resin phase at zero (or atmospheric) pressure. The activity coefficients of glycerol in water at 0°C. are reported by Lewis and Randall (10). These values were estimated to change by not more than ± 0.003 at 25°C. by vapor-pressure data from Carr, Townsend, and Badger (2). The osmotic pressure for this case was reported to be 200 atm. by Glueckauf (5) and 75 atm. by Gregor (7). The partial molal volume of glycerol can be calculated from density data, and the concentrations at equilibrium from Figure 4. The resulting stoichiometric molal activity coefficients for glycerol in the resin phase are given in Table 4.

TABLE 4. ACTIVITY COEFFICIENTS OF GLYCEROL IN THE RESIN PHASE

Glycerol molality in resin phase	Activity coefficients $\gamma_{g,r}^*$		
	Osmotic pressure P_r , atm.		
	200	75	1
0.26	0.973	1.456	1.756
0.12	0.976	1.460	1.761
0.29	0.990	1.480	1.787
0.59	1.007	1.508	1.820
1.20	1.048	1.567	1.889
3.12	1.197	1.790	2.160

Thus it is seen that the activity coefficient in the resin phase is sensitive to the value assigned to the osmotic pressure. This observation emphasizes that fundamental data in the form of activities and osmotic pressure are not available to permit quantitative application of the theoretical equation.

The usefulness of this equation for predicting the qualitative behavior of phase equilibria will be illustrated. The following data show the effect of glycerol upon the activity coefficient of hydrochloric acid (9).

TABLE 5. MEAN ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN GLYCEROL-WATER SOLUTIONS AT 25°C.

Molality of hydrochloric acid	Activity coefficients of hydrochloric acid, weight % of glycerol in solvent	
	3.1	21.2
0.01	0.902	0.885
0.1	0.798	0.775
1.0	0.810	0.810
2.0	1.019	1.030
4.0	1.792	1.914

Thus for molalities of 2.0 and 4.0 the concentration of the hydrochloric acid in the resin phase would be expected to increase slightly as glycerol is added to the solvent. This same effect is noted for sodium chloride in Figure 3. However for concentrations of less than 1 molal the reverse happens. The salt data tends to confirm this below 5%, but the results are not conclusive. A similar comparison of the effect of the electrolyte upon the distribution of the nonelectrolyte should be more striking, but activity data are not available for the comparison.

It would be convenient to extend these equilibrium data to other Dowex-50 resins. The structure and properties of Dowex 50 indicate that the fundamental properties of the resin that can be changed are resin capacity (equivalent weight) and cross linkage (divinyl benzene content). These properties should be sufficient to fix the variables pertaining to the resin in Equation (4). Since Dowex 50 can usually be assumed to possess one sulfonic acid group per styrene molecule (3), the resin capacity can also probably be correlated as a function of divinyl benzene content. Therefore, the latter should be sufficient to correlate these equilibrium data to other Dowex 50 resins. Correlations of this type have been reported for ethylene glycol and water (12) and potassium chloride and water (8).

NOTATION

$a_{j,e}^*$ = activity of component j in the external phase at zero pressure

$a_{j,r}^*$ = activity of component j in the resin phase at zero pressure

D = diameter of a resin bead immersed in a specified solution

D_0 = diameter of the same bead immersed in pure water

P_r = osmotic pressure of the resin phase

R = gas constant

T = temperature

$\bar{V}_{i,r}$ = partial molal volume of component j in the resin phase

V_R' = initial volume of the air-dry resin

V_s' = initial volume of the solution added to the cell

V_R'' = final volume of the resin at equilibrium

V_s'' = final volume of the external solution at equilibrium

ΔV_T = change in total volume

X_s = concentration of sodium chloride in the external phase, wt. %

X_g = concentration of glycerol in the external phase, wt. %

Y_s = concentration of sodium chloride in the internal phase, wt. %

Y_g = concentration of glycerol in the internal phase, wt. %, where the internal phase is defined as the solution in the resin phase on a resin-free basis

$\gamma_{g,r}^*$ = stoichiometric molal activity coefficient for glycerol in the resin phase at zero pressure

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