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Ion Exchange Equilibria under Pressure

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Previous work on the ionization equilibria of weak acids and bases at high pressures suggested that compression should favor the transfer of protons from a weakly acidic resin to a weakly basic one in a mixed bed system, and that the resulting increase of ionization should extract cations and anions from the surrounding solution. In agreement with this idea it has now been observed that the equilibrium concentration of a solution of sodium chloride around a mixture of De-Acidite M and Zeo-Karb 226 resins is almost halved when the pressure is raised from 1 to 3,000 atm. The change is completely reversible.

The measurements indicate that the proton transfer process involves a contraction of about 15 cc. mole^{-1}, which is remarkably close to the analogous contraction [15 to 18 cc. mole^{-1}] that occurs when a proton is transferred from a free carboxylic acid to an amine in solution.

Many measurements have been made of the influence of pressure on ionic equilibria in homogeneous solutions, and the general pattern of behavior is now quite clear (*1* to *3*). Without exception, weak electrolytes tend to become stronger when the pressure is raised, and ion pairs tend to dissociate. Qualitatively, and to some degree, quantitatively, the effects can be understood in terms of the classical macroscopic theory of electrostriction (*1*, *2*).

On the other hand very little work has been done on heterogeneous systems of the kind that are involved in ion exchange processes between solutions and resins. The only published experimental results in this field are some that Horne et al. (*4*) obtained for the equilibrium between potassium and strontium ions and hydrogen ions in a sulfonic acid resin at pressures up to 6,600 atm. The changes, under pressure, were rather small.

The purposes of the present paper are to consider briefly the kinds of effects that pressure might be expected, theoretically, to have on ion exchange equilibria, and to present some new data concerning the uptake of sodium chloride from aqueous solutions by a mixed bed resin.

THEORETICAL CONSIDERATIONS

The task of developing a rigorous molecular theory of ion exchange equilibria is enormously difficult. Rice and his colleagues (*5, 6*) have made some progress in that direction, but their theory still involves a number of parameters whose values can neither be calculated nor measured and whose pressure dependence is entirely unknown. For the present purpose it is more profitable to employ simpler models which at least allow predictions to be made about the influence of pressure. In describing the models it will be convenient to consider separately strongly acidic and strongly basic resins on the one hand, and weakly acidic and weakly basic resins on the other.

Strongly Acidic and Strongly Basic Resins

In general the binding of ions within a resin can arise from: (1) the formation of covalent bonds of the kind that exist between protons and carboxylate groups in weak polycarboxylic acids, (2) the formation of specific ion pairs of the Bjerrum type enhanced by the abnormally low local dielectric constant that exists in resins, (3) the attraction of the net electrostatic field of all the distributed charges in the polymer network, and (4) the formation of stable ionic complexes.

The treatment that follows will consider the influence of pressure on only the second of these factors, which is undoubtedly an important one in strongly acidic and strongly basic resins.

The definition of what constitutes an ion pair is necessarily arbitrary. Here, the authors will adopt Fuoss's criterion that ions can be considered to be paired only when they are within the contact distance a of each other, not merely when they come within the Bjerrum critical distance q of each other. From that criterion, Fuoss (*7*) calculated that the molar equilibrium constant for the association of two oppositely charged ions of valency z_1 and z_2 in a medium of dielectric constant ϵ at an absolute temperature T is:

$$K_c = \frac{4\pi N a^3}{3000} \exp\left(\frac{|z_1 z_2|\, e^2}{\epsilon k T a}\right) \qquad (1)$$

On the molality scale of concentrations, the association constant becomes

$$K_m = \rho K_c \qquad (2)$$

If a is assumed to be independent of pressure, then it is possible to estimate the way in which K_m should vary with pressure, simply by taking account of the corresponding changes of ϵ and ρ. In fact, the pressure dependence of K_m can be written in the form:

$$-\frac{RT\,\partial \ln K_m}{\partial P} = -\frac{N\,|z_1 z_2|\, e^2}{a}\,\frac{\partial \epsilon^{-1}}{\partial P} - \frac{RT\,\partial \ln \rho}{\partial P} = \Delta \overline{V}_a \qquad (3)$$

where $\Delta \overline{V}_a$ denotes the theoretical change of partial molar volume that accompanies the formation of ion pairs.

Experimentally it has been found (*8*) that Fuoss's theory [and Equation (2) in particular] gives a good description of the effects of pressure on ion pair associations in aqueous solutions of magnesium sulfate and lanthanum ferricyanide. It is therefore justifiable to apply it to analogous equilibria in ion exchange resins, although there is naturally a good deal of uncertainty about the most appropriate value to use for $\partial \epsilon^{-1}/\partial P$. In the absence of any direct evidence to the contrary, the authors will assume here that both this derivative and the compressibility term $\partial \ln \rho/\partial P$ have the same values in a resin gel as they have in pure water. Insertion in Equation (2) of the values $\partial \epsilon^{-1}/\partial P = -6.09 \times 10^{-7}$ atm.$^{-1}$ (*9*) and $\partial\ ln\ \rho/\partial P = 4.622 \times 10^{-5}$ atm.$^{-1}$ (*10*) for water at 25°C. and 1 atm. gives:

$$\Delta \overline{V}_a/\text{cc. mole}^{-1} = +8.351 \frac{|z_1 z_2|}{a \text{ (in Å.)}} - 1.13 \qquad (4)$$

In this formula, the interionic distance a can be taken to be the same as the Debye-Hückel parameter for the particular pair of ions concerned. For most electrolytes, including acids and bases, its value lies in the range 3 to 5 Å., so that on the average $\Delta \overline{V}_a$ is about +1.0 cc. mole^{-1} for 1 : 1 electrolytes, +3.0 cc. mole^{-1} for 1 : 2 electrolytes, and +7.2 for 2 : 2 electrolytes.

When an ion exchange process

$$\overline{AB} + C \rightarrow \overline{AC} + B \qquad (5)$$

occurs in a strongly acidic or strongly basic resin, ion pairs AB are replaced by ion pairs AC and the accompanying volume change is the difference between the values of $\Delta \overline{V}_a$ for the formation of the two species. It follows from Equation (4) that the exchange of ions of the same valency is unlikely to involve a very significant volume change unless their radii are considerably different. On the other hand, the exchange of ions of different valencies may cause quite large volume changes. For example, if A and B are singly charged but C is doubly charged, the change of volume will be about +2 cc. mole^{-1} and the equilibrium constant for the exchange (5) will be reduced by about 9% if the pressure is raised from 1 to 1,000 atm.

Although this theory is admittedly crude, it may have some value in predicting pressure effects. Certainly the conclusions drawn in the last paragraph are qualitatively consistent with the results of some recent volumetric experiments (*11*), which indicate that the replacement of Na^+ by K^+ in a number of fully ionized anionic resins causes an average contradiction of only —0.4 cc. equiv.$^{-1}$, whereas the replacement of Na^+ by ½ Mg^{2+} causes an average expansion of +7.2 cc. equiv.$^{-1}$.

Weakly Acidic and Weakly Basic Resins

In pure water the ionogenic groups of weakly acidic and weakly basic resins are almost completely unionized. But in the presence of a salt [for example, sodium chloride] they become partially ionized in the following ways:

$$\overline{RCO_2H} + Na^+ + H_2O \rightleftarrows \overline{RCO_2^-Na^+} + H_3O^+ \qquad (6)$$

$$\overline{R_3N} + Cl^- + H_2O \rightleftarrows \overline{R_3NH^+Cl^-} + OH^- \qquad (7)$$

Here, $\overline{RCO_2H}$ and $\overline{R_3N}$ denote polycarboxylic acid and polyamine resins, respectively.

In contrast to the equilibria of strong electrolyte resins, discussed in the last section, the most important factor in this type of exchange process is that an electrostatic bond is formed in place of a covalent one. Such a change always causes a substantial contraction of the system as a whole, because the ionic groups exert strong attractive forces on the surrounding water molecules, even when the ions are associated as ion pairs. It follows that an increase of pressure should displace the equilibria (6) and (7) to the right in the same way that it enhances the ionization of weak electrolytes in solution (*1, 2*).

Clearly any theoretical attempt to predict the magnitude of the pressure effect must be based on consideration of the states of hydration of the reacting species. A fairly realistic model is one which supposes that the degree of electrostriction of water around ions in the resin gel is not very different from that in the bulk solution, and that the increase of electrostriction which occurs when the acidic or basic groups ionize can be calculated from classical electrostatic theory, assuming the neutral groups to be essentially unhydrated. The latter calculation may be based on either Born's or Bernal and Fowler's formulas for the free energy of hydration of ions, allowing for the effect of pressure on the dielectric constant of water and on the radii of typical ions (*2, 12*). Both theories lead to the conclusion that reactions of types (6) and (7) should involve contractions of the order of 20 cc. mole^{-1}. This is very much greater than the changes calculated in the last section for ion pairing equilibria, and it is to be expected that the pressure effects will be correspondingly larger.

Finally, it is interesting to consider a mixed bed resin in which reactions (6) and (7) occur simultaneously and the hydrogen and hydroxyl ions neutralize each other:

$$\overline{\mathrm{RCO_2H}} + \overline{\mathrm{R_3N}} + \mathrm{Na^+} + \mathrm{Cl^-} \rightleftarrows \overline{\mathrm{RCO_2^-Na^+}} + \overline{\mathrm{R_3NH^+Cl^-}} \quad (8)$$

The net reaction consists in the transference of protons from the acidic to the basic resin and the absorption of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions into the resin. It is to be expected that by far the most important factor in the total volume change will be the increase of electrostriction that accompanies the creation of new ionic charges. Compression should shift the equilibrium to the right and increase the uptake of sodium chloride by the mixed resin. The experiments to be described in the next section show that this happens.

EXPERIMENTAL

Materials

The resins used to make the mixed bed were De-Acidite M, a crosslinked polystyrene amine resin, and Zeo-Karb 226, a cross-linked polyacrylic acid resin, both manufactured by the Permutit Company, Ltd., England. They were mixed in an equivalent ratio of 1:1.

Before each measurement, a small quantity of the mixed resin was equilibrated with 0.05 molal sodium chloride solution by stirring it with a very large excess of the solution for several days. After this treatment the equilibrium loading of the resin was found to be about half the full resin capacity, that is, about 0.5 milliequiv./cc. of wet settled resin. The resin was then placed, together with an equal volume of supernatant 0.05 molal sodium chloride solution, in a high pressure vessel and allowed to establish a new equilibrium with the solution under pressure.

Experimental Technique

The pressure vessel was a stainless steel cylinder of outside diameter 2¾ in., having a blind bore ⅝ in. in diameter and 6 in. long.

About 25 cc. of the mixture of resin and solution, together with a small stainless steel ball, were placed in the cylinder and then compressed by pushing a ⅝ in. diameter plunger into the hole by means of a hydraulic press (cf. reference *13*). The pressure seal at the end of the plunger was made with a Bridgman unsupported-area packing consisting of one rubber and two copper rings mounted on the stem of a stainless steel "mushroom" (*14*). When the desired pressure was reached, the plunger was locked in place with a collar nut in the manner described by Stillman (*15*) and Itskevich (*16*); the assembly was then removed from the press and the resin mixture stirred for 12 hr. by rotating the cylinder about a radial axis at 2 rev./min. The motion of the stainless steel ball produced very efficient stirring and the 12 hr. were more than adequate to establish equilibrium at the new pressure. At the end of that time the resin was allowed to settle under pressure; the mixture was then rapidly decompressed and a sample of the supernatant solution taken as quickly as possible through a micro filter tube and analysed to determine its chloride content.

The internal pressure in the cylinder was not measured directly, nor, because of frictional effects, could it be calculated in a simple way from the cross-sectional area of the plunger and the applied thrust. Instead it was derived from a calibration of the whole apparatus based on observations of well-known freezing transitions in different liquids. The quoted values of pressures are probably reliable to ± 30 atm.

The equilibrations were carried out at room temperature, which seldom varied by more than 1° or 2°C. during any particular run.

RESULTS AND DISCUSSION

The results are briefly summarized in Table 1. In addition to the data presented there, measurements were made of the capacities of the individual acidic and basic resins and of their equilibrium compositions in neutral solutions of sodium chloride. Also, experiments were carried out in a high pressure optical cell to confirm that the volumes of the resin beds were not measurably altered by hydrostatic compression. The reversibility of the changes of equilibrium was demonstrated in experiments 4 and 5 of

TABLE 1. EFFECT OF PRESSURE ON THE CONCENTRATIONS OF SOLUTIONS OF SODIUM CHLORIDE IN CONTACT WITH A MIXED BED RESIN

Experiment No.	Temperature, °C.	Volume of settled resin bed, cc.	Volume of supernatant sodium chloride solution, cc.	Applied pressure P, atm.	Initial concentration of sodium chloride solution at 1 atm. mole kg.$^{-1}$	Final concentration of sodium chloride solution at P atm., mole kg.$^{-1}$	Relative equilibrium product K'_P/K'_1	
							First approximation	Second approximation
1	23.8	12.3	12.9	460	0.0502	0.0462	1.18	1.24
2	23.0	11.7	13.3	1,040	0.0502	0.0413	1.48	1.67
3	24.0	11.7	13.3	1,440	0.0496	0.0354	1.96	2.40
4	22.0	11.4	13.6	2,200	0.0508	0.0313	2.63	3.49
5	23.5	11.8	13.1	3,000	0.0513	0.0273	3.53	4.94
6	23.2	11.4	13.6	3,000	0.0502	0.0273	3.38	4.68
7	23.5	11.7	13.3	3,000	0.0433	0.0257	2.84	3.65
8	22.0	9.1	15.8	3,000	0.0438	0.0282	2.41	3.25
9	29.0	6.9	18.1	3,000	0.0443	0.0320	1.93	2.64

Table 1, in which, after the release of pressure and the removal of small samples of solution for analysis, the mixtures were stirred for 12 hr. at atmospheric pressure. The concentrations of sodium chloride returned to 0.0502 and 0.0510 mole kg.$^{-1}$, respectively.

It is clear from columns 6 and 7 of Table 1 that compression always increased the uptake of salt by the resin bed. The results can be discussed quantitatively in terms of an equilibrium product K', defined by

$$K' = \frac{\overline{m}_{BHCl}\,\overline{m}_{ANa}}{\overline{m}_B\,\overline{m}_{AH}\,m_{Na}\,m_{Cl}} \tag{9}$$

where $\overline{m}_B$ denotes the number of moles of unionized amine groups per kilogram of gel water in the basic resin; $\overline{m}_{BHCl}$ denotes the corresponding molality of ionized groups, and m_{Cl} denotes the equilibrium molality of chloride ions in the external solution. $\overline{m}_{AH}$, $\overline{m}_{ANa}$, and m_{Na} are the analogous quantities for the acidic resin and sodium ions.

Under the experimental conditions, the resin bed contained considerably more salt that the whole of the surrounding solution, so that as a rough approximation it might be assumed that the only quantities in (9) that would change significantly with pressure would be m_{Na} and m_{Cl}. To that approximation, K' is inversely proportional to the square of the molality of sodium chloride in solution. The eighth column of Table 1 lists relative values of K' calculated on that basis, the subscripts P and 1 indicating values at P atm and 1 atm.

An improved calculation would take account of the changes of $\overline{m}_B$, $\overline{m}_{BHCl}$, $\overline{m}_{AH}$, and $\overline{m}_{ANa}$ by allowing for the amount of extra salt that was absorbed into the resin when the pressure was raised. To do this it is convenient to treat the mixed bed as if it were a single resin. Considering, as an example, experiment 1, the initial salt content of the gel water of the mixed bed at 1 atm. was 2.24 molal, and since the total resin capacity was 4.87 molal the average concentration of unionized groups was 2.63 molal. The corresponding values under pressure could not be measured directly, but they can be calculated from the known amounts of resin and solution and from the observed change in the solution concentration. The respective values are 2.27 and 2.60 molal at 460 atm. The use of these values to represent both $\overline{m}_{BHCl}$, $\overline{m}_{ANa}$ on the one hand, and $\overline{m}_B$, $\overline{m}_{AH}$ on the other (this step involves an averaging between the two resins that may not be entirely justifiable) alters the primitive value of K'_P/K'_1 from 1.18 to 1.24. Other results calculated in this manner are listed in the last column of Table 1.

There is a fairly uniform trend in K'_P/K'_1 with increasing pressure, and the initial slope of the curve corresponds to a value $\Delta V = -15.1$ cc. mole^{-1}, where ΔV is defined by

$$\Delta V = -\frac{\mathrm{R}T\,\partial \ln (K'_P/K'_1)}{\partial P} \tag{10}$$

It is the change of volume for the absorption reaction (8). It should be noted, from (9) that the definition of K' omits activity coefficients and it follows that ΔV represents the volume change for reaction at the local concentrations existing in the experiments (see, for example, reference 2, p. 135), not for a reaction between hypothetical standard states.

A very significant feature of the results is that the value of ΔV is remarkably close to the analogous contraction of 15 to 18 cc. mole^{-1} that occurs when a proton is transferred from a free carboxylic acid to a free amine in solution (*2*, p. 158). The conclusions to be drawn from this, and from the earlier theoretical discussion, are that the Na^+ and Cl^- ions have very nearly the same effective volumes in the resins as in the external solution and that the proton transference involves almost as large an increase of electrostriction as it does in a homogeneous solution. It appears that the amine and carboxylic acid groups in the resins behave as if they were free bases and acids. This is a rather surprising conclusion, but it is consistent with analogous findings by Weiss (*17*) concerning the influence of temperature on ion exchange processes.

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NOTATION

a = interionic contact distance
$A, B, ..$ = chemical species in solution
$\overline{A}, \overline{B}, ..$ = chemical groups in resins
e = electronic charge
k = Boltzmann's constant
K_c = molar scale equilibrium constant
K_m = molal scale equilibrium constant
m = molality in the bulk solution
$\overline{m}$ = molality in a resin
N = Avogadro's number
P = pressure
R = gas constant
T = absolute temperature
z = valence of an ion

Greek Letters

ϵ = dielectric constant
ρ = density of solvent, g./cc.
ΔV = change of molar volume

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