

DISSOCIATION EQUILIBRIUM OF A WEAK-ELECTROLYTIC ANION EXCHANGE RESIN

(STUDIES IN POLYELECTROLYTES XLII)

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Introduction

The mechanism of ion exchange of weak-electrolytic anion (or cation) exchange resins is most complicated, because, in addition to ionic distribution according to the Donnan membrane equilibrium, the change of dissociation constant of ionizable groups inside the resin must be taken into account. This subject has already been studied by several authors.¹⁾⁻⁵⁾ By their studies, it has been made clear that the dissociation of ion exchange resin differs entirely from that of simple electrolyte and is best computed in the same way as the dissociation of polyelectrolytes. However, strictly speaking, it would be better to compute the dissociation of ionizable groups inside resin by using pH of the solution inside the resin than to compute it by using pH outside, because the pH outside has only an indirect relationship with the dissociation constant.

In the present study, by assuming the Donnan membrane equilibrium, the ionic concentrations inside resin are calculated from the concentrations in the equilibrium solution, and the ionic concentrations are used to calculate the dissociation constant of ionizable groups inside the resin.

Fundamental Consideration

Notations used are as follows :

C = concentration HCl in equilibrium solution,

C_s = concentration of added salt in equilibrium solution,

x = concentration of HCl absorbed into the resin as an extraneous electrolyte,

y = concentration of salt absorbed into the resin as an extraneous salt,

z = concentration of chloride ion which served to neutralize the base group inside the resin,

(x, y, z are expressed by equivalents per 1,000 g absorbed water),

Q = maximum exchange capacity of the resin expressed by equivalents per 1,000 g absorbed water.

f^S, f^R = activity coefficients of ions in the equilibrium solution and resin phase respectively.

Let us consider that an amount of ion exchange resin of weak base type is placed in a solution of hydrochloric acid and its salt and left until an equilibrium is attained. Then, the concentration of chloride ion in the equilibrium solution (C_{Cl}^S) is $C + C_s$ and that in the resin (C_{Cl}^R) is $x + y + z$.

Resin phase	Solution phase
R NH ⁺Cl ⁻ (z)	H ⁺ Cl ⁻ (C)
H ⁺Cl ⁻ (x)	Na ⁺ Cl ⁻ (C _s)
Na ⁺Cl ⁻ (y)	
R N..... (Q-z)	

FIG. 1

If it is assumed that the ionic distribution inside and outside resin is given by the Donnan theory on membrane equilibrium, among the concentrations defined above there are the following relationships:

$$\frac{f_{\text{Cl}}^{\text{R}} C_{\text{Cl}}^{\text{R}}}{f_{\text{Cl}}^{\text{S}} C_{\text{Cl}}^{\text{S}}} = \frac{1}{k_1} \frac{f_{\text{Na}}^{\text{S}} C_s}{f_{\text{Na}}^{\text{R}} \cdot y} = \frac{1}{k_2} \frac{f_{\text{H}}^{\text{S}} C}{f_{\text{H}}^{\text{R}} x} \quad (1)$$

where k are the terms concerning the osmotic pressure, as pointed out by Gregor.⁶¹ Among these concentrations, both C and C_{Cl}^{S} can easily be calculated by titration and C_s is given by the difference between C and C_{Cl}^{S} . The value of C_{Cl}^{R} can be calculated from the absorbed water and the decrease in the chloride concentration of solution. (When extraneous salt is absent, that is $C_s = 0$, C_{Cl}^{R} can be very easily calculated from the decrease of hydrogen concentration.) Therefore, the pH and salt concentration inside resin are calculated from these measurable quantities using Eq. (1), as follows:

$$\begin{aligned} \text{pH}^{\text{R}} &= -\log (f_{\text{H}}^{\text{R}} \cdot x) = -\log \left(\frac{1}{k_2} \frac{f_{\text{H}}^{\text{S}} \cdot f_{\text{Cl}}^{\text{S}}}{f_{\text{Cl}}^{\text{R}}} \right) - \log \left(\frac{C \cdot C_{\text{Cl}}^{\text{S}}}{C_{\text{Cl}}^{\text{R}}} \right) \\ &= -\log (k_{\text{H}} \cdot f_{\text{H}}^{\text{R}}) - \log \left(\frac{C \cdot C_{\text{Cl}}^{\text{S}}}{C_{\text{Cl}}^{\text{R}}} \right) \end{aligned} \quad (2)$$

$$y = k_{\text{Na}} \frac{C_s - C_{\text{Cl}}^{\text{S}}}{C_{\text{Cl}}^{\text{R}}} \quad (3)$$

where

$$k_{\text{H}} = \frac{1}{k_2} \frac{f_{\text{H}}^{\text{S}} \cdot f_{\text{Cl}}^{\text{S}}}{f_{\text{H}}^{\text{R}} \cdot f_{\text{Cl}}^{\text{R}}}, \quad k_{\text{Na}} = \frac{1}{k_1} \frac{f_{\text{Na}}^{\text{S}} \cdot f_{\text{Cl}}^{\text{S}}}{f_{\text{Na}}^{\text{R}} \cdot f_{\text{Cl}}^{\text{R}}} \quad (4)$$

and, expecting when x and y are very large, z can be considered equal to C_{Cl}^{R} . In the present experimental condition, x and y are certainly small. The first term of Eq. (2) can not be measured, but it may be almost constant and, moreover, it may not deviate greatly from zero, considering that k_{H} corresponds to the exchange equilibrium constant of strong base ion exchange resin. Therefore, let us define the measurable pH inside resin as follows:

$$\begin{aligned} \text{pH}^{\text{R}} &= \text{pH}^{\text{R}} + \log (k_{\text{H}} \cdot f_{\text{H}}^{\text{R}}) \\ &= -\log \frac{C \cdot C_{\text{Cl}}^{\text{S}}}{C_{\text{Cl}}^{\text{R}}} \end{aligned} \quad (5)$$

Thus pH^{R} is linear to pH^{S} .

The maximum exchange capacity (Q) being defined

$$Q = \lim_{C \rightarrow \infty} z$$

solutions of high ionic concentration must be used to determine the value of Q . The x in the resin, therefore, becomes large and the approximation of $z \doteq C_{\text{Cl}}^{\text{R}}$ turns out to be insufficient. Then, let us employ the following second approximation for z to calculate the value of Q using the quantity of HCl absorbed from HCl solutions without extraneous salt,

$$\begin{aligned} z &\doteq C_{\text{Cl}}^{\text{R}} - k_{\text{H}}^{-1} \cdot x \\ &\doteq C_{\text{Cl}}^{\text{R}} - \frac{C^2}{C_{\text{Cl}}^{\text{R}}} \end{aligned}$$

This approximation may be good because it has already been reported that k_{H} approaches unity as C increases.⁷⁾⁸⁾

Inside the resin, the ionizable group shows the following ionization:



The thermodynamic dissociation constant of this ionization is expressed by

$$\begin{aligned} K_D &= \frac{(\text{OH}^-)(\text{R} - \text{NH}^+)}{(\text{R} - \text{N})} \\ &= \frac{K_{\text{W}} \cdot f_{\text{R} \cdot \text{NH}} \cdot z}{f_{\text{H}}^{\text{R}} \cdot x \cdot f_{\text{R} \cdot \text{N}} \cdot (Q - z)} = \frac{K_{\text{W}} \cdot f_{\text{R} \cdot \text{NH}} \cdot z \cdot (x + y + z)}{k_{\text{H}} \cdot f_{\text{H}}^{\text{R}} \cdot f_{\text{R} \cdot \text{N}} \cdot C(C + C_s)(Q - z)} \end{aligned} \quad (8)$$

where () denotes activity and K_{W} is the dissociation constant of water molecule. However, inasmuch as the behavior of $f_{\text{R} \cdot \text{N}}$, $f_{\text{R} \cdot \text{NH}}$ and k_{H} never be presumed, it is more convenient to define the new dissociation constant as follows:

$$\mathbf{K} = K_D \frac{k_{\text{H}} \cdot f_{\text{H}}^{\text{R}} \cdot f_{\text{R} \cdot \text{N}}}{K_{\text{W}} \cdot f_{\text{R} \cdot \text{NH}}} = \frac{z(x + y + z)}{C(C + C_s)(Q - z)} \quad (9)$$

It is true that \mathbf{K} can not be expected to be constant as the result of this definition, but it can be accepted as reasonable to assume that the term of activity coefficients should not show a variation of more than ten times within the present experimental condition, activity coefficients and k_{H} may not vary greatly with experimental conditions, as can be presumed from a number of studies on strong base (or acid) ion exchange resin. Therefore, it seems certain that such a great variation of \mathbf{K} as seen in the present study is not due to the variation in activity coefficients, but, in fact, is due to the variation in K_D which is caused by the electrostatic effect of ionized groups. Except for the existence of k_{H} term, we encounter the same problem in studies on the dissociation of soluble polyelectrolytes, and in this field, too, the same assumption can be accepted.

It is the present purpose to investigate the degree of dissociation inside resin, *i.e.* how the dissociation constant varies with the exchanged amount of counter ion. The relationship of the dissociation constant with the degree of dissociation or with pH in polyelectrolyte solutions has been fully studied by many researchers, and as a result the following empirical relationship have been established,

$$\begin{aligned} (\text{Kern})^9) & \quad \text{pK} = \text{pK}_0 - A \cdot \text{pH} \\ (\text{Kagawa } et \text{ al.})^{10)} & \quad \text{pK} = \text{pK}_s - m \cdot \log\left(\frac{1 - \alpha}{\alpha}\right) \end{aligned}$$

(Henderson-Hasselbalch-Katchalsky)¹¹⁾

$$\text{pH} = \text{pK}_a + n \cdot \log\left(\frac{1-\alpha}{\alpha}\right)$$

where pK means $-\log K$ and where pK_0 , pK_s , pK_a , A , m , n are constants expressing the dissociation character of the polyelectrolyte. These equations have the same meaning, with the following relationships existing among constants in all three equations;

$$m = A/1 - A, \quad n = 1/1 - A.$$

From the theoretical point of view also, many investigators have reported studies on the dissociation of polyelectrolyte, and as a result, it was revealed that the dissociation character of soluble poly-base can be expressed by the following equation:¹¹⁾

$$\text{pH} = \text{pK} + \log\left(\frac{1-\alpha}{\alpha}\right) + 0.434 \frac{e\psi_a}{kT} \quad (14)$$

where ψ_a is the surface electrical potential of ionizable group and e , k , and T are respectively, unit charge, Boltzmann constant and absolute temperature.

To investigate the applicability of Eqs. (10)-(14) to the solution inside ion exchange resin, pK and pH^R must be used instead of pK and pH , but the ambiguous terms in pK and pH^R are included in the constant terms of Eqs. (10)-(14).

Experiments

The weak base ion exchange resin used is Amberlite IR-45, which consists of polystyrene skeleton. The sample is completely purified by electric dialysis before being used. The hydrochloric acid is used as the neutralizing agent and sodium and potassium chloride used as the extraneous salts.

About one gram of the dried resin is put into a container with 50 cc solution of hydrochloric acid and a chloride salt, and kept at 25° C for 2 days shaking it several times a day until an equilibrium is attained. Then, the resin is put into a glass filter and is separated from the solution by centrifugation at 3,000 rpm for 25 min. The water content of the resin is calculated from the separated resin. The concentration of HCl before and after equilibrium is determined by titration with a NaOH standard solution using a micro-buret. Concentration of chloride ion is determined by potentiometric titration using a AgNO₃ standard solution. From the water content of the resin and the decrease of NaOH or chloride ion, the chloride ion concentration inside resin is calculated.

In terms of C , C_s , C_{Cl}^S , C_{Cl}^R thus determined, pH^R , pK and z can be calculated from Eqs. (5), (7) and (9). In Fig. 2, z against C for salt-free systems to determine the value of Q . The maximum exchange value (Q) is equal to the limiting value of z at $C = \text{infinite}$. Although there were two series of experiments in which sample used were put at our disposal at different times and were purified by slightly different procedures, giving a somewhat different value of Q , the difference of Q did not turn out to make any observable difference in the successive results so long as the value of Q determined for each series of experiments was used

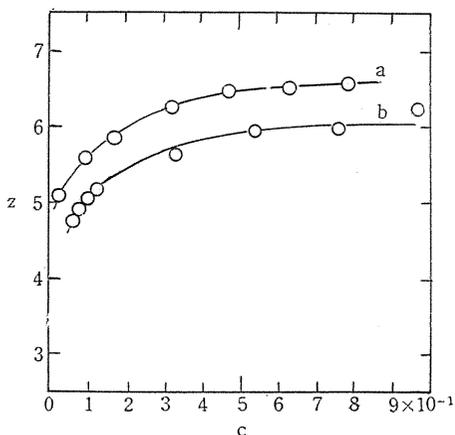


FIG. 2. Determination of the exchange capacity of weak-electrolytic anion exchange resin.

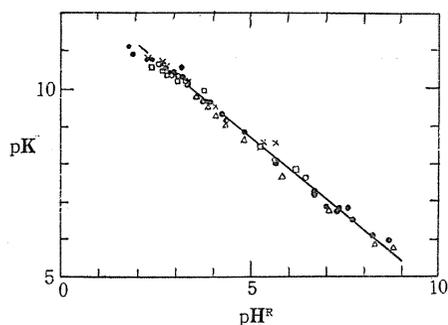


FIG. 3. Relationship between pK and pH^R inside resin.
 • HCl, × 1/10 N NaCl+HCl, Δ 1/100 N NaCl+HCl, □ 1/10 N KCl+HCl, ○ 1/100 N KCl+HCl.

for calculation. In Fig. 3, pK is plotted against pH^R to check Kern's equation (10). In Fig. 4, pK is plotted against $pHCl$ ($= -\log C_{HCl}$) of the outside solution for reference. While there is no notable relationship between pK and $pHCl$, there is good linearity between pK and pH^R as was shown by Kern for polyelectrolyte solution. Eqs. (11) and (12), however, do not hold satisfactorily for the experiment, because in this case A happens to be 0.82 and, hence, the deviations from the linearity in Fig. 3 are greatly exaggerated when Eqs. (11) and (12) are used instead of Eq. (10). The relationship between pH^R and $\log\left(\frac{1-\alpha}{\alpha}\right)$

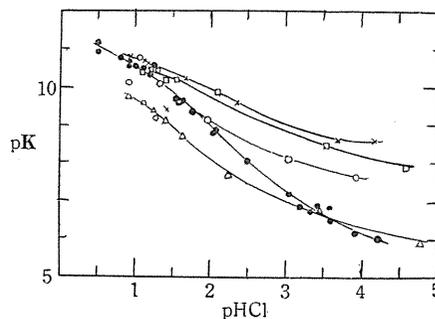


FIG. 4. Relationship between pK and pH outside resin.

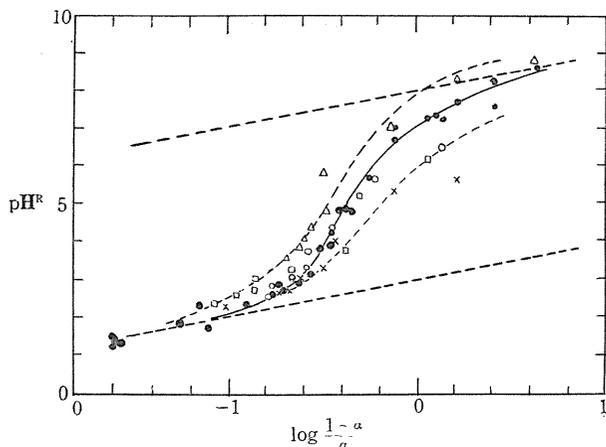


FIG. 5. Relationship between pH^R and $\log\left(\frac{1-\alpha}{\alpha}\right)$. Each straight broken line corresponds to the dissociation of a mono-functional base.

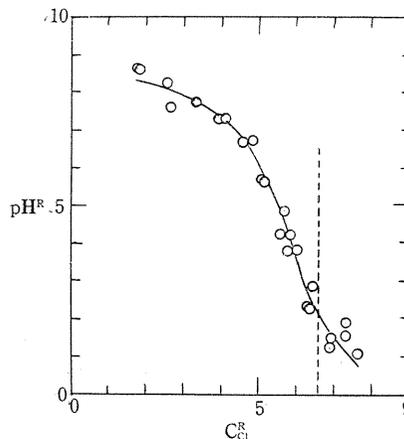


FIG. 6. Titration curve inside resin. The broken line shows the exchange capacity obtained from Fig. 2.

is shown in Fig. 5, where the dissociation inside resin approaches the dissociation of monovalent simple base at both limits of $\alpha = 1$ and 0. The difference between two asymptotic lines for $\alpha = 1$ and 0, $(\Delta\text{pH})_{\alpha=1}^{\alpha=0}$, which means $\left(0.434 \frac{e\psi_{\alpha}}{kT}\right)_{\alpha=1}$ in Eq. (14), is found to be about 5. In Fig. 6, the relationship between pH^R and C_{Cl}^R for series a in Fig. 2 is shown. This curve corresponds to the titration curve of soluble polyelectrolyte.

Discussion

The following results are deduced from Figs. 2-6: (1) Theories on the ionization of polyelectrolyte could be employed for the ionization of weak base ion exchange resin, if pH and ionic concentrations inside resin are used. (2) The fact that the ionizing character approaches that of monovalent simple acid at both limits of $\alpha = 1$ and 0 has not yet been experimentally observed for $\alpha = 1$ when using soluble polyelectrolyte, although it has already been anticipated by several authors.¹⁰⁾ That the ion exchange resin clearly shows an ionization similar to monovalent simple acid even at $\alpha = 1$, may be because the ion exchange resin shows little variation of volume, while soluble polyelectrolytes show remarkable changes of polymer configuration. (3) As was pointed out by Honda,¹⁾ the addition of extraneous salt exerts little influence upon the ionization inside the resin. This is due to the very low concentration of the salt inside the resin. (4) Inspection of Fig. 6 shows that the maximum exchange capacity (Q) obtained from Fig. 2 seems to be too large. To clarify such a discrepancy, the Donnan membrane equilibrium, Eq. (2), which is the basis of calculation should be examined more precisely.

If the change of the surface electrostatic potential ψ_{α} by the change of ionization degree α be theoretically calculated, the ionization of ion exchange resin could be made clear on the basis of Eq. (14). Michaeli and Katchalsky¹²⁾ used the theory of Katchalsky and Lifson¹³⁾ to calculate the free energy of the system, *viz.*, ψ_{α} and introduced a theoretical equation for the relationship between ionization degree α and pH of the outside solution. They showed that the equation is in good agreement with the experiments for methacrylic acid gel. In the present experiment, however, the ionic concentration inside resin is too high and hence ψ_{α} calculated from the Katchalsky and Lifson theory is too small to give $(\Delta\text{pH}^R)_{\alpha=1}^{\alpha=0} = 5$. All other theories concerning the calculation of ψ_{α} in the polyelectrolyte solution may also give the same results because the ionic concentration inside resin is tremendously high. Therefore, as a trial let us suppose the following model for ionic distribution inside resin: The electrostatic potential inside resin is almost flat and, hence, counter ions distribute almost uniformly inside resin, that is, each counter ion is as an average 5-6 Å from fixed group. Then it may be accepted as reasonable that each of the two nearest fixed charges exerts an electrostatic effect of as much as e/Dr upon an unionized group, and the electrostatic effects from other fixed charged groups and movable counter ions cancel out each other to give little effect upon the unionized group. If we assume such a model, it follows that

$$(\Delta\text{pH})_{\alpha=1}^{\alpha=0} = \left(0.434 \frac{e\psi_{\alpha}}{kT}\right)_{\alpha=1} = 6.$$

Therefore, so long as the discussion is limited within the present experiment, the model of uniform counter ion distribution is suitable for ion exchange resin.

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