EQUILIBRIUM CHARACTERISTICS OF ION EXCHANGE BETWEEN AN OH-TYPE STRONG ANION EXCHANGE RESIN AND DILUTE Cl^- SOLUTION

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Introduction

An OH-type strong anion exchange resin has been used in many industrial separation processes^{2,4}, and its equilibrium characteristics are a significant basic element of those processes³. However, only a few studies⁶⁻⁸ of them have been made. Furthermore, few experimental data for dilute solutions have been reported.

In this study, the equilibrium characteristics between the OH-type resin and NaCl or CaCl_2 aqueous solution at the various low concentrations were measured by a batch or column method. The experimental results obtained are discussed.

1. Experimental Procedure

The equilibrium between an OH-type strong anion exchange resin and a dilute Cl^- solution was measured by two methods.

One was a usual batch method. The stocked OH-type resin was equilibrated with Cl^- solution of various concentrations in a glass Erlenmeyer flask. Another was by a column method that was adopted in order to avoid CO_2 in both solution and air, which would influence the equilibrium relation. The procedure is as follows.

After a known weight of the stocked OH-type resin was put into an acrylic column with water jacket (at 298 K), fine conditioning of the resin was done by using CO_2 -free OH^- and Cl^- solution, respectively, to remove CO_2 completely from the resin. Finally, the packed resins were turned into the OH-type and washed rapidly in ultrapure water (its specific electric resistance was more than $16 \text{ M}\Omega\cdot\text{cm}^{-1}$ at 298 K). Then, washing the bed, the known-concentration mixed solution of OH^- and Cl^- was fed into the column at constant flow. During the column operation, air from a feed reservoir was made contact with alkaline solution in a gas washer bottle in order to remove CO_2 from the air. Both OH^- and Cl^- were eluted from the equilibrated resin by the $1.0 \text{ NaNO}_3 \text{ kmol}\cdot\text{m}^{-3}$ solution. These ions' concentra-

tions in effluent were measured by respective titration methods.

All solutions used were fully deaerated under low pressure (2 mmHg) at room temperature.

2. Experimental Results and Discussion

The equilibrium relations of the OH-type resin and NaCl solution by the batch method are shown in Fig. 1. The isotherms show the "S" or the lower convex shape and seems to be affected by C_0 . Here, C_0 means the total concentration of OH^- and Cl^- . This figure suggests that the equilibrium relation measured by the batch method is likely affected by dissolved gases in water.

To confirm this point, measurement by the column method was conducted. Figure 2 shows equilibrium relations which were measured at various C_0 content by that method.

Applying the mass action law to the ion exchange reaction, the equilibrium constant $K_{\text{OH}}^{\text{Cl}}$ is expressed by Eq. (1).

$$K_{\text{OH}}^{\text{Cl}} = \frac{y_{\text{Cl}} \cdot x_{\text{OH}}}{(1 - y_{\text{Cl}}) \cdot x_{\text{Cl}}} \quad (1)$$

where $x = C / C_0$, and $y = q / Q$. C and q denote the concentrations of ion in liquid and resin phase respectively. Q is the ion exchange capacity of the resin.

The solid lines in this figure show the isotherms by Eq. (1).

The effect of C_0 on $K_{\text{OH}}^{\text{Cl}}$ is shown in Fig. 3. Weaton's results⁸ are also shown in this figure. In ideal monovalent ion exchange, the equilibrium constant shows a constant value. When $C_0 = 100 \text{ mol}\cdot\text{m}^{-3}$, the results of this study coincide fairly well with their data. $K_{\text{OH}}^{\text{Cl}}$ was approximately constant when $C_0 > 100 \text{ mol}\cdot\text{m}^{-3}$. However, it decreased with C_0 when $C_0 < 100 \text{ mol}\cdot\text{m}^{-3}$. Even though the amount of dissolved gasses in water is reduced, $K_{\text{OH}}^{\text{Cl}}$ depends on C_0 for the dilute solution. Recently, it is said⁵ that removal of dissolved gases in water enables more effective ion exchange separation and that, especially, degassing of treated water immediately before an anion exchange bed operation is advanta-

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Fig. 1 Experimental equilibrium relations by the batch method. a) $C_0 = 100 \text{ mol} \cdot \text{m}^{-3}$, b) $10 \text{ mol} \cdot \text{m}^{-3}$, c) $5 \text{ mol} \cdot \text{m}^{-3}$, d) $2.5 \text{ mol} \cdot \text{m}^{-3}$.

Fig. 2 Experimental equilibrium relations by the column method

geous. In this study, $K_{\text{OH}}^{\text{Cl}}$ obviously was not constant when $C_0 < 10 \text{ mol} \cdot \text{m}^{-3}$ (345 ppm as Cl). The effect of C_0 on $K_{\text{OH}}^{\text{Cl}}$ suggests the influence of dissolved gases on the equilibria.

Weaton and Bauman⁸⁾ investigated various anion exchange systems and reported that only the OH^- - Cl^- system did not obey Gregor's theory¹⁾ which was established for almost all ion exchange systems. They suggested that the hydrated diameter of OH^- was extremely large, and that the ion exchange equilibrium which was concerned with OH^- showed a discrepancy between theoretical and experimental results.

The relation between C_0 and Q is shown in **Fig. 4**. The Q values obtained were almost constant and agreed with ion exchange capacity which was measured when $C_0 = 500 \text{ mol} \cdot \text{m}^{-3}$.

The equilibrium relations of the OH^- -type resin and

Fig. 3 Effect of C_0 on $K_{\text{OH}}^{\text{Cl}}$ by the column method

Fig. 4 Effect of C_0 on Q by the column method

CaCl_2 solution were also studied, though the figures are omitted. For both $K_{\text{OH}}^{\text{Cl}}$ and Q , no significant differences between NaCl and CaCl_2 were found.

Conclusions

The equilibrium ion exchange relations of the OH^- -type resin and Cl^- solution were measured at the various low concentrations by the two methods. The influence of dissolved CO_2 on the equilibrium relations was significant in the batch method. The column method was adopted to reduce the effect of CO_2 . $K_{\text{OH}}^{\text{Cl}}$ decreased with C_0 , and an almost linear correlation was observed between $K_{\text{OH}}^{\text{Cl}}$ and $\log C_0$ when $C_0 > 100 \text{ mol} \cdot \text{m}^{-3}$. It is suggested that the effect of trace amount of dissolved gases in water is involved.

The values of Q were almost constant and agreed with the theoretical ion exchange capacity.

For both characteristics $K_{\text{OH}}^{\text{Cl}}$ and Q , no significant differences between NaCl and CaCl_2 were found.

Nomenclature

C	= liquid phase concentration	$[\text{mol} \cdot \text{m}^{-3}]$
C_0	= $C_{\text{OH}} + C_{\text{Cl}}$	$[\text{mol} \cdot \text{m}^{-3}]$
q	= resin phase concentration	$[\text{mol} \cdot \text{m}^{-3}]$
K	= equilibrium constant	$[-]$
Q	= ion exchange capacity	$[\text{mol} \cdot \text{m}^{-3}]$

$$\begin{array}{lcl} x & = & C / C_0 \\ y & = & q / Q \end{array} \quad \begin{array}{l} [-] \\ [-] \end{array}$$

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