

DEIONIZATION EQUILIBRIA BETWEEN MIXED CATION AND ANION EXCHANGE RESINS AND A DILUTE NaCl SOLUTION

TAKESHI KATAOKA, AKINORI MUTO* AND TADAAKI NISHIKI

Department of Chemical Engineering, College of Engineering,
University of Osaka Prefecture, Gakuen-cho 1-1, Sakai, Osaka, 593

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The equilibrium relation between mixed cation and anion exchange resins and a dilute salt in water are investigated. Considering the equilibrium characteristic values of each ion exchange and also the mixed-volume fraction of both resins, equilibrium equations are derived on the basis of both cation and anion exchange reactions and the neutralization reaction between H^+ and OH^- eluted from the resins. When both resins are mixed in equal equivalence for ion exchange, the equilibrium relation becomes a rectangular isotherm and is not affected by a concentration of a salt, ionic valence of species composing the salt, or the equilibrium constants of both ion exchanges. When mixed in unequal equivalence, the deionization equilibrium is influenced by the above factors. Especially, the effect of the mixed volume fraction on the equilibrium relationships depends greatly on the valence of ions composing the salt.

The experimental results using aqueous NaCl solution showed good agreement with the calculated ones.

Introduction

Deionized water, which is produced by high removal of ions from aqueous phase, is widely used in many industries, such as microelectronics and pharmaceuticals. In the deionization process, removal of a dilute salt by mixed cation and anion exchange resins is an important selective operation.

Cation and anion exchange equilibria have been investigated for various ion exchange systems^{4,6}. However, few theoretical or experimental studies of the deionization equilibrium by mixed resins have been reported. Heretofore, deionization by mixed resins has been treated as adsorption of a salt¹. There are only a few studies on the rate on the basis of cation or anion exchange properties^{2,3}.

It is important for effective operation to clarify the details of the deionization equilibrium relationships between mixed resins and dilute solution.

The aim of this paper is to elucidate the equilibrium relationship of desalination by mixed resins. This relation, which is applicable to deionization of a salt consisting of multivalent ions, is investigated by considering both cation and anion exchange reactions, and a neutralization reaction. The calculated results by these relationships are compared with experimental results for NaCl as a salt removed from water.

1. Ion Exchange Relationships

1.1 Equilibrium expressions

Desalination proceeds by the following cation and

anion exchange reaction (Eqs. (1) and (2)), and the neutralization reaction between H^+ and OH^- eluted from each resin (Eq. (3)).



Here, M and A respectively represent cation and anion of a removed salt. Z_M and Z_A show the ionic valence of M and A.

Applying the mass action law to Eqs. (1)-(3), the following equilibrium relationships are established.

$$K_H^M = \frac{q_M c_H^{Z_M}}{q_H^{Z_M} c_M} = \frac{q_M c_H^{Z_M}}{(Q_H - Z_M q_H)^{Z_M} c_M} \quad (4)$$

$$K_{OH}^A = \frac{q_A c_{OH}^{Z_A}}{q_{OH}^{Z_A} c_A} = \frac{q_A c_{OH}^{Z_A}}{(Q_{OH} - Z_A q_A)^{Z_A} c_{OH}} \quad (5)$$

$$K_W = C_H C_{OH} \quad (6)$$

Here, K_H^M , K_{OH}^A , and K_W show the equilibrium constant of a cation and an anion exchange, and an association constant of water, respectively. q and Q denote the concentration in liquid phase and resin phase, and the ion exchange capacity of a resin, respectively. From the mass balance relation at equilibrium, Eqs. (7) and (8) are given as follows.

$$C_M = C_{M,0} - \frac{z_M q_M v_H}{V_T} \quad (7)$$

* Received June 3, 1993. Correspondence concerning this article should be addressed to A. Muto.

$$C_A = C_{A,0} - \frac{z_A q_A v_{OH}}{V_T} \quad (8)$$

Here, $C_{M,0}$ and $C_{A,0}$ are the initial concentrations of M and A respectively. V_T shows the volume of a solution, and v_H and v_{OH} denote the H^+ -, and OH^- -type resin volumes, respectively.

Equation (9) is established from the condition of electroneutrality,

$$z_M c_M + c_H = z_A c_A + c_{OH} \quad (9)$$

Total concentration of ions at equilibrium is expressed by Eq. (10).

$$c_T = c_M + c_A + c_H + c_{OH} \quad (10)$$

Initial concentration of the salt is as $C_0 (= C_{M,0} + C_{A,0})$.

Equations (4)-(8) can be rearranged to Eqs. (11)-(17), using the following dimensionless values: $x_i = c_i/C_0$ ($i = M, A, H, OH, T$), $y_M = Z_M q_M / Q_H$, $y_A = Z_A q_A / Q_{OH}$

$$K'_a = K_H^M \left(\frac{Q_H}{C_{M,0}} \right)^{Z_M-1} = \frac{y_M \cdot x_H^{z_M}}{(1-y_M)^{z_M} x_M} \quad (11)$$

$$K'_b = K_{OH}^A \left(\frac{Q_{OH}}{C_{A,0}} \right)^{Z_A-1} = \frac{y_A \cdot x_{OH}^{z_A}}{(1-y_A)^{z_A} x_A} \quad (12)$$

$$K_W = x_H x_{OH} c_0^2 \quad (13)$$

$$x_M = \frac{C_{M,0}}{C_0} - \frac{Q_H v_H}{V_T C_0} y_M \quad (14)$$

$$x_A = \frac{C_{A,0}}{C_0} - \frac{Q_{OH} v_{OH}}{V_T C_0} y_A \quad (15)$$

$$z_M x_M + x_H = z_A x_A + x_{OH} \quad (16)$$

$$x_T = x_M + x_A + x_H + x_{OH} \quad (17)$$

Combining Eqs. (13) and (16), the following relations are given:

$$x_H = \left(\frac{1}{2} \right) \left\{ - (z_M x_M - z_A x_A) + \sqrt{(z_M x_M - z_A x_A)^2 + 4 \frac{K_W}{C_0^2}} \right\} \quad (18)$$

$$x_{OH} = \left(\frac{1}{2} \right) \left\{ - (z_A x_A - z_M x_M) + \sqrt{(z_A x_A - z_M x_M)^2 + 4 \frac{K_W}{C_0^2}} \right\} \quad (19)$$

Using Eqs. (14), (15), (18) and (19), dimensionless total concentration of ions at equilibrium is expressed as follows:

$$x_T = 1 + \sqrt{(z_M x_M - z_A x_A)^2 + 4 \frac{K_W}{C_0^2}} + p \quad (20)$$

where

$$p = - \frac{Q_H v_H y_{Na} + Q_{OH} v_{OH} y_{Cl}}{V_T C_0} \quad (21)$$

The equilibrium relations of desalination by the mixed cation and anion exchange resins are obtained by

the above equations (Eqs. (11)-(21)). In particular, when the salt is NaCl ($M = Na^+$, $A = Cl^-$, $Z_M = 1$, $Z_A = 1$), the following expressions are applicable:

$$K_H^{Na} = \frac{y_{Na} x_H}{(1-y_{Na}) x_{Na}} \quad (22)$$

$$K_{OH}^{Cl} = \frac{y_{Cl} x_{OH}}{(1-y_{Cl}) x_{Cl}} \quad (23)$$

$$x_{Na} = \frac{1}{2} - \frac{Q_H v_H}{V_T} y_{Na} \quad (24)$$

$$x_{Cl} = \frac{1}{2} - \frac{Q_{OH} v_{OH}}{V_T} y_{Cl} \quad (25)$$

$$x_H = \left(\frac{1}{2} \right) \left\{ - (x_{Na} - x_{Cl}) + \sqrt{(x_{Na} - x_{Cl})^2 + 4 \frac{K_W}{C_0^2}} \right\} \quad (26)$$

$$x_{OH} = \left(\frac{1}{2} \right) \left\{ - (x_{Cl} - x_{Na}) + \sqrt{(x_{Cl} - x_{Na})^2 + 4 \frac{K_W}{C_0^2}} \right\} \quad (27)$$

$$\begin{aligned} x_T &= x_{Na} + x_{Cl} + x_H + x_{OH} \\ &= 1 + \sqrt{(x_{Na} - x_{Cl})^2 + 4 \frac{K_W}{C_0^2}} + p \end{aligned} \quad (28)$$

where

$$p = - \frac{Q_H v_H y_{Na} + Q_{OH} v_{OH} y_{Cl}}{V_T C_0} \quad (29)$$

The mixed volume ratio of cation and anion exchange resin, m_H (on the volume basis of H^+ -type resin), is defined as follows (Eq. (30)):

$$m_H = \frac{v_H}{(v_H + v_{OH})} = \frac{1}{(1 + m'_H)} \quad (30)$$

Here, $m'_H (= v_{OH} / v_H)$ means the mixed volume ratio of both resins.

According to the above equations (Eqs. (22)-(30)), the equilibrium relations of ion exchange for Na^+ and Cl^- , are obtained as Eqs. (31) and (32) respectively.

$$\begin{aligned} y_{Na} &= \frac{K_H^{Na} x_{Na}}{K_H^{Na} x_{Na} + \left(\frac{1}{2} - x_{Na} \right)} + \frac{\left(\frac{1}{2} - x_{Na} \right)}{K_H^{Na} x_{Na} + \left(\frac{1}{2} - x_{Na} \right)} \dots \\ &= \frac{(\lambda K_H^{Na} K_{OH}^{Cl} - K_H^{Na} - \lambda K_{OH}^{Cl}) x_{Na} x_{Cl} + \frac{1}{2} K_H^{Na} x_{Na} + \frac{1}{2} \lambda K_{OH}^{Cl} x_{Cl}}{(K_H^{Na} K_{OH}^{Cl} - K_H^{Na} - K_{OH}^{Cl}) x_{Na} x_{Cl} + \frac{1}{2} K_H^{Na} x_{Na} + \frac{1}{2} K_{OH}^{Cl} x_{Cl}} \end{aligned} \quad (31)$$

$$\begin{aligned} y_{Cl} &= \frac{K_{OH}^{Cl} x_{Cl}}{K_{OH}^{Cl} x_{Cl} + \left(\frac{1}{2} - x_{Cl} \right)} + \frac{\left(\frac{1}{2} - x_{Cl} \right)}{K_{OH}^{Cl} x_{Cl} + \left(\frac{1}{2} - x_{Cl} \right)} \dots \\ &= \frac{((1/\lambda) K_H^{Na} K_{OH}^{Cl} - K_{OH}^{Cl} - (1/\lambda) K_H^{Na}) \dots}{(K_H^{Na} K_{OH}^{Cl} - K_{OH}^{Cl} - K_H^{Na}) \dots} \\ &= \frac{x_{Na} x_{Cl} + \frac{1}{2} (1/\lambda) K_H^{Na} x_{Na} + \frac{1}{2} K_{OH}^{Cl} x_{Cl}}{x_{Na} x_{Cl} + \frac{1}{2} K_H^{Na} x_{Na} + \frac{1}{2} K_{OH}^{Cl} x_{Cl}} \end{aligned} \quad (32)$$

Here,

Table 1. Capacity and equilibrium constants of each cation and anion exchange

a) typical values used in the theoretical calculation	
capacity [kmol·m ⁻³]	$Q_H = 3.00$ $Q_{OH} = 2.00$
equilibrium constant [-]	$K_H^M = 1.5$ $K_{OH}^A = 7.0$
b) measured values by experiment	
capacity [kmol·m ⁻³]	$Q_H = 2.86$ $Q_{OH} = 1.68$
equilibrium constant [-]	$K_H^{Na} = 1.56$ $K_{OH}^{Cl} = 7.29$

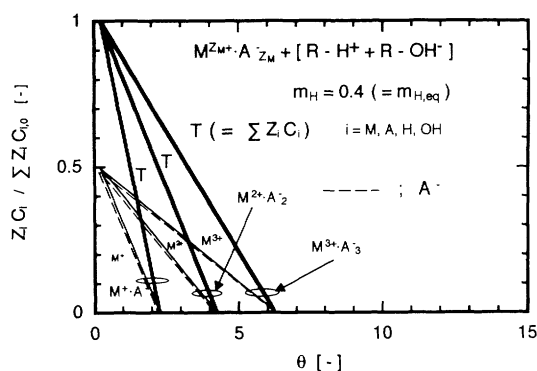


Fig. 1 Relationships between θ and concentration of ions at equilibrium solution

$$\lambda = \left(\frac{Q_{OH}}{Q_H} \right) \left(\frac{1 - m_H}{m_H} \right)$$

In both equations, the first term on the right side shows the ion exchange relation of a single resin, and the second one expresses the contribution to the equilibria by mixing resins.

When both resins are mixed at equal normality ($Q_H v_H = Q_{OH} v_{OH}$), the following relation is obtained.

$$m_{H,eq} = Q_{OH} / (Q_H + Q_{OH}) \quad (33)$$

Therefore, $\lambda = 1$, and $y_{Na} = y_{Cl} = 1$.

1.2 Simulation results and discussion

To clarify the effects of some factors on the deionization equilibrium behavior, the equilibrium relations were calculated by the equations described in the above section. The characteristic values used in the calculation are listed in **Table 1 a**.

1) The case in which both ion exchange resins are mixed at equal normality: $m_H = m_{H,eq}$

For both cation M^{Z_M+} and anion A^{Z_A-} , the equilibrium relations become a rectangular isotherm, and the result is independent of ionic valence.

The relations between the concentrations of each and/or total ions and an amount of the mixed resin are

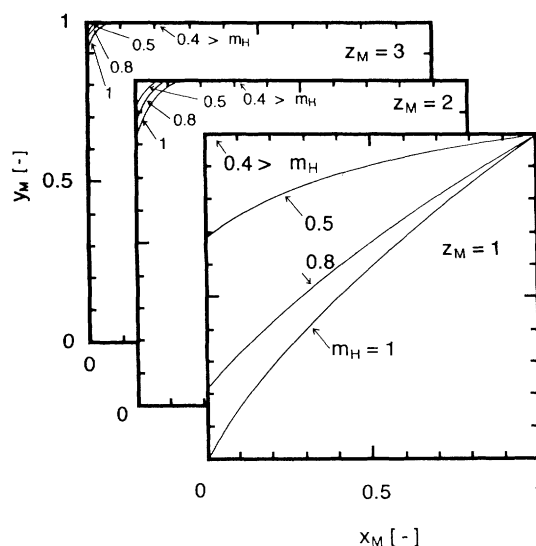


Fig. 2 Equilibrium relations of cation between liquid and resin phase. $C_0 = 1 \text{ mol} \cdot \text{m}^{-3}$

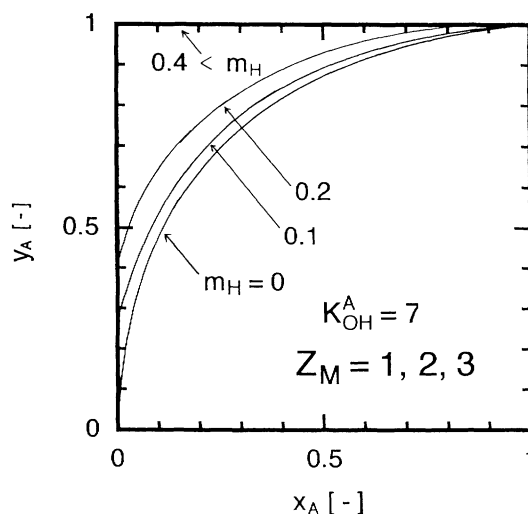


Fig. 3 Equilibrium Relations of anion between liquid and resin phase. $C_0 = 1.0 \text{ mol} \cdot \text{m}^{-3}$

shown in **Fig. 1**.

From this figure, it is found that the total concentration of ions, C_T , straightly decreases with increasing amount of the resins. The minimum amount of the resins for complete deionization increases with ionic valence of a removed salt. The relations $Z_M C_M = Z_A C_A$, $C_H = C_{OH} \cong 0$ ($\cong 10^{-7}$, $\text{pH} = 7$) are kept at equilibrium solution values, even when the salt is not completely removed from the water.

2) The case in which the two ion exchange resins are not mixed at equal normality: $m_H \neq m_{H,eq}$

The effect of the mixed volume ratio of the two resins on the deionization equilibrium is shown in **Figs. 2** (for cation M) and **3** (for anion A).

The line in the figures presents the calculated results for the cases of $Z_M = 1 \sim 3$ and $Z_A = 1$.

As shown in **Fig. 2**, in spite of ionic valence, addition of the anion exchange resin increases the adsorbed

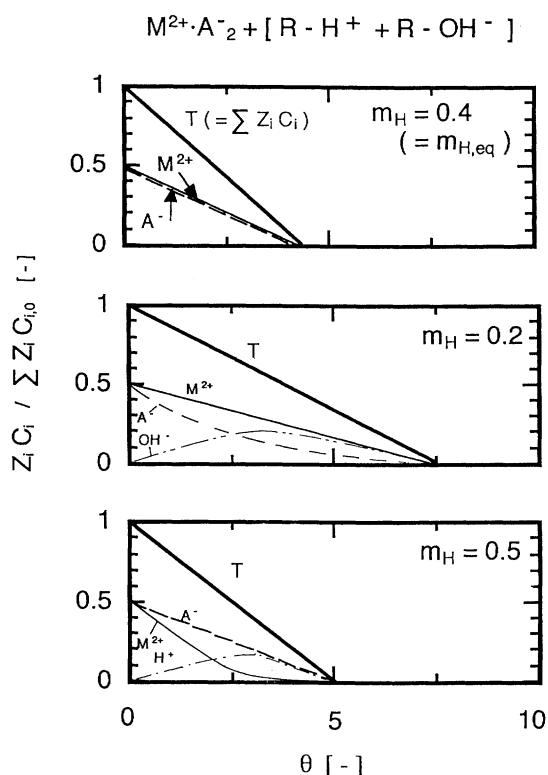


Fig. 4 Effect of m_H on relationships between θ and concentration of ions at equilibrium solution

fraction of M to the cation exchange resin. When $m_H \leq 0.4$, the equilibrium relations showed rectangular isotherms. The effect of the mixed volume ratio m_H on the deionization isotherms is more remarkable when $Z_M = 1$ than when Z_M is multi valent. This result suggests that the mixed volume ratio is an important factor in removing a salt that includes a mono valent ion.

As Fig. 3 shows, the equilibrium relation of the anion is not affected by Z_M , that is, by the ionic valence of the non-counter ion for the anion. This implies that the deionization isotherm is not influenced by the ionic valence of the non-counter ion. The tendency of m_H to increase with the amount of adsorbed anion is also seen in this figure.

Figure 4 shows the effect of m_H on the relation between the equilibrium liquid-phase concentration and the amount of the mixed resins. The lines in the figure express the calculated results for deionization of a salt consisting of a divalent ion (such as $M^{2+} \cdot A_2^-$). As for the minimum amount of the resins required to remove the salt, a mixture of the two resins at equal normality ($m_H = 0.4$) needs the least amount.

The relation between pH of the equilibrium solution and m_H is shown in **Fig. 5**. The calculation condition is the same as in Fig. 4. When $m_H = 0.4$ (equal normality mixing), the equilibrium solution is held to be neutral ($C_H = C_{OH} = 10^{-7} \approx 0$) at a given θ . When $m_H = 0.2$, the equilibrium solution includes M^{Z_M+} , A^- and OH^- , so the solution becomes alkaline, because the amount of OH^- eluted from the anion exchange resin is more than that of

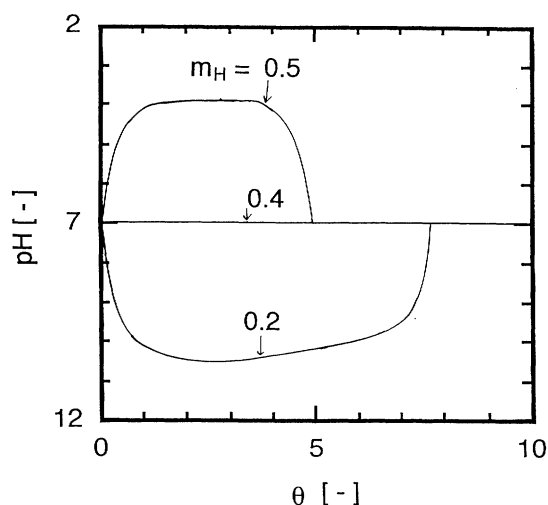


Fig. 5 pH values of equilibrium solution at various m_H . $C_0 = 1 \text{ mol} \cdot \text{m}^{-3}$

H^+ moved from the cation exchange resin and OH^- exists in the solution after the neutralization reaction.

2. Experimental

2.1 Experimental procedure

Both an H^+ -type strong cation exchange resin, SK1B, and an OH^- -type strong anion exchange resin, SA10A, were used. They were prepared by the usual conditioning method. Especially, conditioning of the OH^- -type resin was done immediately before the experiments in order to prevent CO_2 in the air from being adsorbed onto the resin.

An amount of the OH^- -type resin was rapidly weighed after removing surface water by a centrifuge (300 rpm, 30s). Both the weighed H^+ -type and OH^- -type resins were immediately contacted in a flask at various volume ratios of the resins and NaCl solution. The equilibrium relationships were obtained by measuring Na^+ and Cl^- concentration in aqueous solutions at equilibrium. Temperature was regulated at 298 K, and all the chemicals used were of special reagent grade. All solutions were prepared by using ultrapure water which was deaerated at 2-7 mmHg. The Na^+ and Cl^- concentrations in the solution were determined by emission spectroscopy and ion chromatography, respectively.

2.2 Experimental results and discussion

The equilibrium constants and capacities for both ion exchanges ($R - H^+ + Na^+ = R - Na^+ + H^+$, $R - OH^- + Cl^- = R - Cl^- + OH^-$) were measured by batch experiment. The experimental values of ion exchange properties for each resin are shown in **Table 1. b**).

A comparison of the calculated results using the values in Table 1. b) and the experimental ones at various m_H values is shown in **Fig. 6**. At equal-normality mixing ($m_H = m_{H,eq} = 0.370$), the experimental equilibrium isotherms of both Na^+ and Cl^- became rectangular, as predicted by the described calculation results. In the figure, both the computed and experimental results are

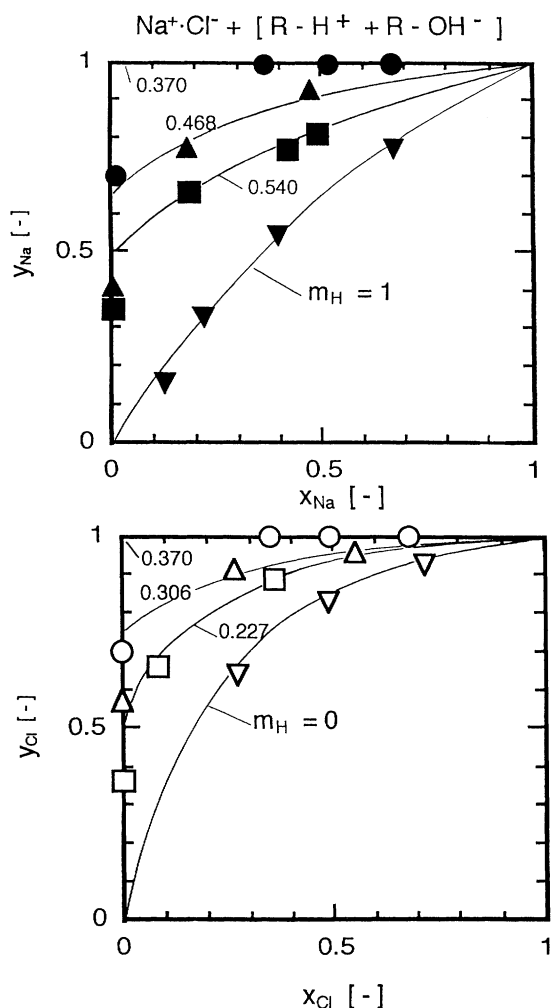


Fig. 6 Comparison of calculated and experimental results of equilibrium relations of NaCl at various m_H .
 $C_0 = 1.71 \text{ mol} \cdot \text{m}^{-3}$ (100 ppm as NaCl)

presented not only at various mixed volume ratios m_H ($= 0.227 \sim 0.540$) but also at single ion exchange ($m_H = 0, 1$). The plots obtained by experiment are in agreement with the calculated lines for each m_H . This shows that the presented expressions can predict the deionization equilibrium relationships well.

The relation between total ion concentration C_T and the amount of the mixed resins is illustrated in **Fig. 7**. When both resins are mixed at equal normality ($m_H = m_{H,eq} = 0.370$), total concentration is always the lowest at any θ . Agreement of experimental and calculated results was also good at various m_H . These results suggest that the mixed volume ratio m_H is an important element in effective desalination by the mixed resins.

Conclusions

Deionization equilibrium relations were derived, considering not only both cation and anion exchange

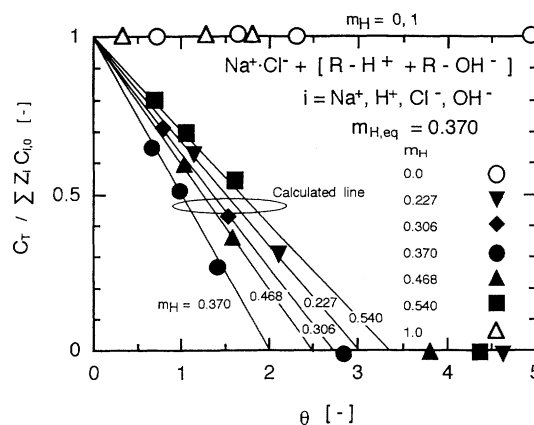


Fig. 7 Comparison of calculated and experimental values of equilibrium concentrations of ions at various m_H .
 $C_0 = 1.71 \text{ mol} \cdot \text{m}^{-3}$ (100 ppm as NaCl)

reactions but also the neutralization of H^+ and OH^- eluted from the resins. The experimental results obtained by using NaCl as a dilute salt are in good agreement with the calculated ones. It is found that the deionization equilibrium could be presented by the expressions described here.

Nomenclature

C	= concentration in liquid phase	$[\text{mol} \cdot \text{m}^{-3}]$
C_0	= initial concentration in liquid phase	$[\text{mol} \cdot \text{m}^{-3}]$
K	= equilibrium constant of ion exchange	$[-]$
K_W	= dissociation constant of water	$[\text{mol}^2 \cdot \text{m}^{-6}]$
m_H	= mixed volume ratio	$[-]$
$m_{H,eq}$	= mixed volume ratio at equal-normality mixing	$[-]$
Q	= ion exchange capacity of a resin	$[\text{mol} \cdot \text{m}^{-3}]$
q	= concentration in resin phase	$[\text{mol} \cdot \text{m}^{-3}]$
T	= total concentration of ions in liquid phase ($= \sum Z_i C_i$)	$[\text{equivalent} \cdot \text{m}^{-3}]$
V_T	= volume of solution in a tank	$[\text{m}^3]$
v_i	= volume of i -type resin	$[\text{m}^3]$
x_i	= C_i / C_0 ($i = M, A, H, OH$)	$[-]$
y_i	= q_i / Q	$[-]$
z_i	= ionic valence of i	$[-]$

$$\theta = \frac{v_H Q_H + v_{OH} Q_{OH}}{C_0 V_T} \quad [-]$$

<Subscripts>

A	= anion
M	= cation

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