

EXPERIMENTAL INVESTIGATION OF THE MASS TRANSFER MODEL FOR A DEIONIZATION PROCESS BY MIXED STRONG CATION AND ANION EXCHANGE RESINS

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Introduction

The deionization operation of water by mixed cation and anion exchange resins is one of the important processes to product ultra pure water. In practice, operational conditions have been obtained almost empirically^{6, 8)}.

Recently, higher purity of ultra pure water and more efficient producing operation have been required. Haub and Fouch presented a mass transfer model of deionization by mixed resins¹⁾. Their model was only applicable to the deionization process of monovalent ions under liquid phase diffusion controlling.

Some authors^{4, 5)} have investigated deionization processes by mixed resins under more extensive conditions. The equilibrium relationship of deionization by mixed resins has been studied both theoretically and experimentally⁴⁾. Furthermore, the mass transfer model in which both liquid and resin phase diffusion resistances, ionic valence and mixed fraction of the two resins were considered was also presented and discussed on the basis of the simulation results⁵⁾.

In this study, a stirred tank experiment for deionization by mixed resins was done. The mass transfer model is verified and discussed on the basis of the experimental results.

1. Experimental

The stirred tank experimental apparatus is basically the same as that used in the previous paper²⁾. Especially, in this study, to avoid CO₂ dissolving from the air through the experiment, the surface of the solution was covered by a floated plastic plate with a small mouth for feeding resin or collecting the solution. And also the stainless stirring rod and paddle were coated by teflon resin to prevent being contaminated with impurities.

Both an H⁺-type cation exchange resin (DIAION SK1B) and an OH⁻-type anion exchange resin (DIAION SA10A) were prepared by conventional conditioning methods. Before the experiment, the final conditioning of OH⁻-type resin was done using degassed 1.0 kmol·m⁻³ NaOH solution to remove impurities such as adsorbed CO₃²⁻ and HCO₃⁻ from the resin. A 0.5 dm³ solution of known concentration was prepared in the stirred tank at constant temperature (298 K). The rotating rate of the paddles was kept at 6.67 s⁻¹ in order to disperse the resins in the solution. Then, known weights of both resins were fed into the solution instantaneously. During the experiment, small portions of the solution were collected to measure the concentration changes of ions with time. The concentrations of Na⁺ and Ca²⁺ were determined by emission spectroscopy. The concentration of Cl⁻ was measured by both Fajan's method and the ion chromatography method.

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Table 1. Values used for calculating deionization rate

self-diffusivity of each ion [$\text{m}^2 \cdot \text{s}^{-1}$]	
liquid phase	
$D_{\text{H}} = 9.31 \times 10^{-9}$	$D_{\text{OH}} = 5.23 \times 10^{-9}$
$D_{\text{Na}} = 1.35 \times 10^{-9}$	$D_{\text{Cl}} = 20.3 \times 10^{-9}$
$D_{\text{Ca}} = 7.92 \times 10^{-10}$	
Resin phase	
$\bar{D}_{\text{H}} = 9.42 \times 10^{-10}$	$\bar{D}_{\text{OH}} = 2.40 \times 10^{-10}$
$\bar{D}_{\text{Na}} = 1.33 \times 10^{-10}$	$\bar{D}_{\text{Cl}} = 9.00 \times 10^{-11}$
$\bar{D}_{\text{Ca}} = 5.74 \times 10^{-11}$	
liquid phase mass transfer coefficient [$\text{m} \cdot \text{s}^{-1}$]	
$k_{\text{L, Na}}^0 = 1.10 \times 10^{-4}$	$k_{\text{L, Cl}}^0 = 1.48 \times 10^{-4}$
$k_{\text{L, Ca}}^0 = 7.77 \times 10^{-5}$	
ion exchange equilibrium constant [-]	
$K_{\text{H}}^{\text{Na}} = 1.56$	$K_{\text{OH}}^{\text{H}} = 7.29$
$K_{\text{H}}^{\text{Ca}} = 4.80$	
ion exchange capacity [$\text{kmol} \cdot \text{m}^{-3}$]	
$Q_{\text{H}} = 2.86$	$Q_{\text{OH}} = 1.68$
diameter of a resin particle [m]	
$d_{\text{p, H}} = 6.25 \times 10^{-4}$	$d_{\text{p, OH}} = 6.49 \times 10^{-4}$

Table 2. Experimental conditions

salt	initial concentration	mixed volume fraction
	C_0 [$\text{mol} \cdot \text{m}^{-3}$]	m_{H} [-]
NaCl	1.71	0.370
	2.50	0.370
	10.0	0.198, 0.370, 0.638
	100.0	0.370
CaCl ₂	1.25	0.370

2. Measurement of Physical Properties of Ion Exchange Systems

Physical properties of the experimental ion exchange systems are tabulated in **Table 1**. Liquid phase self diffusivities are estimated by limiting equivalent conductivity of each ion. Resin phase self diffusivities are measured in the stirred tank experiment. A solution concentration of $0.5 \text{ kmol} \cdot \text{m}^{-3}$ was adopted to make resin phase mass transfer resistance significant. The obtained values were nearly equal to the reported ones³. Equilibrium relations and ion exchange capacities were measured by a batch method at 298 K. Mean diameters of the resin particle were determined by averaging the diameter of one hundred particles.

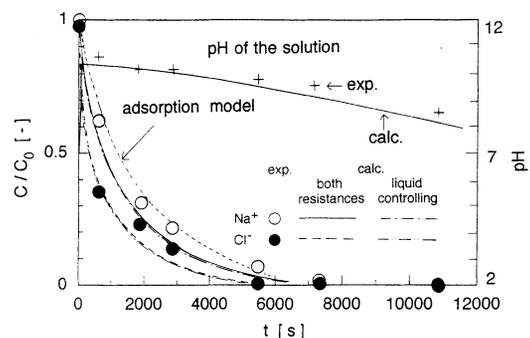
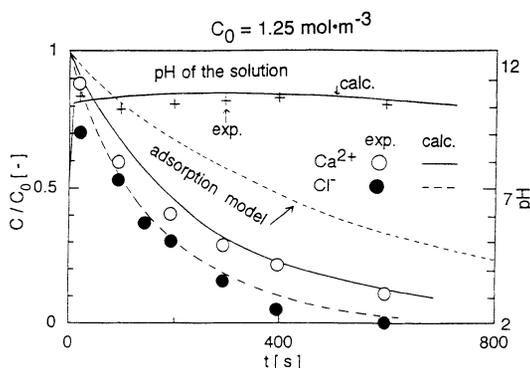
The liquid phase mass transfer coefficient was estimated with the correlation presented by Ohashi *et al.*⁷.

3. Experimental Results and Discussion

The experimental conditions are listed in **Table 2**.

Figure 1 shows the comparisons of experimental and calculated concentration changes of the deionization process for $1.71 \text{ mol} \cdot \text{m}^{-3}$ NaCl solution. Both resins were mixed at equal-normality ($m_{\text{H}} = m_{\text{H, eq}}$). The total ion exchange capability of the mixed resins was the same as the total concentration of both cation and anion contained in the initial solution.

From the previous paper⁵, it is suggested that deionization for low initial concentration as in Fig. 1 ($C_0 = 1.71 \text{ mol} \cdot \text{m}^{-3}$) proceeds under liquid phase mass transfer control. The calculation results under liquid phase control corresponded roughly to the result obtained

**Fig. 1** Comparison of calculated and experimental concentration and pH changes in NaCl + [R-H⁺ + R-OH⁻] system**Fig. 2** Comparison of calculated and experimental concentration and pH changes in Ca₂Cl + [R-H⁺ + R-OH⁻] systems

through considering both liquid and resin phase diffusion resistances. These calculated lines were also in good agreement with experimental results.

When $C_0 = 100 \sim 2.5 \text{ mol} \cdot \text{m}^{-3}$, the theoretical deionization curves—we only considered both diffusion resistances—corresponded to the measured results with the figure omitted. These results support the effect of initial concentration of a solution on the resistance's contribution to the deionization rate suggested in the previous paper⁵.

In the course of deionization, the pH value of the solution changed with time. The solution became alkaline just after starting the process and then gradually approached to neutral because the anion exchange rate is faster than the cation exchange rate.

Figure 2 shows the deionization process of CaCl₂ solution when the two resins are mixed at equal normality. Agreement of the calculated lines with the experimental results suggests that this model is applicable to the deionization process of a salt containing multivalent ions. In this case, the solution also became alkaline in the course of deionization.

In Figs. 1 and 2, the dotted lines show the theoretical one in which the deionization process is regarded as adsorption of a salt. The details of this adsorption model were described elsewhere⁵. There are great discrepancies between the calculated line based on the adsorption model and experimental data. These disagreements are

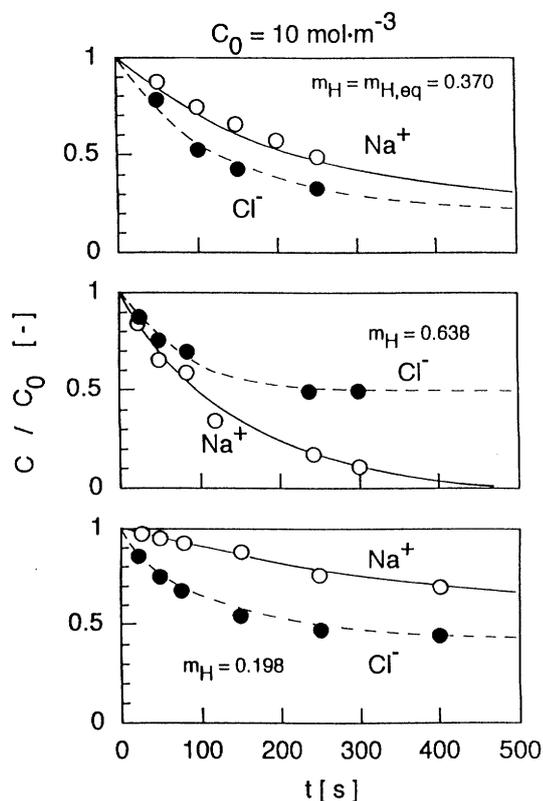


Fig. 3 Comparison of calculated and experimental concentration under various mixed volume ratios of the two resins in NaCl + [R-H⁺ + R-OH⁻] system

thought to arise because the effect of the neutralization reaction on ion exchange rate is not considered in the adsorption model.

There may be some cases in which the two resins are mixed at non equal normality ($m_H \neq m_{H,eq}$) such as when the treated water is not neutral or it contains weak acid species such as silica. The deionization process under various mixed volume ratios was also studied at $C_0 = 10 \text{ mol}\cdot\text{m}^{-3}$. The concentration changes of both Na⁺ and Cl⁻ are shown in **Fig. 3**. The simulated lines agreed with the experimental results not only when $m_H = m_{H,eq}$ but also when m_H

$\neq m_{H,eq}$. Calculated results using this model predicted the ion exchange rate very well for various values of m_H .

Conclusion

A stirred tank experiment using the mixed resins was done to check the proposed mass transfer model. Results calculated by the model agreed with experimental ones. During the deionization process, the pH value of the solution varied with time. The model is found to be applicable to deionization under various ionic valences and initial concentrations of a salt and mixed volume ratio. These results suggest that the details of mass transfer mechanism for the deionization process using mixed resins may be described by this model.

Nomenclature

C	= liquid phase concentration	[mol·m ⁻³]
C_0	= initial concentration in liquid phase	[mol·m ⁻³]
K	= equilibrium constant of ion exchange	[-]
m_H	= mixed volume ratio defined by $v_H / (v_H + v_{OH})$	[-]
$m_{H,eq}$	= mixed volume ratio at equal normality mixing	[-]
Q	= ion exchange capacity of a resin	[mol·m ⁻³]
q	= resin phase concentration	[mol·m ⁻³]
v	= volume of a resin	[m ³]

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-	= resin phase
*	= equilibrium
H	= H ⁺
OH	= OH ⁻

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