BREAKTHROUGH CURVE FOR LIQUID PHASE DIFFUSION CONTROLLING IN IRREVERSIBLE ION EXCHANGE

TAKESHI KATAOKA AND HIROYUKI YOSHIDA*

Department of Chemical Engineering, University of Osaka Prefecture, Sakai, 591

When the ion exchange reaction shown by Eq. (1) is accompanied by the instantaneous irreversible reaction expressed by Eq. (2) and $D^{n\mp}$ ion is the only noncounter ion in the liquid phase, the concentration of $B^{n\pm}$ ion at the solid-liquid interface is always zero.

For such ion exchange systems, the analytical solutions of breakthrough curve for liquid phase diffusion controlling is given as follows.

$$\left. \begin{aligned} x_B &= \exp(-6\xi) \\ y_B &= 6\tau \exp(-6\xi) \end{aligned} \right\}, 0 \leq \tau \leq 1/6 \quad (3)$$

$$x_B = y_B = \exp\{6(\tau - \xi) - 1\}, 1/6 \leq \tau \leq \xi + 1/6 \quad (4)$$

$$x_B = y_B = 1, \xi + 1/6 \leq \tau \quad (5)$$

$\mathcal{D}_{BD}$, the effective diffusivity of B ion, is used to calculate τ and ξ , and is expressed by Eq. (6)³⁾.

$$\mathcal{D}_{BD} = 2\mathcal{D}_B\mathcal{D}_D / (\mathcal{D}_B + \mathcal{D}_D) \quad (6)$$

Eq. (4) is the same equation proposed by Vermeulen *et al.*^{1,4)}.

Breakthrough time τ_B and exhaustion time τ_E are given by Eqs. (7) and (8), respectively.

$$\tau_B = (\ln x_B^B + 6\xi + 1)/6 \quad (7)$$

$$\tau_E = (\ln x_B^E + 6\xi + 1)/6 \quad (8)$$

The length of exchange zone, ξ_{zone} is expressed as

$$\xi_{\text{zone}} = (1/6) \ln(x_B^E/x_B^B) \quad (9)$$

Utilization U defined by the following equation is shown as.

$$\begin{aligned} U &= \text{breakthrough capacity} / \text{bed capacity} \\ &= \{\xi + (1 - x_B^B + \ln x_B^B)/6\} / \xi \\ &= \{\tau_B - x_B^B/6\} / \{\tau_B - (1 + \ln x_B^B)/6\} \end{aligned} \quad (10)$$

Experimental Equipment and Procedure

The principal parts of the equipment made of acrylic resin is shown in Fig. 1. The dimensions of the column packing the resin beads (© in Fig. 1) are 10 mm dia. and 50, 100 and 200 mm height. After the resin particles were packed in the column ©, degassed

distilled water at constant temperature was passed into the bed for about ten minutes. Next, the inlet of the column © was shut by the sliding plate, and parts ④ and ⑤ were filled by the feed solution. Then, glass beads of the same diameter as the resin particles maintained at experimental temperature were packed into ⑥.

Thereafter the sliding plate was rapidly moved, and the feed solution allowed to flow down the column at a constant flow rate.

Table 1 shows the experimental systems and conditions used in this study.

Breakthrough Curve

Fig. 2 shows the experimental results of the breakthrough curve in R-H-NaOH and R-OH-HCl systems. The solid and dotted lines are the theoretical ones calculated from Eq. (4).

Experimental results for R-H-NaOH system agree fairly well with Eq. (4) except for final part.

In the R-OH-HCl system, the degree of fitting between experimental and theoretical values is not better than the case of R-H-NaOH system. Because the resin beads of R-OH type presented a lot of congregated clusters, the distribution of void fraction in the

Fig. 1 Main part of experimental equipment

Received November 5, 1975.

Presented at the Hokuriku Meeting of The Soc. of Chem. Engrs., Japan, at Toyama, July, 1974.

Table 1 Experimental systems and conditions

System	Resin	Feed solution concentration [N]	Bed height [cm]	Temperature [°C]
R-H+NaOH→R-Na+H ₂ O (R-H+Na ⁺ ⇌R-Na+H ⁺) (H ⁺ +OH ⁻ →H ₂ O)	DIAION SK1B (D _p =0.481 mm)	0.001 0.002 0.004	5 10 20	25
R-OH+HCl→R-Cl+H ₂ O (R-OH+Cl ⁻ ⇌R-Cl+OH ⁻) (OH ⁻ +H ⁺ →H ₂ O)	DIAION SA10A (D _p =0.486 mm)	0.004	5	25

Fig. 2 Breakthrough curves of R-H-NaOH and R-OH-HCl systems, respectively

Fig. 4 Relation between utilization U and breakthrough time τ_B

Fig. 3 Breakthrough time τ_B and exhaustion time τ_E

bed is not uniform and the flow pattern does not become a uniform one.

k^* used for the calculation of ξ and τ was evaluated by the following equation²⁾.

$$j^* = \left(\frac{1-\varepsilon}{\varepsilon} \right)^{1/3} \frac{k^* S c^{2/3}}{u_f / \varepsilon} = 1.85 Re'^{-2/3}$$

Breakthrough Time τ_B and Exhaustion Time τ_E

Fig. 3 indicates the relations between τ_B and ξ and between τ_E and ξ . These experimental results agree fairly well with Eqs. (7) and (8), respectively.

Utilization U

U is shown in **Fig. 4**. The theoretical curve represents good agreement with the measured values. As the theoretical curve shows clearly, U increases little with an increase of τ_B at $\tau_B > 3$. Accordingly, in the

course of designing ion exchange system, to adopt the large value of τ_B or ξ in order to increase the value of U is not a reasonable design.

Nomenclature

C	= liquid phase concentration	[meq./cm ³]
C_0	= feed solution concentration	[meq./cm ³]
$\mathcal{D}$	= liquid phase diffusivity	[cm ² /sec]
$\mathcal{D}_{BD}$	= $2\mathcal{D}_B\mathcal{D}_D/(\mathcal{D}_B+\mathcal{D}_D)$, liquid phase effective diffusivity	[cm ² /sec]
D_p	= diameter of resin particle	[cm]
H	= bed height	[cm]
k^*	= liquid phase mass transfer coefficient	[cm/sec]
n	= integer	[—]
Q	= total exchange capacity	[meq./cm ³ ·resin]
q	= resin phase concentration	[meq./cm ³ ·resin]
Re'	= $D_p u_f \rho / (1-\varepsilon) \mu$	[—]
Sc	= $\mu / \rho \mathcal{D}_{BD}$	[—]
Sh	= $k^* D_p / \mathcal{D}_{BD}$	[—]
t	= time	[sec]
U	= breakthrough capacity/bed capacity	[—]
u_f	= superficial velocity	[cm/sec]
v	= linear velocity	[cm/sec]
x	= C/C_0	[—]
x^B	= breakthrough concentration	[—]
x^E	= exhaustion concentration	[—]
y	= q/Q	[—]
z	= axial dimension of bed	[cm]
ε	= void fraction	[—]
μ	= viscosity	[g/cm·sec]
ξ	= $(Sh/Re' Sc)(z/D_p)$	[—]
ξ_{zone}	= length of exchange zone	[—]
ρ	= density	[g/cm ³]
τ	= $k^*(t-z/v)C_0/(D_p Q)$	[—]
τ_B	= breakthrough time	[—]
τ_E	= exhaustion time	[—]

<Subscripts>

- A, B = counter ion
 D = non-counter ion reacting with A
 BD = molecular ($B^{n\pm}D^{m\mp}$)

Literature Cited

- 1) Hiester, N. K. and T. Vermeulen: *Chem. Eng. Prog.* **48**,

505 (1952).

- 2) Kataoka, T., H. Yoshida and K. Ueyama: *J. Chem. Eng. Japan*, **5**, 132 (1972).
3) Kataoka, T., H. Yoshida and Y. Shibahara: *ibid.*, **9**, 130 (1976)
4) Vermeulen, T.: *Ind. Eng. Chem.*, **45**, 1664 (1953).

MEASUREMENTS OF THE RELATIVE HUMIDITY OF SATURATED AQUEOUS SALT SOLUTIONS

CHIKAO ARAI*, SHUJI HOSAKA¹, KOJI MURASE² AND YOSHIKI SANO
Department of Textile Chemical Engineering, Shinshu University, Ueda, 386

Introduction

In order to control the relative humidity of air, saturated aqueous solutions of inorganic salts have been widely used in a laboratory.

There are several methods available for determining the value of the relative humidity over the saturated salt solution. In many cases the vapor pressure of water in equilibrium with the solution is measured and then the ratio p/p_s is calculated. A large number of experimental results based on this method have been reported. The results appearing in the literature^{2,5,6)}, however, differ up to several percentages. It may be considered that the disagreement have been due to the following:

1) Vapor pressures are usually measured in an apparatus made of glass tubing. To make easy experimental operations, glass stopcocks or taper joints etc. are attached to the apparatus. Therefore a small amount of air may leak through these glass implements;

2) The conventional manometer is not accurate enough for low vapor pressure measurements;

3) In a few reported cases the measurements may have been carried out with unsaturated solutions;

In the present study, the authors attempted first to avoid the above points. Although the apparatus had a construction similar to that appearing in the literature^{2,5)}, no glass stopcocks or taper joints were attached in the main part of the apparatus. Using a pair of reading scales of a Göttingen manometer with minimum scale 1/50 mm, the differences in the heights

of the manometric liquid are read with good precision. Moreover, a magnetic stirrer makes it easy to prepare saturated salt solutions within the cell.

The values measured after the modifications showed a good reproducibility, and agreed well with the values estimated from the activities of salts in solutions.

Values of the Relative Humidity

A saturated salt solution with excess salt was prepared as a slushy mixture of water (distilled after ion exchange) and a salt of special chemical grade.

Values of the relative humidity were measured for saturated solutions of eleven salts and an alkali at temperatures from 10° to 50°C. The results are shown in **Table 1**. Each value is the average of several runs. The value for sodium hydroxide at 10°C is not shown since a stable value of vapor pressure was not obtained due to the complex solid phase of sodium hydroxide. The standard deviation of the value is also shown as an index of fluctuation from the average. From these values, it is evident that our measurements have excellent reproducibility.

Vapor pressures calculated from the values of relative humidity fall on the straight line in the Cox-diagram. If a hydrate salt in solid phase converts to a lower hydrate salt at a given temperature, for example, $\text{LiCl} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{LiCl} \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ at 18.5°C, the phase transition would break the line of the diagram. The relative humidity changes measured around the transition point are shown in **Table 2**.

Comparison with Estimated Values

To ascertain further the accuracy of the data, we compared the present data with values estimated from the activities of salts which can be usually determined with high degree of accuracy by various

Received January 30, 1976.

Presented at the 40-th Annual Meeting of The Soc. of Chem. Engrs., Japan, at Nagoya, April 1975.

¹ Arisawa Seisakusho Co. Ltd., Jyo-etsu, 943.

² Dupont Far-East Co., Tokyo, 107.