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# A Study on the Adsorption of Gold(III) with Macroporous Crosslinked Polyacrylate MET Resins. III. Liquid Diffusion Process

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## ABSTRACT

The breakthrough operations for gold tetrachloride in hydrochloric acid solution on a fixed bed were carried out with different kinds of MET resins, different radii of particles, different linear flow velocities, and different media concentrations at temperature of 25 ± 0.5°C. The values of HETP were calculated from the experimental breakthrough curves. It was demonstrated that the rate of mass transfer was controlled by the liquid diffusion process. Two sets of thicknesses of the liquid film were calculated from the experimental HETP values and the conditional parameters, respectively. By comparing the two sets of liquid film thicknesses, we find that the adsorption double layer on the resin/solution interface plays an important role in the liquid mass transfer process.

## INTRODUCTION

In the preceding papers of this research program (1, 2), we conducted investigations on adsorption equilibria and particle diffusion processes

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concerning adsorption of gold tetrachloride from aqueous chloride solutions with macroporous crosslinked polyacrylate (MET) resins (corresponding to XAD-7). Equilibrium and kinetic data, such as selectivity coefficients and particle interdiffusion coefficients, were obtained from the experiments. The equilibrium adsorption mechanism and particle diffusion process were researched carefully. In order to have a thorough study on the adsorption of gold(III) with MET resins, we carried out experiments on the breakthrough operations for this paper. The values of HETP for all experimental runs were calculated, and the rates of mass transfer were demonstrated to be governed by the liquid diffusion process. Thus, the experimental data afforded us an opportunity to investigate the liquid diffusion process in detail.

The liquid diffusion process is a very important and complex topic in the field of ion-exchange research. The rate of the process is usually described by the diffusion constant of the liquid film, $R_F$, and the liquid mass transfer coefficient $K_L$.

Based on the concepts of a concentration gradient and of a liquid film, Boyd et al. (3) derived the equation

$$R_F = 3D/(2r_0\lambda\sigma) \tag{1}$$

where $\lambda$ and $D$ are the linear distribution coefficient and the liquid diffusion coefficient of the species, respectively; $r_0$ is the radius of the resin particle; and $\sigma$ the thickness of the liquid film (in which the concentration gradient is assumed to be linear).

Based on the concept of a driving force of diffusion and a boundary layer, Carberry (4) derived the equation

$$K_L = 1.15(V/\alpha_0)(N_{Re})^{-1/2}(N_{Sc})^{-2/3} \tag{2}$$

where V is the linear flow rate, $\alpha_0$ is the void fraction of the column, $N_{Re}$ is the Reynolds number [$N_{Re} = 2r_0V/(\alpha_0\eta)$], and $N_{Sc}$ is the Schmidt number [$N_{Sc} = \eta/D$]. $\eta$ is the kinematic viscosity of the fluid. Equation (2) is derived under the condition that the flow rate is confined in a wide regime in which a boundary layer is developed and destroyed repeatedly as the fluid journeys through the bed.

In this paper the experimental results were treated by using the above equations. Two sets of liquid film thicknesses were calculated and compared with each other. The effects of the structure of MET resin on the liquid film thickness were researched. According to our investigation, we found that the liquid film thicknesses in the breakthrough process were uncommonly large and that the adsorption double layer on the resin/solution interface played an important role in the liquid mass transfer process.

## THEORETICAL DISCUSSION

### HETP Estimation

Martin and Synge (5) applied the concept of Height of the Theoretical Plate, familiar to industrial chemists who dealing with rectification or solvent-extraction columns to ion-exchange chromatography. Powell and Spedding derived an equation that can be used to calculate the equilibrium HETP value (*H*eight *E*quivalent to the *T*heoretical *P*late) in a breakthrough process (6). In the present experiment, $AuCl_4^-$ and $Cl^-$ anions are counterions in the ion-exchange reaction (1). Thus Powell and Spedding's equation can be rewritten as

$$h/\log \alpha_{Cl^-}^{AuCl_4^-} = L_1^2/\log \frac{(\chi_{AuCl_4^-}/\chi_{Cl^-})_2}{(\chi_{AuCl_4^-}/\chi_{Cl^-})_1} \tag{3}$$

where $h$ refers to the value of equilibrium HETP, $\alpha_{Cl^-}^{AuCl_4}$ is the selectivity coefficient of $AuCl_4^-$ ion to $Cl^-$ ion, $(\chi_{AuCl_4^-}/\chi_{Cl^-})_2$ and $(\chi_{AuCl_4^-}/\chi_{Cl^-})_1$ are mole fraction ratios located on the breakthrough curve, and the distance from $(\chi_{AuCl_4^-}/\chi_{Cl^-})_2$ and $(\chi_{AuCl_4^-}/\chi_{Cl^-})_1$ is $L_1^2$. This equation is suitable for the breakthrough curves under equilibrium conditions and has the shape of a double logarithmic curve (7).

### Determination of the Controlling Step

Glueckauf (8) presented a quantitative discussion on ion exchange and adsorption chromatography. Based to the formulas of mass transfer of particle diffusion and liquid diffusion, he derived equations for calculating HETP values due to diffusions in resin and in solution phases

$$H_F = \frac{4V\sigma r_0}{3D(1 - \alpha_0)} \tag{4}$$

$$H_P = \frac{2r_0^2 V}{14\overline{D}(K_d + \alpha_0)} \tag{5}$$

where $H_F$ and $H_P$ refer to Glueckauf HETP values due to diffusions in resin and in solution phases, respectively; $\overline{D}$ is the diffusion coefficient of ionic species in the resin phase; and $K_d$ is the distribution factor.

Because the value of $\sigma$ decreases with an increase in the linear flow velocity V (9), the correlation can be expressed as

$$\sigma \propto 1/(V)^{\beta} \tag{6}$$

Combining Eqs. (4) and (6):

$$H_F \propto r_0(V)^{\gamma} \qquad 0 < \gamma < 1 \tag{7}$$

Thus, if the mass transfer of the breakthrough process is controlled by the liquid diffusion step, the Glueckauf HETP value will be directly proportional to $r_0$ and $V^{\gamma}$ according to Eq. (7). If particle diffusion is the controlling step in the mass transfer of the breakthrough process, the Glueckauf HETP value will be directly proportional to the value of $r_0^2$ and V according to Eq. (5).

It can be concluded from the above discussion that $r_0$ and V are the two main factors in studying the mechanism of the breakthrough process. By careful analysis of the relationships between HETP value and the two factors, the controlling rate step in the mass transfer of the breakthrough process could be determined.

## Estimate of the Thickness of Liquid Film

### Estimate from HETP Value

If mass transfer is controlled by the liquid diffusion step, the equilibrium HETP value obtained from the breakthrough curve is determined by Eq. (4). It has already been demonstrated that the Glueckauf HETP, $H$, is just two times as large as the equilibrium HETP, $h$, namely, $H = 2h$ (7). Therefore, we can estimate the thickness of the liquid film by substituting this equation into Eq. (4):

$$\sigma_E = \frac{3(1 - a_0)Dh}{2r_0 V} \tag{8}$$

where $\sigma_E$ is the thickness of the liquid film calculated from the equilibrium HETP.

### Estimate from the Boundary-Layer Model

Carberry (4) derived an equation for calculating the mass transfer coefficients in the fluid-particle molecular mass transfer process in a fixed bed in terms of a simplified boundary-layer theory. In his equation the influence of the liquid film on mass transfer is considered from the viewpoint of hydrodynamics. The equation is demonstrated by data from the literature (4) and was employed by other scientists in their article (10). Carberry's equation (Eq. 2) can be rewritten as

$$K_L = 1.15D^{2/3}V^{1/2}(2r_0\alpha_0)^{-1/2}\eta^{-1/6} \tag{9}$$

Comparing the boundary layer model with the liquid film diffusion model, a relationship between the mass transfer coefficient and the thickness of the liquid film can be obtained:

$$K_L = D/\sigma \tag{10}$$

Consider the flux rate of adsorbate from the flow phase into the fixed phase of a unit bed volume in the column process $dQ_b/dt$. The following equation may be written according to the definition of mass transfer coefficient $K_L$ (4) and liquid film diffusion constant $R_F$ (3)

$$dQ_b/dt = K_L S_0 (C_\infty - C) = R_F n_0 (Q_\infty - Q) \tag{11}$$

where $Q_b$ is the total amount of adsorbate per bed volume; $C_\infty$ and $Q$ represent the concentrations at equilibrium and at the present time in the solution phase adjacent to the resin phase, respectively; and $Q_\infty$ and $Q$ are the amounts of adsorbate per resin particle at equilibrium and at the present time, respectively. The surface area per bed volume, $S_0$, can be written as $S_0 = 3(1 - \alpha_0)/(2r_0)$, and the number particles per bed volume, $n_0$, is given by $n_0 = 3(1 - \alpha_0)/(4\pi r_0)$. By proper manipulation:

$$K_L = \frac{2}{3} r_0 \lambda R_F = \frac{D}{\sigma} \tag{12}$$

Combining Eqs. (9) and (10), a theoretical equation for calculation of the thickness of the liquid film is obtained:

$$\sigma_T = 1.23 \alpha_0^{1/2} D^{1/3} r_0^{-1/2} \eta^{1/6} v^{-1/2} \tag{13}$$

where $\sigma_T$ is the theoretical thickness of the liquid film.

According to this equation, one can predict the thickness of the liquid film from only the conditional parameters of the experiment without considering the breakthrough curves.

## EXPERIMENTS AND RESULTS

### Apparatus

The breakthrough operations were conducted in a jacketed glass column (0.65 cm i.d. × 10 cm packed length). The column was packed by adding a slurry of pretreated resin (1, 2). A carefully packed bed with a horizontal top is necessary in order to get satisfactory bands. An HL-1 model corrosion-resistant metering pump made in Shanghai, People's Republic of China, was used to deliver solution, and a BSZ-100 model fraction collector made in Shanghai was used to fractionate the effluents.

### Reagent

*Hydrochloric acid solution*: Prepared from analytical grade concentrated acid.

*Feed solution*: Proper quantities of Au(III) salt (analytical grade $HAuCl_3 \cdot HCl \cdot 3H_2O$) were dissolved in aqueous hydrochloric acids of different concentrations (0.250, 0.500, 0.750, and 1.00 $mol \cdot dm^{-3}$ HCl) to form feed solutions of $5.10 \times 10^{-5}$ $mol \cdot dm^{-3}$ of gold tetrachloride.

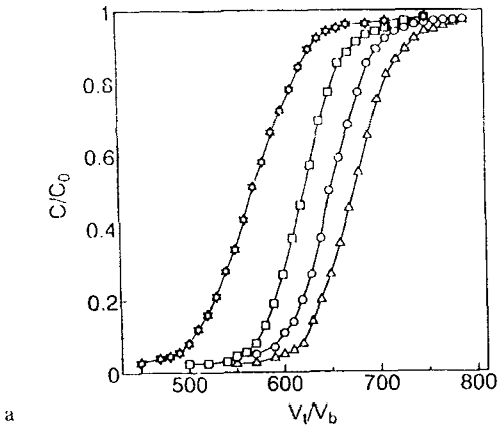

FIG. 1a Breakthrough curves with MET-601 resin. Variation of the radius. Height of bed = 10.7 cm, $\bar{V}$ = 10.0 cm·min$^{-1}$, $C_{HCl}$ = 0.500 mol·dm$^{-3}$, (△) $r_0$ = 3.1 × 10$^{-3}$ cm, (○) $r_0$ = 3.5 × 10$^{-3}$ cm, (□) $r_0$ = 4.7 × 10$^{-3}$ cm, (☆) $r_0$ = 3.1 × 10$^{-3}$ cm.

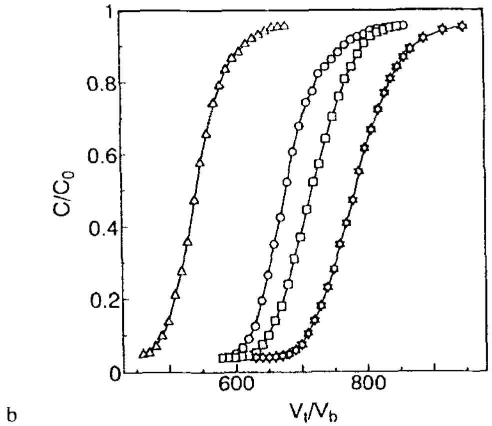

FIG. 1b Breakthrough curves with MET-601 resin. Variation of the acidity. Height of bed = 11.3 cm, $\bar{V}$ = 10.0 cm·min$^{-1}$, $r_0$ = 3.5 × 10$^{-3}$ cm, (△) $C_{HCl}$ = 0.250 mol·dm$^{-3}$, (○) $C_{HCl}$ = 0.500 mol·dm$^{-3}$, (□) $C_{HCl}$ = 0.750 mol·dm$^{-3}$, (☆) $C_{HCl}$ = 1.00 mol·dm$^{-3}$.

## Procedure

After the column was carefully packed, 200 cm$^3$ of aqueous hydrochloric acid with a concentration the same as that of the hydrochloric acid in the feed solution was passed slowly through the bed so that the resin was equilibrated with the aqueous hydrochloric acid of the feed. The gold

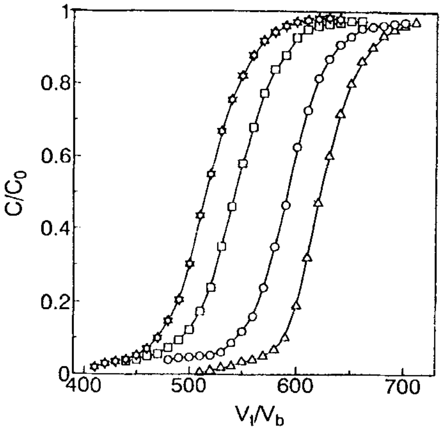

FIG. 1c Breakthrough curves with MET-601 resin. Variation of the velocity. Height of bed = 10.2 cm, $r_0 = 3.5 \times 10^{-3}$ cm, $C_{HCl} = 0.500$ mol·dm$^{-3}$, (△) $\bar{V} = 4.25$ cm·min$^{-1}$. (○) $\bar{V} = 8.00$ cm·min$^{-1}$, (□) $\bar{V} = 10.0$ cm·min$^{-1}$, (☆) $\bar{V} = 12.8$ cm·min$^{-1}$.

concentration in the feed was maintained at $5.10 \times 10^{-5}$ mol·dm$^{-3}$ for all experimental runs. This concentration value ensured that the breakthrough operations were conducted in the linear parts of the adsorption isotherm curves (1). The temperature was controlled at 25 ± 0.5°C for all runs. The experimental breakthrough curves were plotted as the ratio of the gold concentration in the effluent ($C_{AuCl_4^-}$) to that in the feed ($C^0_{AuCl_4^-}$) as the $Y$-axis, and the ratio of the cumulative volume of effluent ($V_t$) to the volume of bed ($V_b$) as the $X$-axis. The void fraction of column was found to vary between 0.7 and 0.5.

## Analysis

The gold concentration in the fractionated effluent was determined with a Hitachi 180-80 model atomic absorption spectrophotometer. The standard samples were made from spectrum grade metal gold, and the concentration of hydrochloric acid in the standard samples was the same as that in the feed solution.

## Experimental Results

The breakthrough experiments were carried out by using different kinds of MET resins, radii of particles, and concentrations of hydrochloric acid in the feed solutions and the linear flow velocities. Because of the large number of combinations, it is impossible to present all the experimental curves here. Figures 1a, 1b, and 1c show only the experimental break-

TABLE 1
List of Conditions and Equilibrium HETP Values for All Experimental Runs

| Run | Resin | $r_0$ (cm × $10^3$) | $C_{HCl}$ (mol·dm$^{-3}$) | V (cm·min$^{-1}$) | $h$ (cm) |
|---|---|---|---|---|---|
| 1 | MET-601 | 3.1 ± 0.2 | 0.500 | 10.0 | 1.28 |
| 2 | | 3.5 ± 0.2 | " | " | 1.34 |
| 3 | | 4.7 ± 0.3 | " | " | 1.79 |
| 4 | | 5.3 ± 0.3 | " | " | 1.94 |
| 5 | | 3.5 ± 0.2 | 0.250 | " | 1.31 |
| 6 | | " | 0.750 | " | 1.36 |
| 7 | | " | 1.00 | " | 1.39 |
| 8 | | " | 0.500 | 4.25 | 1.17 |
| 9 | | " | " | 8.00 | 1.29 |
| 10 | | " | " | 12.8 | 1.38 |
| 11 | MET-602 | 3.3 ± 0.2 | 0.500 | 10.0 | 0.926 |
| 12 | | 4.1 ± 0.2 | " | " | 1.20 |
| 13 | | 4.7 ± 0.2 | " | " | 1.34 |
| 14 | | 5.3 ± 0.2 | " | " | 1.55 |
| 15 | | 4.1 ± 0.2 | 0.250 | " | 1.17 |
| 16 | | " | 0.750 | " | 1.22 |
| 17 | | " | 1.00 | " | 1.25 |
| 18 | | " | 0.500 | 4.30 | 0.995 |
| 19 | | " | " | 7.45 | 1.12 |
| 20 | | " | " | 13.1 | 1.28 |
| 21 | MET-604 | 3.2 ± 0.2 | 0.500 | 10.0 | 1.19 |
| 22 | | 3.9 ± 0.2 | " | " | 1.32 |
| 23 | | 4.5 ± 0.3 | " | " | 1.55 |
| 24 | | 5.7 ± 0.3 | " | " | 1.87 |
| 25 | | 3.9 ± 0.2 | 0.250 | " | 1.30 |
| 26 | | " | 0.750 | " | 1.34 |
| 27 | | " | 1.00 | " | 1.37 |
| 28 | | " | 0.500 | 4.11 | 1.15 |
| 29 | | " | " | 7.73 | 1.26 |
| 30 | | " | " | 13.0 | 1.39 |
| 31 | MET-801 | 3.9 ± 0.2 | 0.500 | 10.0 | 0.729 |
| 32 | | 4.8 ± 0.3 | " | " | 0.840 |
| 33 | | 5.8 ± 0.4 | " | " | 1.10 |
| 34 | | 6.3 ± 0.4 | " | " | 1.16 |
| 35 | | 3.9 ± 0.2 | 0.250 | " | 0.677 |
| 36 | | " | 0.750 | " | 0.767 |
| 37 | | " | 1.00 | " | 0.801 |
| 38 | | " | 0.500 | 4.08 | 0.563 |
| 39 | | " | " | 8.14 | 0.687 |
| 40 | | " | " | 12.5 | 0.778 |
| 41 | MET-802 | 3.3 ± 0.2 | 0.500 | 10.0 | 1.54 |
| 42 | | 4.2 ± 0.2 | " | " | 1.91 |
| 43 | | 4.8 ± 0.3 | " | " | 2.20 |

TABLE 1 Continued

| Run | Resin | $r_0$ (cm × $10^3$) | $C_{\mathrm{HCl}}$ (mol·dm$^{-3}$) | V (cm·min$^{-1}$) | $h$ (cm) |
|---|---|---|---|---|---|
| 44 | | 7.2 ± 0.4 | " | " | 3.32 |
| 45 | | 4.8 ± 0.3 | 0.250 | " | 2.05 |
| 46 | | " | 0.750 | " | 2.37 |
| 47 | | " | 1.00 | " | 2.47 |
| 48 | | " | 0.500 | 1.44 | 1.11 |
| 49 | | " | " | 3.26 | 1.49 |
| 50 | | " | " | 11.1 | 2.28 |
| 51 | MET-804 | 3.9 ± 0.3 | 0.500 | 10.0 | 0.829 |
| 52 | | 4.1 ± 0.3 | " | " | 0.902 |
| 53 | | 5.4 ± 0.4 | " | " | 1.03 |
| 54 | | 6.2 ± 0.3 | " | " | 1.23 |
| 55 | | 3.9 ± 0.3 | 0.250 | " | 0.759 |
| 56 | | " | 0.750 | " | 0.871 |
| 57 | | " | 1.00 | " | 0.930 |
| 58 | | " | " | 4.22 | 0.596 |
| 59 | | " | " | 8.04 | 0.763 |
| 60 | | " | " | 12.8 | 0.911 |
| 61 | MET-1002 | 3.8 ± 0.2 | 0.500 | 10.0 | 0.750 |
| 62 | | 5.0 ± 0.3 | " | " | 0.935 |
| 63 | | 5.7 ± 0.4 | " | " | 1.02 |
| 64 | | 6.2 ± 0.4 | " | " | 1.18 |
| 65 | | 3.8 ± 0.2 | 0.250 | " | 0.684 |
| 66 | | " | 0.750 | " | 0.840 |
| 67 | | " | 1.00 | " | 0.944 |
| 68 | | " | 0.500 | 4.06 | 0.492 |
| 69 | | " | " | 8.05 | 0.677 |
| 70 | | " | " | 12.2 | 0.823 |
| 71 | MET-1004 | 3.2 ± 0.3 | 0.500 | 10.0 | 0.680 |
| 72 | | 4.3 ± 0.2 | " | " | 0.790 |
| 73 | | 4.6 ± 0.3 | " | " | 0.876 |
| 74 | | 5.5 ± 0.3 | " | " | 1.04 |
| 75 | | 4.3 ± 0.2 | 0.250 | " | 0.677 |
| 76 | | " | 0.750 | " | 0.900 |
| 77 | | " | 1.00 | " | 1.02 |
| 78 | | " | 0.500 | 4.00 | 0.523 |
| 79 | | " | " | 8.01 | 0.715 |
| 80 | | " | " | 12.3 | 0.867 |

through curves with MET-601 as an example. The equilibrium HETP values for the breakthrough processes have been calculated by applying Eq. (1). The value of the selectivity coefficient, $\alpha_{\mathrm{Cl}^-}^{\mathrm{AuCl}_4^-}$, needed in Eq. (1) was obtained in the first paper of this research program (1). Table 1 lists the conditions and the estimated $h$ values for all of the experimental runs.

### The Effect of Particle Radius on the Equilibrium HETP *h*

A linear relationship between the values of $h$ and the particle radius $r_0$ for all kinds of MET resins was found. Figure 2 shows plots of $h$ versus $r_0$ for some resins are a series of straight lines passing through the origin. It is clear that the value of $h$ is directly proportional to $r_0$ for all breakthrough processes.

### The Effect of Linear Flow Velocity on *h*

Plots of the logarithm of $h$ versus the logarithm of V for all MET resins also shows a group of straight lines, and the slopes of the lines are values between 0 and 1 for all resins. Figure 3 shows the plot of lg $h$ versus lg V for some resins. Table 2 summarizes the correlation between $h$ and the $h/r_0$ ratio, and the relationship between $h$ and the linear flow velocity.

### The Controlling Step of Rate of Mass Transfer

According to the results shown in Table 2, relationships between $h$ and $r_0$ and between $h$ and V are in agreement with the conditions of a liquid film controlling process as discussed in Theoretical Discussion Section. Therefore, the mass transfer of the breakthrough process for all runs is controlled by the liquid diffusion step.

### The Thickness of Liquid Film

Table 3 shows the values of the liquid film thicknesses as calculated by Eqs. (8) and (11). $\sigma_E$, determined from the experimental equilibrium

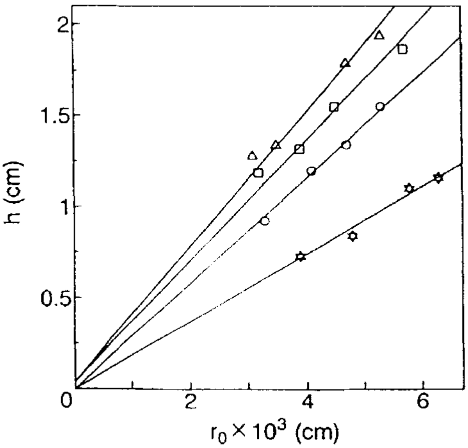

FIG. 2 Plots of the equilibrium HETP versus the particle radius. (△) MET-601, (○) MET-602, (□) MET-604, (☆) MET-801, (——) fitting line.

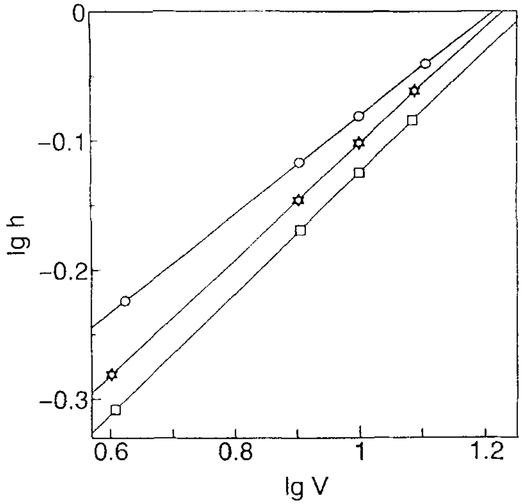

FIG. 3 Plots of lg $h$ versus lg $V$. (△) MET-804, (○) MET-1002, (□) MET-1004, (——) fitting line.

HETP by Eq. (6), represents a true value of the liquid mass transfer process whereas $\sigma_T$, calculated from the experimental condition parameters by Eq. (11), represents the predicted value based on the boundary-layer model (4). It was found that $\sigma_E$ is 10 or more times larger than $\sigma_T$ for each kind of resin, and that $\sigma/r_0$ is larger than 1 for all MET resins. It should be noted that for a gel-type resin, $\sigma/r_0$ is usually not larger than 1. The result that $\sigma_E$ is much larger than $\sigma_T$ and $r_0$ suggests that the nature of the parameter $\sigma_E$ is very different from the usual concept of the thickness of a liquid film, which has been described as a stationary layer surrounding the resin particle. A concentration gradient persists in this layer.

## The Effect of Kinematic Viscosity $\eta$ on $\sigma_E$ Value

The viscosity of the feed solutions was changed by varying the concentration of hydrochloric acid in the solutions. The viscosity coefficients of hydrochloric acid solutions with different concentrations was found from

TABLE 2

The Correlation between $h$ and $r_0$, V (condition: 25 ± 0.5°C, 0.500 mol·dm$^{-3}$ HCl)

| Resin (MET-) | 601 | 602 | 604 | 801 | 802 | 804 | 1002 | 1004 |
|---|---|---|---|---|---|---|---|---|
| $(h/r_0) \times 10^{-2}$ | 3.1 | 2.8 | 2.9 | 1.8 | 2.3 | 1.3 | 1.5 | 1.8 |
| $\gamma$ ($h \propto V^{\gamma}$) | 0.17 | 0.22 | 0.15 | 0.29 | 0.35 | 0.38 | 0.47 | 0.45 |

TABLE 3

Two Thicknesses of Liquid Film and $\sigma_E/r_0$ Values[a] (condition: 25 ± 0.5°C, 0.500 mol·dm$^{-3}$, V = 10.0 cm·min$^{-1}$.)

| Resin (MET-) | 601 | 602 | 604 | 801 | 802 | 804 | 1002 | 1004 |
|---|---|---|---|---|---|---|---|---|
| $\sigma_T \times 10^3$ (cm) | 1.2 | 1.3 | 1.3 | 1.3 | 1.9 | 1.3 | 1.2 | 1.3 |
| $\sigma_E \times 10^2$ (cm) | 2.5 | 2.0 | 2.2 | 1.2 | 1.1 | 1.4 | 1.3 | 1.3 |
| $\sigma_E/r_0$ | 5.3 | 4.9 | 5.6 | 2.5 | 2.6 | 3.1 | 2.6 | 3.0 |

[a] The liquid diffusion coefficients of $AuCl_4^-$ ion used in the calculation of $\sigma_T$ and $\sigma_E$ were obtained in another paper (11). For example, for 0.500 mol·dm$^{-3}$ solution at 25 ± 0.5°C, $D = 1.2 \times 10^{-5}$ cm$^{-2}$/s.

Ref. 12. Plots of the logarithm of $\sigma_E$ versus the logarithm of $\eta$ show a series of lines. The slopes of the lines, $\theta$, are listed in Table 4. Thus we have

$$\sigma_E \propto \eta^\theta \tag{14}$$

It is found from Table 4 that the exponent $\theta$ is much larger than predicted by the boundary-layer model equation (Eq. 11, in which $\theta = 1/6$), and $\theta$ varies for different kinds of resin. Based on this result, a relationship between $\sigma_E$ and $\eta$ stronger than that described by Eq. (11) is assumed to exist in the system investigated. By studying the structural parameters of MET resins, similar tendencies in the variation of $\theta$ and the specific surface area $S$ are found. MET-601, 602, and 604 with lower $\theta$ values have small values of $S$; MET-801, 802, and 804 with higher $\theta$ values have relative high $S$ values; and MET-1002 and 1004 with the highest $\theta$ values possess the largest values of $S$. This result leads to the conclusion that the stronger relationship between $\sigma_E$ and $\eta$ may be related to the specific surface area of a resin. The value of $S$ for every kind of resin is listed in Table 4 for comparison.

TABLE 4

Relationship between $\sigma_E$ and $\eta$[a] (condition: 25 ± 0.5°C, V = 10.0 cm/min)

| Resin (MET-) | 601 | 602 | 604 | 801 | 802 | 804 | 1002 | 1004 |
|---|---|---|---|---|---|---|---|---|
| $\theta$ ($\sigma_E \propto \eta^\theta$) | 2.1 | 3.0 | 2.4 | 6.0 | 7.4 | 8.8 | 12 | 18 |
| $S$ (m$^2$/g) | 124 | 192 | 137 | 255 | 272 | 268 | 361 | 334 |

[a] The kinematic viscosity values for solutions with certain concentrations of hydrochloric acid were obtained from the literature (12).

## The Effect of the Specific Surface Area on $\sigma_E$

According to Tables 3 and 4, the values of $\sigma_E$ for MET-601, 602, and 604, which have smaller values of $S$ (not larger than 200 $m^2/g$), are about two times as large as those for MET-801, 802, 804, 1002, and 1004, which have larger $S$ values (larger than 255 $m^2/g$). Therefore, the specific surface area also has an apparent influence on $\theta$.

## An Explanation on the Nature of $\sigma_E$

The experimental results show that $\sigma_E$ is larger than $r_0$. It is difficult to understand this in terms of the concept of the thickness of a liquid film (3, 7) which was defined as the stationary layer surrounding the resin particle. Thus, it is proper to regard $\sigma_E$ as a value representing the resistance to the liquid diffusion process in the present system.

The fact that $\sigma_E$ is very large may be explained by the outer layer (diffuse layer) of the adsorption double layer on the resin/solution interface.

As discussed in the second paper of this research program (2), the double layer on the MET resin/solution interface may be strong enough to influence the diffusion process. If the liquid diffusion process is considered, there should be two opposite influences of the double layer on $\sigma_E$:

1. The $AuCl_4^-$ and $Cl^-$ ions in the outer layer of the double layer resist the transfer of $AuCl_4^-$ ion from solution to the surface of the resin. This is the main reason why the value of $\sigma_E$ is larger than the value of $\sigma_T$ as predicted by the traditional concept of a liquid film.
2. A proton ion passing by the double layer will lose some hydrated water molecules under the influence of the electrostatic field, and thus the viscosity of the medium near a resin particle will decrease to a small extent. The friction between water molecules in an ionic solution is stronger than in pure water. This is due to the fact that water molecules in an ionic solution are affected by the ionic species and become less movable. According to Ref. 13:

$$\eta/\eta_0 = 1 + A\sqrt{C} \tag{15}$$

where $\eta_0$ is the viscosity of a solution with the ionic concentration $C$ equal to zero. Thus, the value of $\eta$ increases with an increase in concentration of ionic solutions. But in the electrostatic field of the adsorption double layer, the moving $H^+$ ion will gain the surface adsorption energy and lose some hydrated water molecules under the effect of the electrostatic field. Therefore, a decrease in the number of hydrated water molecules leads to a decrease in the viscosity of the solution in the local place. The viscosity decrease will make $\sigma_E$ decrease a little.

According to these considerations the experimental results could be interpreted as follows.

***a) The Effect of the Specific Surface Area on $\sigma_E$.*** Since the specific surface area of a MET resin is sufficiently large, there may exist a double layer on the resin/solution interface. The $AuCl_4^-$ ion attracted in the double layer acts as an electrical repulsion on the $AuCl_4^-$ ion diffusing from the bulk solution. This causes the $\sigma_E$ value to be much larger than the $\sigma_T$ value predicted from the boundary-layer model, and even greater than $r_0$. The specific surface area of a MET resin also influences the viscosity of any media passing through the double layer. The viscosity of the media in the double layer will decrease with an increase in specific surface area because the charge density of the double layer increases with the $S$ value. This will make the value of $\sigma_E$ decrease to a small extent. Thus, the result is that $\sigma_E$ is generally larger than $\sigma_T$ and $r_0$, and it will decrease to a small extent with any increase of the specific surface area $S$. Tables 2, 3, and 4 show the results.

***b) The Relationship between $\sigma_E$ and $\eta$.*** By comparing Eqs. (9) and (12), it is seen that there is a stronger relationship between $\sigma_E$ and $\eta$ than predicted from the boundary-layer model. This result may also be attributed to the influence of the double layer. Since the value of $\eta$ of the solution surrounding a resin particle is influenced by the adsorption double layer, the diffusion coefficient $D$ in this region would be changed as $\eta$ changes, and $\sigma_E$ would be changed as $D$ changes. Therefore, there is a much stronger relationship between $\sigma_E$ and $\eta$ than is predicted by Eq. (11), and $\sigma_E$ for each MET resin apparently increases with an increase in medium acidity.

***c) $\sigma_E$ and $r_0$.*** By combining Eqs. (6) and (8) it was found that $\sigma_E$ has nothing to do with $r_0$ for MET resins. This result is different from that obtained with gel-type resins. Because the main factor determining $\sigma_E$ in the present experiment is the adsorption double layer, the particle radius does not have any influence on the value of $\sigma_E$.

## The Empirical Formula of $\sigma_E$

Based on the above discussion, we put forward an empirical formula for $\sigma_E$ for the column process of the adsorption of Au(III) with MET resin from hydrochloric acid solution:

$$\sigma_E = \sigma_0 \alpha_0^{1/2} r_0^0 \eta^\theta \mathbf{V}^\gamma, \qquad 0 < \gamma < 1 \tag{16}$$

where $\sigma_0$ is the value of $\sigma_E$ when $\mathbf{V}$ and $\eta$ are equal to unity.

## CONCLUSIONS

The main conclusion to be drawn from the present study are as follows.

1) The rate of mass transfer of the breakthrough process under the experimental condition was controlled by the liquid diffusion step.

2) The value of $\sigma_E$, the experimental thickness of a liquid film, was much larger than that predicted by the boundary-layer model. The relationships between the conditional parameters and $\sigma_E$ were analyzed, and it was considered that the liquid diffusion process may be influenced greatly by the adsorption double layer on the MET resin/solution interface.

3) An empirical formula for $\sigma_E$ for the column process of the adsorption of gold tetrachloride from hydrochloric acid solution with a MET resin was proposed. It is noted that the particle radius has no effect on the value of $\sigma_E$. This is interpreted to mean that $\sigma_E$ is mainly determined by the adsorption double layer on the interface.

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