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

II. Particle Diffusion Process

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ABSTRACT

The kinetic behaviors of the adsorption of gold(III) with macroporous crosslinked polyacrylate (MET) resins from hydrochloric acid solutions were studied by employing the "shallow-bed" technique. The MET resins (corresponding to XAD-7) used in the study vary in structural characteristics. The particle interdiffusion coefficients for every kind of MET resins at four temperatures (25, 35, 45, and 55°C) were calculated from the experimental data, and the kinetic properties were carefully researched. It was found that the experimental results can be interpreted in the light of the concept of the adsorption double layer on the resin/solution interface.

INTRODUCTION

The resin-in-pulp (RIP) process has been researched as an alternative to the carbon-in-pulp (CIP) process for the extraction of gold from solution for many years. One of the important advantages for RIP processes is

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that synthetic resins are generally superior to activated carbons with respected to the rate of mass transfer of ions. Consequently, the RIP process may need less time than the CIP process to extract gold from the liquid phase. From this point of view, the kinetic property is an important consideration in the selection of a resin for gold adsorption in order to establish a highly efficient RIP process. Thus, an accumulation of detailed kinetic data as a reference for evaluation of a gold separation system and a full understanding of the kinetic behaviors in the adsorption of gold with resin are of great significance. On the other hand, the development of synthesis technology of organic resins in recent years has made it possible to produce various kinds of resins with special structures. It was found that macroporous resins are generally better than gel-type resins in the mass transfer of ions and molecules, and the excellent kinetic properties of macroporous resins are connected with their special structures (1, 2). This is important for the synthesis of macroporous resins for certain purposes such as the extraction of gold from the leach liquor of ores. If we know how certain structural parameters affect kinetic behaviors, we could synthesize resins with special structural characteristics in order to get special kinetic properties. Therefore, the correlation of kinetic properties and such structural parameters such as specific surface area, density, and porosity is an interesting subject for research in the effort to find organic gold adsorbents of high quality.

Amberlite XAD-7 (Rohm & Haas) has drawn attention as a good adsorbent of gold since Fritz and Miller (3) used it in the separation of gold from many other noble metals. Even though many chelate resins with better selectivity and higher capacities for gold extraction have been synthesized in recent decades, XAD-7 resin with its excellent kinetic properties can still serve as a representative of gold adsorbents.

The macroporous crosslinked polyacrylate (MET) resins made by the Institute of Polymer Chemistry, Nankai University, People's Republic of China, are similar to XAD-7 in composition and have various structural characteristics. Eight kinds of MET resins were employed in the present research. The "shallow-bed" technique was used to investigate the interparticle kinetic process of gold being adsorbed from hydrochloric acid solutions. The particle diffusion coefficients and the activation energies were obtained. The experimental results were carefully studied by comparing the kinetic behaviors and the structural parameters of the resins.

MATERIAL AND METHODS

Adsorption

Eight kinds of MET resin were used in the research. The dried resins were cleaned of preservative agents and polymerization residuals by three successive washings with acetone, 1.0 mol·dm^{-3} hydrochloric acid solution, and deionized water. The cleaned resins were wet-screened to produce various fractions of mesh size, and then all of the fractions were washed with a large quantity of 0.50 mol·dm^{-3} hydrochloric acid solution. The fractions of the swollen resins were photographed by microscopy. Not less than one hundred particles on the photograph for every kind of resin were measured, and the spherical radii of the fractions were calculated statistically. The cleaned resin fractions were put in a desiccator over a saturated sodium chloride solution at 25 ± 0.5°C before use until the weights of the resins were constant. The spherical radii of the fractions used in the present research and some other properties of the MET resins (4) are shown in Table 1.

Reagents

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 0.500 mol·dm^{-3} hydrochloric acid to form 2.00×10^{-4} mol·dm^{-3} $HAuCl_3$ + 0.500 mol·dm^{-3} HCl solution.

Acetone–0.10 mol·dm^{-3} Hydrochloric acid solution: Prepared by mixing 5 volumes of acetone with 1 volume of aqueous 0.10 mol·dm^{-3} HCl solution.

Procedure

The ion-exchange kinetic measurements were carried out by using the "shallow-bed" technique (4). The resin (0.1–0.2 g) was weighed onto the

TABLE 1
Spherical Radius and Some Properties of MET Resins Used in the Present Paper

Resin (MET-)	Matrix density ρ^0 (g·cm^{-3})	Apparent density ρ (g·cm^{-3})	Specific surface area S (m^2·g^{-1})	Mean pore diameter d (Å)	Pore volume v (cm^3·g^{-1})	Spherical radius r_0 (cm × 10^3)
-601	1.31	0.81	124	76.3	0.47	3.5 ± 0.2
-602	1.27	0.76	192	54.4	0.52	4.1 ± 0.3
-604	1.29	0.58	137	120	0.94	3.9 ± 0.2
-801	1.25	0.69	255	61.4	0.66	3.9 ± 0.2
-802	1.23	0.51	272	67.0	0.91	6.6 ± 0.2
-804	1.33	0.43	268	116	1.56	3.9 ± 0.3
-1002	1.34	0.60	361	51.5	0.93	3.8 ± 0.2
-1004	1.34	0.47	334	83.0	1.39	4.3 ± 0.2

sintered disk of a self-fabricated glass column with a water jacket to form a tiny resin bed with a depth of less than 0.2 cm. A thermostat was used to maintain the column and the feed solutions at certain temperatures (25 ± 0.5, 35 ± 0.5, 45 ± 0.5, and 55 ± 0.5°C). A conditioning solution (0.500 mol·dm^{-3} HCl solution) was slowly flowed through the bed so that the resin in the column was equilibrated with the medium condition of the feed solution. The feed solution was then forced by a meter pump to pass through the resin bed with a constant velocity of 20 cm·s^{-1} for periods of 0.2–5 minutes. The flow rate was great enough to ensure that there was no significant concentration gradient along the length of the bed and no significant variation in the composition of the feed solution passing through the bed. Before the elution of gold from resin, the bed was washed with 10 cm^3 of 0.500 mol·dm^{-3} hydrochloric acid solution to clean out any feed solution remaining in the void of bed. The adsorbed gold was then eluted three times from the resin with 10 cm^3 of the acetone–0.1 mol·dm^{-3} hydrochloric acid solution and determined by following procedure. The capacity of the resin was determined by the equilibrium experiments conducted in the first paper of this research program (4).

Analysis

The acetone contained in the effluent was removed by heating with a infrared lamp of modest radiant intensity and adding small quantities of 0.500 mol·dm^{-3} HCl solution three times as the sample was dried. Then the solution was moved to a 25 cm^3 volumetric flask and diluted to volume with 0.500 mol·dm^{-3} HCl solution. The gold content was determined with a Hitachi 180-80 model atomic absorption spectrophotometer. The standard samples were made from spectrum-grade metal gold, and the background solution of the standard samples was aqueous 0.500 mol·dm^{-3} hydrochloric acid.

RESULTS AND DISCUSSIONS

The experiment was carried out with all eight kinds of MET resins listed in Table 1 at temperatures 25 ± 0.5, 35 ± 0.5, 45 ± 0.5, and 55 ± 0.5°C. The experimental kinetic curves are not presented here.

Boyd's Equation Fitting

Based to the initial and boundary conditions of the "shallow-bed" method, Boyd et al. (5) derived the *F–Bt* equation describing the kinetics of ion exchange controlled by the diffusion process with a constant diffusion coefficient. The *F–Bt* equation can be written as

$$F = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \frac{\exp(-Btn^2)}{n^2} \tag{1}$$

$$B = \pi^2\overline{D}/r_0^2 \tag{2}$$

where F is the fractional attainment of equilibrium, t is time, r_0 is the radius of the spherical particle, and B and $\overline{D}$ are the diffusion constant and diffusion coefficient, respectively.

Two important fundamental limitations were presumed for the derivation of Eq. (1) (5): a) The ion-exchange reaction is limited between two isotopic counterions; b) The resin used in the research was a gel-type resin whose structure is much more homogeneous than that of the macroporous resins. These conditions ensured that the equation used in the treatment of the experimental data was without significant errors. Other researchers (6) showed that the limitations could be extended to diffusion between the counterions of different element with gel-type resins to obtain "particle inter-diffusion coefficients." As for macroporous resins, because of their much more heterogeneous structures, there has not been a final conclusion as to whether the F–Bt equation is suitable for use in the treatment of the experimental results. However, when the relationship between Bt and t calculated by the equation from the kinetic curves is linear, we can still employ the equation to determine the values of B and $\overline{D}$ shown in Eqs. (1) and (2). In this case, the $\overline{D}$ values can be regarded as "apparent" or "theoretical equivalent" diffusion (or interdiffusion) coefficients related to the particle diffusion processes, no matter what detailed physical chemistry properties they may have.

All of the experimental kinetic curves were numerically treated by using Eq. (1) on a microcomputer. It was found that the Bt is proportional to t for all the resins. As examples, Fig. 1 shows the plots of Bt versus t for MET-604, 804, and 1004. The results suggest that the F–Bt equation can be used in the present experiment and that the parameters calculated should have a theoretical equivalent significance. Table 2 shows that the values of B calculated from the slopes of the fitting lines and the values of $\overline{D}$ calculated by Eq. (2) at four different temperatures.

The Delay Time in Diffusion Process

It was found that most of the Bt–t lines do not pass through the origin of the coordinate. This result suggested that the $AuCl_4^-$ ion was not adsorbed onto the resin at the beginning of adsorption and the adsorption generally has a delay-period of 0.1–1 minute. The phenomenon was also discovered in other particle diffusion processes (8) conducted with macroporous resins. This will be discussed further in the following paragraph.

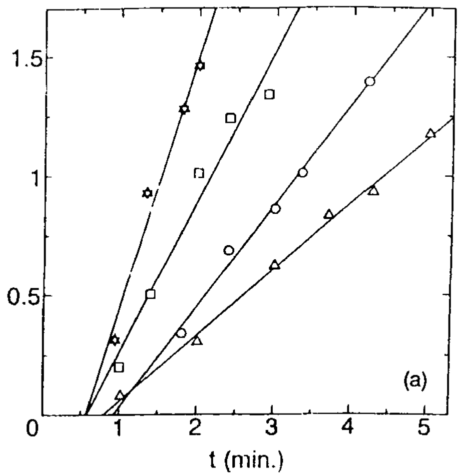

FIG. 1 Plots of Bt versus t for some MET resins. (a) MET-604, (b) MET-804, (c) MET-1004. (△) 25°C, (○) 35°C, (□) 45°C, (✡) 55°C, (——) fitting line.

TABLE 2
Kinetic Parameters for MET Resins

Resin (MET-)	$B \times 10^3$ (s^{-1}) $\bar{D} \times 10^9$ ($cm^2 \cdot s^{-1}$)	T (K)				ΔE_a ($J \cdot mol^{-1}$)
		289	308	318	328	
−601	B	5.13	6.58	8.35	10.1	17.9
	$\bar{D}$	6.4	8.2	10	13	
−602	B	5.75	6.76	7.94	9.95	14.4
	$\bar{D}$	10	11	14	17	
−604	B	4.61	7.00	10.5	17.4	34.9
	$\bar{D}$	7.1	11	16	27	
−801	B	10.9	13.4	16.2	21.1	17.3
	$\bar{D}$	17	21	25	33	
−802	B	9.07	7.75	6.08	5.86	−12.6
	$\bar{D}$	40	34	27	26	
−804	B	14.8	12.6	10.8	9.37	−12.3
	$\bar{D}$	23	20	17	14	
−1002	B	13.2	10.6	8.26	6.81	−17.8
	$\bar{D}$	19	16	12	10	
−1004	B	10.9	9.12	7.26	6.47	−14.4
	$\bar{D}$	20	17	14	12	

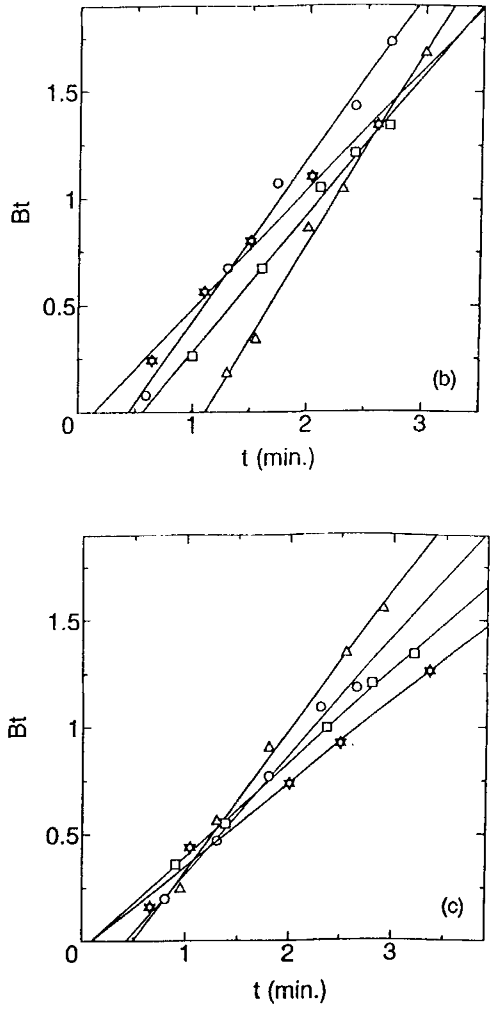

FIG. 1 Continued

The Estimate of ΔE_a

Since the process of diffusion was considered to be an activation mechanism (7), the activation energy within a relatively small range of temperatures can be calculated according to Arrhenius' formula

$$\overline{D} = \overline{D}_0 \exp\left(\frac{\Delta E_a}{RT}\right) \tag{3}$$

where ΔE_a is the activation energy. Combining Eq. (3) with Eq. (2), we have

$$\ln B = \ln B_0 - \frac{\Delta E_a}{RT} \tag{4}$$

Thus, ΔE_a can be obtained from the slope of curve $\ln B$–$1/T$. Based to this method, plots of $\ln B$ versus $1/T$ were drawn and it was found that there were linear relationships between the two values (Fig. 2). The activation energy ΔE_a associated with the particle diffusion process was calculated for all MET resins, and they are also listed in Table 2. It is seen that MET-601, 602, 604, and 801 resins are very different from MET-802, 804, 1002, and 1004 resins according to their activation energies. The first four resins have activation energies with positive values while the last four have activation energies with negative values. Thus, it is reasonable to divide the MET resins into two groups.

The Variation of Particle Interdiffusion Coefficient

It can been seen from Table 2 that for the resins in Group I (those with a positive activation energy), the value of $\overline{D}$ increases with an increase in temperature, while for the resins in Group II (those with a negative activation energy), the value of $\overline{D}$ increases with an increase in temperature. At 25°C the $\overline{D}$ values for Group II are about 2–3 times as large as those for Group I. Due to their complexity, it is difficult to find any obvious correlation between the structural parameters of the resins and the corresponding values of the particle interdiffusion coefficient. In the following paragraph we will concentrate on a discussion of the correlation between the activation energy of diffusion and the structural characteristics of the resins.

The Effect of the Specific Surface Area S on ΔE_a

By comparing the structural parameters of MET resins of the two groups, it is readily seen that the values of the specific surface area S of the resins in Group I are smaller than those of the resins in Group II. For most of the resins in Group I, the specific surface area values are smaller than 200 $m^2 \cdot g^{-1}$ whereas the S values are not smaller than 268 $m^2 \cdot g^{-1}$ for all the resins in Group II. Although MET-801 has a specific surface area ($S = 255$ $m^2 \cdot g^{-1}$) with a value close to those of the resins in Group II, it possesses a positive ΔE_a value. This may be attributed to its relatively large apparent density ρ.

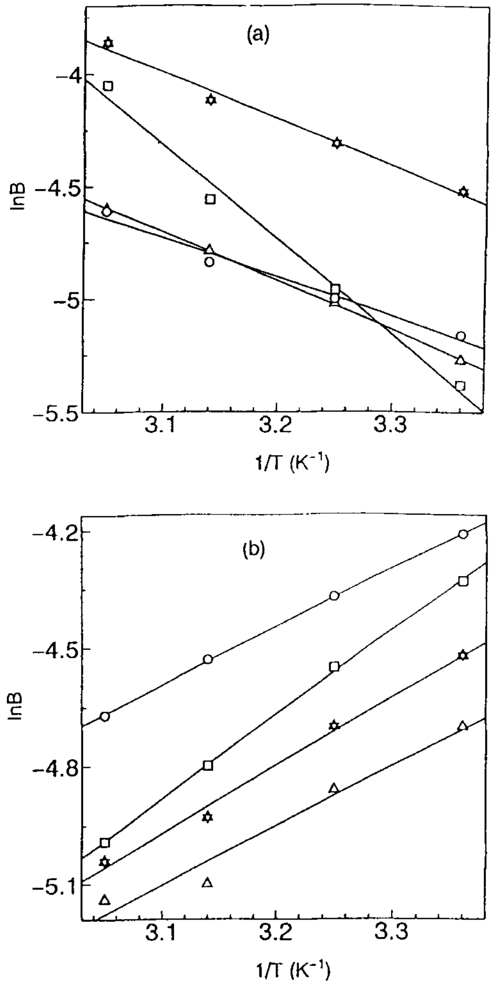

FIG. 2 Plots of ln *B* versus 1/*T*. (a) (△) MET-604, (○) MET-602, (□) MET-604, (✡) MET-801, (——) fitting line. (b) (△) MET-802, (○) MET-804, (□) MET-1002, (✡) MET-1004, (——) fitting line.

The Effect of the Apparent Density on ΔE_a

By comparing the structural parameters of MET-801 and 802, we find that the values of their specific surface area *S* and mean pore diameter *d* are close to each other, but there is a large difference in their ΔE_a values. MET-801 has a positive ΔE_a value and MET-802 has a negative value.

The only apparent difference in the structural parameters of the two resins is the apparent density. Therefore, the large difference in their ΔE_a values may be attributed to the difference in their apparent densities.

The Effect of the Mean Pore Diameter *d* on ΔE_a

By examining the resins in Group I, we found that ΔE_a values increase with an increase of the structural parameters of *d*, the mean pore diameter. The fact that MET-604 has the largest ΔE_a value may be attributed to its largest *d* value. In Group II, MET-804 and 1004 have similar ρ and *S* values, so the difference between their ΔE_a values should be attributed to the difference between their *d* values. The *d* value of MET-804 is larger than that of MET-1004, and the ΔE_a value of MET-804 is also larger than that of MET-1004, as is the case of Group I.

It can be concluded from the above discussion that the specific surface area *S* of a resin has a capital influence on the activation energy. The variation of the specific surface area may change the nature of the process. The apparent density ρ and the mean pore diameter *d* can also affect the activation energy value.

An Explanation in Light of the Concept of the Electric Double Layer

Due to its large specific surface area and the naked active functional groups, a macroporous resin may have a strong surface adsorption electric double layer on the resin/solution interface. Some articles (1, 8) discussed this phenomenon and investigated the influence of the adsorption double layer on the ion-exchange kinetics for macroporous resins. The double layer on the macroporous resin/solution interface should be similar to that on the colloid/solution interface (9). The structure of the adsorption double layer in the conditions of the present experiment may be as follows. Some of the $AuCl_4^-$ and Cl^- ions attracted by the protonized functional groups on the surface of the resin are rigidly held in a two-dimensional array to form the inner layer of the double layer (Stern layer); the other $AuCl_4^-$ and Cl^- ions attracted are not rigidly held in the two-dimensional array and tend to diffuse away from the interface to form the outer layer (Gouy layer) of the double layer (9). Figure 3 shows the schematic of the adsorption electrical double layer on the resin/solution interface.

If the electrostatic field of the adsorption double layer on the MET resin/solution interface is strong enough, it is reasonable to think that it will influence the diffusion process of the $AuCl_4^-$ ion. Thus, the activation energy (ΔE_a) can be divided into two parts which are associated with the different diffusion steps in the process. One part of the activation energy

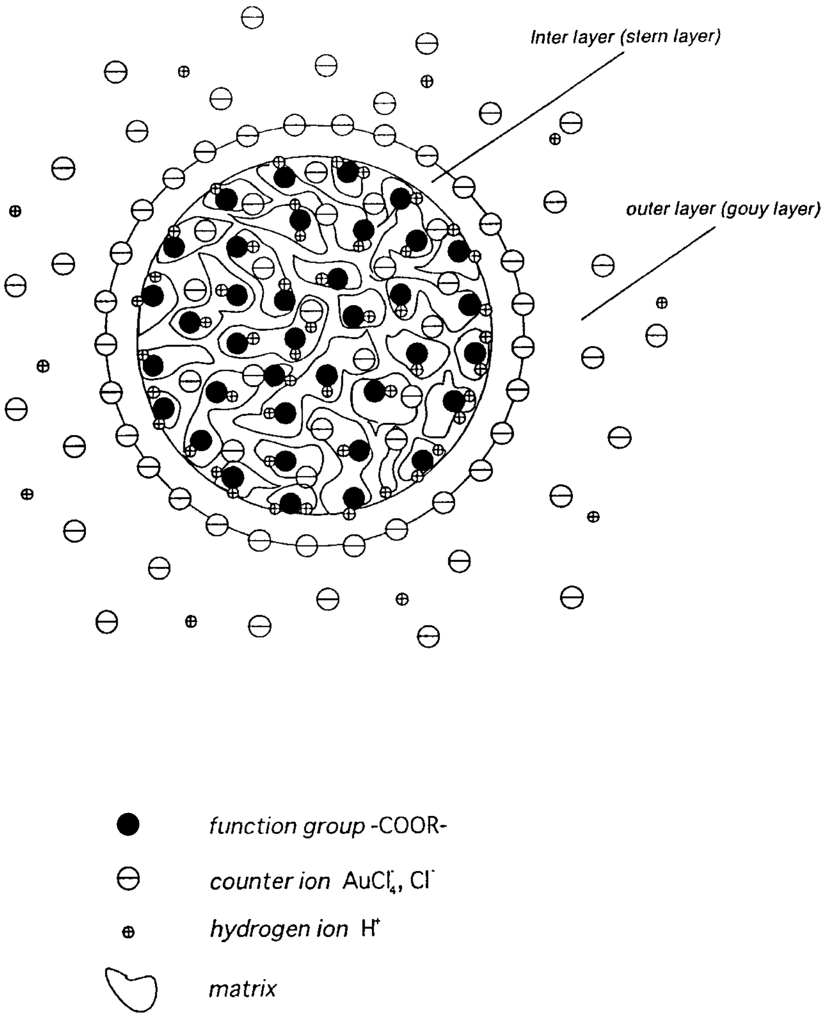

FIG. 3 Diagram of the adsorption double layer on the resin/solution interface.

is related to the diffusion step through the inner layer of the double layer (ΔE_{a1}), the other part is associated with the diffusion step through the resin phase (ΔE_{a2})

$$\Delta E_a = \Delta E_{a1} + \Delta E_{a2} \tag{5}$$

It is just the first term on the right-hand side of Eq. (5), ΔE_{a1}, that is affected by the double layer on the interface. As it crosses the inner layer of the double layer, the $AuCl_4^-$ ion will gain surface adsorption energy from the double layer, and this energy will become one part of the diffusion activation energy of the particle interdiffusion process. The greater the surface adsorption energy obtained, the smaller the ΔE_{a1} value will be. If the surface adsorption energy obtained is greater than the energy consumed in reaching the activation state, the value of ΔE_{a1} will be negative, and the surface adsorption energy obtained may be so great that the value of ΔE_a is changed to a negative value because of the effect of the negative value of ΔE_{a1}.

According to this consideration, the experimental results and the relationship between ΔE_a and the relevant structural parameters of the resin can be interpreted as follows.

The Explanation of the Delay Time

When a MET resin is in contact with the gold(III) solution, the double layer on the interface begins to be charged with $AuCl_4^-$ ions. $AuCl_4^-$ ions cannot enter the phase until the double layer arrives at a saturated state, which will take a period of time. In this period, $AuCl_4^-$ ions are only absorbed on the surface of the resin and can be easily eluted by other electrolytes such as the aqueous hydrochloric acid used in this experiment. Therefore, the experimental results showed that the Bt–t curve did not pass through the origin of the coordinate.

The Relationship between ΔE_a and the Specific Area S

The greater the specific surface area is, the higher the charge density of the double layer will be, and the stronger the electrostatic field will be. Since the resins in Group II have much larger specific surface areas than those in Group I, an $AuCl_4^-$ ion will obtain a much greater surface adsorption energy when it crosses the inner layer of a Group II resin than a Group I resin. This may explain why the ΔE_a values for resins in Group I are positive and the ΔE_a values for Group II are negative.

The Relationship between ΔE_a and the Mean Pore Diameter d

As the mean pore diameter decreases, the curvature of the pores increases. This also causes the charge density of the double layer and the electrostatic field to increase. The surface adsorption energy obtained by a $AuCl_4^-$ ion will increase with an increase in the electrostatic field of the adsorption double layer. Thus, the value of ΔE_a will decrease with a decrease in the value of d.

The Correlation of ΔE_a and the Apparent Density ρ

After crossing the adsorption double layer, $AuCl_4^-$ ions diffuse in the resin phase. The activation energy associated with this diffusion step is represented by ΔE_{a2} in Eq. (5). It has been found that the adsorption of $AuCl_4^-$ in the resin phase can be regarded as a "homogeneous" adsorption (4). Therefore, the apparent density ρ is an important factor for diffusion in the resin phase. The larger the value of ρ is, the greater will be the barrier for $AuCl_4^-$ ions to overcome in order to diffuse in the resin phase, and the value of ΔE_{a2} will increase as the increase of the value of ρ becomes larger. Therefore, the value of ΔE_a increases as the value of ρ increases. This can explain why MET-801 and 802, which have similar S and d values, are so different in their ΔE_a values.

We have found that the concept of an adsorption double layer is very helpful in understanding the results of our experiments. The successful explanation leads us to think that adsorption double layers do exist at the interface of macroporous MET resins and affect the particle diffusion process.

CONCLUSION

The main conclusions to be drawn from this study are as follows.

1) The kinetic curves for MET resins in the adsorption of $AuCl_4^-$ ions from hydrochloric acid solutions were experimentally obtained at four different temperatures by the "shallow-bed" technique. After using Boyd's equation, the experimental data for every resin and at different temperatures showed a linear relationship between Bt and t values. Based on this result, the particle interdiffusion coefficients and the activation energies were calculated.

2) It was found that there is an apparent relationship between the activation energy and the relevant structural parameters of MET resins. The specific surface area S is main influence on the activation energy of the diffusion. Variation of S may change the nature of the diffusion process. The apparent density ρ and the mean pore diameter d can also affect the activation energy value.

3) The relationship between the activation energy and the relevant structural parameters of the resin are complicated, and only by introduction of the concept of an adsorption double layer on the resin/solution interface can the effects of the structural parameters on the ion-exchange kinetics be explained satisfactorily.

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