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

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ABSTRACT

Equilibrium data for the adsorption of gold tetrachloride from aqueous solutions of four different concentrations of hydrochloric acid (0.250, 0.500, 0.750, and 1.00 mol·dm^{-3} HCl) by macroporous crosslinked polyacrylate (MET) resins which have the same functional groups and different structural characteristics have been obtained at a temperature of 25 ± 0.5°C. It was found that the mechanism of adsorption can be regarded as simple ion exchange, and that the adsorption of gold in the resin phase is a "homogeneous" adsorption. The equilibrium constants and the capacities for the adsorption of gold by MET resins were estimated, and the influence of the acidity of the solutions on the equilibrium parameters were discussed.

INTRODUCTION

The carbon-in-pulp (CIP) process is a conventional technology for the extraction of gold from cyanide media. Many successful hydrometallurgical plants have demonstrated that the CIP process is very practical. There

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are still some disadvantages in the method; for example, the activated carbon requires periodic thermal reactivation for the removal of absorbed organic materials, the elution of carbon has to be carried out at high temperature and in a pressure vessel, and appreciable amounts of gold included in sulfuric ore materials are not easily leached out with alkaline cyanide solutions. Therefore, there is great interest in developing other technologies for gold recovery. The extraction of gold from leach solutions by means of synthesized resins is one of these new methods requiring research [i.e., resin-in-pulp (RIP) process] (1). Although great progress has been made in the use of resins for gold recovery (2), there are still many unsolved fundamental problems. Only a few articles have discussed kinetic behavior in the extraction of gold by resins on the influence of resin structure on the behavior of gold adsorption. Both equilibrium and kinetic properties and the effect of resin structure on these properties are very important for evaluating the of method, selecting the resins, designing the technological process, and synthesizing resins with special structures and properties for the RIP process.

Amberlit XAD-7 is an adsorption resin made by Rohm & Haas Company. Due to its good selectivity and kinetic features, XAD-7 was investigated as a separation reagent both for the analysis of gold in samples containing other metal ions (3) and for the extraction of gold from leach liquors (4). Thus, it can be used as a representative resin to carry out research on the basic processes of gold recovery on synthesized resins.

A macroporous crosslinked polyacrylate (MET) resin series has been synthesized by the Institute of Polymer Chemistry, Nankai University, China. These resins are similar to XAD-7 in their functional groups and differ from each other in their structural characteristics. Based on this, MET resins were employed in this research program. We have conducted a study on the equilibrium and kinetic process of adsorption of gold from aqueous chloride solution, and on the relationship between the resin structural features and the adsorption behavior.

For the present paper, equilibrium experiments were carried out. Eight sets of isotherms for MET resins in solutions of four concentrations of hydrochloric acid were obtained. The results are discussed, and the experimental data will be used in the third paper of this research program.

MATERIAL AND METHODS

Adsorbent

The MET resin series was prepared (5) by the copolymerization reaction of α-methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) in the presence of toluene. The reaction took place in water at

40°C for 4 hours and then at 80°C for 2 hours. After that, any toluene existing in the particle matrix was eliminated by distillation and the spherical resin products were obtained. The preparation procedure is illustrated in Fig. 1.

The method of preparation made MET resins possess special structure properties: unclasped macro- and micropores, relative large specific surface area, etc. An electron micrograph (SEM photograph) showed the resin structure (5): the microspheres formed continuous chains which constituted the matrix, and the pores were like many caverns between the chains. By changing the composition of reactants, a series of MET resins with various structural characteristics was obtained. It was found that an increase in the crosslinking agent EGDM led to an increase in pore volume and specific surface area of the resin. For example, MET-602, 802, and 1002 were prepared with the same ratio of toluene to MMA but different percentages of EGDM (60, 80, and 100%). Their pore volumes were 0.47, 0.91, and 0.93 $cm^3 \cdot g^{-1}$, and their specific surface areas were 192, 272, and 361 $m^2 \cdot g^{-1}$ respectively. Some of the relevant information about the MET resins studied in this research program are presented in Table 1.

Preliminary Treatment of Resin

The dried resins were cleaned of preserving agents and polymerization residuals by successive washings with acetone, 1.0 $mol \cdot dm^{-3}$ hydrochloric acid solution, and deionized water three times. They were then washed by a large quantity of 0.5 $mol \cdot dm^{-3}$ hydrochloric acid solution. The cleaned resins were placed in a desiccator over a saturated sodium chlo-

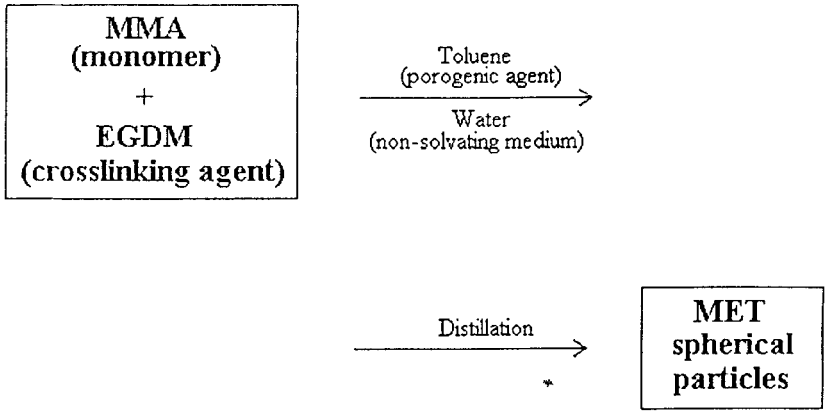

FIG. 1 Schematic preparation of MET resins.

TABLE 1
The Formation and Structural Information on the MET Resin Series

Resin (MET—)	$R\left(\frac{\text{toluene}}{\text{MMA}}\right)$	EGDM (%)	Matrix density ρ° ($g \cdot cm^{-3}$)	Apparent density ρ ($g \cdot cm^{-3}$)	Specific surface area S ($m^2 \cdot g^{-1}$)	Mean pore diameter d (Å)	Pore volume v ($cm^{-3} \cdot g^{-1}$)
—601	1	60	1.31	0.81	124	76.3	0.47
—602	1.5	60	1.27	0.76	192	54.4	0.52
—604	2.5	60	1.29	0.58	137	120	0.94
—801	1	80	1.25	0.69	255	61.4	0.66
—802	1.5	80	1.23	0.51	272	67.0	0.91
—804	2.5	80	1.33	0.43	268	116	1.56
—1002	1.5	100	1.34	0.60	361	51.5	0.93
—1004	2.5	100	1.34	0.47	334	83.0	1.39

ride solution at the temperature of 25 ± 0.5°C until the weight of resin did not vary with time.

Reagent

Hydrochloric acid solution: Prepared from analytical grade concentrated acid.

Gold tetrachloride solution: Proper quantities of gold agent ($AuCl_3 \cdot HCl \cdot H_2O$, analytical grade) were dissolved in hydrochloric acid solutions of different concentrations (0.250, 0.500, 0.750, and 1.00 $mol \cdot dm^{-3}$) to form gold tetrachloride solutions.

Isotherm Procedure

A bottle point isotherm procedure was used to conduct all adsorption equilibrium experiments. Fixed resin dosages of 0.05–0.1 g were placed in 150 cm^3 stoppered glass bottles with $HAuCl_4$–HCl solutions of known concentrations and volumes. The stoppered bottles were placed in a thermotank adjusted to 25 ± 0.5°C and shaken for 24 hours within which the equilibria were established as shown by preliminary experiments. Then the solutions were separated by a centrifugal method. The analysis for gold(III) in the aqueous phase, before and after adsorption, was carried out using an Hitachi 180-80 model atomic absorption spectrophotomter. The concentrations in the resin phase were calculated according to the mass balance. Experiments were conducted with all eight MET resins in hydrochloric acid solutions of four concentrations (0.250, 0.500, 0.750,

and 1.00 mol·dm^{-3} HCl). The equilibrium gold concentrations in the solutions were between 5×10^{-5} and 2.6×10^{-3} mol·dm^{-3}.

RESULTS AND DISCUSSIONS

Experimental Results

The equilibrium data for the adsorption of gold with eight kinds of MET resins are shown in Figs. 2a–2h. It can be seen that favorable adsorption isotherms were obtained in all cases. An increasing adsorption capacity with increasing concentration of hydrochloric acid in solution is also evident, although for some resins the capacities in solutions of 0.500 and 0.750 mol·dm^{-3} HCl overlapped slightly.

It was also found that MET-601, 602, 604, and 801 had higher capacities than MET-802, 804, 1002, and 1004 in the same hydrochloric acid solutions. This phenomenon is thought to be affected by the structures of the resins, and it is discussed in the following part.

Modeling of Adsorption

MET resins are characterized by weak ester groups —CO_2R—. The mechanism of adsorption of gold(III) anion suggested in the literature (4) is either solvation:

$$\text{R—CO}_2 + \text{AuCl}_4^- = \text{R—CO}_2\text{AuCl}_3 + \text{Cl}^- \quad (1)$$

or simple ion exchange:

$$\text{R—CO}_2 + \text{H}_2\text{O} = \text{R—CO}_2\text{H}^+ + \text{OH}^- \quad (2)$$

$$\text{R—CO}_2\text{H}^+ + \text{AuCl}_4^- = \text{R—CO}_2\text{H}^+\text{AuCl}^- \quad (3)$$

Preliminary experiments showed that Cl^- ion was also adsorbed on the resins. Thus, the ion-exchange mechanism is more likely to occur in the adsorption process.

If the ion-exchange mechanism is presumed, the reaction formula can be written as

$$\text{AuCl}_4^- + \overline{\text{Cl}^-} = \overline{\text{AuCl}_4^-} + \text{Cl}^- \quad (4)$$

where the bar denotes the ion under it is in the resin phase, and the ion-exchange equilibrium can be described by

$$\overline{M}_{\text{AuCl}_4^-} = \frac{\overline{M}_T K_P M_{\text{AuCl}_4^-}/M_{\text{Cl}^-}}{(1 + M_{\text{AuCl}_4^-} K_P/M_{\text{Cl}^-})} \quad (5)$$

$$\overline{M}_T = \overline{M}_{\text{AuCl}_4^-} + \overline{M}_{\text{Cl}^-} \quad (6)$$

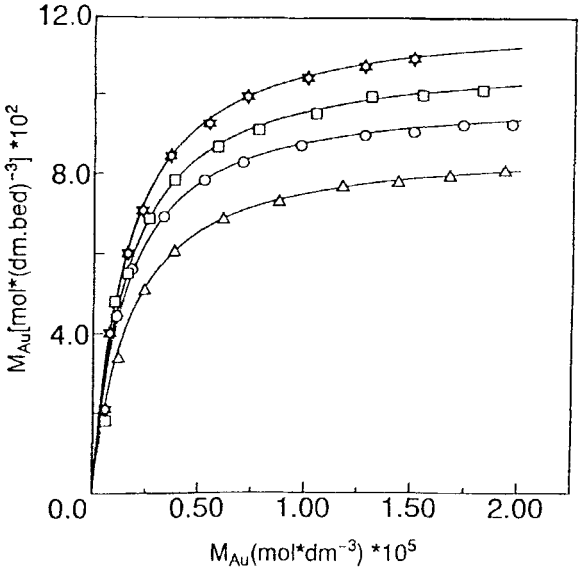

FIG. 2a Isotherms of adsorption of Au(III) with MET-601 resin. (△) 0.250 mol·dm^{-3} HCl, (○) 0.500 mol·dm^{-3} HCl, (□) 0.750 mol·dm^{-3} HCl, (☆) 1.00 mol·dm^{-3} HCl, (——) fitting lines.

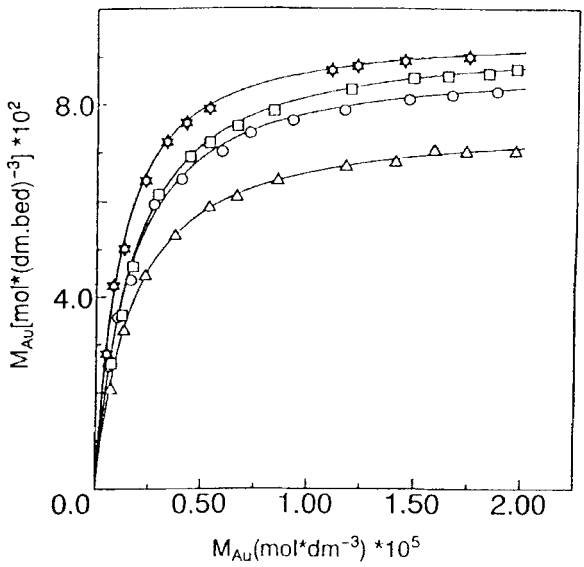

FIG. 2b Isotherms of adsorption of Au(III) with MET-602 resin. Symbols as in Fig. 2a.

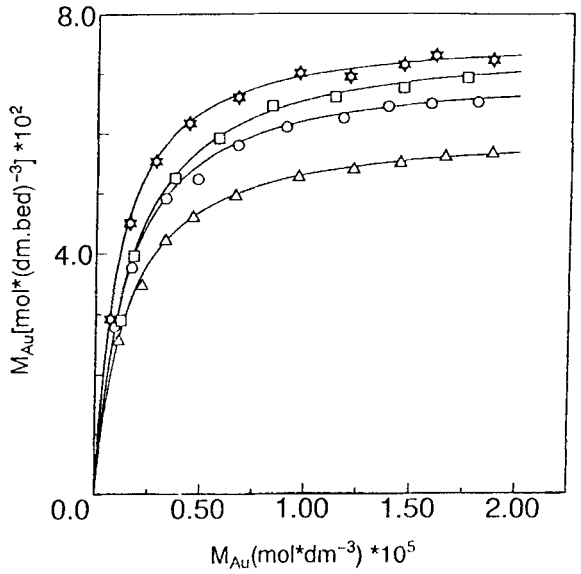

FIG. 2c Isotherms of adsorption of Au(III) with MET-604 resin. Symbols as in Fig. 2a.

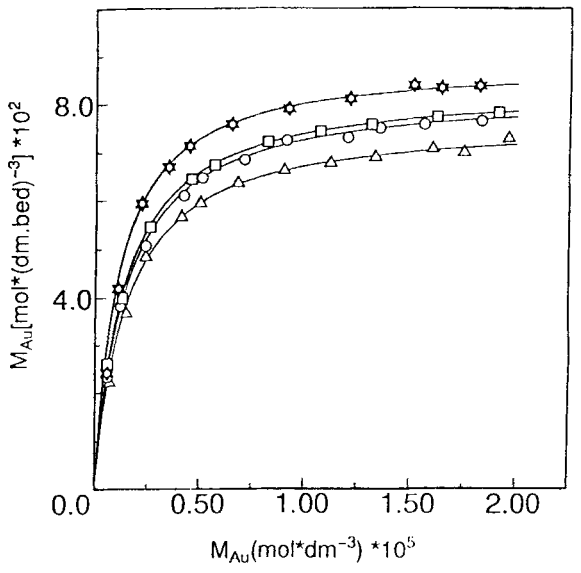

FIG. 2d Isotherms of adsorption of Au(III) with MET-801 resin. Symbols as in Fig. 2a.

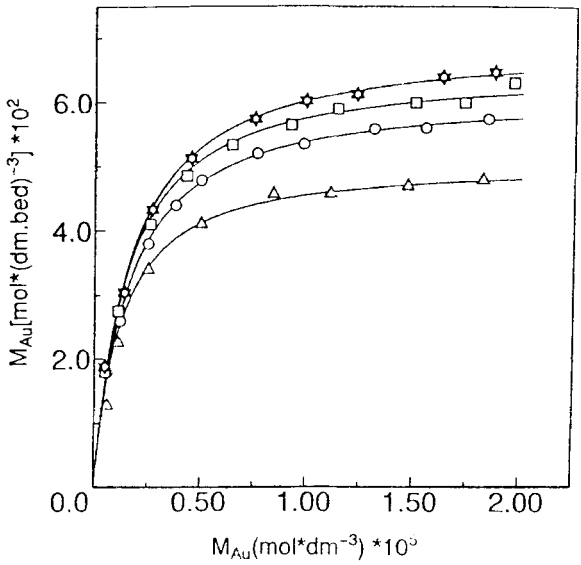

FIG. 2e Isotherms of adsorption of Au(III) with MET-802 resin. Symbols as in Fig. 2a.

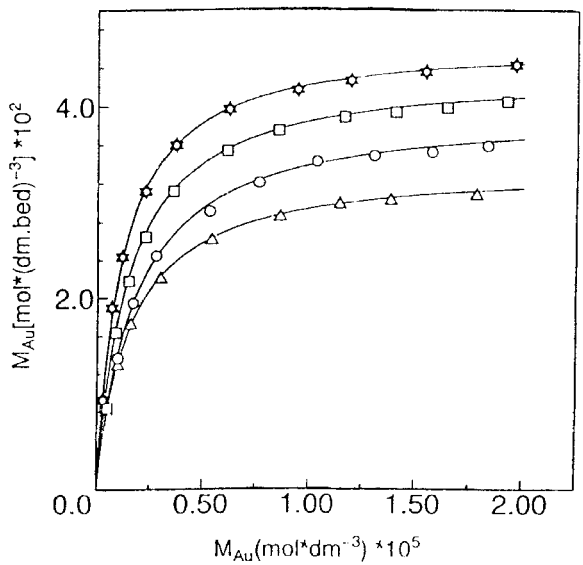

FIG. 2f Isotherms of adsorption of Au(III) with MET-804 resin. Symbols as in Fig. 2a.

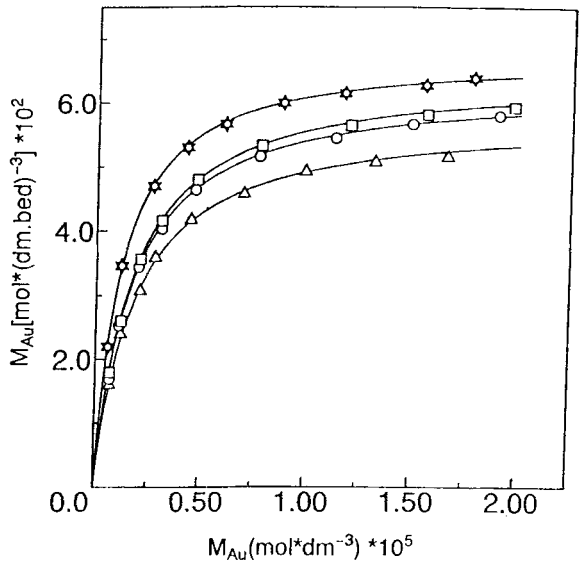

FIG. 2g Isotherms of adsorption of Au(III) with MET-1002 resin. Symbols as in Fig. 2a.

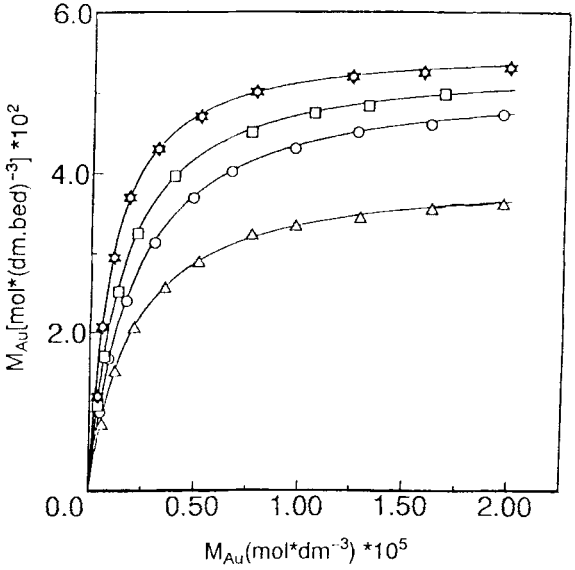

FIG. 2h Isotherms of adsorption of Au(III) with MET-1004 resin. Symbols as in Fig. 2a.

Equation (7) was used to fit the experimental points, and the curves in Figs. 2a–2h show the equation fits. The averaged relative errors between the fitted and experimental values were not larger than 6%. These results show that the adsorption of Au(III) in chloride solution with MET resins can be regarded as an ion-exchange mechanism in our experimental conditions. From the slope and the intercept on the Y axis of the fitted line, it is possible to estimate the values of $\overline{M}_T$ and K_P for every isotherm by using Eq. (7). The value of K_P in this case is equal to that of the selectivity coefficient of $AuCl_4^-$ and Cl^-, $a_4^{AuCl^-}$. K_P will be used in the calculation of HETP for breakthrough operation in the third paper of this research program. $\overline{M}_T$ will be used in the calculation of the particle interdiffusion coefficient in the second paper of this program. All the parameters estimated from the isotherms are listed in Table 2.

Effect of Acidity on K_P

It is readily seen from Table 2 that the value of K_P increases with an increase in medium acidity. This can be explained by the ion-exchange mechanism shown by Eqs. (2) and (3). Since the association of hydrogen

TABLE 2
Equilibrium Parameters of the Adsorption of Gold(III) with MET Resins

Resin (MET—)	$K_P \times 10^{-3}$ / $\overline{M}_T \times 10^2$ [mol·(dm·bed)$^{-3}$]	Concentration of HCl (mol·dm^{-3})			
		0.250	0.500	0.750	1.00
—601	K_P	1.5	3.4	4.8	6.5
	$\overline{M}_T$	8.7	10	11	12
—602	K_P	1.5	3.3	4.6	9.4
	$\overline{M}_T$	7.7	9.0	9.5	9.6
—604	K_P	1.7	3.5	4.7	9.5
	$\overline{M}_T$	6.1	7.1	7.6	7.7
—801	K_P	1.7	3.7	5.5	9.1
	$\overline{M}_T$	7.7	8.3	8.4	8.9
—802	K_P	2.1	3.3	5.1	6.2
	$\overline{M}_T$	5.1	6.2	6.6	7.0
—804	K_P	1.6	2.8	5.2	8.9
	$\overline{M}_T$	3.4	4.0	4.4	4.7
—1002	K_P	1.4	3.0	4.4	8.5
	$\overline{M}_T$	5.8	6.3	6.5	6.8
—1004	K_P	1.4	2.6	5.3	8.1
	$\overline{M}_T$	4.0	5.2	5.4	5.6

ions is the first step in the adsorption of gold, the hydrogen ion content in the resin phase influences its adsorption behavior. An increase in the concentration of HCl in the solution phase makes the dielectric constant of the resin phase decrease, so the stability of the ion pair $H^+AuCl_4^-$ increases (6), the equilibrium (Eq. 4) is moved to the right-hand side, and the value of K_P consequently increases.

Effect of Acidity on $\overline{M}_T$

It is also seen from Table 2 that the capacity of every MET resin increases as the acidity of the medium is increased. This result agrees with those of Fritz and Miller (3) and Edwards et al. (4) for studies carried out in the same range of medium acidity with XAD-7. The reason for this is that, in the experimental range of hydrochloric acid concentrations, the ester groups in the resin phase are not fully protonated (i.e., there are still some ion-exchange sites available as the concentration of hydrochloric acid in the solution is being increased), and therefore an increasing capacity of MET resin for gold(III) is observed with an increasing concentration of hydrochloric acid in solution.

The Structure of MET Resin and K_P

It is noted that the K_P value for different kinds of MET resins did not vary greatly in solutions with the same hydrochloric acid concentration. For example, the values of K_P for all MET resins in solutions of 0.750 mol·dm^{-3} HCl vary only between 4.6×10^3 and 5.5×10^3 mol·(dm·bed)$^{-3}$. Compared with the variation of $\overline{M}_T$ in the same conditions, the change of K_P is relatively small for every chloride solution. This fact reveals that the value of K_P has a weaker correlation with the structural characteristics of the resin than it does for gel-type ion exchangers, in which the equilibrium constants might change several times with the structural features, such as degree of crosslinking (7). The macropores in MET resins should be mainly responsible for this fact because they make the sieve effect on $AuCl_4^-$ ion ineffective.

The Apparent Density ρ and $\overline{M}_T$

By plotting the capacity $\overline{M}_T$ versus the apparent density ρ at every medium acidity, a linear relationship is observed. The absolute correlation coefficient of the linear fitting at every medium acidity is larger than 0.97. As an example, Fig. 3 shows the linear relationship between $\overline{M}_T$ and ρ for a 0.500 mol·dm^{-3} HCl solution. Attempts to find relationships between $\overline{M}_T$ and other structural parameters, such as specific surface area S and

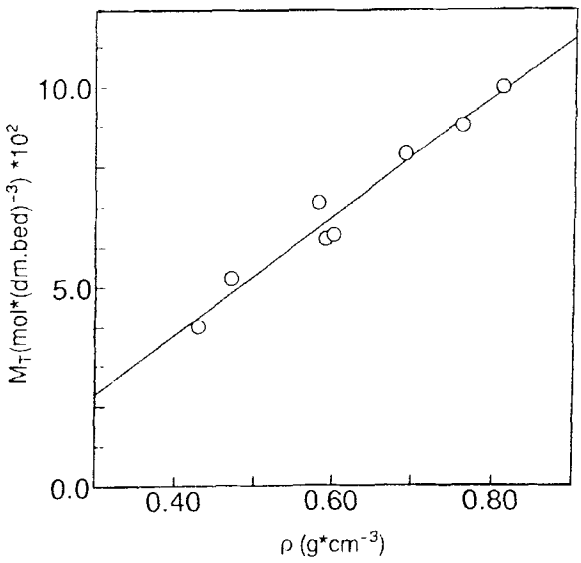

FIG. 3 Plot of the adsorption capacity versus the apparent density of MET resins. Temperature: 25 ± 0.5°C. Medium: 0.500 mol·dm^{-3} HCl.

pore volume v, failed. Thus, it is concluded that the $AuCl_4^-$ ion is not only being adsorbed in the pores of the resin but also adsorbed in the matrix. In other words, the $AuCl_4^-$ ion is distributed in the whole resin phase, and the adsorption of gold(III) with MET resins can be regarded as a "homogeneous" adsorption.

CONCLUSIONS

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

1) According to the discussion on the experimental results, the adsorption mechanism of MET resins for Au(III) is regarded as an ion-exchange mechanism. The equilibrium constants and capacities have been calculated for eight kinds of MET resins in four solutions of different concentrations of hydrochloric acid from the ion-exchange equilibrium equation.

2) The solution acidity is found to influence the values of K_P and $\overline{M}_T$. This is because the first step of the adsorption reaction is the association of hydrogen ion by the functional groups of the resins.

3) It is found that the structural parameters have relatively little influence on the values of K_P when the acidity of the solution was not changed,

whereas the value of $\overline{M}_T$ increased proportionally as the apparent density increased. Therefore, the adsorption of gold(III) on the MET resin phase is a "homogeneous" adsorption.

REFERENCES

1. C. A. Fleming and G. Cromberg, *J. S. Afr. Min. Metall.*, *84*, 125 (1984).
2. Anon, *Coal, Gold Base Miner S. Afr.*, *26*, 75 (1978).
3. J. S. Fritz and W. G. Miller, *Talanta*, *18*, 323 (1971).
4. R. I. Edwards et al., *Theory Pract. Ion Exchange*, *40*, 1 (1976).
5. X. Lin et al., *Acta Polym Sinica*, p. 17 (1988) (in Chinese).
6. G. H. Morrison et al., *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1957, p. 31.
7. R. Dybczyn'ski, *J. Chromatogr.*, *50*, 498 (1970).

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