Highly Selective Adsorption Resins. I. Preparation of Chitosan Derivatives Containing 2-Pyridylmethyl, 2-Thienylmethyl, and 3-(Methylthio)propyl Groups and Their Selective Adsorption of Precious Metals

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Crosslinked *N*-(2-pyridylmethyl)chitosan, *N*-(2-thienylmethyl)chitosan, and *N*-[3-(methylthio)propyl]chitosan were newly synthesized. The amino group of the active adsorption site of chitosan was protected by Schiff's base formation prior to being crosslinked by 2-(chloromethyl)oxirane. The final chitosan derivatives were obtained by reducing the imine moiety of the Schiff's bases with sodium borohydride. The adsorption behavior of metal ions on the chitosan derivatives was examined from a solution containing hydrochloric acid using a batchwise method. These chitosan derivatives exhibited high selectivities and excellent loading capacities for gold(III), palladium(II), and platinum(IV) over base metals in hydrochloric acid. In order to elucidate the adsorption species of palladium(II) on the chitosan derivatives, the effect of the chloride ion concentration on the distribution ratio in the adsorption of palladium(II) was examined. The adsorption capacities of these chitosan derivatives for palladium(II) were found to be about 2.5—3 times greater than that of the cross-linked original chitosan. The desorption of palladium(II) was performed to an extent of 70% by a single batchwise treatment with aqueous thiourea solution.

The precious metals, especially, gold(III), palladium(II), and platinum(IV), are very important in industry.[1] These metals occur in nature associated with major base metals such as copper, nickel, and cobalt. Therefore, it is important from both analytical and industrial points of view that the individual precious metals are separated not only from the base metals but also from each other to a high purity and with a high percentage of recovery. Thus, it is desirable to develop new adsorbents with high selectivity for these metals.

Adsorption techniques, especially those using chelating resins, have been widely applied in the fields of analytical chemistry and separation chemistry. A large number of chelating polymers have been developed so far and some of these are commercially available. In recent years, much attention has been paid to the adsorption of metal ions on various kinds of microorganisms or biomass such as algae and fungi as well as on their cell components: alginic acid,[2] cellulose,[3] chitin, and chitosan[4] because they are abundant and inexpensive. Among these natural polymers, chitosan has been widely applied as an effective coagulating agent[5] in activated sludge plants and for recovering proteins from food processing factories because of its excellent coagulation behaviors. Furthermore, Muzzarelli et al.[6—8] carried out a series of studies on the chromatographic separations of metal ions with some chitosan derivatives. Since chitosan and its derivatives are soluble in acidic solution, crosslinking between polymer chains has been carried out. However, this treatment results in a significant decrease in the adsorption capacity since the crosslinking reagent forms chemical bonds at the active adsorption site. Ohga et al.[9] proposed to prepare resins by crosslinking metal-complexed chitosans to overcome this disadvantage. They concluded that their product exhibits a high loading capacity nearly equal to that of the original chitosan. In addition, high selectivity to the metal ion employed as the "template" was realized in similar to that previously reported by Nishide et al.[10] Thus far, a number of chitosan derivatives for metals have been developed, however, few studies on the adsorption of platinum group metals on chitosan derivatives which contain heteroaromatic nitrogen, and sulfur atoms or a methylthio group have been reported.[11]

In the present paper, the authors describe the preparation of new crosslinked chitosan derivatives containing a pyridyl group, thienyl group or methylthio group. We also found that Schiff's base formation is effective in protecting the amino group prior to the crosslinking reaction. Furthermore, the authors found that the chitosan derivatives synthesized according to the method developed in this study are useful as selective adsorbents for precious metals.

Experimental

Chemicals. 2-Pyridinecarbaldehyde, 2-thiophenecarbaldehyde, and 3-(methylthio)propionaldehyde were supplied from Tokyo Kasei Ltd., Co., and were used without further purification.

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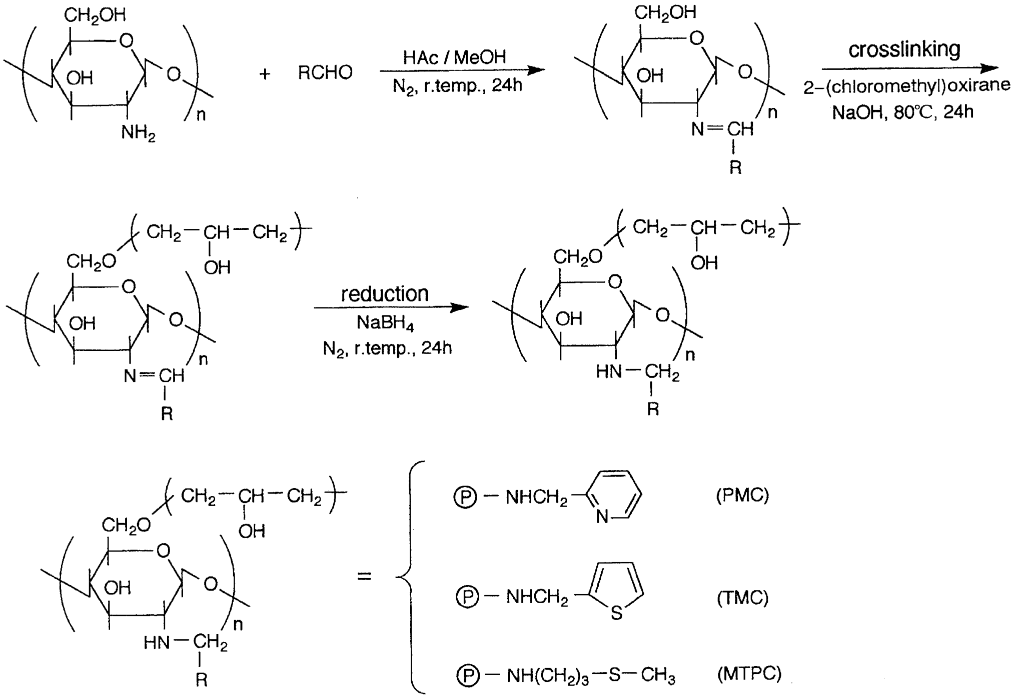
The metal solutions were prepared by dissolving the reagent grade corresponding metal chloride into hydrochloric acid. Samples of chitosan powder from shells of prawns were kindly donated by Katokichi Co., Ltd., Kan-onji, Japan. The degree of deacetylation of the samples was greater than 95% and they were used as delivered without further purification. Other reagent grade reagents were used without further purification. All aqueous solutions were prepared with deionized water.

Preparation of Chitosan Derivatives. *N*-(2-Pyridylmethyl)chitosan (PMC), *N*-(2-thienylmethyl)chitosan (TMC), and *N*-[3-(methylthio)propyl]chitosan (MTPC) were prepared through Schiff's base formation between the amino groups of chitosan and the corresponding aldehydes as shown in Scheme 1. That is, these chitosan derivatives were prepared by the reaction of chitosan (0.1 mol) with a 10-fold excess of the corresponding aldehydes in a mixture (1 dm^3) of aqueous acetic acid and methanol at room temperature. After 24 h, the reaction products were filtered and washed with diethyl ether and ethanol to remove excess aldehydes and then with deionized water to neutrality. Thus, chitosan derivatives as light yellow gels were obtained as the corresponding intermediates. These gels were immersed in dimethyl sulfoxide (1 dm^3) to make them swell, followed by addition of 2-(chloromethyl)oxirane (0.3 dm^3), and then stirred for 24 h. After filtration, the gels were crosslinked in 0.1 mol dm^{-3} aqueous sodium hydroxide solution at 80 °C for 24 h. Under these conditions, it was confirmed that pyridine rings were rarely (<5%) or not quaternized and the thiophene rings were not forming a sulfonium salt during the crosslinking reaction. Subsequently, the crosslinked chitosan derivatives were reduced by portionwise addition of sodium borohydride into the aqueous suspension of the chitosan derivatives. The final products were washed with ethanol and then with deionized water to neutrality. After drying in vacuo, they were ground and sieved to smaller than 100 mesh size. The Schiff's bases of the intermediates and the final products were identified by their IR spectra. In the IR spectra for the intermediate of PMC, characteristic peaks appeared at around 1635 and 859 cm^{-1} due to a C=N linkage and a substituted pyridyl group, respectively. In the IR spectra for the intermediate of TMC, characteristic peaks appeared at around 1634 and 765 cm^{-1} due to a C=N linkage and a substituted thienyl group, respectively. In the IR spectra for the intermediate of MTPC, characteristic peaks appeared at around 1652 cm^{-1} due to a C=N linkage. The reduction of the Schiff's base was confirmed by the disappearance of the peak due to the C=N linkage. The degree of substitution for these chitosan derivatives was determined to be more than 0.90 using the C/N ratio of elemental analysis. These chitosan derivatives were synthesized with favorable reproducibility.

Adsorption Procedures. About 0.1 g of sieved chitosan derivatives and 20 ml of aqueous solution containing metal ion were shaken in a stoppered 50 ml glass flask immersed in a thermostated water bath maintained at 30 °C.

i) Adsorption Rate. In order to determine the time to achieve equilibration, the time-course of palladium(II) adsorption on TMC, PMC, and MTPC was examined by sampling from the mother solution of 1 mol dm^{-3} hydrochloric acid at appropriate intervals. The experimental results are shown in Fig. 1. In all cases, a rapid decrease in palladium(II) concentration was observed and equilibrium was attained after about 1 h. Consequently, the adsorption time was determined as 24 h, also taking into account the convenience of the experimental operation.

ii) Adsorption Equilibria. The initial metal concentration was adjusted to 1 mmol dm^{-3} by dissolving metal chloride in 0.01—6 mol dm^{-3} hydrochloric acid. The initial and equilibrium metal concentrations in the aqueous solutions were determined by titration with EDTA or by using a Seiko (Hamamatsu, Japan) model SPS-7500 atomic absorption spectrophotometer. The amount of adsorbed metal ion was calculated from the concentration change in the aqueous solution before and after the equilibration, the volume of the aqueous solutions (20 ml) and the weight of the dry gel. The distribution ratio (D [dm^3 kg^{-1}]) was defined as the ratio of the amount of metal ions adsorbed on a dry adsorbent (q [mmol g^{-1}])



Scheme 1. Synthesis and chemical structures of chitosan derivatives.

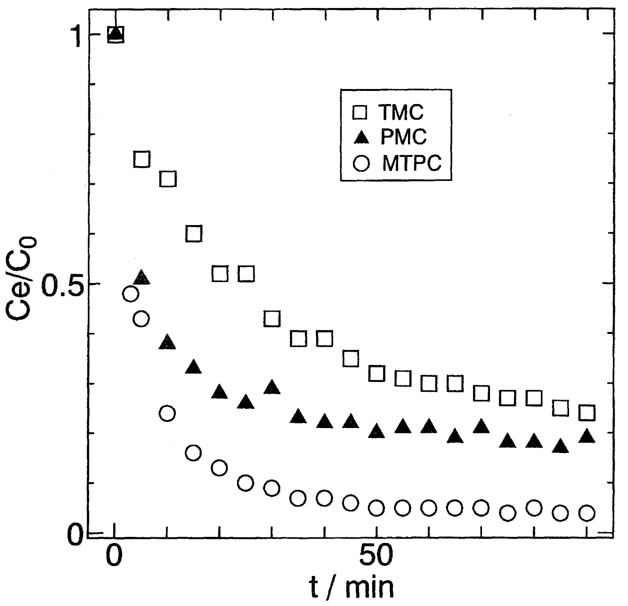


Fig. 1. Relationship between adsorption ratio of palladium(II) and contact time ($[HCl] = 1\ mol\,dm^{-3}$).

to its equilibrium concentration (C_e $[mol\,dm^{-3}]$) in an aqueous solution. The hydrochloric acid concentration was measured by neutralization titration.

Desorption Procedures. Aqueous thiourea solution and thiourea solution containing hydrochloric acid of various concentrations were used as eluents of palladium(II) using a batchwise method. The contact time for desorption was 24 h. The eluent percent was defined as the ratio of the amount of palladium(II) desorbed to the amount of palladium(II) adsorbed.

Results and Discussion

Figures 2, 3, and 4 show the relationship between the distribution ratio of metal ions and the equilibrium concentration of hydrochloric acid in the adsorption of metal ions on PMC, TMC, and MTPC, respectively. As is evident from Fig. 2, PMC has a high selectivity for gold(III), palladium(II), platinum(IV), and mercury(II) over copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II), and iron(III). Among these base metals, copper(II), nickel(II), and cadmium(II) were adsorbed to some extent at a low concentration of hydrochloric acid, while iron(III), cobalt(II), and zinc(II) were not adsorbed in the concentration range of hydrochloric acid examined here. On the other hand, as seen from Figs. 3 and 4, TMC and MTPC which contain a "soft" sulfur atom,[12] showed little or no affinity towards most of the base metals mentioned above, while they exhibited a higher selectivity for palladium(II), gold(III), and platinum(IV) than that of PMC.

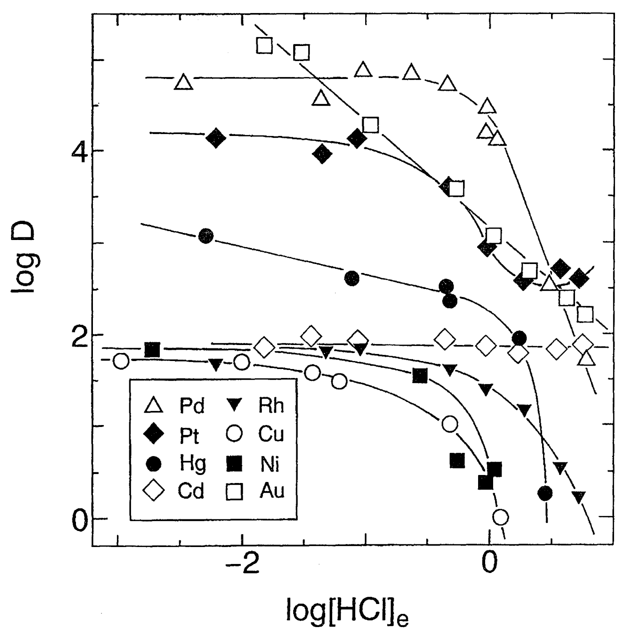


Fig. 2. Relationship between distribution ratio ($[dm^3\,kg^{-1}]$) of metal ions and equilibrium concentration of hydrochloric acid in the adsorption on PMC.

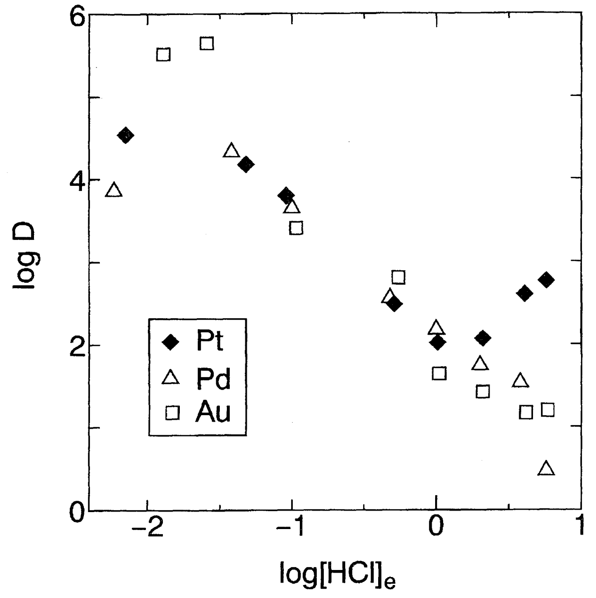


Fig. 3. Relationship between distribution ratio ($[dm^3\,kg^{-1}]$) of metal ions and equilibrium concentration of hydrochloric acid in the adsorption on TMC.

In order to elucidate the adsorption species of palladium(II) on these chitosan derivatives, a quantitative investigation of the adsorption of palladium(II) was conducted by examining the effect of chloride ion on the distribution ratio at a constant concentration of hydrogen ion ($[H^+] = 0.1\ mol\,dm^{-3}$). The concentration of chloride ion was changed by adding ammonium chloride to $0.1\ mol\,dm^{-3}$ hydrochloric acid. The adsorption results of palladium(II) on PMC and TMC are shown in Figs. 5 and 6, respectively. The plots in these figures lie on straight lines with a slope of −2. Considering that palladium(II) exists as a dianionic species, $PdCl_4{}^{2-}$, the adsorption equilibria were presumed as follows. Palladium(II) was considered to be adsorbed according to an anion exchange mechanism accompanied by a chelate formation reaction, while releasing two chloride ions per unit palladium ion, as shown by Eqs. 1, 2 and Eqs. 4; 5 on PMC and TMC, respectively. Overbars indicate the solid phase of the

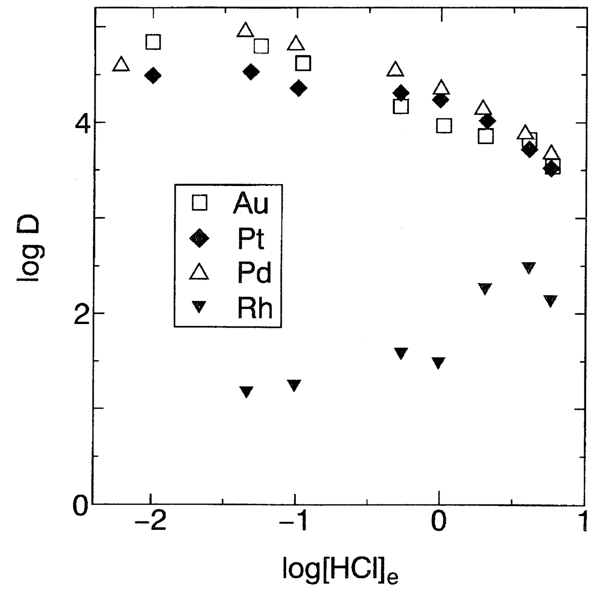


Fig. 4. Relationship between distribution ratio ([dm^3 kg^{-1}]) of metal ions and equilibrium concentration of hydrochloric acid in the adsorption on MTPC.

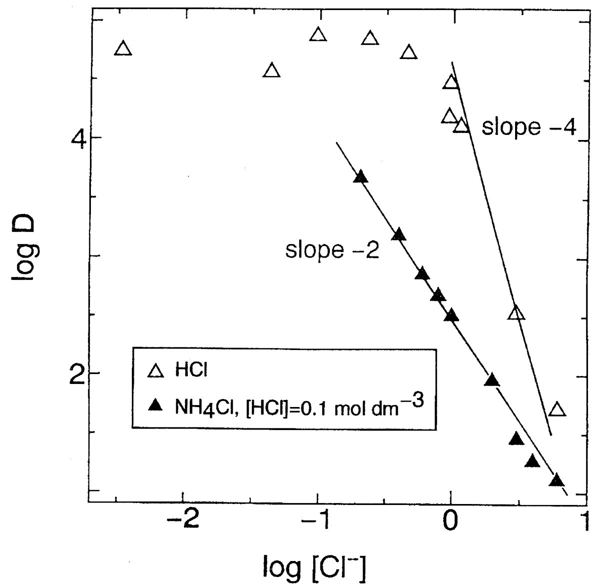


Fig. 5. Effects of chloride ion and hydrochloric acid concentrations on the distribution ratio ([dm^3 kg^{-1}]) on PMC.

chitosan derivatives.

$$\overline{\mathrm{PMC}} + 2\mathrm{H}^+ + 2\mathrm{Cl}^- \rightleftharpoons \overline{\mathrm{PMC(HCl)_2}} \tag{1}$$

$$\overline{\mathrm{PMC(HCl)_2}} + \mathrm{PdCl_4}^{2-} \rightleftharpoons \overline{\mathrm{PMC(H_2PdCl_4)}} + 2\mathrm{Cl}^- \; ; \; K_1 \tag{2}$$

Thus, the distribution ratio is indicated by the following equation from Eqs. 1 and 2.

$$\log D = -2\log\,[\mathrm{Cl}^-] + \log K_1[\overline{\mathrm{PMC(HCl)_2}}] \tag{3}$$

In a similar manner, the adsorption equilibria and the distribution ratio in the case of TMC may be represented as follows:

$$\overline{\mathrm{TMC}} + \mathrm{H}^+ + \mathrm{Cl}^- \rightleftharpoons \overline{\mathrm{TMC(HCl)}} \tag{4}$$

$$\overline{\mathrm{TMCHCl}} + \mathrm{PdCl_4}^{2-} \rightleftharpoons \overline{\mathrm{TMC(HPdCl_3)}} + 2\mathrm{Cl}^- \; ; \; K_2 \tag{5}$$

Thus, the distribution ratio is indicated by the following equation from Eqs. 4 and 5.

$$\log D = -2\log\,[\mathrm{Cl}^-] + \log K_2[\overline{\mathrm{TMC(HCl)}}] \tag{6}$$

Here, Eqs. 3 and 6 suggest that the plots of $\log D$ against $\log\,[\mathrm{Cl}^-]$ lie on a straight line with a slope of -2 since $[\overline{\mathrm{PMC(HCl)_2}}]$ and $[\overline{\mathrm{TMC(HCl)}}]$ are constant under the present experimental conditions. These equations reasonably explain the experimental results shown in Figs. 5 and 6. Accordingly, the adsorption equilibria of palladium(II) on

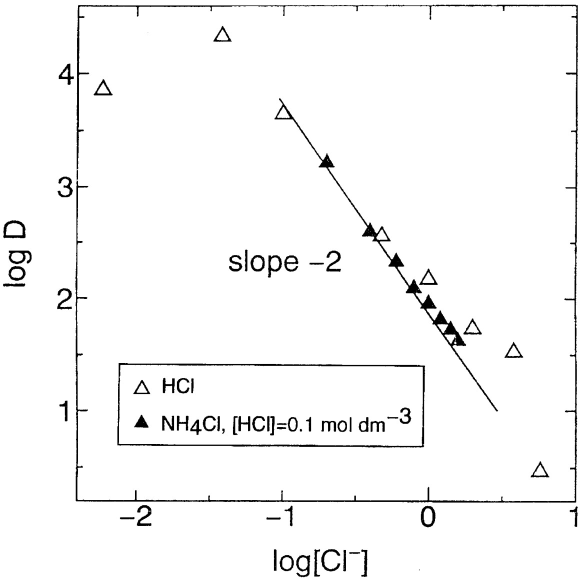


Fig. 6. Effects of chloride ion and hydrochloric acid concentrations on the distribution ratio ([dm^3 kg^{-1}]) on TMC.

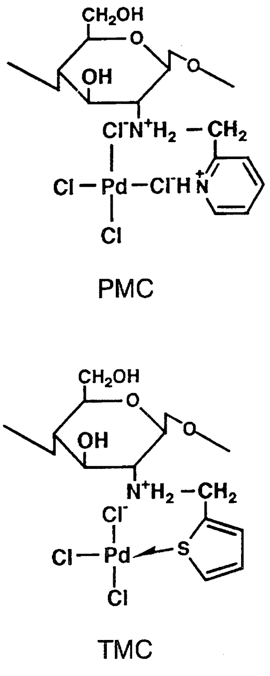


Fig. 7. Chemical structures of palladium(II)–chitosan derivatives complexes for PMC and TMC.

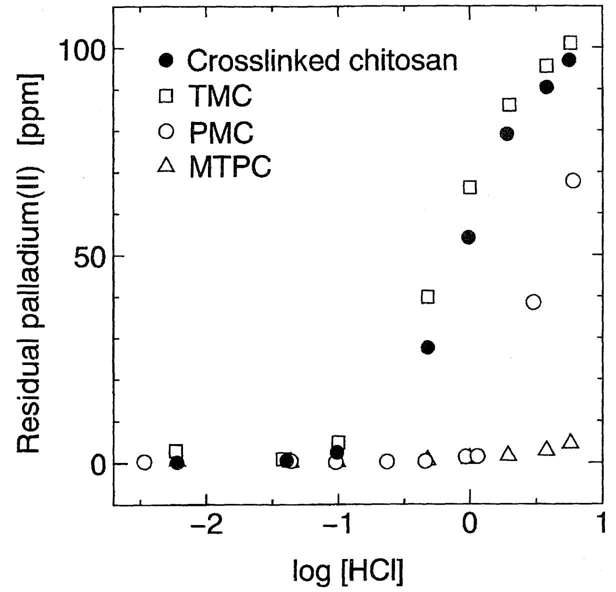


Fig. 8. Plots of residual palladium(II) against hydrochloric acid concentration.

PMC and TMC can be described by Eqs. 2 and 5, respectively. The chemical structures of the palladium–chitosan derivative complexes are illustrated in Fig. 7. In the adsorption of palladium(II) from hydrochloric acid on PMC as shown in Fig. 5, the plots of $\log D$ against log [HCl] indicate a straight line with a slope of -4. This result suggests the effect of hydrogen ion concentration on the distribution ratio of palladium(II), however, further investigation is necessary to elucidate the adsorption equilibria in the region of highly concentrated hydrochloric acid.

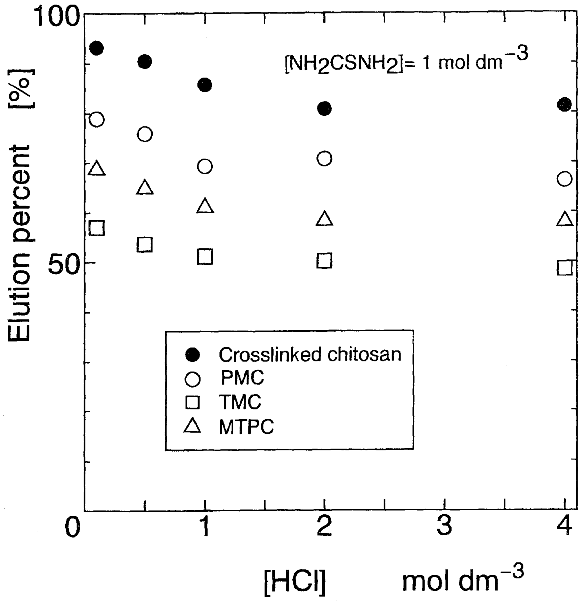


Fig. 10. Plots of elution percent of palladium(II) aginst the concentration of hydrochloric acid contained in 1 mol dm^{-3} aqueous thiourea solution.

A relative comparison of the adsorption ability of these chitosan derivatives was examined under a batch process for recovery of palladium(II) from hydrochloric acid. Figure 8 shows the plots of residual palladium(II) against the concentration of hydrochloric acid. All of the chitosan derivatives tested were found to be effective for the removal of nearly 100% of the initial palladium(II) at their optimum conditions. Especially, MTPC showed a high percentage of recovery for palladium(II) over a wide concentration range of hydrochloric acid. PMC showed a high percentage of recovery below 1 mol dm^{-3} hydrochloric acid, while TMC and crosslinking copper–complexed chitosans, which were prepared by the same method as in previous papers,[13,14] were effective below 0.1 mol dm^{-3} hydrochloric acid. Among these chitosan derivatives, the high selectivity of MTPC may be understood by considering that palladium(II) is a "soft" acid which prefers to associate with "soft" ligand stoms on the basis of the HSAB concept.[12] On the other hand, a large difference in adsorption behavior between TMC and MTPC was observed in the high concentration region of hydrochloric acid, though they likewise contain sulfur atoms. It is considered that the higher adsorption activity of MTPC is attributed to the existence of a propyl chain spacer unit, which would allow for better flexibility of the main ligating atom, the sulfur atom.

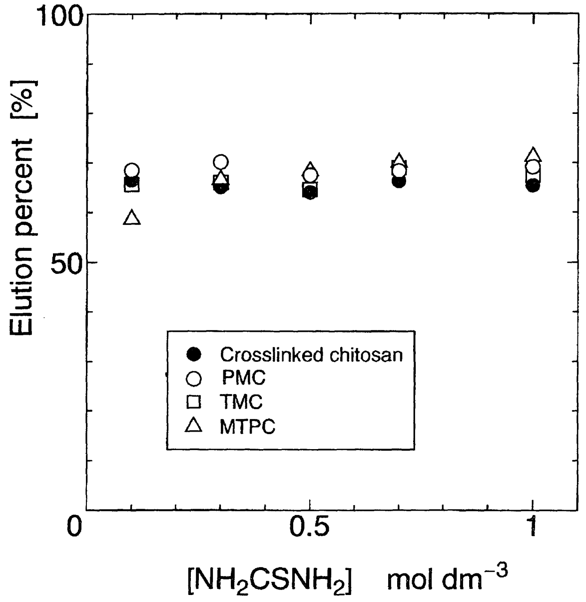


Fig. 9. Plots of elution percent of palladium(II) aginst the concentration of thiourea in the desorption of palladium(II).

The adsorption capacities of palladium(II) were examined from 0.01 mol dm^{-3} hydrochloric acid on PMC, TMC, and MTPC. From the experimental results, the adsorption capacities for palladium(II) were 5.8, 4.8, and 5.8 mmol g^{-1}, respectively; the adsorption capacities of the chitosan derivatives newly developed in the present study are about 2.5—3 times that of crosslinked copper–complexed chitosan.[13] The results mentioned above suggest that the present chitosan derivatives were crosslinked without a significant lowering of the adsorptive activity, and that the sulfur atom or the nitrogen atom of the pyridyl group takes part in the adsorption of precious metals.

In addition, the experimental results for elution of palladium(II) by a one time batch method are shown in Figs. 9 and 10 with aqueous thiourea solution and thiourea solution containing hydrochloric acid of various concentrations, respectively. In the desorption of palladium(II) with aqueous thiourea solution as shown in Fig. 9, the elution percent was about 70% for all of the chitosan derivatives. As shown in Fig. 10, addition of hydrochloric acid to 1 mol dm^{-3} aqueous thiourea solution results in an improvement of the elution percentage of palladium(II) for crosslinked chitosan and PMC, the sulfur atom of which is not contained as a donating atom. On the other hand, the elution percentage of palladium(II) with a mixture of thiourea and hydrochloric acid decreased compared with that with only thiourea for TMC and MTPC containing a sulfur atom. Further studies are necessary to elucidate these desorption mechanisms.

The adsorption characteristics of PMC, TMC, and MTPC suggest that these chitosan derivatives are useful for the selective separation and purification of palladium(II), gold(III), and platinum(IV) from hydrochloric acid containing large amounts of base metals.

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