

Noble Metal Ion Sorption by Pyridyl and Bipyridyl Group-Containing Chelating Polymers

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Received 11 November 1999; accepted 22 May 2000

ABSTRACT: A series of eighteen 4-vinylpyridine and 4-methyl-4'-vinylbipyridine copolymers with different crosslinkers was examined as sorbents for the noble metal ions of Ag(I), Au(III), Pd(II), and Pt(II) from aqueous solutions. The chelating polymers possess appreciable sorption selectivity for Au(III) over Ag(I) and for Pd(II) over Pt(II). Binding abilities of the copolymers toward the noble metal ions vary as the identity of the chelating heterocyclic amine moiety and the structure of the crosslinkers are altered. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 207–213, 2001

Key words: chelating polymers; pyridyl and bipyridyl groups; sorption; noble metal ions

INTRODUCTION

The recovery of ions of noble metals (e.g., silver, gold, and the platinumides) from waste solutions is an important economical and ecological problem that is attracting the ever-increasing attention of researchers. Polymeric sorbents containing various chelating groups have been successfully utilized in noble metal ion separations.¹ In particular, polymers with heterocyclic amines units (e.g., pyrazol, piperazine, tetrahydroindole, and benzimidazole) exhibit efficient sorption of Pd(II) and Pt(II) from aqueous solutions.²

Recently, we reported the selective binding of the hazardous heavy metal ions of Cu(II) and Hg(II) by a series of new chelating polymers with pyridyl (Py)

and bipyridyl (Bipy) donor groups.³ We envisioned that the incorporation of such ligands into organic polymers could also provide efficient sorption of noble metal ions, since Py and Bipy derivatives possess good complexing abilities for Ag(I), Au(III), Pd(II), and Pt(II) in solution⁴ and some derivatives show high affinity for Pd(II) when immobilized on silica.⁵ We now report Ag(I), Au(III), Pd(II), and Pt(II) sorption from aqueous solutions by 14 previously prepared (**1–14**)³ and two new (**15** and **16**) 4-vinylpyridine (VPy) and 4-methyl-4'-vinylbipyridine (MVBipy) copolymers with different dimethacrylate crosslinkers (Table I).

EXPERIMENTAL

Materials

Reagent-grade starting materials and solvents were purchased from commercial suppliers. MES buffer, 2-[*N*-morpholino]ethanesulfonic acid hydrate, was purchased from Sigma (St. Louis, MO). The free-radical initiator 2,2'-azobisisobutyroni-

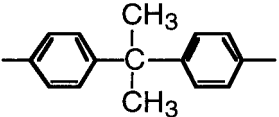
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Contract grant sponsor: Texas Higher Education Coordinating Board–Advanced Research Program.

Contract grant sponsor: Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy; contract grant number: DE-FG03-94ER14416.

Journal of Applied Polymer Science, Vol. 80, 207–213 (2001)
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Table I VPy and MVBipy Copolymers with Different Dimethacrylate Crosslinkers, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{—X—CO}_2\text{C}(\text{CH}_3)=\text{CH}_2$, at a 2/1 Crosslinker/Chelating Monomer Molar Ratio

Spacer X in the Crosslinker	Chelating Group	
	Py	Bipy
$\text{—}(\text{CH}_2)_2\text{—}$	1	8
$\text{—}(\text{CH}_2)_4\text{—}$	2	9
$\text{—CH}_2\text{—}\langle\bigcirc\rangle\text{—CH}_2\text{—}$	3	10
$\text{—}(\text{CH}_2)_6\text{—}$	4	11
	5	12
$\text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—}$	6	13
$\text{—CH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{—}$	7	14
$\text{—CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{—}$	15	16

trile (AIBN) from Aldrich (Milwaukee, WI) was purified by recrystallization from absolute ethanol below 40°C in subdued light, dried *in vacuo* at room temperature over P_2O_5 , and stored *in vacuo* in the dark at below -10°C . MVBipy was prepared by a literature procedure.⁶ The synthesis of copolymers **1–14** was reported earlier.³ Anhydrous methanol was prepared by refluxing the reagent-grade solvent for 2–3 h over magnesium turnings in the presence of iodine followed by distillation.

Equipment

IR spectra were measured with a Perkin–Elmer Model 1600 FTIR spectrophotometer. TGA analysis was performed with a Shimadzu TGA-50 thermogravimetric analyzer with a temperature increase rate of $10^\circ\text{C}/\text{min}$. A Perkin–Elmer Model 5000 atomic absorption spectrophotometer was used to determine the metal ion concentrations in aqueous solutions before and after contact with the polymer. Elemental analyses were performed by Desert Analytics Laboratory (Tucson, AZ). The circulating water bath for temperature control during polymer syntheses utilized a Lauda Model B1 thermocouple-controlled heating unit and a Lauda Model C pump connected to a 2-L glass container.

Synthesis of 3-Thia-1,5-dipentylene Dimethacrylate (TDMA)

Methacryloyl chloride (3.42 g, 32.7 mmol) was added to a 50 mL of diethyl ether and 0.03 g (ca.

1% wt) of the stabilizer hydroquinone in a 150-mL reaction flask equipped with a reflux condenser, addition funnel, and calcium chloride drying tube. A mixture of 3-thia-1,5-pentanediol (2.00 g, 16.4 mol), 25 mL of diethyl ether, and 4.13 g (36.5 mmol) of triethylamine was added dropwise. The reaction mixture was stirred magnetically for 2 h at room temperature. Then, 50 mL of water was added and the mixture was stirred for 5 min. The organic layer was separated, washed with water (3×50 mL), and dried over MgSO_4 . The solvent was evaporated *in vacuo* at room temperature to give a yellow oil that was purified by chromatography on a short column of alumina with dichloromethane as the eluent to provide 2.80 g (66%) of TDMA⁷ as a clear colorless liquid.

IR (neat): ν 1731 (C=O), 1632 (C=C), 1161 (C—O) cm^{-1} . $^1\text{H-NMR}$ (CDCl_3): δ 2.00 (s, 6H), 2.85 (t, 4H), 4.35 (t, 4H), 5.20 (s, 2H), 5.60 (s, 2H), 6.10 (s, H).

General Procedure for the Preparation of VPy and MVBipy Copolymers with TDMA (**15** and **16**, respectively)

To 5.00 mL of a methanol–benzene solution (1:1 by volume) in a 34×24 -cm reaction tube was added 5.10 mmol of the monomer (VPy or MVBipy) and the mixture was stirred with a magnetic stirring bar until the monomer completely dissolved. TDMA (10.20 mmol) was added with a pipette and the mixture was stirred until a solution was obtained. After this, AIBN (0.050 g) was added and stirring was continued to provide a solution that was degassed by the freeze–pump–thaw method. The solution was frozen with a dry ice–acetone bath and the reaction tube was evacuated with a vacuum pump. The contents of the tube were allowed to thaw at room temperature. This procedure was repeated three times. After this, the reaction tube was partially immersed in a 60°C water bath and the reaction was allowed to proceed for 18 h. The solvent was decanted and the solid was washed three times with 50 mL of methanol–benzene (1:1 by volume). The product was dried *in vacuo* at 100°C for 24 h and ground with a Wigg-L-BugTM apparatus into a fine powder (<100 mesh).

15: 87% yield. ANAL. Calcd: C, 60.25%; H, 6.92%; N, 2.44%; S, 10.13%. Found: C, 60.25%; H, 7.01%; N, 2.67%; S, 9.73%. **16**: 93% yield. ANAL. Calcd: C, 63.81%; H, 6.69%; N, 4.80%; S, 8.23%. Found: C, 63.76%; H, 6.86%; N, 4.53%; S, 8.15%. IR (KBr): ν 1726 (C=O), 1461, and 1144 (C—O) cm^{-1} for both **15** and **16**.

Single-species Noble Metal Ion Sorption

A mixture of 50 mg of the polymer and 5.00 mL of 10.0 mM aqueous solution of AgNO_3 or KAuCl_4 or a 1.00 mM solution of K_2PdCl_4 or K_2PtCl_4 (pH 6.5, buffer MES) was shaken for 24 h in a 30-mL, pear-shaped flask at room temperature with a Burrel wrist-action shaker. The solid was filtered and the filtrate was analyzed for metal ion content by atomic absorption spectrophotometry.

Determination of Pd(II) Sorption Constants for Copolymers 1 and 8

Aqueous solutions (pH 6.5, MES buffer) with different Pd(II) concentrations (2.00–20.0 mM) were prepared by dilution of a 20.0 mM aqueous solution of K_2PdCl_4 with 50.0 mM aqueous KCl solution. A mixture of 10.0 mg of **1** or 12.5 mg of **8** (20.0 μmol of the chelating groups in each polymer sample) and 5.00 mL of the aqueous K_2PdCl_4 /KCl solution was shaken for 24 h at room temperature with a Burrel wrist-action shaker. The solid was filtered and the filtrate was analyzed for metal ion content by atomic absorption spectrophotometry. K values were determined from graphs of $1/a$ versus $1/C_{\text{Pd}}$.

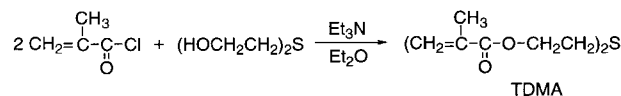
RESULTS AND DISCUSSION

Synthesis and Characterization of the Copolymers 15 and 16 with Sulfur Atoms in the Spacers

Soft electron acceptors of Ag(I), Au(III), Pd(II), and Pt(II) are known to possess great affinity for soft⁸ sulfur donor atoms. We anticipated that the introduction of a thioether group into the crosslinker of Py- and Bipy-containing copolymers would provide additional binding sites for noble metal ions and provide enhanced noble metal ion sorption. Therefore, new polymers **15** and **16** (Table I) were prepared by free-radical copolymerization of VPy and MVBipy, respectively, with TDMA.

TDMA was synthesized earlier in unspecified yield by transesterification of methacrylic acid with 3-thia-1,5-pentandiol in the presence of anhydrous K_2CO_3 .⁷ The procedure required a sixfold excess of methacrylic acid. Our alternative procedure for the synthesis of TDMA in 66% yield is presented in Scheme 1.

Our previous study³ showed that copolymers prepared from a 2/1 ratio of dimethacrylate/Vpy monomers exhibited the most efficient heavy



Scheme 1

metal ion binding in a series of copolymers in which the crosslinker/chelating monomer ratio was varied from 1 to 8. Therefore, copolymers **1–14** were synthesized with a crosslinker/chelating monomer ratio of 2.³ Likewise, copolymers **15** and **16** were prepared with two TDMA monomers for each chelating monomer.

The new copolymers were characterized by IR spectroscopy and elemental analysis. Disappearance of the vinyl group C=C stretching absorbance in the IR spectra verified complete conversion of the monomers into the polymeric product.

Thermogravimetric analysis of **15** and **16** showed that these copolymers possess high thermal stability. No polymer decomposition was observed below 300°C.

Noble Metal Ion Separations by VPy and MVBipy Copolymers 1–16 with Different Dimethacrylate Crosslinkers

Single-species sorption of silver(I), gold(III), palladium(II), and platinum(II) from neutral aqueous solutions by copolymers **1–16** was studied. The sorption propensities of the compounds and their extrapolated selectivities, that is, those calculated from the single-ion experiments, are discussed below.

Silver(I) and Gold(III) Sorption

As evident from the data presented in Figure 1, most of the copolymers **1–16** exhibited quite high levels of Au(III) sorption with appreciable selectivity for Au(III) over Ag(I). In contrast, the sorption capacities of **1–16** for Ag(I) varied significantly as the identity of chelating group was changed from Py to Bipy. Thus, the Bipy-containing copolymers [Fig. 1(b)] showed more efficient Ag(I) binding than that of the related Py-containing compounds [Fig. 1(a)]. Evidently, a Ag(I) complex with an immobilized bidentate Bipy donor group is more stable than is that with a monodentate Py unit.

Since Au(III) sorption was conducted from aqueous KAuCl_4 solutions [in contrast to the sorption of Ag(I) from aqueous nitrate media], complexation of the former might proceed by a

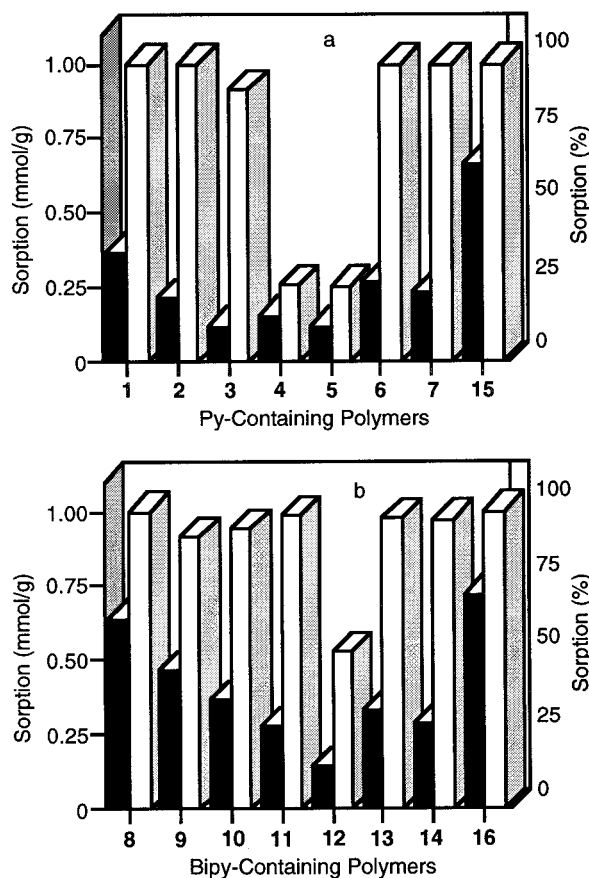


Figure 1 (■) Silver(I) and (□) gold(III) sorptions by (a) VPy and (b) MVBipy copolymers with different crosslinkers from aqueous 10.0 mM AgNO₃ or KAuCl₄ solutions, respectively.

dual mechanism involving both cationic and anionic gold-containing species.^{4b} However, the mechanistic study of Au(III) sorption by copolymers 1–16 was outside the scope of this study.

The difference in Ag(I) and Au(III) sorption from aqueous solutions by the copolymers varied as the crosslinker structure was changed. For Ag(I) sorption, this tendency was more pronounced. Thus, the binding of Ag(I) by the Py-containing copolymers 1–5 and Bipy-containing copolymers 8–12 [Fig. 1(a,b), respectively] decreased when the length and branching of the alkylene chain in the crosslinker were enhanced. This trend may indicate that each Ag(I) is coordinated by more than one Py (Bipy) group of the polymer. Then, if the distance between the chelating groups is increased and/or bulky substituents in the spacers cause spatial hindrance for a metal ion approach to the Py (Bipy) moieties, the sorption ability of the polymer will be reduced. In

agreement, VPy and MVBipy copolymers with bisphenol A dimethacrylate as the crosslinker (5 and 12, respectively) exhibited the weakest Ag(I) sorption from aqueous solution for the polymer series.

The diminished sorption ability for Ag(I) by copolymers with long hydrocarbon spacers between the Py (Bipy) groups improved significantly when a soft⁸ sulfur donor atom was introduced into the crosslinker. Thus, sulfur-containing copolymers 15 and 16 showed the most efficient Ag(I) sorption. The introduction of hard⁸ oxygen atoms in the crosslinkers of copolymers 6, 7, 13, and 14 had a much smaller effect on Ag(I) binding.

Efficient Au(III) sorption by the Py- and Bipy-containing copolymers remained almost unchanged as the length of the aliphatic spacer was varied, except for copolymer 4. However, low Au(III) sorption was noted for copolymers 5 and 12 which have branched aromatic hydrocarbon spacers.

The Au(III) sorption capacities of copolymers containing sulfur donor atoms (15 and 16) and oxygen donor atoms (6, 7, 11, and 12) in the crosslinkers were essentially the same as the high Au(III) binding levels of copolymers 1–3 and 8–11 that contain no heteroatoms in the spacers. On the other hand, copolymers 15 and 16 showed enhanced sorption of Ag(I), as mentioned above. Therefore, introduction of the soft sulfur coordination centers in the spacers of copolymers 15 and 16 diminished the Au(III)/Ag(I) selectivities of these copolymers relative to those of 1–14. This feature of copolymers 15 and 16 could be a disadvantage for their use in noble metal ion separations.

Pd(II) and Pt(II) Sorption

Data for the sorption of Pd(II) and Pt(II) by copolymers 1–16 are presented in Figure 2. As is readily apparent, most of the copolymers showed highly efficient sorption of Pd(II) with discrimination from Pt(II).

Remarkable Pd(II)/Pt(II) selectivities were observed for the Bipy-containing sorbents [Fig. 2(b)]. Under the experimental conditions, copolymers 10, 11, 13, and 14 provided nearly complete removal of Pd(II) from an aqueous solution, while Pt(II) sorption by these polymers was below the detection limit. In contrast, the analogous Py-containing copolymers possessed an appreciable affinity for Pt(II) [Fig. 2(a)] and, therefore, a much lower sorption selectivity for Pd(II) over Pt(II).

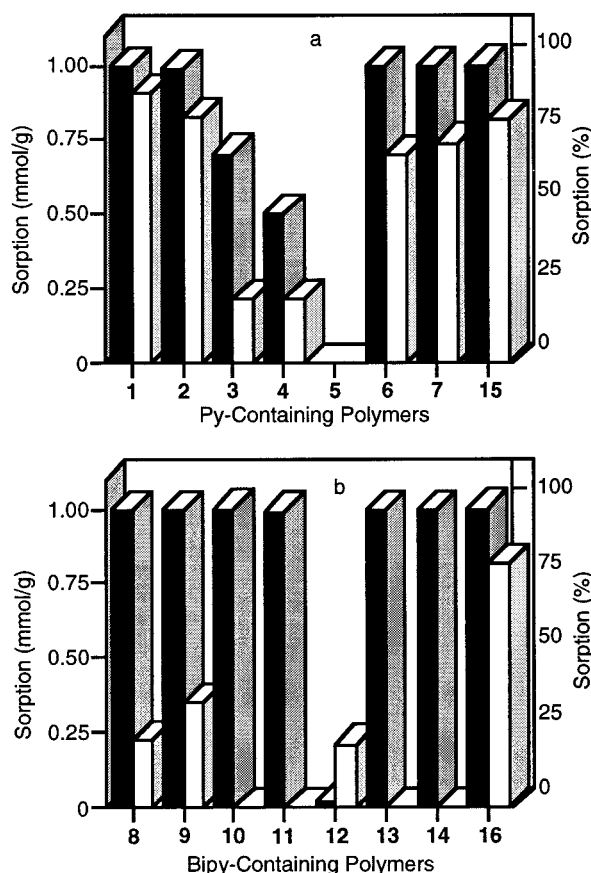


Figure 2 (■) Palladium(II) and (□) platinum(II) sorptions by (a) VPy and (b) MVBipy copolymers with different crosslinkers from aqueous 1.00 mM K_2PdCl_4 or K_2PtCl_4 solutions, respectively.

Levels of Pd(II) and Pt(II) sorption by Py-containing copolymers 1–4 decreased as the length of the aliphatic hydrocarbon chain in the crosslinker increased. In contrast, highly efficient Pd(II) sorption by the analogous Bipy-containing compounds was insensitive to the length of the hydrocarbon spacer. We postulate that this dissimilarity arises from differing compositions of the Pd(II) complexes formed by immobilized Py and Bipy chelating groups. Thus, we propose that with the Vpy copolymers each Pd(II) prefers to be coordinated by two monodentate Py units, while with the MVBipy copolymers 1:1 metal-to-Bipy complexes are formed.

Use of branched bisphenol A dimethacrylate as a crosslinker in copolymer 5 resulted in complete loss of both the Pd(II) and Pt(II) binding ability. An analogous dramatic effect of the branched spacer on the Pd(II) sorption capacity was observed for the related Bipy-containing copolymer

12. However, it is surprising that copolymer 12, despite anticipated steric hindrance for metal ion complexation, retained a moderate Pt(II) sorption ability. Therefore, 12 is the only copolymer which exhibits sorption selectivity for Pt(II) over Pd(II).

The VPy copolymers 6 and 7 with oxygen atoms in the crosslinkers and sulfur-containing 15 exhibited significantly greater sorption of Pd(II) and Pt(II) relative to that of 3 and 4 which contain no heteroatoms in their long hydrocarbon spacers [Fig. 2(a)]. For 6 and 7, this result was unexpected since coordination of soft Pd(II) and Pt(II) coordination with hard⁸ ether oxygen donor atoms is unusual. Probably, with an oxygen atom in the crosslinker, it may coordinate K^+ of the K_2PdCl_4 (K_2PtCl_4). This reaction would be accompanied by ion-pairing with the platinide-containing anion and thereby increase the overall Pd(II) or Pt(II) uptake from an aqueous solution.

Unlike the Py-containing copolymers, introduction of hard⁸ oxygen donor atoms in the crosslinkers of the Bipy-containing analogs 13 and 14 did not alter the binding ability of these copolymers for Pd(II) and Pt(II) relative to that of copolymers 10 and 11 which have long-chain spacers, but no heteroatoms. The long spacer-containing copolymers 10, 11, 13, and 14 did not detectably sorb Pt(II) from the aqueous solution, in contrast with copolymers 8 and 9 in which the Bipy units are separated by shorter crosslinkers. This observation suggests that Pt(II) sorption by the Bipy-containing copolymers may proceed via 1:1 metal-to-Bipy complexation, as assumed (*vide supra*) for Pd(II) binding. If this were the case, the level of Pt(II) sorption will decrease when the distance between the chelating groups is enhanced, unless a soft⁸ donor atom is incorporated into the crosslinker. Indeed, copolymer 16 with a soft sulfur donor atom in the spacer exhibited a dramatic increase of Pt(II) sorption relative to that observed for all of other Bipy-containing copolymers [Fig. 2(b)]. However, the enhanced complexing ability of 16 for Pt(II) results in the loss of the very high Pd(II)/Pt(II) selectivity that is characteristic for this series of chelating polymers.

Determination of Pd(II) Sorption Constants for the VPy and MVBipy Copolymers with Ethylene Glycol Dimethacrylate

For quantitative characterization of the complexing ability of immobilized Py and Bipy chelating groups for Pd(II), copolymers of ethylene glycol dimethacrylate with VPy and MVBipy (1 and 8,

respectively) were chosen. In these copolymers, the heterocyclic amine units are separated by short ethylene spacers and, thus, may form complexes with different metal-to-ligand stoichiometries. Also, copolymers **1** and **8** do not contain any donor centers in the crosslinkers that could interfere with Pd(II) binding by the Py and Bipy moieties.

With excess Cl^- , Pd(II) is present in aqueous solution mostly as $[\text{PdCl}_3]^-$ and $[\text{PdCl}_4]^{2-}$ anionic species which interact with Py and Bipy groups immobilized in the polymer surface (L_{im}) in accord with the following equation:



where $n = 1$ or 2 and the same values are assumed to be the most probable for m . Determination of the complex stability constant as the equilibrium constant for eq. (1) is quite complicated. However, Pd(II) sorption by **1** and **8** may be characterized by the conventional Langmuir equation:

$$\theta = a/a_\infty = KC_{Pd}/(1 + KC_{Pd}) \quad (2)$$

where θ is the relative metal loading of the sorbent; a and a_∞ , the observed and maximal adsorption values [e.g., numbers of moles of Pd(II) species sorbed by the polymer sample], respectively; K , the sorption constant; and C_{Pd} , the equilibrium Pd(II) concentration in the aqueous solution. Equation (2) is easily transformed into eq. (3):

$$1/a = 1/a_\infty(1 + 1/KC_{Pd}) \quad (3)$$

The values of a_∞ and K may be determined from a plot of $1/a$ versus $1/C_{Pd}$. The maximal metal-to-ligand stoichiometry for sorption is evaluated as a_∞/N_L , where N_L is a number of moles of chelating groups in the polymer sample.

As calculated from the elemental analyses data,³ copolymers **1** and **8** contained 2.00 and 1.60 mmol/g of chelating groups, respectively. For the Pd(II) sorption studies, samples of **1** and **8** with $N_L = 20.0 \mu\text{mol}$ were utilized. The sorption data are presented in Figure 3.

The monotonous curves of a versus N_{Pd}/N_{Bipy} [Fig. 3(a)], where N_{Pd} is the number of moles of Pd(II) in the aliquot of an aqueous solution, with $N_{Pd} > N_{Py}$, become linear in a plot of $1/a$ versus $1/C_{Pd}$ [Fig. 3(b)]. From these graphs, values of the maximal Pd(II) adsorption, sorption constant, and maximal sorption capacity of the copolymers

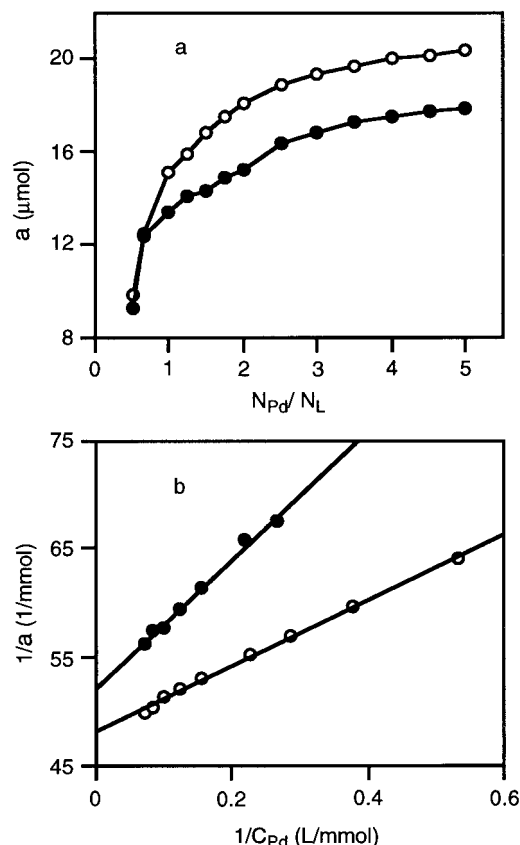


Figure 3 Dependence of (a) a versus N_{Pd}/N_L and (b) $1/a$ versus $1/C_{Pd}$ for Pd(II) sorption by copolymers (●) **1** and (○) **8**.

1 and **8** [e.g., the maximal number of moles of sorbed Pd(II) per gram of sorbent, c_m] were calculated (Table II).

With $N_{Pd} > N_{Py}$, both of the copolymers were found to bind Pd(II) as 1:1 complexes. The K value determined for the Bipy-containing **8** was about as twice large as that for the Py-containing **1**. Since the constant for complexation-based metal ion sorption determined from the Langmuir equation (eq. 2) may be considered analogous to the stability constant of the corresponding complex,⁹ the binding strength of Pd(II) with monodentate Py immobilized in **1** is only approximately one-half that for the analogous complex formed by bidentate Bipy incorporated into copolymer **8**.

CONCLUSIONS

A series of chelating copolymers containing Py and Bipy groups separated by spacers with differing structures are found to be efficient noble

Table II Pd(II) Sorption from Aqueous K_2PdCl_4 Solutions by VPy and MVBipy Copolymers with Ethylene Glycol Dimethacrylate

Copolymer	Chelating Group	Maximal Pd(II) Adsorption, a_∞ (mmol)	Maximal Sorption Stoichiometry, a_∞/N_L	Sorption Constant, K (L/mol)	Maximal Sorption Capacity, c_m (mmol/g)
1	Py	1.92×10^{-2}	0.96	8.74×10^2	1.92
8	Bipy	2.08×10^{-2}	1.04	1.59×10^3	1.66

metal ion sorbents that possess selectivity for Au(III) over Ag(I) and for Pd(II) over Pt(II). The binding abilities of the copolymers toward the noble metal ions vary as the crosslinker structure and chelating group identity were changed in the copolymer. New VPy and MVBipy copolymers with TDMA containing a sulfur donor atom in the spacer possess enhanced sorption capacities for Ag(I), Au(III), Pd(II), and Pt(II). However, they exhibited diminished selectivities relative to those of analogous copolymers with no heteroatoms in the crosslinker.

This research was supported by the Texas Higher Education Coordinating Board-Advanced Research Program and the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy (Grant DE-FG03-94ER14416).

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