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Preparation of Site-Selective Ion-Exchange Resins

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Abstract

Ion-exchange resins were prepared by copolymerization of styrenic monomers with metal ion complex compounds bearing polymerizable ligands. Removal of the metal ions by acid washing produced sites in the resins which contained ligands configured to match the bonding characteristics of the ions used in their construction. This template procedure was performed with Ni^{2+} and Cu^{2+} ions, and comparisons were made of exchange capacities and equilibrium constants for templated and untemplated resins. Templated resins showed order of magnitude capacity preferences for the ion used in their preparation. Equilibrium constants were found to be inversely related to capacities.

INTRODUCTION

It has been demonstrated that enhancement of selectivity in sorption processes may be obtained by templating active sites in sorbents (*1*). This template process usually involves preparation of the sorbent in the presence of the species to be absorbed, followed by the removal of the templating species to leave stereospecific sites in the sorbent. A number of investigators have used such techniques in the preparation of selective silica-based sorbents (*2–5*).

Recently work has been done with template syntheses of polymer-based sorbents. Wulff and his associates published a number of papers concerning polymers designed as enzyme analogues (*6–8*). The method employed involved attachment of vinyl groups to organic template molecules to produce polymerizable derivatives, and copolymerization with a matrix monomer and crosslinking agent. Subsequent removal of the template species left cavities in the polymer. The cavities had shapes and arrangements of binding groups which correspond to the structure of the template. Other groups using analogous methods with organic molecular template species include those of Fuji, Mosbach, Neckers, Sarhan, and Shea (*9–13*).

There are a few reports in the literature concerning stereoselective polymers prepared by templating with inorganic ions. First reports were due to the groups of Kabanov and Nishide (*14*, *15*). These groups produced templated ion-exchange resins by first preparing linear polymers from monomers able to coordinate metal ions. The linear polymers were then placed in contact with solutions of metal ions, and were allowed to equilibrate in order to produce polymer–metal compounds in which the polymer conformation had been adjusted to coordinate the metal ions as optimally as possible. The compounds were then isolated and crosslinked in an effort to preserve the polymer conformation, and the metal ions were removed by acid washing. Exchange experiments were performed, and it was generally observed that templated resins showed increased sorption capacities relative to untemplated resins, indicating that the templating process can make a resin selective for the template species. Equilibrium constants for the exchange of template species were reported to be enhanced in some cases (*16*, *17*).

The groups of Neckers and Nishide performed copolymerizations with metal ions present in the reaction mixtures (*18*, *19*). The monomers present were divinyl benzene (DVB) and polymerizable ligands such as vinylimidazole and 4-vinyl-4′-methylbipyridine. After removal of the metal ions by acid washing, the resins produced exhibited increased sorption capacities for all ions, and particularly for the ion present during polymerization. Nishide's group reports an increase in equilibrium constant for the exchange of Ni^{2+} due to the template effect, though other information concerning equilibrium constants is not presented by either group.

It is the purpose of the current work to employ methods similar to those outlined above to prepare site-selective ion-exchange resins, and that the exchange properties of such resins be investigated. The approach taken differs from earlier work in that the first step will be to prepare polymerizable metal ion complex compounds by coordination of metal ions with ligand molecules which contain vinyl groups. These compounds will then be copolymerized with styrenic matrix monomers and DVB to produce ion-exchange resins in which templated exchange sites will be dispersed in an inert environment. Removal of the ions by acid washing should provide resins with configured sites sufficiently isolated from each other to eliminate mutual distortions during exchange experiments and optimize coordination and selectivity.

EXPERIMENTAL

With the exception of the items named below, all reagents were obtained from commercial suppliers and used without purification. 4-Vinylpyridine (VPY) was distilled before use because of partial autopolymerization.

4-Vinylbenzoic acid (VBA) was freshly prepared by the method of Broos et al. (*20*). Standard solutions of metal ions were prepared for use in atomic absorption analyses by dissolution of highly pure metals in nitric acid.

Copper acrylate prepared as described by Edmondson and Lever was dissolved in diethyl ether and a stoichiometric amount of VPY was added (*21*). The solution changed color from blue to green, and, upon standing, green crystals were observed to form in the solution. Evaporation produced a green solid, the infrared spectrum of which showed peaks consistent with complexed pyridyl groups. Elemental analysis was performed by Desert Analytics for C, H, and N with the following results: C = 50.1%, H = 4.0%, N = 4.2%. Calculated values for $Cu_2(C_3H_3O_2)_4(VPY)_2$ are C = 50.2%, H = 4.2%, N = 4.5%.

Cu^{2+}, Ni^{2+}, and Ag^+ salts of VBA were prepared by literature methods (*22*, *23*). Elemental analysis performed by Desert Analytics on the Ni^{2+} salt for C and H showed C = 52.8%, H = 4.7%. Calculated values for the trihydrate give C = 53.1%, H = 5.0%.

Free radical copolymerizations were carried out in bulk. The matrix monomers were styrene (STY) or vinylbenzylchloride (VBC), and the crosslinking agent was DVB. Polymerization was initiated by addition of azobisisobutyronitrile (AIBN) followed by heating to 60°C. Solvents were required for solution of the metal ion compounds in the styrenic matrix monomers. The solvents employed included chloroform (CHL), toluene (TOL), dimethylformamide (DMF), methyl isobutyl ketone (MIK), dimethylsulfoxide (DMSO), and pyridine (PY). All polymerizations were performed with reaction mixtures sealed in screw-cap glass vials under inert atmosphere. The feed compositions and reaction conditions for the resins are given in Table 1.

Resins were ground as finely as possible and washed with solvents such as acetone to remove soluble components. They were gradually exposed to water by gradient elution of increasing water concentration in acetone. When fully hydrated, the resins were exposed to acid solutions until metal ions were no longer removed. The hydrogen form resins were then water washed to remove excess acid, and were ready for metal ion loading and further experimentation.

Washed resins were loaded with Cu^{2+} and Ni^{2+}, simultaneously, or with each after the other, using batch mode equilibrations. They were water washed until eluted water was found to be metal free. After air drying for 24 h, samples were weighed into plastic bottles and combined with water. The pH of each mixture was adjusted by addition of dilute HNO_3 and an overnight equilibration was allowed with the mixture gently stirring in a controlled temperature chamber maintained at 30 ± 2°C. A portion of the solution was removed from the mixture, and the pH of what remained was

TABLE 1
Feed Compositions and Reaction Conditions

Resin	Complex (%)	DVB (%)	Matrix monomer	Temperature (°C)	Time (h)	Solvent (mL)
			Ni Templated			
59A, B	2	2½	STY	60	20	1.0 CHL
60A, B	2	2½	VBC	60	20	1.0 CHL
101A, B	2	2½	STY	60	20	1.0 CHL
101C, D	2	2½	VBC	60	20	1.0 CHL
131A, B	2	1½, 2½	STY	60	20	1.0 CHL, 0.02 TOL
131C, D	2	1½, 2½	VBC	60	20	1.0 CHL, 0.02 TOL
170A, B	1	1, 4	STY	60	20	0.5 DMF, 1.0 MIBK
170C, D	1	1, 4	VBC	60	20	0.5 DMF, 1.0 MIBK
200A, B	4	1, 2½	STY	60	20	1.0 DMF, 1.0 MIBK
200C, D	4	1, 2½	VBC	60	20	1.0 DMF, 1.0 MIBK
204A	1	4	STY	60	20	1.0 DMF, 1.0 MIBK
204B	1	2½	VBC	60	20	1.0 DMF, 1.0 MIBK
217A–D	1, 2	1, 2½	STY	50	13	0.6 or 0.8 PY
217E–G	1, 5	4, 5	STY	50	13	0.5 or 1.5 PY
			Ag Templated			
93A, B	1½	1	STY	60	20	1.0 DMSO
205A–C	1½	2½	STY	60	20	1.0 DMSO
			Cu Templated			
124A, B	3	2½	STY	60–70	42	1.0 CHL
223A, B	1, 2	2½	STY	60–65	48	0.7 PY

further adjusted by addition of concentrated HNO_3. After a second overnight equilibration period, another portion of the solution was removed. Resins were re-used after water washing. Repeated extraction without loading indicated that all available metal ions were removed by this procedure.

Metal ion content of removed solutions was determined by atomic absorption (AA) techniques. The spectrometer used was a Varian AA-1475, with single element Ni and Cu lamps. Standard solutions of the metal ions were prepared by dilution of 1000 ppm stock solutions prepared by dissolution of highly pure metals in nitric acid.

RESULTS AND DISCUSSION

Calculations of the metal-ion capacity and the equilibrium constant were obtained for each polymer from the weight of the polymer, the amount of water to which the polymer was exposed, the pH of the solution after the first adjustment and equilibration, the amount of solution removed from the polymer, and the concentration of metal ion observed in each of the solutions removed from the polymer. The capacity of a polymer was equivalent to the amount of metal ion removed from the polymer in both parts of each extraction. The equilibrium constant was determined by the acid concentration and metal ion concentration in the water phase and in the polymer phase. The H^+ concentration in the water phase was equal to 10 raised to the −pH power, where −pH was the negative of the pH of the solution in contact with the polymer at equilibrium. The metal ion concentration in the water phase was taken as the concentration observed by AA analysis of the solution in contact with the polymer at equilibrium,

TABLE 2
Sample Calculations[a]

Label	Item	Value	Units	Formula
A	+ cap water[b]	38.153	g	
B	+ eq water[c]	44.130	g	
C	+ polymer	15.031	g	
D	Tare	13.639	g	
E	Polymer	1.392	g	C–D
F	eq water	29.099	g	B–C
G	cap water	23.104	g	A–C
H	+ removed water	22.700	g	
I	Tare	6.527	g	
J	Removed water	16.173	g	H–I
K	pH	3.09		
L	eq solution Ni^{2+}	0.15	ppm	
M	cap solution Ni^{2+}	0.12	ppm	
N	eq solution Ni^{2+}	7.4×10^{-5}	mm	S*F
O	Removed Ni^{2+}	4.1×10^{-4}	mm	N*J/F
P	Ni^{2+} capacity	6.4×10^{-5}	mm/g	(M/58710)*G/E + O/E
Q	$[H^+]$	8.1×10^{-4}	mm/mL	10^{-K}
R	$[NiR_2]$	1.0×10^{-5}	mm/g	P − N/E
S	$[Ni^{2+}]$	2.6×10^{-6}	mm/mL	L/58710
T	[HR]	1.1×10^{-4}	mm/g	2*N/E
U	*K*	2.3×10^2		$Q^2*R/(S*T^2)$
V	Log *K*	2.4		

[a] These data were obtained from a simultaneous double exposure of 59A.

[b] cap water refers to the water in contact with polymer after the addition of concentrated nitric acid and equilibration.

[c] eq water refers to the water in contact with polymer after the addition of dilute nitric acid and equilibration.

TABLE 3
101 Series Resins

Property	101A	101B	101C	101D
		Single Ion Exposures		
Log $K_{H,Ni}$	3.35	3.19	2.90	3.49
Capacity	8.87×10^{-4}	4.88×10^{-4}	1.03×10^{-3}	8.59×10^{-4} mm/g
Log $K_{H,Cu}$	1.91	4.84	4.26	4.97
Capacity	1.36×10^{-5}	5.3×10^{-6}	6.0×10^{-6}	4.2×10^{-6} mm/g
Log $K_{H,Ni}$	3.06	2.75	2.22	1.76
Capacity	3.22×10^{-4}	4.78×10^{-4}	8.64×10^{-4}	1.04×10^{-3} mm/g
Log $K_{H,Cu}$	6.1	7.58	6.81	6.74
Capacity	$<1 \times 10^{-6}$	3.3×10^{-6}	3.2×10^{-6}	3.2×10^{-6} mm/g
		Summary of Single Exposures		
Log $K_{H,Ni}$	3.2 ± .2	2.9 ± .3	2.5 ± .4	2.6 ± 1.2
Capacity	6.0×10^{-4}	4.8×10^{-4}	9.5×10^{-4}	9.5×10^{-4} mm/g
Log $K_{H,Cu}$	4.0 ± 3.0	6.2 ± 1.9	5.5 ± 1.8	5.9 ± 1.3
Capacity	7.2×10^{-6}	4.4×10^{-6}	4.6×10^{-6}	3.7×10^{-6} mm/g
		Double Exposures: Cu Then Ni		
Log $K_{H,Ni}$	4.62	4.10	2.61	3.01
Capacity	1.61×10^{-4}	1.77×10^{-4}	6.47×10^{-4}	4.40×10^{-4} mm/g
Log $K_{H,Cu}$	err	err	6.21	4.20
Capacity	5.1×10^{-6}	7.6×10^{-6}	4.4×10^{-6}	6.7×10^{-6} mm/g
Log $K_{H,Ni}$	2.48	3.20	1.68	1.82
Capacity	1.19×10^{-4}	1.06×10^{-4}	2.28×10^{-4}	1.84×10^{-4} mm/g
Log $K_{H,Cu}$	6.14	4.89	6.27	2.11
Capacity	4.18×10^{-5}	8.6×10^{-6}	5.0×10^{-6}	7.6×10^{-5} mm/g
		Double Exposure: Ni Then Cu		
Log $K_{H,Ni}$	3.47	3.58	2.75	3.03
Capacity	9.98×10^{-5}	8.91×10^{-5}	2.08×10^{-4}	1.85×10^{-4} mm/g
Log $K_{H,Cu}$	3.97	8.38	5.82	5.66
Capacity	2.45×10^{-5}	8.8×10^{-6}	7.6×10^{-6}	5.7×10^{-6} mm/g
		Simultaneous Double Exposure		
Log $K_{H,Ni}$	2.20	2.18	0.920	1.38
Capacity	8.32×10^{-5}	9.80×10^{-5}	2.71×10^{-4}	2.11×10^{-4} mm/g
Log $K_{H,Cu}$	5.02	4.58	4.14	4.92
Capacity	4.8×10^{-6}	8.3×10^{-6}	1.13×10^{-5}	1.97×10^{-5} mm/g

(*continued*)

TABLE 3 (*continued*)

Property	101A	101B	101C	101D
Single Exposures after Acetone Washing				
Log $K_{H,Ni}$	-0.535	-0.323	2.52	2.45
Capacity	7.16×10^{-4}	7.75×10^{-4}	6.19×10^{-5}	5.45×10^{-5} mm/g
Log $K_{H,Cu}$	0.635	1.17	3.79	4.77
Capacity	4.73×10^{-4}	4.86×10^{-4}	2.93×10^{-5}	5.9×10^{-6} mm/g
Log $K_{H,Ni}$	err	5.65	6.59	err
Capacity	5.47×10^{-5}	7.64×10^{-5}	1.39×10^{-5}	7.0×10^{-6} mm/g
Log $K_{H,Cu}$	3.40	2.74	3.89	3.71
Capacity	2.53×10^{-4}	2.15×10^{-4}	3.90×10^{-5}	2.62×10^{-5} mm/g
Simultaneous Double Exposure after Acetone Washing				
Log $K_{H,Ni}$	err	err	err	5.03
Capacity	1.59×10^{-5}	1.83×10^{-5}	1.37×10^{-5}	3.0×10^{-6} mm/g
Log $K_{H,Cu}$	1.55	2.33	3.45	4.41
Capacity	1.44×10^{-4}	7.85×10^{-5}	2.95×10^{-5}	1.01×10^{-5} mm/g

converted from ppm to molarity units. The concentration of metal ions in the polymer phase was calculated as the capacity of the polymer less the amount of metal ion that was exchanged into solution at equilibrium, divided by the weight of the polymer. The H^+ concentration in the polymer phase was calculated as twice the amount of divalent metal ion in solution at equilibrium divided by the polymer weight. An example of these calculations appears in Table 2.

The log K and capacity values calculated from data obtained in exchange experiments conducted with resins in the 101 series are presented in Table 3. After a number of experiments in aqueous media, these resins were washed with acidic acetone solutions in order to determine if swelling in the absence of templating metal ions would alter the observed selectivities. Data obtained before and after acetone swelling are presented in this table. Summary data acquired before acetone exposure are presented for all of the resins in Table 4.

The resins of the 59 and 60 series provided the first indications of selectivity in that the Ni^{2+} capacities observed were larger than the Cu^{2+} capacities. The 101 series resins represent a later replication of these series, where the capacity based selectivity is more pronounced. It is also notable from data concerning these resins that while capacities are greater for Ni^{2+}, equilibrium constants are larger for Cu^{2+}. This trend is borne out in

TABLE 4
Summary of Resin-Exchange Properties[a]

Resin series	Complex (%)	DVB (%)	Log $K_{H,Ni}$	Ni capacity (10^{-5} mm/g)	Log $K_{H,Cu}$	Cu capacity (10^{-5} mm/g)
			Ni Templated			
59, 60	2	2½	2.7 ± 0.7	17 ± 11	3.7 ± 1.6	10 ± 10
101	2	2½	2.7 ± 0.9	39 ± 32	5.3 ± 1.6	1.4 ± 1.9
131	2	1½, 2½	1.6 ± 0.9	43 ± 32	4.4 ± 1.0	3.7 ± 4.7
170	1	1, 4	2.9 ± 0.7	29 ± 42	4.5 ± 1.1	4.0 ± 3.0
200	4	1, 2½	2.0 ± 0.9	28 ± 20	5.5 ± 1.2	2.6 ± 2.8
204	1	2½, 4	3.0 ± 1.0	65 ± 106	3.5 ± 0.3	6.2 ± 2.3
217A–D	1, 2	1, 2½	3.8 ± 0.7	31 ± 42	6.3 ± 1.6	20 ± 15
217E–G	1, 5	4, 5	3.5 ± 0.9	52 ± 88	5.4 ± 0.4	3.5 ± 2.9
			Ag Templated			
93	1.5	2½	3.7 ± 1.0	6.0 ± 3.9	4.3 ± 1.2	2.3 ± 1.2
205	1.5	1, 2½	3.1 ± 2.0	5.7 ± 5.2	3.4 ± 2.1	52 ± 55
			Cu Templated			
124	3	2½	2.5 ± 1.5	11 ± 12	1.8 ± 0.3	58 ± 41
223	1, 2	2½	4.7 ± 0.8	7.5 ± 8.4	1.8 ± 0.3	101 ± 56

[a] The exchange properties given are mean values ± standard deviations for all resins in each series, excluding experiments performed after acetone washing. All entries represent at least four experimental values.

all of the resins that were templated with Ni^{2+}: there is roughly an order of magnitude preference for Ni^{2+} in terms of capacity, but Cu^{2+} exchange is characterized by higher equilibrium constants.

The resins that were not templated for Ni^{2+} did not show selectivity for Ni^{2+} in terms of capacity. Those prepared with silver vinylbenzoate were intended to provide resins in which the functional groups would not tend to be paired by association with a divalent ion. Such preparation provided material that served the role of blank resins. Exchange experiments revealed higher Cu^{2+} capacities than Ni^{2+} capacities where there was a clear distinction. The equilibrium constants were also found to be larger for Cu^{2+} than for Ni^{2+}, though differences were not large.

Resins in the 124 and 223 series were templated for Cu^{2+} instead of Ni^{2+}. Only small amounts of these materials were obtained from each polymerization attempt due to the presence of Cu^{2+}. The capacities and equilibrium constants measured for exchange of Cu^{2+} and Ni^{2+} by these resins showed an enhancement in Cu^{2+} capacity as expected. The equilibrium constants measured did not show a preference for Cu^{2+}, but were instead larger for Ni^{2+}.

CONCLUSIONS

It has been observed that sorption of inorganic ions by ion-exchange resins can be enhanced by templating the resin for the ion of choice during preparation. The method used in this work provides active sites which have been configured to match a given ion and are dispersed in a matrix that is inactive in terms of exchange.

The results of exchange experiments performed with templated resins indicate that sorption capacities are enhanced for the ion used as the template species. It has been further observed that equilibrium constants measured in the exchange experiments do not follow the capacity trend, nor do they follow solution stability constant trends. The equilibrium constants are observed to decrease with increasing capacity, so that the ion used as the template in preparation exhibits a lower than usual equilibrium constant though its sorption capacity is increased relative to untemplated resins.

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