Uptake of Zinc, Nickel, and Chromium by *N*-Isopropyl Acrylamide Polymer Gels

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ABSTRACT: Pure *N*-isopropyl acrylamide (NIPA) polymer gel and NIPA copolymers containing 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 2-acetamidoacrylic acid (AAA), and acrylic acid (AA) were prepared and evaluated with respect to their capability for taking up zinc, nickel, and chromium ions from solutions. AAA-containing NIPA gels were found to take up these metal ions most efficiently. Titration of these gels verified the strong acidic nature of the AMPS–NIPA gel and the weakly acidic nature of the AA–NIPA and AAA–NIPA gels. The ion-exchange capacities, derived from the titration curves, were, however, rather low in all cases. NIPA gels are known to collapse at temperatures about 32°C. This, however, was found to have no effect on the ion-exchange behavior of the gels. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 355–362, 1998

Key words: NIPA copolymer gels; uptake of Zn, Ni, and Cr ions; ion-exchange capacities; effect of temperature on metal uptake

INTRODUCTION

Poly(*N*-isopropyl acrylamide) (PNIPA) has been widely studied due to its interesting thermal properties in aqueous solutions. Aqueous PNIPA solutions precipitate at a lower critical solution temperature (LCST) around 32°C due to a phase transition between the hydrated and dehydrated states of the polymer side chains.[1–4] Water-swollen crosslinked PNIPA networks swell and shrink at temperatures below and above the LCST, correspondingly.[1,5]

The microstructure of the NIPA gel can be strongly influenced by the reaction conditions.[1,6,7] Polymerization in an aqueous solution below the critical temperature produces a transparent homogeneous gel, whereas the gels synthesized above the LCST are turbid, indicating a heterogeneity of the polymer network. A heterogeneous macroporous NIPA gel can swell and shrink several thousand times faster than can a nonporous homogeneous gel of the same composition and dimension.[1,6] In this work, heterogeneous macroporous copolymeric NIPA gels were prepared, since it was assumed that large pore sizes greatly facilitate the chemical accessibility and diffusion of ions and larger molecules.

PNIPA has been tested for several applications in biotechnology, such as in drug release, film technology, flocculation, and water treatment.[1,2,8] The concept of thermoresponsive polymers and gels as a new matrix of an ion-exchange resin in this study is based on the possibility of the synthesis of high-porosity gels in which the pore structure and size are not permanent, but can be reversibly changed or reduced with the temperature.

2-Acrylamido-2-methylpropane sulfonic acid (AMPS) has been used as a comonomer because of its thermal and hydrolytic stability. This monomer contains a spacer which allows the charged group to have a relatively high mobility when linked to a polymer backbone. Also, 2-acetami-

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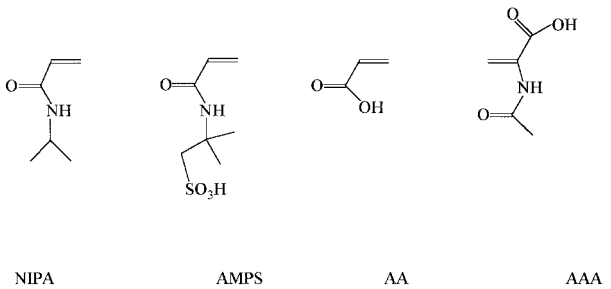
doacrylic acid (AAA) has been copolymerized with NIPA. AAA is an ionic vinyl monomer having two functional groups, that is, carboxyl and acetamido groups, and it is known to form complexes with di- and trivalent metal ions.[9] Acrylic acid (AA) was chosen as the third comonomer.



EXPERIMENTAL

Materials

N-Isopropyl acrylamide (NIPA; Polysciences Inc.) was recrystallized from hexane before use. Acrylic acid (AA; Fluka) was purified by using De-Hibit-100 macroreticular ion-exchange resin for the removal of the inhibitors. 2-Acetamidoacrylic acid (AAA) was prepared by refluxing a toluene (500 mL) solution of puruvic acid (0.5 mol) and acetamide (0.25 mol) over 4 h. The crude AAA was removed by filtration from the supernatant toluene, and it was recrystallized twice from ethanol.[10] 2-Acrylamido-2-methylpropane sulfonic acid (AMPS; Merck) and *N,N′*-Methylene bisacrylamide (BIS; Serva) were used as received.

Preparation of NIPA Gels

Homopolymeric and six copolymeric NIPA gels were prepared by free-radical polymerization in water above the LCST to get heterogeneous macroporous gels. The comonomers added into NIPA in various ratios were AMPS, AAA, and AA. The chemical composition of the copolymers refers here to the molar ratio of the monomers in the feed of the polymerization reaction. For example, NIPA(98)–AMPS(2) refers to a product in which 98 mol % of NIPA and 2 mol % of AMPS were used in the reaction mixture. Monomers and 5 mol % of the crosslinking monomer BIS were dissolved in water to obtain a 15 wt % solution. Thereafter, the pregel solutions were purged with nitrogen for about 30 min and 2 mol % of potassium persulfate ($K_2S_2O_8$) as the initiator was added to the solutions and the polymerization reactions were carried out at 60°C for 1.5 h. The resulting gels were cut into pieces and immersed in pure water for several days to remove unreacted residues. After purification, the gels were dried first ambiently and then under a vacuum at room temperature. This polymerization procedure resulted in heterogeneous gels where most of the polymer mass resided in closely packed clusters randomly distributed in the gel structure.[11]

Determination of Water Contents of the Dried Gels

Since the uptake parameters, described later, are calculated on the dry weight basis of the polymers, the water contents of the dried NIPA gels were determined with a Mettler 850 thermobalance heating up to 250°C. The heating rate was 10°C/min.

Determination of Zn, Ni, and Cr Uptake on NIPA Gels in Buffer Solutions

Since the gels containing acidic carboxylic and sulfonic acid groups vary in their acidities, the solution pH affects the metal-uptake values. Therefore, to obtain comparative data at the same pH values, the metal-uptake determinations were first carried out with NIPA, NIPA(98)–AMPS(2), and NIPA(98)–AA(2) gels in a 0.056*M* sodium citrate buffer solution having a pH of 4.0. Batches of this solution were made 0.01 m*M* in respect to zinc, nickel, and trivalent chromium ($ZnCl_2$, $NiCl_2 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$). Eight-milliliter samples of these solutions were equilibrated by vigorously shaking with 0.08-g samples of wet gels for 1–3 days in 10-mL plastic centrifuge tubes at two temperatures: 20 ± 1°C and 40 ± 2°C. Thereafter, the gels were removed from the solution phase by first centrifuging for 10–30 min at 25,000–50,000*g* and then filtering with 0.2- or 0.45-μm filters, after which the metal concentration of the supernate was determined. During the centrifugation, the temperature was the same as that used in the shaking. The pH values of the supernates were determined and found to be practically identical with that in the initial buffer solutions.

In addition, the same kind of procedures were made with NIPA(98)–AMPS(2) for chromium uptake in a 0.067*M* phosphate solution (62% Na_2HPO_4–38% KH_2PO_4) having a pH of 7.0. To determine the effect of the buffer ions on the metal uptake, the tests were made in a 0.01-m*M* Cr solution without a buffer as well.

Titration of Gels with NaOH Solution: Determination of Distribution Coefficients of Ni, Zn, and Cr as a Function of pH

For the titration of the NIPA, NIPA(98)–AMPS(2), NIPA(98)–AA(2), and NIPA(98)–AAA(2) gels and determination of the distribution coefficients of Ni, Zn, and Cr, 0.3-g polymer samples were equilibrated in plastic centrifuge tubes with 30 mL of a 0.1*M* NaCl solution having a Ni, Zn, or Cr concentration of 0.01 m*M* followed by gradual addition of NaOH to the system. After each 2–3 days' shaking, the gels were centrifuged for 30 min at 25,000*g* and the pH values of the supernates were determined and 1-mL fractions of the supernates were pipetted for metal-concentration measurements. Thereafter, 5–100 μL of 0.1*M* NaOH was added to the tubes and the procedure was repeated. The temperature in these experiments was 21 ± 1°C. To study the effect of the amount of AAA in the gel, these experiments were also done with gels which had a higher proportion of AAA in the reaction mixture: NIPA(90)–AAA(10) and NIPA(80)–AAA(20).

Determination of Distribution Coefficients of Ni, Zn, and Cr at Various Temperatures

To study the effect of temperature (10, 20, 30, 40°C) on the metal uptake by NIPA, NIPA(98)–AMPS(2), NIPA(98)–AA(2), and NIPA(98)–AAA(2), 0.08-g gel samples were equilibrated for 48 h with 0.1*M* NaCl, which was 0.01 m*M* with respect to Ni, Zn, or Cr. To have an approximately similar pH value of 6.5–7.5 in each trial, NaOH was added to the solutions in amounts derived from the titration curves.

Determination of Metal Concentrations

Chromium concentrations of the solutions contacted with the gels were determined with an atomic absorption spectrophotometer (AAS) using a graphite furnace. For the determination of nickel and zinc concentrations, the solutions were labeled with radioactive tracers ^{63}Ni and ^{65}Zn, the activities of which were determined with a liquid scintillation counter and a gamma scaler, respectively.

Calculation of Distribution Coefficient

As a quantitative measure for the metal uptake, the distribution coefficient (K_D) was calculated for each metal/gel system. K_D is a typical quantity used for trace metal uptake and it reflects the selectivity of the metal-uptaking polymer to the studied ions at given conditions. The distribution coefficient is the ratio of the metal-ion concentration in the polymer to that in the solution phase after contact with the metal-containing solution. K_D is calculated in the following way: $K_D = (C_i/C - 1) \times V/m$ (mL/g), where C_i and C are the metal concentrations in the solution before and after contact, respectively; V, the solution volume (mL); and m, the dry polymer mass (g). In general, K_D is an equilibrium quantity. In this study, however, the attainment of equilibrium was not verified, but it was assumed that it was reached within the time of equilibration.

RESULTS

Water Contents of the Dried Gels

The water contents of the dried NIPA gels were in the range of 5.8–10.6% and the temperatures required to release all water, according to the TGA curves, in the range of 169–237°C.

Uptake of Zn, Ni, and Cr in Buffer Solutions at pH 4.0 and 7.0

In sodium citrate buffer solutions, none of the gels tested, NIPA, NIPA(98)–AMPS(2), and NIPA(98)–AA(2), took up any metal ions at either of the test temperatures, 20 and 40°C. This could have been caused by three possible reasons:

1. The sodium concentration of about 0.1*M*. Later, it will be seen that this was not the reason since at least some of these gels took up metal ions in 0.1*M* NaCl solution at pH 4.0 (see Figs. 2–5).
2. A low solution pH, which prevented the dissociation of acidic groups capable of binding metal ions. It is obvious from Figure 1 that the gels, excluding the AMPS–NIPA gel, were weakly acidic. The low pH of 4.0 certainly must have been one reason for the absence of metal uptake, but it does not completely explain why the gels did not take up any metal ions at all, since some uptake was observed in 0.1*M* NaCl solutions at the same pH value (Figs. 2–5).

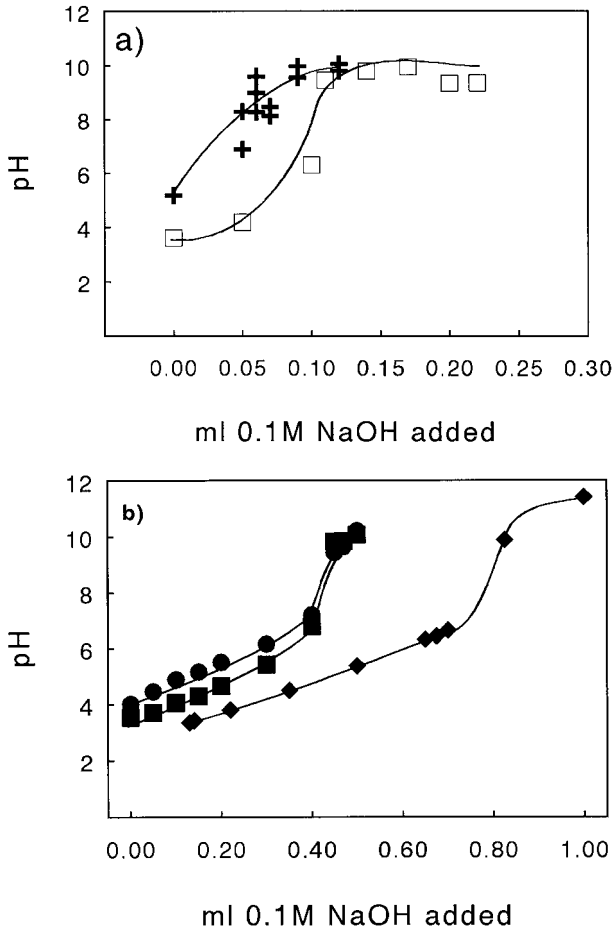


Figure 1 Titration curves of NIPA gels. (a) (+) NIPA; (□) NIPA–AMPS. (b) (●) NIPA–AA; (■) NIPA(98)-AAA(2); (♦) NIPA(80)–AAA(20). Titration with 0.1*M* NaOH.

3. The presence of complexing citrate anions. Citrate does not form very strong complexes with transition-metal ions; for example, the stability constant for the formation of the monocomplex with Ni is only intermediate 5.90 (log K).[12] However, a large excess of citrate ions resulted in the situation where the Ni ions were present practically entirely as a citrate complex at pH 4, as analyzed by the SPE program.[13] This is likely the reason that no metal uptakes were observed. The stability of the Zn–citrate complex is comparable to that of Ni and the situation was the same. The fact that the gels could not strip the metals from their citrate complexes reveals that none of them form strong complexes with these metals.

In the phosphate buffer at pH 7.0, some Cr(III) uptake could be seen (Table I). The distribution coefficient values were, however, rather low, and practically identical at both temperatures. The distribution coefficient from a pure water solution with the same chromium concentration was much higher, close to 10,000. The equilibrium pH in these solutions was two units lower due to the dissociation of the AMPS group and possible Cr for hydrogen exchange. Analysis of the solution species with the SPE program revealed that the main species at pH 5 was $Cr(OH)^{2+}$, and at pH 7, $Cr(OH)_2^+$. The phosphate complex of chromium is so weak (log K of MHL 2.56)[12] that no complex was present in the conditions used. Again, as in the case of citrate buffer solution, it can be con-

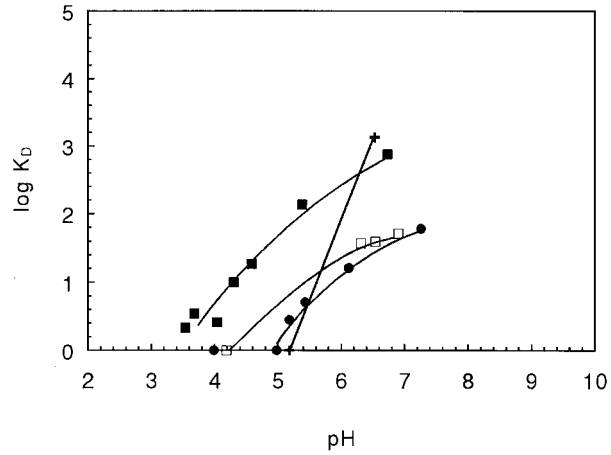


Figure 2 Distribution coefficient of Ni on (+) NIPA, (□) NIPA–AMPS, (●) NIPA-AA, and (■) NIPA–AAA gels as a function of pH. Initial Ni concentration 0.01 m*M*.

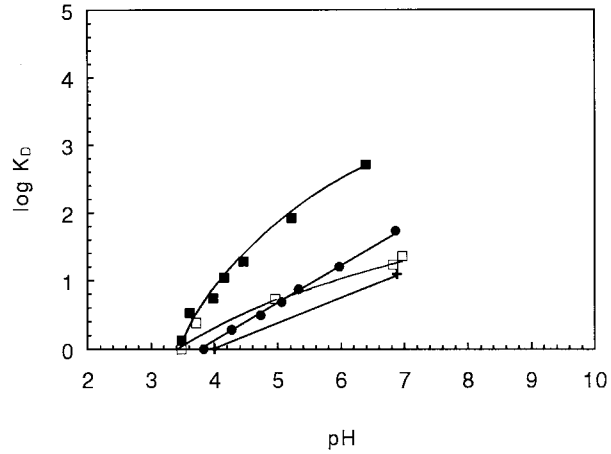


Figure 3 Distribution coefficient of Zn on (+) NIPA, (□) NIPA–AMPS, (●) NIPA–AA, and (■) NIPA–AAA gels as a function of pH. Initial Zn concentration 0.01 m*M*.

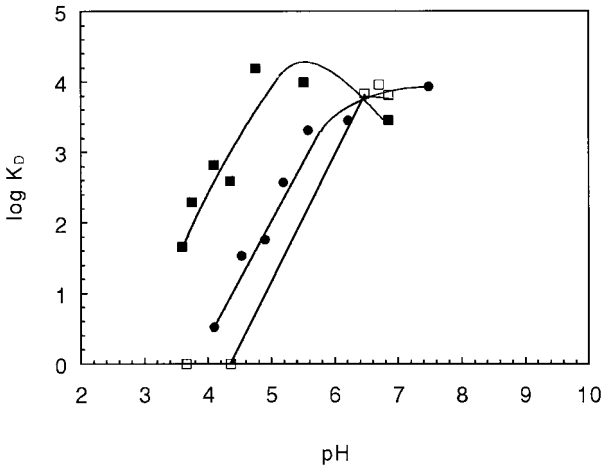


Figure 4 Distribution coefficient of Cr^{3+} on (□) NIPA–AMPS, (●) NIPA–AA, and (■) NIPA–AAA gels as a function of pH. Initial Cr concentration 0.01 m*M*.

cluded that the NIPA–AMPS gel does not form strong complexes, since it cannot strip chromium from $Cr(OH)^{2+}$.

Acidic Properties and Ion-exchange Capacities of NIPA Gels

Titration of NIPA gels revealed that the pure NIPA gel had no acidic properties, and no inflection point could be seen in the titration curve, as would be expected [Fig. 1(a)]. The NIPA–AMPS gel showed a curve characteristic for strong cation exchangers; a strong inflection point was observed at a pH of about 6 [Fig. 1(a)]. This is also understandable since sulfonic acid, part of the AMPS group, is known to be strongly acidic. The ion-exchange capacity calculated from the consumption of NaOH at the inflection point was 0.037 meq $g_{(dry\ gel)}$. This value is very low compared to ordinary sulfonic acid containing ion-exchange resins which have ion-exchange capacities up to 5 meq per dry gram. This NIPA–AMPS gel had only 2 mol % of AMPS, which explains the low capacity.

NIPA–AA and NIPA–AAA gels behaved in a very similar manner [Fig. 1(b)]. Both gave a titration curve characteristic for weakly acidic ion exchangers: weak inflection at a higher pH value of about 8. AA and AAA have carboxylic acid groups which are weakly acidic and have inflection points at the observed pH range. The ion-exchange capacities were 0.16 meq/$g_{(dry\ gel)}$ for both gels. Although this value is higher than for the AMPS gel, it is still rather low compared to ordinary carboxylic acid containing ion-exchange resins which have ion-exchange capacities up to 10 meq per dry gram. As in the case of NIPA–AMPS, the NIPA–AA and NIPA–AAA gels had only 2 mol % of these acidic components.

Figure 1(b) shows the titration curve also for the NIPA–AAA gel which had 20 mol % of AAA in the reaction mixture. The shape on the curve was identical to that of the gel having only 2 mol % of AAA. The ion-exchange capacity, however, was approximately twice higher: 0.30 meq $g_{(dry\ gel)}$. It is surprising that the increase in ion capacity was only twofold when the AAA content increased 10-fold in the reaction mixture. This may indicate that only a fraction of AAA reacted with NIPA and remained in the gel after rinsing.

Uptake of Ni, Zn, and Cr as a Function of pH

The NIPA–AAA gel was found to take up most efficiently all metal cations studied, Ni, Zn, and trivalent Cr, over the whole pH region of 3–8.5. (Figs. 2–5). All the other gels behaved in a rather similar manner, except that the pure NIPA gel took up nickel as efficiently as did the NIPA–AAA gel at pH values above 6. None of the gels took up metal ions below the pH values of 3–4 and the distribution coefficient increased with pH at the higher pH region. This is what would be expected for cation exchangers containing weakly acidic groups, such as carboxylic acid which are present in AA and AAA. For strong acid-containing exchangers, such as NIPA–AMPS, one would expect higher distribution coefficients at the low pH region but this was not observed.

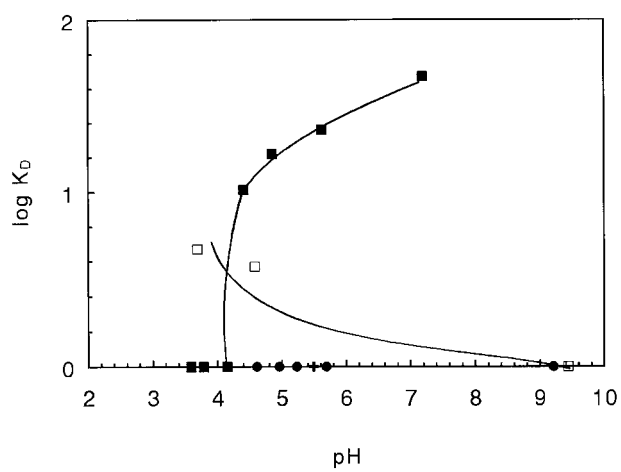


Figure 5 Distribution coefficient of Cr^{6+} on (□) NIPA–AMPS, (●) NIPA–AA, and (■) NIPA–AAA gels as a function of pH. Initial Cr concentration 0.01 m*M*.

Table I Distribution Coefficient of Cr(III) on NIPA(98)–AMPS(2) Gel From a 0.01-m*M* Chromium Solution and a Phosphate Buffer Solution Having the Same Cr Concentration at Two Temperatures

Solution	Logarithm of Distribution Coefficient (mL/g)	
	Temperature 20°C	Temperature 40°C
0.01-m*M* Cr(III) solution, equilibrium pH 5.0	3.93	3.70
0.01-m*M* Cr(III) in phosphate buffer at pH 7.0	0.88	0.82

Metal hydrolysis also had some effect on the observed K_D values in the higher pH region. In 0.01-m*M* solutions, Cr^{3+} starts to precipitate as a hydroxide at pH 7.4; Ni^{2+}, at pH 8.0; and Zn^{2+}, at pH 8.2. Since the gels had taken up considerable proportions of these metals already at lower pH values, the actual concentrations were lower than the initial 0.01 m*M*. Thus, the precipitation started at higher pH values than those given above. Because of hydroxide precipitation, no K_D values were included in Figures 2–5 at pH values above 8 for chromium and above 8.5 for nickel and zinc.

The pH dependence of pure NIPA gel can be rationalized in the following way: The nitrogen atoms in the —NH— groups were probably protonated at low pH values, forming $—NH_2^+A^-—$ groups, where A^- is an anion, chloride in this case. In these protonated groups, the nitrogen atom did not have a free-electron pair capable of forming coordination bonds with transition metals. At higher pH values, however, nitrogen was depropotonated and the gel could thus bind metal ions. It is possible that in the other NIPA gels, having AMPS, AA, and AAA, these nitrogen atoms were also responsible for the metal-ion uptake. Taking into account the fact that the contents of the acid groups were rather low, coordination with nitrogen atoms could have been the major factor in the metal uptake by all the gels.

The reason for the better metal-uptake efficiency of NIPA–AAA gels could have been the fact that in its structure the acid group and the nitrogen are closer to each other than in the other gels. This makes it possible that the transition metal is bound at the same time both by ion exchange to the carboxylic group and by coordination to the nitrogen and, thus, a strong five-ring chelate is formed. This kind of bond is stronger than ionic and coordination bonds alone.

All the other gels but pure NIPA took up chromium more efficiently than did other metal ions (Fig. 5). This is understandable since chromium has a valence of three and thus the electrostatic interaction in the bond to acidic groups is stronger than with divalent nickel and zinc ions. Hexavalent chromium was more or less excluded by the gels. Only the NIPA–AAA gel took up some Cr^{6+} but to a much lesser extent than did Cr^{3+}. Also, the NIPA–AMPS resin took up very little Cr^{6+} but only in the acidic region.

In conclusion, the following selectivity series can be drawn from the results shown in Figures 2–5:

Zn: NIPA–AAA > NIPA–AA = NIPA–AMPS > NIPA

Table II Distribution Coefficient of Nickel on NIPA Gels at Various Temperatures

	NIPA		NIPA–AMPS		NIPA–AA		NIPA–AAA	
T (°C)	log K_D	pH_{eq}	log K_D	pH_{eq}	log K_D	pH_{eq}	log K_D	pH_{eq}
10	2.34	6.56	3.87	8.08	3.81	7.64	4.61	7.67
20	1.52	6.52	3.26	7.55	4.15	7.38	4.04	7.15
30	2.21	6.64	3.76	7.80	4.58	7.45	4.33	7.36
40	1.67	6.57	4.49	7.58	4.27	7.36	3.78	7.26

Initial nickel concentration 0.01 m*M* in a 0.1*M* NaCl solution. AMPS, AA, and AAA contents of the gels was 2%.

Table III Distribution Coefficient of Zinc on NIPA Gels at Various Temperatures

	NIPA		NIPA–AMPS		NIPA–AA		NIPA–AAA	
T (°C)	log K_D	pH_{eq}	log K_D	pH_{eq}	log K_D	pH_{eq}	log K_D	pH_{eq}
10	2.16	6.48	3.33	7.21	2.35	6.63	2.87	6.75
20	1.71	6.32	2.93	6.90	2.00	6.65	3.25	6.70
30	1.57	6.62	2.79	7.10	2.90	6.84	2.88	6.90
40	1.85	6.67	3.85	7.08	3.03	6.87	3.70	6.88

Initial zinc concentration 0.01 mM in a 0.1M NaCl solution. AMPS, AA, and AAA contents of the gels was 2%.

Ni: NIPA–AAA = NIPA > NIPA–AA = NIPA–AMPS
Cr^{3+}: NIPA–AAA > NIPA–AA > NIPA–AMPS > NIPA
Cr^{6+}: NIPA–AAA > NIPA–AMPS > NIPA–AA = NIPA
NIPA: Ni > Cr^{3+} > Zn > Cr^{6+}
NIPA–AMPS: Cr^{3+} > Ni = Zn > Cr^{6+}
NIPA–AA: Cr^{3+} > Ni = Zn > Cr^{6+}
NIPA–AAA: Cr^{3+} > Ni = Zn > Cr^{6+}.

Effect of AAA Amount in NIPA Gels on Metal Uptake

The amount of AAA in the NIPA gels had no essential effect on the metal-uptake values. If all AAA had been bound to the NIPA gels and the AAA groups were responsible for the metal uptake, the increase in the AAA amount from 2 to 20% would be reflected in a 10-fold increase in the distribution coefficient, which certainly was not the case. Figure 1(b) shows that increase of the AAA amount in the reaction mixture from 2 to 20% increased the ion-exchange capacity only twofold. Therefore, it seems probable that only a fraction of the AAA reacted with the NIPA, as already noted.

Uptake of Ni, Zn, and Cr as a Function of Temperature

No systematic effect of temperature on the metal uptake can be seen (Tables II–IV). The differences of distribution coefficient values, even rather large in some cases, are expected to have been caused by two main factors: variation of the equilibrium pH and chemical inhomogeneity of the polymers.

CONCLUSIONS

AAA-containing NIPA gels take up metal ions more efficiently than do the pure NIPA gel and AA–NIPA and AMPS–NIPA gels. In all the gels, there are free-electron pairs bearing nitrogen groups which can form coordination bonds with transition metals. In addition, sulfonic acid groups in AMPS gels and carboxylic acid groups in AA and AAA gels can take up metal ions by ion exchange. It is possible that in AAA gels both these mechanisms take part in the uptake process and a five-ring chelate is formed. In all the gels, the concentrations of acidic groups were rather low and therefore it is probable that the complexing nitrogen atoms were mostly responsible for

Table IV Distribution Coefficient of Chromium(III) on NIPA Gels at Various Temperatures

	NIPA		NIPA–AMPS		NIPA–AA		NIPA–AAA	
T (°C)	log K_D	pH_{eq}	log K_D	pH_{eq}	log K_D	pH_{eq}	log K_D	pH_{eq}
10	4.16	6.11	3.85	6.85	4.10	6.32	3.71	6.75
20	3.43	5.95	—	—	4.03	6.50	—	—
30	3.94	6.25	3.98	7.03	4.13	6.51	3.71	6.73
40	4.08	6.16	3.84	6.97	4.02	6.64	3.43	6.67

Initial chromium concentration 0.01 mM in a 0.1M NaCl solution. AMPS, AA, and AAA contents of the gels was 2%.

the metal uptake. Increasing the concentration of the acid group in the reaction probably did not increase its concentration in the gel product in a corresponding manner. Collapse of the NIPA gels at the critical temperature has no effect on their ion-exchange behavior. The gels studied in this article were heterogeneous in nature; corresponding homogeneous gels may behave in a different manner with respect to temperature.

REFERENCES

1. S. H. Gehrke, *Adv. Polym. Sci.,* **110,** 81 (1993).
2. F. M. Winnik, *Macromolecules,* **23,** 233 (1990).
3. G. Chen and A. S. Hoffman, *Macromol. Rapid Commun.,* **16,** 175 (1995).
4. E. Vesterinen, H. Tenhu, and A. Dobrodumov, *Polymer,* **35,** 4852 (1994).
5. M. Shibayama and T. Tanaka, *Adv. Polym. Sci.,* **109,** 1 (1993).
6. Q. Yan and A. S. Hoffman, *Polymer,* **36,** 887 (1995).
7. E. Vesterinen, A. Dobrodumov, and H. Tenhu, *Macromolecules,* **30,** 1311 (1997).
8. Y. Deng and R. Pelton, *Macromolecules,* **28,** 4617 (1995).
9. S. Masuda, T. Kobayashi, T. Tomida, T. Inoue, M. Tanaka, and Y. Asahi, *Polymer,* **34,** 4562 (1993).
10. R. S. Asquith, K. L. Gardner, and K. W. Yeung, *J. Polym. Sci. Polym. Chem. Ed.,* **16,** 3275 (1978).
11. E. Vesterinen and H. Tenhu, to be published.
12. A. E. Martell, R. M. Smith, and R. J. Motekaitis, *Critically Selected Stability Constants of Metal Complexes, Database, Version 2.0,* Texas A&M University, College Station, TX, 1995.
13. A. E. Martell and R. J. Motekaitis, *Determination and Use of Stability Constants,* VCH, 1988.