Talanta 134 (2015) 538–545

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Effect of template ion–ligand complex stoichiometry on selectivity of ion-imprinted polymers

Katri Laatikainen [a,*], Dutduan Udomsap [b], Heli Siren [c], Hugues Brisset [b], Tuomo Sainio [a], Catherine Branger [b,**]

[a] Lappeenranta University of Technology, Laboratory of Separation Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland
[b] University of Toulon, MAPIEM, EA 4323, 83957 La Garde, France
[c] University of Helsinki, Department of Chemistry, P.O. Box 55, FI-00014 Helsinki, Finland

## ARTICLE INFO

*Article history:*
Received 25 August 2014
Received in revised form
19 November 2014
Accepted 22 November 2014
Available online 8 December 2014

*Keywords:*
Ion imprinted polymers
2-(Aminomethyl)pyridine
Nickel
Inverse suspension polymerization

## ABSTRACT

In order to highlight the importance of the complex stoichiometry during ion imprinted polymer (IIP) synthesis, we investigated the effect of the complex structure on IIPs selectivity by adjusting the complex stoichiometry before polymerization. 2-(aminomethyl)pyridine monomer (amp) was chosen as a functionalized ligand for nickel(II) ions and a polymerizable vinylbenzyl derivative (Vbamp) was prepared. Complex formation was studied by varying the nickel/Vbamp ratio and recording absorption spectra of the complexes at the polymerization conditions. Using a least-squares minimization scheme, the complex species distribution was successfully established. From these results, it was possible to choose the metal/ligand stoichiometry in the complex (1:1; 1:2 or 1:3) by adjusting the initial metal/ligand ratio. IIPs were then prepared by inverse suspension copolymerization of Vbamp with ethyleneglycol dimethacrylate (EDMA). Highly porous particles with good nickel binding capacity and good Ni/Zn selectivity even at acidic conditions were obtained. Equilibrium uptake of Ni(II) at pH 7 ranged from 0.12 to 0.2 mmol $g^{-1}$ and relative selective coefficient was as high as 260 for the IIP prepared using the $Ni(Vbamp)_2$ complex.

## 1. Introduction

Ion exchange and adsorption are safe and environmentally acceptable technologies for the recovery of valuable metals from either dilute or concentrated aqueous solutions. Industrial applications such as hydrometallurgy require selective, fast, inexpensive and stable ion-exchangers and adsorbents. Furthermore, it is also essential that the separation material can be regenerated using minimum amount of chemicals and energy. One type of ion exchangers and adsorbents are solid chelating separation materials, in which chelating ligands have been attached to solid matrix. These ligands act as donors of electrons and form coordinative bonds with metal cation acting as the central atom in metal chelates and complexes [1]. Thus, metal selectivity of such materials depends mainly on the ligand selectivity [2,3]. Although several commercial chelating materials have been available since the 1970s [4,5], there are still many applications for which sufficiently selective commercial ion exchangers or adsorbents are not found from the markets. Thus, development of new highly selective ion exchangers and adsorbents remains a very challenging topic.

Imprinting technology is one solution for the preparation of separation materials with high selectivity. Synthetic imprinted polymers include in their network selective recognition sites prepared using a template (usually a molecule or an ion) incorporated in the polymer matrix during the polymerization process. Subsequent removal of the template is necessary for recognition to occur in the spaces created by the template [6]. Consequently, imprinted polymers present remarkable recognition properties that can be compared to those of natural biological receptors such as antibodies [7,8], molecularly imprinted polymers (MIPs) and ion-imprinted polymers (IIPs) were described for the first time in the same period, 1972 [9,10] and 1976 [11] respectively, but real development in imprinted materials has taken place more recently [11]. The main difference between MIP and IIP techniques is that MIPs generally interact via hydrogen bonds or van der Waals interactions with the template molecules, whereas IIPs form coordinative complexes with the template metal ions. Consequently, IIPs can be considered as chelating resins with improved selectivity due to the introduction of an imprinting effect during their preparation.

Four approaches have been used for the preparation of IIPs; copolymerization of a ligand carrying a polymerizable functionality,

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[*] Corresponding author. Tel.: +358 401823138.
[**] Corresponding author. Tel.: +33 494146729.
*E-mail addresses:* Katri.Laatikainen@lut.fi (K. Laatikainen), branger@univ-tln.fr (C. Branger).

http://dx.doi.org/10.1016/j.talanta.2014.11.050
0039-9140/

trapping of a ligand (without such a functionality), crosslinking of linear polymer chains and surface imprinting (which can involve chemical immobilization or trapping procedure) [12,13]. In all cases, the key step is the formation of the complex between the ligand and the metal ion. The complex can be isolated before polymerization but this requires an additional step in the IIP synthesis. For this reason, it can be more convenient to just mix the ligand and the metal ion to form the complex in the pre-polymerization medium before the polymer formation. Because of its simplicity, absorption spectroscopy is most commonly used to verify the complex structure before polymerization [14–20]. Continuous variation analysis originally introduced by Job [21] and ligand titration are normally used to produce the spectral data. In many cases, however, highly selective chelating ligands form more than one complex with the template metal ion and advanced chemometric methodology is needed to analyze the overlapping spectra. Least-squares (LS) minimization [22] is one of the methods that enable calculation of complex species distribution from the spectral data [23].

The objective of the present study is to investigate the effect of the template–ligand complex structure on IIP selectivity by adjusting the complex distribution before polymerization. For that purpose, absorption spectra were recorded at different metal/ligand ratios and the complex species distributions were obtained by analyzing the spectral data with a least-squares (LS) minimization scheme [22]. From these results, it was possible to choose the metal/ligand stoichiometry in the complex (1:1; 1:2 or 1:3) by simply adjusting the initial metal/ligand ratio in the polymerization mixture. To the best of our knowledge, such a route has never been investigated till now. It offers the advantage to control the complex stoichiometry in a very easy fashion without tedious isolation of the complex. As the complex stoichiometry might influence the selectivity of the binding sites of the IIPs, such an approach is expected to enhance the performance of the prepared IIPs.

Using this strategy, nickel-selective IIPs were prepared with 2-(aminomethyl)pyridine (amp) as the ligand. Amp is known to form complexes with nickel even at mildly acidic conditions [29]. Furthermore, stability constants of different Ni–amp and Zn–amp complexes indicate selective binding of nickel over zinc [30]. Amp was functionalized with a vinylbenzyl group (Vbamp) in order to be used as the functional monomer during the IIPs synthesis via the chemical immobilization route. Other nickel-selective chelating materials have been developed mainly for analytical applications such as selective separation and pre-concentration of nickel from aqueous solutions [24–28] Some of these materials were used to remove nickel from zinc solutions [24,25,28]. Although they had good selectivity, they suffered from low uptake capacity which prevented their use for industrial purpose. The aim of this work is to enhance selectivity while reaching high binding capacity.

The complex formation was therefore studied with Vbamp by varying the Ni(II)/Vbamp ratio and the anion (nitrate or perchlorate). Ni-selective IIP particles were prepared by inverse suspension polymerization with initial Nickel/Vbamp ratios corresponding to 1:1, 1:2 and 1:3 Ni/Vbamp complexes. The effect of this complex stoichiometry on the Ni(II)/Zn(II) selectivity was investigated at pH 4 and 7 in sulfate media. As has been shown in our previous studies, chelating adsorbents are potential also for purification of concentrated $ZnSO_4$ solutions, although only removal of copper has been found useful adsorbent so far [29].

## 2. Experimental

### 2.1. Materials

The chemicals 2-(aminomethyl)pyridine (2-picolylamine, 99%, Sigma-Aldrich), 3-vinylbenzaldehyde (97%, Sigma-Aldrich), $NaBH_4$ (99.99%, Sigma-Aldrich), toluene (99.9%, Sigma-Aldrich), ethanol (99.8%, Fluka), diethyl ether (99.9%, inhibitor free, Sigma-Aldrich), and $MgSO_4$ (99.5%, anhydrous, Sigma-Aldrich) were reagent grade and used without further purification.

Mineral oil (heavy, Sigma-Aldrich), 2,2-azobis(2-methylpropionitrile) (AIBN) (98%, Sigma-Aldrich), methanol (99.9%, Sigma-Aldrich), 2-methoxyethanol (99.9%, Sigma-Aldrich), $Ni(NO_3)_2 \cdot 6H_2O$ (98.5%, Sigma-Aldrich), $Ni(ClO_4)_2 \cdot 6H_2O$ (98%, Sigma-Aldrich), and chloroform (99.9%, Sigma-Aldrich) were reagent grade chemicals and used in the polymerization of non-imprinted and nickel-imprinted polymers. Ethylene glycol dimethacrylate (EDMA) (98%, Acros) used in the polymerization was washed with 10% NaOH (99.9%, Sigma-Aldrich), dried on $MgSO_4$ and distilled to remove inhibitors.

$Zn(NO_3)_2 \cdot 6H_2O$ (98%, Sigma-Aldrich), $ZnSO_4 \cdot 7H_2O$ (99%, Sigma-Aldrich), $NiSO_4 \cdot 6H_2O$ (99%, Fluka), $HNO_3$ (69%, Sigma-Aldrich), $KNO_3$ (99%, Sigma-Aldrich), $Na_2SO_4 \cdot 10H_2O$ (99%, Sigma-Aldrich) were used in binding experiments. Aqueous solutions were prepared, using deionized water (conductivity less than 0.1 $\mu S\ cm^{-1}$).

### 2.2. Instrumentation

$^1H$ and $^{13}C$ NMR spectra were obtained using a Bruker AVANCE 400 MHz Ultrashield spectrometer using DMSO-$d_6$ as solvent.

BET surface area, BJH pore volume and pore size were measured using $N_2$ adsorption (Micromeritics Gemini V). Particles were analyzed using scanning electron microscopy (SEM, JEOL JSM-5800).

The absorption spectra of the Ni–Vbamp complexes were measured at 25 and 80 °C with UV–vis spectrophotometers (Agilent 8453, Jasco V670) equipped with a thermostated cuvette holder. Quartz cuvette with a light path of 1 cm was used. The concentrations of the sample solutions are estimated to be correct within 2%. The accuracy of the spectra was tested by repeating a measurement 4 times over a period of hours. The average absolute difference in the wavelength range 400–1000 nm was 0.001 absorbance unit. Stability constants were estimated using the HypSpec program based on least-squares minimization scheme [22]. Detailed description of the calculations can be found from Refs. [22,23].

FTIR spectra were obtained using the standard KBr pellet method (Perkin–Elmer Frontier FTIR). Number of scans was 64 and resolution was 4 $cm^{-1}$.

Total amount of N, C and H in the polymers was determined by elemental analysis according to DIN 51732. Metal ion concentrations were determined by plasma emission spectroscopy (Iris Intrepid II XDL ICP-AES). All samples were analyzed at least twice and the duplicate determinations agreed within 5%.

### 2.3. Synthesis of 1-(pyridin-2-yl)-N-(3-vinylbenzyl)methanamine (Vbamp)

1-(Pyridin-2-yl)-N-(3-vinylbenzyl)methanamine (Vbamp) was synthesized according to well-known Schiff base reaction and reduction of the corresponding imine. 1.0 g of 3-vinylbenzaldehyde (7.6 mmol) and 0.98 g of 2-(aminomethyl)pyridine (9.1 mmol) were dissolved in 40 mL of toluene. The solution was refluxed for 30 min and water was removed using a Dean-Stark apparatus. Remaining toluene was evaporated and the crude product was dissolved in 200 mL of ethanol and dried with anhydrous $MgSO_4$. After removal of ethanol, a light yellow viscous liquid was obtained. This crude imine compound ((1-pyridin-2-yl)-N-(3-vinylbenzylidene)methanamine) was reduced without further purification. It was dissolved in 200 mL of dried ethanol. 2.86 g of $NaBH_4$ (75.6 mmol) was added and the reaction mixture was refluxed for 2.5 h under nitrogen. 15 mL of water was then added and the mixture was left at 4 °C overnight. The precipitate was filtered off and the solution was evaporated to 25 mL before addition of 25 mL of diethyl ether. The mixed solution was washed four times with water and the organic phase was dried with

$MgSO_4$ before evaporating the solvent. Vbamp was purified by silica gel chromatography using ethyl acetate as eluent. 2.0 g (8.9 mmol) of light yellow viscous liquid was obtained (yield=51.8%). $^1$H NMR (DMSO-$d_6$; δ in ppm): 8.49 (d, 1H, position 3 of pyridinyl), 7.74 (dt, 1H, position 5 of pyridinyl), 7.45(d and s, 2H, positions 6 of pyridinyl and 4 of benzyl), 7.34-7.21 (m, 4H, positions 4 of pyridinyl and 2,4 and 6 of benzyl), 6.73 (dd, 1H, CH of vinyl), 5.82 (dd, 1H, $CH_2$ of vinyl, cis to benzyl), 5.25 (dd, 1H, $CH_2$ of vinyl, trans to benzyl), 3.79 (s, 1H, $CH_2$ between NH and pyridinyl), 3.73 (s, 1H, $CH_2$ between NH and benzyl).

### 2.4. *Complexation of nickel with 1-(pyridin-2-yl)-N-(3-vinylbenzyl) methanamine*

Complexation between nickel and Vbamp monomer was studied in methanol and 2-methoxyethanol mixture (50:50, v/v) using $Ni(NO_3)_2 \cdot 6H_2O$ or $Ni(ClO_4)_2 \cdot 6H_2O$ salts as the nickel source. The combined concentration of the nickel and Vbamp was kept constant but the mole ratio of the ligand and metal was varied. Typically 14 spectra at different mole ratios were recorded. The spectra were recorded at 25 and 80 °C. The complex distribution at equilibrium was calculated using commercial program HypSpec [22] based on least-squares (LS) minimization scheme.

### 2.5. *Synthesis of ion imprinted and non-imprinted polymers*

The Ni/Vbamp complex was prepared by dissolving Vbamp and $Ni(NO_3)_2.6H_2O$ or $Ni(ClO_4)_2 \cdot 6H_2O$ in 10 mL of a mixture of methanol and 2-methoxyethanol (50:50, v/v) using Ni/Vbamp molar ratios as described in Table 1.

The Ni/Vbamp complex was first formed by stirring the solution of Vbamp and nickel salt for 1 h under nitrogen. Then 4.4 mL of EDMA (23.5 mmol) and 0.1 g of AIBN (0.65 mmol) were added. 80 mL of mineral oil was mixed in a 500 mL round-bottomed flask with nitrogen purging and the organic phase was added quickly. Polymerization was carried out by refluxing at 80 °C for 4 h with stirring rate of 200 rpm under nitrogen. Formed polymer particles were filtered, washed with 50 mL of chloroform and extracted in Soxhlet equipment for 24 h with a chloroform–acetone mixture (1:1). Finally, the particles were dried under vacuum at 25 °C for 24 h. Non-imprinted polymers (NIPs) were prepared under identical conditions except for omission of the nickel template. The yields for the NIP and IIPs were as follows: NIP=76%, IIPNO3 2:1=83%, IIPNO3 1:2=97%, IIPNO3 1:4=68%, and IIPClO4 1:2=91%.

Leaching of the template was studied by treating 0.01 g of polymers with 10 mL of a $H_2SO_4$ solution (0.5, 1, 3 or 5 mol $L^{-1}$) in plastic tubes. The tubes were shaken at room temperature for 2 h and analyzed by scanning electron microscopy coupled with X-ray fluorescence (SEM, JEOL JSM-5800 with an X-ray fluorescence detector from Thermo Fisher Scientific Inc.) by measuring nickel in the polymers at least from 5 particles and from 10 measuring points in each particle. Leaching was also monitored by FTIR measurements after treatment with 1 M NaOH.

**Table 1**
Polymer preparation conditions.

| Polymer | Nickel source | $n_{Ni}$, mmol | $n_{Vbamp}$, mmol | Ni/Vbamp, mole ratio |
|---|---|---|---|---|
| NIP | – | – | 2.3 | – |
| IIPNO3 2:1 | $Ni(NO_3)_2 \cdot 6H_2O$ | 4.6 | 2.3 | 2 |
| IIPNO3 1:2 | $Ni(NO_3)_2 \cdot 6H_2O$ | 1.2 | 2.3 | 0.5 |
| IIPNO3 1:4 | $Ni(NO_3)_2 \cdot 6H_2O$ | 0.6 | 2.3 | 0.25 |
| IIPClO4 1:2 | $Ni(ClO_4)_2 \cdot 6H_2O$ | 1.2 | 2.3 | 0.5 |

### 2.6. *Batch sorption measurements*

After Soxhlet extraction and drying, 0.01 g of the unleached polymers were treated with 10 mL 5 M $H_2SO_4$ during 2 h in a shaker in order to remove the nickel template (leading to what is later referred to as leached polymers).

Before batch sorption measurements, polymers were subjected to an acid–base pretreatment in a glass column. The polymer particles were treated consecutively with 1 BV of 5 M $H_2SO_4$, 5 BV of water, 5 BV of 1 M NaOH and 5 BV of water (BV is the volume of the bed formed by the particles). The cycle was repeated three times and finally the polymers were rinsed copiously with water and then dried under vacuum at 25 °C for 24 h.

Acid titration curves of NIP and IIPs were measured in nitrate and sulfate solutions in order to determine the nitrogen contents of these polymers. All measurements were made at 25 °C and at a constant supporting ionic strength $I_s$=0.1 mol $L^{-1}$ adjusted with $KNO_3$ or $Na_2SO_4$. A constant amount of polymer (0.01 g) was weighed in glass vials containing different concentrations of nitric or sulfuric acid. The liquid volume of all samples was 10 mL. The samples were shaken at room temperature for at least 2 days and then kept several hours at 25 °C before measurement of the equilibrium pH. All titrations were repeated at least twice and the difference between duplicate data points was less than 3%.

Sorption isotherms of nickel from pure solutions and nickel and zinc from their mixtures in NIP and IIPs were measured at room temperature ($T$=20–22 °C) at pH 4 and 7 (±0.1). 0.01 g of polymer was weighed in plastic tubes containing the metals in nitrate or sulfate media. The liquid volume of all samples was 10 mL. pH of the samples was kept constant by intermittent addition of sulfuric acid or sodium hydroxide. The bottles were shaken at room temperature for 7 days and then the metals were leached out with 5 M $H_2SO_4$ from the polymers. The bound amounts were calculated from the analyses of the desorption solution. The values are given per unit weight of dry base-form adsorbent.

Selectivity coefficient, $K_{Zn}^{Ni}$, is calculated according to Eq. (1) [31], in which $q$ and $c$ are the metal uptake (mmol $g^{-1}$) and concentration (mol $L^{-1}$), respectively.

$$K_{Zn}^{Ni} = \frac{q_{Ni} c_{Zn}}{c_{Ni} q_{Zn}} \tag{1}$$

The effect of ion imprinting on selectivity was studied with relative selectivity coefficient, $k'$, as defined in Eq. (2) [32]. $(K_{Zn}^{Ni})_{IIP}$ is the selectivity coefficient of imprinted polymer and $(K_{Zn}^{Ni})_{NIP}$ is the selectivity coefficient of non-imprinted polymer.

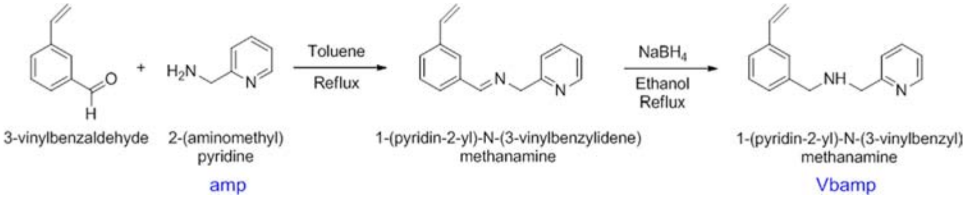
$$k' = \frac{(K_{Zn}^{Ni})_{IIP}}{(K_{Zn}^{Ni})_{NIP}}. \tag{2}$$

## 3. Results and discussion

### 3.1. *Complexation of nickel with Vbamp*

The ligand 2-(aminomethyl)pyridine (amp) was modified into a polymerizable monomer in order to be covalently bound in the polymer matrix. For that purpose, Vbamp (Vinylbenzyl-amp) was prepared in two steps according to Scheme 1. Despite many attempts, pure imine intermediate compound (1-(pyridin-2-yl)-N-(3-vinylbenzylidene)methanamine) could not be isolated. However, its formation was evidenced by $^{13}$C NMR (DMSO-$d_6$; δ in ppm); 162.87 (C=N of imine), 66.07 ($CH_2$ between N and pyridinyl). Therefore, the crude compound was successfully used in the reduction step to give Vbamp.

The structure and species distribution of the Ni–Vbamp complexes were investigated in order to control the stoichiometry of



**Scheme 1.** Synthesis of Vbamp.

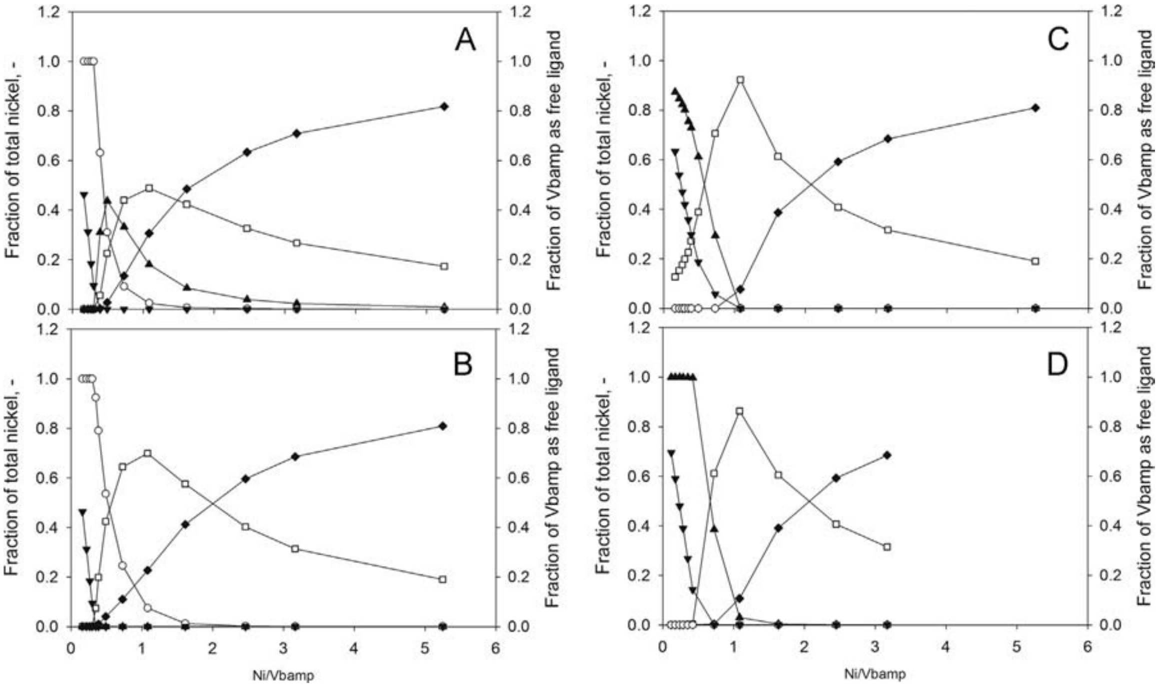


**Fig. 1.** Complex distributions calculated from UV–vis spectra using HypSepc program[22] between nickel and Vbamp at different Ni/Vbamp ratios using $Ni(NO_3)_2 \cdot 6H_2O$ (A and B) or $Ni(ClO_4)_2 \cdot 6H_2O$ (C and D) as the nickel source at 25 °C (A and C) and 80 °C (B and D). Free nickel = diamonds, Ni(Vbamp) = squares, $Ni(Vbamp)_2$ = triangles up, Ni $(Vbamp)_3$ = circles, free Vbamp = triangles down. Solvent mixture = methanol/2-methoxyethanol (50:50 v/v).

the complexes introduced in the IIPs. Distribution of the complex species was determined by analyzing the absorption spectra recorded in a solvent mixture of methanol/2-methoxyethanol (50:50, v/v) (solvent of polymerization), at 25 °C and 80 °C (temperature of polymerization). The Ni/Vbamp ratio was varied from 0.1 to 5.3 using $Ni(NO_3)_2 \cdot 6H_2O$ or $Ni(ClO_4)_2 \cdot 6H_2O$ as the nickel source. The complex distribution curves were calculated using HypSpec program [22].

The influence of Ni/Vbamp mole ratio on the distribution of nickel and Vbamp in complexes of different stoichiometry is displayed in Fig. 1. The results are given as mole fraction of total nickel present as free nickel and in the complexes and as mole fraction of Vbamp present as uncomplexed free ligand.

The data measured with nitrate anion are shown in Fig. 1 (A) and (B), and it is clear that part of the Vbamp remains in the solution and does not take part in the complexation reactions, when the Ni/Vbamp ratio is below 0.5. When free Vbamp is not anymore present in the solution (Ni/Vbamp ratio above 0.5), free nickel starts to be present in the solution. The higher is the Ni/Vbamp ratio, the higher is the amount of free nickel in the solution. In the case of perchlorate anion, the situation is similar, except that free Vbamp remains in solution at Ni/Vbamp ratios below 1 whereas above Ni/Vbamp ratio 1, free nickel appears in the solution. In practice, only the amount of free Vbamp which does not take part to the complexation reaction is important for the polymer properties, because the uncomplexed nickel ions are not incorporated in the polymer. Uncomplexed Vbamp will not produce selective imprinted sites of IIP but will create complexing sites analogous to those found in the non-imprinted polymer.

Temperature affects significantly the complex formation between nickel and Vbamp. Moreover, when temperature was increased from 25 to 80 °C, some precipitates were formed. They were isolated and analyzed by FTIR. They were identified as $[Ni(Vbamp)_2]^{2+}$ complex in nitrate medium and $[Ni(Vbamp)_3]^{2+}$ complex in perchlorate medium in accordance with the literature data [33,34]. It seems therefore that solubility of the 1:2 complex in the nitrate system and the 1:3 complex in perchlorate system in methanol and 2-methoxyethanol solvent mixture (50:50 v/v) is very low. Reasons for this behavior observed also in the precipitation of 1:2 and 1:3 Ni–amp complexes are, however, unknown [33–35]. Calculation of the distribution curves was successful only by assuming that the 1:2 complex in the nitrate case and the 1:3 complex in the perchlorate case precipitated completely from the system (Fig. 1(B) and (D)). The stability constants of $[Ni(Vbamp)]^{2+}$, $[Ni(Vbamp)_2]^{2+}$, and $[Ni(Vbamp)_3]^{2+}$, in nitrate and perchlorate media, used in the calculations (Fig. 1) (in methanol and 2-methoxyethanol (50:50, v/v) solvent mixture at 25 and 80 °C) are shown in Table 2.

According to these results, it appears that the stoichiometry of the complex(es) formed in the polymerization medium at the polymerization temperature can be simply controlled by the initial Ni/Vbamp ratio. For instance, the 1:3 complex can be selectively formed in nitrate medium in a solvent mixture that is suitable for IIP synthesis by using a four-fold excess of Vbamp with respect to nickel (Fig. 1(B)).

**Table 2**
Stability constants of $[Ni(Vbamp)]^{2+}$, $[Ni(Vbamp)_2]^{2+}$, and $[Ni(Vbamp)_3]^{2+}$ in nitrate and perchlorate media in methanol and 2-methoxyethanol (50:50, v/v) solvent mixture and at 25 and 80 °C.

| Anion | Temperature | | | | | |
|---|---|---|---|---|---|---|
| | 25 °C | | | 80 °C | | |
| | log $\beta_1$ | log $\beta_2$ | log $\beta_3$ | log $\beta_1$ | log $\beta_2$ | log $\beta_3$ |
| $NO_3^-$ | 7.226 | 13.816 | 19.970 | 6.469 | – | 17.459 |
| $ClO_4^-$ | 7.098 | 9.196 | – | 7.058 | 11.746 | – |

### 3.2. Polymer synthesis and characterization

Non-imprinted polymers (NIP) and ion-imprinted polymers (IIP) were prepared by polymerizing Vbamp in the absence or presence of nickel salt, respectively, with ethylene glycol dimethacrylate (EDMA) as the cross-linker. In order to obtain regular polymer particles, inverse suspension polymerization was applied using a previously published procedure [36]. Mineral oil was used as the continuous non-polar phase and methanol/2-methoxyethanol (50:50 v/v) as the polar porogen phase.

Four different IIPs were prepared by varying the Ni/Vbamp ratio and the anion (Table 2) to get different complex stoichiometries in the IIPs and to study their effect on the Ni/Zn selectivity. According to the complex distributions shown in Fig. 1, all Vbamp complexed with nickel to form predominantly the 1:1 complex, when the IIP was prepared in nitrate medium with Ni/Vbamp mole ratio of 2:1 (abbreviated here as IIPNO3 2:1). In the case of IIPNO3 1:2, the ligand and the metal ion form a mixture containing mainly the 1:1 (42%) and 1:3 (54%) complexes. For IIPNO3 1:4, Vbamp reacts with nickel forming only the 1:3 complex. However, there is still about 20% Vbamp which has not taken part in the complexation reaction. In the case of IIPClO4 1:2 polymer, 10% of the Vbamp remains free and the remaining Vbamp reacts with nickel forming 80% of the 1:2 complex and 20% of the 1:1 complex. The complex distributions in Fig. 1 are given as mole fraction of total nickel present as free nickel and in the complexes and as mole fraction of Vbamp present as uncomplexed free ligand.

FTIR analyses were made on the NIP and the IIPs before and after leaching (Figs. 2 and 3). The spectrum of the Vbamp monomer (Fig. 2(B)) reveals stretching bands of C=C (from vinyl, benzene and pyridine) and C=N bands of pyridine at 1575, 1593, and 1630 cm$^{-1}$. These bands can be found in the non-imprinted polymer (Fig. 2(A)) with a slight shift of the 1630 band to 1638 cm$^{-1}$, probably due to the presence of some unreacted vinyl groups of EDMA.

According to Bruda et al. [33], the C=N stretching band of amp shifts from 1593 cm$^{-1}$ to 1610 cm$^{-1}$ when complexed with nickel. A similar observation was done on the spectra of IIPs before leaching nickel out of the polymers (Fig. 2(A)); the C=N band present at 1593 cm$^{-1}$ in the NIP moved to 1610 cm$^{-1}$ in the IIPs spectra. In the case of IIPNO3 1:4 polymer, the band at 1593 cm$^{-1}$ was also observed because substantial amount of free Vbamp was present in the polymerization medium for this polymer composition (Table 3).

In the case of ion-imprinted polymers, leaching of the template ion can be difficult because of strong interactions between the ion and the polymer matrix via the ligand moiety. Leaching of nickel from the polymers with 0.5, 1, 3, and 5 M $H_2SO_4$ was studied by analyzing the leached materials using scanning electron microscopy with an X-ray fluorescence detector. Broken particles were used in order to obtain the nickel content inside the particles. According to the results, complete leaching of nickel out of the polymers required acid concentration 5 mol L$^{-1}$. This result is in accordance with a previous study made with a commercial chelating adsorbent containing amp as functional group [29]. The results were confirmed by analyzing the FTIR spectra of the IIPs (Fig. 3) after acid treatment with 5 M $H_2SO_4$ (and after a NaOH treatment at similar conditions as in Fig. 2). These spectra were very similar to that of the NIP. The shift of the C=N band from 1595 to 1611 cm$^{-1}$ was no longer observed, showing the disruption of the coordinative bond between the nitrogen atom and nickel, and therefore proving the efficiency of the leaching treatment.

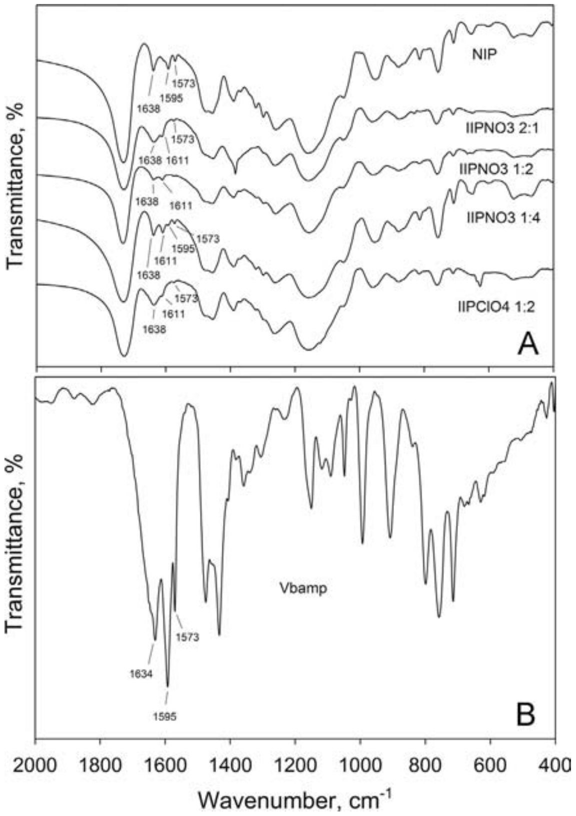


**Fig. 2.** FTIR spectra (KBr pellets) of unleached IIPNO3 2:1, IIPNO3 1:2, IIPNO3 1:4, and IIPClO4 1:2 polymers (A) and Vbamp (B).

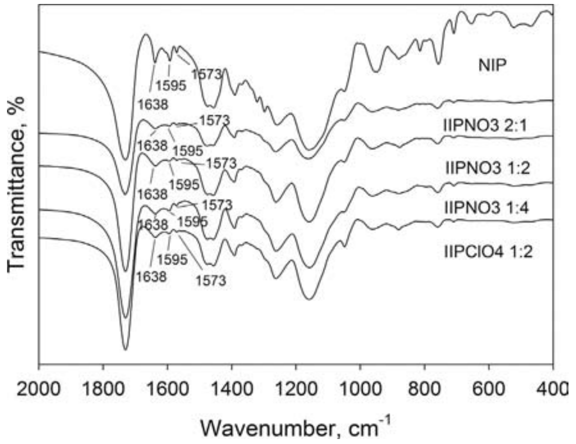


**Fig. 3.** FTIR spectra (KBr pellets) of IIPNO3 2:1, IIPNO3 1:2, IIPNO3 1:4, and IIPClO4 1:2 polymers after leaching and base treatment.

Nitrogen adsorption measurements were performed on the IIPs and NIP leading to the determination of BET surface areas, pore volumes and average pore sizes (Table 4). For any application requiring materials with high binding capacities, large surface area, pore volume and pore size are needed. According to results

**Table 3**
Polymer synthesis conditions and complex distributions calculated from UV–vis spectra at 80 °C in methanol/2-methoxy-ethanol (50:50 v/v) solvent mixture using HypSec program [22].

| Polymer | Initial experimental ratio Ni/Vbamp | Fraction of total nickel (calculated) | | | | Fraction of total Vbamp (calculated) |
|---|---|---|---|---|---|---|
| | | Free (Ni) | 1:1 Complex | 1:2 Complex | 1:3 Complex | Free (Vbamp) |
| NIP | 0 | – | – | – | – | – |
| IIPNO3 2:1 | 2 | 0.5 | 0.5 | 0 | 0 | 0 |
| IIPNO3 1:2 | 0.5 | 0.04 | 0.42 | 0 | 0.54 | 0 |
| IIPNO3 1:4 | 0.25 | 0 | 0 | 0 | 1 | 0.2 |
| IIPClO4 1:2 | 0.5 | 0 | 0.18 | 0.82 | 0 | 0.1 |

**Table 4**
Properties of NIP, IIPNO3 2:1, IIPNO3 1:2, IIPNO3 1:4, and IIPClO4 1:2.

| | **NIP** | **IIPNO3 2:1** | **IIPNO3 1:2** | **IIPNO3 1:4** | **IIPClO4 1:2** |
|---|---|---|---|---|---|
| Initial Ni/AMP ratio (mol/mol) | 0 | 2.0 | 0.5 | 0.25 | 0.5 |
| $S_{\mathrm{BET,\ unleached}}$, $m^2/g$ | 202 | 215 | 242 | 135 | 175 |
| $S_{\mathrm{BET,\ leached}}$, $m^2/g$ | – | 103 | 207 | 77 | 138 |
| Average pore diameter$_{\mathrm{unleached}}$, nm | 11.9 | 8.8 | 4.5 | 8.5 | 11.8 |
| Average pore diameter$_{\mathrm{leached}}$, nm | – | 10.6 | 7.8 | 8.5 | 10.5 |
| Total porous volume$_{\mathrm{unleached}}$, $cm^3/g$ | 0.48 | 0.29 | 0.11 | 0.21 | 0.28 |
| Total porous volume$_{\mathrm{leached}}$, $cm^3/g$ | – | 0.18 | 0.49 | 0.12 | 0.22 |
| Nickel content$_{\mathrm{theoretical}}$, mmol/g | – | 0.37 | 0.24 | 0.12 | 0.24 |
| Nickel content, mmol/g[a] | – | 0.38 | 0.19 | 0.10 | 0.18 |
| Nitrogen content$_{\mathrm{unleached}}$, mmol/g[b] | 0.81 | 1.41 | 1.13 | 0.97 | 1.1 |
| Nitrogen content$_{\mathrm{leached}}$, mmol/g[b] | 0.69 | 0.72 | 0.66 | 0.71 | 0.69 |
| Nitrogen content$_{\mathrm{acid\ titration}}$, mmol/g[c] | 0.65 | 0.61 | 0.60 | nd. | 0.61 |
| Accessibility (%)[d] | 94 | 84 | 91 | – | 88 |
| Nickel binding capacity at pH 4, mmol/g[e] | 0.08 | 0.12 | 0.10 | 0.08 | 0.10 |
| Nickel binding capacity at pH 7, mmol/g[e] | 0.11 | 0.20 | 0.16 | 0.11 | 0.16 |

nd – not determined.

[a] Determined on the leaching solutions of IIPs using ICP-AES.

[b] According to elemental analysis.

[c] Determined by acid titration on leached polymers.

[d] Calculated as the ratio between the nitrogen amount measured by acid titration and the nitrogen content determined by elemental analysis.

[e] Determined from binding isotherms (Fig. 4).

shown in Table 4, all synthesized polymers meet this requirement. However, significant differences can be observed in the values measured for unleached and leached polymers. This is quite unexpected [37] and might be due to acid–base pretreatment which was made before the leached materials were analyzed. Comparison of the leached IIPs with NIP shows that NIP has higher surface area, pore volume and pore diameters. This might be explained by the formation of bridges between walls of the pores due to the nickel complex in IIPs leading to a decrease of pore size and surface area [36].

Theoretical nickel contents can be compared with nickel contents in the IIPs determined by ICP-AES in acid leaching solutions (Table 4). Determined nickel contents were analyzed after Soxhlet extraction and acid leaching. Theoretical nickel contents of IIPNO3 2:1, and IIPNO3 1:4 polymers agree well with the values determined experimentally. In the cases of IIPNO3 1:2 and IIPClO4 1:2, the difference between theoretical and analyzed contents is more significant. For those polymers, about 20% of the nickel–Vbamp complexes may have not polymerized and unpolymerized material has been removed during Soxhlet extraction and acid leaching.

The nitrogen contents of the NIP and IIPs were analyzed by elemental analysis for unleached and leached polymers (Table 4). Unleached polymers were analyzed after Soxhlet extraction and leached polymers were analyzed after Soxhlet extraction and acid leaching. Theoretical nitrogen contents of NIP and IIPs (without taking nickel into account) are calculated to be 0.91 mmol $g^{-1}$ for all polymers. These values are 20% higher than those measured by elemental analysis on NIP and leached IIPs. Consequently, about 80% of Vbamp was incorporated in the polymer network and 20% of unpolymerized material was removed in Soxhlet extraction and acid leaching. This is in agreement with the results obtained from nickel content calculations. Furthermore, nitrogen contents before acid leaching are higher than those measured after leaching. For IIPNO3 resins, this is due to the presence of nitrate counter-ion in the unleached polymers. For NIP and IIPClO4 1:2, such a decrease can only be explained by a leaching of some non-polymerized Vbamp monomers which were not removed by Soxhlet extraction. The nitrogen contents of leached IIPs were also measured by acid titration method using sulfuric acid and nitric acid without significant difference between sulfate and nitrate anion in the results. Accessibility (expressed in %) was calculated as being the ratio between the nitrogen content measured by acid titration and by elemental analysis for leached samples [38]. Accessibility values are very high indicating that the ligands are easy to reach by nickel ions present in aqueous solutions.

### 3.3. *Sorption of nickel/zinc salts*

Nickel binding properties were studied using NIP and leached IIPs at pH 4 and 7 in sulfate and nitrate solutions. As no significant effect of the anion on the nickel uptake was observed, nickel binding isotherms are shown only for sulfate solutions (Fig. 4). All isotherms have similar shapes independent of pH but the maximum binding capacities of polymers are different and depend on the solution pH (Table 4). Typically, IIPs suffer from low uptake capacity [26,27], while the nickel binding capacities determined in the present study at pH 7 are about one order of magnitude higher, probably because of the high ligand accessibility. However, values similar to those measured here have also been reported in the literature [24,25].

Lowest uptake capacities of nickel were reached in the case of NIP and IIPNO3 1:4 at both pH values. Highest nickel capacity was found for the IIPNO3 2:1 polymer, but at pH 4 there was no significant difference between IIPNO3 2:1, IIPNO3 1:2 and IIPClO4 1:2 polymers. Imprinting factors (defined as the ratio of the IIP maximum binding capacity divided by that of the NIP) at pH 4 for the IIPNO3 2:1, IIPNO3 1:2, IIPNO3 1:4 and IIPClO4 1:2 are 1.5, 1.3, 1.0 and 1.3, respectively. At pH 7 a slight increase of imprinting factors (1.8, 1.5, 1.1 and 1.7, respectively) is observed. Because the amount of Vbamp was the same in NIP and IIPs before complex formation and polymerization, the explanation must be found from the complex structures in the polymers before polymerization. In the IIPNO3 2:1 polymer, only 1:1 complex was present before polymerization. Thus, it seems that when there is only 1:1 complex in the polymer structure, it has a positive effect at neutral conditions on the nickel capacity as compared with other complex distributions studied here. At pH 4, where also competition between acid and nickel is important, this effect cannot be seen from the isotherm results so clearly. In the case of IIPNO3 1:4, only the 1:3 complex is found in the solution before polymerization

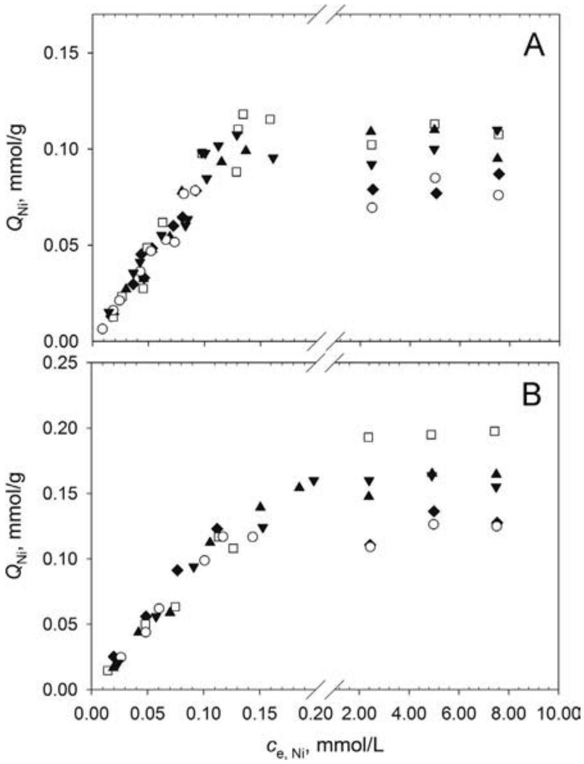


**Fig. 4.** Ni isotherms of NIP (diamonds), IIPNO3 2:1 (squares), IIPNO3 1:2 (triangles up), IIPNO3 1:4 (circles), and IIPClO4 1:2 (triangles down) at pH 4 (A) and pH 7 (B) at room temperature with ionic strength 0.1 M $Na_2SO_4$.

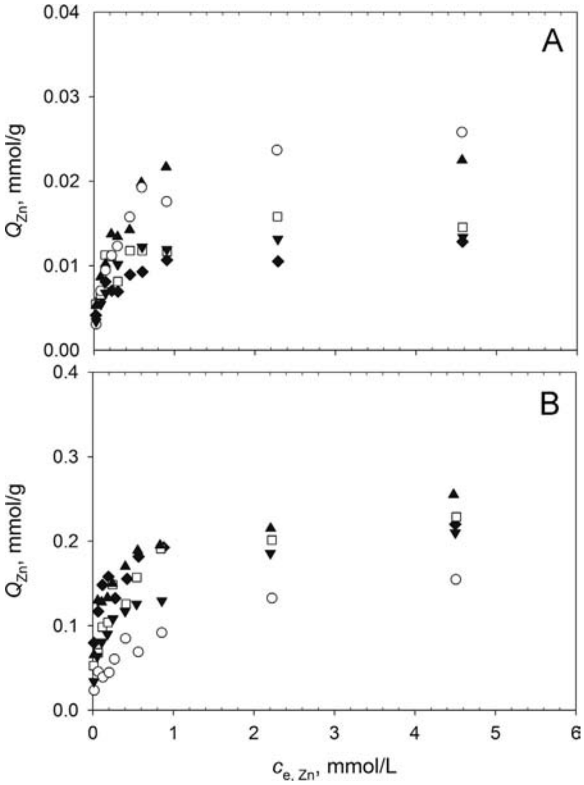


**Fig. 5.** Zn isotherms of NIP (diamonds), IIPNO3 2:1 (squares), IIPNO3 1:2 (triangles up), IIPNO3 1:4 (circles), and IIPClO4 1:2 (triangles down) at pH 4 (A) and pH 7 (B) at room temperature in ionic strength 0.1 M $Na_2SO_4$.

(Table 3) but at the same time, about 20% of the Vbamp monomer remains free. This appears to make the nickel binding properties similar as in NIP.

As mentioned in Section 3.2, theoretical nickel capacities of IIPs agree well with the actual nickel amounts analyzed after Soxhlet extraction and acid leaching. Similar trend can be noticed by comparing the measured maximum nickel capacities (Table 4) with the theoretical capacities. At pH 7, the values agree quite well except for IIPNO3 2:1. The values measured at pH 4 are, however, substantially lower due to the competition by the acid.

In this study, the synthesized polymers were characterized in terms of nickel/zinc selectivity and therefore also zinc isotherms were needed. Measurements were again done at pH 4 and 7 and the results are shown in Fig. 5.

IIPNO3 1:2 and IIPNO3 1:4 have the highest zinc capacity at pH 4 (Fig. 5(A)), while the values of NIP, IIPNO3 2:1, IIPNO3 1:4 and IIPClO4 1:2 are almost 50% lower. At pH 7 (Fig. 5(B)) all zinc capacities are higher and it is noteworthy that IIPNO3 1:4 has significantly lower zinc capacity than NIP and other IIPs. The very low zinc uptake observed for all materials at pH 4 is in accordance with our previous results obtained with a commercial amp-functionalized chelating adsorbent [29].

### 3.4. *Ni/Zn selectivity*

The effect of the Ni–Vbamp complex structure on the selectivity of the IIPs was investigated in the case of the competitive uptake of nickel and zinc. According to the results shown in Table 5, selectivity coefficients (defined in Eq. (1)) increase when initial zinc concentration is increasing from 0.3 to 30 mmol $L^{-1}$. Moreover, pH has dramatic effect on the selectivity. In Table 5 relative selectivity coefficients giving information about the effect of ion imprinting to the selectivity of the polymers are also shown.

The selectivity experiments were done in sulfate solutions at pH values 4 and 7. At pH 7, selectivity is identical for NIP and IIPs. At pH 4, the situation is completely different and an imprinting effect can be observed. According to Table 5, IIPClO4 1:2 has highest Ni/Zn selectivity at all initial zinc concentrations. At the highest zinc concentration (30 mmol/L), $K_{Zn}^{Ni}=262$. This value is 3–7 times higher than values reported in the literature [24,25,28]. It seems that when the 1:2 complex is dominant before polymerization (80% of nickel exists as the $[Ni(Vbamp)_2]^{2+}$ complex, see Table 3), it significantly improves the selectivity of the imprinted polymer. On the other hand, the amount of free Vbamp in the polymerization mixture impairs the selectivity properties. In the case of IIPNO3 1:4 polymer, only the 1:3 complex is found in the solution before polymerization. However, there is also 20% free Vbamp monomer in the solution, which makes IIPNO3 1:4 polymer similar in selectivity properties as NIP. In the case of IIPClO4 1:2 there was only 10% free Vbamp in the solution before polymerization and the free ligand thus has less influence on the selectivity.

Higher selectivity coefficients observed at pH 4 are most probably due to competition by the acid. As discussed in Section 3.3, nickel adsorption is about 2 times lower at pH 4 than at pH 7 whereas the adsorbed amount of zinc decreases to one tenth. Furthermore, as can be seen from Table 5, the selectivity coefficients increase with increasing initial zinc concentrations. This can be explained with different shapes of binding isotherms of nickel and zinc. Consequently, the ratio of the metals in the adsorbent is not directly proportional to the concentration ratio in the solution.

## 4. Conclusions

In this study, the effect of template complex structure on selectivity of ion-imprinted polymers was investigated. According to the results obtained, the relative amounts of complexes with

**Table 5**
Selectivity coefficients and relative selectivity coefficients of the NIP and IIPS with nickel and zinc concentrations 0.3 mmol/L nickel and 0.3, 3, and 30 mmol/L zinc at pH 4 and 7 at room temperature in ionic strength 0.1 M $Na_2SO_4$.

| Materials | $c^0_{Ni}$, mmol/L | $c^0_{Zn}$, mmol/L | pH | $K^{Ni}_{Zn}$ | $k'$ |
|---|---|---|---|---|---|
| NIP | 0.3 | 0.3 | 4 | 7 | – |
| IIPNO3 2:1 | 0.3 | 0.3 | 4 | 4 | 0.6 |
| IIPNO3 1:2 | 0.3 | 0.3 | 4 | 7 | 1.0 |
| IIPNO3 1:4 | 0.3 | 0.3 | 4 | 5 | 0.7 |
| IIPClO4 1:2 | 0.3 | 0.3 | 4 | 12 | 1.6 |
| NIP | 0.3 | 3 | 4 | 16 | – |
| IIPNO3 2:1 | 0.3 | 3 | 4 | 23 | 1.4 |
| IIPNO3 1:2 | 0.3 | 3 | 4 | 36 | 2.2 |
| IIPNO3 1:4 | 0.3 | 3 | 4 | 9 | 0.5 |
| IIPClO4 1:2 | 0.3 | 3 | 4 | 50 | 3.0 |
| NIP | 0.3 | 30 | 4 | 55 | – |
| IIPNO3 2:1 | 0.3 | 30 | 4 | 59 | 1.1 |
| IIPNO3 1:2 | 0.3 | 30 | 4 | 54 | 1.0 |
| IIPNO3 1:4 | 0.3 | 30 | 4 | 30 | 0.6 |
| IIPClO4 1:2 | 0.3 | 30 | 4 | 262 | 4.8 |
| NIP | 0.3 | 0.3 | 7 | 2 | – |
| IIPNO3 2:1 | 0.3 | 0.3 | 7 | 2 | 0.8 |
| IIPNO3 1:2 | 0.3 | 0.3 | 7 | 2 | 0.9 |
| IIPNO3 1:4 | 0.3 | 0.3 | 7 | 2 | 1.0 |
| IIPClO4 1:2 | 0.3 | 0.3 | 7 | 4 | 1.7 |
| NIP | 0.3 | 3 | 7 | 9 | – |
| IIPNO3 2:1 | 0.3 | 3 | 7 | 3 | 0.3 |
| IIPNO3 1:2 | 0.3 | 3 | 7 | 3 | 0.4 |
| IIPNO3 1:4 | 0.3 | 3 | 7 | 2 | 0.3 |
| IIPClO4 1:2 | 0.3 | 3 | 7 | 7 | 0.7 |
| NIP | 0.3 | 30 | 7 | 33 | – |
| IIPNO3 2:1 | 0.3 | 30 | 7 | 42 | 1.3 |
| IIPNO3 1:2 | 0.3 | 30 | 7 | 32 | 1.0 |
| IIPNO3 1:4 | 0.3 | 30 | 7 | 14 | 0.4 |
| IIPClO4 1:2 | 0.3 | 30 | 7 | 33 | 1.0 |

different stoichiometry depend significantly on the initial Ni/Vbamp ratio, nickel salt anion, and temperature. It was shown that determining the complex distribution before polymerization gives a stronger basis for explaining selectivity and imprinting factors of the imprinted polymers and offers new tools in developing highly selective ion-imprinted polymers. The results obtained indicate that the template complex structure adjusted before polymerization also determines the complex structure in the polymer, and has major effect on selectivity of polymers and also metal capacities of the polymers. The highest Ni/Zn selectivity was reached with the IIPClO4 1:2 polymer, which was polymerized from a mixture containing 20% of nickel as $[Ni(Vbamp)]^{2+}$ and 80% as $[Ni(Vbamp)_2]^{2+}$. Moreover, only 10% of the ligand was uncomplexed. This means that without troublesome isolation reactions and purification steps, it is possible to establish a desired complex structure by adjusting properly the metal/ligand ratio and thus significantly increase the selectivity of the imprinted polymer.

## Acknowledgments

Financial support from the Research Foundation of Lappeenranta University of Technology, Magnus Ehrnrooth Foundation and Finnish Cultural Foundation, South Karelia Regional Fund are gratefully acknowledged. The authors are thankful to Ms. Anne Hyrkkänen and D.Sc. Tuomas Sihvonen for assistance with the experimental and analytical work.

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