# Coordination of Cu(II) and Ni(II) in polymers imprinted so as to optimize amine chelate formation

Leonid S. Molochnikov[a], Elena G. Kovalyova[a], Andrei A. Zagorodni[b,*],
Mamoun Muhammed[c], Yusif M. Sultanov[c], Aiaz A. Efendiev[d]

[a]*Department of Inorganic Chemistry, Ural State Wood Technology University, Siberian Highway 37, 620100 Ekaterinburg, Russian Federation*
[b]*Division of Materials Chemistry, Royal Institute of Technology, 10044 Stockholm, Sweden*
[c]*M.F.Nagiev Institute of Theoretical Problems of Chemical Technology, Azerbaijan Academy of Sciences, G. Javid Avenue 29, 370143 Baku, Azerbaijan Republic*
[d]*Institute of Polymer Materials, Azerbaijan Academy of Sciences, Samed Vurgun Street 124, 373204 Sumgait, Azerbaijan Republic*

## Abstract

Molecular imprinting has become an established technique. However, little was done on direct investigation of the sorbents produced. In the present work, en ESR method was used for the investigation of the complex formation processes within the sorbents imprinted with copper(II) and nickel(II). The sorbents were synthesized from a mixture of linear low molecular weight polyethyleneimine oligomers. The composition, structure and distribution of complexes in the resin phase were investigated. The effects of the synthesis conditions, loading degree and water content were examined. The presence of certain copper complexes was found to be a convenient characteristic of the imprinting efficiency. The optimum synthesis conditions for obtaining sorbents imprinted with copper(II) or nickel(II) were identified. The imprinting results in the improvement of the stability of the complexes and the selectivity and working capacity of the sorbents. The imprinted samples are also characterized by a more even distribution of chelating sites. The synthesis conditions and loading by ions allow for the regulation of the ratio between individual complexes and magnetic associates in the resin phase. This is a critical point on the future use of the metal containing imprinted sorbents as catalysts.
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## 1. Introduction

Molecular imprinting has become an established technique for preparing robust molecular recognition elements for a wide variety of target molecules [1,2]. The imprinting process requires a template molecule or ion that organizes functional and cross-linking polymerizable molecules during the polymerization process [3,4]. High selectivity of the obtained materials to a particular substance leads to the possibility of creating highly efficient separation processes [5–7] and highly stable catalytic sites [6,8–10]. There are also studies on the use of imprinted materials targeted to design specific receptors or molecular sensors [1, 6] and novel medications [11].

Kabanov put forward the principle of preparation of

polymers with tertiary structure optimized for sorption of the corresponding substrate [12]. Wulff described 'molecular imprinting' of multiple organic functionality in organic polymers [13]. One of the authors of the present paper together with Kabanov and Orudzhev proposed a new principle for the preparation of chelating polymers [14–16]. The principle consists of the purposeful conformational rearrangement of non-cross-linked polyelectrolyte macromolecules into positions favorable for complex formations with certain metal ions. Subsequent cross-linking preserves these conformations. The similar procedure was later used by other researchers for preparation of polymers able to separate mixture of ions and organic compounds [17–19]. Therefore, the sorption process is not opposed by an elastic force due to the distortion of the polymer chains. This results in the thermodynamically favorable sorption of ions forming certain coordination structures.

**Nomenclature**

| | |
|---|---|
| $A$ | hyperfine coupling constant; |
| $\bar{A}$ | apparent hyperfine coupling constant describing the result of the coalescence of two ESR signals with similar parameters; |
| $b$ | coefficient depending on the pattern of the paramagnetic centers distribution, the shape of the ESR line, and the rate of the spin-lattice relaxation; |
| $C$ | concentration; |
| $\langle C_{Cu} \rangle$ | local concentration of copper ions within a group of Cu-complexes located close enough for dipole–dipole interactions; |
| $g$ | $g$-factor; |
| $N$ | number of ESR responding copper ions; |
| $Q$ | ion exchange capacity; |
| $q_{Cu^{2+}}$ | amount of functional groups associated with copper ions; |
| $q_{RNH_2^+}$ | amount of functional groups associated with protons; |
| $RNH_2^+$ | protonated functional group of the resin; |
| $t$ | time; |
| $\alpha$ | protonation degree; |
| $\beta$ | constant of complex stability; |
| $\Delta H_{1/2}$ | width of the low field component altered by dipole–dipole interaction, measured at half the line height; |
| $\Delta H_{1/2}^0$ | original width of the low field component, measured at half the line height; |
| $\eta$ | fraction of copper ions contributing to the isotropic signal; |
| $\lambda$ | distribution coefficient; |
| $\lambda^0$ | standardized distribution coefficient; |
| $\parallel$ | notation indicating the direction of the magnetic field along the fourth order symmetry axis of the complex; |
| $\perp$ | notation indicating the direction of the magnetic field perpendicular to the fourth order symmetry axis of the complex. |

The new concept of polymer synthesis requires new methods in order to investigate the process and the product. The difficulty of studying the resin phase is a basic problem of sorbents investigation. The ESR method was selected due to the possibility of examining certain complexation processes in non-transparent media. Introduction of paramagnetic ions (as labels) allows an ESR investigation of the resin phase structure [20,21]. This approach is based on the sensitivity of the spin Hamiltonian parameters to the symmetry of the crystal field and to the delocalization of the electron density. This method was used for investigation of structure, sorption processes, and catalytic properties of sorbents imprinted with Cu(II) and Co(II) [22–26]. However, no attempt was done to characterize efficiency of the imprinting, nor to recognize the difference between non-imprinted, imprinted, and partially imprinted samples.

The main purpose of the present research is to find a method and criteria to measure the imprinting efficiency. ESR methodology was developed and applied to optimize the synthesis procedure. In general, the results obtained validate the concept of imprinting.

Resins based on mixture of linear low molecular weight polyethyleneimine oligomers (designated below by LLM PEI) were selected for this investigation. The composition, structure and distribution of complexes in the resin phase were investigated by ESR. The effects of the synthesis conditions, loading degree, and water content were examined.

The results obtained allowed for a number of novel conclusions concerning the state of sorbed ions in differently imprinted samples. The technique developed and conclusions obtained can be extended to many other types of functional polymers.

## 2. Experimental

### 2.1. Reagents

Inorganic reagents of analytical quality were used as obtained. All solutions were prepared using double-distilled water.

LLM PEI, a commercial product of AO 'Uralkhimplast' (Nizhni Tagil, Russian Federation) is a mixture of oligomers with structure

$$H_2N-(-CH_2-CH_2-NH-)_n-CH_2-CH_2-NH_2 \qquad (1)$$
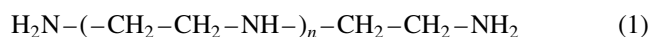
Some of molecules have a branched structure.

The product of reaction between epichlorohydrin and ammonia (ECHA) was prepared as described by Efendiev et al. [27]. One mole of $NH_4OH$ (aqueous solution) was added drop-wise to 2 mol of epichlorohydrin at 60 °C at

vigorous agitation. ECHA had the structure:

$$(Cl-CH_2-CH-CH_2)_2-NH-CH_2-CH-CH_2 \quad (2)$$
$$\qquad\qquad OH \qquad\qquad H^+Cl^- \qquad O$$
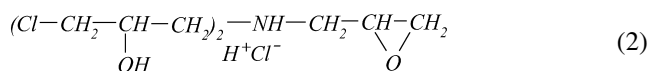
## 2.2. Synthesis of imprinted sorbents

The sorbents were prepared on the basis of LLM PEI and ECHA. $Cu^{2+}$ or $Ni^{2+}$ chloride or sulfate was dissolved in water. To prepare the desired complexes, the solution was added to LLM PEI in a volume ratio of 1:1. The amount of the ions added varied from 1 to 3 mmol per 1 g LLM PEI. Then, the obtained oligomer ECHA was mixed with corresponding amount of complex of $Cu^{2+}$ or $Ni^{2+}$ with LLM PEI and kept with constant stirring for 3 h at 80 °C, followed by 2 h at 100–105 °C. The weight ratio of LLM PEI and ECHA varied between 1:1 and 1:3. The metal ions were eluted from the obtained cross-linked material with 1 M HCl as corresponding salts of hydrochloric acid. The metal ions were recovered completely as confirmed by ESR tests. The configuration of LLM PEI cross-linked with ECHA is presented by structure (3):
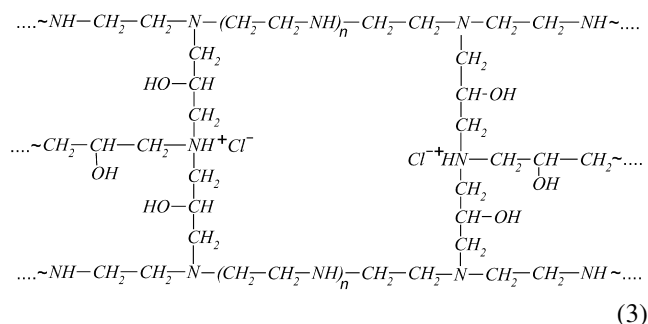
$$\text{(structure 3)} \quad (3)$$

The preferred structure has $n = 4$. The non-imprinted samples intended for reference experiments were prepared by the same procedure except for the introduction of any metals. Details of the sample preparation are given in Table 1.

## 2.3. Determination of basic resin characteristics

The water content and static ion exchange capacity ($Q$) were determined by a conventional method [28], as follows.

Samples of air-dry resin were weighed simultaneously with samples intended for each experiment and were dried (110 °C, 4 h). The water content was calculated from the weight loss. The dry resin weight was used for all calculations.

The static ion exchange capacity was defined as the number of moles of functional groups available for the $OH^- - Cl^-$ exchange per 1 g of dry resin. To determine the ion exchange capacity the sample ($OH^-$ form) was equilibrated with HCl (0.1 M) for 7 days. The equilibrium solution was titrated by NaOH (0.1 M) to calculate the amount of HCl consumed.

## 2.4. Determination of standardized distribution coefficients

Resin samples of 0.1 g were equilibrated with 100 ml of $Cu(NO_3)_2$. The concentration of the solution varied, not exceeding 0.1 M. The lowest limit was defined for each sample by detectability of copper in the equilibrium solution. The distribution coefficients ($\lambda$) were calculated as the ratio between amounts of copper sorbed by the resin and remaining in the solution. Standardized distribution coefficients were obtained by extrapolation of the $\lambda = f(C)$ dependence to zero concentration:

$$\lambda^0 = \lim_{C \to 0} \lambda \quad (4)$$

## 2.5. Sorption experiments

The sorption experiments were performed under static conditions. The protonation reaction

$$R = NH \cdots HOH + HCl \leftrightarrow R = NH_2^+ Cl^- + H_2O \quad (5)$$
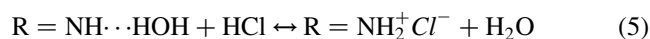
was taken into consideration for sample preparation. The protonation degree ($\alpha$) was defined as the ratio between amount of functional groups associated with protons and the ion exchange capacity measured as described above:

$$\alpha = \frac{q_{RNH_2^+}}{Q} \quad (6)$$

where $q_{RNH_2^+}$ represents the amount of protonated functional groups per 1 g of dry resin. Samples with chosen protonation degrees were prepared as follows. A sample of air-dry resin was kept in deionized water (24 h) in order for swelling to complete. After removal of the surrounding water the sample was placed in solution of electrolyte for 1 week to obtain the desired protonation degree. The sample was removed from the solution and washed with water until the desired value of pH was obtained. The conditions are presented in Table 2.

The resin (0.1 g of air-dry) in 24 ml of metal sulfate solution was used for each sorption experiment. The initial concentration varied while maintaining a constant pH 4 to get different resin loading degrees. The loading degree was defined as a percent of functional groups involved in the complex formation assuming, for simplicity, coordination number four for each metal ion participating in the complex formation. This acidity level was selected because copper does not form hydroxo complexes in aqueous solutions at pH 4. The contact time was 1 week. After equilibration, the phases were separated by filtration, and the equilibrium solution was analyzed. The amount of copper ions involved in complex formation (within the resin phase) was measured by the ESR method as described below. The chelating ability of the samples was characterized by the percent of resin amino groups involved in complex formation (at the saturation of the sample by copper).

Table 1
Characteristics of the samples prepared

| Sample | Weight ratio LLM PEI:ECHA | Metal introduced for imprinting | Amount of the metal introduced, mmol $g^{-1}$ of LLM PEI | Swelling degree, % | $Q$, mmol $g^{-1}$ of dry resin |
|---|---|---|---|---|---|
| *Samples imprinted with copper* | | | | | |
| *AN*-31*i*1*Cu*1.5 | 1:1.5 | $Cu^{2+}$ | 1 | 120 | 9.33 |
| *AN*-31*i*2*Cu*1.0 | 1:1.0 | $Cu^{2+}$ | 2 | 180 | 9.37 |
| *AN*-31*i*2*Cu*1.3 | 1:1.3 | $Cu^{2+}$ | 2 | 150 | 9.35 |
| *AN*-31*i*2*Cu*1.5 | 1:1.5 | $Cu^{2+}$ | 2 | 140 | 9.33 |
| *AN*-31*i*2*Cu*2.0 | 1:2.0 | $Cu^{2+}$ | 2 | 120 | 9.26 |
| *AN*-31*i*2*Cu*2.5 | 1:2.5 | $Cu^{2+}$ | 2 | 110 | 8.08 |
| *AN*-31*i*2*Cu*3.0 | 1:3.0 | $Cu^{2+}$ | 2 | 100 | 7.44 |
| *AN*-31*i*3*Cu*1.5 | 1:1.5 | $Cu^{2+}$ | 3 | 160 | 9.33 |
| *Samples imprinted with nickel* | | | | | |
| *AN*-31*i*1*Ni*1.5 | 1:1.5 | $Ni^{2+}$ | 1 | 100 | 9.33 |
| *AN*-31*i*2*Ni*1.0 | 1:1.0 | $Ni^{2+}$ | 2 | 180 | 9.37 |
| *AN*-31*i*2*Ni*1.5 | 1:1.5 | $Ni^{2+}$ | 2 | 140 | 9.33 |
| *AN*-31*i*2*Ni*2.0 | 1:2.0 | $Ni^{2+}$ | 2 | 110 | 9.26 |
| *AN*-31*i*2*Ni*2.5 | 1:2.5 | $Ni^{2+}$ | 2 | 100 | 8.08 |
| *AN*-31*i*2*Ni*3.0 | 1:3.0 | $Ni^{2+}$ | 2 | 90 | 7.44 |
| *AN*-31*i*3*Ni*1.5 | 1:1.5 | $Ni^{2+}$ | 3 | 160 | 9.33 |
| *Non-imprinted samples* | | | | | |
| *AN*-31*n*1.0 | 1:1.0 | – | – | 120 | 9.18 |
| *AN*-31*n*1.3 | 1:1.3 | – | – | 110 | 9.15 |
| *AN*-31*n*1.5 | 1:1.5 | – | – | 100 | 9.05 |
| *AN*-31*n*2.0 | 1:2.0 | – | – | 80 | 8.62 |
| *AN*-31*n*2.5 | 1:2.5 | – | – | 70 | 7.48 |
| *AN*-31*n*3.0 | 1:3.0 | – | – | 60 | 7.27 |

## 2.6. Estimation of copper mobility in the resin phase

Swollen samples were exposed to a solution containing $CuSO_4$ (0.1 M) and $NiSO_4$ (0.1 M) for 4 min. Nickel salt was added in order to obtain better resolution of the ESR spectra. The phases were rapidly separated. The excess of the solution was removed by fast rinsing. In some experiments, the solvent film was removed from the grain surface by filter paper. Sequential series of ESR measurements were performed to monitor the spectra alteration as a function of the time elapsed from the moment of phase separation. The solutions contained ethanol (up to 50%) in order to reduce the diffusion. The same water–ethanol mixtures were used for all samples to acquire values suitable for comparison.

## 2.7. Determination of compound concentrations

The total metal concentrations were determined by conventional titration with EDTA. Cu(II) in the presence of Ni(II) or Zn(II) was determined by a spectrophotometric method in complex with 2,2′-diquinolyl dissolved in 3-methyl-1-butanol at $\lambda = 540$ nm [30].

pH was measured by a '1 in 3' combined electrode with a model 340 pH meter (Corning Inc., NY). The accuracy of these measurements was within 0.01.

## 2.8. ESR investigations

ESR spectra were recorded by an automatic X-band ESR spectrometer PS 100. × (Advanced Analytical Instruments Inc. Minsk, Belarus) at room temperature (20–22 °C) and were processed with the spectrometer's standard software. Some spectra were also recorded with use of Bruker Model ESP300 X-band spectrometer. A crystal of ruby ($Cr^{3+}$ in $Al_2O_3$) was used as an internal reference (standard) for standardizing the intensity of spectra obtained. Response of the standard can be observed in the spectra presented in Section 3. Both water-swollen and air-dry samples were investigated. The conventional ESR parameters $g_\parallel$ and $A_\parallel$ were used to characterize the complexes. The number of ESR-responding copper ions ($N$) was estimated by double integration of the spectrum and subsequent comparison with reference measurements (single crystal of $CuSO_4 \cdot 5H_2O$ with known number of spins). $N$ was calculated separately for isotropic and anisotropic signals. The experimental spectra were modeled by a sum of separately obtained isotropic and anisotropic signals. Details of the method can also be found in work of Sharma and Borovik [25]. The anisotropic signal was modeled by a spectrum of the sample with minimal loading by copper (see, for example, Fig. 1, curve 1). The peculiar anisotropic signal was recorded for each sorbent and for each degree of imprinting. The difference between anisotropic signals is due to different copper complexes formed. The spectrum obtained for

Table 2
Conditions of sorption experiments

| Targeted | Electrolyte solution | | Washing to pH |
|---|---|---|---|
| $\alpha$ | Reagent | Amount of reagent, %[a] | |
| 0 | 0.1 M NaOH | 120 | 9.5 |
| 0.4 | 0.1 M HCl | 40 | Calculated for each sample[b] |
| 1 | 0.1 M HCl | 120 | 4.0 |

[a] The amount of the solution is expressed as a percent ratio of the reagent amount to the total exchange capacity of the resin sample.

[b] The pH value was calculated for each sample on the basis of the potentiometric investigation with the use of pH sensitive nitroxide radicals [29].

*AN*-31*i*3*Ni*1.5 (Fig. 1, curve 6) loaded with a mixture of copper and nickel was selected to model the isotropic signal. The isotropic signal is broad and insensitive. Hence, the same spectrum was used for all models. The anisotropic and isotropic signal spectra were spin-density quantified and normalized prior to the simulation. An iterative method was used for the calculations. The estimated errors in the simulated spectra were $\sim 10\%$.

The low field component was re-recorded with high resolution (the sweep width was 20 mT). The difference between the line width of different spectra was up to 30% (differently imprinted samples of the same material), corresponding to 10% of the spectrum span. Such a method allowed reliable registration of the line width difference. The difference in the width of the copper(II) low field component of the ESR spectra was used to calculate the average local concentrations of the copper-ions ($\langle C_{Cu} \rangle$) [31] as follows

$$\Delta H_{1/2} - \Delta H_{1/2}^0 = b \langle C_{Cu} \rangle \quad (7)$$

where $\Delta H_{1/2}^0$ and $\Delta H_{1/2}$ are the original width of the spectrum low field component and the width altered by dipole–dipole interaction, respectively. The width of the low field component is measured at half of its height. $b$ in expression (7) is a coefficient which depends on the following independent parameters: the pattern of the paramagnetic centers distribution, the shape of the ESR line, and the rate of spin–lattice relaxation. The value $b = 3.60$ mT mol$^{-1}$ was used in our calculations to estimate $\langle C_{Cu} \rangle$. This value was obtained experimentally by Kokorin and Shubin for frozen solutions of Cu(H$_2$N–CH$_2$–CH$_2$–NH$_2$)$_2$(NO$_3$)$_2$ in 1:1 water–methanol [31]. The value is in good agreement with theoretically calculated $b = 3.49$ mT mol$^{-1}$ [32,33]. The characteristic $\langle C_{Cu} \rangle$ represents the local concentration of copper ions within a group of Cu-complexes located close enough for dipole–dipole interactions to occur. Applicability of Eq. (7) to the systems investigated was tested in separate experiments. A linear dependence of $\Delta H_{1/2}$ on copper content in the sample was found as predicted by

Eq. (7). This dependence is not sensitive to presence of another metal ion (Zn$^{2+}$). Application of Eq. (7) to other systems (linear and cross-linked polyelectrolytes) has been theoretically justified by Kokorin et al. [31, 34].

## 3. Results and discussion

A number of imprinted samples of the LLM PEI based polymer were prepared as described (see Section 2). Characteristics of the samples are presented in Table 1. The goal of the imprinting is to preserve functional group positions favorable to complex formations with certain metal ions. Therefore, a similarity between structures of the complexes formed in the resin phase and in aqueous solution (with the initial soluble polyelectrolyte LLM PEI as the ligand) was selected as the criterion of the imprinting efficiency.

### 3.1. Copper(II) complexes with LLM PEI

Three different Cu$^{2+}$ complexes can be identified in aqueous solutions of LLM PEI by ESR (Table 3) [22,35]. The complexes are not in a quick equilibrium, allowing them to be identified separately. It was shown that the same complexes are formed in mixtures of LLM PEI and oligomer of epichlorohydrin and ammonia (ECHA), i.e. the presence of ECHA does not affect the copper–LLM PEI complex formation under the conditions studied [22]. Complex formation is strongly dependent on pH. Structures of the complexes are shown in Fig. 2. An increase of the pH of the media results in the increase of the number of
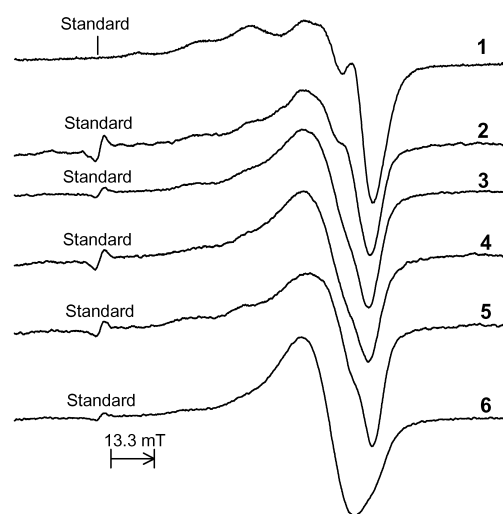


Fig. 1. ESR spectra of Cu(II) in swollen *AN*-31*i*3*Ni*1.5 loaded at $\alpha = 0.4$. **1–4**-the resin was equilibrated with Cu$^{2+}$; **5**-the resin was equilibrated with 1:100 mixture of Cu$^{2+}$ and Zn$^{2+}$; **6**-the resin was equilibrated with 1:100 mixture of Cu$^{2+}$ and Ni$^{2+}$. The loading by metals at the equilibrium was: **1**-2% Cu$^{2+}$; **2**-6% Cu$^{2+}$; **3**-13% Cu$^{2+}$, **4**-17% Cu$^{2+}$, **5**-4% Cu$^{2+}$ and 4% Zn$^{2+}$; **6**-4% Cu$^{2+}$ and 8% Ni$^{2+}$. The standard sample was Cr$^{3+}$ in Al$_2$O$_3$.

deprotonated amino groups along polymeric chains, thus increasing the possibility of adjacent amino groups forming a complex with the same copper ion. The difference between ESR spectra of the three complexes observed at different pH confirms this suggestion. Most of the nitrogen atoms along one LLM PEI chain are protonated in acidic solutions. The probability of deprotonation for two adjacent nitrogens in one chain is very low. Hence, copper complexes formed under acidic conditions, most likely, include only nitrogen atoms of different polymeric chains or, in some cases, nitrogen atoms positioned far from each other along one chain (complex CI, Fig. 2). Absence of chelating rings allows for the flexibility of the chains surrounding the metal ion, and a square-planar structure can be formed. Reduction of the media acidity results in the formation of another square-planar complex CII. Two pairs of nitrogen atoms at opposite sides of the square are connected by ethylene bridges. The difference in g-factor clearly indicates the presence of five-member rings (−copper−nitrogen−methylene−methylene−nitrogen−) as shown in Table 3. The complex denoted as CIII involves three or four adjacent nitrogen atoms of the chain. Only one ethylene unit is connected to each pair of nitrogen atoms, resulting in the distortion of the complex planar shape (see Fig. 2). In the distorted structure the coordinated nitrogen atoms are located out of the perfect planar positions. Such alterations are clearly reflected by changes in the hyperfine coupling constant but do not affect the value of g-factor. Analogous changes in ESR spectra were observed by other authors for similar systems characterized by *trans* symmetry of the distortions and by relatively small deviations of ligands from the planar positions [36,37]. In the investigated system the distortion is indicated by the lower hyperfine coupling constant $A_\parallel$ of CIII then that of complex CII.

### 3.2. Formation of copper(II) complexes in the LLM PEI-based sorbents

Synthesis of the imprinted sorbents was performed at neutral or weak-alkali pH. Under these conditions $Cu^{2+}$ forms only the complex CIII in aqueous solutions of LLM PEI and ECHA [22,35]. Previous investigations showed that the polycondensation does not affect the structure of complexes [22,23]. ESR characteristics of copper complexes in the resin phase do not differ from the values presented in Table 3.

ESR spectra of Cu(II) sorbed by the investigated resins resulted from a superposition of one or two anisotropic signals and one isotropic signal (Fig. 1). The isotropic signal is represented by a wide spectral line having a nearly symmetrical shape. The anisotropic signals have a good resolution in the low field region. They are typical of Cu(II) having $D_{4h}$ crystal field symmetry and belong to well-distanced copper-ions. The isotropic spectrum is a result of an exchange interaction between complexes of copper located near one another (the distance between them is

Table 3
ESR characteristics of Cu-complexes formed in solutions of LLM PEI and LLM PEI-ECHA

| Complex | pH range of formation[a] | $g_\parallel \pm 0.005$ | $A_\parallel \pm 0.3$, mT |
|---|---|---|---|
| CI | 3.0–4.0 | 2.214 | 18.0 |
| CII | 4.0–5.5 | 2.205 | 17.8 |
| CIII | 5.5–12.5 | 2.202 | 16.0 |

[a] Protonation of LLM PEI amino groups prevents any significant complex formation at pH < 3.

around 0.8 nm [38]). In all cases the g-factor of the symmetric line ($g_0$) was equal to the $\bar{g}$ values calculated with the use of the anisotropic signal parameters:

$$\bar{g} = \frac{g_\parallel + 2g_\perp}{3} \tag{8}$$

The $g_0 = \bar{g}$ equality proves that the isotropic signal belongs to the same complexes as the anisotropic one. The difference between the complexes causing anisotropic and isotropic signals is only their location within the resin matrix. The anisotropic signal corresponds mainly to copper ions located in smaller micro-pores. The isotropic signal can characterize the complexes located in larger pores with a significant number of amino groups. This conclusion is confirmed by ESR spectra of the samples containing different amounts of water. Reduction of the water content results in an increase of the isotropic signal intensity (swelling degree of the resins is present in Table 1). This might be explained by shrinkage of the resin at the air drying and the shortening of the distances between sorbed copper ions. The drying does not affect the anisotropic signal, indicating the absence of changes in the complex structures.

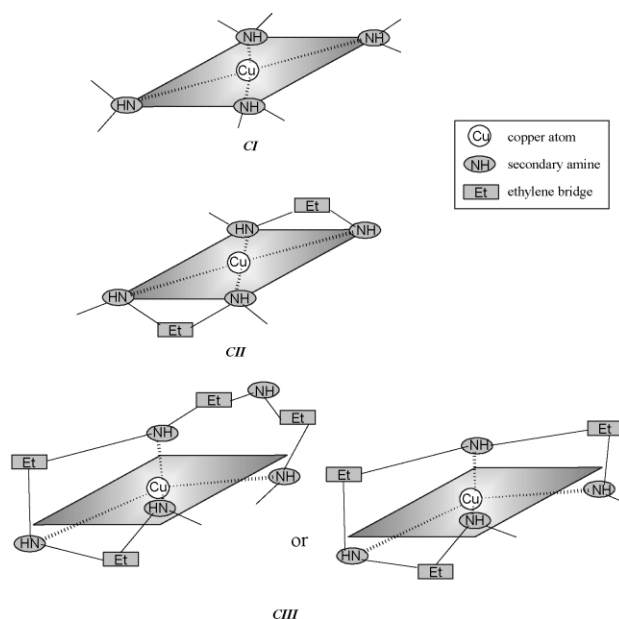The introduction of copper(II) in protonated sorbents



Fig. 2. Complexes formed by copper(II) in LLM PEI solutions. Water molecules are omitted for simplicity of the schemes.

($\alpha \rightarrow 1$) results in the formation of CI complexes only. Under these conditions imprinted sorbents do not exhibit any difference in complex formation from non-imprinted samples. Deprotonation of amino groups ($\alpha \sim 0.4$ and $\alpha \rightarrow 0$) results in resin interstitial conditions favorable to the forming of CII and/or CIII complexes. The ratio between the amounts of CIII and CII depends on the sorbent synthesis conditions, i.e. on the imprinting efficiency. Only CII complexes can be identified in non-imprinted samples. The dependence of the ratio CIII:CII in the imprinted sorbents on the ratio LLM PEI:ECHA used in the sorbent synthesis was initially investigated. As stated above, the hyperfine coupling constant is most sensitive to changes in the symmetry of immediate surroundings of the $Cu^{2+}$ ions. Dependence of $\bar{A}_{\parallel}$ on the fraction of LLM PEI used for the synthesis of AN-31i2Cu and AN-31i2Ni is shown in Fig. 3. $\bar{A}_{\parallel}$ represents the spectral response which appears as the result of a coalescence of two anisotropic signals with similar parameters. $\bar{A}_{\parallel}$ can be considered as an apparent characteristic useful for describing the overall ESR response. The loading degree ($Cu^{2+}$) in these experiments was 7–8% of the ion exchange capacity. The value of $\bar{A}_{\parallel}$ plotted at beginning of the Y-axis (Fig. 3) corresponds to aqueous solutions of LLM PEI. This value remains unchanged in samples synthesized with a LLM PEI fraction between 1.0 and 0.5. The increase of $\bar{A}_{\parallel}$ at increase of the ECHA fraction in the synthesis mixture indicates a gradual alteration of the copper complex. The reason for this increase is the coalescence of the ESR signals of two copper complexes (CIII and CII) with similar spectral characteristics. The increase of the ECHA amount used in the synthesis results in the reduction of the complex CIII fraction. However, some amount of CIII is formed in the imprinted samples at any LLM PEI:ECHA ratio. The contribution of CIII can explain the smaller value of $\bar{A}_{\parallel}$ in comparison with the $A_{\parallel}$ value of the pure CII complex. Unfortunately, the similarity between CII and CIII ESR characteristics does not allow to perform truly quantitative estimation of the content of these complexes. However, variations of the contribution of CII are clearly indicated by corresponding variations of $A_{\parallel}$ between 16.2 mT (CIII) and 17.8 mT (CII). As was written above, the similarity between the structures of the complexes formed in the resin phase and in aqueous solution was selected as a criterion of the imprinting efficiency. Thus, the LLM PEI:ECHA ratios 1:1–1:1.5 can be considered as favorable for the imprinting. Samples synthesized at other ratios of LLM PEI:ECHA also contain some amount of the complex CIII. However, the greater amount of CII indicates low efficiency of the imprinting.

A similar change in the ratio between CIII and CII complexes can be observed when studying the effect of the metal amount introduced at the sorbents synthesis. Copper is preferably sorbed as the complex CIII by sorbents synthesized in the presence of 2–3 mmol of Cu(II) or Ni(II) per 1 g LLM PEI. Complex CII is preferably formed in the

samples synthesized with less than 2 mmol of metal per 1 g LLM PEI.

Introduction of higher amount of metal into the LLM PEI at this stage created difficulties for the cross-linking procedure due to two reasons. First, more metal occupies more functional groups of LLM PEI and fewer groups remain available for cross-linking. Second, macromolecules loaded with metal are more rigid that creates a mechanical hindrance for the cross-linking. We also found that the increase of the metal amount above 3 mmol per 1 g LLM PEI does not improve sorption properties of the cross-linked sorbents.

In conclusion, successful imprinting can be achieved at a LLM PEI:ECHA ratio between 1:1 and 1:1.5 and with the amount of the metal introduced between 2 and 3 mmol per 1 g LLM PEI.

The fraction of copper ions contributing to the isotropic signal ($\eta$) was calculated as

$$\eta = N_{isotropic}/(N_{isotropic} + N_{anisotropic}) \tag{9}$$

$\eta$ was found to be sensitive to both the amount of $Cu^{2+}$ sorbed by the sample (Fig. 1, curves 1–4) and to the degree of imprinting (Fig. 4). For water-swollen samples, the fraction of the isotropic signal starts to increase at 7–8% copper loading (calculated per ion exchange capacity) and reaches its maximum at 13–14%. This tendency is characteristic of all the swollen samples investigated. The distribution of copper ions in the resin depends on the adjustment of the functional groups to positions favorable for complex formation with copper. The sorbents imprinted with copper and nickel contain both isolated complexes and exchange coupled associates, even at low loading degrees. An increase in degree of imprinting results in the reduction of $\eta$ sensitivity to the loading degree (curves $1 \rightarrow 2 \rightarrow 3$, Fig. 4). This is an additional confirmation of the fixation of the coordination sites at the synthesis of imprinted samples. The stable ratio between copper complexes located far from
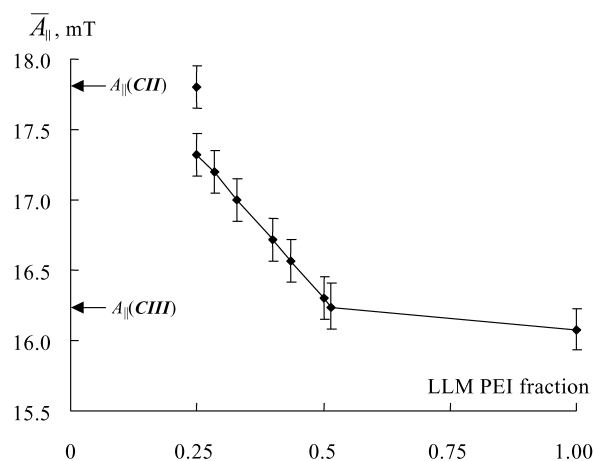


Fig. 3. Dependence of the apparent hyperfine coupling constant on the fraction of LLM PEI in the LLM PEI-ECHA mixture used in the synthesis. The difference between the $\bar{A}_{\parallel}$ values obtained for AN-31i2Cu and for AN-31i2Ni samples cannot be distinguished within the measurement error.

each other and complexes located close enough to form magnetic associates reflects such a ratio as the one in the solution before the cross-linking.

Modification of the LLM PEI:ECHA ratio from 1:1 to 1:1.5 results in the increase of the isotropic signal fraction in ESR spectra for the same loading degree. This can be explained by the decrease of the water content with the increase of the ECHA fraction. This explanation agrees with the above discussion of the difference between the spectra of swollen and air-dry samples. The subsequent increase of the ECHA content in the synthesis (from 1:1.5 to 1:3.0) results in the decrease of the isotropic signal fraction. This can be explained by the increase of the polymeric matrix density resulting from the increase of the cross-linking degree and the increased number of sites suitable for formation of separate copper complexes. This tendency is intensified by the reduction of the imprinting efficiency (see Fig. 3).

Deprotonated forms of the sorbents ($\alpha \rightarrow 0$) have the internal solution pH $\approx$ 8 [29]. Addition of the copper solution caused the fast formation of the hydroxide

$$Cu^{2+} + 2H_2O = Cu(OH)_2 + 2H^+ \qquad (10)$$
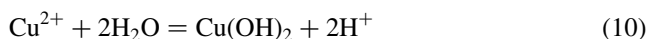
The final equilibrium can be obtained only via the following reaction:

$$Cu(OH)_2 + R(> NH)_4 + 2H^+ = R(> NH)_4Cu^{2+} + 2H_2O \qquad (11)$$
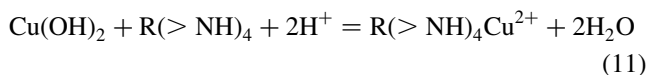
i.e. the relatively slow reaction (11) reverses hydrolysis (10). Equilibrium under these conditions is achieved after at least 10 days of rigorous agitation. The equilibria are characterized by the chelating of significant amounts of $Cu^{2+}$ (up to 30–40% of the ion exchange capacity). CIII and CII complexes as well as their magnetic associates were formed in the resin phase. Formation of copper hydroxide in the resin phase makes the investigation of the system even more difficult. The problem was solved in the following way. It is known that solid $Cu(OH)_2$ does not initiate any ESR response. Therefore, its presence in the samples cannot significantly affect the value of the double integral of the spectrum that was used to characterize the ESR signals initiated by the copper complexes. The amount of copper hydroxide in the resin phase was estimated from the difference between the increase of the total amount of copper sorbed (chemical analysis) and the increase of the ESR spectra response. The significant difference between imprinted and non-imprinted sorbents was found at relatively high loading degrees (10% or higher). The fraction of $Cu^{2+}$ involved in the complex formation was twice as high in the imprinted samples as in the non-imprinted, i.e. imprinting affects the copper distribution between the complexes and hydroxide. This fact confirms the idea of the higher stability of the copper complexes in imprinted sorbents and correlates with the values of the
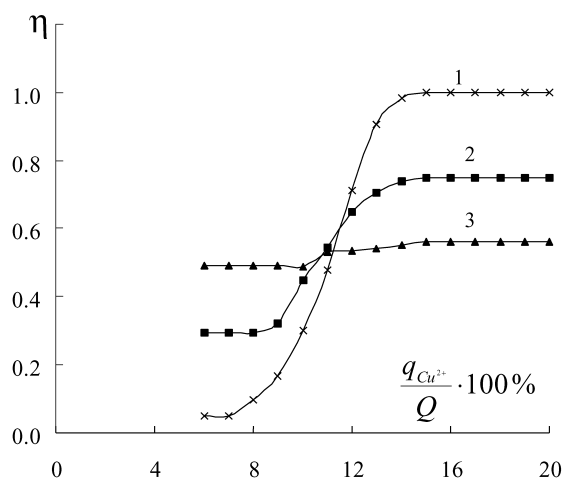


Fig. 4. Dependence of the isotropic signal fraction on the Cu(II) content in the imprinted sorbents (swollen samples): **1**-*AN-31i1Ni1.5*; **2**-*AN-31i2Ni1.5*; **3**-*AN-31i3Cu1.5*.

copper(II) and nickel(II) distribution coefficients standardized to infinite dilution [39], see Fig. 5.

### 3.3. Specific property of sorbents imprinted with nickel(II)

Ni(II) does not induce any response on the ESR spectra under the conditions selected. Therefore, the efficiency of the Ni-imprinting cannot be directly investigated by the ESR method. However, an earlier study demonstrated that at low loading degrees (3–8%) copper forms identical CI– CIII complexes in both Cu- and Ni-imprinted sorbents [23]. This phenomenon takes place despite the difference in the structure of copper and nickel complexes (copper forms preferably planar complexes while nickel forms octahedral complexes). Formation of CIII copper complexes in sorbents imprinted with nickel(II) indicates a partial adjustment of the groups to positions favorable for chelating of copper. This allows the investigation of Ni-imprinted sorbents by the introduction of Cu(II) as a paramagnetic label. It was assumed that the ratio between the copper complexes CIII and CII could be considered to be a criterion for the Ni-imprinting degree. This assumption is justified by positioning of the functional groups favorable for complex formation with copper at the nickel-imprinting. The absence of the CIII copper complexes in the non-imprinted samples might be regarded as additional proof. Loading of the samples over 8% results in the reduction of the CIII:CII ratio. This shows that only limited numbers of sites are suitable for CIII complex formation. It should be noted that the reduction of the CIII:CII ratio with a loading increase is characteristic only for the nickel-imprinted sorbents. It does not take place in the copper-imprinted samples, thus indicating a difference between sorbents imprinted with different metals.

### 3.4. Sorption of ion mixtures

To investigate the behavior of the nickel-imprinted sorbents in binary systems, samples were loaded with $Cu^{2+}$ and $Ni^{2+}$ from solutions containing both ions in different ratios. First, the samples were loaded from solutions containing equal amounts of copper and nickel (molar ratio $Cu^{2+}:Ni^{2+} = 1:1$). Up to total loading degrees of 10%, no differences in the complex composition were found in comparison to the case of only $Cu^{2+}$ sorption. However, the amount of the sorbed copper was much less (twice or more) in comparison to that sorbed in the case of only $Cu^{2+}$ sorption.

Complex formation in the resin phase was found to be different when nickel dominated in the mixture. Loading of the nickel-imprinted samples by the solution containing $Cu^{2+}$ and $Ni^{2+}$ in a 1:100 molar ratio results in the formation of CII copper complexes only. The amount of the copper sorbed is small. On the contrary, the copper-imprinted samples preserve the ability to form CIII complexes even under such unfavorable conditions.

Loading of the sorbents by a mixture of copper and zinc ions (molar ratio $Cu^{2+}:Zn^{2+} = 1:100$) can be characterized by the formation of CIII complexes in both copper- and nickel-imprinted samples. Only CII complexes are formed in the partially imprinted samples (the amount of metal introduced in the synthesis is less than 2 mmol g$^{-1}$ of LLM PEI) under the same conditions.

The specific nature of $Ni^{2+}$ and $Cu^{2+}$ sorption on the nickel-imprinted sorbents can be illustrated by comparing the samples loaded by $Cu^{2+}$–$Ni^{2+}$ and by $Cu^{2+}$–$Zn^{2+}$ mixtures (Fig. 1, curves 5–6). The ions of $Ni^{2+}$ do not generate an ESR response due to their paramagnetic nature, but they participate in exchange interactions and affect

shape of the $Cu^{2+}$ spectrum [31,40]. However, due to a shorter time of the spin-lattice relaxation, widening of the line due to the $Ni^{2+}$ influence is not so pronounced as the widening due to exchange interactions of $Cu^{2+}$ ions [31]. Contribution of the isotropic signal in the spectrum of *AN*-31*i*3*Ni*1.5 loaded with 4% $Cu^{2+}$ and 8% $Ni^{2+}$ (spectrum 6) is significantly higher in comparison with spectrum of the resin loaded with 13% $Cu^{2+}$ (spectrum 3). As stated above, the loading degree was formally calculated for coordination number four for each metal ion participating in the complex formation. In case of the $Ni^{2+}$ coordination with six functional groups, the total loading degree should be estimated as 16% (4% $Cu^{2+}$ and 12% $Ni^{2+}$). However, a comparison of spectrum 6 with spectrum 4 (17% loading with $Cu^{2+}$) results in the same observations. This contribution of the isotropic signal cannot be explained by participation of $Ni^{2+}$ in exchange interactions because the nickel influence on the relaxation of copper ions is much less in comparison with influence of $Cu^{2+}$. Hence, nickel ions primarily occupy thermodynamically favorable sites in small micropores of the nickel-imprinted sorbents. The copper ions occupy the rest of the sites located in the larger cavities. The copper ions are at short distances from one another in such positions and can form magnetic associates. On the contrary, the sorption of the copper–zinc mixture results in copper positioning at favorable sites. The ions located in the small micropores are far from each other, and this is reflected in anisotropic spectral line. This can be considered to be a cause of the high selectivity of the nickel-imprinted sorbents to $Ni^{2+}$. It is especially remarkable because in aqueous solutions copper forms much stronger complexes with ethyleneamines than nickel does. For example, stability constants of triethylenetetraamine complexes can be compared: log $\beta_{Cu} = 20.4$ and log $\beta_{Ni} = 14.0$ [41].

### 3.5. Migration of copper ions within sorbents

The mobility of copper ions in the imprinted and non-imprinted samples was compared. The dependence of the average local concentrations of the copper ions on the time elapsed from the moment of phase separation is shown in Fig. 6. Three samples synthesized under the same conditions were selected for the investigation. The samples sorbed different amounts of copper during the 4 min contact with the solution: *AN*-31*i*2*Cu*1.5 sorbed 0.085 mmol g$^{-1}$, *AN*-31*i*2*Ni*1.5 sorbed 0.067 mmol g$^{-1}$, and *AN*-31*n*1.5- 0.046 mmol g$^{-1}$ of dry resin. However, $\langle C_{Cu} \rangle$ was similar at time zero for all samples. Only complexes including four amines were formed in all three samples. This allows for the comparison of the $\langle C_{Cu} \rangle$ values of different samples. Thus, improved imprinting of the sorbent results in a more even initial distribution of copper.

The following reduction of $\langle C_{Cu} \rangle$ was initiated by the $Cu^{2+}$ migration inside the sorbent grains. The slopes of the curves in Fig. 6 can characterize the diffusion in the radial
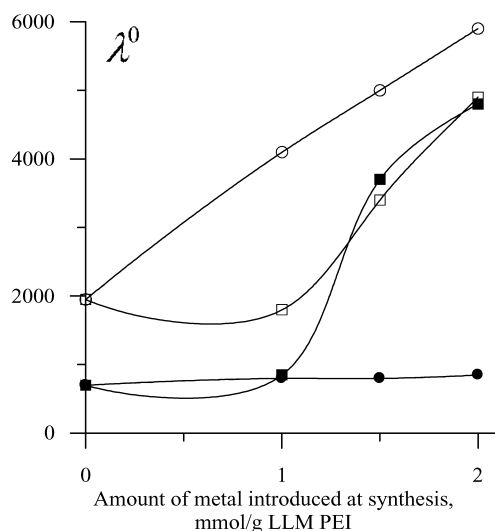


Fig. 5. Dependence of the standardized distribution coefficients on the amount of metal introduced in the synthesis for imprinting. Circular symbols represent sorbents imprinted with $Cu^{2+}$; rectangular symbols represent sorbents imprinted with $Ni^{2+}$; open symbols represent sorption of copper; solid symbols represent sorption of nickel.

direction. The linear character of the dependencies indicates constant rates of diffusion in all three samples. Considering the rate of diffusion, the samples can be ranked as follows:

$$AN\text{-}31n1.5 > AN\text{-}31i2Ni1.5 > AN\text{-}31i2Cu1.5 \qquad (12)$$

The imprinted sorbents swell 1.5 times more then the non-imprinted samples. Hence, the diffusion coefficient decrease in Eq. (12) cannot be explained by the decrease in solvent content. The only explanation for this decrease can be the increase of the binding energy between copper ions and amino groups defined by the sorbent synthesis procedure.

## 4. Conclusions

The degree of imprinting of the sorbents to copper(II) and nickel(II) can be characterized by the formation of the copper complex, CIII, in the resin phase. This is the same complex that is formed between $Cu^{2+}$ and LLM PEI in aqueous solutions at neutral and low-alkali pH.

An introduction of template metal ions in the synthesis mixture does not necessarily result in a fabrication of imprinted sorbents. The optimum synthesis conditions for obtaining sorbents imprinted with copper(II) or nickel(II) were determined using of the method proposed. Successful imprinting can be achieved at a LLM PEI:ECHA ratio between 1:1 and 1:1.5 and with the amount of metal introduced between 2 and 3 mmol per 1 g LLM PEI.

The higher complex stability resulting from the imprinting is caused by the energy benefit due to formation of non-distorted complexes (in comparison with non-imprinted samples). The imprinted polymers are also characterized by a more uniform distribution of chelating sites. All these result in improvement of selectivity and efficient capacity (maximal loading).

The synthesis conditions and loading by ions allow for the regulation of the ratio between individual complexes and magnetic associates in the resin phase This is a critical point on the future use of the metal ions immobilized in the imprinted sorbents as catalysts in various processes.
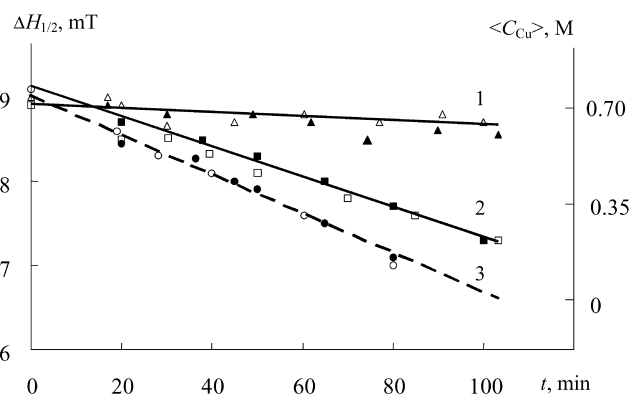
## Acknowledgements

Fig. 6. Time dependence of parameters characterizing the distribution of copper in the samples: 1-AN-31i2Cu1.5; 2-AN-31i2Ni1.5; 3-AN-31n1.5. Open symbols represent samples investigated after the removal of the solvent with filter paper. Solid symbols represent samples examined with the solvent film.

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