In situ complexation versus complex isolation in synthesis of ion imprinted polymers

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A B S T R A C T

In this study, the object is to prove that isolation of complexes made by varying the metal/ligand ratio (in situ complexation) yields similar polymer characteristics, metal binding and selectivity results as polymers synthesized by isolating the complex by precipitation. Complexation between nickel and the N-(4-vinylbenzyl)-2-(aminomethyl)pyridine (Vbamp) monomer was studied in dimethyl sulfoxide (DMSO) and in a DMSO-methanol mixture (50:50, v/v) at 80 °C using a $Ni(NO_3)_2 \cdot 6H_2O$ salt as the nickel source. According to the results, the three nickel/Vbamp complexes could be selectively obtained using specific conditions: for $[Ni(Vbamp)]^{2+}$ the Ni/Vbamp ratio in DMSO was 1.08, for $[Ni(Vbamp)_2]^{2+}$ the Ni/Vbamp ratio DMSO-methanol (50:50, v/v) was 0.49 and for $[Ni(Vbamp)_3]^{2+}$ the Ni/Vbamp ratio in DMSO was 0.3. Ion-imprinted polymers (IIPs) were prepared either with $[Ni(Vbamp)](NO_3)_2$, $[Ni(Vbamp)_2](NO_3)_2$, or $[Ni(Vbamp)_3](NO_3)_2$ complexes as the template. IIP with a $[Ni(Vbamp)_3]^{2+}$ complex, isolated by precipitation prior to polymerization, was also prepared. The results demonstrated that surface properties, nickel binding and selectivity properties were similar for both kind of IIPs – prepared by in situ complexation or isolation of the complex prior to polymer synthesis. Selectivity coefficients of nickel toward zinc for IIPs with $[Ni(Vbamp)]^{2+}$, $[Ni(Vbamp)_2]^{2+}$ and $[Ni(Vbamp)_3]^{2+}$ templates were close to 1038, 1441 and 1463, respectively.

1. Introduction

In the search for highly selective separation sorbents, ion imprinting technique leads to very attractive materials [1]. Their remarkable recognition properties come from their method of preparation. Synthesis of ion imprinted polymers usually consists of three steps: complexation between a polymerizable ligand and the template metal ion, copolymerization of the complex with a matrix-forming monomer and removal of the metal ion after polymerization [2]. The selectivity of the formed ion-imprinted polymers (IIPs) depends on the stability of the complex and on the size and shape of the generated cavities [3]. For the separation of transition metals, IIPs are usually based on chelating ligands, because of their ability to form strong coordinative bonds with metal cations [4]. In the development of ion imprinted materials, the challenge is still to prepare highly selective materials, which efficiently work in actual process conditions. Thus, new ideas improving the synthesis and selectivity of IIPs are still needed [5].

In the synthesis of IIPs, isolation of ligand-metal complexes has been extensively studied [6–13]. Isolation of complexes can be accomplished by crystallization of the complex in a separate step and re-dissolution in the polymerization mixture [6–13]. Crystallization of the complex is a reliable but time-consuming way to isolate the desired structure. Moreover, the back-dissolution step in the polymerization medium is often problematic. An alternative, simple and quick procedure is to form the complex directly in the pre-polymerization medium by mixing the metal and the ligand in a well-defined metal/ligand ratio [14–21]. In this case, the stoichiometry of the complex before polymerization is commonly checked by absorbance spectroscopy [15–18,20–22]. When only one structure of the complex is formed, as in the case of the 1-hydroxy 2-(prop-2′-enyl)-9,10-anthraquinone ligand and uranyl, this method is suitable [20]. However, when multiple complexes form, overlapping spectra are obtained and specific methods are required to determine the distribution of the various complexes. Continuous variation analysis originally introduced by Job [23] and ligand titration are normally used to analyze the spectral data [15,18,21]. However, these are only approximate methods and in the case of more complicated systems, the exact distribution of the complexes in the pre-polymerization medium usually remains unclear. Least-squares

minimization [24] enables calculation of the distribution of the complexes from the spectral data [25–26]. Despite its efficiency, apart from our team [25–26], only Shamsipur et al. [16–17] have implemented non-linear fitting of spectral data for determination of the distribution of complexes before the synthesis of IIPs.

The aim of this study is to prove that isolation of complexes made by varying the metal/ligand ratio and solvent mixture at 80 °C in the pre-polymerization medium (*in situ* complexation) yields similar polymer characteristics, metal binding and selectivity results as polymers made by isolating the complex by crystallization. *In situ* complexation method represents a simple way to control the stoichiometry of Ni/Vbamp complexes, while avoiding a conventional isolation method (crystallization or precipitation). In order to validate the efficiency of this new synthetic route, nickel uptake capacities and nickel/zinc selectivity of the IIPs were compared with those of an IIP prepared from a [Ni(Vbamp)$_3$]$^{2+}$ complex, which was isolated *via* prior polymerization [27]. Furthermore, to the best of our knowledge, no studies concerning IIPs with different stoichiometries between the specific ligand and the metal can be found in the literature. It is noteworthy that there are many excellent papers published recently in which high selective have been achieved, but complex formation study have been ignored although it is presumable that different complex stoichiometries can be formed [28–30]. In this study, we show the effect of the stoichiometry of the complex on material characteristics, metal binding and selectivity properties.

The *N*-(4-vinylbenzyl)-2-(aminomethyl)pyridine (Vbamp) monomer was chosen for this study, because of the ability of the 2-(aminomethyl) pyridine ligand to form three different complexes with nickel and its stability constants for high Ni/Zn selectivity are promising [31]. Complexation between nickel and Vbamp was studied by recording absorbance spectra with different nickel/Vbamp ratios and solvent compositions (dimethyl sulfoxide (DMSO), or a mixture of DMSO and methanol (50:50, v/v) at 80 °C. The distribution of the complexes was obtained by analyzing the spectral data using a least-squared minimization scheme [24–25]. Subsequently, IIPs with three different structures ([Ni(Vbamp)](NO$_3$)$_2$, [Ni(Vbamp)$_2$](NO$_3$)$_2$ and [Ni(Vbamp)$_3$](NO$_3$)$_2$) were prepared by inverse suspension polymerization using ethylene glycol dimethacrylate (EDMA) as the crosslinking agent.

2. Experimental

2.1. Materials and instrumentation

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 chemicals used without further purification. Methanol (99.9%, Sigma-Aldrich), DMSO (99.9% Sigma-Aldrich), Ni(NO$_3$)$_2$·6H$_2$O (98.5%, Sigma-Aldrich), NiSO$_4$·6H$_2$O (99%, Fluka), and Na$_2$SO$_4$·10H$_2$O (99%, Sigma-Aldrich), were used in experiments to form the complexes. Mineral oil (heavy, Sigma-Aldrich), 2,2′-azobisisobutyrontrile (AIBN) (98%, Sigma-Aldrich) and EDMA (98%, Acros) used in the polymerization was washed with a solution of 10% NaOH (99.9%, Sigma-Aldrich), dried on MgSO$_4$ and distilled to remove inhibitors. Aqueous solutions were prepared using deionized water (conductivity less than 0.1 μS cm^{-1}).

Absorbance spectra of the nickel and Vbamp complexes were measured with a UV–vis spectrophotometer (Jasco V670) using a quartz cuvette with a light path of 1 cm. The concentrations of the sample solutions are estimated to be correct within 2%. The accuracy of the spectra was tested by repeating a measurement four times over a period of 4 h. The average absolute difference in the wavelength range 400–1000 nm was 0.001 absorbance unit.

Structures of the nickel and Vbamp complexes after polymerization of IIPs were analyzed using a reflection UV–vis-NIR spectrophotometer

(JASCO V670) equipped with a horizontal integrating sphere attachment (JASCO PIN-757). Spectra were measured between 190 and 1000 nm with a 400 nm·min^{-1} scan speed using the corresponding non-imprinted polymers (NIPs) as a reference.

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

The BET surface area, BJH pore volume and pore size were measured using N$_2$ adsorption (Micromeritics Gemini V). Nitrogen adsorption/desorption isotherms were also measured. Before the measurements were collected, samples were evacuated several hours at a pressure less than 10^{-3} Pa at 50 °C. The shape of the particles was analyzed using scanning electron microscopy (SEM, JEOL JSM-5800).

Metal concentrations were determined by inductively coupled plasma-atomic emission spectroscopy on a ICP-AES (Iris Intrepid IIXDL ICP-AES). All samples were analyzed at least twice and the duplicate determinations agreed within 5%.

2.2. Complexation of nickel with the 2-(aminomethyl)pyridine monomer

The functional monomer, *N*-(4-vinylbenzyl)-2-(aminomethyl)pyridine (Vbamp) was synthesized *via* Schiff base reaction and subsequent reduction of the imine as previously described [26]. The complexation between nickel and Vbamp was studied in DMSO and a DMSO/methanol mixture (50:50, v/v) using Ni(NO$_3$)$_2$·6H$_2$O as the nickel source. The procedure is illustrated in Scheme 1. The experiments were performed in 3 mL glass vials. The combined concentration of the nickel (0.01–0.09 mol L^{-1}) and Vbamp (0.09–0.01 mol L^{-1}) was kept constant (0.1 mol L^{-1}), 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 80 °C using a UV–vis spectrophotometer.

At equilibrium, the distribution of the complexes was calculated using a commercial program (HypSpec) based on the least-squares minimization scheme [24]. Stability constants, extinction coefficients, and concentrations of all absorbing components were simultaneously estimated. For uncomplexed nickel, the extinction coefficients were known from independent measurements. Detailed description of the calculations can be found in our previous paper [25].

2.3. Synthesis of ion-imprinted polymers

Each complex was copolymerized with EDMA crosslinker to prepare IIP1a, IIP1b and IIP1c (with [Ni(Vbamp)](NO$_3$)$_2$), IIP2 (with [Ni(Vbamp)$_2$](NO$_3$)$_2$) and IIP3 (with [Ni(Vbamp)$_3$](NO$_3$)$_2$) by inverse suspension copolymerization. Solutions containing predominantly the complexes with 1:1, 1:2 and 1:3 stoichiometries were prepared from Ni/Vbamp molar ratios of 1.1, 1.5 and 4.0 for [Ni(Vbamp)](NO$_3$)$_2$, 0.5 for [Ni(Vbamp)$_2$](NO$_3$)$_2$ and 0.3 for [Ni(Vbamp)$_3$](NO$_3$)$_2$ (Table 1). The solvents were respectively, DMSO, a DMSO-methanol mixture (50:50, v/v) and DMSO. The volume of the solvent was 10 mL, the mass of Vbamp was kept constant at 0.519 g (0.002 mol) and Ni(NO$_3$)$_2$·6H$_2$O was used as the nickel source (the amount was calculated from the Ni/Vbamp mole ratios). In the case of IIP4, Ni(Vbamp)$_3$(ClO$_4$)$_2$ complex was precipitated by slow evaporation after one day according to Lenoble et al. [27]. Additionally, 4.4 mL (0.02 mol) of EDMA and 0.1 g of AIBN were added, to the solution and stirring under nitrogen was maintained for 15 min. 80 mL of mineral oil was introduced in a 500 mL round-bottom flask and purged with nitrogen for 15 min. The organic phase containing the monomers and AIBN was then added quickly. Polymerization was performed at 80 °C for 4 h under nitrogen with stirring rates of 1000 rpm (IIP1a, IIP1b, IIP1c and IIP2), 250 rpm (IIP3) and 750 rpm (IIP4). The polymer particles formed were filtered, washed with 50 mL chloroform and extracted in a Soxhlet tube for 24 h with a chloroform-acetone mixture (1:1). Finally, the particles were dried under vacuum at 25 °C for 24 h. NIPs were prepared in DMSO (NIP1) and in the DMSO-methanol mixture (50:50, v/v) (NIP2) under