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Complexation of Zn^{2+} with Vinyl Imidazole Containing IMAC Adsorbent: Potentiometric, Kinetic, and Thermodynamic Studies

Vinil İmidazol İçeren IMAK Adsorbanının Zn^{2+} ile Kompleksleşmesi: Potansiyometrik, Kinetik ve Termodinamik Çalışmalar

Research Article

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ABSTRACT

The aim of this paper is to synthesize a cross-linked polymer containing imidazole groups and study its metal ion complex properties under different experimental conditions. Thus, the use of the potentiometric method for the determination of the protonation constant of vinyl imidazole (VIM) and the stability constant of the Zn^{2+} ion complex of VIM was investigated. First to determine the coordination tendency of the vinyl imidazole ligand towards the Zn^{2+} ions in solution, poly(ethylene glycol dimethacrylate-n-vinyl imidazole) [poly(EGDMA–VIM)] microbeads (average diameter 150–200 μm) were synthesized. The microbeads were characterized by N_2 adsorption/desorption isotherms, elemental analysis, energy dispersive spectroscopy (EDS or EDX). Protonation constants of vinyl imidazole and the metal-ligand stability constant of vinyl imidazole with Zn^{2+} ions have been determined potentiometrically in a 0.1 M NaCl medium at 298, 318, and 338 K. The corresponding thermodynamic parameters of protonation and complexation processes (ΔG, ΔH, and ΔS) were derived and discussed. The formation kinetics of Zn^{2+}-vinyl imidazole complex were also investigated, and the process obeyed the pseudo-second-order kinetic model.

Key Words
Vinyl imidazole, insoluble polymers, Zn^{2+}, beads

ÖZET

Bu çalışmanın amacı imidazol grupları içeren çapraz bağlı bir polimerin metal iyonları ile kompleks oluşturma özelliklerinin araştırılmasıdır. Vinil imidazol (VIM) ligandının protonlanma sabiti ile Zn^{2+} iyonları ve VIM ligandları arasında oluşan kompleksin kararlılık sabitinin belirlenmesinde potansiyometrik yöntem kullanıldı. Vinil imidazol ligandının Zn^{2+} iyonlarına olan afinitesinin belirlenmesi için ilk olarak çapları 150–200 μm aralığında değişen poli(etilenglikol dimetakrilat-n-vinil imidazol) [poly(EGDMA–VIM)] mikroküreler sentezlendi. Mikroküreler, elemental analiz, N_2 adsorpsiyon/desorpsiyon izotermleri ve enerji dağılım spektroskopisi (EDS veya EDX) ile karakterize edildi. Vinil imidazol ligandının protonlanma sabiti ile VIM ligandı ile Zn^{2+} iyonları arasında oluşan kompleksin metal-ligand kararlılık sabiti 0.1 M NaCl ortamında 25 °C, 35 °C ve 45 °C sıcaklıkta potansiyometrik olarak belirlendi. Protonlanma ve kompleks oluşumuna ilişkin termodinamik parametreler (ΔG, ΔH, and ΔS) hesaplandı. Zn^{2+}-vinil imidazol kompleksinin oluşum kinetiği incelendi ve yalancı-ikinci-mertebe olduğu belirlendi.

Anahtar Kelimeler
Vinil imidazol, çapraz bağlı polimerler, Zn^{2+}, küreler

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INTRODUCTION

Various chelating ligands are synthesized and used on polymer supports for complexation of metal ions. Amongst the most commonly used ligands iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), carboxymethylated aspartic acid (CM-Asp), and triscarboxymethyl ethylene diamine (TED) were found to be useful. Chelating ligand bearing polymers have been intensively used for complexation of metal ions [1-5]. Zinc is used to generate metal chelate complexes with acrylic acid and crotonic acid [6], iminodiacetic acid [7-9], hyaluronic acid [10], ethylene glycol-bis-(b-aminoethyl ether) N,N,N′,N′-tetra-acetic acid [11], benzoylthiourea [12], imine [13], acrylic acid [14], pyrrolidone [15], dipicolylamine [16], azelaoyl-bis-hydroxamic acid [17], bis[2-(2-mercaptobenzothiazolylethyl) sulfoxide] [18], 2-acrylamidosulphadiazine [19] containing chelating polymers. Except for Zn^{2+} a large varieties of transition-metal ions such as Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{3+} has been studied with chelate polymers. Such reactions result in the formation of complex in which nitrogen, sulphur and oxygen atoms are coordinative bounded to metal ions.

1-Vinyl imidazole is a monodentate ligand that forms complexes with Zn^{2+} ions. In terms of its high chelating ability to metal ions, 1-vinyl imidazole is an attractive monomer candidate of complex formation. Poly(N-vinyl imidazole) and its copolymer hydrogels were studied at binding of Zn^{2+} ions. Up to four imidazoles bind to one Zn^{2+} ion; the log K (where K is association constant) for each imidazole ligand is increasing from $\log K_1 = 1.98$ for binding the first imidazole ligand to $\log K_4 = 2.62$ for binding the fourth imidazole ligand [20]. Galaev et al. [21] reports that the imidazole ligands when coupled with solid matrices because imidazole ligands are spatially separated due to a predominantly 1:1 complex formation, and the proper orientation of the ligands to form a complex with the same Cu^{2+} is unlikely. They explained the successful use of imidazole ligands in metal-affinity precipitation flexibility of the water-soluble polymer as compared with the rigidity of the IMA chromatography matrix.

Understanding of mechanisms of interaction of polymer and metal ions is an important problem in view of potential application of the polymer/metal pair in various fields. Investigations into complex stability constants and coordination numbers between metal ions with adsorbents containing different chelating agents have generally been disregarded, although these factors indicate strong and stable complexes. Only limited studies have concentrated on the acid-base and metal binding properties of new and traditional chelating adsorbents and on changes in the physicochemical properties of immobilized metal chelate complexes [22–25].

In our previous studies, we developed a novel approach for the preparation of a metal-chelating matrix containing vinyl imidazole ligand. In this approach, the comonomer vinyl imidazole (VIM) is polymerized in the presence of a cross-linker ethylene glycol dimethacrylate (EGDMA), and poly(ethylene glycol dimethacrylate-*n*-vinyl imidazole) [poly(EGDMA-VIM)] hydrogel beads were prepared [26]. The most important advantage of this approach over conventional techniques used for metal-chelating matrix preparation is that no need to activate the matrix for the chelating-ligand immobilization exists because the comonomer VIM acted as the metal-chelating ligand.

In order to better understand the complexation mechanism of chelating imidazole ligand bearing polymers, we were studied this subject in present investigation and reported more detailed mechanisms of interaction of vinyl imidazole and Zn^{+2} ions. In this report, poly(ethylene glycol dimethacrylate-n-vinyl imidazole) [poly(EGDMA-VIM)] hydrogel beads were prepared by the copolymerizing of ethylene glycol dimethacrylate (EGDMA) with 1-vinylimidazole (VIM), as described in our previous paper [20]. The potentiometric titration method was used for the determination of the protonation constants of VIM and the stability constants of the Zn^{2+}-VIM complexes at 25 °C, 45 °C, and 65 °C. The protonation and stability constants were determined from potentiometric titration data by using the BEST microcomputer program at three different temperatures. Kinetic studies were also conducted to clarify the Zn^{2+}-VIM complex formation process.

MATERIALS AND METHODS

Materials

Ethylene glycol dimethacrylate (EGDMA) was obtained from Merck (Darmstadt, Germany), purified by passing through active alumina, and stored at 4°C until its use. N-Vinyl imidazole (VIM, Aldrich, Steinheim, Germany) was distilled under a vacuum (74–76°C, 10 mm Hg). Also, 2,2'-Azobisisobutyronitrile (AIBN) was obtained from Fluka A.G. (Buchs, Switzerland). Poly(vinyl alcohol) (PVAL; Mw: 100.000, 98% hydrolyzed) was supplied by Aldrich Chem. Co. (United States of America [USA]). All other chemicals (zinc chloride, [Merck 99%], disodium salt of ethylenediaminetetraacetic acid, [Merck 99%], sodium hidroxyde, and hydrochloric acid) were of an analytical grade and used without further purification. A stock solution of Zn^{2+} was prepared by dissolving the proper amount of $ZnCl_2$ in a small amount of HCl (Merck 37% purity) to prevent hydrolysis. The concentration of free acid in the stock solution of Zn^{2+} was checked by potentiometric titration. The stock solution of Zn^{2+} was standardized complexometrically by ethylenediaminetetraacetic acid (EDTA) titration using the method of Schwarzenbach [27]. All water used in the binding experiments was purified using a Barnstead (Dubuque, Iowa, USA) ROpure LPw reverse osmosis unit with a high-flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpurew organic/colloid removal and ion exchange packed-bed system. All glassware were extensively washed using diluted nitric acid before being used.

Synthesis and characterization of the poly(EGDMA-VIM) microbeads

The poly(EGDMA-VIM) beads were selected as the metal chelating polymer and produced by suspension polymerization technique as described in our previous article [28].

In order to evaluate the degree of VIM incorporation, the synthesized poly(EGDMA-VIM) microbeads were subjected to elemental analysis using a Leco Elemental Analyzer (Model CHNS-932, USA).

The average size and size distribution of the beads were determined via screen analysis performed using standard sieves (Model AS200, Retsch Gmb & Co., KG, Haan, Germany).

Energy dispersive spectroscopy (EDS or EDX) was used to determine the elements (atoms) of which the surface of the sample is composed.

The specific surface area of the beads in a dry state was determined using a multipoint Brunauer-Emmett-Teller (BET) apparatus (Quantachrome Corporation, Autosorb-6, USA).

Potentiometric measurements

Potentiometric titrations were performed on a Schott Titroline Alpha Plus automatic titrator with a combined pH electrode (Schott), which was connected to a computer. All titrations were carried out in a double-walled glass cell. The temperature was kept constant inside the cell at 25.0±0.1ºC, 45.0±0.1ºC, and 65.0±0.1ºC by circulating water from an external thermostat (VWR, precision ±0.1ºC). The pH-meter was calibrated daily using standard buffer solutions (Mettler-Toledo). The combined glass electrode calibration was carried out daily from the titration of a strong acid (HCl, 0.1 M) with a strong base (NaOH, 0.1 M) at the same ionic strength before each titration, as was previously done. The ionic strength of the solutions were adjusted to 0.1 M by NaCl, and a total volume of 50 mL was used for each titration. The data for the potentiometric titrations were treated using the microcomputer program BEST, as previously described [29, 30]. The BEST software was used to minimize the standard deviation of the fit (σ_{fit}) between the observed and calculated pH values for the overall titration data. The species distribution diagram was obtained using the SPE program [31]. Potentiometric titrations were carried out using three different Zn^{2+} concentrations (4.10^{-3} M; 3.10^{-3} M; 2.10^{-3} M).

The methods used in potentiometric titrations for the determination of protonation and stability constants can be summarized as follows:

(a) 5 mL 0.1 M HCl + 5 mL 1 M NaCl (for cell calibration)
(b) 5 mL 0.1 M HCl + n x a mmol vinyl imidazole containing poly[(EGDMA-HVIM)]$^{n+}$ beads + 5 mL 1 M NaCl (for the determination of the protonation constant of VIM) [n=1 to 4]
(c) Solution b + a mmol Zn^{2+} ions (for the determination of the stability constant of Zn^{2+}-VIM complex) [a= 0,01 to 0,02]

Determination of protonation constants

For the determination of protonation constants (log K) of VIM, potentiometric titrations were performed at 25ºC, 45ºC, and 65ºC. Firstly, the VIM content of the poly(EGDMA-VIM) beads that can form a complex with Zn^{2+} ions was determined to be mmol protons (H^+) / g beads by potentiometric titration. The amount of proton is equal to the amount of VIM in the poly(EGDMA-VIM) structure due to the one protonable amine group in the imidazole ring. For this purpose, [poly(EGDMA-*H*VIM)]$^{n+}$ beads were prepared from poly(EGDMA-VIM) beads by protonation of the VIM groups in the poly(EGDMA-VIM) structure according to the following equation:

poly(EGDMA-VIM) + nH^+ <---> [poly(EGDMA-*H*VIM)]$^{n+}$ (1)

Briefly, the poly(EGDMA-VIM) beads (1 g) was transferred in an HCl solution (0.1 M, 100 mL), and the medium was incubated in a shaking water-bath at 100 rpm for 5 hours at room temperature. Following this period, the [poly(EGDMA-*H*VIM)]$^{n+}$ beads were filtered and washed with an excess amount of water. Then, the beads were dried and used for the potentiometric titration experiments. The mmol protons (H^+) per gram [poly(EGDMA-*H*VIM)]$^{n+}$ beads were determined via potentiometirc titration of protons (H^+) with a 0.1 M NaOH solution in a 0.1 M NaCl medium at 25ºC, 45ºC, and 65ºC. The protonation constants of VIM for three different temperatures were calculated from potentiometric titration data using the BEST program. The protonation constant (log K) values were used to calculate the thermodynamic parameters (ΔG, ΔH, and ΔS) of the protonation process.

Determination of stability constants

In order to determine the stability constant (log β) of the Zn^{2+}-vinyl imidazole complex at 25 °C, 45 °C, and 65 °C, potentiometric titrations of Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems prepared at different Zn^{2+}:VIM mole ratios were performed. The four different Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems for which the Zn^{2+}:VIM mole ratios are (1:1), (1:2), (1:3), and (1:4) were prepared by taking into consideration the VIM group content of the [poly(EGDMA-*H*VIM)]$^{n+}$ beads. Potentiometric titrations were conducted as described previously, and the stability constant (log β) values of the Zn^{2+}:VIM complex were calculated at 25ºC, 45ºC, and 65ºC by using the BEST microcomputer program. The thermodynamic parameters (ΔG, ΔH, and ΔS) of the complex formation process were determined.

Batch studies

For the determination of Zn^{2+}:VIM complex stoichiometry, Zn^{2+}-chelated poly(EGDMA-*H*VIM)]$^{n+}$ beads for which Zn^{2+}:VIM ratios are (1:1), (1:2), (1:3), and (1:4) were also prepared in a batch system. A total of 0.25 g of the beads were mixed with 25 mL of aqueous solutions containing Zn^{2+} ions at different concentrations, at a constant pH of 5.0 (adjusted using HCl and NaOH), which was the optimum pH for Zn^{2+} chelate formation at room temperature. The flasks were stirred magnetically at 100 rpm for 3 h (sufficient to reach equilibrium), and the beads were filtered. The concentration of the Zn^{2+} ions in the resulting solution was determined with a graphite furnace atomic absorption spectrometer (Analyst 800/ Perkin–Elmer, USA). The results were used for the determination of the mmol Zn^{2+} ions per mmol VIM in the poly(EGDMA-VIM) chain.

Kinetic studies for complex formation

Kinetic studies of Zn^{2+}-VIM complex formation were investigated by using the potentiometric method. Firstly, 20 mL of an aqueous solution containing Zn^{2+} ions (0.01 M) was prepared at a pH of 5.0. Then, [poly(EGDMA-*H*VIM)]$^{n+}$ beads were added to a Zn^{2+} ions- containing solution,

Table 1. Elemental analysis of poly(EGDMA-VIM) microbeads.

Sample	Elemental analysis (experimental value)			Mole Fractions in copolymer (%)	
	N (wt. %)	C (wt. %)	H (wt. %)	EGDMA	VIM
Poly(EGDMA-VIM)	10.22	51.25	10.71	47.1	52.9

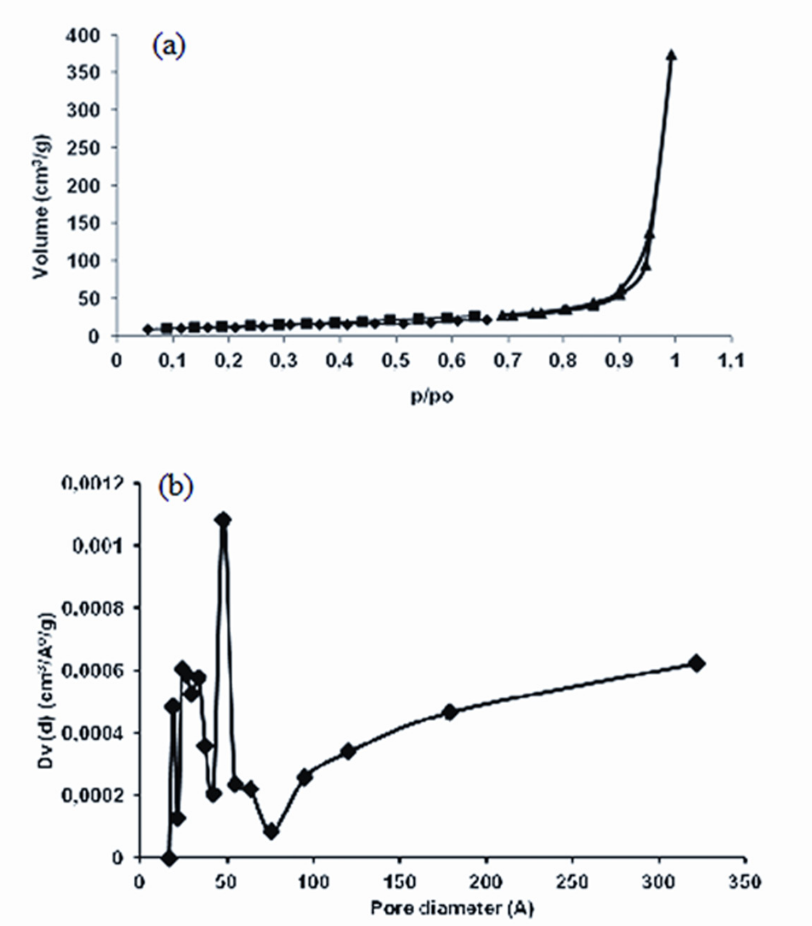

Figure 1. (a) Adsorption/desorption isotherms of nitrogen at 77.40 K and **(b)** pore size distribution obtained by Dv (d) according to average pore diameter for the poly(EGDMA-VIM) microbeads.

and the pH of the solution was measured at 30-s time intervals. The obtained data were used to evaluate the fitting of kinetic models.

RESULTS AND DISCUSSION

Properties of poly(EGDMA-VIM) microspheres

The poly(EGDMA-VIM) beads were prepared in the spherical form in the size range of 150–200 µm. The specific surface area of the poly(EGDMA-VIM) beads was found to be 66.3 m^2/g, which is relatively high due to the roughness of the bead surfaces. The ratio of EGDMA and VIM in the poly(EGDMA–VIM) beads, as calculated from the nitrogen stoichiometry based on the elemental analysis data, is shown in Table 1.

The elemental analysis results suggested that mole fractions of EGDMA and VIM in the copolymer structure are 47.1% and 52.9%, respectively. The ratio of EGDMA to VIM was 1:1. On the other hand, the mole fractions of EGDMA and VIM are calculated using VIM group content of the poly(EGDMA-VIM) structure and determined to be 83.3% and 16.7%, respectively. When compared with elemental analysis results, the decrease in the mole ratio of VIM shows that many vinyl imidazole groups in the

Table SI1. BET surface area, pore volume, and pore size of poly(EGDMA-VIM)

Sample	BET surface area ($m^2 . g^{-1}$)	Pore volume ($cm^3 . g^{-1}$)	Pore size (Angstrom)
poly(EGDMA-VIM)	66.33	0.5896	67.74

poly(EGDMA-VIM) chain can be inaccessible in an aqueous solution. Therefore, the chelation of Zn^{2+} ions can occur mainly on the surface of the beads and in the pores that the hydrated Zn^{2+} ions can diffuse.

In order to obtain information on pore size of the poly(EGDMA-VIM) microbeads, the N_2 adsorption/desorption isotherm was also evaluated. The isotherm and corresponding pore size distribution curve for the poly(EGDMA-MATrp) microbeads are shown in Figure 1. The BET surface area (S_{BET}), pore volume (V_p), and pore size are given in Table SI1.

The average pore size of the poly(EGDMA-VIM) beads was determined to be 67.74 angstrom by using the N_2 adsorption/desorption isotherm data. The ionic radius of a hydrated Zn^{2+} ion (four coordinated) is 0.74 angstrom in an aqueous solution. When the ionic radius of the hydrated Zn^{2+} ion is considered, it can be clearly said that the hydrated Zn^{2+} ions can diffuse into the pores near the surface of the beads and form a chelate with accessible VIM groups.

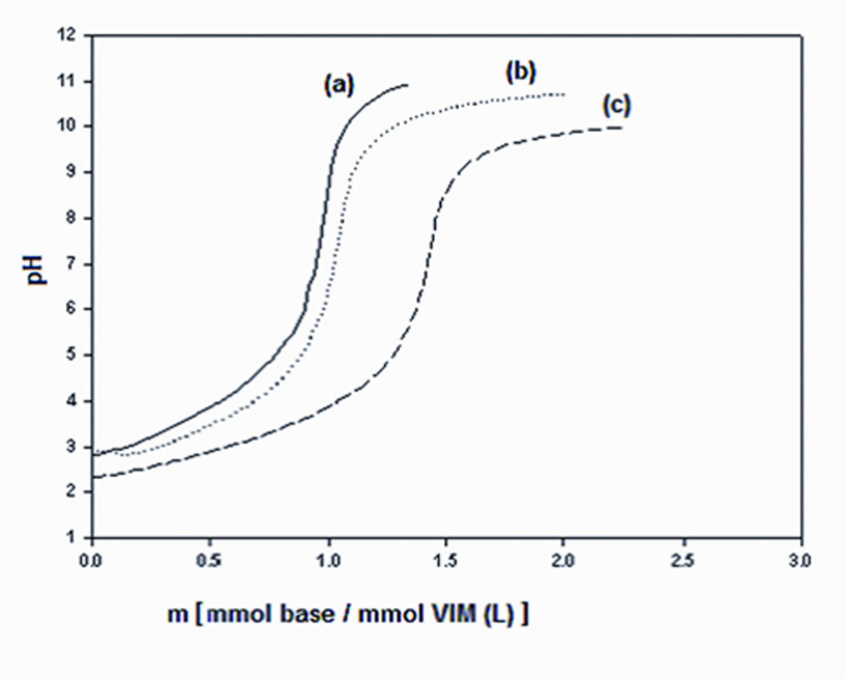

Figure 2. Titration curves of $[poly(EGDMA\text{-}\boldsymbol{H}VIM)]^{n+}$ beads in a 0.1 M NaCl medium at (a) 25 °C, (b) 45 °C, and (c) 65 °C.

Determination of the protonation constant and thermodynamic parameters

The protonation constant (log K) is a value that shows the basicity of the ligand. Log K values of VIM have been determined potentiometrically in

Table 2. Protonation constants (log K ± σ^a) and thermodynamic functions for the protonation of vinyl imidazole in 0.1 M NaCl ionic medium at 25 °C. 45 °C and 65 °C.

Ligand	Temperature (K)	Protonation constants (log K ± σ^a)	Gibbs Energy Change ΔG^0 (kj/mol)	Enthalpy Change ΔH^0 (kj/mol)	Entrophy Change ΔS^0 (J/mol K)
Vinyl imidazole	298	3.61±0.05	-20.60	-45,54	-82.63
	318	3.28±0.06	-19.97		
	338	2.66±0.08	-17.52		

a 0.1 M NaCl medium at 25ºC, 45ºC, and 65ºC. In Figure 2, the titration curves of [poly(EGDMA-*H*VIM)]$^{n+}$ beads in a 0.1 M NaCl medium at 25ºC, 45ºC, and 65ºC were depicted. From the potentiometric titration data of [poly(EGDMA-*H*VIM)]$^{n+}$ beads at 25ºC, the mmol VIM was determined to be 0.868 per g poly(EGDMA-VIM) beads.

Due to the fact that change in temperature affects the activities of the ions as well as the liquid-junction potentials, shifts in the m values of the titration curves occur with increasing temperature. In the titration curve of the [poly(EGDMA-*H*VIM)]$^{n+}$ beads, only a single inflection point exists because the VIM groups in the poly(EGDMA-VIM) chain have one protonable amine group. Log K values of the VIM ligand (L) were calculated from potentiometric data using BEST software at 25ºC, 45ºC, and 65ºC and are provided in Table 2. Values listed in this table can be described by the following equations:

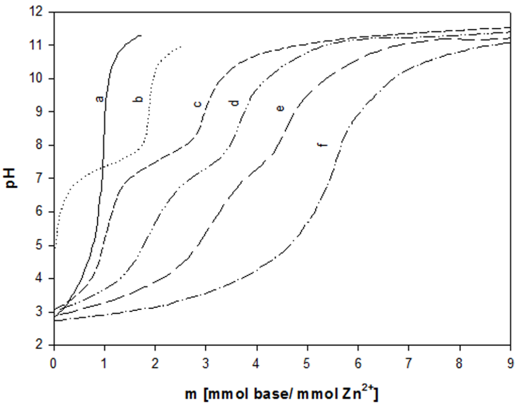

Figure 3. The titration curves of a) [poly(EGDMA-*H*VIM)]$^{n+}$ beads; b) Zn^{2+} ions; c) (1:1); d) (1:2); e) (1:3); and f) (1:4) Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems at 25 °C.

$$L + H^+ \overset{K}{\longleftrightarrow} [LH]^+ \quad K= [LH^+] / [H^+] [L] \qquad (2)$$

where L and [LH$^+$] symbolize VIM and protonated-VIM in the poly(EGDMA-VIM) chain, respectively. K is the equilibrium constant of the protonation reaction.

Thermodynamic parameters—the enthalpy change (ΔH), the Gibbs energy change (ΔG), *and* the enthalpy change (ΔH) of the protonation processes—were also calculated from potentiometric titration data. The ΔG and ΔH values, which one can use to deduce the entropy changes (ΔS), were also calculated for the protonation process of vinyl imidazole. The enthalpy change (ΔH) for the protonation processes was calculated from the slope of the plot log K vs. 1/T using the graphical representation of the van't Hoff equation:

$$-2{,}303RT\log\{K\} = \Delta H - T\Delta S \qquad (3)$$

or

$$\log\{K\} = \frac{-\Delta H}{2.303R}\left(\frac{1}{T}\right) + \frac{\Delta S}{2.303R} \qquad (4)$$

From the Gibbs energy change ΔG and ΔH values, one can deduce the entropy changes (ΔS) using the well-known relationships (5) and (6):

$$\Delta G = -2{,}303RT\log\{K\} \qquad (5)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (6)$$

where the gas constant R = 8.314 J K^{-1} mol^{-1}, log K is a protonation constant for VIM (L) and T absolute temperature. The thermodynamic parameters of the protonation process of VIM were also recorded in Table 2. From these results, the following conclusions can be made:

(a) The log K values decrease with increasing temperature, i.e. the acidity of the vinyl imidazole ligand (L) increases.

b) A negative value of ΔH indicates that the process is exothermic.

c) A negative value of ΔG indicates that the process is spontaneous.

d) The protonation process for vinyl imidazole (L) has a negative value of ΔS due to the increased order.

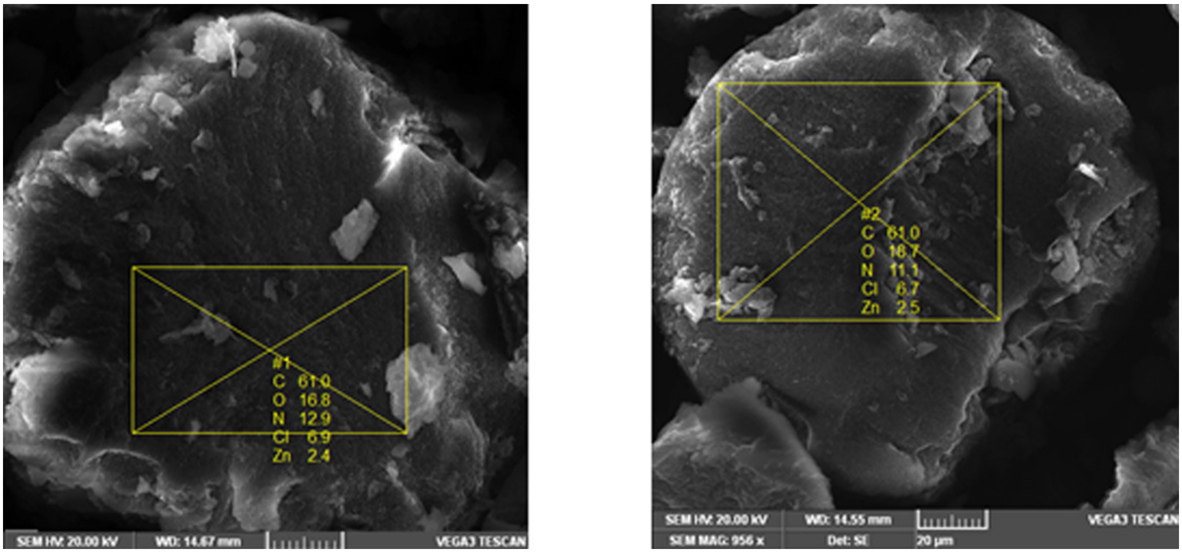

Figure 4. SEM/EDX analysis of Zn^{2+}-chelated poly(EGDMA-VIM) beads prepared at (a) 1:1 and (b) 1:4 Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems.

Analysis of Zn^{2+}-VIM complex formation

Potentiometric titrations of Zn^{2+}:[poly(EGDMA-HVIM)]$^{n+}$ system

In order to clarify the Zn^{2+}-VIM complex formation, potentiometric titrations of Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems were performed. The potentiometric titration experiments were conducted in a 0.1 M NaCl medium for four different Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems, for which metal-to-ligand ratios are (1:1), (1:2), (1:3), and (1:4). The temperature was kept in 25°C. The aqueous solutions containing [poly(EGDMA-*H*VIM)]$^{n+}$ beads and Zn^{2+} ions were also separately titrated with a 0.1 M NaOH solution in a 0.1 M NaCl medium. The titration curves were provided in Figure 3.

Two inflection points were observed in the titration curves of Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems (figures 3 c, d, e, f). While the first inflection points belong to Zn^{2+}-VIM complexes, the second inflection points result from the hydrolysis of Zn^{2+} ions that do not participate in complex formation. When compared with the titration curve of [poly(EGDMA-*H*VIM)]$^{n+}$ beads (Figure 3 a), the shifts in m values that occurred with the first inflections and the decreases in the initial pH values of the titrati-on curves of Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems demonstrate the Zn^{2+}-VIM complex for all of the investigated Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems. When the titration curves regarding (1:1), (1:2), (1:3), and (1:4) Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems were compared with that of Zn^{2+} ions (Figure 3b), it can be said that residual Zn^{2+} ions exist and the hydrolysis of Zn^{2+} ions occurs above a pH of 5.0. The amount of residual Zn^{2+} ions decreased from (1:1) to (1:4) Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems because the ratio of Zn^{2+} to VIM decreased. The presence of residual Zn^{2+} ions at a (1:1) Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ system proves that the stoichiometry of the complexes that formed between Zn^{2+} ions and VIM ligands in the polymeric chain is not 1:1 (Zn^{2+}:VIM). This is because the Zn^{2+} ions in the medium are sufficient to form complexes with all available imidazole groups in the [poly(EGDMA-*H*VIM)]$^{n+}$structure.

Batch studies of Zn^{2+}:[poly(EGDMA-HVIM)]$^{n+}$ system

For the determination of complex stoichiometry, Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems for which

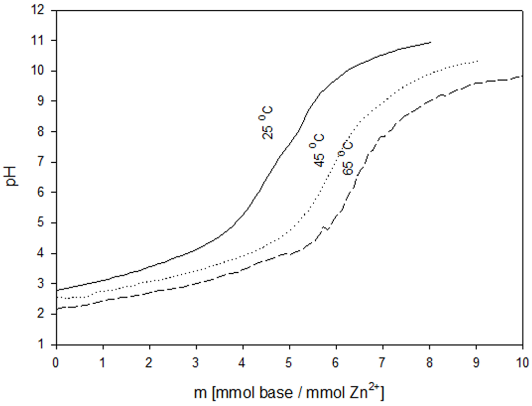

Figure 5. The titration curves of the (1:4) Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ system at 25°C, 45°C, and 65°C.

Table 3. Stability constants (log $\beta \pm \sigma^a$) and thermodynamic functions for the ZnL_2 type complex formation in 0.1 M NaCl ionic medium at 25°C. 45°C and 65°C.

Complex type	Temperature (K)	Stability constants (log $\beta \pm \sigma^a$)	Gibbs Energy Change ΔG^0 (kj/mol)	Enthalpy Change ΔH^0 (kj/mol)	Entrophy Change ΔS^0 (J/mol K)
ZnL	298	5.82±0.08	-4.361	-10.36	-19.88
	318	4.86±0.17	-4.180		
	338	3.54±0.17	-3.552		

Zn^{2+}:VIM ratios are (1:1), (1:2), (1:3), and (1:4) were also studied in batch systems. The Zn^{2+}-chelated poly(EGDMA-VIM) beads were prepared by incubating the poly(EGDMA-*H*VIM)]$^{n+}$ beads in the Zn^{2+} ion solutions. Then, the Zn^{2+}-chelated poly(EGDMA-VIM) beads were separated from the medium. The concentration of the Zn^{2+} ions in the resulting solutions were determined and used for the calculation of Zn^{2+}-VIM complex stoichiometry. It was shown that 2.13, 2.33, 1.84, and 2.20 vinyl imidazole ligand binds per one Zn^{2+} ion on Zn^{2+}-chelated poly(EGDMA-VIM) beads prepared at (1:1), (1:2), (1:3), and (1:4) Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems, respectively. These results show that two vinyl imidazole ligands in the polymeric chain are bound to the one Zn^{2+} ion. In other words, two imidazole groups are close enough to form a complex with the same Zn^{2+} ion, thus providing significant strength of an interaction in the poly(EGDMA-VIM) structure. The results obtained for soluble linear poly(VIM) support these findings [20].

SEM/EDX analysis of Zn^{2+}-chelated beads

In conjunction with generating SEM images, the electrons generate X-rays from the surface of the materials in the sample. The X-rays emitted from the sample can be interpreted using EDX to determine the elements (atoms) of which the surface of the sample is composed as well as the elemental composition of the features on the sample. In order to get information on the surface composition of the Zn^{2+}-chelated poly(EGDMA-VIM) beads, SEM/EDX analysis was conducted for the beads prepared at (1:1) and (1:4) Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ systems. The SEM photographs coupled with surface elemental compositions are given in Figure 4. As can be seen from the figure, surface composition is not significantly changed with a decrease in the Zn^{2+}:VIM ratio. The findings also support that a particular complexation manner in the Zn^{2+}-VIM complex exists in the poly(EGDMA-VIM) chain.

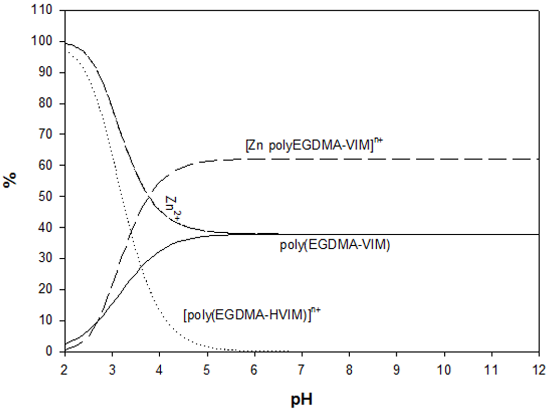

Figure 6. The distribution curves of Zn^{2+} and their coordination species at the Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ system (metal-to-ligand ratio of 1:4).

Determination of the stability constant and thermodynamic parameters

Until now, a limited number of studies have concentrated on Zn^{2+}-vinyl imidazole complex formation [32]. Moreover, none of them were related to Zn^{2+}-vinyl imidazole interaction in insoluble polymer matrix. The poly(EGDMA-VIM) polymer is the first chromatografic adsorbent for which vinyl imidazole can be used as a chelating ligand in the immobilized metal ion affinity. The stability constants (log β) of the ZnL_2 (L is VIM) type complex formation at 25°C, 45°C, and 65°C were calculated using the BEST computer program using the potentiometic titration data from the (1:4) Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ system. The mole ratio of (1:4) was used for the stability constants formation because the amount of residual Zn^{2+} ions is minimal. The titration curves of the (1:4) system at three different temperatures are given in Figure 5. The log β values and thermodynamic parameters for the ZnL_2-type complex formation are provided in Table 3.

When one Zn^{2+} ion binds to two imidazole ligands, the stability constant (log β) of the ZnL_2-type complex was determined to be 5.82±0.08 at 25°C in a 0.1 N NaCl ionic medium. Complexation equilibria of Zn^{2+} ions with linear water-soluble poly(vinyl imidazole) has been investigated potentiometrically. The stability constant (log β_2) of the Zn^{2+} ion complex was reported to be 4.37 for two vinyl imidazole ligands binding to one Zn^{2+} ion [20]. The stability constant value of the ZnL_2-type complex in a poly(EGDMA-VIM) chain is higher than that of the linear poly(VIM). This result shows that cross-linked three dimensional polymeric structure enables more stable complex.

The thermodynamic parameters of the complexation process of vinyl imidazole were calculated according to Equations (3), (4), (5), and (6) and recorded in Table 3. Examination of these values shows that:

a) The stability constants for adsorbent-linked vinyl imidazole complexes decrease with increasing temperature, which means that the stability of the complexes decreases at higher temperatures.
b) The negative value of ΔG for the complexation process suggests the spontaneous nature of such a process.
c) The ΔH values are negative, meaning that these processes are exothermic and unfavorable at higher temperatures.
d) The ΔS values for the ligand complexes are negative, confirming that the complex formation is entropically unfavorable.

The distribution curves of Zn^{2+} and their coordination species that form at the Zn^{2+}:[poly(EGDMA-*H*VIM)]$^{n+}$ system (1:2) were prepared by SPE system and are shown in Figure 6. As can be seen from the distribution curves, 65% of the Zn^{2+} ions participate in the complex formation. The complex formation occurs at a pH of 5.0, and 65% of the [poly(EGDMA-*H*VIM)]$^{n+}$ take part in the complex formation.

Kinetic analysis of complex formation

For testing the dynamic experimental data, the pseudo-first-order kinetic model [33], the pseudo-second-order kinetic model [34], the modified Ritchie's-second-order kinetic model [35] and the intraparticle diffusion model [36] were used at the initial concentration—0,01 M, of Zn^{2+} ions and three temperatures (298, 308, and 318 K) at a pH of 5.0.

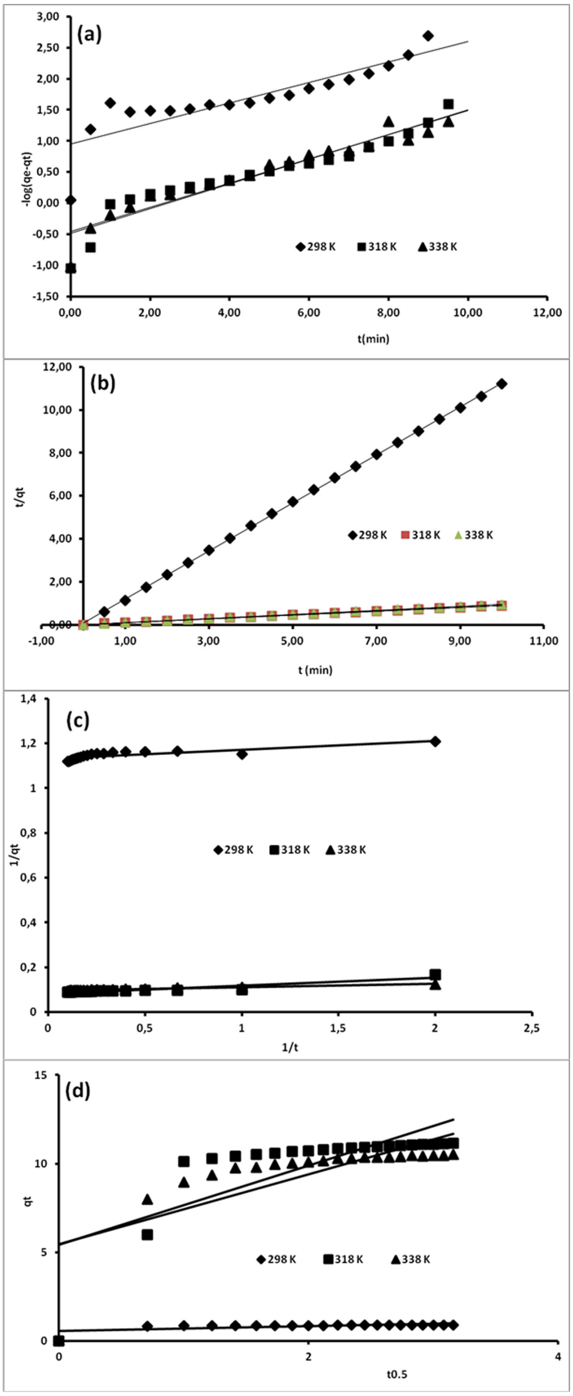

Figure 7. Formation kinetics of the Zn^{2+}-VIM complex at different temperatures: (a) pseudo-first-order, (b) pseudo-second-order, (c) Ritchie's-second-order, and (d) intraparticle diffusion.

Table 4 . Kinetic parameters for the complex formation between Zn^{2+} ions and VIM ligands.

Parameters		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model				Ritchie's-second-order kinetic model			Intraparticle diffusion model	
	Experimental												
Temperature (K)	q_e (mg/g)	k_1x10^{-1} (1/min)	q_{eq} (mg/g)	R^2	h ((mg/g)/min)	k_2 ((g/mg)/min)	q_{eq}(mg/g)	R^2	k_R (1/min)	q_{eq} (mg/g)	R^2	k_ix10^{-1}((mg/g)/min$^{0.5}$)	R^2
298	0.8603	37.86	0.3868	0.7389	91.84	13.59	0.8951	0.9998	28.29	0.8839	0.7159	1.391	0.3836
318	10.43	45.60	1.623	0.8905	17.21	0.4543	11.31	0.9994	2.418	11.92	0.8582	22.43	0.5609
338	9.756	44.82	1.575	0.9203	10.64	0.5388	10.64	0.9998	5.906	10.58	0.9857	19.70	0.5452

The pseudo-first-order kinetic model of Lagergren is given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

where q_e and q_t (mg/g) are the amounts of the Zn^{2+} ions binding at the equilibrium and at time (min), respectively. k_1 (1/min) is the rate constant of the pseudo-first-order adsorption, and q_e is the binding capacity at the equilibrium. The pseudo-second-order kinetic model can be expressed as :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where q_e and q_t (mg/g) have the same definitions as in Equation (7), and k_2 is the pseudo-second-order rate constant at the equilibrium [(g/mg)/min]. The initial complexation rate h ((mg/g)/min) can be determined from k_2 and q_e values using the following equation:

$$h = k_2 q_e^2 \quad (9)$$

The modified Ritchie's-second-order kinetic model:

$$\frac{1}{q_t} = \frac{1}{k_R\, q_e\, t} + \frac{1}{q_e} \quad (10)$$

where q_t and q_e (mg/g) have the same definitions as in Equation (7) and k_R is the rate constant (1/min) of the modified Ritchie's-second-order kinetic model.

The intraparticle diffusion model can be described as :

$$q_t = k_i\, t^{1/2} \quad (11)$$

where q_t (mg/g) has the same definitions as in Equation (7), and k_i is the intraparticle diffusion rate constant [(mg/g)/min$^{1/2}$].

The values of constants in equations (7), (8), (10), and (11) can be obtained from the slopes and intercepts of the fitted curves (Figure 7), and the results are shown in Table 4. The highest correlation coefficient values (0.9999) of the pseudo-second-order model for all of the studied temperatures and the closest q_e (experimental) to q_e (calculated) indicated the second-order nature of the present complexation process.

CONCLUSIONS

In this study, we present the experimental results of the interaction of Zn^{+2} ions with poly(ethylene glycol dimethacrylate-n-vinyl imidazole). Poly(EGDMA-VIM) microbeads were synthesized by suspension polymerization and characterized using N_2 adsorption/desorption isotherms, elemental analysis, an SEM, EDS or EDX, and swelling studies. The protonation constants of VIM and the thermodynamic parameters of the protonation process were calculated at three different temperatures. The values of the protonation constants decreased with increasing temperature. ΔG, ΔH and ΔS values showed that the protonation process is spontaneous, exothermic, and entropically unfavorable. The stoichiometry of the Zn^{2+}-VIM complex was also determined. In the poly(EGDMA-VIM) chain, two vinyl imidazole groups bind to one Zn^{2+} ion. The stability constants and thermodynamic parameters (ΔG, ΔH and ΔS) of the ZnL_2-type complex formation were calculated first in the literature. The results show that the complex formation occurs spontaneously and that the formation process is exothermic and entropically unfavorable. The complex formation process could be best described by the pseudo-second-order kinetic model. Overall, the findings presented in this study are first in the literature for vinyl imidazole containing a solid IMA chromatography matrix.

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