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Thermal Behaviour of Pb (II) Ion Imprinted Interpenetrating Polymer Networks

Girija P.

Associate Professor, Department of Chemistry, S D College, Alappuzha, Kerala, India

Beena Mathew

Associate Professor, School of Chemical Sciences, Mahathma Gandhi University, Kottayam, Kerala, India

Abstract:

Thermogravimetric studies of Pb(II) ion imprinted interpenetrating polymer networks were described. The relative thermal stabilities, decomposition patterns and the kinetic parameters of decomposition of the imprinted, non-imprinted and Pb(II) ion bound polymer networks were followed. Thermal stability of Pb(II) ion bound polymer network is higher compared to Pb(II) ion desorbed polymer.

1. Introduction

Thermogravimetry of metal ion imprinted polymers can reveal the thermal stability acquired by binding with metal ionsⁱ. The thermal stability varies with metal ions and the structure of metal ion imprinted polymers. The thermal stabilities depend on the characteristics of functional polymers and the bound metal ionⁱⁱ. Naturally occurring biopolymers like alginate, extracted from algae, have been known to exhibit excellent adsorption ability for metal ionsⁱⁱⁱ. Due to biodegradable nature and renewable resource of alginate, it could replace synthetic polymer in many applications. Therefore, their thermal degradation and kinetics is very much important. The present paper describes the thermal decomposition behavior of the Pb(II) ion imprinted interpenetrating polymer networks prepared from alginic acid and crosslinked polyacrylamide.

2. Experimental

The Pb(II) ion imprinted and non-imprinted interpenetrating polymer networks were prepared by using alginic acid and functional monomer acrylamide, NNMBMA as crosslinker in presence of initiator potassium persulphate. Fourier transform infrared (FTIR) spectra of the metal ion imprinted, non-imprinted, and the Pb(II) ion bound polymers were recorded between 4000-400 cm⁻¹, using a Perkin Elmer 400 FTIR spectrophotometer. TG curves were recorded on a Shimadzu D-740 thermal analyzer at a heating rate of 10°C/min from 30-900°C under nitrogen atmosphere.

Scheme

3. Results and Discussions

The Pb(II) ion imprinted, non-imprinted and their metal bound polymers were subjected to thermo analytical studies.

The major decomposition was used for the kinetic analysis. The kinetic parameters for the thermal decomposition of metal ion desorbed imprinted and bound polymers were evaluated by the reported integral^{iv} and approximation^v methods using the least square method. The integral equation was used in the form

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - E_a/RT \quad (1)$$

and the approximation equation as:

$$\ln \frac{g(\alpha)}{T^{1.921}} = \ln \left(\frac{AE}{\beta R} \right) + 3.772050 - 1.921503 \ln E - 0.120394 \left(\frac{E}{T} \right) \quad (2)$$

3.1. Characterization

FTIR spectrum of Pb(II) ion imprinted IPN showed absorption at 1627cm⁻¹ which is assigned to carboxyl group of alginic acid and this is shifted to 1638 cm⁻¹ in Pb(II) ion bound polymer networks. This result revealed that carboxyl group of alginate has participated in Pb(II) ion adsorption process. C-H stretching vibrations of both Pb(II) ion imprinted and non-imprinted interpenetrating polymer networks are seen around 2930 and 1514 cm⁻¹ respectively.

3.2. UV-vis. Spectra

The structure and geometry of a metal ion imprinted polymer are largely determined by the microenvironment of the polymer domain. UV-vis. spectrum of Pb(II) ion bound polymer is shown in figure 1. As a result of the interaction of Pb(II) ion with the nonbonding electrons of carboxyl group of alginate chain, a shift in the wavelength maxima takes place [30]. This may be due to $n \rightarrow \pi^*$ transition. Pb(II) ion bound polymer showed bands at 616, 487 and 260 nm. In Pb(II) ion bound MIP these bands are observed at 665 and 370 nm. These bands indicate ligand metal charge transition and $\pi \rightarrow \pi^*$ transitions.

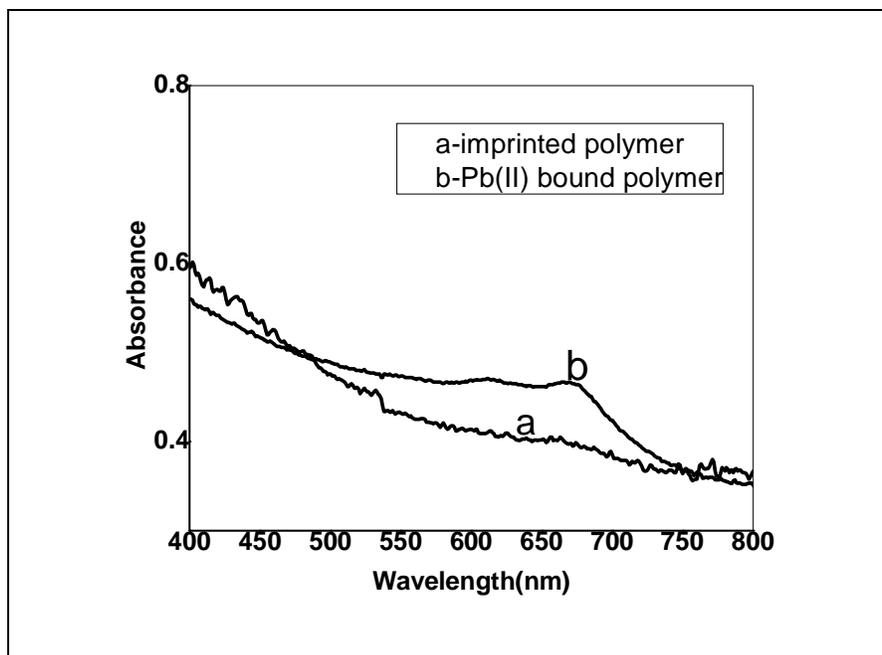


Figure 1: UV- vis. spectra of Pb(II) imprinted and Pb(II) ion bound polymers

3.3. Thermogravimetric Analysis

TG curves of imprinted, non-imprinted and the corresponding Pb(II) ion bound interpenetrating polymer networks reveal the variation of thermal stability with Pb(II) ion binding (figure 2). The thermal decomposition behavior of a metal ion bound polymer depends on the macromolecular characteristics of the polymer support and the type of coordination geometry.^{vi} The thermal decompositions of imprinted and non-imprinted polymer networks showed three stages and their corresponding Pb(II) ion bound polymer networks two stages. In all the cases, the first stage decomposition corresponds to decomposition of the carboxylate group or uncomplexed ligands. The second stage is the major decomposition in which polymer chain breaks and leaving only the metallic residue. According to thermogravimetric analysis imprinted polymer supports 5% weight loss at about 27-100°C due to adsorbed water and the second stage decomposition in the range 110-240°C, which is ascribed to the removal of carboxylate ion or uncomplexed ligands. During the third stage of decomposition at 270-480°C, 56% weight loss is observed, which is attributed to the decomposition of polymer chain. The DTG peak temperature obtained at 408.9°C. While in Pb(II) ion bound IPNs there are 3 stages of decomposition, major decomposition was in the second stage in the range 380-480°C, resulting a mass loss of 40%. The decomposition finishes at 900°C, leaving metallic residue.

TG curves of non-imprinted polymers also showed 4 stages of decomposition. The first decomposition was in the temperature range 30-100°C leaving a mass loss of 15% corresponds to adsorbed water. The second stage decomposition occurs in the range 150-425°C leaving 25% mass loss corresponding to uncomplexed ligands. The third stage is the major decomposition corresponding to 54% mass loss due to polymer rupture. The DTG peak is at 398°C. The decomposition ends at 899.5°C.

In Pb(II) bound non imprinted polymer, the first stage decomposition up to 105°C corresponds to a mass loss of 20% due to adsorbed water, the second stage takes place at 220-300°C leaving 20% mass loss due to the removal of uncomplexed ligands. The third stage decomposition takes place at 305-400°C, leaving a mass loss of 40%, due to the rupture of polymer chain. This also supports the thermal stability of Pb(II) ion bound inter penetrating polymer networks than that of non-bounded polymers. The major decomposition was used for the kinetic analysis.

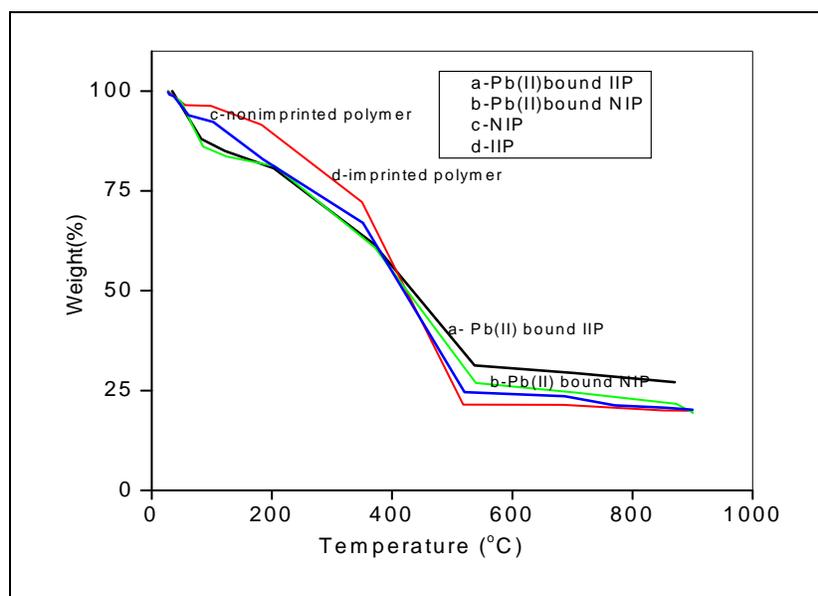


Figure 2: TG curves of Pb(II) ion bound and unbound polymers

Polymer	Decomposition temperature range in TG(°C)		Peak temperature in DTG(°C)	Mass loss(%)
IIP	266	486	395.05	58
NIP	276	410	398.18	54
Pb(II) IIP	286	486	408.90	44
Pb(II) NIP	288	488	390.00	45

Table 1: Phenomenological data for the second stage decomposition of Pb(II) ion imprinted polymers

The phenomenological data for the second stage decomposition of metal ion desorbed ion imprinted, non-imprinted and Pb(II) ion bound polymers are given in Table IV.1. The activation energy, pre-exponential factor, entropy of activation and correlation coefficient are given in Table IV.2. For Pb(II) ion imprinted polymer the temperature range is from 266-486°C with a temperature interval of 220°C. The activation energy obtained according to equation 1 and 2 for imprinted polymer is 14.6 and 14.4 kJ/mole respectively. The same polymer after binding Pb(II) ion the decomposition temperature range is from 286 to 486°C with a temperature interval of 200°C. The activation energy obtained according to equation (1) and (2) for imprinted polymer with Pb(II) ions are 16.28 and 15.57 kJ/mole respectively. The activation energy increases on metal ion binding. This is due to the fact that the thermal stability increases in Pb(II) ion bound polymers and more energy is required for the decomposition.

Polymer	Integral Equation (1)				Approximation Equation (2)			
	E (kJ/mol)	A (S ⁻¹)	ΔS (J)	R	E (kJ/mole)	A (S ⁻¹)	ΔS (J)	R
A	14.61	1.7X10 ⁻³	-304	0.99	14.41	1.03X10 ⁻³	-312	0.99
B	10.23	1.9X10 ⁻⁴	-315	0.99	13.78	1.70X10 ⁻³	-308	0.99
C	32.41	5.8X10 ⁻⁴	-314	0.99	32.44	3.05X10 ⁻⁶	-310	0.99
D	16.28	3.6X10 ⁻³	-298	0.99	15.57	1.90X10 ⁻³	-311	0.99

Table 2: Kinetic parameters of Pb(II) ion imprinted and non-imprinted polymers

(A) - Imprinted polymer, (B) - Non-imprinted polymer, (C) - Pb(II) ion bound imprinted polymer, (D) - Pb(II) ion bound non-imprinted polymer.

The entropy of activation is negative for all polymers. The entropy values of bound polymers are higher than that of unbound polymers. This indicates the increase of randomness during the binding process. The activation energy of non-imprinted polymers is lower than that of ion imprinted polymer, suggesting lower thermal stability. In metal ion bound non-imprinted polymer activation energy is lower than the corresponding metal bound imprinted polymer. The entropy of activation of metal bound imprinted polymers is higher than that of the corresponding non-imprinted metal bound polymer.

4. Conclusion

The Pb(II) ion imprinted polymeric system exhibited much higher value in activation energy suggesting more thermal stability for Pb(II) ion imprinted polymers. Thermal stability increases on metal ion binding. The extra stability of the imprinted polymer-metal complexes arises from the formation of stable ring structures of the metal complexes. The more positive value of entropy of activation suggests the distortion of the polymer chains from their normal position for complexation with metal ions.

5. References

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