

Polymer-supported urea: The effect of hydrogen bonding on lanthanide ion affinities

Yijia Yang, Spiro D. Alexandratos*

Department of Chemistry, Hunter College of the City University of New York, 695 Park Ave., New York, NY 10065, USA

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ABSTRACT

Hydrogen bonding has been proposed as the triggering mechanism for the sorption of lanthanide ions by polymer-supported tetramethylmalonamide (TMMA) and diethylenetriamine (DETA) – substituted malonate ester. In the current study, DETA was immobilized onto cross-linked poly(vinylbenzyl chloride), converted to the urea, and its affinity determined for lanthanide ions from solutions of 2–8 M HCl. Lanthanide affinities significantly increase when the acid concentration exceeds 4 M. The site at which sorption occurs forms after protonation of the carbonyl, stabilization by hydrogen bonding to the interior nitrogen and resultant formation of an iminium ion. This is consistent with the mechanism proposed for the amide polymers. TMMA has the weakest affinities for Ln(III) ions yet is most selective due to attenuation of the (+) charge at the iminium site by two electron-donating methyl groups (=NR₂(+)); DETA-malonamide (MAM) has higher Ln(III) affinities than TMMA but is less selective because the iminium has only one –CH₂– moiety attenuating the (+) charge (=NHR(+)); the urea also forms a secondary iminium but its higher basicity makes its iminium more positively charged than that in DETA–MAM and therefore a stronger ligand. The urea has the highest affinities and is unique in having the lanthanide distribution coefficients correlate with the sum of the first, second and third ionization energies. The implication of this for the sorption mechanism is discussed.

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1. Introduction

Ionic recognition is an essential mechanism within biological systems [1]. Small molecules capable of ionic recognition have many applications in medicine, [2,3] sensor technology, [4] and environmental remediation [5]. The benefits of immobilizing ion-selective ligands onto cross-linked polymers include ease of operation, an absence of organic solvent, regenerability, and no loss of complexant [6].

Lanthanide/actinide separations and recovery of individual lanthanides from within the series have implications for the nuclear fuel cycle [7] and radiochemical applications [8]. The focus of this research is the development of polymer-supported complexants for lanthanide separations. Immobilized *N,N,N',N'*-tetramethylmalonamide (TMMA) displays ionic recognition among the lanthanides since maximum affinities are evident toward the middle of the series [9]. The bell-shaped trend is caused by a shift in the dominant interaction from metal–ligand electrostatic attraction to metal–aqueous-phase affinity (quantified by the enthalpy of dehydration) as the series passes Eu(III). Results with TMMA and diethylenetriamine-substituted malonate monoamide (DETA–MAM) suggest that hydrogen bonding triggers formation of an iminium ion which then becomes the site of ion exchange [9,10].

The complexation mechanism consists of protonation of one of the carbonyls, which is stabilized by hydrogen bonding to the neighboring carbonyl, formation of the iminium site (confirmed by FTIR spectra [11]) and ion exchange of the chloride ion with the lanthanide chlorocomplex. TMMA, with two electron-donating methyl groups moderating the positive charge density at the iminium site is a weaker ligand than DETA–MAM which has only one methylene moiety on its amide nitrogen. The reduced ligand strength makes TMMA more responsive to changes between electrostatic attraction and dehydration enthalpy and leads to maximum affinities within the lanthanide series.

Ureas form stronger hydrogen bonds than amides: this is the basis for the higher melting points of ureas relative to comparable amides [12]. Shifts in FTIR spectra indicate a greater basicity for ureas relative to amides, resulting in the stronger hydrogen bonds [13]. Since hydrogen bonding is central to the affinities displayed by amides for the lanthanide ions from acidic solution, the current report extends the study to the urea ligand in order to determine the effect of its greater basicity on the lanthanide ion affinities.

2. Experimental

2.1. Materials

All chemicals were obtained from Sigma–Aldrich or Acros Chemical and used without further purification unless otherwise

* Corresponding author.

E-mail address: alexsd@hunter.cuny.edu (S.D. Alexandratos).

noted. The preparation of poly(vinylbenzyl chloride) [polyVBC] beads has been described [14]. A particle size of 0.25–0.42 mm was used. Reactions at other than room temperature or reflux were regulated with a temperature controller. Water for metal ion studies and analytical determinations was filtered through a Millipore Direct Q-5 system and had a resistivity of 18.2 M Ω -cm.

2.2. Synthesis of the primary amine

PolyVBC (8.0 g) was swelled in 50 mL of *N*-methyl-pyrrolidone (NMP) for 2 h before mixing with 40.0 g potassium phthalimide and 200 mL NMP. The mixture was stirred at 80 °C for 17 h. The beads were recovered and washed with NMP, water and MeOH; then 100 mL MeOH, 10 mL water, and 50 mL hydrazine monohydrate were added. The mixture was stirred at 65 °C for 17 h. The beads were recovered and washed with MeOH and water, placed in a glass frit funnel, and conditioned with 1 L of H₂O, 1 M NaOH, H₂O, 1 M HCl, and H₂O.

2.3. Synthesis of immobilized diethylenetriamine (DETA)

PolyVBC (5.0 g) was swelled in 100 mL NMP for 2 h before stirring with 50 mL DETA at 80 °C for 17 h. The beads were recovered, washed with NMP, water and MeOH, placed in a glass frit funnel and conditioned as above.

2.4. Synthesis of immobilized urea

The synthesis follows a published procedure [15]. DETA (2.0 g) was stirred with 40 mL conc. HCl at room temperature for 1 h, the HCl removed, and the beads washed with 100 mL water. Aqueous potassium cyanate (20 mL, 20% w/w solution) was added to the beads and the reaction was stirred at room temperature for 17 h. The beads were recovered, washed with saturated sodium bicarbonate and water, placed in a glass frit funnel and conditioned as above. The procedure was repeated with the primary amine.

2.5. Characterization

The polymers were characterized by FTIR spectra, percent solids, and acid, chlorine, and nitrogen capacities. The spectra were obtained on a Bomem MB series FTIR. KBr pellets were prepared

with 0.01 g of polymer and 0.001 g of KBr followed by grinding and compression.

2.6. Metal ion sorption

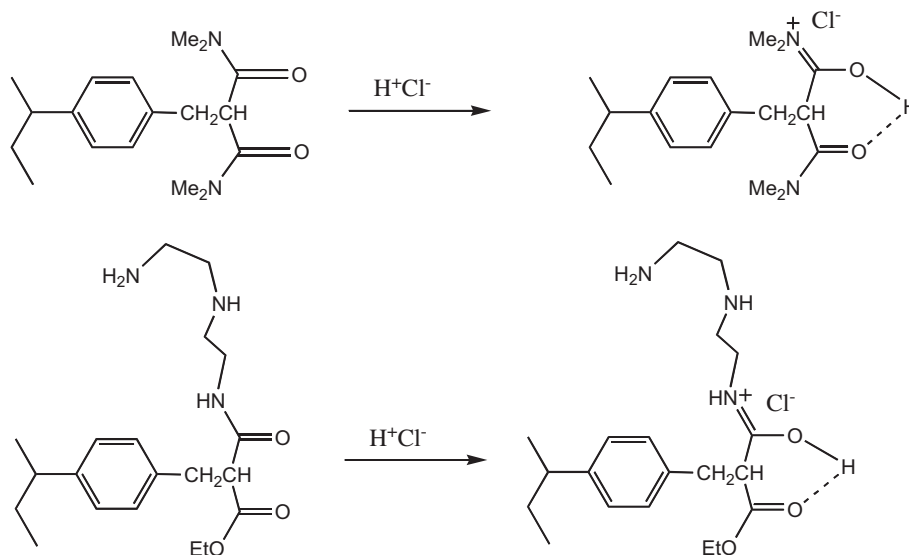
Polymer (0.10 g) was contacted with 5 mL of 10⁻⁴ N solutions of La(III), Ce(III), Nd(III), Eu(III), Tb(III), Ho(III), Yb(III), and Lu(III) chlorides in 2, 4, 6, and 8 M HCl for 17 h on a digital orbital shaker (VWR, DS-500) at a speed of 200 rpm. Each polymer was pre-equilibrated with a solution of HCl of the same acidity as the metal-containing solution. The amount of metal sorbed at equilibrium was determined with an inductively coupled plasma–optical emission spectrometer (Spectroflame M 120E). The results are tabulated as distribution coefficients, *D*, defined as [(mmol Mⁿ⁺)_{polymer}/g_{polymer}]/[(mmol Mⁿ⁺)_{soln}/mL_{soln}] and thus have units of mL/g. Single ion studies are appropriate for fundamental studies in which the focus is on ligand–ion interactions [16].

3. Results

Urea polymers were produced in two ways. The primary amine was prepared first via the Gabriel synthesis (Scheme 2). Complete functionalization is indicated by comparison of the experimental and theoretical nitrogen capacities (5.75 and 5.68 mmol/g, respectively) and the absence of chlorine. Subsequent reaction with KNCO gave the urea with experimental and theoretical nitrogen capacities of 10.3 and 10.9 mmol/g, respectively (Scheme 2). This polymer will be referred to as urea-1.

The DETA polymer was prepared by aminating polyVBC (Scheme 3). Its experimental nitrogen capacity (8.72 mmol/g) is lower than theoretical (9.90 mmol/g) and indicates ~10% bridging by DETA of two benzyl groups. Reaction with KNCO in the next step gave the urea (Scheme 3). The nitrogen capacity of the product (12.0 mmol/g) suggests a ligand with one urea per ligand (11.6 mmol/g, calculated). Since DETA is more reactive at the primary site (e.g., carbon dioxide reacts only at the primary amine [17]), the product is most likely as written in Scheme 3. This polymer will be referred to as urea-3.

FTIR spectra of urea-1 and urea-3 show the carbonyl band at 1645 cm⁻¹, bands at 1437–1452 cm⁻¹ for the asymmetric C–H bend, and a band at 3100–3500 cm⁻¹ for the N–H stretch.



Scheme 1. Formation of the site of ion exchange in the TMMA and DETA–MAM polymers.

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