

# Effect of macrocyclic lactam receptors on extraction of heavy metals and chromate anions

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**Abstract** The article presents the syntheses and extraction properties of new lactam ionophores. These lactam derivatives were easily synthesized via aminolysis of 2,2'-methylenebis(4-chlorophenol) dimethylester with corresponding diamine compounds in methanol–dichloromethane solvent systems at one step, respectively. The extraction studies of lactam ionophores were performed toward dichromate anion and alkaline and transition metals such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ . All the structures of the ionophores were confirmed by spectroscopic techniques and elemental analysis.

**Keywords** Lactam · Chromate extraction · Picrate extraction · Liquid–liquid extraction

## Introduction

Ground water is contaminated with toxic anions and heavy metals due to wastewaters of industrial applications such as fertilizer, pharmaceutical, leather tanning, petroleum refinery, metal processing and dyeing related industries. These type unwanted chemicals causes health problems, when they exceed tolerance limit in water [1]. For example, Chromate and dichromate anions are important because of their high toxicity [2, 3] and also because of their presence in soils and waters [4]. Hexavalent chromium (Cr(VI)) compound are known human carcinogens and have been shown to cause different types of DNA damage, with chromates and dichromates being both mutagenic and

genotoxic. Chromium(VI) requires intracellular reduction for activation, and this in vivo reduction can produce several reactive intermediates such as chromium(V) and chromium(IV) that can target and damage DNA [5]. Chromate and dichromate ( $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) are dianions with oxide functionalities at their periphery. Nevertheless, since the periphery of the anions has oxide moieties, these are potential sites for hydrogen. Chromium(VI) can be toxic as it can diffuse as  $\text{Cr}_2\text{O}_7^{2-}$  or  $\text{HCr}_2\text{O}_7^-$  through cell membranes, and oxidize biological molecules [6]. The maximum permissible levels of Cr(VI) in potable and industrial wastewaters are 0.05 and 0.25 mg/L, respectively [7]. Due to its high solubility, Cr(VI) is very toxic to living organisms compared to Cr(III) [8]. When Cr(VI) is ingested beyond the maximum concentration, it can cause health disorders, such as vomiting and hemorrhage [9]. Therefore, treatment of wastewater containing Cr(VI) prior to discharge is essential. Selectivity signaling of toxic anions is a very important topic for the detection and treatment of the toxic anions in various chemical systems. Furthermore, Toxic metals such as Cd, Hg and Pb are mostly take place in the environment due to natural phenomenon as well as human activities. These metal ions are mostly present in the environment due to fossil fuel combustion, paint, battery and fertilizer industries as well as oil refineries, smelting plants and wastewater [10]. These highly toxic metals are known to cause health problems such as brain damage [11–13], nephropathy [14, 15], sluggishness [10], hyperirritability [16], restlessness [17], infertility [18] and a number of diseases in early aged children [19]. Recently, molecular receptors capable of interacting selectively with toxic anions and cations have been described. For example, many crown ethers were developed for the selective recognition of metal ions and amine salts [20–22]. Both the strength of binding and the

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degree of ionic or molecular recognition will depend upon both the structural and electronic complementarity between host and guest. While virtually all host–guest systems exhibiting molecular recognition will show some degree of both steric and electronic complementarity. Macrocyclic rings have frequently been used as structural components in both supramolecular and supermolecular systems, especially for binding metal ions [23]. Polyoxalactone, polyazalactone and polyether compounds have received very much attention after quite a number of reports on macrocyclic ethers as multidendate ligands binding most cations. Because they form stable complexes both in solution and in the crystalline form, with salt of alkali and other metals [24] and their role in studies on bioprocesses, catalysis, material science, and transport and separation phenomena [25–27]. Polyoxalactones, polyazalactones and polyethers containing hydrophobic exteriors are lipophilic hosts, which can include cations, especially alkali and alkaline earth metal ions for polyethers and transition metals for polyoxalactones and polyazalactones, into their cavities via an ion–dipole interaction [28, 29]. Though enormous number of lactone and crown ether derivatives and their complexes have already been described, many more interesting systems of this type surely await discovery. Although several works regarding the synthesis and complexation of metal cations and toxic anions with macrocyclic ligands as calixarenes and crown ethers present in the literature, number of studies dealing with their complexation between dichromate anion and lactam based receptors is very few.

Therefore, the main focus of this work is the design of new lactam derivatives based ionophores that effectively bind alkali and heavy metals and anions. These ionophores can be useful for multiple applications such as laboratory, clinical, environmental and industrial process analysis. In our previous work [30, 31], we have extended the field of research of design structures based on a polyoxalactone platform for the extraction of alkali ( $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ), transition metal cations ( $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Pb}^{2+}$ ). Herein, we report synthesis and extraction studies of new designed lactam ionophores (**3a–c**) via aminolysis of dimethylester (**2**) with appropriate alkyl diamine derivatives. The bridging of two hydroxy groups at adjacent aromatic rings by diamine units is favored over the bridging of two hydroxy groups at opposite aromatic rings.

## Experimental

### General methods

$^1\text{H}$  spectra were recorded on a Varian 400 MHz spectrometer in  $\text{CDCl}_3$ . Melting points were determined on an

Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. IR spectra were obtained on a Perkin Elmer 1605 FTIR spectrometer using KBr pellets. UV–Vis spectra were obtained on a Shimadzu 160A UV–Vis spectrophotometer. Elemental analyzes were performed using a Leco CHNS-932 analyzer. A Crison MicropH 2002 digital pH meter was used for the pH measurements. Analytical TLC was performed using Merck prepared plates (silica gel 60 F254 on aluminum). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All reagents and starting material used were of standard analytical grade from Fluka, Merck and Aldrich and used without further purification. Dichloromethane was distilled from  $\text{CaCl}_2$  and stored over molecular sieves. Methanol was distilled over  $\text{CaO}$  and stored over molecular sieves. Other commercial grade solvents were distilled, and then stored over molecular sieves. Anions were used as their sodium salts. The drying agent employed was anhydrous  $\text{MgSO}_4$ . All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system. Dimethylester **2** and lactam ionophores **3a–c** was synthesized according to previously described methods [32, 33]. All of the reactions were monitored with thin layer chromatography.

### *Dimethyl 2,2'-(6,6'-methylenebis(2-tert-butyl-4-methyl-6,1-phenylene))bis(oxy)diacetate (2)*

To a suspension of  $\text{K}_2\text{CO}_3$  (11 mmol) in dry acetone (350 mL) was added compound **1** (5 mmol) under a nitrogen atmosphere, and stirred for half an hour at room temperature. Methyl bromoacetate (10.2 mmol) was added dropwise into the mixture by syringe and refluxed for 24 h. Reaction mixture was filtered off and excess solvent was evaporated under reduced pressure and the residue dried in vacuo. The crude product was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  to give light white product **2**. Yield 80%; mp 133 °C; IR (KBr),  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3010–3000 (C–H<sub>aryl</sub>), 2870–2865 (CH<sub>2</sub>), 1750 (CO), 1585–1500 (C=C), 1260 (CO<sub>aryl</sub>), 1165 (CO<sub>alkyl</sub>);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.10 (s, 2H, ArH<sub>meta</sub>); 6.80 (s, 2H, ArH<sub>meta</sub>); 4.80 (s, 4H, O–CH<sub>2</sub>–CO), 4.03 (s, 2H, Ph–CH<sub>2</sub>–Ph), 3.55 (s, 6H, OCH<sub>3</sub>), 2.38 (s, 6H, CH<sub>3</sub>), 1.33 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.3, 151.4, 136.4, 134.9, 131.9, 126.3, 114.8, 70.3, 60.5, 36.7, 31.4, 29.2, 22.7. Mass spec.,  $m/z$  ( $\text{M}^+$ ) (found/calculated) 484.2801/484.2812; Elemental Anal. Calcd. for  $\text{C}_{29}\text{H}_{40}\text{O}_6$ : C, 71.87; H, 8.32. Found: C, 71.81; H, 8.29.

### General procedure for synthesis of lactam ionophores

A solution of the alkyldiamine (3.2 mmol) in methanol (200 mL) was added drop by drop to a solution of the

dimethyl ester compound **2** (1.5 mmol) in dichloromethane (100 mL) for 3 h. The mixture was stirred at room temperature for 48 h and concentrated under reduced pressure. The residue was precipitated with methanol as white powder and solid product was washed with methanol.

#### Lactam ionophore (**3a**)

Yield 65%, mp 136 °C; IR (KBr),  $\nu_{\max}/\text{cm}^{-1}$ : 3010–3000 (C–H<sub>aryl</sub>), 2875–2870 (CH<sub>2</sub>), 1710 (CONH), 1585–1540 (C=C), 1260 (CO<sub>aryl</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.3 (s, 2H, ArH<sub>meta</sub>); 6.9 (s, 2H, ArH<sub>meta</sub>); 5.6 (br s, 2H, CONH), 4.6 (s, 4H, O–CH<sub>2</sub>–CO); 4.0 (s, 2H, Ph–CH<sub>2</sub>–Ph); 3.3 (s, 4H, CH<sub>2</sub>–CH<sub>2</sub>), 2.3 (s, 6H, Ar–CH<sub>3</sub>), 1.3 (s, 18H, *tert*-C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  171.5, 148.4, 133.3, 131.9, 128.0, 126.6, 73.7, 49.1, 35.5, 31.8, 30.3, 21.5; Mass spec.,  $m/z$  (M<sup>+</sup>) (found/calculated) 480.3001/480.3012; Elemental Anal. Calcd. for C<sub>29</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>: C, 72.47; H, 8.39; N, 5.83, Found: C, 72.41; H, 8.41; N, 5.91.

#### Lactam ionophore (**3b**)

Yield 70%, mp 158 °C; IR (KBr),  $\nu_{\max}/\text{cm}^{-1}$ : 3010–3000 (C–H<sub>aryl</sub>), 2875–2860 (CH<sub>2</sub>), 1725 (CONH), 1585–1540 (C=C), 1240 (CO<sub>aryl</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.3 (s, 2H, ArH<sub>meta</sub>); 7.1 (s, 2H, ArH<sub>meta</sub>); 5.8 (br s, 2H, CONH); 4.6 (s, 4H, O–CH<sub>2</sub>–CO); 4.0 (s, 2H, Ph–CH<sub>2</sub>–Ph); 3.1 (t, 4H, CH<sub>2</sub>–CH<sub>2</sub>); 2.3 (s, 6H, Ar–CH<sub>3</sub>); 1.3–1.1 (m, 20H, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub> and *tert*-C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  172.0, 155.4, 134.1, 132.2, 129.6, 128.7, 71.3, 40.1, 35.0, 33.4, 31.7, 28.3, 21.7; Mass spec.,  $m/z$  (M<sup>+</sup>) (found/calculated) 494.3100/494.3112; Elemental Anal. Calcd. for C<sub>30</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>: C, 72.84; H, 8.56; N, 5.66, Found: C, 72.78; H, 8.51; N, 5.62.

#### Lactam ionophore (**3c**)

Yield 55%, mp 176 °C; IR (KBr),  $\nu_{\max}/\text{cm}^{-1}$ : 3010–3000 (C–H<sub>aryl</sub>), 2875–2855 (CH<sub>2</sub>), 1700 (CONH), 1585–1540 (C=C), 1220 (CO<sub>aryl</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.7–7.3 (m, 8H, ArH), 7.1 (s, 2H, ArH<sub>meta</sub>); 5.8 (br s, 2H, CONH), 4.6 (s, 4H, O–CH<sub>2</sub>–CO); 4.0 (s, 2H, Ph–CH<sub>2</sub>–Ph); 2.3 (s, 6H, Ar–CH<sub>3</sub>), 1.3 (s, 18H, *tert*-C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  173.2, 147.9, 138.4, 133.6, 131.9, 128.1, 126.6, 122.7, 74.7, 35.5, 32.1, 28.8, 26.9, 21.6; Mass spec.,  $m/z$  (M<sup>+</sup>) (found/calculated) 556.3303/556.3300; Elemental Anal. Calcd. for C<sub>35</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>: C, 75.51; H, 7.97; N, 5.03, Found: C, 75.58; H, 7.91; N, 5.12.

#### Liquid–liquid extraction

Picrate and dichromate extraction experiments were performed following Pedersen's procedure [34]. 10 mL of a

$2.5 \times 10^{-5}$  M aqueous picrate solution or  $1 \times 10^{-4}$  M dichromate solution (pH of dichromate solution was maintained by 0.01 M KOH/HCl solution) and 10 mL of  $1 \times 10^{-3}$  M solution of compounds (**2** and **3a–c**). In CH<sub>2</sub>Cl<sub>2</sub> were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min then magnetically stirred in a thermostated water-bath at 25 °C for 1 h, and finally left standing for an additional 30 min. The concentration of picrate/dichromate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described [35]. Blank experiments showed that no picrate extraction occurred in the absence of lactam ionophores (**3a–c**). The alkali picrates were prepared as described [36] elsewhere by stepwise addition of a  $2.5 \times 10^{-2}$  M aqueous picric acid solution to a 0.14 M aqueous solution of metal hydroxide, until neutralization which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried in vacuo for 24 h. Transition metal picrates were prepared by stepwise addition of a  $1 \times 10^{-2}$  M of metal nitrate solution to a  $2.5 \times 10^{-5}$  M aqueous picric acid solution and shaken at 25 °C for 1 h.

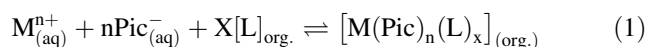
The percent extraction (E%) has been calculated as:

$$E\% = [(A_0 - A)/A_0] \times 100$$

where A<sub>0</sub> and A are the initial and final concentrations of the metal picrate/dichromate before and after the extraction, respectively.

#### Log–log plot analysis

To characterize the extraction ability the dependence of the distribution coefficient D of the cation between the two phases upon the calixarene concentration was examined.



If the general extraction equilibrium is assumed to be given by Eq. 1 the overall extraction equilibrium constant is expressed as Eq. 2.

$$K_{\text{ex}} = \frac{[\text{M}(\text{Pic})_n(\text{L})_x]}{[\text{M}^{n+}][\text{Pic}^-]^n[\text{L}]^x} \quad (2)$$

and the distribution ratio D would be defined by Eq. 3.

$$D = \frac{[\text{M}(\text{Pic})_n(\text{L})_x]}{[\text{M}^{n+}]} \quad (3)$$

one obtains Eq. 4. By introduction it in Eq. 2 and taking log of both sides.

$$\log D = \log (K_{\text{ex}}[\text{Pic}^-]^n) + x \log [\text{L}] \quad (4)$$

With these assumptions a plot of the log D vs. log [L] should be linear and its slope should be equal to the number of ligand molecules per cation in the extraction species.

## Results and discussion

Synthesis of novel lactames **3a–c** were performed by treatment of compound **2** with corresponding amine compounds such as 1,2-diaminoethane, 1,3-diaminopropane and *m*-xylylenediamine for compounds **3a–c**, respectively, in dichloromethane–methanol solutions at room temperature under a nitrogen atmosphere (Scheme 1). All of the host **3a–c** was characterized by IR, NMR spectroscopy and Elemental analysis. Spectroscopic data were in full agreement with those expected. In the IR spectra of the synthesized compounds, diester compound **2** showed characteristic ester peaks at  $1770\text{--}1760\text{ cm}^{-1}$ , while no absorption assignable to hydroxy groups in starting material **1** was observed in the region  $3300\text{--}3500\text{ cm}^{-1}$ . These data can be used to monitor the esterification reaction progress. Furthermore, in the IR spectra of the lactam derivatives **3a–c**, corresponding amide peaks were seen around  $1700\text{--}1725\text{ cm}^{-1}$ . Phenolic hydroxy groups in starting material **1** usually gives rise to a sharp peak at  $\delta$  4–7.5 ppm in the  $^1\text{H}$  NMR spectra, so that the absence of signals in the region  $\delta$  4–7.5 ppm and appearing of new

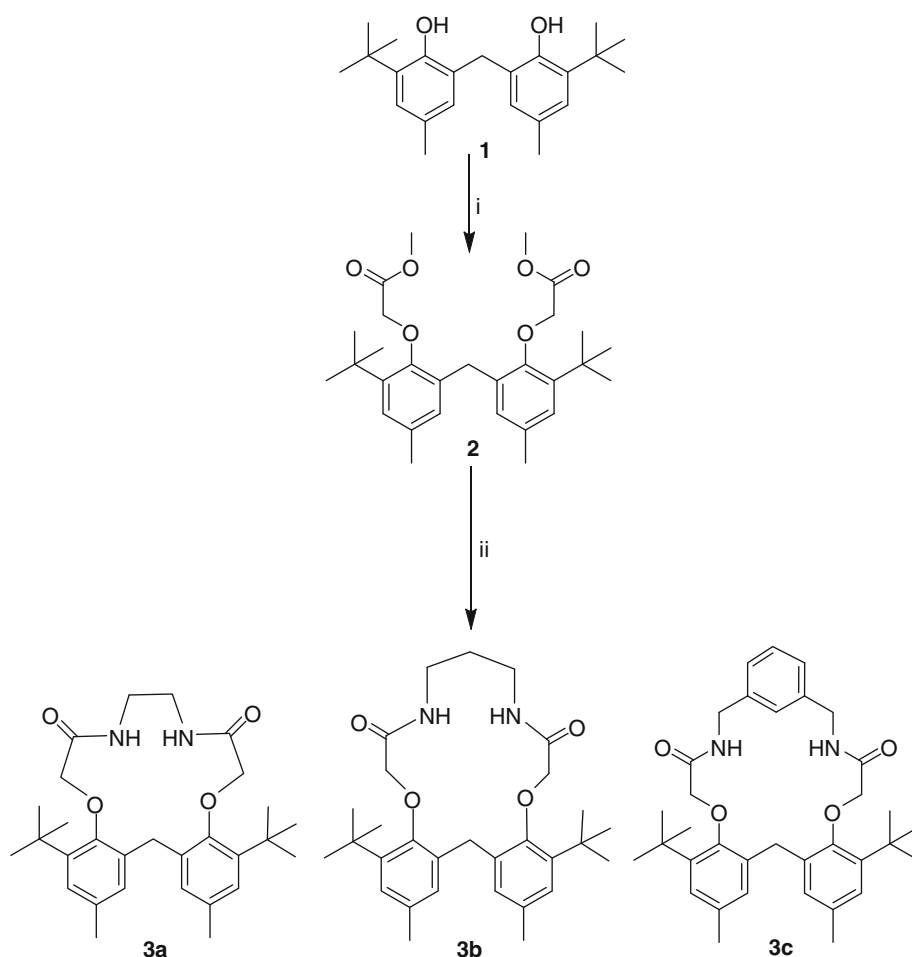
singlet peaks around 3.5 ppm attributable  $-\text{OCH}_3$  and 4.8 ppm attributable  $\text{O}-\text{CH}_2-\text{CO}$  counts in favor of the esterification reaction completion. Furthermore, in the  $^1\text{H}$  NMR spectrum of lactam derivatives **3a–c**, the singlet peak of  $-\text{OCH}_3$  group of compound **2** around 3.5 ppm disappeared as expected and new broad singlet peak attributable NH amide protons appeared around 5.6–5.8 ppm. It was also observed in their IR spectrum, confirming the formation of lactam ionophores **3a–c**. On the other hand, methylene protons in the polyalkyl fragments of **3a–c** were located around  $\delta$  3.3 ppm for **3a**, 1.3–3.1 ppm for **3b** and 4.6 ppm **3c** and methyl bridge protons between phenyl ring were seen around 4.0 ppm. Furthermore, methyl and *tert*-butyl groups of phenyl rings were seen around 1.1–2.3 ppm for receptors **3a–c**.

### Liquid–liquid extraction studies

#### Metal cations

From the extraction data shown in Table 1, neither alkali nor transition metal cations were extracted by the starting

**Scheme 1** (i) Methylbromoacetate,  $\text{K}_2\text{CO}_3$ , acetone, reflux; (ii) corresponding alkyl diamine, dichloromethane/methanol, room temperature



**Table 1** Percentage extraction of alkali and transition metal ions by ionophores **3a–c**

Compound	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Co <sup>2+</sup>	Hg <sup>2+</sup>	Pb <sup>2+</sup>
<b>2</b>	2.0 ± 0.1	3.1 ± 0.1	3.2 ± 0.1	11.1 ± 0.1	70.1 ± 0.1	14.4 ± 0.1
<b>3a</b>	12.2 ± 0.2	10.9 ± 0.2	15.9 ± 0.1	41.5 ± 0.2	78.1 ± 0.1	65.5 ± 0.2
<b>3b</b>	16.4 ± 0.2	11.8 ± 0.2	13.3 ± 0.2	44.3 ± 0.1	81.4 ± 0.2	71.1 ± 0.3
<b>3c</b>	12.5 ± 0.3	13.1 ± 0.1	17.2 ± 0.1	51.2 ± 0.3	80.9 ± 0.2	68.3 ± 0.3

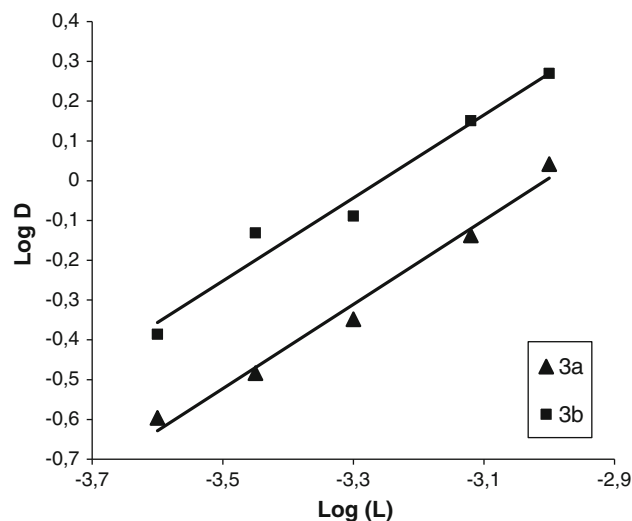
Averages and standard deviations calculated for data obtained from three independent extraction experiments

Aqueous phase: [metal picrate]:  $2.5 \times 10^{-5}$  M; organic phase: dichloromethane, [ligand]:  $1 \times 10^{-3}$  M; at 25 °C, for 1 h

material **1** from aqueous to organic phase. On the introduction of amid groups in lactam ionophores compounds **3a–c** to the two hydroxy groups in starting material **1**, all of these compounds **3a–c** showed a higher affinity toward transition metals such as Co<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup>. However, acyclic compound **2** having esteric groups extracted only Hg<sup>2+</sup>, but alkali metal cations could not be extracted significantly by both lactam ionophores **3a–c** and diester compound **2**. From these observations, we conclude that the size of the macro ring alone does not play a major role in the complexation phenomenon, but the nature and ionic diameter of the metal ions and the effectiveness and aggregation of functional groups are factors in complexation. In the case of ligands **3a–c**, the increased affinity in complexation can be explained by the fact that there is an important role played carbonyl groups having  $\pi$ -electron system and electron-donor nitrogen atoms at the water–dichloromethane interface. Moreover, these phenomenon may reflect the ‘hard and soft acids and bases’ concept introduced by Pearson [37]. As this environment exists due to the presence of  $\pi$ -bonds containing functionalities, where cation– $\pi$  interactions favor the complexation with the more polarizable transition metal ions especially Hg<sup>2+</sup> and Pb<sup>2+</sup> which are known as soft metal cations. Figure 1 shows the extraction into dichloromethane at different concentrations of the ligand **3a** and **3b** for Hg<sup>2+</sup>. A linear relationship between log D versus log [L] is observed with the slope of lines for Hg<sup>2+</sup> by the ligands **3a–b** which is roughly equal to 0.98–0.97, suggesting that the ligands **3a–b** forms a 1:1 complex with Hg<sup>2+</sup>.

#### Chromate anion

The removal of the dichromate anions from water sources gained high attention because of their high toxically affect. Anion recognition and sensing is an increasingly important research topic in supramolecular chemistry due to the importance of various anions in biological and environmental locations. Chromate and dichromate anions are important because of their high toxicity and their presence in soils and waters. The dichromate ions (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/HCr<sub>2</sub>O<sub>7</sub><sup>-</sup>) are anions where the periphery of the anion has



**Fig. 1** Log D versus log [L] for the extraction of Hg picrate by the ligands **3a** and **3b** from an aqueous phase into dichloromethane at 25 °C

oxide moieties. For a molecule to be effective as a host, it is necessary that its structural features are compatible with those of the guest anions. We performed some preliminary evaluations to investigate binding efficiencies of the selected extractants **3a–c** for Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> by using solvent extraction. The results were summarized in Table 2 and Fig. 2.

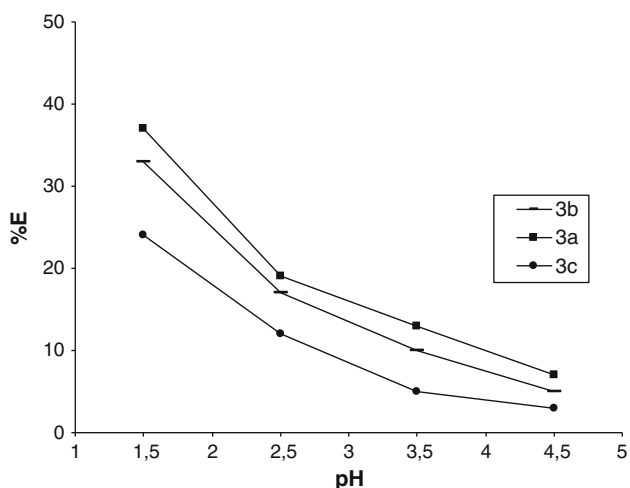
The results showed that Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> could be extracted from aqueous solution into dichloromethane at low pH values. Blank experiments showed that no dichromate anion extraction occurred in the absence of lactam ionophores (**3a–c**). According to our knowledge the obtained data in extraction of **3a–c** can be attributed to a number of reasons. Compounds **3a–c** possesses an amide nitrogen and carbonyl, facilitating hydrogen bonding with the dichromate anion. The next reason is that compounds **3a–c** has a more stable structure because of the bridging of the two amide moieties by alkyl chain. The acidic conditions facilitate the protonation of dichromate anion Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> which in turn interacts with the receptors **3a–c**. Moreover, from the extraction phenomenon it could be concluded that the complexation of dichromate anion just do not depend

**Table 2** Percentage extraction of dichromate ion by ionophores **3a–c** at different pH

Compound	pH			
	1.5	2.5	3.5	4.5
<b>2</b>	<1.0	<1.0	<1.0	<1.0
<b>3a</b>	37.3 ± 0.1	19.5 ± 0.1	13.6 ± 0.1	7.9 ± 0.1
<b>3b</b>	24.5 ± 0.1	12.1 ± 0.1	5.3 ± 0.1	3.7 ± 0.1
<b>3c</b>	33.8 ± 0.1	17.3 ± 0.1	10.1 ± 0.1	5.8 ± 0.1

Averages and standard deviations calculated for data obtained from three independent extraction experiments

Aqueous phase, [metal dichromate]:  $1 \times 10^{-4}$  M; organic phase, dichloromethane, [ligand]:  $1 \times 10^{-3}$  M at 25 °C, for 1 h

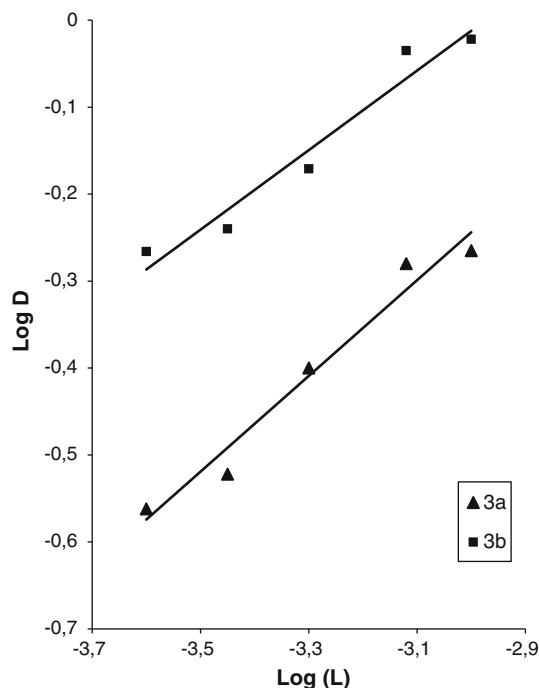
**Fig. 2** Plots of extraction (E%) versus pH following the two-phase solvent extraction of dichromate anion with compounds **3a–c**

upon the pH of solution, but depend upon the conformation and size of the cyclic receptor, and also upon the nature aggregations of the ions around the receptor.

In the Fig. 3, a linear relationship between log D versus log [L] is observed with the slope of lines for dichromate anion by the ligands **3a–b** which is roughly equal to 0.96–0.95, suggesting that the ligands **3a–b** forms a 1:1 complex with dichromate anion. However, it is well known that at more acidic conditions  $\text{Na}_2\text{Cr}_2\text{O}_7$  is converted into  $\text{H}_2\text{Cr}_2\text{O}_7$  and after ionization in an aqueous solution it exists in the  $\text{HCr}_2\text{O}_7^-/\text{Cr}_2\text{O}_7^{2-}$  form. At higher acidic conditions  $\text{HCr}_2\text{O}_7^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  dimers become the dominant  $\text{Cr}^{6+}$  form and  $\text{p}K_{a1}$  and  $\text{p}K_{a2}$  values of these equations are 0.74 and 6.49, respectively.

## Conclusions

In conclusion, the synthesis and ion extraction abilities of lactam ionophores were studied. The toxic anion and metal

**Fig. 3** Log D versus log [L] for the extraction of dichromate anion by the ligands **3a** and **3b** from an aqueous phase into dichloromethane at 25 °C

complexation studies showed that compounds **3a–c** were effective receptors. It could be concluded that the complexation of toxic anion and cation depends on the structural properties of the receptor such as hydrogen binding ability, stability or rigidity, and protonation ability. The lactam derivatives based receptors could be proved to find remarkable applications in the design of chemical sensors, using electrochemical transduction/as conventional ion selective electrodes and solid-state sensors.

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