

Crown moieties as cation host units in model polyamide compounds: Application in liquid–liquid cation extraction and in membrane cation transport

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Abstract

A new model polyamide compound that has a benzo-18-crown-6 moiety in the pendant structure is described. This model interacts with metal cations in the alkaline, earth alkaline, transition metal and heavy metal series. The interaction has been analyzed in terms of competitive cation extraction from aqueous solution by liquid model/dichloromethane phase. In each cation series, K(I), Ba(II), Cr(III), and Hg(II) have been selectively extracted by liquid model polyamide phases.

The interaction of a dense composite model polyamide-cellulose acetate membrane with lead(II) has been studied through its adsorption isotherm, infrared spectra and scanning electron microscopy study of the membranes before and after Pb(II) adsorption. The transport of lead nitrate through the membrane together with that of sodium chloride (for comparison), have been evaluated.

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1. Introduction

The discovery of the ability of biological molecules, such as porphyrins or valinomycin, to selectively bind cations has opened new research fields

in cation purification, extraction, environmentally toxic cation elimination or sensing. An early example of synthetic molecules which mimic Nature are the macrocyclic polyethers, which can selectively interact with cation through ion–dipole interactions of the positively charged cations involving the lone pairs of the ether oxygens. These macrocycles are cyclic polyethers made up of ethylene glycol units, $(\text{OCH}_2\text{CH}_2)_n$, and were called crown ethers by

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C.J. Pedersen in 1967 due to the appearance of *crowns* of the space filling models of the compound in the polyether–metal ion complex [1,2].

The specificity of the interaction of the crown ether with cations makes these compounds useful for preparation of novel materials as metal ion catalysts, molecular imprinting compounds, chirality inducing reagents, ion-exchange membranes, selective solvent extraction separation, selective membrane transport, ionoselective membranes for sensors, etc. [3–8].

We have previously studied the interactions of cations with methacrylic polymers having pendant crown ether moieties [9,10]. In this work, we extend the study to a new model compound of the polyamide bearing a pendant benzo-18-crown-6 ether moiety in each structural unit. The model compound of a polymer is a discrete, low molecular weight molecule that has a chemical structure, which resembles the structural unit of the polymer. The model compounds are used to study some characteristics of the polymers that cannot be studied in the macromolecule. The lack of solubility of the polyamide inhibits their study in liquid–liquid extraction. Thus, the model studied in this work is a host molecule for cations, which acts as probes of the polyamide and can be used in liquid–liquid extraction. Furthermore, the use of the model compound allows evaluation of the interaction and extraction of cations with a single 18-crown-6 host moiety, because in the polyamide, the crown moiety is a part of the pendant polymer backbone, so that the mobility of these subgroups is restricted and some kind of stacking is favored by the comb-like anchor of the pendant crown ether moieties to the main polymer chain [11–13].

In this manuscript, we describe the synthesis of a host molecule for cations, formally a model polyamide compound with a benzo-18-crown-6 moiety in the structure, together with its behavior in liquid–liquid extraction of cations in aqueous solution and its cation binding capabilities in a cellulose acetate matrix. Results of liquid phase of model compounds dissolved in organic solvents, in terms of selective cation uptake, have been obtained. Moreover, the interaction of a composite model polyamide–cellulose acetate dense membrane with lead(II) has been studied by means of its adsorption isotherm, infrared spectra and scanning electron microscopy studies. This membrane has also been tested for the transport of Pb(II) and Na(I).

The data obtained should be useful both for applications in elimination, extraction or purifica-

tions of cations, and also for a selectivity tests to prepare sensor membranes for applications in areas such as spectroscopic cation probes, ion-selective electrodes, or cation selective transport membranes.

2. Experimental

2.1. Materials

All materials and solvents were commercially available and were used as received, unless otherwise indicated. *N*-Methyl-2-pyrrolidone (NMP) was vacuum-distilled twice, over phosphorous pentoxide, and then stored over 4 Å molecular sieves. Lithium chloride was dried at 400 °C for 12 h prior to use. Triphenylphosphite (TPP) was vacuum distilled twice, over calcium hydride, and then stored over 4 Å molecular sieves. Pyridine was dried with reflux over sodium hydroxide for 24 h, and distilled over 4 Å molecular sieves. The synthesis of 4-(3',5'-dicarboxyphenylaminocarbonyl)benzo-18-crown-6 was accomplished according to the procedures previously described [13].

2.2. Model compound: 4-((3,5-bis(phenylcarbamoyl)phenyl)carbamoyl)benzo-18-crown-6 [Mdc6]

In a 50 ml three necked flask fitted with mechanical stirring, 22 mmol of aniline, 10 mmol of 4-(3',5'-dicarboxyphenylcarbamoyl)benzo-18-crown-6 and 1.4 g of lithium chloride were dissolved in a mixture of 6 ml of pyridine, 22 mmol of TPP and 20 ml of NMP. The solution was stirred and heated at 110 °C under a dry nitrogen blanket for 4 h. The system was then cooled at room temperature and the product was precipitated in 300 ml of water. The product, Mdc6 in Scheme 1, was purified by dissolving and re-precipitation (NMP and water, respectively), filtered off and dried overnight at 80 °C in a vacuum oven.

Yield: 80%; mp: amorphous solid ($T_g = 75$ °C). ^1H NMR [400 MHz, deuterated dimethylsulfoxide (DMSO- d_6), δ , ppm]: 10.50 (s, 3H); 8.65 (s, 2H); 8.37 (s, 1H); 7.89 (d, 4H); 7.74 (m, 2H); 7.39 (t, 4H); 7.14 (d, 4H); 6.79 (m, 2H); 4.22 (s, 4H); 3.78 (s, 4H); 3.60 (s, 4H); 3.44 (m, 8H); 1.08 (t, 6H). ^{13}C NMR [400 MHz, deuterated dimethylsulfoxide (DMSO- d_6), δ , ppm]: 165.35; 165.19; 157.49; 151.68; 147.87; 139.91; 139.24; 135.97; 130.31; 129.44; 128.78; 126.73; 123.94; 122.81; 121.95; 121.86; 120.80; 118.86; 115.37; 113.88; 112.86; 70.25; 69.43; 69.12; 69.00; 68.86; 68.41; 65.73;

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