Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Adsorption of amino acid derivatives on calixarene carboxylic acid impregnated resins

Tatsuya Oshima^{a,*}, Ryota Saisho^a, Kaoru Ohe^a, Yoshinari Baba^a, Keisuke Ohto^b

^a Department of Applied Chemistry, University of Miyazaki, 1-1, Gakuen Kibanadai Nishi, Miyazaki 889-2192, Japan ^b Department of Applied Chemistry, Saga University, Honjo 1, Saga 840-8502, Japan

ARTICLE INFO

Article history: Received 21 September 2008 Received in revised form 20 November 2008 Accepted 20 November 2008 Available online 3 December 2008

Keywords: Calixarene Extractant impregnated resin Adsorption Separation Amino acid

ABSTRACT

Macrocyclic host molecules calixarene carboxylic acid derivatives are found to act as powerful extractants for biologically important amino compounds. A series of adsorbents were prepared from a methacrylate-based polymer Amberlite XAD-7 by impregnation with various calixarene derivatives, for adsorptive recovery of amino acid derivatives. The larger macrocycles calix[6]arene and calix[8]arene carboxylic acid derivatives were more effective for adsorption of amino acid derivatives on the impregnated resin than the calix[4]arene derivative. Since adsorption proceeds mainly via electrostatic interaction, the carboxylic acid groups introduced into the calixarene platform were important for adsorption of cationic amino acid derivatives. The adsorption selectivity for amino compounds using adsorbent impregnated with the calix[6]arene carboxylic acid derivative depends simply on the hydrophobicity of the adsorbates.

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1. Introduction

A variety of calixarene derivatives has been developed in the past few decades for molecular recognition of biomolecules [1–6]. The rigid macrocyclic structure of calixarene is versatile as a platform for designing a receptor that binds to a biomolecule via multiple interactions. In particular, various calixarene derivatives have been developed for the recognition of amino compounds. A calix[6]arene carboxylic acid derivative (abbreviated as ^tOct[6]CH₂COOH, whose structure is shown in Fig. 1) has been found to act as a host molecule for the extraction of amino acids. Calix[6]arene has a favorable cavity for inclusion of organic molecules, six ionizable carboxylic acid groups for electrostatic interaction with cationic species, and C₃ symmetry for recognition of the NH_3^+ group [7–10]. This calixarene shows the highest extractability for organic amines under weakly acidic conditions. Liquid–liquid extraction of a cationic protein, cytochrome *c*, using calix[6]arene has also been achieved [11,12].

The macrocyclic compound, calixarene, is attractive as a platform to develop a novel host compound for entrapping biomolecules. However, practical use of calixarene in liquid–liquid extraction is still limited because of its low solubility in organic solvents [13–16]. For instance, the most popular *p-tert*-butyl calix-

* Corresponding author. Fax: +81 985 58 7323.

E-mail address: oshimat@cc.miyazaki-u.ac.jp (T. Oshima).

arenes are dissolved at only millimolar levels in alkyl halides such as chloroform. Consequently, immobilization of calixarene derivatives on polymer matrix has been performed for the recovery of metal ions [17]. Crosslinking of calixarene to polymers has been carried out [18–21], as well as copolymerization of calixarene with other monomers [22–25]. Furthermore, impregnation of resins with calixarene derivatives is also one of the recognized methods for immobilization of calixarenes.

Reagent impregnated resins are easily prepared by physical adsorption in the macropores of the polymer support. The extractabilities and selectivities using the impregnated resins are governed by the characteristics of the extractant. A variety of extractants, as well as calixarene derivatives, have been used for preparing impregnated resins for uptake of metal ions [26–32]. Glennon et al. prepared a resin impregnated with calix[4]arene hydroxamate derivatives for solid phase extraction of metal ions [33]. *p-tert*-Butyl sulfinylcalix[4]arene-impregnated resin has been prepared and used for adsorption of niobium(V) from tantalum(V) [34]. Moreover, adsorption of transition metal ions such as lead(II) on resins impregnated with calixarene carboxylic acid derivatives has been studied [35,36]. The adsorption selectivity of the impregnated resins for divalent metal ions is in accordance with that of the calixarene derivatives in liquid–liquid extraction.

Resins impregnated with calixarene carboxylic acid derivatives were prepared for adsorptive recovery of catecholamines [37]. In the present study, adsorption of amino acid derivatives on resins impregnated with the series of calix[n]arene carboxylic acid derivatives with n = 4, 6, and 8 was studied. The adsorption behavior of





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Fig. 1. Molecular structures of impregnated extractants used in this study.

the impregnated resins was compared with the extraction behavior of the calixarenes in liquid–liquid extraction [6–8]. For the recovery of biomolecules, adsorption directly from an aqueous solution without using organic solvents is preferred to liquid–liquid extraction.

2. Experimental

2.1. Reagents

Fig. 1 shows the molecular structures of and abbreviations for the extractants used in the present study. The extractants *p-tert*-octylcalix[4]arene tetracarboxylic acid derivative (abbreviated as ¹Oct[4]CH₂COOH), *p-tert*-octylcalix[6]arene hexacarboxylic acid derivative (¹Oct[6]CH₂COOH), and *p-tert*-octylcalix[8]arene octa-carboxylic acid derivative (¹Oct[8]CH₂COOH), were synthesized according to the procedures described in previous papers [7,38]. Two calix[6]arene sources for ¹Oct[6]CH₂COOH, namely *p-tert*-octylcalix[6]arene (¹Oct[6]H) and *p-tert*-octylcalix[6]arene hexaeth-yl ester derivative (¹Oct[6]CH₂COOEt), were obtained as precursors for ¹Oct[6]CH₂COOH. Here, ¹Oct[4]CH₂COOH has cone conformation. The final products were purified by recrystallization and identified by means of FT-IR, ¹H NMR, and elemental analysis. Fig. 2 shows the molecular structures of and abbreviations for the amino acid derivatives. Analytical grade amino acid, amino acid esters, and

amino acid β -naphthyl amide derivatives were purchased and used without further purification. L-tryptophan (Trp), L-tryptophan methyl ester hydrochloride (Trp-OMe), L-phenylalanine methyl ester hydrochloride (Phe-OMe), and L-tyrosine methyl ester hydrochloride (Tyr-OMe) were supplied by Aldrich Chemical Co: L-leucine β -naphthyl amide (Leu- β NA), L-lysine β -naphthyl amide (Lys- β NA), L-serine β -naphthyl amide (Ser- β NA), and L-glutamic acid β -naphthyl amide (Glu- β NA) were obtained from Bachem AG. Analytical grade serotonin was purchased from Wako Pure Chemical Industries. The macroporous methacrylate-based polymer Amberlite XAD-7 was purchased from Organo Co., Ltd. It was washed three times with methanol followed by drying *in vacuo*, and used as the polymer matrix of the impregnated resin. All other reagents were reagent grade and were used as received.

2.2. Preparation of the impregnated resins

Pretreated Amberlite XAD-7 (4.00 g) was immersed in a chloroform solution containing 1.00 g of an extractant calixarene derivative. After 40 h, the chloroform was removed *in vacuo*. The procedure was repeated several times until the extractant was completely impregnated in the polymer matrix. The percentage impregnation was calculated as 20%, from the weight percentage of the extractant in the resulting material [35,36].

2.3. Adsorption tests

Adsorption tests were carried out using the conventional batch method [36]. Two aqueous solutions were separately prepared by dissolving 0.2 mmol dm⁻³ of an amino acid (Trp) or an amino acid derivative (Trp-OMe, Phe-OMe, Tyr-OMe, Leu- β NA, Lys- β NA, Ser- β NA, Glu- β NA, or serotonin) in either 100 mmol dm⁻³ hydrochloric acid or glycine solution. The pH in the aqueous solution was adjusted by mixing the two aqueous solutions. The aqueous solution (10 cm³) and 20 mg of an impregnated resin were mixed in a stoppered glass tube, and the mixture shaken in a thermostatted water bath (120 rpm) at 30 °C. After 24 h adsorption, equilibrium was reached. Both the mixture and the initial aqueous solution were then filtered through filter paper. The concentrations of adsorbate before and after adsorption (C_0 and C_e mmol dm⁻³, respectively) were determined using UV–VIS spectrophotometry (JASCO U-best v560) or an HPLC (Shimadzu SPD-10Avp/LC-10ADvp isocratic sys-



Fig. 2. Molecular structures of amino acid derivatives: (a) aromatic amino acid esters; (b) amino acid β-naphthyl amide derivatives and (c) indole compounds.

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