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Polyaminocarboxylic acids rejection by charged nanofiltration membrane

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Abstract

The aim of this work was to investigate the mechanisms behind the rejection of polyaminocarboxylic acids, especially the influence of membrane and solute properties. The rejections of five polyaminocarboxylic acids by commercially available charged nanofiltration membrane (Desal GH, Osmonics) were studied at constant ionic strength, pressure and temperature as a function of the pH. The rejections of polyaminocarboxylic acids with Desal GH spiral-wound membrane varied from 10 to 99% at pH ranging from 1 to 7. Findings of this study indicated that the rejection of polyaminocarboxylic acids was primarily driven by Donnan exclusion and correlated with the net charge of the solute which could be calculated using protonation constants. The effects of molecular weight and molecular parameters on rejection were studied when polyaminocarboxylic acids had a net charge close to zero.

Keywords: Nanofiltration; Polyaminocarboxylic acids; Isoelectric point; Donnan exclusion

1. Introduction

Membrane processes such as reverse osmosis (RO) and nanofiltration (NF) are becoming increasingly wide spread in water treatment applications and two of them can be highlighted: rejection of organic molecules and rejection of inorganic ions. Rejection and transport mechanisms of inorganic ions through nanofiltration membranes have been described in several publications [1–4]. It can be applied for drinking water softening [5,6], selective concentration of uranium traces from sea water [7] or separation of metal by nanofiltration assisted by complexation [8,9].

Rejections of low molecular-weight organic compounds has number of applications in drinking water, wastewater and water reuse [10]. Some micropollutants such as pesticides [11–13], endocrine disrupting compounds and pharmaceutically active compounds [14] can be effectively removed by NF and RO membranes. NF could be also used for treatment of wastewater originated from dyeing process [15,16], biotechnology and fermentation industry especially for the separation and purification of oligosacharides [17] or amino acids [18–22].

The rejection of organic compounds traces represents a complex interaction of steric hindrance, electrostatic repulsion and solute/membrane interactions [10]. Some interactions are fairly well understood. For uncharged low molecular-weight organics, the rejection can be correlated with the size related characteristics of the molecules (Stokes diameter, equivalent molecular diameter and calculated diameter) [23] and log *P* [11]. The rejection of charged low molecular-weight solutes depends upon both solute properties (i.e. size, polarity and charge) and membranes properties (i.e. pore size, charge and hydrophobicity) [10]. Investigations, however, on the mechanisms behind the rejection of organic acids, especially the role of membrane and solutes properties, are limited.

By using polyaminocarboxylic acids with different molecular weight and molecular shape (Table 1), with several well defined protonation constants (Table 2), membrane separation mechanisms could be studied. The main objective of this study is to determine the polyaminocarboxylic acids rejection performance of the Desal GH membrane at constant ionic strength,

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Table 1
List of polyaminocarboxylic acids used in this work

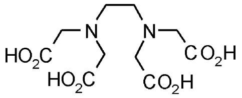
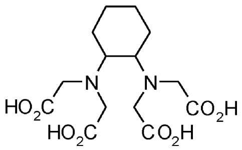
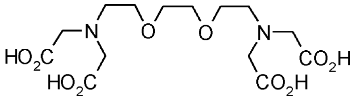
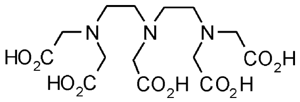
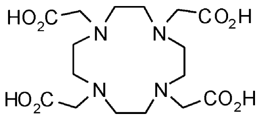
MW (Da)	Polyaminocarboxylic acids	Abbreviations
292		EDTA
346		CDTA
380		EGTA
393		DTPA
404		DOTA

Table 2
Protonation constants of polyaminocarboxylic acids determined by potentiometric titration

	log K_{H1}	log K_{H2}	log K_{H3}	log K_{H4}	log K_{H5}	log K_{H6}
EDTA [26]	10.21	6.11	2.60	2.00	–	–
CDTA [27]	12.30	6.12	3.53	2.42	1.60	–
EGTA [28]	9.47	8.85	2.66	2.00	–	–
DTPA [26]	10.59	8.65	4.28	2.73	2.06	–
DOTA [29]	11.08	9.23	4.24	3.18	1.88	1.71

pressure and temperature as the function of the feed pH. In this work we only focused on charge and steric effects. From these information, it will be possible to develop efficient strategies and give recommendations for the separation of industrial feeds containing charged organics solutes or metals using nanofiltration assisted by complexation [24].

2. Experimental

2.1. Reagents

All solutions were prepared using distilled water that was further purified by passing through a Millipore Alpha-Q reverse osmosis cartridge system (resistivity 18.2 MΩ cm). Ethylenediaminetetraacetic acid (EDTA 99%, Aldrich), *trans*-1,2-diaminocyclohexane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid (CDTA 98%, Acros), ethylenebis(oxyethylene-nitrilo)tetraacetic acid (EGTA 99%, Acros), diethylenetriaminepentaacetic acid (DTPA 97%, Aldrich), and 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid (DOTA > 99%, Guerbet S.A., France) were used without further purification for NF experiments. The structure and molecular weight of the polyaminocarboxylic acid used in this study are given in Table 1.

2.2. Membrane

The commercial Desal GH membrane (Osmonics, USA) selected for this study was a spiral-wound membrane (length 305.0 mm, diameter 47.0 mm, spacer 0.71 mm) constituted of polyamide filtering layers. The active membrane area is 0.25 m^2 and the nominal molecular weight cut-off (MWCO) is estimated by its manufacturer at 2500 Da using polyethylene glycol (PEG). This membrane is suited in low ultrafiltration as compared to the most common NF membranes which generally exhibit a MWCO lower than 1000 Da. The membrane charge represented by the zeta-potential (ζ) has been previously determined by tangential streaming potential measurements as a function of the pH in 1 mM KCl [25] or in the presence of equimolar quantity of $Gd(NO_3)_3$ and DTPA [24] (Fig. 1). As expected, the membrane surface charge is impacted by the ionic strength and by the composition of the solution, but under the different conditions tested, the isoelectric point of the Desal G 10 membrane is between pH 3.5 and pH 4.0.

2.3. Apparatus

NF experiments were performed with a spiral-wound module equipped with a Vessel PV1812 membrane cell (Sepra, Italy) and a schematic flow diagram of the lab-scale membrane system has been previously described [24]. The membrane cell is composed of a cell holder in stainless which supports a maximum of differential pressure and temperature of 42 bar and 50 °C, respectively. Before starting experiments, the Desal GH membrane is conditioned by permeating pure water using a transmembrane pressure of 4.0 bar and a temperature of 20 °C to reach the maximum permeability coefficient of the membrane, $J_w = 2.95$ L/(h bar m^2). During all experiments, the membrane is

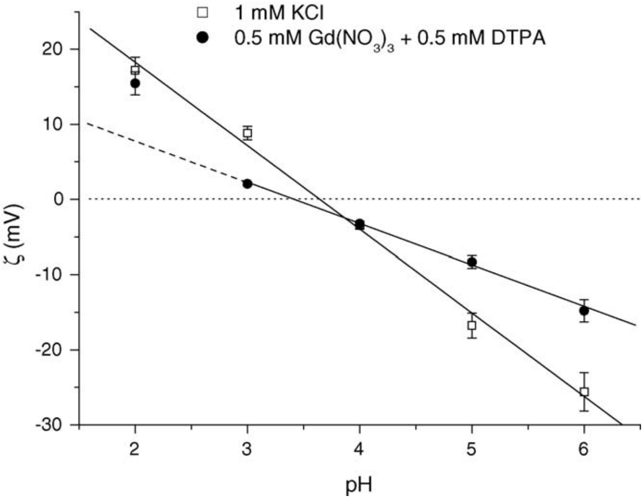


Fig. 1. pH dependence of ζ-potential of Desal GH membrane determined from both 1 mM KCl [25] or [Gd(III)] = [DTPA] = 0.5 mM [24] electrolyte support.