Extraction and membrane transport of lanthanides with dynameric constitutional framework carriers

M. Yahia M. Abdelrahim [a,b], H.H. Osman [a,b], Sophie Cerneaux [a], Nathalie Masquelez [a], Mihail Barboiu [a,*]

[a] Institut Europeen des Membranes, UMR 5635 (CNRS-ENSCM-UM2), Université de Montpellier, Place Eugene Bataillon, F-34095 Montpellier, France
[b] Department of Chemistry, Faculty of Science, Helwan University, Ain-Helwan, Cairo 11795, Egypt

A B S T R A C T

Dynamic covalent polymers or dynamers, generated from reversibly interacting monomers, offer the possibility to generate molecular-controlled materials with addressable domains which are different from these of former monomers and based on structural relationships between the network components. Herein, constitutional dynamic frameworks of Jeffamine-type macromonomers cross-linked via trifunctional core centers have been used as a dynameric-electrolyte network in liquid and solid membrane systems for lanthanide recognition, extraction and transport. The transport is based on the partition ability of lanthanides (La^{+3}, Lu^{+3}, and Eu^{+3}) within functional dynameric network bearing polyether and imine groups. Interestingly, the lanthanides are extracted and selectively transported through the membrane, only in the presence of constitutional cross-linked frameworks, while the former Jeffamine monomers have been shown high extraction yields, but any selectivity. This would be explained by the formation of molecularly addressable recognition "pockets" in which the recognition/diffusional selective percolation pathways might exist. It implies that such dynameric frameworks have high selectivity towards La^{+3}, Lu^{+3} relative to Eu^{+3} that may be separated.

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1. Introduction

Membrane-mediated separations of ionic species are an attractive alternative to other chemical methods (i.e., ion exchange and chromatographic processes) for purification, recovery, etc. [1–3] Numerous artificial membrane transport systems using high-affinity polymeric materials for recognition or channel-forming structures have been developed in the last decades. The design and application of polytopic receptors recognizing cations, anions or molecular species has attracted a great deal of interest as these systems have many potential functions such as extraction and membrane transport processes [2–8].

The extension of molecular recognition and self-assembly properties of discrete carriers and transporting devices would be related to the potential ability of such multifunctional membrane to present molecular controlled properties such as solute multiple molecular recognition by using polytopic receptors [9–12] and the generation of directional diffusion pathways by self-assembly of receptors at the supramolecular level in the membrane material [13–16].

Importing such collective dynamic features into polymeric membrane materials implies developing dynamic polymers "dynamers", generated via reversible covalent reactions between molecular monomers that are dynamic by nature (supramolecular) or by design (molecular) [17–22]. Dynameric membranes for ionic [23] and gas [24–26] separations have been recently developed. We learned from these studies that compared with a physical mixture of classical polymers, the mixtures of dynamers give access to new homogenous species presenting controllable modulation of their structure at molecular level, in response to external stimuli or experimental conditions. This is playing an important role in the ability to control the separation properties by using the collective properties of membrane material components. For all these reasons, functional dynamic polymers "dynamers" may be used to conceive novel membrane materials.

Herein, our efforts are turned towards the synthesis and the fabrication of "dynameric" frameworks used as collective extractors or carrier systems in liquid membranes and as thin-layer films for solid membranes. Jeffamine-based materials are well known polymer electrolyte systems used in particular in solid state electrochemical devices [27], but also to solubilize luminescent lanthanide cations with potential optical applications [28]. Therefore, the objectives of this work are to conceive and to investigate such constitutional Jeffamine-type dynameric

* Corresponding author.
E-mail address: mihail-dumitru.barboiu@univ-montp2.fr (M. Barboiu).

frameworks in liquid and solid membrane systems for the selective extraction and transport of the lanthanide cations (La^{3+}, Lu^{3+}, and Eu^{3+}). The transport performances (permeability, selectivity and partition coefficients) are evaluated by using the solution-diffusion model.

2. Materials and methods

2.1. Materials

Benzene-1,3,5-tricarbaldehyde (TCA) (98%, Manchester Organics Ltd), Jeffamine D-2000 and Jeffamine T-3000 were used to prepare the dynameric membranes. TCA was used as the core connectors of the membrane structures. Jeffamines D-2000 and T-3000 were used as macromonomers and purchased from Huntsman Holland BV. All the products were used as received without further purification. For all the experiments, chloroform was used as a solvent and purchased from Sigma Aldrich. Lanthanum (III) chloride (99%, Alfa Aesar), Lutetium (III) chloride (99%, Sigma Aldrich), and Europium (III) chloride hexahydrate (99%, Janssen Chimica) have been used as the source of the lanthanides ions. Ascorbic acid (98%, Sigma) and Arsenazo III (98%, Fluka) were used for the UV-spectroscopy quantitative determination of lanthanides.

2.2. The synthesis of the dynameric materials P1-P7

A series of dynameric materials **P1**-**P7** with molecular formula $\mathbf{1_{1-x} \cdot 2 \cdot 3_x}$ have been synthesized by using Benzene-1,3,5-tricarbaldehyde (TCA), **1** the linear Jeffamine2000, **2** star-type Jeffamine3000, **3** macromonomers and as reagents. The cross-linking degree of the polymer was varied by changing the molar fraction of linear J-D2000 and cross-linked J-T3000 Jeffamines, while the molar fraction of TCA core center was held constant (Table 1). The dynameric materials **P1**-**P7** were synthesized according to the following procedure: the suitable amounts of reagents have been dissolved in 50 mL of chloroform, placed in 100 mL round bottom flask and then refluxed at 70 °C under stirring overnight. Two thirds of the solvent was then evaporated and the resulted solution was casted in a Teflon plate then placed inside an oven and successively dried at 60 °C and 120 °C for more than two days.

2.3. Solvent extraction experiments

The solvent extraction experiments were performed using a definite amounts of **P1**-**P7** dissolved in 5 mL of chloroform in contact with 5 mL of aqueous solutions of 200 ppm La^{3+}, Lu^{3+}, Eu^{3+} and then the biphasic systems were shacked overnight at room temperature. Samples of the aqueous phase were taken and analyzed by UV-Spectrophotometry by using Arsenazo III to determine the unextracted amount of the metal ion in the aqueous

solution, as previously reported [29]. The uptake percentage can be calculated from the absorbance values using the following equation: %uptake=$(Abs._{int.}-Abs._{fin.})/Abs._{int.}$, where: ($Abs._{int.}$) is the absorbance of the standard initial solution before extraction, while ($Abs._{fin.}$) is the same but after the extraction experiment.

2.4. Facilitated transport procedure through the liquid and solid membranes

We performed the single transport dialysis experiments of the lanthanides through solid and liquid membranes. In case of solid membranes, the membrane transport experiments were performed with a bi-compartmental device, magnetically stirred at room temperature (Fig. 1a). It consisted of two PTFE cell devices separated by the solid membrane ($S=5.32$ cm^2). Nitrogen permeation measurements were performed to ensure that they were dense and defect free. The liquid membrane experiments were performed under magnetic stirring by using a conventional U-tube glass cell, at room temperature (Fig. 1b). In both cases, the feed phase was an aqueous solution with a volume of 50 mL and a concentration of 200 ppm of each lanthanide metal ions ($LaCl_3.6H_2O$ / $LuCl_3.6H_2O$ / $EuCl_3.6H_2O$). The receiving phase consisted of 50 mL of deionized water. The concentrations of La^{3+}, Lu^{3+}, and Eu^{3+} were monitored at different time intervals using UV- spectrophotometry [29]. The permeabilities (P) and the partition coefficient ratio (α) of ions have been determined from experimental concentration versus time profiles using the previously reported solution-diffusion models [10,30].

2.5. Instrumental techniques

FTIR experiments have been performed by using a Nicolet Nexus Fourier transform spectrometer (speed of mirror=0.6329 cm s^{-1}, iris aperture=100, detector DTGS) equipped with a diamond ATR accessory Golden Gate whose resolution is 4 cm^{-1}. The swept frequency range covers the area of the mid-infrared 400–4000 cm^{-1}. The acquisition of the spectra is performed in transmittance mode (64 scans). ^{1}H NMR spectra have been recorded by using a BRUKER NMR ADVANCE 300 MHz spectrometer. Deuterated chloroform ($CDCl_3$) EURISO-TOP was used as solvent. Thermogravimetric profiles have been obtained on a heat-balance type TGAQ50 Thermal Analysis under flow of inert gas (nitrogen). 5–15 mg of polymer material was placed in a platinum crucible, then heated from -80 °C to 500 °C at a temperature gradient of 10 °C/min. TA Universal Analysis software has enabled us to record and calculate the evolution of the mass and its derivative as a function of temperature. The plot of the derivative of the weight loss versus temperature allowed us to distinguish the successive mass loss. Differential Scanning Calorimetric (DSC) measurements were performed on a TA Instruments DSC2920 machine equipped with a module between 150 °C and 400 °C at a heating rate of 10 °C/ min. The exploitation of the results was performed using the TA Universal Analysis software, marketed by TA Instruments. The sample, mass of about 2–5 mg was placed in an aluminum crimped and sealed vial so that the measurement is more accurate because the mass of the sample is constant. The surface and cross section of the solid membrane films imaging were analyzed using a Hitachi S4800 Scanning Electron microscope. The acceleration voltage ranges from 0.1 kV to 30 kV. The maximum magnification is 800,000 × . The scanning electron microscope is operated with an electron beam intensity of 10 kV. 2 cm^2 pieces of the sample were cut in a liquid nitrogen environment to avoid distorting the material surface or cross section. The chemical composition of the surface of the membranes has been analyzed using a Hitachi S4500 Field microscope equipped with a Thermofisher EDX detector for chemical analysis

Table 1
Composition of the synthetized polymeric materials **P1** to **P7**.

Dynamer	Mass, g ($x=$molar ratio in the mixture)		
	TCA	D2000	T3000
P1	0.1 (1)	1.86 (0.5)	0
P2	0.1 (1)	1.55 (1.25)	0.32 (0.17)
P3	0.1 (1)	1.24 (1)	0.61 (0.33)
P4	0.1 (1)	0.93 (0.75)	0.93 (0.5)
P5	0.1 (1)	0.62 (0.5)	1.25 (0.67)
P6	0.1 (1)	0.31 (0.25)	1.54 (0.83)
P7	0.1 (1)	0	1.86 (1)