Synthesis of Noncyclic Carriers for Cerium Ion Transport through Polymer Inclusion Membrane

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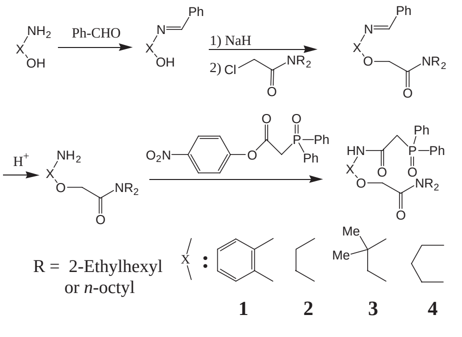
Noncyclic ionophores having both diphenylphosphinyl methylcarbamoyl and *N*,*N*-di(2-ethylhexyl)carbamoylmethoxy groups were synthesized for cerium ion transport through polymer inclusion membrane. The derivative of 3-aminopropanol having these groups was found to be an excellent carrier over 2-aminoethanol derivatives.

Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO),[1] *N*,*N*,*N*′,*N*′-tetraoctyl-3-oxapentanediamide (TODGA),[2] and macrocyclic derivatives based on calixarenes,[3] resorcinarenes,[4] etc. have been reported to be excellent extractants and carriers for lanthanoid and actinoid metal ions. They can be used for the separation of valuable metal ions and radioactive wasted actinoid ions.[2] If they are available not only as extractants but also carriers for the separation technology, they could be utilized for effective separation processes such as treatment of radioactive wastewater. In particular, separation through liquid membranes does not need to use a large amount of ionophores (carriers) for the separation of the target ions. Therefore, synthesis of carriers, which can be used in the membrane systems, is one of the important goals.

In this paper, we report the synthesis of a new hybrid-type carrier having not only CMPO moiety but also TODGA moiety partly because both carbamoylmethylphosphine oxide of CMPO and oxamethylamide of TODGA have a strong coordinative ability toward lanthanoid and actinoid ions, and the transport behavior through polymer inclusion membranes (PIM)[5] using them as carriers. Scheme 1 shows the reaction process. That is, ω-aminoalcohol protected by benzaldehyde reacts with *N*,*N*-di(2-ethylhexyl or *n*-octyl)carbamoylmethyl chloride in DMF to give *N*,*N*-di(2-ethylhexyl)carbamoyl-methoxyalkylamine derivatives after deprotection of benzaldehyde. The mixture of amine derivatives and *p*-nitrophenyl (diphenylphosphinyl)-acetate[3b] were stirred in dry and ethanol-free chloroform at 45 °C for three days to result in the formation of ionophores having both diphenylphosphoryl methylcarbamoyl and *N*,*N*-di(2-ethylhexyl or *n*-octyl)carbamoylmethoxy groups. They were confirmed by NMR, ESI-mass, Precise Mass, and IR.[6]



Scheme 1. Reaction process of synthesis of carriers, **1–4**.

In order to investigate the effect of the structure, some alkylene groups and *ortho*-phenylene group were introduced as a spacer between diphenylphosphorylmethylcarbamoyl and *N*,*N*-di(2-ethylhexyl or *n*-octyl)carbamoylmethoxy groups.

Cellulose triacetate was used to form the PIM and to support ligand in solvent (2-nitrophenyl *n*-octyl ether/ NPOE).[7] The PIM was prepared using a procedure, which is described in detail elsewhere.[8] We tried to transport cerium ion by using the PIMs containing ligands **1**–**4** newly synthesized. In the initial conditions, feed phase contains 200 ppm cerium nitrate 0.05 M nitric acid, and 2.95 M of sodium nitrate, on the other hand, strip phase contains distilled and deionized water. Both phases were stirred with stirrer bar at 600 rpm at 40 °C. The details of the transport apparatus and the experimental procedure are described elsewhere.[8] Figure 1 shows an example of transport of cerium ion through PIMs containing ligands **1**–**4** with time. Under these conditions, more than 90% of cerium ion in the feed phase can be transported into the strip phase with ligands except **1** within 3 h. Ligand **4** is the best carrier among them. The transport ability of dimethyl-substituted ligand **3** is better than that of ligand **2**, probably because its lypophilicity increases and freedom of rotation of C–C bond decreases. Trimethylene derivative **4** can transport cerium ion very effectively as shown in Figure 1. Trimethylene chain might be advantageous to make 2:1 complex with cerium ions because the two functional groups can smoothly work as chelating agent. On the other hand, the transport ability of phenylene derivative **1** drastically decreases compared

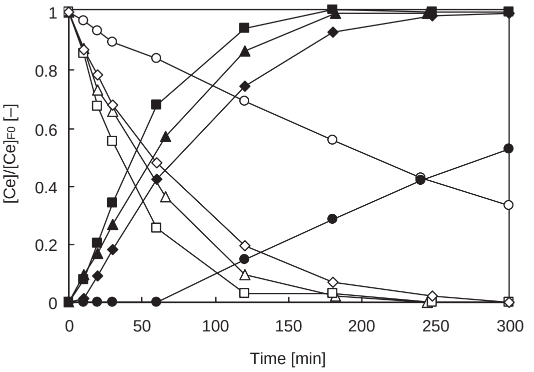


Figure 1. Transport of Ce(III) through PIM with carriers, **1**–**4**; conditions: membrane thickness 49 µm, Feed: 200 ppm Ce$(NO_3)_3$ in 0.05 M HNO_3/2.95 M $NaNO_3$, Strip: water, Temp: 40 °C, Stirring: 600 rpm. 1 : ●○, 2 : ◆◇, 3 : ▲△, 4 : ■□ (filled symbols: strip, open symbols: feed).

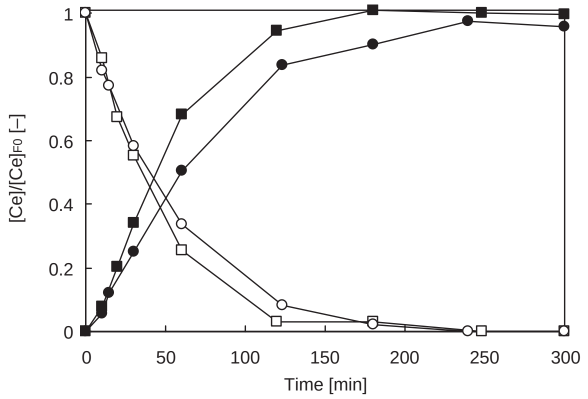


Figure 2. Transport of Ce(III) through PIM with carriers, **4** and TODGA; conditions: same as Figure 1. **4** : ■□, TODGA : ●○ (filled symbols: strip, open symbols: feed).

with ligand **2**. Forming intermolecular, stable complex with cerium ion, the rigid benzene part between two functional groups would work disadvantageously.

The transport ability of **4** was compared with TODGA,[2] which is one of the best potent candidates for lanthanoid or actinoid extractants and carriers, under the same conditions. Figure 2 shows the transport behaviors of two carriers. Ligand **4** surpasses TODGA in the transport ability for cerium ion. Carrier **4** should also be one of the most potent carriers for lanthanoid ions through polymer inclusion membranes.

In the membrane system (PIM), these compounds could act as a tetradentate, otherwise at least tridentate complexing agent. Although ESI mass spectroscopy of the mixture of these compounds with cerium nitrate in NPOE was measured, any mass number of the complex with cerium ion was not clearly detected under the same conditions (40 eV, positive mode, in acetonitrile). However, in FAB mass spectroscopy of the same mixture (matrix: 3-nitrobenzyl alcohol; ionization mode: positive), mass number of 1461.3 due to the 2:1 complex, $[(\text{ligand }\mathbf{4})_2 + \text{Ce}(\text{NO}_3)_2]^+$ (calcd 1460.7) was detected. CMPO was reported to make 2:1 complex with lanthanoid or actinoid ions in the extraction systems,[9] whereas TODGA makes 2:1 or 3:1 complex with those metal ions.[2b] These results suggest that ligand **4** might form 2:1 complex with cerium(III) ion as illustrated in Figure 3.

Thus, the newly prepared hybrid-type carriers having both properties of CMPO and TODGA can work as excellent carriers of cerium(III) ion in polymer inclusion membrane (PIM) system. Further investigation on the synthesis of new carriers is now in progress.

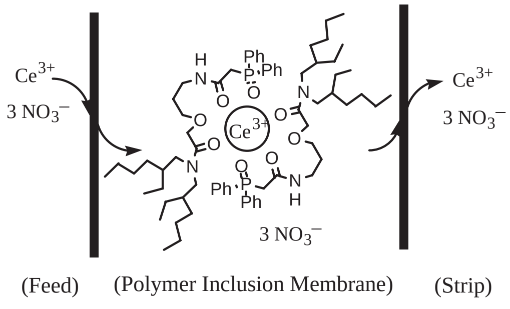


Figure 3. Postulated 2:1 complexation of **4** with cerium(III) ion in the transport through PIM.

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6 Only **1** has *n*-octyl groups as substituent R. Selected data for carriers **1**–**4**: **1**: ^{1}H NMR (CDCl$_3$, ppm) 0.89 (t, 6H, CH$_3$), 1.2 (broad, 20H, CH$_2$), 1.5 (m, 4H, CH$_2$), 2.24 (s, 3H, Ar-CH$_3$), 3.26 (m, 4H, N-CH$_2$), 3.54 and 3.59 (s, 2H, P-CH$_2$-CO), 4.72 (s, 2H, CO-CH$_2$-O), 6.75 (d, 1H, Ar-H), 6.78 (s, 1H, Ar-H), 7.5 (m, 6H, Ar-H), 7.8 (m, 4H, Ar-H), 8.08 (d, 1H, Ar-H), 9.92 (s, 1H, NH); Precise Ms: Calcd: 646.39, Found: 646.396. **2**: ^{1}H NMR (CDCl$_3$, ppm) 0.89 (t, 12H, CH$_3$), 1.26 (broad, 16H, CH$_2$), 1.6 (m, 2H, CH), 3.05 (d, 2H, N-CH$_2$), 3.40 (m, 2H, N-CH$_2$), 3.36 and 3.40 (s, 2H, P-CH$_2$-CO), 4.13 (s, 2H, CO-CH$_2$-O), 7.5 (m, 6H, Ar-H), 7.7 (m, 4H, Ar-H), 7.9 (broad, 1H, N-H); Precise Ms: Calcd: 584.37, Found: 584.372. **3**: ^{1}H NMR (CDCl$_3$, ppm) 0.90 (m, 12H, CH$_3$), 1.18 (s, 6H, CH$_3$), 1.27 (broad, 16H, CH$_2$), 1.64 (m, 2H, CH), 3.05 (d, 2H, N-CH$_2$), 3.32 (m, 2H, N-CH$_2$), 3.32 and 3.37 (s, 2H, P-CH$_2$-CO), 4.13 (s, 2H, CO-CH$_2$-O), 7.46 (m, 6H, Ar-H), 7.84 (m, 4H, Ar-H), 8.05 (s, 1H, N-H); Precise Ms: Calcd: 612.41, Found: 612.399. **4**: ^{1}H NMR (CDCl$_3$, ppm) 0.89 (m, 12H, CH$_3$), 1.26 (broad, 16H, CH$_2$), 1.64 (m, 2H, CH), 1.65 (m, 2H, CH$_2$), 3.07 (d, 2H, N-CH$_2$), 3.24 (m, 2H, NCH$_2$), 3.31 (t, 2H, N-CH$_2$), 3.35 and 3.40 (s, 2H, P-CH$_2$-CO), 3.42 (t, 2H, O-CH$_2$), 4.11 (s, 2H, CO-CH$_2$-O), 7.5 (m, 6H, Ar-H), 7.8 (m, 4H, Ar-H), 7.85 (s, 1H, N-H); Precise Ms: Calcd: 598.39, Found: 598.387.

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