Kemp's Acid Imides as Uphill Transport Carriers for Alkaline Earth Metal Ions

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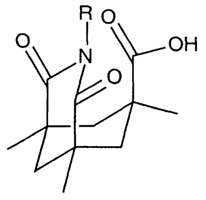
N- Substituted- 1, 3, 5 - trimethylcyclohexane- 3, 5 - imido- 1 - carboxylic acids efficiently transported Ca^{II} and Mg^{II} from alkaline earth metal ion mixtures against their concentration gradient through a chloroform liquid membrane.

Extensive study has been performed on ionophores for metal ion extraction and transport and many efficient ionophores have been developed.[1] Although they are well designed, they contain macrocyclic structures and are therefore not synthetically simple. Versatile and simple ionophores are still desired for metal ion separation and recovery not only from an academic, but also industrial and environmental points of view. As an extension of our study on metal ionophores, [2,3] we report a new carrier for alkaline earth metal ions having one carboxylic acid moiety to coordinate metal ions and an imide moiety to increase lipophilicity and help to stabilize the coordinated metal.

The versatility of Kemp's triacid as a key structure of molecular recognition and molecular assembly used by Rebek *et al.* is well known.[4] This versatile character results from its unique structure, that is, three axial carboxyl groups on a cyclohexane ring stabilized by three equatorial methyl groups. However there are few reports on its application to metal ion chelating agents or carriers.[5] We desired to use one carboxyl group of Kemp's triacid as a main coordinating group for metal ions.

We prepared imide acids[6] from the reaction of the anhydride acid chloride of Kemp's triacid and primary amines as in the literature.[7] Decreasing the number of coordinating groups by this reaction also works to increase the solubility of the derivative in organic solvents. Organic solubility of ionophores is an important factor for their application as transport agents.

The prepared imide acids, **1** and **2**, were examined for alkali and alkaline earth metal ion transport ability. A U-tube glass cell was used to study ion transport ability as reported previously.[3] The source phase was a tris-buffered solution containing metal ions and the receiving phase was 0.1 mol dm^{-3} nitric acid solution. These aqueous solutions were separated by a chloroform solution containing imide acid **1** or **2**. The experimental temperature was controlled at 25.0 ± 0.2 °C and each phase mechanically stirred at 200 rpm. Concentrations of the transported and remaining metal ions in the receiving and source phases, respectively, were monitored by atomic absorption spectroscopy (Shimadzu AA-680 & Seiko SAS-760). Control experiments were performed without the imide acids and almost no ion transport was observed, except for Ba^{II}, which was transported 6~11% under the present conditions. Therefore we concluded that Ba^{II} transport was uniquely influenced by the tris-buffered solution system.



1; R = p-n-$C_4H_9C_6H_4$
2; R = n-$C_{18}H_{37}$

Table 1 summarizes the results for the amount of ions transported for single ion and competitive ion transport experiments after 2 days. Run 1 shows that imide acid **1** selectively transports Li^I from the weakly basic solution of a mixture of alkali metal ions. The selectivity is as good as for acyclic polyether reported by Hiratani *et al.*,[8] which had quinolyl and carboxylic acid moieties as terminal groups, but the quantity of alkali metal ions transported by **1** was much less. Comparison of the structures of acyclic polyether[8] and imide acid **1** yields a possible explanation. The ether oxygen atoms of the acyclic polyether may work to stabilize the complexes in chloroform phase, but there are no ether oxygens in the imide acid. Since more than 90% of Na^I and K^I and about 83% of Li^I remained in the source phase after 2 days, low extraction ability of **1** for alkali metal ions in general is obvious.

It was shown that the imide acid **1** transports alkaline earth

Table 1. Amount of Alkali Metal and Alkaline Earth Metal Ions Transported after 2 days[a]

Run	Carrier	Metal ions transported to the receiving phase / mol%[b] (μmol)							Selectivity
		Li	Na	K	Mg	Ca	Sr	Ba	
1	**1**	6.7 (10)	1.3 (2)	1.3 (2)	-	-	-	-	Li/Na = 5.2, L/K = 5.2
2	**1**	6.8 (10)	-	-	-	-	-	-	
3	**1**	-	-	-	20 (30)	70 (105)	4 (6)	13 (20)	Ca/Mg = 3.5, Ca/Sr = 17.5
4	**1**	-	-	-	26 (39)	71 (106)	-	-	Ca/Mg = 2.7
5	**1**	-	-	-	61 (92)	-	-	-	
6	**1**	-	-	-	-	91 (136)	-	-	
7	**2**	2.9 (4.4)	2.5 (3.7)	1.8 (2.7)	-	-	-	-	
8	**2**	-	-	-	22 (33)	55 (82)	4.3 (6.4)	22 (32)	Ca/Mg = 2.5, Ca/Sr = 12.8

a; Initial transport conditions (25°C): source phase - 10 mmol dm^{-3} metal chloride tris-buffered solution, pH ~9.0~9.4, 15 cm^3; liquid membrane - 0.15 mmol of imide acid chloroform solution, 30 cm^3; receiving phase - 0.1 mol dm^{-3} HNO_3, 15 cm^3.
b; mol% = 100 x (moles of ion M^{z+} transported) / (initial moles of ion M^{z+} in the source phase)

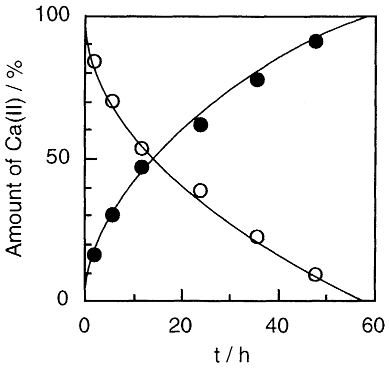


Figure 1. Time dependence of the amounts of Ca(II) in the source (O) and receiving (●) phase using carrier **1**.

metal ions an order of magnitude more effectively than alkali metal ions (runs 1 and 3). The acyclic polyether by Wierenga *et al.*[10] and the chelating agents having two imide acid moieties by Rebek *et al.*[5] also show high Ca^{II} transport ability comparable to that of natural ionophore A23187, although the selectivities were not reported. The present data for **1** and **2**, which contain a small cleft or cavity, indicate a large size cleft or cavity, as in the chelating agents by Rebek *et al.*[5] and Gloe *et al.*,[11] is not always necessary for selective ion transport. Furthermore simple lipophilic monoacids, like stearic and adamantane acetic acids, provide very little alkaline earth metal ion transport. Rather, the ionophore must have the appropriate balance between formation and decomposition of metal complex at the membrane interfaces.

The transport selectivity of **1** was examined by competitive ion transport experiments (runs 3 and 4) and single ion transport of Ca^{II} and Mg^{II} (runs 5 and 6). Run 3 shows that **1** has high Ca^{II}-selectivity over Ba^{II} and Sr^{II} and fairly good selectivity over Mg^{II}. This Ca^{II}/Ba^{II} selectivity was comparable to that of acyclic polyethers having two carboxyl groups developed by Hiratani *et al.*[9] Interestingly, taking into account Ba^{II} transport without carrier, the selectivity ratio for Ca^{II}/Ba^{II} would be much higher. The selectivity ratio for Ca^{II}/Mg^{II} is higher for the competitive experiments in runs 3 and 4, about 3.1, than that calculated from the ratio of runs 5 and 6, about 1.5. This is a commonly observed phenomenon, ascribed to the ions competing for ionophore in runs 3 and 4 or simply being transported without competition as in runs 5 and 6. The imide acid **2** shows almost the same results for both alkali metal and alkaline earth metal ions (runs 7 and 8). Therefore the structure of the **R** group on the nitrogen atom has little effect on the transport ability.

A typical time dependence of concentrations in the source and receiving phases for carrier **1** is shown for Ca^{II} (run 6) in Figure 1. The transport rate gradually decreases with time but, after a day, the Ca^{II} concentration in the receiving phase is higher than that of the source phase. Uphill transport of metal ion is apparently achieved due to the pH difference, that is, deprotonation of the carboxyl group at the membrane/source phase interface and re-protonation at the membrane/receiving phase interface drives the transport process.

To simulate capture of metal ions from the source phase for the transport experiments, extraction experiments were performed. A 1 mmol dm^{-3} $CHCl_3$ solution of **1** extracted about 9% of Mg^{II} and about 25% of Ca^{II} from 1 mmol dm^{-3} tris-buffered solutions of the ions at 25 ± 1 °C. These results are consistent with the selectivity of the transport experiments. Among the kinetic factors for transport, that is uptake and releasing rates, the former is slower, meaning uptake is the rate-determining step.

In summary, we have shown that imide acids, **1** and **2**, easily prepared from Kemp's acid were good carriers for alkaline earth metal ions from weakly basic to acidic solutions. The ionophores were very efficient and selective for Ca^{II} and Mg^{II} among alkaline earth metal ions.

References and Notes

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