Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Izatt, R. M. , Eblerhardt, L. , Clark, G. A. , Bruening, R. L. , Bradshaw, J. S. , Cho, M. H. and Christensen, J. J.(1987) 'Macrocycle-Mediated Transport in a Bulk 1.5 M HNO_3-$CHCl_3$-0.01 M HNO_3 Membrane System of Pd^{2} and M^{n} from Pd^{2} M^{n} Mixtures', Separation Science and Technology, 22: 2, 701 — 710
To link to this Article: DOI: 10.1080/01496398708068976
URL: http://dx.doi.org/10.1080/01496398708068976

SEPARATION SCIENCE AND TECHNOLOGY, 22(2&3), 701-710, 1987

Macrocycle-Mediated Transport in a Bulk 1.5 M HNO_3-$CHCl_3$-0.01 M HNO_3 Membrane System of Pd^{2+} and M^{n+} from Pd^{2+}-M^{n+} Mixtures

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ABSTRACT

Pd^{2+} has been transported using sulfur substituted macrocycles as carriers and several M^{n+} (M^{n+} = Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Tl^+, Cd^{2+}, and Pb^{2+}) have been transported using 18-crown-6 (18C6) and sulfur substituted macrocycles as carriers in a 1.5M $HNO_3/CHCl_3$/0.01M HNO_3 bulk liquid membrane system. Competitive Pd^{2+}-M^{n+} transport studies have also been carried out for the same systems. The cyclic polyether 18C6 transports M^{n+} selectively over Pd^{2+} for all M^{n+} except Li^+, Mg^{2+}, and Cd^{2+}. In the cases of these three cations, no transport was found for either Pd^{2+} or M^{n+}. Generally, the sulfur substituted macrocycles transport Pd^{2+} selectively over M^{n+}.

INTRODUCTION

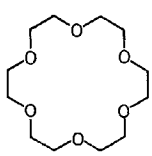
Macrocycle-mediated bulk liquid membrane cation transport has been studied extensively (1-13). In many instances, a particular cation is transported selectively over other cations from two-cation (14-20), three-cation (21), and multi-cation (22) mixtures.

Interest in the development of techniques for the separation of palladium lead to the present liquid membrane transport study. Recovery of palladium is important because of its usefulness as a catalyst, in electrical components, and in applications based upon

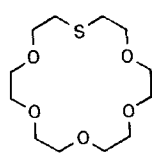
its resistance to corrosion (23). Liquid membrane technology may become important to the field of resource recovery in the near future. Bulk liquid membrane transport experiments are useful for deducing transport principles and for the identification of transport selectivities. The transport principles may be applied to practical membrane types, such as supported and emulsion liquid membranes, for efficient transport.

The chemistry of palladium is similar to that of platinum, i.e. both metals form anionic complexes with halide ions. Palladium, however, differs from platinum in forming a Pd^{2+} hydrated species in acid solutions of non-complexing anions (24). The existence of Pd^{2+} should make it possible to form Pd-macrocycle^{2+} complexes, like those formed with other divalent metal ions. Complex formation between Pd^{2+} and macrocycles should also lead to the transport of Pd^{2+} across liquid membranes, which transport has been achieved with other divalent metal ions, such as Pb^{2+} (4,14).

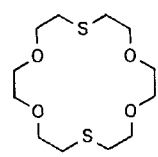
Few Pd-macrocycle^{2+} complexes have been reported in the literature. Crystal structure data of the $PdCl_2$-$T_2$18C6 complex



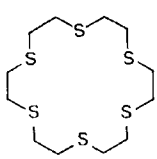
18-Crown-6 (18C6)



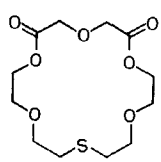
Thia-18-Crown-6 (T18C6)



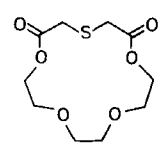
1,10-Dithia-18-Crown-6 ($T_2$18C6)



Hexathia-18-Crown-6 ($T_6$18C6)



Diketothia-18-Crown-6 (DKT18C6)



Diketothia-15-Crown-5 (DKT15C5)

Fig. 1. Macrocycles used in this study.

(25) and the $Pd(SCN)_2$-$T_2$18C6 complex (26) (see Figure 1 for the structure of $T_2$18C6 and of the other macrocycles used in the study) show Pd^{2+} coordination to be square planar with bonding to the two sulfur atoms of the macrocycle ring and to the two anions present in each complex. The oxygen donor atoms of the macrocycle ring do not coordinate with Pd^{2+}. These results are consistent with the greater affinity of Pd^{2+} for ligands containing sulfur donor atoms than for ligands with oxygen donor atoms (24). As a result of these data, a series of macrocycles containing sulfur donor atoms were selected as potential carriers of Pd^{2+} for the present transport study. The 18C6 macrocycle was also studied for comparison purposes.

Transport experiments were conducted using the macrocyclic carriers in Fig. 1 for the individual transport of Pd^{2+} as its nitrate salt and the competitive transport of Pd^{2+} and M^{n+} from binary mixtures of the nitrate salts of Pd^{2+} and of M^{n+}, where M^{n+} = Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Tl^+, Cd^{2+}, and Pb^{2+}. The source phases and receiving phases were made acidic in order to preclude Pd^{2+} hydrolysis in water and its subsequent precipitation as $Pd(OH)_2$. In order to understand the effect of acid upon transport of M^{n+}, experiments were conducted using a single nitrate solution of each M^{n+} as the source phase.

EXPERIMENTAL

The transport experiments were performed as described earlier (4), except that a 1.5 M HNO_3-$CHCl_3$-0.01 M HNO_3 liquid membrane system was used. The organic membrane was 3.0 ml of chloroform which, initially, was made 1.0 mM in the macrocycle and was situated between 0.8 ml of aqueous source phase and 5.0 ml of aqueous receiving phase. The single salt source phase solutions were 0.1 M $M(NO_3)_n$ in 1.5 M HNO_3 except for the $Ba(NO_3)_2$ solution which was 0.02 M in 1.5 M HNO_3 because of the lower solubility of $Ba(NO_3)_2$. The binary salt source phase solutions were 0.05 M $Pd(NO_3)_2$/0.05 M $M(NO_3)_n$ in 1.5 M HNO_3 except for the $Pd(NO_3)_2$/$Ba(NO_3)_2$ binary mixture which was 0.01 M $Pd(NO_3)_2$/0.01 M $Ba(NO_3)_2$ in 1.5 M HNO_3. The receiving phase was in all cases 0.01 M HNO_3.

The phases were stirred using small teflon magnetic stirrer bars placed in the chloroform layers and driven at 120 rpm by Hurst synchronous motors for 24 hours. After this period of time, 2.5 ml samples of the receiving phases were removed and analyzed for the metals of interest using a Perkin Elmer Model 603 atomic absorption spectrophotometer. The measured flux values (moles transported $s^{-1} \cdot m^{-2}$), J_M, were multiplied by 10^8 to obtain the J_M values in Tables 1 and 3. Each J_M value is the average of three separate determinations. The standard deviations are ~±12% and never exceed ±33%. Generally, the large standard deviations are for those systems which show little transport. The J_M values given are valid for the $CHCl_3$-source phase boundary. The J_M values across the $CHCl_3$-receiving phase boundary can be calculated by multiplying the

J_M values in Tables 1 and 2 by 0.286. The value of 0.286 is calculated from the difference between the source phase-membrane and receiving phase-membrane interfacial surface areas. The cell dimensions are given in reference (4). The experiments were run at room temperature (23-25°C), except for those systems containing Ag^+, which were covered with a dark box and were maintained at ~30°C.

The chemicals used and their sources are: $LiNO_3$ (MCB, Baker); $NaNO_3$ (Mallinckrodt, Baker); KNO_3 (Baker, Fisher); $Mg(NO_3)_2$

TABLE 1
M^{n+} Flux Values (J_M = moles transported $s^{-1} \cdot m^{-2}$) X 10^8 Through a 1.5M HNO_3-$CHCl_3$-0.01M HNO_3 Bulk Liquid Membrane System for Source Phases Containing 0.1 M $M(NO_3)_n$ and Using Various Macrocyclic Carriers[a]

M^{n+}	Macrocycles					
	18C6	T18C6	$T_2$18C6	DKT18C6	DKT15C5	$T_6$18C6
Pd^{2+}	0	35	54	27	1	0[b]
Li^+	0		0			0
K^+	346	5	0	0		0
Rb^+	216		0			0
Cs^+	46		0			0
Mg^{2+}	0.2			0.2		0.2
Ca^{2+}	13			0.3		0.4
Sr^{2+}	438		0			0
Ba^{2+}[c]	53		0.2			0.2
Ag^+[d]	216	398	66	40		53[b]
Tl^+	532		4			0.1
Cd^{2+}	0		0			0
Pb^{2+}	142	649	173	0.1		0.1

[a]Blank experiments containing no macrocyclic carrier typically gave flux values of ~0.2 X 10^{-8} moles $s^{-1} \cdot m^{-2}$ or less for each M^{n+}; [b]Precipitation occurred at the source phase-membrane interface; [c]$Ba(NO_3)_2$ = 0.02 M; [d]Temperature of cell is ~30°C.

TABLE 2

Log K Values for 1:1 M^{n+}-Macrocycle Interaction at 25°C[a]

Macrocycle	M^{n+}													
	Pd^{2+}	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ag^+	Tl^+	Cd^{2+}	Pb^{2+}
18C6	b	c	0.8	2.03	1.56	0.99	c	<0.5	2.72	3.87	1.50	2.27	2[d]	4.27
			4.36[e]	6.06[e]	5.32[e]	4.79[e]		3.86[e]	>5.5[e]	7.04[e]	4.58[e]	5.34[e]		(7.44)[f]
T18C6			2.57[e]	3.61[e]	2.99[e]					3.4[e]	>5.5[e]			
$T_2$18C6	>7[g]			1.15[e]							4.34	0.93		3.13
											(7.42)[h]	(4.00)[i]		(6.30)[f]

[a]Valid in H_2O unless otherwise indicated; reference 30; [b]Log K very small in 1.0 M HNO_3; reference 28; [c]Log K very small in CH_3OH; reference 29; [d]Valid in 0.1 M HNO_3; reference 31; [e]Valid in CH_3OH; reference 30; [f]Log K(CH_3OH) values are estimated by adding 3.17 (the difference between log K(CH_3OH) and log K(H_2O) for Ba^{2+}-18C6 interaction) to the log K(H_2O) values for Pb^{2+}-18C6 and Pb^{2+}-$T_2$18C6 interactions; [g]Valid in 1.0 M HNO_3; this work; [h]Log K(CH_3OH) value is estimated by adding 3.08 (the difference in log K(CH_3OH) and log K(H_2O) for Ag^+-18C6 interaction) to log K(H_2O) for Ag^+-$T_2$18C6 interaction; [i]Log K(CH_3OH) value is estimated by adding 3.07 (the difference in log K(CH_3OH) and log K(H_2O) for Tl^+-18C6 interaction) to log K(H_2O) for Tl^+-$T_2$18C6 interaction.

(Mallinckrodt, Fisher); HNO_3, $CHCl_3$ (Fisher); $RbNO_3$, $CsNO_3$ (Aldrich, Alfa); $Pd(NO_3)_2$ (Alfa); $Ca(NO_3)_2$, $Pb(NO_3)_2$ (Baker, B&A); $Sr(NO_3)_2$ (Fisher, ACS); $Ba(NO_3)_2$ (Baker, JTB); $AgNO_3$ (Baker, Aldrich); $TlNO_3$ (ICN); $Cd(NO_3)_2$ (B&A); 18C6, T18C6, $T_3$18C6 (Parish); $T_6$18C6 (Professor Stephen Cooper, Harvard University); DKT18C6, DKT15C5(27). All chemicals were reagent quality and were used without further purification.

RESULTS AND DISCUSSION

Single Salt Systems

It was found that $Pd(NO_3)_2$ transported very little from acidic solutions using oxygen and nitrogen donor atom crown ether and cryptand carriers. Sulfur donor atom crown ethers were much more efficient as $Pd(NO_3)_2$ carriers (28). Results from the present study for the transport of $Pd(NO_3)_2$ using various macrocycle carriers are given in Table 1 as flux values. Very little Pd^{2+} transport occurs using 18C6. This is to be expected because of the small interaction between Pd^{2+} and 18C6 in acidic solution (28), as was estimated using a calorimetric technique described earlier (29). Successive substitution of one and two oxygen donor atoms of 18C6 with sulfur results in the successive increase in Pd^{2+} fluxes as indicated for the Pd^{2+} fluxes in Table 1 obtained using T18C6 and $T_2$18C6. Preliminary calorimetric results show that the log K(1.0 M HNO_3) value for Pd^{2+}-$T_2$18C6 interaction is several log K units higher than the log K(1.0 M HNO_3) value for Pd^{2+}-18C6 interaction. In the case of $T_6$18C6, a very strong Pd^{2+}-$T_6$18C6 interaction would be expected. Formation of an orange precipitate at the source phase-membrane interface indicates complexation occurs. The lack of Pd^{2+} transport in this case is probably due to little release of Pd^{2+} from $T_6$18C6 into the receiving phase because of strong complexation between Pd^{2+} and $T_6$18C6. The lower fluxes of Pd^{2+} with DKT18C6 and DKT15C5 relative to the other sulfur macrocycles may be due to greater macrocycle partitioning and, hence, loss of DKT18C6 and DKT15C5 to the aqueous phases due to the presence of carbonyl oxygens on the macrocycle ring.

Transport of several cations from single salt solutions containing nitric acid has been studied using 18C6, T18C6, $T_2$18C6, DKT18C6, and $T_6$18C6. The transport trends from macrocycle to macrocycle for each cation are similar to the previous results in neutral source solutions in which 18C6 transported alkali cations, alkaline earth cations, Ag^+ (4), and Tl^+ (17) better than $T_2$18C6. It is interesting to note that of the macrocycles studied, T18C6 transports Ag^+ and Pb^{2+} better than any other macrocycle. Lamb, et al. (5) observed that there is an optimum log K(CH_3OH) value for M^{n+}-macrocycle interaction for which M^{n+} transport is greatest. The transport of M^{n+} decreases rapidly as the log K(CH_3OH) value becomes less than or greater than the optimum value. The optimum log K(CH_3OH) values were found to be 5.5-6.0 for monovalent cations and 6.5-7.0 for divalent cations. The better transport of Ag^+ and Pb^{2+}

TABLE 3
Pd^{2+} and M^{n+} Flux Values (J_M = moles transported $s^{-1} \cdot m^{-2}$) X 10^8 Through a 1.5M HNO_3-$CHCl_3$-0.01M HNO_3 Bulk Liquid Membrane System for Source Phases Containing 0.05 M $Pd(NO_3)_2$/0.05 M $M(NO_3)_n$ Mixtures and Using Various Macrocyclic Carriers

Cation	Macrocycles					
	18C6	T18C6	$T_2$18C6	DKT18C6	DKT15C5	T^{6}18C6[a]
Pd^{2+}	0.2	38	56	34	1	0.1
Li^+	0.1	0	0	0	0	0
Pd^{2+}	0.1	49	54	33	1	0
Na^+	6	3	3	3	3	3
Pd^{2+}	0	36	61	32	1	0.1
K^+	362	1	0.3	0.4	0.4	0.8
Pd^{2+}	0	37	61	33	2	0
Rb^+	215	0	0	0	0	0
Pd^{2+}	0	51	56	30	2	0
Cs^+	23	0.6	0	0	0	0
Pd^{2+}	0.	40	58	35	1	0.1
Mg^{2+}	0.2	0.1	0.8	0	0.2	0
Pd^{2+}	0	41	59	29	2	0
Ca^{2+}	11	0.3	0.4	0.3	0.1	0.2
Pd^{2+}	0.6	41	60	32	2	0
Sr^{2+}	329	0.1	0.1	0	0	0.1
Pd^{2+}[b]	0	38	60	31	2	0
Ba^{2+}[b]	63	8	0.2	0.8	0.4	0.3
Pd^{2+}[c]	0	58	52	18[d]	1	0.1
Ag^{+}[c]	189	8	2	0.3[d]	0.2	2
Pd^{2+}	0.1	54	60	30	1	0
Tl^+	661	0.1	0.1	0.1	0.2	0.1
Pd^{2+}	0.1	37	48	30	2	0
Cd^{2+}	0	0	0	0	0	0
Pd^{2+}	0.1	39	52	32	1	0
Pb^{2+}	289	7	2	0.2	0.2	0.2

[a]Precipitation occurred at the source phase-membrane interface; [b]$Pd(NO_3)_2$ = 0.01 M, $Ba(NO_3)_2$ = 0.01 M; [c]Temperature of cell is ~30°C; [d]Small amount of precipitation occurred at the receiving phase-membrane interface.

with T18C6 as compared to 18C6 and $T_2$18C6 is probably due to more optimal log K values for Ag^+-T18C6 and Pb^{2+}-T18C6 interactions relative to the corresponding 18C6 and $T_2$18C6 interactions. Table 2 contains log K values for M^{n+}-macrocycle interactions. No log K data are available for Ag^+-T18C6 and Pb^{2+}-T18C6 interactions, however, the values would be expected to lie between those for the corresponding 18C6 and $T_2$18C6 interactions. Substitution of oxygen donor atoms with sulfur donor atoms increases the log K values for Ag^+-macrocycle interaction and decreases the log K values for Pb^{2+}-macrocycle interaction as seen in Table 2 for Ag^+ and Pb^{2+} interactions with 18C6 and $T_2$18C6. The macrocycle $T_6$18C6 produces little transport for any of the cations studied except Ag^+. In the case of Ag^+, some transport occurs in spite of the presence of a white precipitate formed at the source phase-membrane interface. The presence of nitric acid in the source phase has produced cation fluxes that are of the same magnitude as those observed earlier for neutral source phase solutions at ten times the cation concentrations (4, 17).

Binary Salt Systems

In competitive transport experiments for binary systems containing Pd^{2+} and one other cation, Pd^{2+} is transported selectively over the other cation (Table 3) using the sulfur macrocycles, except for the Pd^{2+}/Na^+-DKT15C5 system and several of the $T_6$18C6 systems. The selective transport of Pd^{2+} over other cations with the sulfur macrocycles is probably a reflection of the greater affinity of sulfur containing macrocycles for Pd^{2+} compared to that for the other cation. Transport results for Ag^+ and Pb^{2+} (Table 1) show both of these cations to have larger fluxes than Pd^{2+} with T18C6 and $T_2$18C6 in single salt systems. However, competitive binary studies show Pd^{2+} to be transported selectively in these systems. This phenomenon has been observed before (13). In the cases of T18C6 and $T_2$18C6, the log K values for their interactions with Ag^+ and Pb^{2+} are probably closer to their optimum values than those for Pd^{2+}, as indicated by the greater flux values of Ag^+ and Pb^{2+} with these macrocycles in single systems. The selective transport of Pd^{2+} over both Ag^+ and Pb^{2+} in the binary systems using T18C6 and $T_2$18C6 indicates a greater stability for the Pd^{2+}-macrocycle complexes relative to those for Ag^+ and Pb^{2+}. Preliminary calorimetric data show that the log K(1.0 M HNO_3) value for Pd^{2+}-$T_2$18C6 interaction is much greater than those for the corresponding interactions for Ag^+ and Pb^{2+}. The log K(1.0 M HNO_3) value for Pd^{2+}-$T_2$18C6 interaction is much greater than the optimum value for divalent cations. This large log K value is probably responsible for the flux of Pd^{2+} with $T_2$18C6 being less than the fluxes of Ag^+ and Pb^{2+} with $T_2$18C6.

ACKNOWLEDGMENT

We acknowledge support for this research by the National Science Foundation through Grant Number CPE-8119634. We also express appreciation to Gypzy LindH for doing several of the atomic absorption analyses and some of the transport experiments.

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