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Effect of Receiving Phase Anion on Macrocycle-Mediated Cation Transport Rates and Selectivities in Water—Toluene—Water Emulsion Membranes

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Effect of Receiving Phase Anion on Macrocycle-Mediated Cation Transport Rates and Selectivities in Water–Toluene–Water Emulsion Membranes*

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Abstract

Relative transport rates of metal nitrates (Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, and Pb^{2+}) were measured alone and in combination with either Pb^{2+}, Ag^+, or Tl^+ in a water–toluene–water emulsion membrane system. The toluene phase contained the surfactant Span 80 and the crown ether dicyclohexano-18-crown-6 (DC18C6). The aqueous receiving phase contained the lithium salt of one of the following anions: pyrophosphate, thiosulfate, hydroxide, chloride, formate, nitrate. In the case of the metal combinations, chloride and formate ions were not studied. Unless significant complexation occurred both between the transported cation and the anion in the receiving phase and between the cation and DC18C6 in the membrane phase, there was little or no transport of the cation from the source phase to the receiving phase. Selective removal of Pb^{2+} and of Ag^+ from binary mixtures of these cations with each of the cations listed was demonstrated using the emulsion membrane.

INTRODUCTION

This paper is the third in a series intended to identify and systematically evaluate factors which affect the macrocycle-mediated transport of cations from cation mixtures using emulsion membranes. In our previous communications (*1*, *2*), we showed that the crown ether dicyclohexano-18-crown-6 (DC18C6) incorporated into the organic layer of a water in organic liquid in

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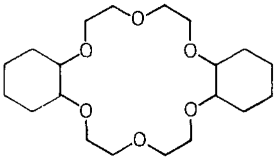

Dicyclohexano-18-Crown-6
(DC18C6)

water emulsion membrane system could in minutes selectively transport Pb^{2+} over any metal ion studied and Tl^{+} over most metal ions investigated from the source phase into an interior receiving phase containing 0.050 *M* $Li_4P_2O_7$.

We now report the effect of receiving phase anion concentration and type on the relative rates of DC18C6-mediated transport of several metal nitrate salts. By choosing the appropriate receiving phase anion, either Pb^{2+} or Ag^{+} was transported selectively relative to all other metal ions tested.

EXPERIMENTAL

The emulsion system was formulated from the organic membrane phase and the aqueous receiving and source phases as described previously (*1*). The organic phase consisted of toluene (Fisher) in which was dissolved the carrier DC18C6 [mixture of cis-syn-cis and cis-anti-cis isomers (*3*), Parish Chemical Co.], and 3% v/v of the nonionic surfactant Span 80 (Emulsion Engineering). The source phase contained nitrate salts of either one or two of the following metal ions which were obtained in the highest purity available and were used without further purification: Na^{+}, Sr^{2+} (Mallinckrodt); K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Pb^{2+} (Baker); Rb^{+}, Cs^{+} (Alfa); Tl^{+} (ICN Pharmaceuticals); Ag^{+} (Sargent Welch). The receiving phase contained a 0.050 *M* lithium salt of one of the following anions: pyrophosphate, thiosulfate, hydroxide, chloride, formate, nitrate. The nitrate (Alfa), chloride (Mallinckrodt), and hydroxide (Matheson, Coleman, and Bell) were obtained as their reagent grade lithium salts. The reagent grade sodium salts of formate (Spectrum), pyrophosphate (Mallinckrodt), and thiosulfate (Fisher) were converted to the corresponding lithium salts by the ion-exchange procedure described previously (*2*). The lithium salt was used because in previous work (*3*) DC18C6 was shown to form much weaker complexes with Li^{+} than with other cations used in the study. Thus, Li^{+} in the receiving phase would be least likely to compete with the other cations for the

DC18C6 carrier in the membrane. Enrichment ratio, used to express cation transport in these systems, is defined as $E = (C_f^r/C_i^s)$, where C_f^r = final cation concentration in the receiving phase and C_i^s = initial cation concentration in the source phase. Since the volume of the receiving phase was one-tenth that of the source phase, a maximum value of 10 may be obtained for E if complete transfer of the cation from the source phase to the receiving phase occurs.

Measured amounts of the emulsion (consisting of membrane and receiving phases) and source phases were stirred together continuously at 600 rpm (*1*). Samples for analysis were obtained at 0 and 10 min (*2*). Metal analyses were carried out using a Perkin-Elmer model 603 atomic absorption spectrophotometer. Each experiment was done at least in triplicate. In several cases the same system was determined several times including preparation of new emulsions for each determination. The precision of the enrichment ratios in these determinations was ±10% or better. The Pb^{2+} determinations in Tables 1, 3, and 5 provide cases in point. The average of these Pb^{2+} enrichment values is 7.9 with a standard deviation of 0.6.

RESULTS AND DISCUSSION

Enrichment ratios for Pb^{2+} as a function of receiving phase anion ($P_2O_7^{4-}$) and membrane phase carrier (DC18C6) concentrations are given in Table 1. In general, E increased with both DC18C6 and $P_2O_7^{4-}$ concentrations. The apparent small increase in E with increasing crown concentration at O M $P_2O_7^{4-}$ may be due to partitioning of Pb^{2+} into the membrane because of an increasing number of DC18C6 molecules available to complex with Pb^{2+}.

The effect on the transport rate of decreasing receiving phase volume while

TABLE 1
Effect of DC18C6 and $P_2O_7^{4-}$ Concentrations on Pb^{2+} Enrichment Ratios Measured at 10 Minutes

Crown concentration in membrane (*M*)	$P_2O_7^{4-}$ Concentration in receiving phase (*M*)				
	0.0	0.001	0.005	0.010	0.050
	Enrichment Ratio (E)				
0.000	0.3	0.0	0.1	0.0	0.6
0.001	0.8	1.4	1.4	1.8	2.2
0.005	1.0	1.9	2.8	2.9	4.1
0.010	1.5	2.3	3.7	3.6	5.4
0.020	1.5	2.5	4.3	5.1	7.3

maintaining the concentration of lithium pyrophosphate at 0.05 *M* and of DC18C6 at 0.2 *M* was examined. With the receiving phase as small as 3 mL per 9 mL of organic phase, complete transport of the Pb^{2+} was seen within 10 min. When an experiment was performed with no receiving phase present, little extraction of Pb^{2+} into the toluene was observed. The effect on Pb^{2+} enrichment ratios of decreasing the receiving phase volume at 0.005 *M* $P_2O_7^{4-}$ is shown in Table 2. The quantity *E* remains relatively constant, but the final concentration of Pb^{2+} in the source phase increases with decreasing receiving phase volume. From this result one can conclude that the total amount of Pb^{2+} transported is directly related to the number of moles of $P_2O_7^{4-}$ present.

Effect of Receiving Phase Anion Type-Single Extraction

The initial and final M^{n+} concentrations in the source phase and the enrichment ratios as a function of receiving phase anion for single cation transport with DC18C6 are presented in Table 3. Generally, a direct correlation is found between the binding constant of the metal ion to the anion (log *K* values in Table 3) and *E*, i.e., the larger the binding constant the greater the enrichment ratio, unless a stable M^{n+}-macrocycle complex is not formed. The movement of the cation from the source phase into the organic phase requires that a stable M^{n+}-macrocycle complex be formed. However, the stability of this complex must be less than that of the M^{n+}-anion species in the receiving phase for cation transport to occur. The alkaline earth cations provide an illustration of these effects Neither Mg^{2+} nor Ca^{2+} form stable complexes with DC18C6 and their transport is negligible even though they form stable $P_2O_7^{4-}$ and, in the case of Mg^{2+}, OH^- complexes. On the other hand, Sr^{2+} and Ba^{2+} form stable complexes with both DC18C6 and $P_2O_7^{4-}$.

TABLE 2
Effect of Receiving Phase Volume on Pb^{2+} Enrichment Ratio[a]

Volume of receiving phase (mL)	Enrichment ratio, *E*	Final concentration (μg/mL) of Pb^{2+} in source phase
10	8.6	19
8	8.9	40
5	11[b]	53
2	11[b]	102

[a] Concentration of $Li_4P_2O_7$ in receiving phase = 0.005 *M* and of DC18C6 in toluene = 0.01 *M*.

[b] An *E* value greater than 10 is possible since the receiving phase is less than 10 mL.

TABLE 3

Initial (i) and Final (f)[a] Cation Concentrations (μg/mL) in the Source Phase for Single Cation Transport Together with the Enrichment Ratio (E) as a Function of Receiving Phase Anion (either $P_2O_7^{4-}$, $S_2O_3^{2-}$, OH^-, Cl^-, $HCOO^-$, or NO_3^-)[b]

	$P_2O_7^{4-}$				$S_2O_3^{2-}$				OH^-			
M^{n+}	log K[c]	i	f	E	log K[c]	i	f	E	log K[c]	i	f	E
Na^+	2.35	108	106	0.2	0.8	122	130	0.0	−0.70	98	103	0.0
K^+	2.3	103	92	1.1	0.92	98	102	0.0	[d]	104	103	0.1
Rb^+	[e]	134	92	3.1	[e]	117	119	0.0	[d]	115	110	0.4
Cs^+	2.3	189	166	1.2	[e]	103	106	0.0	[d]	106	100	0.6
Ag^+	[e]	107	62	4.2	8.87	130	5	9.6	*−7.84*	82	8	9.0
Tl^+	1.69	84	2	9.8	1.91	108	106	0.2	0.49	128	109	1.5
Mg^{2+}	5.7	128	131	0.0	1.84	130	132	0.0	*−10.74*	97	97	0.0
Ca^{2+}	5.60	86	80	0.7	1.90	73	74	0.0	1.30	156	144	0.8
Sr^{2+}	5.4	83	37	5.5	2.04	113	103	0.9	0.96	163	144	1.2
Ba^{2+}	4.64	135	81	4.0	2.33	79	68	1.4	0.64	188	182	0.3
Pb^{2+}	11.24	120	18	8.5	2.56	131	119	0.9	*−16.79*	133	66	5.0
Zn^{2+}	12.80	122	107	1.2	2.40	124	125	0.0	*−17.15*	126	91	2.8

	Cl^-				$HCOO^-$				NO_3^-			
M^{n+}	log K[c]	i	f	E	log K[c]	i	f	E	log K[c]	i	f	E
Na^+	−0.78	106	109	0.0	[e]	136	131	0.4	−0.3− −0.5	112	112	0.0
K^+	[d]	122	118	0.3	[e]	224	218	0.3	−0.26	131	140	0.0
Rb^+	[d]	117	115	0.2	[e]	131	133	0.0	[e]	150	160	0.0
Cs^+	−0.45	105	107	0.0	[e]	106	110	0.0	0.04	102	102	0.0
Ag^+	−9.75	94	62	3.4	[e]	90	91	0.0	−0.18	85	86	0.0
Tl^+	0.66	97	94	0.3	[e]	105	108	0.0	0.38	122	125	0.0
Mg^{2+}	[d]	129	130	0.0	1.43	130	132	0.0	[d]	122	124	0.0
Ca^{2+}	[d]	70	68	0.3	1.43	197	212	0.0	0.31	134	146	0.0
Sr^{2+}	[d]	150	148	0.1	1.39	146	151	0.0	0.54	149	153	0.0
Ba^{2+}	[d]	203	198	0.2	1.38	197	194	0.2	0.94	191	194	0.0
Pb^{2+}	1.59	88	79	1.0	0.78	161	140	1.3	1.15	109	98	1.0
Zn^{2+}	−0.5	128	130	0.0	1.97	122	119	0.2	[d]	118	120	0.0

[a] After 10 min.

[b] The anion and DC18C6 concentrations were 0.05 and 0.02 M respectively.

[c] Log K values are for the 1:1 reaction of M^{n+} with the anion to form an aqueous species except in the cases where insoluble products are formed and solubility products are given (italics) (*4–6*).

[d] No evidence of complexation.

[e] Log K value unknown.

The high E values in these cases indicate that the M^{2+}–$P_2O_7^{4-}$ complexes are formed preferentially. In the case of Tl^+, a low binding constant for Tl^+ with $P_2O_7^{4-}$ is reported (Table 3), yet there is a large amount of transport. Our experimental results leading to the large E values have been verified several times. We do not have an explanation for this exception, but redetermination of the Tl^+–$P_2O_7^{4-}$ binding constant appears desirable.

Effect of Receiving Phase Anion Type-Binary Metal Ion Transport

In describing transport from cation mixtures, a separation factor between cations A and B is defined as $\phi(M_1/M_2) = (C_f^r/C_f^s)_{M_1}/(C_f^s/C_f^r)_{M_2}$ where C is the metal concentration in ppm, subscript f refers to the final concentration, and superscripts r and s refer to the internal receiving and external source phases, respectively.

Transport data are given in Table 4 for a series of binary mixtures of metal ions where either $P_2O_7^{4-}$, $S_2O_3^{2-}$, OH^-, or NO_3^- is present in the receiving phase at 0.050 *M*. The DC18C6 concentration in the toluene phase was initially 0.02 *M*. With NO_3^-, little if any, metal ion transport is seen. This result correlates with the data in Table 3 in that there was little enrichment for any metal tested alone when NO_3^- was present in the receiving phase. With $S_2O_3^{2-}$ present, significant extraction was observed for Ag^+ over all the other metal ions tested. This result is consistent with the data in Table 3 as Ag^+ is the only metal ion with a significant enrichment ratio with this anion. Significant enrichment is shown by Pb^{2+} and Ag^+ when run individually with OH^- (Table 3). In binary systems with OH^- in the receiving phase, Pb^{2+} was extracted selectively over all other cations present except Zn^{2+} where significantly lower Pb^{2+} transport is found. Ag^+ was selectively transported over all cations tested with the exceptions of Pb^{2+} and Zn^{2+}. The low enrichment ratios for Pb^{2+} and Ag^+ when in binary systems with Zn^{2+} are probably a result of the formation of anionic Zn^{2+}–OH^- species which are more stable than either corresponding anionic Pb^{2+}–OH^- or AgOH(s) species (7). Consistent with this argument, the log K_{sp} value for $Zn(OH)_2$(−17.15) is lower than that of either AgOH (Log $K_{sp} = -7.84$) or $Pb(OH)_2$ (log $K_{sp} = -16.79$). It is interesting that in either H_2O or methanol, Zn^{2+} does not react with DC18C6 whereas Ag^+ and Pb^{2+} form stable complexes. In order to determine whether or not DC18C6 was necessary for Zn^{2+} transport, Zn^{2+} enrichment values obtained for runs that were identical (0.05 *M* $P_2O_7^{4-}$ receiving phase) except for DC18C6 concentration were compared. For a DC18C6 concentration of 0.2 *M*, an E value of Zn^{2+} of 2.8 was obtained, and for a run with no DC18C6 in the

TABLE 4

Initial (i) and Final (f)[a] Cation Concentrations (μg/mL) in the Source Phase for Several Metal Cations (M_2) with Either Pb^{2+}, Ag^+, or Tl^+ (M_1) Together with the Enrichment Ratio (E) and the Separation Factor, $\phi(M_1/M_2)$ for Each Binary Cation System as a Function of Receiving Phase Anion (either $P_2O_7^{4-}$, $S_2O_3^{2-}$, OH^-, or NO_3^-)[b]

M_1	i	f	E	M_2	i	f	E	$\phi(M_1/M_2)$
				$P_2O_7^{4-}$				
Pb^{2+}	126	1	9.9	Na^+	106	108	0.0	c
Pb^{2+}	132	2	9.8	K^+	74	74	0.0	c
Pb^{2+}	127	7	9.4	Rb^+	114	114	0.0	c
Pb^{2+}	133	1	9.9	Cs^+	97	99	0.0	c
Pb^{2+}	129	2	9.8	Ag^+	80	77	0.4	1630
Pb^{2+}	123	2	9.8	Tl^+	119	115	0.3	1739
Pb^{2+}	116	1	9.9	Mg^{2+}	135	136	0.0	c
Pb^{2+}	128	2	9.8	Ca^{2+}	93	92	0.1	5796
Pb^{2+}	126	1	9.9	Sr^{2+}	81	75	0.7	1562
Pb^{2+}	75	30	6.0	Ba^{2+}	127	120	0.6	26
Pb^{2+}	135	2	9.9	Zn^{2+}	141	140	0.1	9310
				$S_2O_3^{2-}$				
Ag^+	120	65	4.6	Na^+	126	123	0.2	35
Ag^+	130	43	6.7	K^+	90	108	0.0	c
Ag^+	118	73	3.8	Rb^+	132	139	0.0	c
Ag^+	113	47	5.8	Cs^+	93	102	0.0	c
Ag^+	193	85	5.6	Tl^+	74	79	0.0	c
Ag^+	117	76	3.5	Mg^{2+}	130	130	0.0	c
Ag^+	131	35	7.3	Ca^{2+}	93	111	0.0	c
Ag^+	190	25	8.7	Sr^{2+}	294	328	0.0	c
Ag^+	138	56	5.9	Ba^{2+}	130	139	0.0	c
Ag^+	214	96	5.5	Pb^{2+}	76	76	0.0	c
Ag^+	115	88	2.3	Zn^{2+}	116	126	0.0	c
				OH^-				
Pb^{2+}	140	43	6.9	Na^+	108	115	0.0	c
Pb^{2+}	109	3	9.7	K^+	123	114	0.7	448
Pb^{2+}	114	24	7.9	Rb^+	114	112	0.2	210
Pb^{2+}	108	45	5.8	Cs^+	118	114	0.3	40
Pb^{2+}	124	1	9.9	Ag^+	115	97	1.6	663
Pb^{2+}	106	36	6.6	Tl^+	132	131	0.1	255
Pb^{2+}	160	0	10.0	Mg^{2+}	163	164	0.0	c
Pb^{2+}	100	9	9.1	Ca^{2+}	136	122	1.0	88
Pb^{2+}	107	22	7.9	Sr^{2+}	165	160	0.3	124
Pb^{2+}	135	11	9.2	Ba^{2+}	114	73	3.6	20
Pb^{2+}	112	80	2.9	Zn^{2+}	115	96	1.7	2
Ag^+	123	52	5.8	Na^+	113	113	0.0	c
Ag^+	88	35	6.0	K^+	76	94	0.0	c

(continued)

TABLE 4 (continued)

M_1	*i*	*f*	E	M_2	*i*	*f*	E	$\phi(M_1/M_2)$
				OH^-				
Ag^+	106	5	9.5	Rb^+	121	121	0.0	[c]
Ag^+	85	17	8.0	Cs^+	112	114	0.0	[c]
Ag^+	74	11	8.5	Tl^+	100	94	0.6	90
Ag^+	94	17	8.2	Mg^{2+}	77	94	0.0	[c]
Ag^+	86	15	8.3	Ca^{2+}	74	68	0.8	54
Ag^+	96	19	8.0	Sr^{2+}	126	108	1.4	24
Ag^+	82	0	10.0	Ba^{2+}	88	105	0.0	[c]
Ag^+	132	125	0.5	Zn^{2+}	125	95	2.4	0
				NO_3^-				
Pb^{2+}	132	126	0.5	Na^+	116	114	0.2	3
Pb^{2+}	84	75	1.1	K^+	121	97	2.0	0
Pb^{2+}	178	174	0.2	Rb^+	145	160	0.0	[c]
Pb^{2+}	224	207	0.8	Cs^+	152	152	0.0	[c]
Pb^{2+}	142	134	0.6	Ag^+	90	87	0.3	2
Pb^{2+}	71	62	1.3	Tl^+	94	90	0.4	3
Pb^{2+}	133	122	0.8	Mg^{2+}	105	122	0.0	[c]
Pb^{2+}	147	139	0.5	Ca^{2+}	134	124	0.7	1
Pb^{2+}	134	128	0.4	Sr^{2+}	136	142	0.0	[c]
Pb^{2+}	124	116	0.6	Ba^{2+}	94	101	0.0	[c]
Pb^{2+}	113	110	0.3	Zn^{2+}	121	125	0.0	[c]
Tl^+	142	136	0.4	Na^+	166	163	0.2	2
Tl^+	109	107	0.2	K^+	117	107	0.9	0
Tl^+	201	197	0.2	Rb^+	153	157	0.0	[c]
Tl^+	200	197	0.2	Cs^+	159	161	0.0	[c]
Tl^+	201	199	0.1	Ag^+	92	93	0.0	[c]
Tl^+	82	77	0.6	Mg^{2+}	122	124	0.0	[c]
Tl^+	155	147	0.5	Ca^{2+}	174	178	0.0	[c]
Tl^+	135	138	0.0	Sr^{2+}	148	143	0.3	[c]
Tl^+	84	81	0.4	Ba^{2+}	110	140	0.0	[c]
Tl^+	119	123	0.0	Zn^{2+}	117	117	0.0	[c]

[a] After 10 min.

[b] The anion and DC18C6 concentrations were 0.05 and 0.02 *M*, respectively.

[c] Undefined.

TABLE 5
Pb^{2+} and Sr^{2+} Concentrations (C) (μg/mL) in the Source Phase Together with Enrichment Ratios (E) as a Function of Time (min) for Pb^{2+} and Sr^{2+} Single and Pb^{2+}–Sr^{2+} Binary Cation Systems

Sr^{2+}			Pb^{2+}		
min	C	E	min	C	E
Pb^{2+} and Sr^{2+}, Single Cation Systems					
0	83	0.0	0	108	0.0
3	63	2.4	3	70	3.5
6	51	3.9	6	47	5.6
10	37	5.5	10	24	7.8
15	19	7.7	15	7	9.4
20	10	8.8	20	6	9.4
Pb^{2+}–Sr^{2+}, Binary Cation System					
0	78	0.0	0	118	0.0
3	77	0.1	3	28	7.6
6	75	0.4	6	20	8.3
10	66	1.6	10	21	8.2
15	55	2.9	15	23	8.1
20	43	4.5	20	22	8.1

membrane, an E value of 0.0 was obtained. From this result we conclude that Zn^{2+} complexation with DC18C6 must occur in toluene, allowing Zn^{2+} to reach the receiving phase where a stable anionic Zn^{2+}–OH^- complex is formed. The Pb^{2+}–Zn^{2+} binary system determinations using LiOH in the receiving phase were repeated several times. In each case the result was the same. Pb^{2+} transport was markedly lower when Zn^{2+} was present, and Zn^{2+} transport was unchanged from its single ion value. Determinations were also made in which the Pb^{2+} and Zn^{2+} E values were measured at intervals of 3, 6, 10, 15, and 20 min. The E values increased with time at the same rate for both cations (Pb^{2+}: E = 2.3, 2.4, 3.0, 3.6, 4.1; Zn^{2+}: E = 1.2, 0.8, 1.7, 2.2, 3.9). This result suggests that Zn^{2+} and Pb^{2+} must bind DC18C6 about equally in toluene.

The data presented in Tables 1–4 allow three conclusions to be drawn with respect to the selectivity shown by emulsion membranes toward specific cations either in single cation or dual cation experiments. First, partitioning of the cation into the organic phase is determined primarily by the relative strength of the cation–crown ether complex compared to cation hydration. For example, Mg^{2+} does not complex with DC18C6 and therefore no transport is seen even though an anion, OH^-, which interacts with Mg^{2+} to form $Mg(OH)_2$ (log $K_{sp} = -10.74$) is present in the receiving phase. The remaining cations either are known to form complexes with DC18C6 of moderate to high stability (*8*) or, as in the case of the Zn^{2+}–OH^- system, apparently form stable DC18C6 complexes in toluene. Therefore, they partition into the membrane and are transported to the receiving phase. Second, partitioning of the metal from the membrane phase to the receiving phase is closely related to the strength of the complex formed between the cation and the receiving phase anion. The stronger the complex formed, the more complete is the release of the cation to the receiving phase. For example, metal nitrate complexes are very weak and so no transport is seen. On the other hand, $P_2O_7^{4-}$ complexes strongly with Pb^{2+} (log $K = 11.24$); hence, complete transport of Pb^{2+} from the source phase to the receiving phase occurs within minutes. However, when $S_2O_3^{2-}$ is used as the receiving phase anion, no Pb^{2+} transport is seen with the same membrane carrier, but complete Ag^+ transport is observed. The latter result it consistent with the observation that Ag^+ complexes strongly with $S_2O_3^{2-}$ (log $K = 8.87$) while Pb^{2+} does not. Third, for the case in which both metal ions in a mixture complex with the receiving phase anion, the relative transport rates of the two metal ions will be determined by the relative magnitudes of the log K values for formation of their crown ether complexes. The metal ion that forms the most stable complex with the crown ether will be transported first followed by the other. For example, we have observed that for the Pb^{2+}–Sr^{2+} mixture using 0.050 M $P_2O_7^{4-}$ in the receiving phase, the Pb^{2+} is transported rapidly with Sr^{2+} transport proceeding simultaneously, but at a slower rate. This effect is illustrated in Table 5 where E values as a function of time for Pb^{2+} and Sr^{2+} when present alone and as a mixture are compared. The data show that the presence of Sr^{2+} has little effect on the E value for Pb^{2+}. However, the E value for Sr^{2+} during the first 6 min is reduced sharply when Pb^{2+} is present. After 6 min Sr^{2+} transport accelerates and the Sr^{2+} enrichment value after 20 min ($E = 4.5$) approaches the 10 min value obtained when Sr^{2+} is present alone ($E = 5.5$). These results are consistent with the relative log K values for reaction of these cations with either isomer of DC18C6, the value for Pb^{2+} being larger by ~1.8 log K units (*3*).

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