Separation Science and Technology

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

Transport of $AgBr^{2-}$, $PdBr_4^{2-}$, and $AuBr_{4-}$ in an Emulsion Membrane System Using K-Dicyclohexano-18-crown-6 as Carrier

Reed M. Izatt[a]; Glen A. Clark[a]; James J. Christensen[a]
[a] Departments of Chemistry and Chemical Engineering, Brigham Young University, Provo, Utah

To cite this Article Izatt, Reed M. , Clark, Glen A. and Christensen, James J.(1987) 'Transport of $AgBr^{2-}$, $PdBr_4^{2-}$, and $AuBr_{4-}$ in an Emulsion Membrane System Using K-Dicyclohexano-18-crown-6 as Carrier', Separation Science and Technology, 22: 2, 691 — 699

To link to this Article: DOI: 10.1080/01496398708068975

URL: http://dx.doi.org/10.1080/01496398708068975

SEPARATION SCIENCE AND TECHNOLOGY, 22(2&3), 691-699, 1987

Transport of $AgBr^{2-}$, $PdBr_4^{2-}$, and $AuBr_4^-$ in an Emulsion Membrane System Using K^+-Dicyclohexano-18-crown-6 as Carrier

REED M. IZATT, GLEN A. CLARK, and JAMES J. CHRISTENSEN

DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING
BRIGHAM YOUNG UNIVERSITY
PROVO, UTAH 84602

ABSTRACT

Silver, palladium, and gold have been transported through a 1.5 M KBr/toluene/0.025 M MgS_2O_3 (or $Mg(NO_2)_3$) emulsion membrane system as $AgBr_2^-$, $PdBr_4^{2-}$, and $AuBr_4^-$, respectively, using K^+-dicyclohexano-18-crown-6(DC18C6) as carrier. The transport studies are carried out in $AgBr_2^-$, $PdBr_4^{2-}$, and $AuBr_4^-$ single solutions and in $AgBr_2^-/PdBr_4^{2-}$, $AgBr_2^-/AuBr_4^-$, and $PdBr_4^{2-}/AuBr_4^-$ binary solutions. The presence of DC18C6 in the toluene membrane is found to greatly enhance ion transport. When MgS_2O_3 is in the receiving phase, $AuBr_4^-$ is found to transport well even without DC18C6 in the membrane. The transport of $AgBr_2^-$, $PdBr_4^{2-}$, and $AuBr_4^-$ is greater for those systems containing MgS_2O_3 in the receiving phase than for those with $Mg(NO_3)_2$. In binary studies with MgS_2O_3 in the receiving phase, $PdBr_4^{2-}$ is transported selectively over $AgBr_2^-$ and $AuBr_4^-$ is transported selectively over either $PdBr_4^{2-}$ or $AgBr_2^-$.

INTRODUCTION

Macrocycles have been used as cation carriers in emulsion liquid membranes for the transport of cations across an otherwise impermeable organic membrane (1-7). Concurrent transport of an anion with the cation occurs when neutral macrocycle carriers are used. Recently, the transport of the metal anionic complex,

$AgBr_2^-$, by M^{n+}-DC18C6 carriers was shown, where M^{n+} = K^+, Na^+, or Li^+, and where M^{n+} is the co-transported cation. In these cases, the transport rate of $AgBr_2^-$ was found to be correlated to the log K value for the M^{n+}-DC18C6 interaction (8). Thus, transport of $AgBr_2^-$ was greatest in the case of K^+ because of the larger log $K(H_2O)$ value for K^+-DC18C6 interaction compared to those for the other M^{n+}-DC18C6 interactions.

A desire to study transport behavior of other metal bromo anionic complexes has lead to the present study. The objectives of this work have been to investigate K^+-DC18C6-mediated transport of $AgBr_2^-$, $PdBr_4^{2-}$, and $AuBr_4^-$ from single and binary solutions of their K^+ salts. In the competitive transport studies, binary mixtures of two of these complex anions are used in order to determine transport selectivities. The effect of receiving phase composition on transport has also been studied through the incorporation of either MgS_2O_3 or $Mg(NO_2)_3$ into the receiving phase.

EXPERIMENTAL

Materials

The following materials were obtained in the highest available purity from the indicated sources: AgBr and $AuBr_3$ (Alfa); $PdBr_2$ (Aldrich); KBr (Wasco); MgS_2O_3 (Fluka); $Mg(NO_3)_2$ (Mallinckrodt); toluene (Fisher, spectranalyzed); Span 80 (ICI Americas); and DC18C6 (mixture of isomers, Parish).

Procedure

Solutions of the K^+ salts of $AgBr_2^-$, $PdBr_4^{2-}$, and $AuBr_4^-$ were made by dissolving either AgBr, $PdBr_2$, or $AuBr_3$ in 1.50 M KBr. UV-Visible spectra were run of the yellow colored solutions of $PdBr_4^{2-}$ and $AuBr_4^-$. Comparison with literature spectra for $PdBr_4^{2-}$ (9) and $AuBr_4^-$ (10) confirmed the existence of these species in solution.

The emulsion membrane system consists of an aqueous source phase containing the ion(s) to be transported and an emulsion, which in turn consists of an organic membrane phase and an aqueous receiving phase into which the ion(s) are to be transported. The emulsion is prepared by blending 16 ml of 0.025 M MgS_2O_3 or 0.025 M $Mg(NO_3)_2$ receiving phase, and 16 ml of pure toluene or 0.01 M DC18C6 in toluene, with 0.48 ml of the neutral surfactant, Span 80 (sorbitan monooleate) at high speed for 10 minutes. The presence of either $S_2O_3^{2-}$ or NO_3^- in the receiving phase will affect ion transport dramatically because of the strong interactions of $S_2O_3^{2-}$ with Ag^+ (11) and Pd^{2+} (12) and because of the weak interactions of NO_3^- with Ag^+ (11) and Pd^{2+} (13).

A small quantity of prepared emulsion (1.8 ml) is added to each of 4 transport cells (small beakers) containing 9.0 ml of source phase. The concentrations of the bromo complexes are ~1 x 10^{-3} M in the single solutions and ~5 x 10^{-4} M in the binary solutions. The dimensions of each transport cell (beaker) are 60.0 mm in height by 28.5 mm in internal diameter. A glass propeller stirrer is suspended into each beaker and is used to mix emulsion into the source phase. In order to achieve reproducible stirring, all 4 propellers are turned simultaneously at 600 rpm by synchronous Hurst motors at room temperature (21-24°C). The propellers are stopped at different time intervals; 3, 6, 10, and 15 minutes. After stirring is stopped, the emulsion is allowed to separate for 2 minutes before sampling the source phase. The source phase metals are analyzed with a Perkin-Elmer 603 atomic absorption spectrophotometer (Norwalk, CT) using the method of standard additions. Samples at time 0 are obtained by sampling the source phase before addition of the emulsion. Three separate transport runs are made at each time interval using fresh emulsion each time. The standard deviations between runs average about ±10%.

Emulsion breakage is determined for each transport run by analysis of Mg^{2+} in the source phase. Emulsion breakage is usually ~2% for 15 minutes of stirring and is never more than 7%.

RESULTS AND DISCUSSION

Single Systems

The addition of DC18C6 (Figure 1) to the toluene phase increases transport of $AgBr_2^-$, $PdBr_4^{2-}$ and $AuBr_4^-$ as indicated by the data in Table 1. This increase in transport is a direct consequence of increased salt partitioning to the membrane phase due to the formation of lipophilic K-DC18C6$^+$ cationic complexes. Partitioning of these complex anions is greater with K-DC18C6$^+$ than with K^+. In the case of the $AuBr_4^-$, the presence of DC18C6 in the membrane causes a yellow precipitate to form in the source phase upon stirring with the emulsion. The precipitate dissolves after about 10 minutes of stirring. The composition of the precipitate is probably [K-DC18C6$^+$][$AuBr_4^-$]. In order to avoid precipitation, $AuBr_4^-$ transport experiments were conducted in the absence of

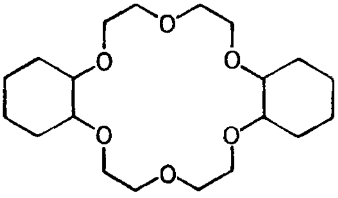

Fig. 1. Dicyclohexano-18-crown-6 (DC18C6).

TABLE 1
Concentration (μg/ml) as a Function of Time of $AgBr_2^-$, $PdBr_4^{2-}$, and $AuBr_4^-$ In Source Phases for Single Systems With or Without DC18C6 and Containing 0.025 M MgS_2O_3 or 0.025 M $Mg(NO_3)_2$.

Ion	Minutes	0.01 M DC18C6		No DC18C6	
		MgS_2O_3	$Mg(NO_3)_2$	MgS_2O_3	$Mg(NO_3)_2$
$AgBr_2^-$	0	104	107	107	101
	3	76	82	99	100
	6	65	72	98	103
	10	49	62	93	98
	15	47	62	89	101
$PdBr_4^{2-}$	0	114	106	113	98
	3	77	95	111	96
	6	67	93	107	97
	10	46	93	105	92
	15	26	88	100	97
$AuBr_4^-$	0	200	195	226	227
	3	-	-	183	220
	6	-	-	160	225
	10	-	-	146	220
	15	6	35	115	209

DC18C6. Thus, $AuBr_4^-$ transports even without DC18C6 present (Table 1).

Receiving phase composition also has a dramatic influence on ion transport. Transport to the MgS_2O_3 receiving phase is greater than transport to the $Mg(NO_3)_2$ receiving phase (Table 1). These results are consistent with the greater affinity of $S_2O_3^{2-}$ over NO_3^- for Ag(I), Pd(II) and Au(III). The log $\beta_3(H_2O)$ value for Ag^+-$3S_2O_3^{2-}$ and the log $\beta_4(H_2O)$ value for Pd^{2+}-$4S_2O_3^{2-}$ interactions are 14.2 (11) and 35 (12), respectively. By comparison, the log $K(H_2O)$ values for Ag^+-NO_3^- and Pd^{2+}-NO_3^- interactions are -0.2 (11) and 1.2 (13), respectively. No log $K(H_2O)$ data are available for the interaction of Au(III) species with either $S_2O_3^{2-}$ or NO_3^-.

However, the much faster transport of $AuBr_4^-$ with $S_2O_3^{2-}$ than with NO_3^- is evidence for greater affinity of Au(III) for $S_2O_3^{2-}$ than for NO_3^-. Addition of $S_2O_3^-$ to $AuBr_4^-$ source solutions results in a solution color change from yellow to colorless, indicating complexation of Au(III) by $S_2O_3^{2-}$.

Binary Systems

When MgS_2O_3 is in the receiving phase and DC18C6 is in the membrane, $PdBr_4^{2-}$ is transported selectively over $AgBr_2^-$ (Figure 2). Substitution of $Mg(NO_3)_2$ for MgS_2O_3 results in decreased transport of both $PdBr_4^{2-}$ and $AgBr_2^-$ (21 and 26% transport, respectively, at 15 minutes). The greater transport of $PdBr_4^{2-}$ in the MgS_2O_3 system probably results from the much greater affinity of $S_2O_3^{2-}$ for Pd^{2+} (12) than for Ag^+ (11).

In competitive transport experiments, $AuBr_4^-$ is transported selectively over both $AgBr_2^-$ (Figure 3) and $PdBr_4^{2-}$ (Figure 4) when MgS_2O_3 is in the receiving phase. When $Mg(NO_3)_2$ is in the

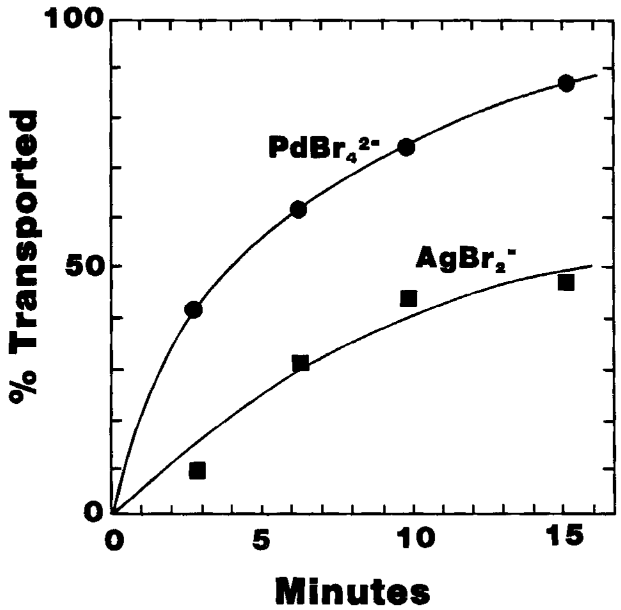

Fig. 2. Percent transport of $AgBr_2^-$ and $PdBr_4^{2-}$ from a binary mixture using a 0.01 M DC18C6 in toluene membrane and a 0.025 M MgS_2O_3 receiving phase.

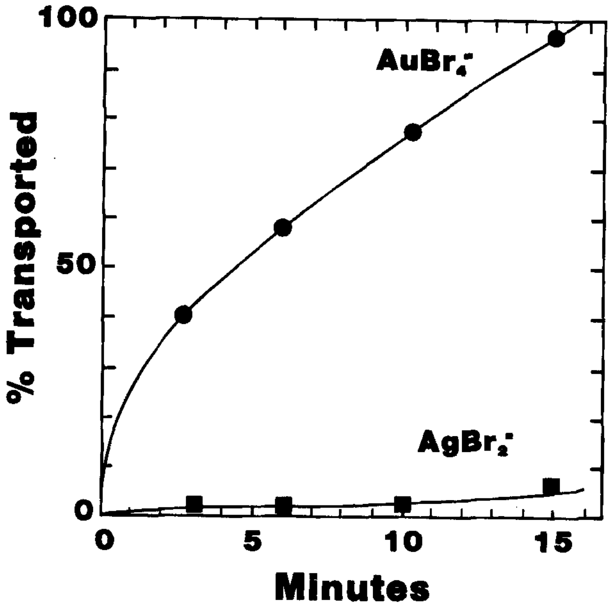

Fig. 3. Percent transport of $AgBr_2^-$ and $AuBr_4^-$ from a binary mixture using a pure toluene membrane and a 0.025 M MgS_2O_3 receiving phase.

receiving phase, little transport is seen for any of the metals. In these cases, at the 15 minute level, $AgBr_2^-$ and $AuBr_4^-$ showed 8 and 12 percent transport, respectively, while $PdBr_4^-$ and $AuBr_4^-$ each showed 14 percent transport. The explanation for the high transport rates of $AuBr_4^-$ in the systems containing MgS_2O_3 is probably two fold. First, $AuBr_4^-$ should partition more to the membrane phase than $PdBr_4^{2-}$ because of the less negative hydration enthalpy for $AuBr_4^-$ [ΔH_{hydr} = -40.9 kcal/mole (14)] than for $PdBr_4^{2-}$ [ΔH_{hydr} = -165.5 kcal/mole (14)]. These hydration enthalpies are consistent with the expected lower surface charge density of $AuBr_4^-$ relative to that of $PdBr_4^{2-}$. Both $AuBr_4^-$ and $PdBr_4^{2-}$ are low spin square planar complexes with similar sizes. This occurs because of the similar ionic radii of four coordinated Au(III) [r = 0.68Å (15)] and Pd(II) [r = 0.64Å (15)] and because of the same number of Br^- ions bonded to the central metal ion in each complex. The lower surface charge density of $AuBr_4^-$ is a result of its smaller charge and the greater electronegativity of Au(III) versus Pd(II). The hydration enthalpy, ΔH_{hydr}, for $AgBr_2^-$ is not available for comparison with those for $AuBr_4^-$ and $PdBr_4^{2-}$.

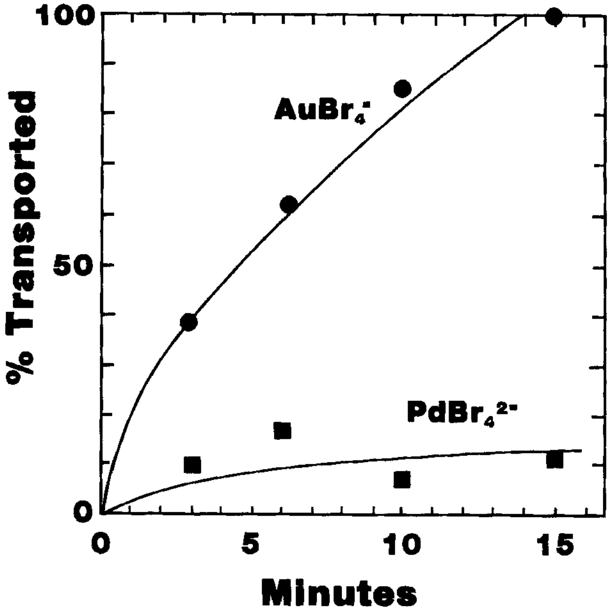

Fig. 4. Percent transport of $PdBr_4^{2-}$ and $AuBr_4^-$ from a binary mixture using a pure toluene membrane and a 0.025 M MgS_2O_3 receiving phase.

Second, in the Au(III)/Pd(II) system, the large increase and selective transport of $AuBr_4^-$ in going from the $Mg(NO_3)_2$ to the MgS_2O_3 system suggests that the log K value for Au(III)-$S_2O_3^{2-}$ interaction is about equal in magnitude to that for Pd(II)-$S_2O_3^{2-}$ interaction. In the $PdBr_4^{2-}$-$AgBr_2^-$ binary system, where $PdBr_4^{2-}$ is transported selectively, $PdBr_4^{2-}$ transport like that of $AuBr_4^-$ is greatly improved with MgS_2O_3 in the receiving phase. Assuming $S_2O_3^{2-}$ to have nearly equal affinity for Au(III) in $AuBr_4^-$ and for Pd(II) in $PdBr_4^{2-}$, the selective transport of $AuBr_4^-$ over $PdBr_4^{2-}$ would then be a result of the greater partitioning of $AuBr_4^-$ to the membrane phase. The selective transport of $AuBr_4^-$ over $AgBr_2^-$ is probably a result of greater affinity of $S_2O_3^{2-}$ for Au(III) in $AuBr_4^-$ over that for Ag(I) in $AgBr_2^-$. Although $AuBr_4^-$ may partition more to the membrane phase than $AgBr_2^-$, partitioning would also be a major contributing factor to the selective transport of $AuBr_4^-$. The log K(H_2O) values for Au(III)-$S_2O_3^{2-}$ interactions and the hydration enthalpy, $\Delta H_{hydr.}$, of $AgBr_2^-$ need to be determined before the transport selectivities can be understood fully.

CONCLUSIONS

Bromo complexes of precious metals are transported through an emulsion liquid membrane consisting of 0.1 M DC18C6 in toluene. In the cases of $AgBr_2^-$ and $PdBr_4^{2-}$, the presence of DC18C6 in the toluene phase and MgS_2O_3 in the receiving phase is a prerequisite for achieving transport of 50% or greater. In the case of $AuBr_4^-$, nearly 50% transport occurs from single salt solutions even without DC18C6 when MgS_2O_3 is in the receiving phase.

In competitive transport experiments involving a mixture of two of the bromo complexes, $PdBr_4^{2-}$ is transported selectively over $AgBr_2^-$ and $AuBr_4^-$ is transported selectively over either $PdBr_4^{2-}$ or $AgBr_2^-$ when MgS_2O_3 is in the receiving phase. The $AuBr_4^-$ transport results are particularly interesting because approximately 97% of the $AuBr_4^-$ is transported compared to 12% of the $PdBr_4^{2-}$ and only 6% of the $AgBr_2^-$.

ACKNOWLEDGMENT

We acknowledge support of this work by the National Science Foundation through grant number CPE-8119634. We would also like to thank Gypzy LindH for help with metal analyses.

REFERENCES

1. M.P. Biehl, R.M. Izatt, J.D. Lamb, and J.J. Christensen, Sep. Sci. Technol., 17, 289 (1982).

2. R.M. Izatt, M.P. Biehl, J.D. Lamb, and J.J. Christensen, Sep. Sci. Technol., 17, 1351 (1982).

3. J.J. Christensen, S.P. Christensen, M.P. Biehl, S.A. Lowe, J.D. Lamb, and R.M. Izatt, Sep. Sci. Technol., 18, 363 (1983).

4. R.M. Izatt, D.V. Dearden, D.W. McBride, Jr., J.L. Oscarson, J.D. Lamb, and J.J. Christensen, Sep. Sci. Technol., 18, 1113 (1983).

5. R.M. Izatt, D.V. Dearden, E.R. Witt, D.W. McBride, Jr., and J.J. Christensen, Solvent Extr. Ion Exch., 2, 459 (1984).

6. J. Strzelbicki and R.A. Bartsch, J. Membr. Sci., 10, 35 (1982).

7. R.A. Bartsch, W.A. Charewicz, and S.I. Kang, J. Membr. Sci., 17, 97 (1984).

8. R.M. Izatt, G.A. Clark, and J.J. Christensen, J. Membr. Sci., 24, 1 (1985).

9. L.I. Elding, Inorg. Chim. Acta, 6, 647 (1972).

10. L.I. Elding and A.B. Groning, Acta Chem. Scand. A, 32, 867 (1978).

11. Critical Stability Constants (R.M. Smith and A.E. Martell, eds.), Vol. 4, Plenum, New York, 1976.

12. Critical Stability Constants (R.M. Smith and A.E. Martell, eds.), Vol. 5, Plenum, New York, 1982.

13. C.K. Jorgensen and V. Parthasarathy, Acta Chem. Scand. A, 32, 957 (1978).

14. R.M. DeJonge, J. Inorg. Nucl. Chem., 38, 1821 (1976).

15. R.D. Shannon, Acta Cryst. A, 32, 751 (1976).