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 Qi, Zhang , Sasakura, T. and Cussler, E. L.(1984) 'Liquid Membrane Separations of Potassium Iodide from Mixed Brines', Separation Science and Technology, 19: 13, 963 — 975
To link to this Article: DOI: 10.1080/01496398408058341
URL: http://dx.doi.org/10.1080/01496398408058341

SEPARATION SCIENCE AND TECHNOLOGY, **19**(13-15), pp. 963-975, 1984-85

Liquid Membrane Separations of Potassium Iodide from Mixed Brines

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Abstract

Liquid membranes containing the polyether dibenzo-18-crown-6 dissolved in chlorinated hydrocarbons were used to separate potassium iodide from brines of sodium chloride and other salts. Product purity is 95% or better. The separations largely proceed via the transport of polyether-potassium iodide complexes; transport of other species is much less important. These systems can be formulated as emulsion liquid membranes to give the rapid fluxes required for practical application.

Separation of mixed brines is commonly accomplished by fractional crystallization (*1*). This process is inexpensive and frequently produces products of very high purity. However, it can be ineffective if the desired product has a high solubility or a low concentration. Then an alternative separation process may be preferred.

 0149-6395/84/1913-0963$3.50/0

We have been investigating an alternative separation of mixed brines which uses emulsion liquid membranes. These membranes are most easily visualized as a thin organic layer, stabilized by surfactants, and containing a complexing agent selective for one of the ions in the brine. All the ions are insoluble in the organic layer alone, but one specific salt will dissolve in the organic layer when the complexing agent is added.

The specific membrane studied here uses the macrocyclic polyether dibenzo-18-crown-6 to separate potassium iodide from a mixture of sodium salts. Membranes with this polyether have been extensively studied because of their high selectivity for potassium over other cations (*2–8*). Other related polyethers show similar selectivities (*9*, *10*). These membranes have also been used to separate potassium salts containing different anions (*11–14*). However, we believe that our studies are the first to separate simultaneously potassium and iodide from mixed brines.

In this article, we have three objectives. First, we want to demonstrate that polyether-containing membranes can selectively separate potassium iodide. Second, we need to delineate the mechanism responsible for this separation. Third, we want to develop these membranes as emulsions which give very rapid separations. The experiments by which we seek to achieve these objectives are described below.

EXPERIMENTAL

All salts (Fisher) were regent grade and were used as received. Of the solvents, chloroform was purified once by distillation, but *o*-dichlorobenzene was used as received. The macrocyclic polyether dibenzo-18-crown-6, synthesized from catechol and dichloro-diethylether (*15*), was recrystallized three times from acetone. The resulting pure white crystals had a melting point of 162–164°C, consistent with that reported previously (*15*). Substituted polyethers, purchased from Parish Chemical (Provo, Utah), were used without further purification. The emulsion membranes also contained a copolymer of isobutylene succinic anhydride and tetraethylpentamine (ECA 5025, Exxon Research and Engineering, Clinton, New Jersey). This polymer is surface active and stabilizes the emulsion membranes. It was used without further purification.

Two types of liquid membranes were used. In preliminary studies we used a "Schulman bridge," which is essentially a U-tube (*16*). About 12 mL of a chloroform solution of the polyether is placed in the bend of the U-tube, which has a cross-sectional area of 1 cm^2. A receiving phase, 10 mL of initially pure water, was placed in the right-hand arm of the U-tube, and a source phase, 30 mL of a solution of potassium iodide and other salts, was placed in the left-hand arm. Three magnetic stirring bars were positioned in

the tube, one immersed in the chloroform and the others near each water–chloroform interface. When these three bars were rotated faster than 55 rpm, we obtained reproducible results. Thus in the Schulman bridge, the "membrane" is really the boundary layers near the water–chloroform interfaces.

We also wanted to show that the separations across such boundary layers will also occur in a commercially attractive membrane geometry. To do so, we made experiments with emulsion liquid membranes, also called "liquid surfactant membranes" (*14, 17–20*). These membranes are essentially a water-in-oil-in-water emulsion (*21*).

Our emulsion liquid membranes were made as follows. About 30 mL of the receiving phase (pure water) was encapsulated by stirring at 1740 rpm for 30 min in 50 mL of liquid membrane (a chlorobenzene solution of the polyether and 1% of the thickener ECA 5025). The resulting emulsion was suspended by stirring at 200–240 rpm in 100 mL of the source phase (containing potassium iodide and other salts). The resulting water-in-oil-in-water emulsion constitutes the emulsion membrane. After a desired time the stirring was stopped, the emulsion was allowed to settle, and the source phase was decanted. The remaining emulsion, including the receiving phase, was diluted 1:1 with a mixture of equal parts petroleum ether and isopropyl alcohol. This dilution breaks the emulsion. The receiving phase was decanted and analyzed; the organic phase was distilled to remove the petroleum ether and the alcohol and then recycled.

The aqueous solutions were analyzed as follows (*22*). Sodium and potassium were measured by atomic adsorption spectroscopy using a Buck model 200. Calcium and magnesium were measured by titration with EDTA. Iodide was determined by first adding bromine to yield iodate, then adding potassium iodide to produce iodine, and finally titrating the iodine with sodium thiosulfate. Bromide was measured by adding sodium hypochlorite to yield bromate, then adding iodide to yield iodine, and again titrating with thiosulfate. Sulfate and carbonate were found by titration with barium chloride and hydrochloric acid, respectively. Chromate was measured by visible spectroscopy using a Perkin-Elmer/Hitachi model 139. Finally, chloride was not measured directly but was inferred from electrical neutrality; titration of chloride with silver nitrate is severely compromised by the presence of iodide and bromide.

RESULTS AND DISCUSSION

This paper has three objectives. First, we want to show that potassium iodide can be separated from mixed brines by use of liquid membranes. Second, we want to identify the mechanism by which these membranes

function. Third, we want to report separations based on emulsion liquid membranes, a geometry of practical potential. These objectives are best discussed sequentially.

The selectivities possible for potassium iodide are demonstrated by the results in Table 1. The concentrations shown in the source phase are those present initially; the concentrations shown in the receiving phase are the averages of those measured after 12 h in at least two independent experiments. The selectivity for potassium iodide is high. For example, when the source phase contains roughly equal amounts of potassium, sodium, chloride, and iodide, the receiving phase is better than 99% potassium iodide, with minor amounts of sodium and chloride. No divalent anions were ever detected in the receiving phase. Thus the sequence for selectivity is KI $\gg$ KCl > NaI > NaCl $\gg$ divalent salts. The results for bromide are similar but less selective.

The mechanism by which these membranes function is clarified by the results in Table 2. These results show that the flux of potassium iodide depends on the product of potassium and iodide concentrations. For example, the flux when $[K^+]$ equals 0.4 *M* and $[I^-]$ equals 1.6 *M* is nearly the same as the flux when $[K^+]$ and $[I^-]$ both equal 0.8 *M*. Similarly, the flux when $[K^+]$ equals 0.4 *M* and $[I^-]$ equals 1.2 *M* is within experimental error of the flux when $[K^+]$ equals 1.2 *M* and $[I^-]$ equals 0.4 *M*. Note that the iodide flux will be increased if the brine contains more potassium, and not just more potassium iodide, a result with practical implications. Note also that the presence of other ions has no significant effect on the fluxes observed.

The variation of flux and concentration shown in Table 2 suggests a specific mechanism for potassium iodide transport. This mechanism has six important features:

(1) All solutions are ideal, including the source solution and the membrane.
(2) The receiving phase concentrations are essentially zero.
(3) The polyether reacts reversibly with potassium and iodide to produce a complexed ion pair within the membrane.
(4) This reaction is so fast that it is essentially at equilibrium at each membrane interface.
(5) Only negligible amounts of potassium or iodide exist as ions or uncomplexed ion pairs within the membrane.
(6) The diffusion coefficients of the polyether and of the polyether–potassium iodide complex are equal.

These features have considerable precedent (*2, 8, 11, 13, 14*). The most

TABLE 1
The Selectivities of a Liquid Membrane at 25°C Containing 0.02 *M* Dibenzo-18-crown-6 in Chloroform[a]

Experimental conditions	Concentration of ions (*N*)									Purity of KI[a] or KBr (wt%)
	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	Br^-	I^-	SO_4^{2-}	CO_3^{2-}	
Source phase	1.000	1.000		0.200	1.000		1.000	0.200		99.0
Receiving phase	0.115	0.002		0.000	0.003		0.114	0.000		
Source phase	1.000	1.000	0.100	0.100	1.200		1.000			99.2
Receiving phase	0.138	0.002	0.000	0.000	0.003		0.137			
Source phase	1.000	1.200			1.000		1.000	0.100	0.100	99.3
Receiving phase	0.113	0.002			0.003		0.112	0.000	0.000	
Source phase	1.000	1.000		0.200	1.000	1.000		0.200		99.5
Receiving phase	0.182	0.005		0.000	0.017	0.170		0.000		
Source phase	1.000	1.000	0.100	0.100	1.100	1.100				94.1
Receiving phase	0.164	0.005	0.000	0.000	0.016	0.152				
Source phase	1.100	1.100			1.000	1.000		0.100	0.100	95.6
Receiving phase	0.155	0.005			0.012	0.148		0.000	0.000	

[a]The purity of KI or KBr is defined as the percentage of KI or KBr in the total salts in the receiving phase. This purity and the receiving phase concentrations are those measured after 12 h.

TABLE 2
The Flux of Potassium Iodide at 25°C vs the Composition of Ions in the Source Phase[a]

Source phase compositions, M					
$[K^+]$	$[I^-]$	$[Na^+]$	$[SO_4^{2-}]$	$\frac{1}{[K^+][I^-]}$, M^{-2}	$\frac{1}{J}$, $10^8 \frac{s}{mol}$
0.20	0.20	1.80	1.80	25.00	3.23
0.40	0.40	1.60	1.60	6.26	1.12
0.40	0.40	1.60	1.60	6.25	1.00
0.20	1.20	1.80	0.80	4.17	0.70
0.40	0.80	1.60	1.20	3.13	0.66
0.60	0.60	1.40	1.40	2.78	0.60
0.60	0.60	1.40	1.40	2.78	0.58
1.20	0.40	0.80	1.60	2.08	0.51
0.40	1.20	1.60	0.80	2.08	0.50
0.80	0.80	1.20	1.20	1.56	0.44
0.80	0.80	1.20	1.20	1.56	0.43
0.40	1.60	1.60	0.40	1.56	0.41

[a]The membrane phase contains 0.01 M dibenzo-18-crown-6 in chloroform solution.

restrictive is probably #4, for mobile carrier membranes are known which do not approach this limit (*23*). However, polyethers are known to react very rapidly with ions, often producing complexes with no net charge (*24*).

If this mechanism is that involved here, then the flux J can be shown to be (*2, 3, 25, 26*)

$$J = \frac{DA}{l}\left(\frac{K[P][K^+][I^-]}{1 + K[K^+][I^-]}\right) \tag{1}$$

where D is the constant diffusion coefficient, A is the membrane area, l is its equivalent thickness, K is the polyether–ion pair equilibrium constant, and [P] is the total polyether concentration, including both its complexed and uncomplexed forms. This equation is easily rearranged:

$$\frac{1}{J} = \left(\frac{l}{DA[P]}\right) + \left(\frac{l}{DAK[P]}\right)\left(\frac{1}{[K^+][I^-]}\right) \tag{2}$$

Equation (2) predicts that the reciprocal of the flux should vary linearly with the reciprocal of the product of potassium and iodide concentrations. That this is true is shown by the results in Fig. 1.

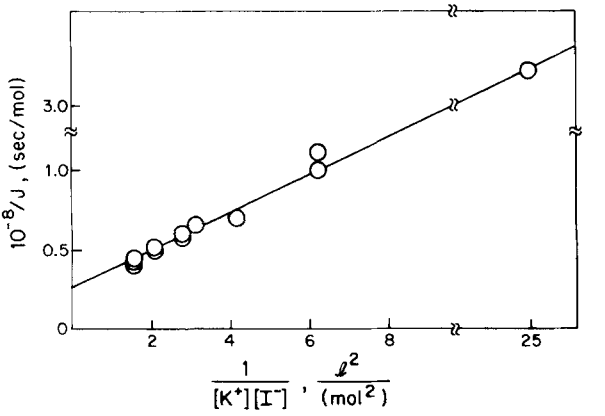

FIG. 1. Potassium iodide flux vs concentration. The reciprocal of the flux varies linearly with the reciprocal of the product of potassium and iodide concentrations. These fluxes, which are independent of the other ions present, are found from the time derivative of the measured concentrations. They are consistent with a mobile carrier mechanism involving a polyether–potassium iodide complex.

We can test this mechanism further by comparing the intercept and slope in Fig. 1 with those expected from Eq. (2). We expect D in chloroform is about 1×10^{-5} cm^2/s, l is about 50×10^{-4} cm, A is 1 cm^2, and [P] is 0.01 M. Thus from Eq. (2) we expect an intercept of 0.5×10^8 s/mol, which is close to the observed value. Similarly, from the slope in Fig. 1, we find K is about 3 ℓ^2/mol^2.

Equations 1 and 2 also predict that the flux J is proportional to the total carrier concentration [P]. Whether this is true is tested by the results in Fig. 2. The flux varies linearly with polyether concentration up to about 0.009 M, verifying the predictions of Eqs. (1) and (2) over this range. Above this concentration the variation shows a sudden break. The reason is a visible precipitate, forming within the membrane phase. Since at these concentrations no precipitate forms without potassium iodide present, we suspect that it is the polyether–ion pair complex. We expect precipitation will occur whenever the product of the concentrations of potassium, iodide, and polyether exceeds 0.009 M^3. To our bemusement, the flux with precipitate present continues to increase, albeit slightly. We are not sure why this occurs; it may be due to convection of the precipitated solid in the membrane phase.

We used chemically substituted analogues of dibenzo-18-crown-6 in an effort to increase the flux to still higher values. This did not work, for the solubility of these analogues was not much greater than that of the unsubstituted polyether. However, at low polyether concentrations, we

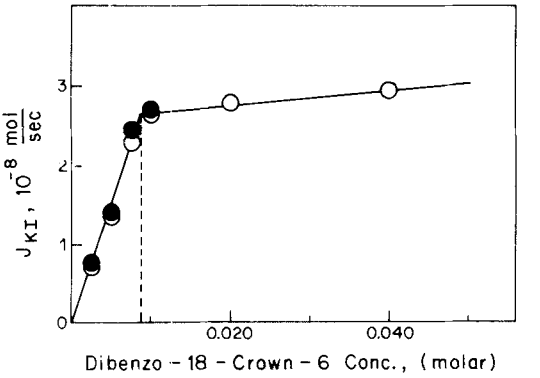

FIG. 2. Potassium iodide flux vs polyether concentration. The flux varies linearly with polyether concentration below 0.009 *M* polyether, consistent with predictions of the mobile carrier mechanism described in the text. Above this concentration, a visible precipitate-containing carrier formed in the membrane. For the open circles, the source solution contained 1.0 *M* KI; for the filled circles, it contained 1.0 *M* NaI and 0.5 *M* K_2SO_4.

found that adding aliphatic side chains to the polyether has little effect on the transport rate, as shown in Fig. 3. Lamb et al. (*8*) found similar results.

This constant flux is important, for the substituted carriers are less soluble in water than the dibenzo-18-crown-6. As a result, membranes using substituted carriers lose less carrier into the water and have the potential for longer life. At the same time, the constant fluxes inferred from Fig. 3 are surprising and so of theoretical interest. The side chains can almost double the molecular weight of the mobile carrier, and hence should reduce its diffusion coefficient by around 30%. Equation (1) predicts that this should decrease the flux by the same amount; such a decrease is not observed. We are not sure why this is so. We suspect it may be due to ion pairs moving quickly from one carrier molecule to the next, producing a mechanism more like a bucket brigade than the more common picture of interfacial reaction, diffusion, and reverse reaction at the other interface (*26*).

We now have shown that this type of membrane is selective for potassium iodide, and we have shown that the results are consistent with transport of polyether–potassium iodide ion pairs. We next turn to our final objective, demonstrating these separations using emulsion liquid membranes.

Typical results using emulsion liquid surfactant membranes are shown in Fig. 4. In this figure the data correspond to two separate experiments. In

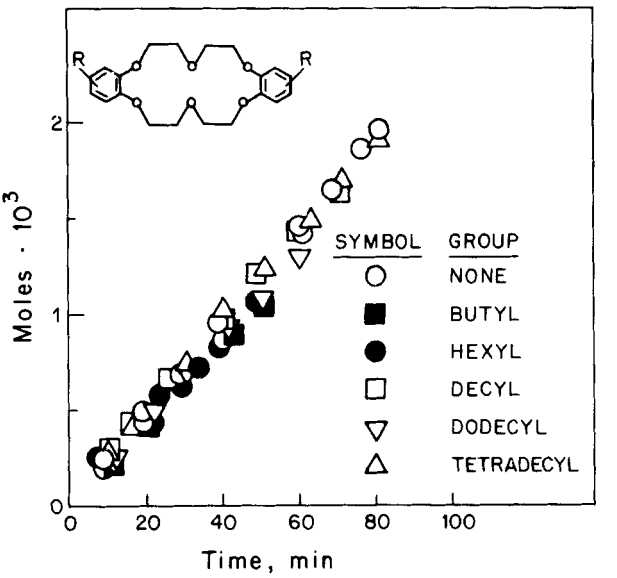

FIG. 3. Potassium iodide transport for substituted analogues of the carrier dibenzo-18-crown-6. The amount transported is independent of the substitutions in the carrier present at 1×10^{-3} *M*. This constancy suggests a strategy for reducing carrier loss and hence increasing membrane life.

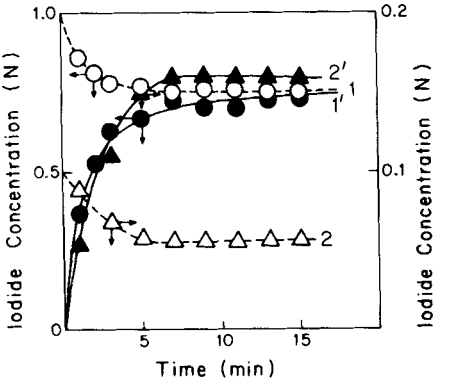

FIG. 4. Potassium iodide fluxes across emulsion liquid membranes at 30°C. Two different experiments are shown in this figure. In the first, a source phase initially of 1.0 *M* KCl and 1.0 *M* NaI (Curve 1 and open circles) diffuses into initially pure water (Curve 1′ and filled circles). In the second experiment, a source phase initially of 0.9 *M* KCl, 0.9 *M* NaCl, and 0.1 *M* NaI (Curve 2 and open triangles) diffuses into pure water (Curve 2′ and filled triangles). In both experiments, the membrane contained 0.02 *M* dibenzo-18-crown-6 and 0.5 wt% ECA 5025 in dichlorobenzene.

Experiment 1, shown by the scale on the left, the source solution initially contained 1.0 *M* KCl and 1.0 *M* NaI. The iodide concentration in the source phase drops smoothly, as shown by Curve 1; at the same time, the iodide concentration in the receiving phase shown by Curve 1′ rises smoothly to meet it. In the second experiment shown in Fig. 4, the source phase inititally contained 0.9 *M* KCl, 0.9 *M* NaCl, and 0.1 *M* NaI. Its iodide concentration, given on the right-hand scale, changed as shown by Curve 2. At the same time, the iodide concentration in the receiving phase rose abruptly past that in the source phase, as shown by Curve 2′. This increase in iodide concentration beyond that in the source results because the flux does not depend on iodide concentration, but rather on the product of iodide and potassium concentrations. This again demonstrates the importance of the polyether–ion pair complex which was discussed above.

The emulsion liquid membranes used for Fig. 4 are chemically different than those used in Figs. 1–3. The emulsion liquid membranes consist of the polyether dissolved in dichlorobenzene and thickened with the surface-active polymer ECA 5025. The resulting solutions have the high viscosity necessary for stable emulsion membranes. In contrast, the experiments in Figs. 1–3 were made by adding polyether to chloroform. While the polyether is soluble in both dichlorobenzene and chloroform, the thickening polymer is insoluble in chloroform. Moreover, the vapor pressure of chloroform is so high that stable emulsions are not easy to obtain with other thickeners. When we recognize that the membranes in Fig. 4 have a much higher viscosity than those in Figs. 1–3, the fast fluxes in Fig. 4 are still more dramatic. These larger fluxes are a consequence of the large surface area per solution volume characteristic of emulsion membranes.

The speed and product purity possible with these emulsion systems is underscored by the results in Table 3. In both sets of experiments a product of about 95% purity is obtained in less than 10 min. In the second set the concentration of potassium iodide produced is higher than the iodide concentration in the source solution. These results look very promising.

However, Table 3 also shows the uncertain reproducibility characteristic of emulsion liquid membranes: the product purity found here is lower and varies more than for the Schulman bridge experiments reported in Table 1. The reduced purity probably results from encapsulation of small amounts of source solution into the membrane phase. We believe that this irreproducibility is inherent in the use of emulsions. As part of our development of the membrane formulation used for Fig. 4 and Table 3, we studied emulsion stability by encapsulating 0.1 *M* sodium dichromate within the emulsion droplets. We then measured the color released vs time as an indication of membrane breakup. We found that emulsion membrane

TABLE 3
Separation of Potassium Iodide Using Emulsion Liquid Membranes[a]

No.[b]	Contact time (min)	Concentration of salts in receiving phase (*M*)			Purity of KI (%)
1A	5	0.773	0.020	0.040	96.0
1B	7	0.752	0.021	0.051	95.3
1C	7	0.772	0.014	0.037	96.8
2A	5	0.140	0.008	0.008	95.7
2B	7	0.158	0.021	0.009	92.7
2C	9	0.182	0.013	0.013	94.6

[a]These membranes contain 0.02 dibenzo-18-crown-6 and 0.5% (wt) ECA 5025 in dichlorobenzene.

[b]The source solution used in Expt 1 contains 1.00 *M* KCl and 1.00 *M* NaI. That used in Expt 2 contains 0.90 *M* KCl, 0.90 *M* NaCl, and 0.10 *M* NaI.

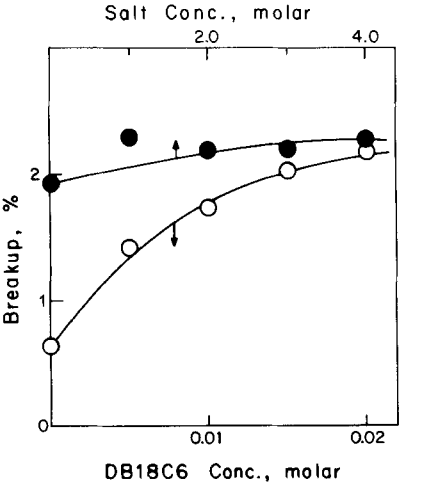

FIG. 5. Emulsion liquid membrane stability. Membrane stability varies with almost every aspect of the system, including the concentrations of added salt and of polyether. The reasons for these variations are unclear.

stability varied with everything we considered including salt concentration and polyether concentration (Fig. 5). Increased emulsion breakup with added salt is often the result of reduced electrostatic repulsion between droplets (*27*). However, in this case the electrical charge should be somewhat less important because the surface active thickener is *non*ionic. The increased emulsion breakup with increased polyether concentration is a mystery.

Thus, in this article we have described liquid membranes capable of separating potassium iodide from sodium chloride and other salts. The membranes contain the polyether dibenzo-18-crown-6 or its analogues as a mobile carrier; the membrane flux is consistent with carrier-assisted diffusion of potassium iodide ion pairs. This system is easily adapted to the emulsion liquid membrane geometry, where it gives fast fluxes of practical potential.

Acknowledgments

Zhang Qi is grateful to the Academia Sinica of the People's Republic of China for a research fellowship. Support for this research came from the National Science Foundation grants CPE 8207917 and CPE 8025304.

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Received by editor March 14, 1984
Revised June 14, 1984