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

Facilitated Transport of Alkali Metal Ions Across Bulk Liquid Membrane Containing Phenoxy Compounds as Carrier

Jayshree Ramkumar[a]; B. Maiti[a]; S. K. Nayak[a]; P. K. Mathur[a]
[a] ANALYTICAL CHEMISTRY DIVISION, BHABHA ATOMIC RESEARCH CENTRE, MUMBAI, INDIA

Online publication date: 07 December 1999

To cite this Article Ramkumar, Jayshree , Maiti, B. , Nayak, S. K. and Mathur, P. K.(1999) 'Facilitated Transport of Alkali Metal Ions Across Bulk Liquid Membrane Containing Phenoxy Compounds as Carrier', Separation Science and Technology, 34: 10, 2069 — 2077
To link to this Article: DOI: 10.1081/SS-100100756
URL: http://dx.doi.org/10.1081/SS-100100756

SEPARATION SCIENCE AND TECHNOLOGY, **34**(10), pp. 2069–2077, 1999

Facilitated Transport of Alkali Metal Ions across Bulk Liquid Membrane Containing Phenoxy Compounds as Carrier

JAYSHREE RAMKUMAR and B. MAITI
ANALYTICAL CHEMISTRY DIVISION

S. K. NAYAK
BIO-ORGANIC DIVISION

P. K. MATHUR*
ANALYTICAL CHEMISTRY DIVISION

BHABHA ATOMIC RESEARCH CENTRE
MUMBAI 400 085, INDIA

ABSTRACT

The carrier activity of several phenoxy ethers toward the facilitated transport of alkali metal ions through a chloroform bulk liquid membrane has been studied. A brief description of the synthesis of carrier compounds has been given, and the mechanism of transport process has been discussed. The organic carriers are protonated on the receiving side of a permeation cell, and the protons are exchanged with the metal ions at the membrane interphase of the feed side. Protonation of carriers has been confirmed from electronic spectral studies. A high degree of selectivity for Na^+ transport has been observed when 1,2-bis-(2-acetyl phenoxy) ethane is used as carrier whereas dibenzo-[*a*,*e*]-3,4-dihydroxy-3,4-dimethyl-7,10-dioxocyclodeca-1,5-dione facilitated selective transport of K^+.

INTRODUCTION

Transport of metal ions across a membrane plays an important role in many biochemical processes (1, 2). Of the different types of membranes, liquid

* To whom correspondence should be addressed.

membrane is considered to be a very useful separation tool due to its simplicity and low operation cost, and a bulk liquid membrane has the additional advantage of higher stability although the transport rate is slow.

In our previous studies we reported the transport of cations (3, 4), anions (5, 6), and organic molecules (7) through a Nafion/modified Nafion membrane. Transport of alkali metal ions through a Nafion membrane modified with crown ethers has also been reported (8). Crown ethers are synthetic macrocyclic compounds known to form unusually stable complexes with alkali metal ions, and they often demonstrate a high degree of cation selectivity (9, 10). Therefore, they have been studied as a model carrier for the transport of cations across cell membranes (11). Although a high degree of cation selectivity has been attributed to the cage size of the ionophore, the formation of stable complexes with a metal ion is the primary reason for the facilitated transport process. Our interest was to look for other carriers capable of forming stable complex to serve as suitable carriers for metal ions. In the transport of alkali metal ions using diethylene glycol dibenzoate as a carrier in a bulk liquid membrane (12), the stability of the metal ion complexes and the carrier activity are likely due to the presence of an ether linkage. This prompted us to examine the carrier activity of some phenoxy ethers. In the present paper we study the transport of alkali metal ions through a bulk liquid membrane of chloroform containing the phenoxy compounds as carriers.

EXPERIMENTAL

All reagents used were of analytical grade. Metal ion solutions (0.1 M) were prepared by weighing appropriate amounts of their chloride salts and dissolving them in deionized water.

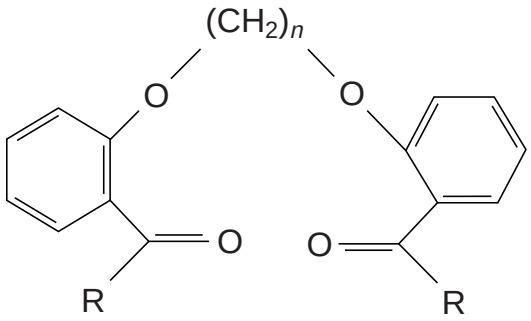
The carrier compounds used for the transport experiments are listed in Table 1. They were synthesized by the reduction of 2-hydroxy acetophenone followed by reaction with the appropriate dibromoalkane. In the case of Compound *e*, ring closure due to the formation of a C—C linkage through the carbon atoms of the two carbonyl groups was effected by refluxing with $TiCl_3$ and Mg metal in dry tetrahydrofuran under an argon atmosphere followed by the addition of a stoichiometric amount of Compound *a*.

A general procedure for the synthesis is given in Scheme 1. The details of the synthesis and characterization of these compounds and a few others will be published elsewhere.

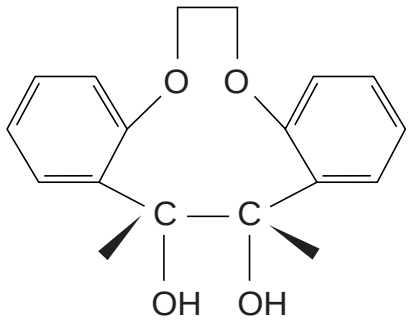
These carrier compounds are almost insoluble in water but freely soluble in chloroform. The bulk membrane phase consists of a chloroform solution of these carriers. Liquid membrane experiments were conducted using the setup shown in Fig. 1. A 10^{-3} M chloroform solution (50 mL) of phenoxy ether compounds was placed at the bottom of a glass beaker (height 8 cm and i.d. 7

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

TABLE 1
Organic Compounds Used as Carriers for the Transport Experiments

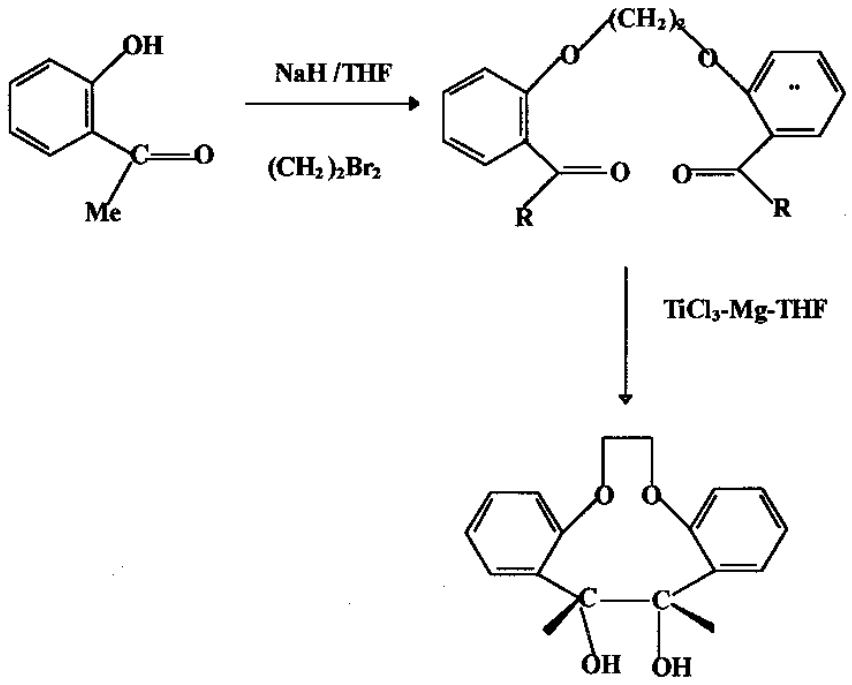


Code	R	*n*	Name
a	Me	2	1,2-Bis(2-acetyl phenoxy) ethane
b	H	2	1,2-Bis(2-formyl phenoxy) ethane
c	Me	4	1,4-Bis(2-acetyl phenoxy) butane
d	H	4	1,4-Bis(2-formyl phenoxy) butane



e			Dibenzo-[*a*,*e*]-3,4-dihydroxy-3,4-dimethyl-7,10-dioxocyclodeca-1,5-diene

cm). A glass cylindrical tube (i.d. 2.3 cm) open at both ends was suspended vertically 1 cm above the bottom of the beaker and well below the surface of the chloform membrane. The source solution was 10 mL of 0.1 M metal salt solution placed carefully on top of the chloroform layer inside the cylinder. 25 mL of aqueous hydrochloric acid solution was placed atop the outer ring of chloroform. This served as the receiving solution. The organic phase was stirred with a magnetic stirrer while the aqueous phases were mechanically stirred. The pH of the aqueous phases were measured using an EIL 7030 pH meter (India) equipped with a combination electrode. The transport studies were carried out at 25 ± 1°C. The concentrations of the metal ions in the re-



SCHEME 1 Synthesis of phenoxy ether compounds.

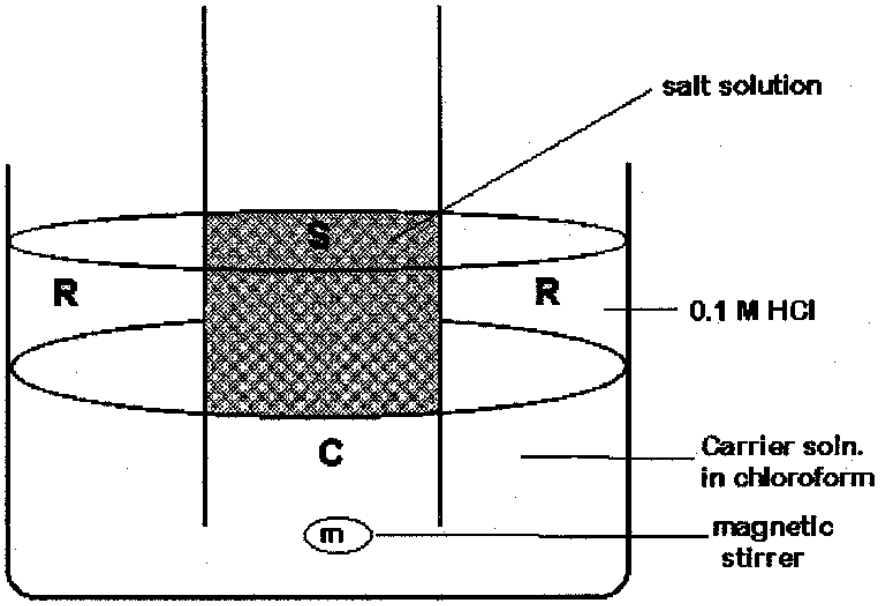


FIG. 1 Experimental setup for ion transport system. R = receiving phase; S = source phase; C = chloroform layer with carrier; m = magnetic stirrer.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

ceiving phase were determined after a definite time interval using an atomic absorption spectrometer (Hitachi 180-80 polarized Zeeman AAS). The carrier concentration measurement and the recording of their electronic spectra were carried out using a Shimadzu 120 UV-Visible double beam spectrophotometer.

RESULTS AND DISCUSSION

The results for the single ion transport of Li^+, Na^+, and K^+ are given in Table 2. The table gives the concentrations of the carrier and of the metal ions after 24 hours. The concentration of the carrier in the bulk organic phase was about 10^{-3}M. Although the compounds are insoluble in water, it was found from measurement of the carrier concentration at the end of the experiment that a small amount of carrier bleeded from the membrane during the experiment. However, this did not show any remarkable effect on the uphill transport of the metal ions. An increase in the aciditity increased the extent of bleeding, but a decrease in the acidity of the receiving phase reduced the permeation rate. Hence, the optimum acidity was arrived at by trial and error, and the experiments were finally carried out using 0.1 M hydrochloric acid solution in the receiving side. In spite of the bleeding of carriers, the amounts of metal ions transported were quite high and comparable with those obtained using crown ethers as carriers under identical experimental conditions (13).

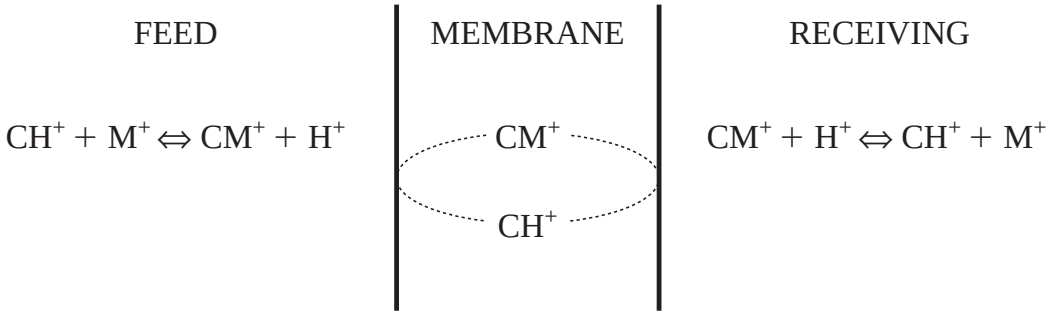
It was seen that the pH of the feed solution gradually decreased while that of the receiving phase increased. This suggests a coupling mechanism for the transport process. The ether oxygen atoms of these carriers are presumably protonated at the interphase between the two liquids at the receiving side and

TABLE 2
Variation of Concentration of Carriers and Metal Ions after 24 Hours

Carrier	Initial concentration of carrier (mmol)	Final concentration of carrier (mmol)	Concentration (mmol) of metal ions transported after 24 hours			Selectivity order
			Li^+	Na^+	K^+	
a	2.33	1.23	0.13	1.31	0.31	$Na^+ > K^+ > Li^+$
b	2.13	2.01	0.10	0.22	0.15	$Na^+ > K^+ > Li^+$
c	1.05	0.87	0.32	0.32	0.69	$K^+ > Na^+ > Li^+$
d	1.70	1.10	0.04	0.50	0.34	$Na^+ > K^+ > Li^+$
e	—	—	0.08	0.09	0.73	$K^+ > Na^+ > Li^+$

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

the protons exchange with metal ion at the feed side as shown below:



where C and M represent carrier and metal ion, respectively. The measurement of H^+ concentration in the source phase suggests that the ratio of moles of metal ion transported to the receiving solution to that of H^+ ion is 1:1. Thus, this mechanism involves a net transfer of metal ions from the feed to the receiving phase and an equivalent amount of H^+ moving in the opposite direction. Protonation of carriers has been confirmed from separate experiments. The UV-visible spectra of the chloroform solutions of the carriers are shown in Fig. 2(A). The spectra show strong absorption maxima around 325 nm. Compounds *b* and *d* have additional maxima at 345 and 360 nm, respectively. The organic solutions were equilibrated with 0.1 M HCl for 24 hours, and the spectra of the organic layers were recorded again. The absorbance values for all the bands reduced considerably (spectra not shown in Fig. 2), suggesting loss of carriers from the organic phase during equilibration with acid. The spectra of the acid extracts are shown in Fig. 2(B). In general, there is a reduction in the intensity of the peak in the spectra of the chloroform solutions of the compounds at 325 nm and a simultaneous appearance of a new peak between 360 nm and 380 nm. These changes in the spectral features are attributed to the protonation of these compounds during equilibration of the chloroform solutions with acid. The acid extracts were then neutralized using dilute NaOH and equilibrated with fresh chloroform. These chloroform extracts showed spectra (Fig. 2C) identical to those obtained for the original chloroform solutions of these carriers. Coupled with the decrease of the pH of the feed solution, the spectra not only confirms the protonation of the carriers but also the reversibility of the protonation–deprotonation reaction. The ion-exchange mechanism of transport was further confirmed by taking solutions of picrate salts of the metal ions as the feed solution. Transport of the colored picrate anions to the receiving compartment could not be visually observed or spectrophotometrically determined even after carrying out the transport experiment for more than 24 hours. However, the transport of the cations was confirmed from their concentration measurements. Table 2 also gives a picture of carrier activity of each of the carriers toward Li^+, Na^+, and K^+. Coupled with the uphill transport, a degree of selectivity of the carriers for differ-

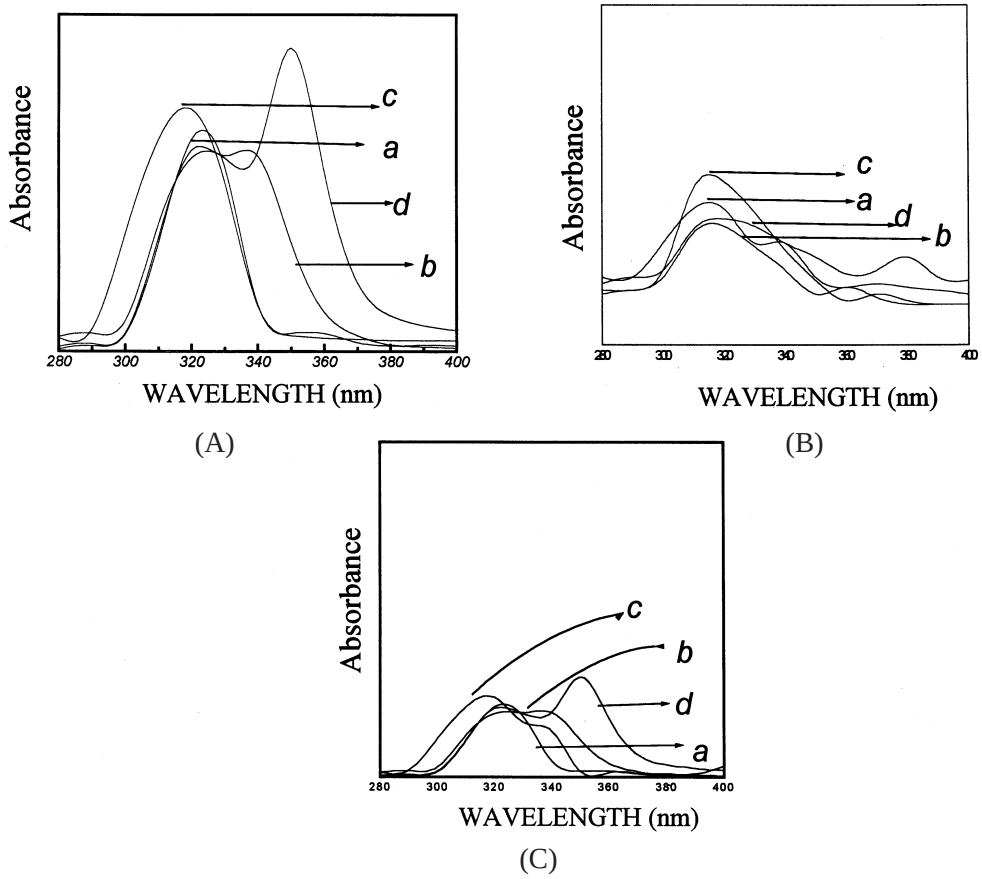


FIG. 2 Electronic spectra of carrier compounds in (A) chloroform solution, (B) aqueous acid extract, and (C) chloroform after neutralization and reextraction. *a*, *b*, *c*, and *d* denote the carrier compounds as listed in Table 1.

ent metal ions has been observed. Since the experiments were carried out for single ion transport, the word "selectivity" actually denotes the amount of metal ions transported during a fixed period of time (24 hours). Carriers *a* and *e* show a high degree of selectivity toward the transport of Na^+ and K^+, respectively. The selectivity is expected to be governed by the stability of the metal–carrier complex. Substitution on the ligands is not expected to have any significant effect on the transport. Some electron-withdrawing groups, of course, would marginally increase the basicity of the ether oxygen atoms which are believed to enhance the ion-exchange process operative in the transport. If the carrier activity had been due to the chelation of metal ions, the structure of the ligands and the substitutions on them would have influenced the transport property of the carriers. On the other hand, if transport was due to the accommodation of metal ions in the ionophore, as in the case of crown ethers, the size of the cavity would have been the important factor for the

transport process. Compound *e* was specifically chosen because it has a closed ring structure. The carrier activity of this compound was expected to be different from the others (*a–d*), and it was expected that the mechanism of ion transport by this compound would be similar to the one observed for crown ethers. However, the experimental observations suggested an ion-exchange mechanism for the carrier activity of this compound also.

It is worthwhile to compare the transport mechanism of these carriers with those of crown ethers. First of all, crown ethers are planar compounds which accommodate the cations within their ionophores and the accompanying anions, thus resulting in the transport of the metal salts as a whole through the hydrophobic liquid membrane. The present carriers have open structures (except *e*), and protonation of ether oxygens followed by cation exchange is responsible for transport. The linkage of ether oxygen through CH_2 groups does not imply a planar arrangement of the oxygen atoms of the ligand. In the case of compound *e* the spatial orientation of the OH and CH_3 groups suggests a nonplanar geometry. In spite of this, all the compounds show sufficient carrier activity toward the transport of alkali metal ions.

The ion-exchange mechanism of transport suggests the electrostatic nature of the metal–carrier bond, but it is interesting to note that methyl substitution has a positive effect on the carrier activity of the compounds but the selectivity order does not appear to be affected significantly.

CONCLUSION

Phenoxy ethers have been found to be effective carriers for the transport of alkali metal ions across a bulk liquid membrane. The mechanism of cation transport could be a coupled transport process involving protonation followed by cation exchange. Compounds *a* and *e* have been found to be selective for Na^+ and K^+, respectively. The transport rates are comparable to those observed for the well-known crown-ether carriers. Studies on the carrier activity of similar compounds would be of interest for the study of some biochemical processes. Since ion exchange is the operating mechanism of transport processes, it would be interesting to study the carrier activity of these compounds toward divalent cations.

REFERENCES

1. B. C. Pressman, *Inorganic Biochemistry, Vol. 1* (G. L. Eichohorn, Ed.), American Elsevier, New York, NY, 1973, p. 203.
2. W. E. Morf and W. Simon, in *Progress in Macrocyclic Chemistry, Vol. 1* (R. M. Izatt and J. J. Christensen, Eds.), Wiley, New York, NY, 1979.
3. J. Ramkumar, K. S. Shrimal, B. Maiti, and T. S. Krishnamoorthy, *J. Membr. Sci., 116*, 31 (1996).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

4. J. Ramkumar, B. Maiti, and P. K. Mathur, *Sep. Sci. Technol.*, *33*, 2423 (1998).
5. E. K. Unnikrishnan, S. D. Kumar, and B. Maiti, *J. Membr. Sci.*, *137*, 133 (1997).
6. J. Ramkumar, E. K. Unnikrishnan, B. Maiti, and P. K. Mathur, *Ibid.*, *141*, 283 (1998).
7. J. Ramkumar, B. Maiti, and T. S. Krishnamoorthy, *Ibid.*, *125*, 269 (1997).
8. T. Hayashita and R. A. Burtsch, *Ibid.*, *116*, 243 (1996).
9. J. D. Lamb, R. M. Izatt, and J. J. Christensen, in *Coordination Chemistry of Macrocyclic Compounds* (G. A. Melson, Ed.), Plenum Press, New York, NY, 1979.
10. C. J. Penderson, *J. Am. Chem. Soc.*, *89*, 7017 (1967).
11. T. Eggers, in *Membranes, Vol. 3* (G. Elsenman, Ed.), Dekker, New York, NY, 1975, p. 1.
12. D. Mishra and U. Sharma, *Indian J. Chem.*, *35A*, 1014 (1996).
13. J. D. Lamb, R. M. Izatt, and J. J. Christensen, *J. Membr. Sci.*, *9*, 83 (1981).

Received by editor May 26, 1998
Revision received September 1998

PAGE 2078 IS BLANK

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Request Permission or Order Reprints Instantly!