Transport Studies of Iodine Through Liquid Membrane System

U. S. VURAL and M. ERSOZ*

Department of Chemistry, Faculty of Arts and Sciences, Selcuk University, Konya 42079, Turkey

SYNOPSIS

Transport of iodine by a charge-transfer mechanism through a bulk organic liquid membrane system containing calixarene based on donor-type carriers was studied. It was found that the transport of iodine is facilitated by n-donor carriers depending on the pH of the source phase. The color of iodine solutions on the source side turned from brown to colorless. The passage of iodine through the organic bulk liquid membrane was governed by donor–acceptor interaction between n-donor atoms in the carrier and σ-acceptor (iodine atoms) and by the diffusion of an n–σ-type charge-transfer complex in the membrane followed to release by the Lewis acid–base interaction in the aqueous phase. The transport by the new carrier arises both from the different extraction equilibrium constants between the aqueous phase and donor–acceptor interaction with iodine and the carrier in the organic phase. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Calixarenes have gained an important place over the past two decades in host–guest chemistry because of their ability to form complexes with ions and neutral organic molecules; they also have attractive structural properties for the construction of many biomimetic systems.[1] Calixarenes are cyclic oligomers made up by phenolic units. The cyclic structure suggests the potential use of calixarenes as specific receptors for metal ions.[1] Calixarenes may be functionalized by groups containing donor types of atoms which are able to form charge-transfer complexes with some acceptors. These interesting properties provoked our interest in the use of calixarenes as a carrier for the transport of iodine and the elucidation of the possible interaction between the carrier and iodine by the charge-transfer mechanism.

The kinetics of charge-transfer complex formation seem to depend strongly on the structure of the donor and acceptor as well as on the solvent. Charge-transfer complexes have attracted a considerable

role in chemical reactivity, pharmacology, molecular physics, biochemistry, and biophysics as well as in biological reactions of living organisms.[2-8] There have been many studies of charge-transfer complexes which have been used for polymerization and copolymerization reactions, photoconductivity, formation and modification of liquid crystals, etc.[9-13]

In this study, some new derivatives of calixarenes (I_4-EPO, I_4-HPA, and I_6-benzoyl) were obtained by the reaction of calixarenes with epichlorohydrin, monochloroglyoxime, and benzoylchloride. The derived calixarenes have donor properties. However, the transport of acceptors through charge-transfer complexes with donor types of carriers has not been studied in the liquid membrane systems. Preliminary experiments show that the donor types of calixarene derivatives are capable of transporting iodine.

EXPERIMENTAL

Materials

All chemicals were obtained from Merck and were of analytical grade. Reagent-grade chloroform and carbon tetrachloride was used as the membrane solvent.

Preparation of Membranes

The p-tert-butylcalix[4]aren and p-tert-butylca-lix[6]aren were prepared according to the Gutsche method.[14,15] The functional calixarenes were obtained by the benzylation with benzoyl chloride as I_6-benzoyl, epoxidation with epichlorohydrin as I_4-EPO, and glyoximation with monochloroglyoxime as I_4-HPA according to the literature[16–22] and the chemical structure of the synthesized materials are shown in Scheme 1.

Transport Experiments

Transport experiments were performed in a conventional U-tube glass cell with magnetic stirring at room temperature. The solution compositions of source phase and receiver phase are listed in Table I.

Aliquots (400 μL) of the aqueous solutions of both phases were withdrawn at appropriate intervals and then diluted by a factor of 25. The pH of both sides was monitored by using an Orion model 720 pH meter. The concentration of iodine on both sides of the membrane were measured by a UV-visible spectrophotometer (Shimadzu UV-160A) at 420 nm. Each experiment was repeated at least twice, and the results were consistent within ±10%.

RESULTS AND DISCUSSION

Solutions containing the interacting electron donor (D) and electron acceptor (A) species exhibit not only the absorption bands of D and A but most often also show a new band or bands which are assignable to charge-transfer transitions of the complex. The intensity of this band could be used as a measure of the concentration of the complex. The equilibrium or extraction equilibrium constant that involves the
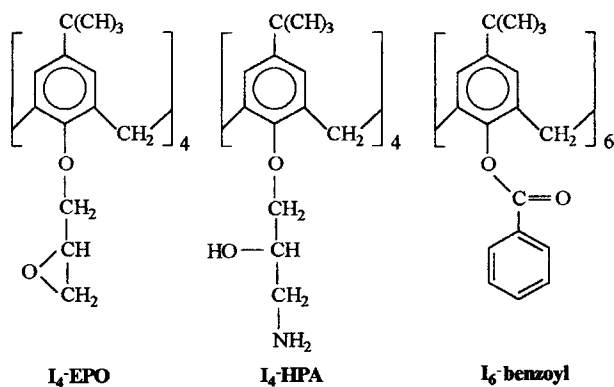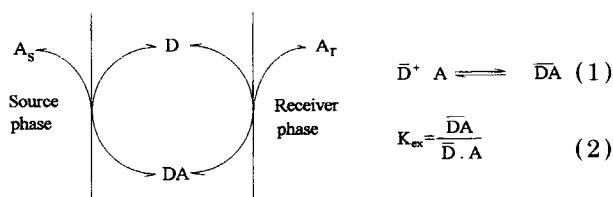

Scheme 1

Table I Composition of Source and Receiver Phase Solutions

Source solution, 10 mL

pH 2–7, I = 0.2 with 100 mmol KCl
5.5 mmol iodine in water
50 mmol citric acid
25 mmol Na_2HPO_4
The pH of buffer solution concentration is adjusted in the desired pH range

Receiver phase, 10 mL

pH 10, I 0.2 with 100 mmol KCl
100 mmol H_3BO_4
100 mmol NaOH

Membrane phase, 10 mL

I_4-EPO	13.29 mmol in $CHCl_3$
I_4-HPA	7.8 mmol in $CHCl_3$
I_6-benzoyl	7.5 mmol in CCl_4

formation of a charge-transfer complex from (D) and (A) can be represented schematically as shown in Scheme 2.

$$\overline{D}^+ A \rightleftharpoons \overline{DA} \quad (1)$$

$$K_{ex} = \frac{\overline{DA}}{\overline{D} \cdot A} \quad (2)$$

Scheme 2

An acceptor is taken from the source phase into the membrane to form a charge-transfer complex $\overline{DA}$, and the complex traverses the two boundary layers by diffusion to release A (receiver phase). The process is driven by the concentration gradient $C_{A,s} \gg C_{A,r}$.

When the rate for complex formation and dissociation between carrier and iodine is fast (equilibrium assumption), the concentration of species at the interfaces are related through the overall extraction equilibrium constant, K_{ex}. The symmetry assumption requires that all concentration gradients be equal at the steady state.[23] A steady-state concentration profile is shown in Scheme 3.

The steady-state flux of A is given by Fick's law[23]:

$$J_A = \frac{D}{2l}(DA_{i,s} - DA_{i,r}) \quad (3)$$

Scheme 3
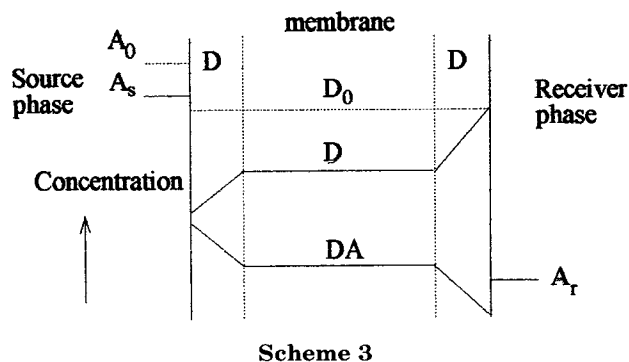
where i indicates the interfacial concentration; J_A, the transport of the acceptor; D, the diffusion coefficient; l, the apparent thickness of the membrane (organic) phase; DA_s and DA_r, the concentration of the acceptor with the carrier between the source and receiver interfaces, respectively. The equilibrium assumption also provides a mass balance equation, since for the total concentration of the carrier, every point must be equal (L_0).[23] As a result,

$$J_A = \frac{K_{ex}DL_0}{2l} \frac{A_s - A_r}{(1 + K_{ex}A_s)(1 + K_{ex}A_r)} \quad (4)$$

The initial concentration is $A_r = 0$ and that throughout the experiment is $A_s \gg A_r$. When K_{ex} is small, $K_{ex}A_s \ll 1$ (and $K_{ex}A_r \ll 1$)[23]; thus,

$$J_A \cong \frac{DL_0}{2l} K_{ex}A_s \quad (5)$$

As $K_{ex}A_s$ increases, the term $(1 + K_{ex}A_s)$ thus becomes

$$J_A \cong \frac{DL_0}{2l} \frac{K_{ex}A_s}{(1 + K_{ex}A_s)} \quad (6)$$

Some examples of the changes in concentration of iodine in the source phase and receiver phase with time for the three carriers are shown in Figure 1. For all values in the source phase, the concentration of iodine on the receiver phase increased, whereas on the source phase, it was just the opposite. The solution on one side of the membrane is acidic or neutral, and the solution on the other side is alkaline.

To clarify the charge-transfer mechanism of the iodine transport by carriers, a curve-fitting using the equations for transport was performed on the results of the transport experiment using the iodine in the source phase. The values of K_{ex} shown in Table II were used for eq. (6), and the experimental

value of J_A was used to determine $(D/l)(L_0)$. The results of the curve-fitting using eq. (6) is shown in Figures 2 and 3, which agrees with the experimental results.

Iodine is an electron acceptor and a Lewis acid. Iodine, the most polarizable of the halogen mole-
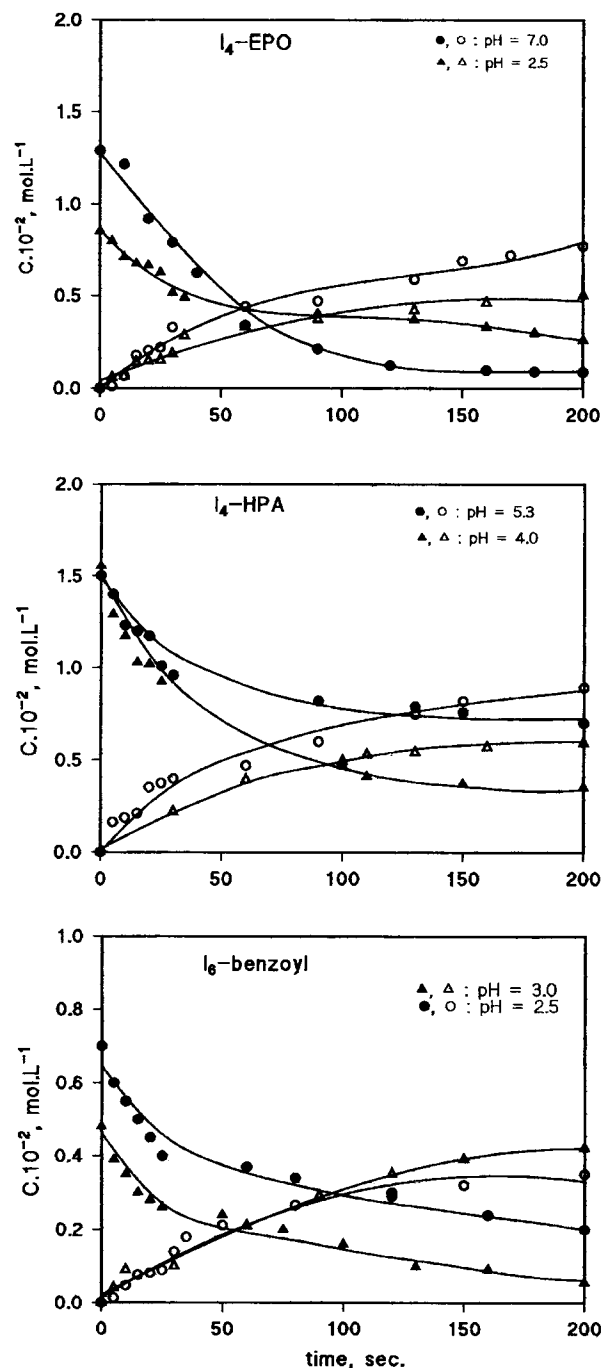

Figure 1 Changes in concentration of iodine with time through organic liquid carriers membranes. Solid symbols: source phase; open symbols: receiver phase.
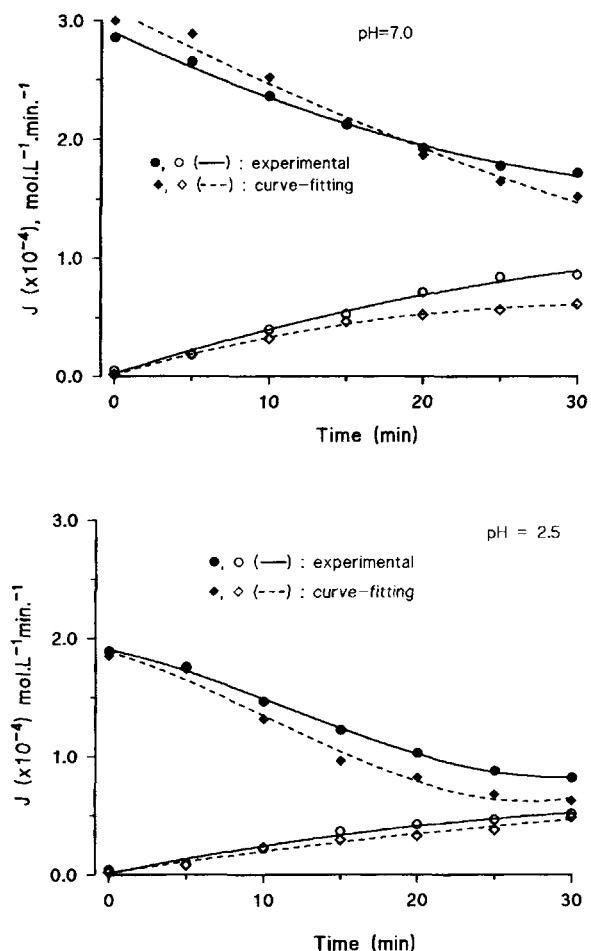
Figure 2   The curve-fitting of iodine transport by carrier I_4-EPO. Effect of the initial pH on the source phase. Solid symbols: source phase; open symbols: receiver phase.

cules, is violet in the solid and gas phases and is brown in nondonor solvents such as chloroform, water, acetone, or ethanol, all of which are Lewis bases. The color changes because the solvent–solute complex which is formed from the lone pair of donor molecules O or N atoms and a low-lying σ^* orbital of dihalogen has a strong optical absorption. The strong visible absorption spectra of I_2 arise from transitions from filled to low-lying unfilled orbitals, providing a hint that the empty orbitals may be low enough in energy to serve as acceptor orbitals in Lewis acid–base complex formation. The transition responsible for the new absorption band is observed when a charge-transfer complex is formed. The orbital from which the electron originates in the transition is predominantly the lone-pair orbital; thus, transition occurs and the transition transfers an electron from the base to the acid.

The general transport formula of the carrier-mediated transport of an ion pair in a diffusion-limited

process gives the relationship between the transport rate and the type of carrier. If two atoms of iodine are transported by two donor atoms of carrier I_4-HPA, the transport rate by carrier I_4-HPA is twice faster than that by carrier I_4-EPO and I_6-benzoyl. Only one iodine atom is probably transported by the carriers I_4-EPO and I_6-benzoyl, and the difference in the transport rate between the carriers also comes from the term of the extraction equilibrium constant, as shown in Table II. As described above, the transport rate depends on the quantity of the donor atoms and may be conformation of the carrier, the electronegativity of the donor atoms, and the pH of the source phase.

The transport flux of iodine was observed in the order I_4-HPA > I_4-EPO > I_6-benzoyl, which is related to donor atoms in the carriers. The transport flux of iodine by carrier I_4-HPA is faster than that by carriers I_4-EPO and I_6-benzoyl. The case of I_4-HPA, which has two donor atoms which are O and
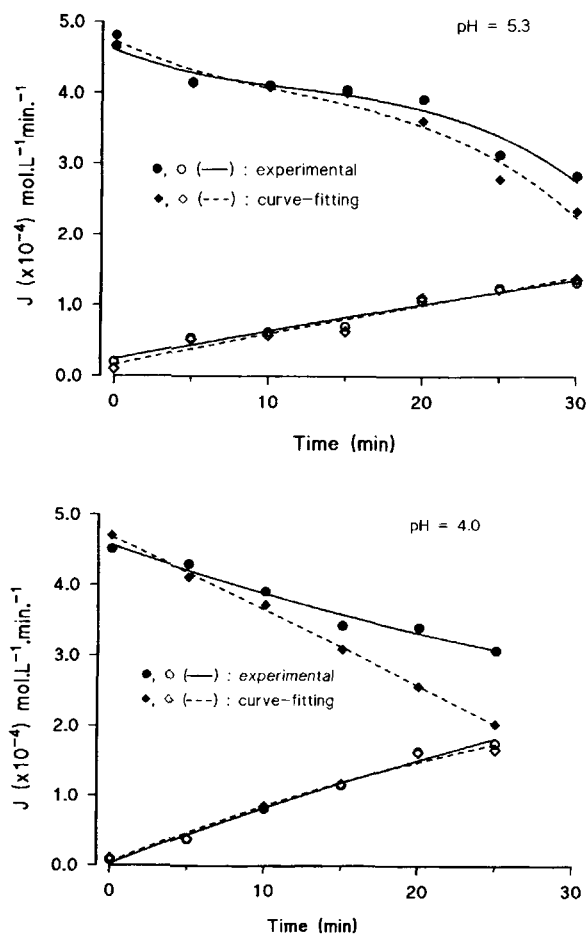

Figure 3   The curve-fitting of iodine transport by carrier I_4-HPA. Effect of the initial pH on the source phase. Solid symbols: source phase; open symbols: receiver phase.

Table II Transport Flux and Extraction Equilibrium Constants for Iodine Through Used Carriers

Carrier	pH	I_{max} (mol L^{-1} min^{-1})	K_{ex} (L mol^{-1})
I_4-HPA	5.3	3.96×10^{-3}	2.540
	4.0	5.07×10^{-3}	1.792
I_4-EPO	7.0	1.80×10^{-4}	1.578
	2.5	7.18×10^{-5}	1.088
I_6-benzoyl	3.0	4.50×10^{-4}	0.991
	2.5	4.70×10^{-4}	0.540

N, plays a very important role in the transport of iodine. These n-donor-type atoms may interact with two iodine atoms, and the other carriers only may interact with one iodine atom. Therefore, it is expected that the efficiency of transport of iodine is affected by the quantity of the donor atoms of the carriers.

The pH affects the iodine flux. Increasing the pH value of the source phase, the iodine flux increases. First, the iodide ion may react with the carrier molecules through the oxygen and nitrogen atoms and a large number of iodine atoms seep into the organic phase from the aqueous phase and react with the carrier host molecules. This was experimentally confirmed, as shown in Table II, which lists the extraction equilibrium constants and the transport flux of iodine by carriers from the aqueous solution to the chloroform solutions for I_4-HPA and I_4-EPO and carbon tetrachloride for I_6-benzoyl under the same experimental condition.

As shown in Table II, the transport flux of iodine in the liquid membrane containing three carriers was facilitated markedly. It is known that the affinity of calixarenes for alkali metal cations increases with increasing size of the metal cations. Therefore, it may be expected that the partly positive iodine, which might be a primary interacting part of the present host–guest system, could favorably interact with the binding site, the pseudocavity of the carrier, to give a charge-transfer complex. The pseudocavity of the carrier consists of the oxygen n-donor atoms of epoxy and benzoyl groups and oxygen and nitrogen n-donor atoms of the amino groups. The partly positive iodine group of the guest is anchored in the n-donor atoms in the pseudocavity of the carrier by the charge-transfer interaction between I $\cdots\cdots\overset{+\delta}{\cdots}\cdots\cdots$ O— or I $\cdots\cdots\overset{+\delta}{\cdots}\cdots\cdots$ N— which is the interaction between acceptor and donor atoms.

The absence of the carriers in the transport of iodine was also conducted as a control experiment. In that case, the transport of iodine was observed from the source phase to the organic phase according to its distribution coefficient between the aqueous phase and the organic phase, but no transport was observed from the organic phase to the receiver phase. In comparison, the transport of iodine without carriers could be negligible.

The primary observation of this study is that varying the pH in the source phase can significantly impact the transport rate of iodine through the calixarene-based liquid membrane by the charge-transfer mechanisms. For example, the iodine transport at neutral pH was observed to be more than that for lower pH on the source phase. To answer the questions, we need to examine the transport mechanism in this system. In the general case, the charge-transfer model has to consider both the diffusion and reaction processes. The solution to this model for the charge-transfer mechanisms is that the reaction kinetics should be well defined. The complete reversible reaction and complex formation for the charge-transfer reaction is a complicated function of the acceptor, donor, and complex and their concentrations, pH, solvent interaction, etc.

REFERENCES

1. C. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, 1989.
2. R. Foster, *J. Phys. Chem.*, **84**, 2135 (1980).
3. J. Latha, S. Palaniappan, and D. N. Sathyarayana, *Indian J. Chem.*, **33A**, 104 (1994).
4. K. Tamaru and M. Ichikawa, *Catalysis by Electron Donor-Acceptor Complexes*, Kondansha, Tokyo, 1975.
5. M. A. Slifkin, *Charge Transfer Interactions of Biomolecules*, Academic Press, London, 1971.
6. M. Elsadek, S. Eladl, M. Aboukull, and S. M. Sakr, *Talanta*, **40**, 585 (1993).
7. A. S. Perez, M. J. G. Matilla, and J. H. Mendez, *Anal. Lett.*, **26**, 721 (1993).
8. J. Molnar, J. Fischer, and M. J. Nakamura, *Int. J. Gen. Mol. Microbiol.*, **62**, 309 (1992).
9. A. Deronizer and M. Essakalli, *J. Phys. Chem.*, **95**, 1737 (1991).
10. D. Markovitsi, H. Bengs, and H. Ringsdorf, *J. Chem. Soc. Faraday Trans.*, **88**(9), 1275 (1992).
11. T. Li, S. Li, and S. Fu, *J. Macromol. Sci.-Chem. A*, **28**(7), 673 (1993).
12. H. Z. Chen, M. Wang, L. X. Feng, and S. L. Yang, *J. Photochem. Photobiol. A-Chem.*, **70**, 179 (1993).

13. R. D. Calleja, P. J. Klar, E. S. Martinez, J. Behrens, J. Kudnig, and G. Klar, *J. Mater. Chem.*, **3,** 489 (1993).

14. C. D. Gutsche and M. Iqbal, *Org. Synth.*, **68,** 234 (1990).

15. C. D. Gutsche, B. Dhawan, M. Leonis, and D. Stewart, *Org. Synth.*, **68,** 238 (1990).

16. H. S. Irwin, *Enzyme Kinetics*, Wiley, New York, 1975.

17. K. A. See, F. R. Fronczek, W. H. Watson, R. M. Kashyap, and C. D. Gutsche, *J. Org. Chem.*, **56,** 7256 (1991).

18. C. D. Gutsche and K. A. See, *J. Org. Chem.*, **57,** 4527 (1992).

19. J. S. Rogers and C. D. Gutsche, *J. Org. Chem.*, **57,** 3152 (1992).

20. E. S. Hemdan and J. Porath, *J. Chromatogr.*, **323,** 247 (1985).

21. R. A. Kurbanova, A. V. Ragimov, and N. R. Bektasi, *Doklad Akad. Nauk. Azerb.*, **17,** 37 (1987).

22. S. G. Entelis, V. V. Evreinov, and A. I. Kuzaev, *New Concepts in Polymer Science: Reactive Oligomers*, VSP BV, Utrecht, 1989.

23. T. M. Fyles, in *Inclusion Aspects of Membrane Chemistry: Principles of Artificial Membrane Transport of Ions by Synthetic Ionopheres.*, T. Osa and J. L. Atwood, Eds., Kluwer, Dordrecht, 1991, Vol. 2, p. 59.

24. S. Tsuchiya and M. Seno, *J. Phys. Chem.*, **98,** 1682 (1994).