A Kinetic Investigation of a Carrier-Mediated Transport Through a Bulk Liquid Membrane

Yaftian, Mohammad Reza*[+]

Department of Chemistry, Faculty of Science, Zanjan University, P.O.Box 45195-313 Zanjan, I. R. IRAN

Burgard, Michel

ECPM, Université Louis Pasteur, 25, Rue Bequrel, 67200 Strasbourg, FRANCE

ABSTRACT: *The kinetics of the potassium thiocyanate transport mediated by dicyclohexyl-18-crown-6 (L) through a bulk liquid membrane is studied experimentally and theoretically. The proposed model is based on the assumption of a pure diffusion of the complex salt $[K\bullet L]^+SCN^-$ through the liquid membrane stagnant films at the interfaces. It illustrates the connection between liquid-liquid extraction equilibrium data and transport rates. The evaluation of the transfer coefficient allows to evaluate the organic stagnant films thickness, the stationary state transport rate and the time lag.*

KEY WORDS: *Kinetics, Transport, Liquid membrane, Diffusion, KSCN, DC18C6.*

INTRODUCTION

The liquid membrane can be defined as a liquid phase separating two fluid phases. In practical cases, these two fluids are aqueous while the liquid membrane itself is a water-immiscible organic layer.

Since the pioneering work of S*chulman et al.* [1] many experimental and technical liquid membrane systems have been elaborated and developed [2]. Regardless of the type of liquid membrane, transfer of a chemical solute between the aqueous phases can be considered as a simultaneous extraction and stripping process.

As already described by *Izatt et al.* [3], the liquid membrane acts as a solvent for a transported solute whose transport is governed by its solubility in the membrane.

The most interesting case arises when this solubility can be controlled by a chemical reaction between the transported solute and an extractant-carrier molecule which forms a solute-carrier complex. This kind of transport is called facilitated or carrier-mediated transport [2].

It is generally considered that the transfer mechanism involves several steps, including interface reaction and diffusion processes [4]. The rationalization of the related transfer kinetics is simplified if one can identify the limiting steps of the transfer process under the experimental conditions used. In many cases, transfer rates have been described using the two films model in which one assumes that transfer is controlled by diffusion.

* *To whom correspondence should be addressed.*

+ *E-mail: yaftian@mail.znu.ac.ir*

1021-9986/06/4/17 7/$/2.70

In this paper, we present a simple mathematical model describing the transfer kinetics of KSCN through a liquid membrane which is a solution of dicyclohexyl-18-crown-6 (L) in chloroform. This system has been selected because the ability of DC18C6 to selectively complex [5] and efficiently transport [6] the potassium ions, among the alkali metal ions, has been well studied and reported. These abilities have been attributed to the size adaptation of the metal ion with the cavity of the crown ether.

EXPERIMENTAL

Membrane transport experiments were conducted in a glass U-shaped tube (Fig. 1, diameter 41 mm and arm height 150 mm), immersed in a thermostated water bath maintained at 25°C. The cell was filled with 160 ml of a chloroform solution of dicyclohexyl-18-crown-6 (Fluka) solution (0.002 M) in chloroform (Merck) in contact with 80 ml of a 0.1 M solution of potassium thiocyanate (Fluka) in one of the arms, and 80 ml distilled water in the other. It is confirmed that without dicyclohexyl-18-crown-6, transfer of potassium across the chloroform membrane does not take place. One uniform mixer was inserted into each arm and two synchronous motors (Heidolph RZR 2000) provided a constant rotation of the mixers, ensuring stirring of the phases without perturbation of the interfaces. Transport was started by stirring the phases (100 rpm). Appearance of the cation in the receiving phase was monitored by determination of thiocyanate ions simultaneously transported across the membrane. Thus, an aliquot of 2 ml was removed from phase each half hour (for three hours) and diluted to 4 ml with $Fe(NO_3)_3$ (Fluka) (0.02 M) in 0.2 M HNO_3 (Merck). The concentration of SCN^- was measured spectrophotometrically at 480 nm (Perkin-Elmer 550S) using a molar absorptivity coefficient of 4400 l mol^{-1} cm^{-1} at 25°C [7]. Changes in the volume of the receiving phase due to successive removal of material, were taken into account in the final calculation. In order to maintain the position of the interfaces, 2 ml of the feed phase were also removed at each titration point. At the end of the experiment, the concentration of potassium thiocyanate in the organic phase was determined by withdrawal of 5 ml of the chloroform layer and stripping it with 5 ml of distilled water. The amount of dissolved KSCN was measured according to the method described above. Finally, in order to determine the equilibrium extraction

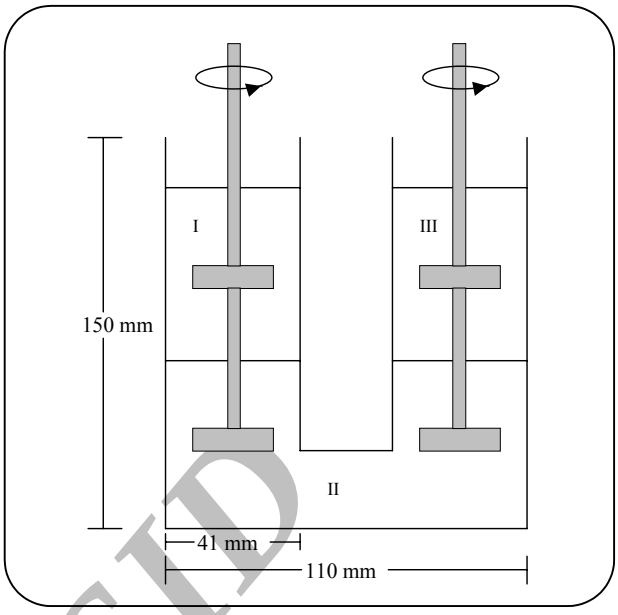

Fig. 1: U-shaped glass tube used for the transport experiment. I: feed phase; II: membrane; III: receiving phase.

concentration (C_1), 10 ml of aqueous potassium thiocyanate (0.1 M) and an equal volume of a solution of dicyclohexyl-18-crown-6 in chloroform were placed in a tube immersed in the thermostated bath at 25°C. The mixture was stirred magnetically for 20 minutes before the phases were allowed to settle and 2 ml of the organic phase were removed. This solution was stripped with 5 ml of distilled water and used for spectroscopic determination as described above.

RESULTS AND DISCUSSION

The simplest setup for liquid membrane experiments is certainly the U-shaped tube where the organic phase lies at the bottom and the two arms contain a feed and a receiving phase (Fig. 1).

The feed phase is a concentrated potassium thiocyanate aqueous solution (concentration: C_f) while the receiving phase is distilled water. The transport process (Fig. 2), firstly, involves formation of a complex between KSCN and dicyclohexyl-18-crown-6 (KLSCN) at the feed/membrane interface. After crossing the membrane, the complex is dissociated at the membrane/receiving phase.

Both steps are described by an interfacial reaction:

$$K^+_{i,aq} + SCN^-_{i,aq} + L_{i,org} \rightleftharpoons KLSCN_{i,org} \qquad (1)$$

where "i" denotes a species at the interface, "aq" a species at the aqueous side and "org" a species at the membrane side.

The rate of transport can be studied by monitoring the potassium concentration in the receiving phase (C_r) and in the membrane phase (C_m) as a function of time (Table 1 and Fig. 3).

The so-called double films model can be used to describe the evaluation of the concentration of potassium in these phases. This model considers a *fickian diffusion* for the solute through stagnant layers existing on either side of a given interface (Fig. 4). The mechanism of the transport is described by means of the concentration profile of the involved species:

Step 1- Diffusion of KSCN through the aqueuse stagnant layer at the first interface characterized by the salt concentration gradient C_f-C_{fi} with:

$$C_{fi} = [K^+_{i,aq}]_1 = [SCN^-_{i,aq}]_1$$

Step 2- Complex (KLSCN) formation at the first interface. The interfacial concentrations are related via the equilibrium constant (K_{ex}) of reaction (1):

$$C_1 = [KLSCN_{i,org}]_1 = K_{ex} C_{fi}^2 [L_{i,org}]_1 = \frac{K_{ex} L_0 C_{fi}^2}{1 + K_{ex} C_{fi}^2} \quad (1)$$

with $[L_{i,org}]_1 = L_0 - C_1$

Step 3- Diffusion of the complex KLSCN through the organic stagnant layer at the first interface characterized by the complex concentration gradient C_1-C_m.

Step 4- Diffusion of the complex through the organic stagnant layer at the second interface characterized by the complex concentration gradient C_m-C_2.

Step 5- KSCN release into the receiving phase by complex dissociation according to the equilibrium (1). The concentration at the second interface are also related via K_{ex} :

$$C_2 = [KLSCN_{i,org}]_2 = K_{ex} C_{ri}^2 [L_{i,org}]_2 = \frac{K_{ex} L_0 C_{ri}^2}{1 + K_{ex} C_{ri}^2} \quad (2)$$

with $[L_{i,org}]_2 = L_0 - C_2$.

Step 6- KSCN diffusion through the aqueous stagnant layer at the second interface characterized by the concentration gradient C_{ri}-C_r with:

$$C_{ri} = [K^+_{i,aq}]_2 = [SCN^-_{i,aq}]_2$$

Table 1: Experimental concentration of the transported complex in the receiving phase (C_r) and the membrane(C_m) versus time.

Time (s)	C_r (M)	C_m (M)
1800	1.36×10^{-5}	-
3600	4.91×10^{-5}	-
5400	9.44×10^{-5}	-
7200	1.54×10^{-4}	-
9000	2.23×10^{-4}	-
10800	3.00×10^{-4}	2.58×10^{-4}

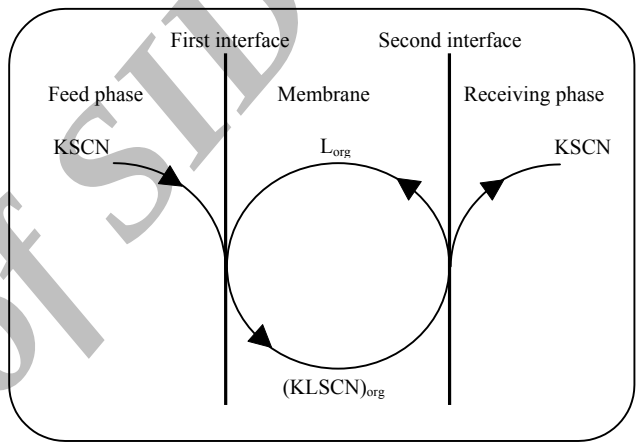

Fig. 2: Schematic representation of the mechanism of KSCN transport through a liquid membrane containing a carrier (L).

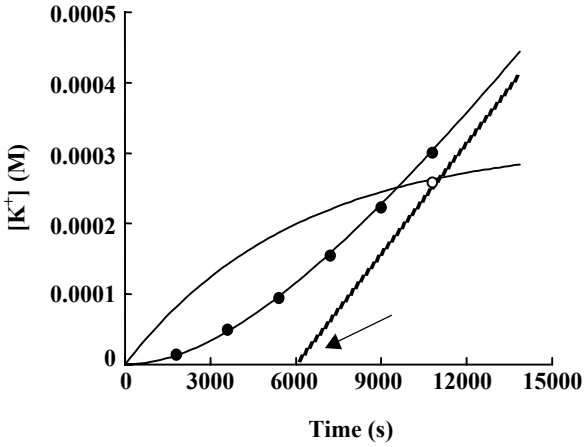

Fig. 3: Calculated (lines) and experimental concentrations of potassium thiocyanate in the receiving (filled circles) and membrane (empty circle) phases versus time using DC18C6 as carrier at 25 °C. Feed phase : 0.1 M potassium thiocyanate (80 ml); receiving phase : distilled water (80 ml); membrane phase : 0.002 M of DC18C6 in chloroform; stirring speed : 100 rpm.

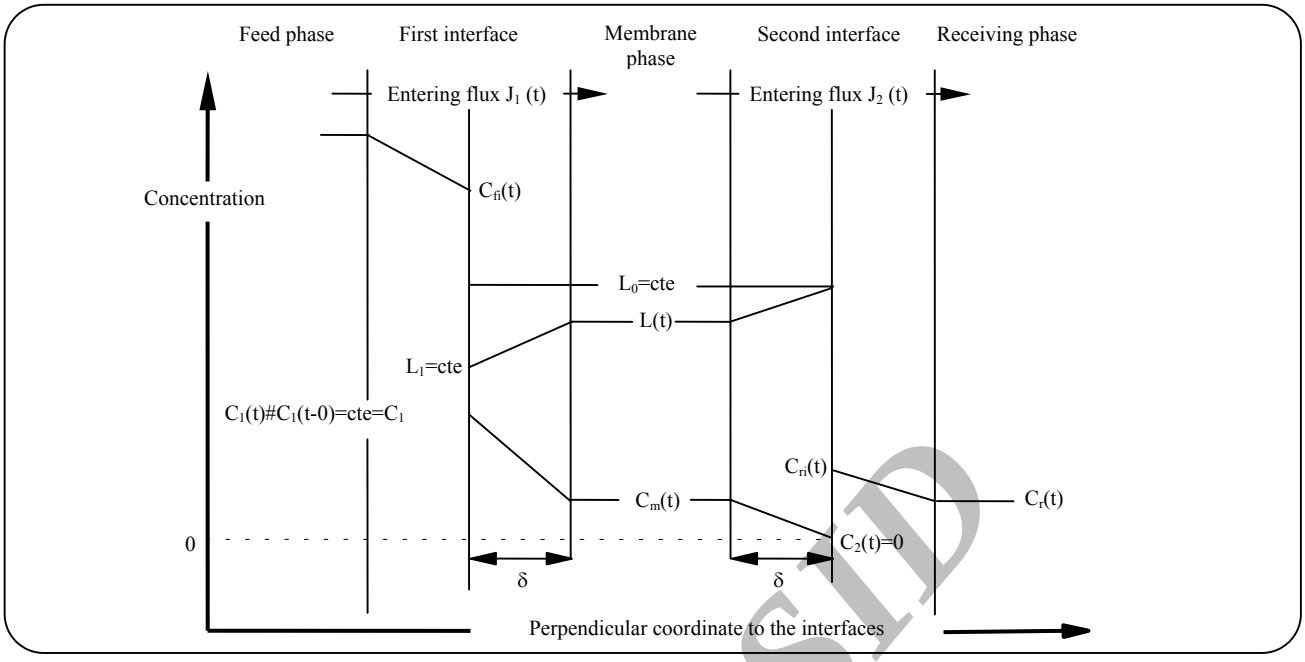

Fig. 4: Diffusion layers and the concentration gradients in the transport process.

Based on the Fick's law, the molar flux (J) is related to the concentration gradient ΔC by the equation:

$$J = K\Delta C = \frac{D}{\delta}\Delta C \qquad (3)$$

with k, mass transfer coefficient; D, diffusion coefficient of the complex KSCN; and δ, thickness of the organic stagnant film. At any time, the entering flux J_1 can be expressed as :

$$J_1 = k_{aq1}(C_f - C_{fi}) = k_{org1}(C_1 - C_m) \qquad (4)$$

where k_{aq1} and k_{org1} are respectively the mass transfer coefficient in the aqueous and membrane phases. A similar relation holds for the membrane leaving flux :

$$J_2 = k_{aq2}(C_{ri} - C_r) = k_{org2}(C_m - C_2) \qquad (5)$$

For symmetry reasons:

$k_{aq1} = k_{aq2} = k_{aq}$, $k_{org1} = k_{org2} = k_{org}$.

Additional assumptions are made:

- high KSCN concentration in the feed phase can be considered as a time independent concentration (C_f = KSCN concentration at any time),

- within the conditions (slow transfer corresponding to a low gradient) one can assume $C_{fi} \# C_f$.

These assumptions allow to calculate the complex concentration C_1 which is also time independent using the equilibrium constant corresponding to equilibrium (1):

$$C_1 = \frac{K_{ex} L_0 C_f^2}{1 + K_{ex} C_f^2} \qquad (6)$$

($[K^+]_{aq} = [SCN^-]_{aq} = C_f$)

An extraction experiment carried out in a separatory funnel provides the organic KLSCN concentration (C_1) from C_f (see experimental section). The deduced K_{ex} value (47 M^{-2}) can be considered as low and thus at any time $C_2 = 0$ (see appendix). Therefore the eq. (5) becoms:

$J_2 = k_{aq}(C_{ri} - C_r) = k_{org} C_m$.

The rate of transport (n') can be presented by:

$n' = S J$ (S : interface area)

Assuming the rate determining step is the diffusion of the solute through the organic stagnant films, the rate of which is given by:

$$n'_1(t) = S_1 J_1(t) = S_1 k_{org1}(C_1 - C_m(t)) \qquad (7)$$

while the rate at which this species exits the membrane becomes:

$$n'_2(t) = S_2 J_2(t) = S_2 k_{org2} C_m(t) = V_r \frac{dC_r(t)}{dt} \qquad (8)$$

By applying the conservation law,

$$n_1'(t) = n_2'(t) + V_m \frac{dC_m(t)}{dt} \quad (9)$$

and allowing for symmetry reasons,

$S_1 = S_2 = S$ and $k_{org1} = k_{org2} = k_{org}$.

Integration of eq. (9) provides the expression for the complex concentration within the membrane, $C_m(t)$, (boundary condition : t=0; C_m=0);

$$C_m(t) = \frac{C_1}{2}(1 - \exp[-\frac{2\,k_{org}\,S\,t}{V_m}]) \quad (10)$$

Therefore, the concentration of potassium in the receiving aqueous phase, $C_r(t)$, can be calculated according to eq. (8) (boundary condition : t=0; $C_r(t)$=0) as follows :

$$C_r(t) = \frac{k_{org}\,S\,C_1}{2\,V_r}t - \frac{C_1\,V_m}{4\,V_r} + \frac{C_1\,V_m}{4\,V_r}\exp[-\frac{2\,S\,k_{org}\,t}{V_m}] \quad (11)$$

The analysis of the experimental results is carried out by means of a graphical representation (Excel) whereby the theoretical curves are normalized to the experimental results using an appropriate value of k_{org} (1.01×10^{-3} cm/s). In fact, eq. (11) describes the "approach to the steady-state flow" [8] through the liquid membrane. For $t\rightarrow\infty$ expression eq. (11) approaches the line;

$$C_r(t)_{steady} = \frac{k_{org}\,S\,C_1}{2\,Vr}t - \frac{C_1\,V_m}{4\,V_r} \quad (12)$$

the slope of which;

$$n_{2\,steady}' = \frac{k_{org}\,C_1\,S}{2\,V_r} \quad (13)$$

being the steady-state transport rate corresponding to the boundary conditions (C_1= constant, $C_2(t)$=0 at any time).

In addition, the analysis allows to determine the time lag (t_l) [6] which is defined as the intercept of the line (eq. 12) on the "t" axis : $C_r(t_l)_{steady} = 0$

$$\frac{k_{org}\,S\,C_1}{2\,V_r}t_l - \frac{C_1\,V_m}{4\,V_r} = 0,$$

$$t_l = \frac{V_m}{2\,S\,k_{org}} \quad (14)$$

Considering the Fick's first law, the transfer coefficient, k_{org}, is expressed in terms of the diffusion coefficient of the complex and the thickness of the organic stagnant film (δ): $k_{org} = D/\delta$. In addition, the *Wilke-Chang* equation [9] (see notations):

$$D = \frac{1.17\times10^{-13}\,(\xi\,M)^{0.5}\,T}{V^{0.6}\,\eta} \quad (15)$$

provides a satisfactorily evaluation of the diffusion coefficient (1.29×10^{-5} cm^2s^{-1}) if the molar volume of the diffusing complex, V, can be estimated. This relationship between D and V shows the influence of the size of the diffusing complex on the transfer kinetics [10].

The molar volume of the DC18C6-K complex ($V = 362$ cm^3mol^{-1}) is estimated here by using a group contribution method [11]. Hence, it is seen that this experiment provides information on the organic stagnant film thickness ($\delta \approx 0.01$ cm).

CONCLUSIONS

A simple method based on the two films model is used, successfully, for investigating the kinetics of the transport of potassium thiocyanate through a bulk liquid membrane containing dicyclohexyl-18-crown-6 in chloroform. The derived equations allow to evaluate the variation of the salt concentration in the membrane and receiving phases by using an appropriate value for transfer coefficient. The model provides, also, the evaluation of the steady-state transfer rate and the time lag of the process.

This approach is used for the estimation of the organic stagnant thickness as well as the diffusion coefficient of the transported species.

Appendix

The deduced K_{ex} value (47 M^{-2}) can be considered as low and can be used to relate the species in equilibrium at the second interface:

$$C_2 = \frac{K_{ex}\,L_0\,C_{ri}^2}{1 + K_{ex}\,C_{ri}^2} \quad (i)$$

C_{ri} is of the order of magnitude of C_r which is very weak; therefore, for low K_{ex} and very low C_{ri}:

$C_2 \# K_{ex}L_0C_{ri}^2$ with $K_{ex}L_0 \# 0.1\ M^{-1}$.

The expression of C_2 can be introduced in the double expression for J_2:

$$J_2 = k_{aq}(C_{ri} - C_r) = k_{org}(C_m - K_{ex}L_0C_{ri}^2)$$

$$\frac{k_{aq}}{k_{org}}(C_{ri} - C_r) = C_m - K_{ex}L_0C_{ri}^2 \quad \text{(ii)}$$

For an equal stirring speed, k_{aq} and k_{org} are of the same order of magnitude and the ratio $\alpha = k_{aq}/k_{org}$ can be considered as in the range: $0.1 < \alpha < 10$. The eq. (ii) becomes:

$$\alpha C_{ri} - K_{ex}L_0C_{ri}^2 = C_m + \alpha C_r \quad \text{(iii)}$$

Considering the range of value for C_{ri} ($0 < C_{ri} < 10^{-3}$ M), it is clear that $K_{ex}L_0C_{ri}^2$ can be neglected with respect to αC_{ri}. Thus, eq. (iii) becomes: $\alpha C_{ri} \# C_m + \alpha C_r$ or $\alpha(C_{ri} - C_r) \# C_m$. This clearly shows that within the experimental conditions, the complex concentration at the receiving interface is very low and can be negligible with respect to C_m (i.e. $C_2 = 0$).

Notations

C_f	Potassium thiocyanate concentration in the feed phase (cte = 0.1 M)
$C_r(t)$	Potassium thiocyanate concentration in the receiving phase (M)
C_1	Complex concentration of KLSCN in the stagnant film of the organic phase at the feed interface (determined by liquid-liquid extraction, 6.3×10^{-4} M)
$C_m(t)$	Complex concentration in the membrane (M)
$C_2(t)$	Concentration of KLSCN at the receiving interface (≈ 0)
ΔC	Concentration gradient (M)
D	Diffusion coefficient of solute, KSCN, in the chloroform layer ($cm^2\ s^{-1}$)
I	Interfacial species
$J_1(t)$	Solute flux through the stagnant film at the feed interface at each time (mol s^{-1} cm^{-2})
$J_2(t)$	Solute flux through the stagnant film at the receiving interface at each time (mol s^{-1} cm^{-2})
K_{ex}	Concentration equilibrium constant ($\approx 47\ M^{-2}$)
k_{org1}	Coefficient of transfer (mass transfer coefficient) through the organic stagnant film at the feed interface (cm s^{-1})
k_{org2}	Coefficient of transfer (mass transfer coefficient) through the organic stagnant film at the receiving interface (cm s^{-1})
L_0	Initial carrier concentration in the membrane (0.002 M)
L_1	Free carrier concentration at the feed interface (M)
L(t)	Free carrier concentration in the membrane (M)
M	Molecular weight of the chloroform (119.5 g mol^{-1})
n_1', n_2'	Entering rate of KSCN at the feed and receiving interface (mol s^{-1})
S_1, S_2	Interfacial areas ($S_1=S_2=S=13.2\ cm^2$)
T	Time (s)
Tl	Time lag (6000 s)
T	Absolute temperature (298 K)
V	Molar volume of the solute (362 cm^3 mol^{-1}, ref. 11)
V_f, V_r	Volume of the feed and receiving aqueous phases (80 ml)
Vm	Membrane volume (160 ml)
δ	Organic stagnant film thickness, that is same for two interfaces (cm)
η	Chloroform viscosity (0.542 cP or mPa.s)
ξ	Association coefficient of chloroform (equal to 1 for the non-associating solvents)

Received : 31th October 2004 ; Accepted : 13th March 2006

REFERENCES

[1] Rosano, H. L., Schulman, J. H. and Weisbuch, J. B. *Ann. N. Y. Acad. Sci.*, **92**, 457 (1961).

[2] Boyadzhiev, L. and Lazarova, Z. In "Membrane Separations Technology, Principles and Applications", Noble, R. D. and Stern, S. A. (Eds.), Elsevier Science, New York, Chapter 7 (1994).

[3] Lamb, J. D., Christiensen, J.J. and Izatt, R.M., *J. Chem. Educ*., **57**, 227 (1980).

[4] Lamb, J. D., Christiensen, J. J., Izatt, S. R., Bedke, K., Astin, M.S. and Izatt, R.M., *J. Am. Chem. Soc*., **102**, 3399 (1980)

[5] Izatt, R. M., Bradshaw, J. S., Nielsen, S. A., Lamb,

J. D. and Christensen, J. J., *Chem. Rev.*, **85**, 271 (1985).

[6] Izatt, R. M., Haws, R. M., Lamb, J. D., Dearden, D. V., Brown, P. R., McBride, D. W. and Christensen, J.J., *J. Membr. Sci.*, **20**, 273 (1984).

[7] Arnaud-Neu, F., Fanni, S., Guerra, L., McGregor, W., Ziat, K., Schwing-Weill, M.J., Barrett, G., Mc Kervey, M. A.; Marrs, D. and Seward, E. M., *J. Chem. Soc. Perkin Trans.*, **2***,* 113 (1995).

[8] Crank, J. "The Mathematics of Diffusion" Clarendon Press: Oxford, p 52 (1986).

[9] Hines, A. L. and Maddox, R. N., *"*Mass Transfer, Fundamentals and Applications" Prentice-Hall Publisher; New Jersey, p 29 (1985).

[10] Yaftian, M. R., Burgard, M., Matt, D., Wieser C., Dieleman, C., *J. Incl. Phenom.,* **27**, 127 (1997).

[11] Marcus, Y. and Asher, L. E., *J. Phys. Chem*., **82**, 1246 (1978).