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Kinetic Study of an Effective Pb(II) Transport through a Bulk Liquid Membrane Containing Calix[6]arene Hexaester Derivative as a Carrier

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The article describes transport of Pb(II) through bulk liquid membrane (BLM) containing calix[6]arene hexaester derivative (1) as a carrier. The effect of various parameters such as temperature, carrier concentration, stirring speed and type of solvent on the Pb(II) transport efficiency of the carrier through BLM was evaluated. The activation energy values for the extraction and re-extraction were found as 56.33 kJ mol^{-1} and 14.79 kJ mol^{-1}, respectively. These values demonstrate that the process is diffusionally controlled by Pb(II). Observations indicate that the membrane entrance and exit rate constants (k_1, k_2) increase with increasing stirring speed as well as carrier concentration and decrease with increasing temperature. The effect of solvent on k_1 and k_2 was found to be in the order of $CH_2Cl_2 > CHCl_3 > CCl_4$.

Keywords bulk liquid membrane; calixarene; kinetic parameters; Pb(II) toxicity

INTRODUCTION

Lead, a widespread constituent of the earth's crust has long been recognized as a harmful environmental pollutant and its contamination in the environment is largely anthropogenic mainly due to the use of leaded gasoline, industrial processes, and solid waste combustion (1). According to WHO guideline maximum permissible limit of lead is 0.01 mg L^{-1} (2). Adverse effects of lead on human health include damage to the brain and the nervous system among children (3). In adults joint pain, reproductive, and hypertension problems are well reported in the literature (4,5). Besides this, soil and water organisms also suffer from lead poisoning (6).

Several methods for the removal of dissolved heavy metals from wastewaters including precipitation (7), ion exchange, oxidation – reduction (8), sorption (9–12), extraction, filtration, electrochemical treatment, and evaporative recovery (13) are reported previously. However, these processes often have certain disadvantages including incomplete metal removal, requirement of expensive equipments, reagents as well as utilization of high energy and generation of toxic sludge along with other waste products. Recently, liquid membrane (LM) techniques, i.e., organic liquid in contact with two separated aqueous phases have drawn more attention of analytical chemists due to vast prospective separation methods particularly in cases where solute concentrations are comparatively low and other techniques cannot be applied efficiently. The LM technology has been effectively used to treat aqueous streams contaminated with heavy metal ions like copper, zinc, cadmium, nickel, mercury, and lead (14–20).

The extraction chemistry of this technique is fundamentally the same as that of liquid–liquid extraction, but the transport is governed by kinetic rather than equilibrium parameters by a non-equilibrium mass transfer. In LM processes, the extraction, stripping, and regeneration operations are combined in a single stage (21,22). An efficient and appropriate carrier in the LM separation technology is of critical value to facilitate the selective removal of toxic contaminants and desired substances, in particular.

Among LM technologies, due to its simplicity and availability of constant mass transfer area, BLM is the simplest design for performing liquid membrane processes. As a result, this technique finds its use in small-scale operations and is a popular choice in applications that are in developmental stages (23). Although, the BLM configurations employed by various workers (24–30) are not completely the same, but the principle is similar; however, they are often used to study the transport properties of novel carriers (31). Moreover, in view of the high selectivity for specific applications, synthesis of new type of calixarene based ionophores have vastly been carried out (34–38).

Calixarenes, a versatile class of macrocyclic ion receptors are well renowned in supramolecular chemistry (39–41). The highly ordered structure of calixarenes offers not only enormous possibilities for chemical modifications, but also makes them exceptionally practical in the study of selective molecular recognition in supramolecular processes. The

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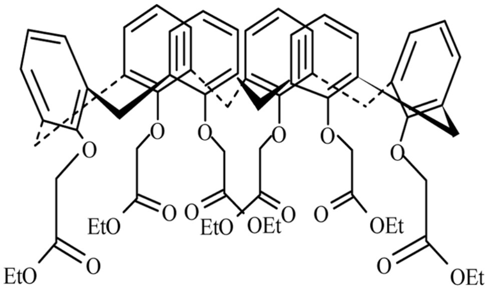


FIG. 1. Calix[6]arene hexaester derivative (**1**).

selective extraction efficiency of calix[6]arene hexaester derivative (**1**) (shown in Fig. 1) for Pb(II) was recently reported by our group (33). Therefore, in the present work calix[6]arene skeleton was selected as a vehicle for modeling such phenomena involving Pb(II) transport through BLM. The effectiveness of **1** as a carrier was explored including the effect of the solvent, the stirring rate, carrier concentration, and temperature on the efficiency of the transport process.

EXPERIMENTAL

Method and Materials

All chemical reagents used for the preparation of solutions were of analytical grade. Deionized water prepared through a Milli-Q system (ELGA Model CLASSIC UVF, UK) was used for preparation of standards. The carrier **1** used in the study was synthesized according to the literature methods (40–42).

A Spectronic® 20 Genesys™ (CAT 4001/4, USA) was used for recording all absorbance. Experimentally, the rotation rates of two Teflon-coated magnetic bars were set to be equal to one another via Gallenkamp magnetic stirrer model APP SS610/5, UK.

Bulk Liquid Membrane Experiments

Co-transport experiments were conducted using a thermostated (Grants Instruments, model W14, Cambridge, England) apparatus at 298 K and transport experiments were carried out in a U-type cell (Fig. 2). An organic solution (15 mL) containing the carrier was placed at the bottom of the cell and two portions of aqueous solutions (10 mL) were carefully added on top of them. Surface area for both of them was 2.5 cm^2. The organic phase was stirred at 90 rpm magnetically. The initial composition of the phases consists of the donor phase (aqueous lead picrate, 2.5×10^{-5} M) (39), membrane phase (carrier **1**, 1.0×10^{-3} M in organic solvent) and acceptor phase (double distilled water). Samples were taken from both water phases (acceptor and donor phases) at regular time intervals and the lead picrate concentration was analyzed by the spectrophotometric method.

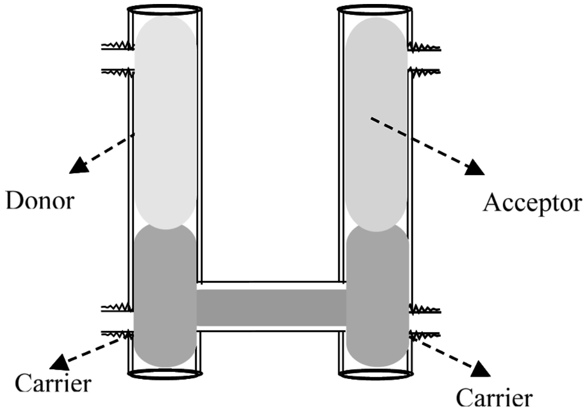


FIG. 2. Bulk liquid membrane apparatus (U-type cell) used for the transport of Pb(II).

RESULTS AND DISCUSSIONS

Kinetic Procedure

The present work is in continuation of our early reports on the transport of Hg(II) from aqueous phase using calix[n]arene derivatives as carriers (19,27–30). In the present work, the kinetic behavior for the transport of Pb(II) as a function of carrier concentration, temperature, type of solvent, and stirring rate was studied in detail. The variation of lead picrate concentration with time was directly measured in both the donor (C_d) and acceptor (C_a) phases, respectively. The reduced dimensionless concentrations were used for experimental purposes;

$$R_d = \frac{C_d}{C_{do}} \; R_m = \frac{C_m}{C_{do}} \; R_a = \frac{C_a}{C_{do}} \tag{1}$$

where C_{do} is the initial Pb(II) concentration in the donor phase, while C_d, C_m, and C_a represent the Pb(II) concentration in donor, membrane and acceptor phases, respectively.

The material balance with respect to the reduced concentrations can be expressed as;

$$R_d + R_m + R_a = 1.$$

From this expression, the kinetic behavior of the consecutive irreversible first order reactions can be described as follows (19,27–30);

$$C_d \xrightarrow{k_1} C_m \xrightarrow{k_2} C_a$$

where k_1 and k_2 are the apparent membrane entrance and exit rate constants, respectively.

At the end of transport experiments (about 200 min., t = 298 K, see below), it has been observed that in favorable circumstances R_d and R_m become zero while R_a reaches a limiting value of 1. This judgment may clarify that the second process of Eq. (2) i.e., transport from the membrane phase to the acceptor phase must be irreversible with the above-mentioned condition whether the first process of Eq. (2) i.e., transport from the donor phase to the membrane phase is irreversible or reversible (44). A conventional extraction experiment under the same donor solution and the membrane phase conditions as transport experiments, demonstrated that more than 94.9% of Pb(II) in a water phase could be extracted into an organic phase, we hence suppose that the reversibility of the first process may be reasonably neglected (45). A quantitative transport of Pb(II) takes place beyond 200 min.

The kinetic scheme for consecutive reaction systems can be described by the following rate equations (19,27–30).

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \tag{3}$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \tag{4}$$

$$\frac{dR_a}{dt} = k_2 R_m = J_a \tag{5}$$

where J is the flux, when $k_1 \neq k_2$; and integrating the above differential equations give;

$$R_d = \exp(-k_1 t) \tag{6}$$

$$R_m = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{7}$$

$$R_a = 1 - \frac{k_1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \tag{8}$$

while the maximum values of R_m and t_{max} (when $dR_m/dt = 0$) can be written as;

$$R_m^{max} = \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \tag{9}$$

$$t_{max} = \left(\frac{1}{k_1 - k_2}\right) \ln\frac{k_1}{k_2} \tag{10}$$

combining Eqs. (9) and (10), the following relationship can be obtained (46).

$$k_2 = \frac{\ln\left(\frac{1}{R_m^{max}}\right)}{t_{max}} \tag{11}$$

Numerical analysis by non-linear curve fitting permits the rate constants to be determined, the value of k_1 is directly obtained by iteration from Eq. (6). This value is introduced as a constant value in Eqs. (7) and (8). An initial value of k_2 is obtained from Eq. (11) and introduced in Eqs. (7) and (8) and iterated.

By considering the first-order time differentiation Eqs. (6)–(8) at t_{max}, one obtains the following equations:

$$\left.\frac{dR_d}{dt}\right|_{max} = -k_1\left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} \equiv J_d^{max} \tag{12}$$

$$\left.\frac{dR_a}{dt}\right|_{max} = k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{max} \tag{13}$$

$$\left.\frac{dR_m}{dt}\right|_{max} = 0 \tag{14}$$

$$-\left.\frac{dR_d}{dt}\right| = \left.\frac{dR_a}{dt}\right| \tag{15}$$

It was noted that at $t = t_{max}$, the system may be in steady state because the concentration of Pb(II) in the membrane does not change with time (Eq. (14)). As a result of this the exit and entrance fluxes are equal and have opposite signs (Eq. (15)). The activation energy value is obtained from the Arrhenius equation using the k_1 and k_2 values at different temperatures.

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \tag{16}$$

It can be seen that R_d versus t yields a decreasing mono-exponential curve whereas the time variation of both R_m and R_a is bi-exponential. The actual numerical analysis was carried out by non-linear curve fitting. The variation of R_d, R_m, and R_a with time through BLM is shown in Fig. 3.

Effect of Carrier Concentration on Pb(II) Transport

The influence of carrier concentration on lead recovery in the acceptor phase was examined at different concentrations ranging from 1×10^{-5} to 1×10^{-3} M in CH_2Cl_2 at

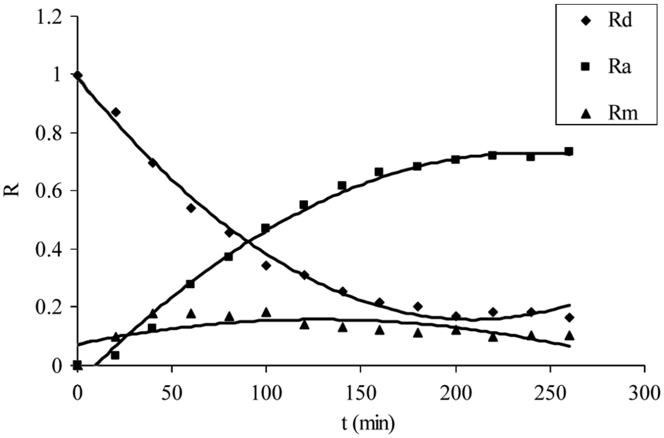
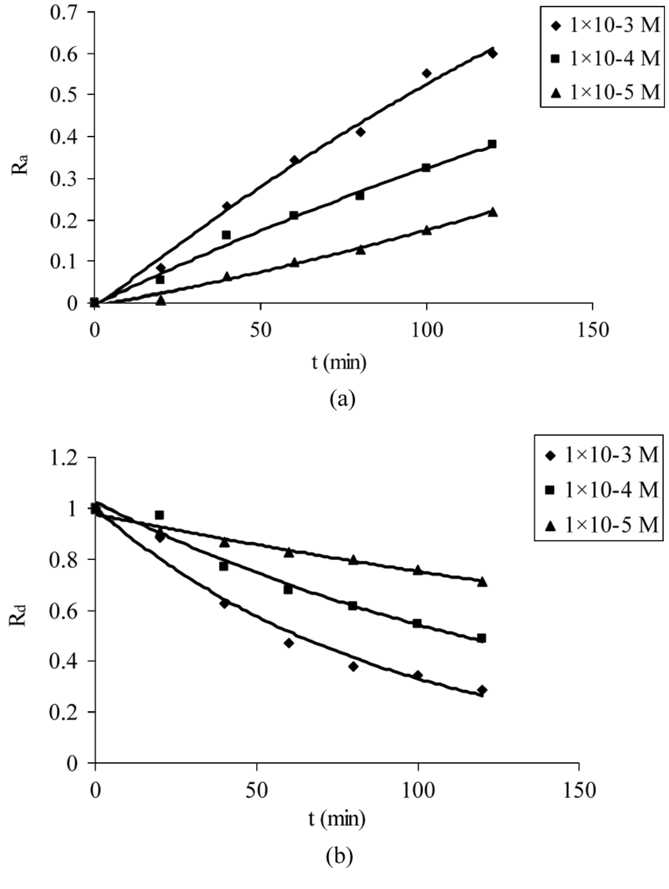


FIG. 3. Time dependence of R_d, R_m and R_a for the transport of Pb(II). Membrane phase: 1×10^{-3} M carrier in chloroform, stirring rate 90 rpm at 298 K.

TABLE 1
Effect of carrier **1** concentration on the kinetic parameters for transport of Pb(II) ions (solvent: CH_2Cl_2, 298 K and 90 rpm)

Conc.	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})	Ion transported (%)
1×10^{-5}	2.10	14.8	0.09	160	−1.52	1.52	51.6
1×10^{-4}	5.50	16.8	0.13	120	−3.19	3.19	54.1
1×10^{-3}	11.0	19.4	0.21	80.0	−5.24	5.24	80.1

298 K and 90 rpm stirring speed (Table 1). It is generally observed that an increase in carrier concentration yields higher rate of lead transport across the membrane. The maximum transport percentage (80%) of Pb(II) was observed at a higher concentration 1×10^{-3} M. This is attributed to the saturated interaction of the carrier and lead picrate between donor aqueous phase and membrane phase. Flux values as well as kinetic constants k_1 and k_2 depend on the carrier concentration and increase readily with the initial carrier concentration as shown in Fig. 4 (a and b). It can be inferred from Eqs. (6)–(8) that dimensionless reduced concentration is related with carrier concentration. In addition, no noticeable movement of the Pb(II) through the BLM was observed in the blank experiments containing no carrier, suggesting that the transport of the lead ions through the BLM occurs in the presence of carrier **1**. This verifies that the transport mechanism across BLM is not so simple but is strongly influenced by carrier concentration.



(a)

(b)

FIG. 4. Time dependence of R_a(a) and R_d(b), for the transport of Pb(II) at different carrier concentrations in CH_2Cl_2, stirring rate 90 rpm at 298 K.

Effect of Stirring Speed on Pb(II) Transport

The stirring speed also influences the transportation of ions through BLM. In the present study, the stirring rate of the membrane phase was carried out at three different stirring rates, 30, 60, and 90 rpm at 298 K, while the carrier (**1**) concentration in $CHCl_3$ was 1×10^{-3} M. The results (Table 2 and Fig. 5) reveal that the flux values, k_1, k_2 increase, while t_{max} decreases with an increase of the stirring speed (27–30,47). It has been observed that 73% of the Pb(II) was transferred to the receiving phase at 90 rpm. However, it is estimated that a stronger agitation promotes the interfacial interaction at the donor–membrane and membrane–acceptor interfaces, by decreasing the thickness of the diffusion layer and thus increases the kinetic rate of chemical reaction on the interface (47).

Effect of Solvent on Pb(II) Transport

The influence of different solvents have also been examined (CH_2Cl_2, $CHCl_3$, and CCl_4) on the transport efficiency of **1** for Pb(II). The kinetic parameters are demonstrated in Table 3 and Fig. 6. The results show that the highest transport efficiency was observed with CH_2Cl_2. The membrane entrance (k_1) and exit (k_2) rate constants as well as the flux (J^{max}) values decrease in order as CH_2Cl_2 (80%) > $CHCl_3$ (73%) > CCl_4 (61%). This is consistent with the literature reported (47). The results are in harmony with the physicochemical properties of the solvents given in Table 4. However, the data imply that the viscosity and polarity are essential factors for solvent selection for BLM phenomena.

Effect of Temperature

The effect of temperature on the transport of Pb(II) across the BLM was investigated at 298, 303, 308, and

TABLE 2
Kinetic parameters of Pb(II) at different stirring rates (solvent: $CHCl_3$; T = 298 K)

Stirring rate (rpm)	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})	Ion transported (%)
30	4.10	6.95	0.16	260	−1.92	1.92	66.8
60	5.20	15.0	0.12	140	−2.96	2.96	69.9
90	10.0	16.9	0.18	100	−4.68	4.68	73.3

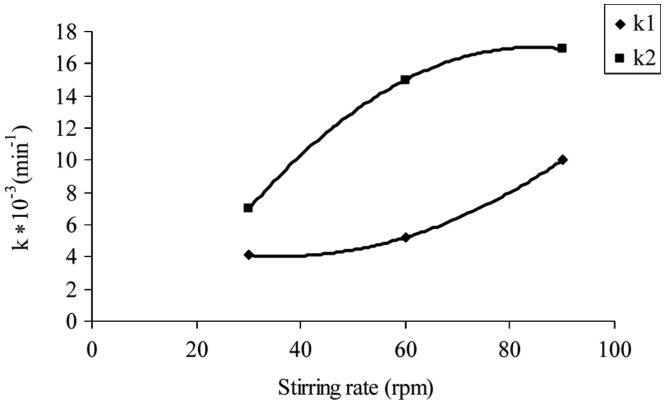


FIG. 5. *Stirring* rate dependence of k_1, k_2 for the transport of Pb(II) at 1×10^{-3} M carrier concentration in $CHCl_3$ at 298 K.

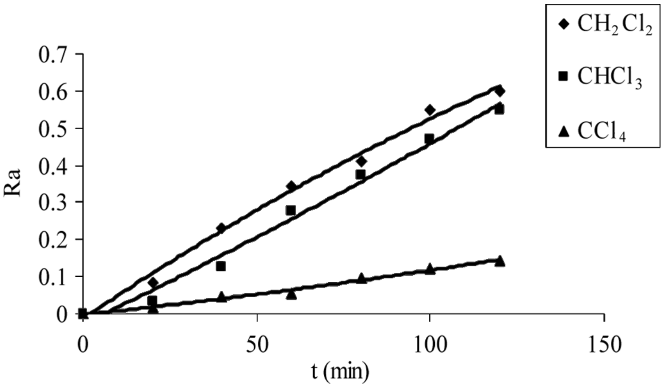


FIG. 6. Time variation v/s R_a for the transport of Pb(II) in different solvents at 1×10^{-3} M carrier concentration, stirring rate 90 rpm at 298 K.

313 K, respectively. The experimental results are shown in Table 5. The results indicate that the kinetic parameters, i.e., k_1 and k_2, as well as J_d^{max} and J_a^{max} decrease with an increase in the temperature. An Arrhenius-type plot is followed perfectly in Fig. 7, which shows that the effect of temperature is higher on k_1, while it is relatively lower on k_2, it is in agreement with the reported results (48). The activation energy values are 56.33 kJ mol^{-1} for extraction and 14.79 kJ mol^{-1} for re-extraction, respectively. E_a values of given process can be used as criteria to determine whether diffusion or chemical reaction is the rate controlling step. The temperature has great impact on rate constants therefore, diffusion controlled processes have lower

TABLE 4
Physicochemical characteristics of solvents (47)

Solvent	ε_0	n_D	μ	η	V_m
CH_2Cl_2	9.08	1.42	1.96	0.44	64.2
$CHCl_3$	4.81	1.45	1.35	0.58	96.5
CCl_4	2.24	1.47	0	0.97	96.5

ε_0 dielectric constant (20°C).
n_D refractive index (20°C).
μ dipole moment (D).
η viscosity (cP).
V_m molar volume (M^{-1}).

TABLE 3
Kinetic parameters of Pb(II) when different solvents are used. (T = 298 K; stirring speed is 90 rpm)

Solvent	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})	Ion transported (%)
CH_2Cl_2	11.0	19.4	0.21	80.0	−5.24	5.24	80.1
$CHCl_3$	10.0	16.9	0.18	100	−4.68	4.68	73.3
CCl_4	1.30	7.13	0.14	280	−0.89	0.89	61.8

TABLE 5
The kinetic parameters of Pb(II) transport using carrier **1** at different temperatures (solvent is CH_2Cl_2; stirring rate is 90 rpm)

Temp. (K)	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})
298	10.0	16.9	0.18	100	−4.68	4.68
303	5.20	14.8	0.17	120	−2.95	2.95
308	3.90	13.2	0.16	140	−2.34	2.34
313	3.30	12.2	0.14	160	−2.03	2.03

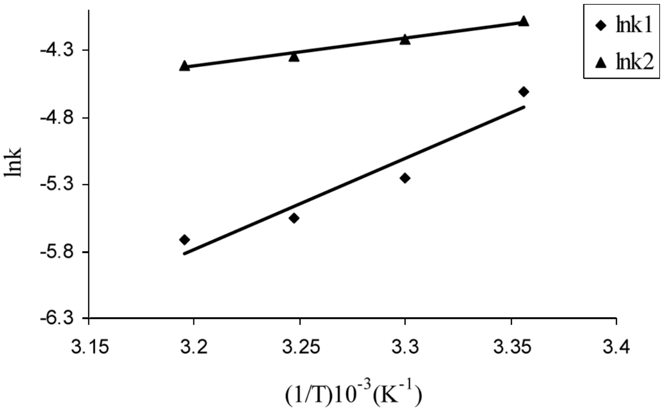


FIG. 7. Arrhenius plots for the transport of Pb(II) in bulk liquid membrane.

E_a value (<84 kJ mol^{-1}) than chemical controlled processes. Thus, the obtained values of E_a specify that the transport of Pb(II) is diffusion controlled processes (49).

Suggested Mechanism

The mechanism for the transport of Pb(II) across the bulk liquid membrane containing **1** as carrier is depicted in Fig. 8. At the interface between the donor and the membrane, the lead picrate ion pair forms complex with ligand, then the $[LPb]^{2+}(Pic)_2^-$ complex diffuses through the membrane. At the interface between the membrane and the acceptor, the ligand ion pair complex is decomplexed and $Pb^{2+}(Pic)_2^-$ is released into the acceptor phase. Finally, the ligand carrier diffuses back across the membrane aqueous boundary layer (47).

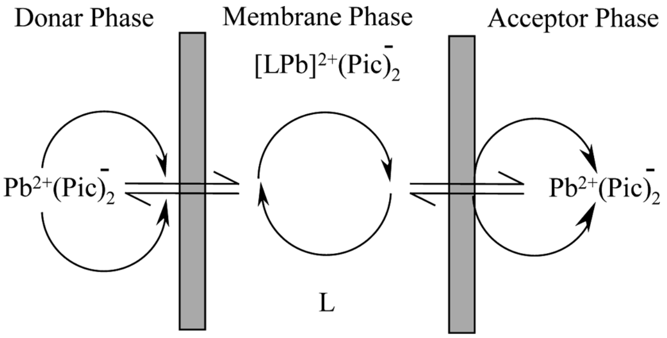


FIG. 8. Mechanism of the ion pair mediated transport through bulk liquid membrane.

Reproducibility of Bulk Liquid Membrane Technique

The reproducibility of the above system was studied by performing five replicate transport experiments. The percent of metal ion transport after 200 min. was 73 ± 2%.

Selectivity of Bulk Liquid Membrane Technique

The interferences of other selected metal cations (Na^+, K^+, Cu^{2+} and Mg^{2+}) on the Pb^{2+} extraction ability of **1** was reported by our group (33). The results reveal that there is no significant effect of interfering metal cations except Na^+ with a little effect on the extraction ability of **1**. It will provide a great evidence for **1** to be used as a selective and efficient carrier for Pb(II) ions in bulk membrane processes. Ultimately, it will be an excellent strategy for reclamation of Pb(II) polluted sites as well as in other environmental/analytical applications.

CONCLUSION

In the present study calix[6]arene hexaester derivative (**1**) has been proved to be a successful carrier for the transport of Pb(II) through BLM at ambient temperature. The mass transfer of Pb(II) has been analyzed on the basis of kinetic laws of two consecutive irreversible first order reactions. By fitting experimental data, apparent rate constants, i.e., k_1, k_2, along with t_{max}, R_m^{max} and the flux values such as J_d^{max}, J_a^{max} have been determined. The effectiveness and reproducibility of transport has proved to be dependent on carrier concentration, type of solvent, stirring speed, and temperature.

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