



# Calix[4]arene derivative bearing imidazole groups as carrier for the transport of palladium by using bulk liquid membrane

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## ABSTRACT

The carrier activity of calix[4]arene containing imidazole groups towards the facilitated transport of palladium(II) through dichloromethane bulk liquid membrane has been studied. The optimum transport conditions were established by the studies on the effect of pH, feed concentration, carrier concentration, receiver phase concentration and transport time. A solution of 1 M hydrochloric acid (HCl) served as receiving phase for maximum transport of the metal ion. Maximum transport efficiency was observed for Pd(II) ion when it was present in the concentration of  $10^{-3}$  M and the transport efficiency after 24 h was found as 95%.

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## 1. Introduction

Recently, the development of an efficient technique for the recovery of valuable metals contained in industrial wastes has come under serious consideration due to the resource scarcity and some hazards of these metals might cause to the global environment of the valuable metals. In most of wastes, target metals are often very rare compared to a primary source and thus their separation is very difficult. Therefore, it is necessary to develop an efficient and low expensive recovery process for such valuable metals [1]. The solvent extraction process has already been industrially applied to the recovery of precious metals [2,3]. However, the extraction rate of precious metals is understood to be kinetically very slow, and as a result a huge amount of extractant and interfacial area are required to operate the process efficiently. Palladium, a member of the platinum group metals, is a noble metal with an increasing technological importance due to its wide application in electrical and electronics industry, jewellery, dentistry and autocatalysts, coating agents and brazing alloys [4–6]. Palladium have very close properties. Only Pd(II) forms, however, hydrate in acidic solutions [7], which may be bound by special carriers like the sulphur containing macrocyclic compounds, e.g., T18C4 (thio-18-crown-6).

The Liquid membrane (LM) technology has been effectively used to treat aqueous streams contaminated with metal ions. Among LM technologies bulk liquid membranes (BLM) are suitable for

screening novel carrier-mediated transport systems on a laboratory scale. In general, the mobile carrier contained in the liquid membrane governs the efficiency and selectivity of the liquid membrane transport and therefore a lot of novel carriers have been explored to create selective separation systems [8]. In recent years, a remarkable increase of the applications of liquid membranes in separation processes is observed [9,10]. Hidalgo et al. used a supporting liquid membrane (SLM) module impregnated with a Cyanex 471 solution for separation of Pd(II) from Pt-containing chloride solutions as well as for the recovery of Pd(II) from waste catalysts [11]. Bulk liquid membrane (BLM) has been studied for preconcentration and separation of palladium with different carriers. Abbaspour and co-workers have reported that 3,4-dihydro-4,4,6-trimethyl-2(1H)-pyrimidinethione (DTPT) ligand sulfur containing is an excellent carrier for selective and efficient transport of Pd(II) [12]. Khayatian et al. used ammonium–dibenzylidiazia-18-crown-6 complex as a highly efficient carrier for the uphill transport of palladium as  $\text{PdCl}_4^{2-}$  complex ion through a chloroform bulk liquid membrane. By using thiocyanate as a metal ion acceptor in the receiving phase, the amount of palladium transported across the liquid membrane after 120 min was  $92.2 \pm 1.4\%$  [13]. Also, Alizadeh et al. successfully applied to the transport of Pd(II) to a BLM with a cationic surfactant hexadecylpyridinium bromide (HDPB) as carrier and the results showed that transport efficiency of Pd(II) for the ten replicate measurements after 110 min was  $97.9 \pm 1.1\%$  [1].

In the last decade, macrocyclic ligands have attracted much attention as novel host compounds for ionic species [14]. In this study, we have focused on the calixarenes, whose cavity can recognize the size of a guest molecule and the framework is available

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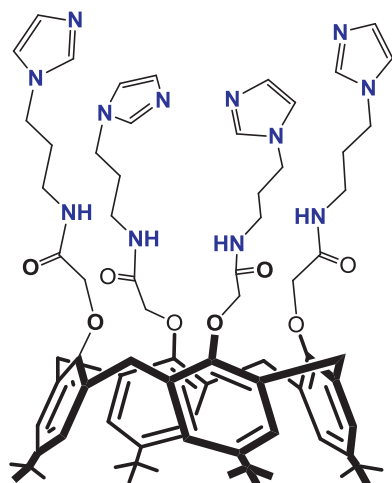


Fig. 1. Calix[4]arene imidazole derivative.

for the arrangement of the functional groups to create a specific affinity for a target guest molecule. Calixarenes represent one of the most important macrocyclic host molecules in supramolecular chemistry together with crown ethers and cyclodextrins. Chemical modification of the calix[4]arene platform gives access to a wide variety of multifunctional ligands suitable for selective ion complexation [15,16]. Their efficiency and economic advantages designate them as the optimal solution for some important problems in science and technology, such as precious metal recovery, toxic product elimination from waste waters, etc. The liquid membrane transport effect is one of the typical supramolecular chemistry characteristics of calixarenes [17,18]. Studies on the effects of calixarenes in liquid membrane transport are not only able to show the ability of calixarenes and their derivatives as fluid carriers in transporting metal cations and the laws of that transport, but are also helpful in understanding the principles, driving force and main factors influencing the transport of metal cations. The present study examines the effectiveness of **3** as a carrier and explores the effect of pH, solvent, stirring rate, transport time, carrier concentration, and temperature on the efficiency of transport process.

## 2. Experimental

### 2.1. Chemicals

The chemical reagents used in bulk liquid membrane experiments were, palladium(II) nitrate, hydrochloric acid, sulfuric acid, nitric acid, ethylenediaminetetraacetic acid, potassium chloride, sodium nitrate, sodium sulfate, dichloromethane, carbon tetrachloride, chloroform from Merck Co. (Darmstadt, Germany). The  $\text{Pd}(\text{NO}_3)_2$  solutions were prepared in B. Robinson buffer solution at pH 2–8 [19]. Doubly distilled water was used throughout. The carrier used in the study are presented in Fig. 1.

### 2.2. Apparatus

The atomic absorption spectrometer (AAS) used for the measurement of metal concentrations was a ContrAA 300 (Analytik Jena, Germany) in air-acetylene flame at wavelength of 247.642 nm. A pH-meter (Orion) equipped with a combined glass–Ag/AgCl electrode was used for pH measurements. The membrane phase was stirred including a teflon-coated magnetic bar by magnetic stirrer (Daihan MSH-20D, Germany). A bulk type liquid membrane cell (Fig. 2) was used in all transport experiments.

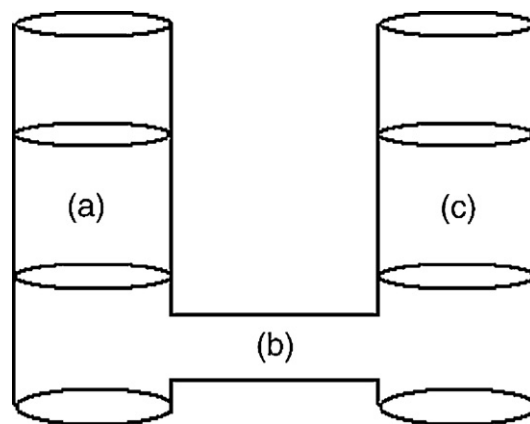


Fig. 2. Bulk liquid membrane cell (a) feeding phase, (b) membrane phase, and (c) receiving phase.

### 2.3. Procedure

Transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter 3.5 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two aqueous phases, was used. The feeding (source) phase contained 10 mL of  $10^{-3}$  M palladium(II) solution and 1 M KCl. The receiving phase included 10 mL of 1 M hydrochloric acid. A dichloromethane layer (10 mL) containing  $10^{-3}$  M of calix[4]arene lay below these two aqueous phases and bridged them. The organic layer with a thickness of 1.6 cm was stirred constantly by a teflon-coated magnetic bar. Determination of the metal ion concentration in both aqueous phases was carried out by spectrometry. The limit of detection calculated as the concentration that gives a reading equal to three-times the standard deviation of a series of the procedural blank signal ( $n = 5$ ), was found to be 0.005 mg/L.

### 2.4. Synthesis

The synthesis of **1–3** was depicted in Scheme 1. Compounds **1–3** were prepared according to the literature methods [20,21] and by adapting known synthetic procedures, respectively.

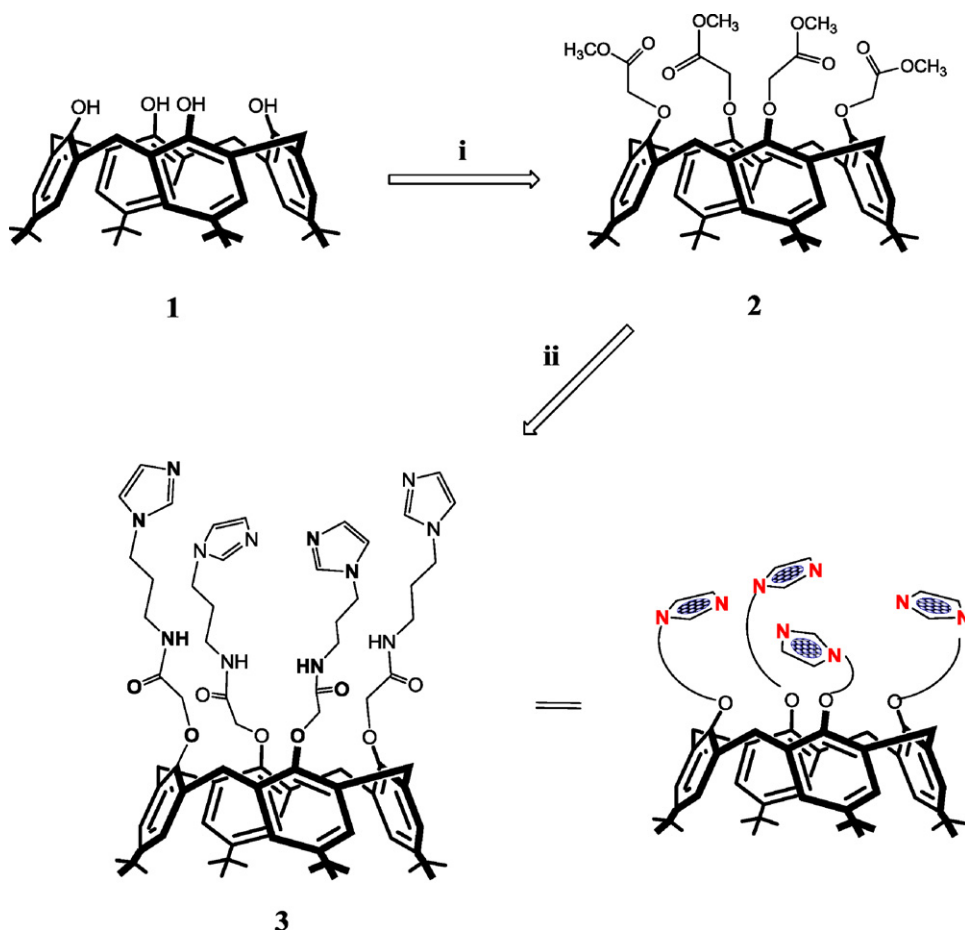
#### 2.4.1. Synthesis of 5,11,17,23-tetra(tert-butyl)-25,26,27,28-tetra(4-propylimidazole acetamide)-calix[4]arene (**3**)

A mixture of tetraester derivative of calix[4]arene (**2**) (1.31 g, 1.0 mmol) and 1-(3-aminopropyl)imidazole (0.51 g, 4.1 mmol) in 60 mL of a 1:1 mixture of methanol:toluene was refluxed for 3 days. The solvents were removed by evaporation under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ . The residue was precipitated with hexane to give pure **3** (80%) as a white solid. Mp 244–250 °C. FT-IR:  $1680\text{ cm}^{-1}$  (NHC=O),  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.10 (s, 36H,  $\text{C}(\text{CH}_3)_3$ ), 2.0 (p, 8H,  $\text{NHCH}_2\text{CH}_2$ ), 3.15 (t, 8H,  $\text{NHCH}_2\text{CH}_2$ ), 3.9 (t, 8H, NCHCH), 3.2 (d, 4H,  $\text{ArCH}_2\text{Ar}$ ), 4.4 (d, 4H,  $\text{ArCH}_2\text{Ar}$ ), 4.42 (s, 8H,  $\text{OCH}_2$ ), 6.8 (s, 8H, ArH), 6.90–7.10 (m, 8H, CH, imidazololy), 7.45 (s, 4H, CH, imidazololy), 8.15 (s, 4H, CONH). Anal. calcd. for  $\text{C}_{76}\text{H}_{100}\text{O}_8\text{N}_{12}$ : C, 69.70; H, 7.70; N, 12.83. Found: C, 70.03; H, 7.72; N, 12.85.

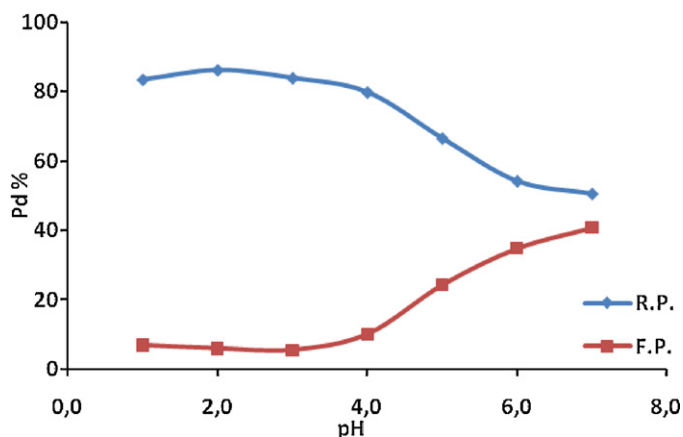
## 3. Results and discussion

### 3.1. Optimization of conditions

The optimum transport conditions were established by the studies on the effect of pH, feed concentration, carrier concentration,



**Scheme 1.** Schematic representation of synthesis of compounds 1–3. Reagents and conditions: (i)  $\text{BrCH}_2\text{CO}_2\text{CH}_3$ ,  $\text{K}_2\text{CO}_3$ , acetone, reflux, 90%; (ii) 1-(3-aminopropyl)imidazole, toluen:MeOH, reflux, 80%.



**Fig. 3.** Effect of pH of feed phase on transport. Conditions: feed phase (F.P.), 10 mL of  $1 \times 10^{-3}$  M Pd(II) and 1 M KCl; liquid membrane phase, 10 mL of  $10^{-3}$  M calix[4]arene; receiving phase (R.P.), 10 mL of 1 M HCl; time of transport, 24 h.

receiver phase concentration, stirring rate, effect of solvent and transport time.

### 3.2. Effect of feed phase pH

The effect of the feed phase pH on the efficiency of metal transport was studied (Fig. 3). It is quite clear that the transport of  $\text{Pd}^{2+}$  ions is influenced by the pH of feed phase. The results revealed that the palladium transport occurs at pH 1.0–4.0. At higher pH values,

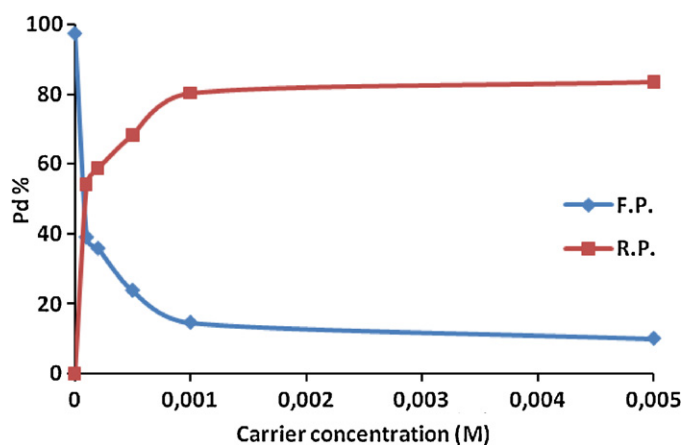
there is a decrease in percentage of transport due to the formation of palladium hydroxide complexes [1]. The optimum value in the present study appears to be about pH 2 in which a high degree of palladium transport is achievable.

### 3.3. Effect of carrier concentration

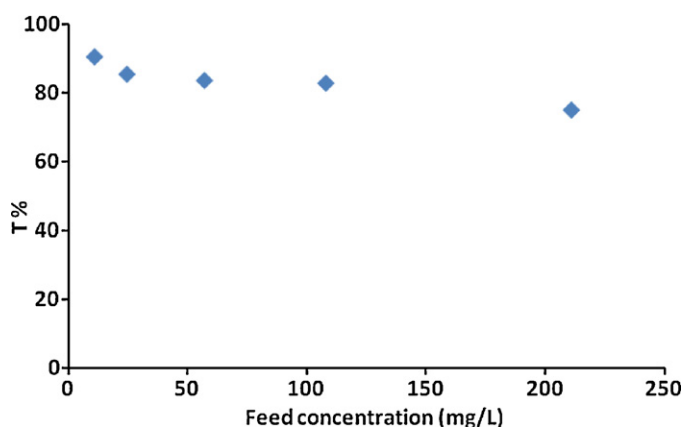
The carrier concentration of organic phase has a significant effect on Pd(II) ion transport across the membrane. It is generally expected to increase with the carrier concentration. The experiments were carried out at different initial carrier concentrations ( $1 \times 10^{-4}$ ,  $2 \times 10^{-4}$ ,  $5 \times 10^{-4}$ ,  $1 \times 10^{-3}$  and  $5 \times 10^{-3}$  M) in dichloromethane at 298 K and 300 rpm. As can be seen from Fig. 4, the Pd(II) transport increases with increasing carrier concentration and when concentration of the carrier is  $1 \times 10^{-3}$  M, the Pd(II) transport reaches a balance.

### 3.4. Effect of feed concentration

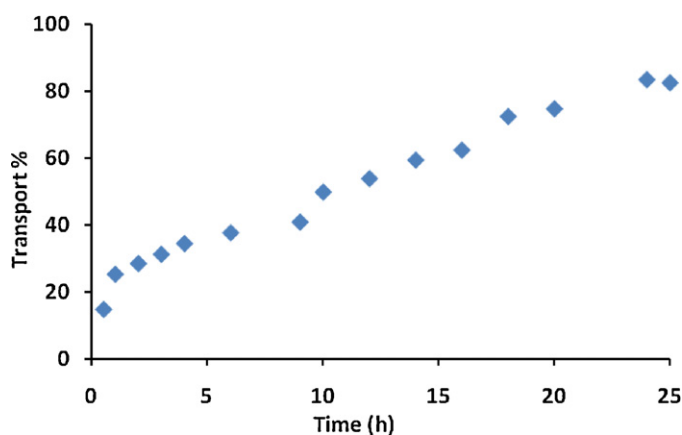
The feed concentration of effect on Pd(II) ion transport across the membrane. It is generally expected to decrease with the feed concentration. The experiments were carried out at different initial feed concentrations  $1 \times 10^{-4}$ ,  $2 \times 10^{-4}$ ,  $5 \times 10^{-4}$ ,  $1 \times 10^{-3}$  and  $5 \times 10^{-3}$  M in dichloromethane at 298 K and 300 rpm. As shown in Fig. 5, the best results have been obtained on the feed concentration of  $1 \times 10^{-3}$  M and this value for the optimum conditions were employed.



**Fig. 4.** Effect of concentration of calix[4]arene on transport. Conditions: feed phase (F.P.), 10 mL of  $1 \times 10^{-3}$  M Pd(II) and 1 M KCl; liquid membrane phase, 10 mL of different concentrations of calix[4]arene; receiving phase (R.P.), 10 mL of 1 M HCl; time of transport, 24 h.



**Fig. 5.** Effect of concentration of feeding phase on transport. Conditions: feed phase, 10 mL of different concentrations Pd(II) and 1 M KCl; liquid membrane phase, 10 mL of  $1 \times 10^{-3}$  M calix[4]arene; receiving phase, 10 mL of 1 M HCl; time of transport, 24 h.



**Fig. 6.** Effect of time on Pd(II) transport. Conditions: feed phase, 10 mL of  $1 \times 10^{-3}$  M Pd(II) and 1 M KCl; liquid membrane phase, 10 mL of  $1 \times 10^{-3}$  M calix[4]arene; receiving phase, 10 mL of 1 M HCl.

### 3.5. Effect of time on transport and kinetic procedures

Fig. 6 shows the time dependence of palladium transport through the liquid membrane under the optimal experimental conditions. It is quite obvious that the extraction of palladium from

the aqueous source phase into the organic membrane occurs very rapidly, so that the extraction seems to be completed after approximately 1 h. However, the release of palladium into the aqueous receiving phase occurs at a slower rate. It was confirmed that about 82% of palladium was transported from the source phase into the receiving phase after 24 h, under the optimal conditions.

The transport experiments were carried out by using the bulk liquid membrane apparatus as presented in Fig. 2. The membrane phase (10 mL), containing the carrier in an organic solution, was placed at the bottom of the cell with a 1.6 cm magnetic stirring bar inside. The membrane phase was stirred at 350 rpm magnetically. An open glass cylinder was inserted into the membrane. The feeding phase (donor phase) (10 mL) contained Pd(II) solution buffered with B. Robinson buffer at pH 2 was added slowly inside cylinder. The receiver phase (acceptor phase) (10 mL) containing 1 M HCl buffered with B. Robinson buffer at pH 5 was placed outside the cylinder. In experiments, variation of Pd(II) concentration with time was directly determined in both feeding (Cd in M) and receiver (Ca in M) phases using AAS at regular time intervals for a 24 h period. The corresponding change of palladium ion concentration in the membrane phase was determined from the material balance between the phases. For practical reason, dimensionless reduced concentrations (R) were used:

$$R_d = \frac{C_d}{C_{d0}}, \quad R_m = \frac{C_m}{C_{d0}}, \quad R_a = \frac{C_a}{C_{d0}} \quad (1)$$

where  $C_{d0}$  is the initial Pd(II) concentration in the feeding phase while  $C_d$ ,  $C_m$  and  $C_a$  represent the Pd(II) concentration in feeding, membrane and receiver phases, respectively. The material balance with respect to the reduced concentrations can be expressed as  $R_d + R_m + R_a = 1$ . When  $R_d$ ,  $R_m$  and  $R_a$  values are inspected, the results suggest that the Pd(II) ion transport obeys the kinetic laws of two consecutive irreversible first-order reaction according to the kinetic scheme [22–25]:



where  $k_1$  and  $k_2$  are pseudo-first-order apparent rate constants of the extraction and reextraction, respectively. The change of carrier concentration and other factors affect feeding, membrane and receiver phases Pd(II) ion concentration. This effect results a change in  $k_1$  and  $k_2$  values. The kinetic scheme, Eq. (2), for consecutive irreversible reactions can be described by the following rate equations [22,26]:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \quad (3)$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \quad (4)$$

$$\frac{dR_a}{dt} = k_2 R_m \equiv J_a \quad (5)$$

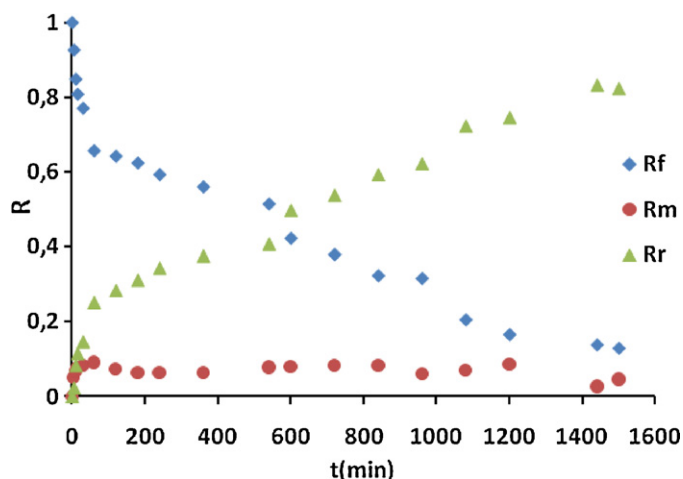
where  $J$  represents the flux. When  $k_1 \neq k_2$ , integrating Eqs. (3)–(5) gives the following expressions:

$$R_d = \exp(-k_1 t) \quad (6)$$

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

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

where  $k_1$  and  $k_2$  values are the apparent extraction and reextraction rate constants, respectively. The kinetic parameters  $k_1$  and  $k_2$  were obtained by fitting Eqs. (6)–(8) to the experimentally obtained data. The observed experimental results reveal that  $R_d$  decreases exponentially with time, accompanied by a simultaneous increase of  $R_a$ ,



**Fig. 7.** Time dependence of  $R_d$ ,  $R_m$  and  $R_a$  for transport of Pd(II). Theoretical curves calculated from Eqs. (6)–(8). Donor phase:  $1 \times 10^{-3}$  M Pd(II) solution buffered at pH 2; acceptor phase: buffered at pH 5; membrane phase:  $1 \times 10^{-3}$  M carrier in dichloromethane, at 350 rpm and 298 K (these values were the optimum conditions).

whereas  $R_m$  presents a maximum at intermediate times. The variation of  $R_d$ ,  $R_m$  and  $R_a$  with time through liquid membrane is shown in Fig. 7. The maximum values of  $R_m$  (when  $dR_m/dt=0$ ) and  $t_{\max}$  may be written as follows:

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

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

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

$$\left. \frac{dR_d}{dt} \right|_{\max} = -k_1 \left( \frac{k_1}{k_2} \right)^{-k_1/(k_1-k_2)} \equiv J_d^{\max} \quad (11)$$

$$\left. \frac{dR_m}{dt} \right|_{\max} = 0 \quad (12)$$

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

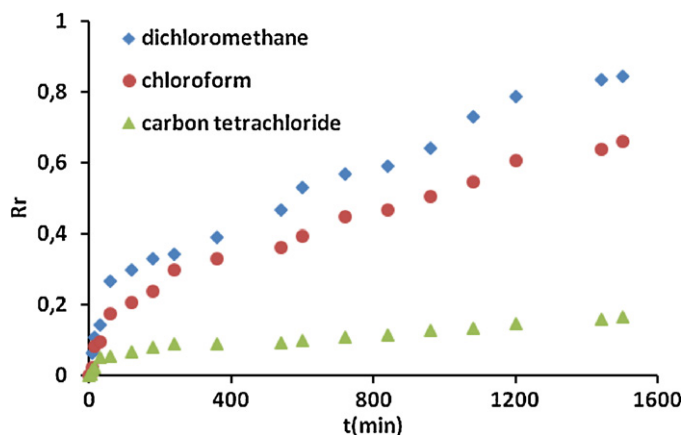
The system is in steady state, so the Pd(II) concentration in the membrane ( $t = t_{\max}$ ) does not vary with time Eq. (12). Because the maximum membrane entrance ( $J_d^{\max}$ ) and exit ( $J_a^{\max}$ ) fluxes are equal but having opposite signs:

$$-J_d^{\max} = +J_a^{\max} \quad (14)$$

The actual numerical analysis was carried out by non-linear curve fitting using a Sigma-Plot software program. The extraction rate constant,  $k_1$ , was obtained from Eq. (6) by using feeding phase data, while the reextraction rate constant,  $k_2$ , was determined from the receiver phase data by using Eq. (8) or indirectly from the membrane phase data calculated ( $k_2$ ) on the basis of Eq. (7).

**Table 1**  
The kinetic parameters for the transport of Pd(II) at different stirring speed.

Stirring Speed (rpm)	$k_1$ ( $\times 10^3 \text{ min}^{-1}$ )	$k_2$ ( $\times 10^3 \text{ min}^{-1}$ )	$t_{\max}$ (min)	$R_a^{\max}$	$J_d^{\max}$ ( $\times 10^3 \text{ min}^{-1}$ )	$J_a^{\max}$ ( $\times 10^3 \text{ min}^{-1}$ )	%Transport
100	1.54	0.22	1478.85	0.65	-0.65	0.65	34.08
150	2.0	0.28	1241.08	0.63	-0.88	0.88	38.75
200	2.46	0.54	956.20	0.60	-1.02	1.02	48.42
300	3.02	1.02	754.76	0.56	-1.56	1.56	69.45
350	3.28	1.86	512.86	0.52	-1.82	1.82	82.20



**Fig. 8.** Solvent dependence of  $R_r$  for the transport of Pd(II). Feed phase:  $1 \times 10^{-3}$  M Pd(II) solution buffered at pH 2; receiving phase: buffered at pH 5; membrane phase:  $1 \times 10^{-3}$  M carrier in solvents, at 350 rpm and 298 K (these values were the optimum conditions).

### 3.6. Effect of stirring rate

The influence of the stirring speed on palladium(II) transport was studied in order to optimize uniform mixing of the solution and to minimize thickness of aqueous boundary layers. In the present investigation, the stirring rate of the membrane phase was carried out at five different stirring rates: (100, 150, 200, 300 and 350 rpm) at 298 K when the carrier concentration was  $1 \times 10^{-3}$  M in dichloromethane. The results are presented in Table 1 which indicate that the stirring rate affects the transport rate of palladium(II) through the liquid membrane it can be concluded that the rate of transport of Pd(II) increased with increasing stirring speed. It is also shown that  $t_{\max}$  and  $R_a^{\max}$  decrease with the increase of stirring speed.

### 3.7. Effect of solvent

The experiments were also accomplished with three solvents:  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ . From the results in Table 2, it can be seen that the order of the amount of the Pd(II) released into the receiving phase varies as:  $\text{CCl}_4 \ll \text{CHCl}_3 < \text{CH}_2\text{Cl}_2$ . The highest transport efficiency was obtained in  $\text{CH}_2\text{Cl}_2$ .  $\text{CCl}_4$  was found to be an unsuitable solvent for the transport of Pd(II) as shown in Fig. 8. This result can be attributed to the distinct difference in solvent polarity between  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$ . This result is in concordance with the previous studies [22,25,27].

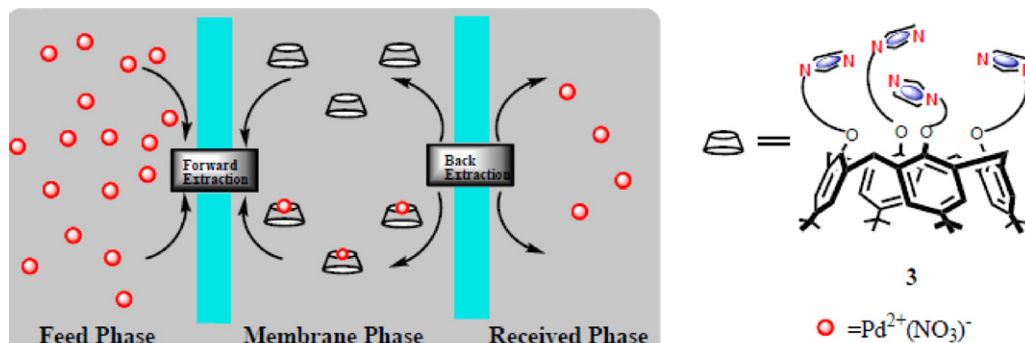
### 3.8. Suggested mechanism

The suggested mechanism for the transport of Pd(II) ion through bulk liquid membrane, which operated in this study, is shown in Fig. 9. The Pd(II) is transported from the feed phase to the received phase via a liquid membrane in the presence of the carrier 3. After complexation of the palladium nitrate ion pair with carrier on the feed phase, the complex diffuses down its concentration gradient. On the received phase, carrier ion pair complex is decomposed

**Table 2**

The kinetic parameters for the transport of Pd(II) at different solvent.

Solvent	$k_1$ ( $\times 10^3 \text{ min}^{-1}$ )	$k_2$ ( $\times 10^3 \text{ min}^{-1}$ )	$t_{\text{max}}$ (min)	$R_a^{\text{max}}$	$J_d^{\text{max}}$ ( $\times 10^3 \text{ min}^{-1}$ )	$J_a^{\text{max}}$ ( $\times 10^3 \text{ min}^{-1}$ )	%Transport
CH <sub>2</sub> Cl <sub>2</sub>	4.24	1.812	350.14	0.53	-1.60	1.60	83.49
CHCl <sub>3</sub>	2.62	1.28	751.12	0.48	-0.78	0.78	63.76
CCl <sub>4</sub>	0.56	0.24	2016.40	0.30	-0.22	0.22	16.06

**Fig. 9.** Mechanism of transport of Pd(II) by using **3** through bulk liquid membrane.**Table 3**Amount of cation transported from various cation mixtures through the membrane.<sup>a</sup>

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1		
Pd <sup>2+</sup>	89	10
Co <sup>2+</sup>	1	96
Zn <sup>2+</sup>	0	97
Ni <sup>2+</sup>	1	96
Cd <sup>2+</sup>	2	95
Mixture 2		
Pd <sup>2+</sup>	92	7
Mn <sup>2+</sup>	1	98
Fe <sup>3+</sup>	0	100
Mg <sup>2+</sup>	3	96

<sup>a</sup> Conditions: feed phase, 10 mL of  $1 \times 10^{-3}$  M of each cation and 1 M potassium chloride; liquid membrane phase, 10 mL of  $10^{-3}$  M calix[4]arene; receiving phase, 10 mL of 1 M hydrochloric acid; time of transport, 24 h.

and palladium nitrate ion pair is released into the received phase. The free carrier diffuses back across the liquid membrane and the cycle starts again. The net result is the transport of Pd(II) from the aqueous source phase to the aqueous receiving phase across the bulk of the organic phase [27].

### 3.9. Transport selectivity

The selectivity of the membrane system was studied at optimum conditions by transporting  $1 \times 10^{-3}$  M of palladium and in the mixture of such as Table 3 shows the percentage transport of palladium ion and other cations.

## 4. Conclusion

In this study, in order to achieve efficiently transport rate, we investigated various factors that affect the transport of Pd(II) through BLM using 5,11,17,23-*tetra* (*tert*-butyl)-25,26,27,28-*tetra*(4-propylimidazole acetamide)-calix[4]arene derivative as a carrier. The highest transport rate was found as 95% by using  $1 \times 10^{-3}$  M carrier in the dichloromethane membrane,  $1 \times 10^{-3}$  M Pd(NO<sub>3</sub>)<sub>2</sub> solution at pH 2 and 5 in the feed and the receiving phases, respectively. In the light of the experimental results obtained, it was demonstrated that calix[4]arene derivative could be regarded

as an effective agent used for transport of Pd(II) from acidic aqueous solution.

## Acknowledgment

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