TRANSPORT BEHAVIOR OF Cr(III), Cd(II), Pb(II), AND Ag(I) IONS THROUGH BULK LIQUID MEMBRANE CONTAINING *p-tert*-BUTYLCALIX[4]ARENE–TETRADIETHYLACETAMIDE AS ION CARRIER

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Received 11 April 2008; Accepted 15 May 2008

ABSTRACT

The study on the transport behavior of Cr(III), Cd(II), Pb(II), and Ag(I) through bulk liquid membrane using p-tert-butylcalix[4]arene-tetradiethylacetamide as ions carrier has been conducted. The aims of this work are to determine the optimum condition, efficiency, and transport selectivity of the carriers for those ions. Both optimum condition and transport efficiency were obtained by determination of the concentration of transported ions with variation of the source phase pH, ion carrier concentration, the nature of decomplexant agent in the receiving phase, and transport time. The transport selectivity of the ion carrier was obtained from the ions competition transport experiments. The amount of Cr(III), Pb(II), Cd(II), and Ag(I) transported across liquid membrane were 11.6, 25.5, 39.5, and 42.1% respectively. The ion carrier is selective for Cd(II), Pb(II), Ag(I), and strongly depends on the nature of decomplexant agent as well as transport mechanism. The remarkable selectivity was shown by the ion carrier to Ag(I) when the transport process was carry out under high concentration of acid in the source phase.

Keywords: *transport, p-tert-butylcalix[4]arene-tetradiethylacetamide, efficiency, selectivity, bulk liquid membrane, heavy metals*

INTRODUCTION

Separation techniques for removing, decreasing, and recovering heavy metals from industrial liquid waste are very important because of the growing environmental protection problem. The most common treatment of industrial liquid waste that involves the precipitation of metal as hydroxide, basic-salt or sulfide, is not effective for metal recovery and for dilute wastewater treatment [1]. In this respect, liquid membrane transport method has shown great potential, especially in cases where solute concentrations in waste are relatively low.

Liquid membrane transport is a relatively new separation method where ions are transported from source phase to receiving phase through membrane that contain ion carriers where separation processes involves extraction, stripping, and regeneration in single unit operation. It can be developed for treatment of liquid waste, especially that contains solute in low concentration [2]. This method has been proposed as a clean technology for their characteristic, such as high selectivity, low energy requirement, continuous processes, the ability to transport species from high concentration to low concentration, low inventory of solvents, etc. [3]. Efficiency and selectivity of transport of ion in this separation processes is highly affected by the nature of the system and the ion carrier [4-6].

Molecules of *p-tert*-butylcalix[n]arene with diethylaetamide groups are potential as ion carrier for separation of metal ions with liquid membrane transport. A calix[n]arene with diethylacetamide group can be synthesized by either reaction of *p-tert*-butylcalix[n]arene with diethyl-2-bromoacetamide [7] or by reaction of a carboxylic derivatives of *p-tert*-calix[4]arene with thionyl chloride followed by amidation using diethylamine [8, 9]. Oxygen and nitrogen atoms in this group act as electron donors for the metal ions in complexation. The compound is soluble in organic solvent such as chloroform, dichloromethane, dichloroethane, etc. [10, 11]. The amide type derivatives of calixarenes have been reported in relation to solvent extraction and ionophore CHEMFETs of some metal ions [7, 9] but the use of this type of compound as ion carrier for heavy metal ions in liquid membrane transport have not been reported yet.

Therefore, this work was carried out to investigate the transport behavior of Cr(III), Cd(II), Pb(II), and Ag(I) ions through bulk liquid membrane containing *p-tert*-butyl-calix[4]arene-tetradiethylacetamide as ions carrier, including the effects of source phase pH, ion carrier concentration in membrane phase, nature of

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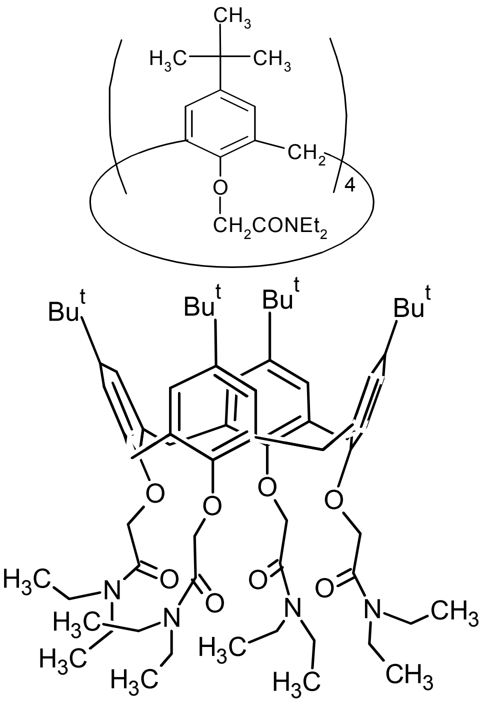

Fig 1. Structure of the ion carrier *p-tert*-butylcalix-[4]arene-tetradiethylacetamide or 5,11,17,23-tetrakis-(*tert*-butyl)-25,26,27,28-tetrakis(diethylcarbamoil-methoxy)-calix[4]arene

decomplexant agent in receiving phase, and transport time on transport efficiency and selectivity. Structure of the ion carrier employed in the present work is shown in Fig 1.

EXPERIMENTAL SECTION

Material

p-tert-Butylphenol, formaldehyde, ethyl-chloro-acetate, diethylamine, thionylchloride, chloroform, $Cr(NO_3)_3$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $AgNO_3$, HNO_3, HCl, H_2SO_4, $Na_2S_2O_3$, and other chemicals were used in the synthesis of *p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[4]arene-tetradiethylacetamide. All chemicals used in this study were the highest purity available from Merck and Aldrich chemical companies and employed without further purification. Whereas, *p-tert*-butylcalix[4]arene-tetracarboxylic acid which was used to synthesis the ion carrier, was prepared according to procedure described in the previous paper [4].

By acylation to *p-tert*-butylcalix[4]arene-tetracarboxylic acid with thionylchloride followed by amidation using diethylamine in a mixture of dry chloroform/K_2CO_3. It was obtained *p-tert*-butylcalix[4]arene-tetradiethylacetamide (47%). This product contain *cone*, *partial cone*, and 1,2-*alternate* conformers: m.p. 280 °C; TLC (SiO_2, $CHCl_3$: ethanol = 1:1 v/v, Rf = 0.84); IR (KBr), 2962.5, 2904.6, 2869.9 cm^{-1} (C-H), 1666.4 cm^{-1} (C=O amide), 1581.5 cm^{-1} (aromatic), 1477.4 cm^{-1} (CH_2), 1431.1 cm^{-1} (C-N), 1361.4 cm^{-1} (CH_3), 1199.6, and 1126.4 cm^{-1} (C-O); ^1H-NMR (500 MHz, $CDCl_3$), δ 6.84, 6.83, 6.77, 5.0 ppm (s, s, s, s, Ar***H***), δ 6.72, and 6.68 ppm (d, d, J = 2.5 Hz, Ar***H***), δ 5.29, and 3.19 ppm (d, d, J = 12.8 – 13.0 Hz, $\mathrm{ArC}\boldsymbol{H_2}\mathrm{Ar}$), δ 4.97 ppm (s, $ArCH_2Ar$), δ 4.93, and 4.76 ppm (d, d, J = 14.7 Hz, $\mathrm{ArC}\boldsymbol{H_2}\mathrm{Ar}$), δ 3.33 ppm (m, J = 6.8 -7.3 Hz, $\mathrm{CON(C}\boldsymbol{H_2}\mathrm{CH_3)_2}$), δ 1.11, and 1.08 ppm (t, t, J = 7.4 Hz, $\mathrm{CON(CH_2C}\boldsymbol{H_3}\mathrm{)_2}$), δ 1.117, 1.115, and 1.02 ppm (s, s, s, 1:1:2, $\mathrm{C(C}\boldsymbol{H_3)_3}$) δ 1.01 ppm (s, $\mathrm{C(C}\boldsymbol{H_3)_3}$); ^{13}C-NMR (500 MHz, $CDCl_3$), δ 169.54 ppm ($\boldsymbol{C}\mathrm{ON(CH_2CH_3)_2}$), δ 154.32 ppm (***C***-O aryl), δ 144.40 ppm (s, ***C**-para* aryl), δ 133.75 ppm (***C**-ortho* aryl), δ 125.46 ppm (***C**-meta* aryl), δ 72.02 ppm ($\mathrm{O}\boldsymbol{C}\mathrm{H_2CON(CH_2CH_3)_2}$), δ 40.95, and 33.98 ppm ($\mathrm{CON(}\boldsymbol{C}\mathrm{H_2CH_3)_2}$), δ 33.60 ppm ($\boldsymbol{C}\mathrm{(CH_3)_3}$), δ 31.60 ppm ($\mathrm{Ar}\boldsymbol{C}\mathrm{H_2Ar}$), δ 31.52 ppm ($\mathrm{C(}\boldsymbol{C}\mathrm{H_3)_3}$), δ 14.46 and 13.32 ppm ($\mathrm{CON(CH_2}\boldsymbol{C}\mathrm{H_3)_2}$).

Instruments

IR spectrometer (Shimadzu FTIR-8201PC), ^1H and ^{13}C-NMR (Jeol JNM-MY500), atomic absorption spectrophotometer (Perkin Elmer 3110), Orion-pH-meter, transport cell (U glass pipe, ϕ_d = 1.25 cm) 30 mL in volume, stirrer bar (1 cm), analytical balance, and reflux apparatus.

Procedure

Preparation of solution

Chloroform was used as liquid membrane. A stock solution of ions carrier was prepared by dissolving an appropriate amount of *p-tert*-butylcalix[4]arene-tetradiethylacetamide in chloroform (membrane) and dilution by this solvent for making solution with different concentrations, i.e. 1.0×10^{-4} – 4.0×10^{-4} mol L^{-1}. The stock of 100 ppm solutions of each metal ions were made by dissolving an appropriate amount of nitrite of metals compound in 1000 mL of distilled water. A metal ion solution, 1.0×10^{-4} mol L^{-1} prepared by dilution of an appropriate amount of a stock solution in distilled water was used as source phase. The pHs of source phase (1.0 – 5.5) were adjusted by addition of HNO_3. Solutions 0.1 – 3.0 mol L^{-1} of HNO_3, were also used as a source phase. Receiving phases were acid solutions with concentrations of 0.1 – 3.0 mol L^{-1} that were prepared by dilution of concentrated HNO_3, HCl and H_2SO_4 in distilled water. Another receiving were solutions of 0.005 – 0.100 mol L^{-1} $Na_2S_2O_3$ that were prepared by dissolving an appropriate amount of $Na_2S_2O_3$ in distilled water.

Transport experiment

Transport experiments were done at 29 ± 1 °C. For transporting cations across liquid membrane, a U bulk-type liquid membrane cell was used. The membrane phase (6 mL), where the ion carrier was dissolved, was separates the two aqueous phases (source and receiving phase, 5 mL). The membrane was stirred at 150 rpm by teflon-coated magnetic bar (1 cm in length). The cell was covered with an aluminium foil or plastic sheet to minimize solvent evaporation. After allowing at a periodic of time, the metal ion concentration of both *aqueous* phase were sampled and measured by atomic-absorption spectroscopy. This procedure was conducted for the variation of source phase pH, concentration of the ion carrier in membrane, nature and concentration of decomplexant agent in receiving phase, and transport time experiments. Transport selectivity of the metal ions was determined by equimolar mixture transport experiment (concentration of each metal ion was 1.0 × 10^{-4} mol L^{-1}) under the optimum condition of single metal ion transport.

RESULT AND DISCUSSION

Behaviors of the metal ions transport were characterized by percentage of metal ion in both source and receiving phase (%M) after transport processes and transport selectivity of metal ion (β) which was calculated using equation below, where $\%M_1$ and $\%M_2$ are percentage of metal ion 1 and 2 transported [4, 5, 12-14].

$$\beta_{M_1/M_2} = \frac{\%M_1}{\%M_2}$$

Effect of the pH of the Source Phase

The effects of the source phase pH on transport efficiency of Cr(III), Cd(II), Pb(II), and Ag(I) ions were investigated (Fig 2). Percentages of the metal ions in

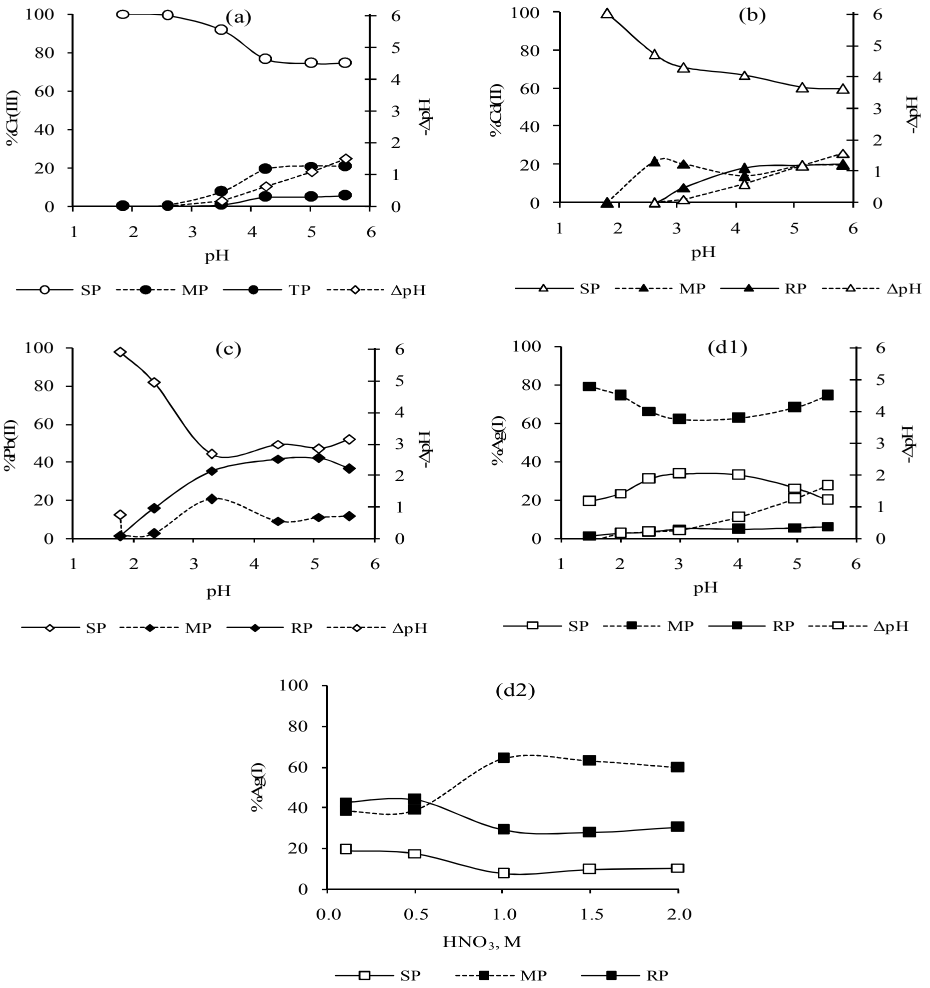

Fig. 2. The pH effects of source phase on transport efficiency of Cr(III) (a), Cd(II) (b), Pb(II) (c), and Ag(I) ions (d1 and d2) by *p-tert*-butylcalix[4]arene-tetradiethylacetamide ($L(CONEt_2)_4$) (SP, source phase; MP, membrane phase; RP, receiving phase)

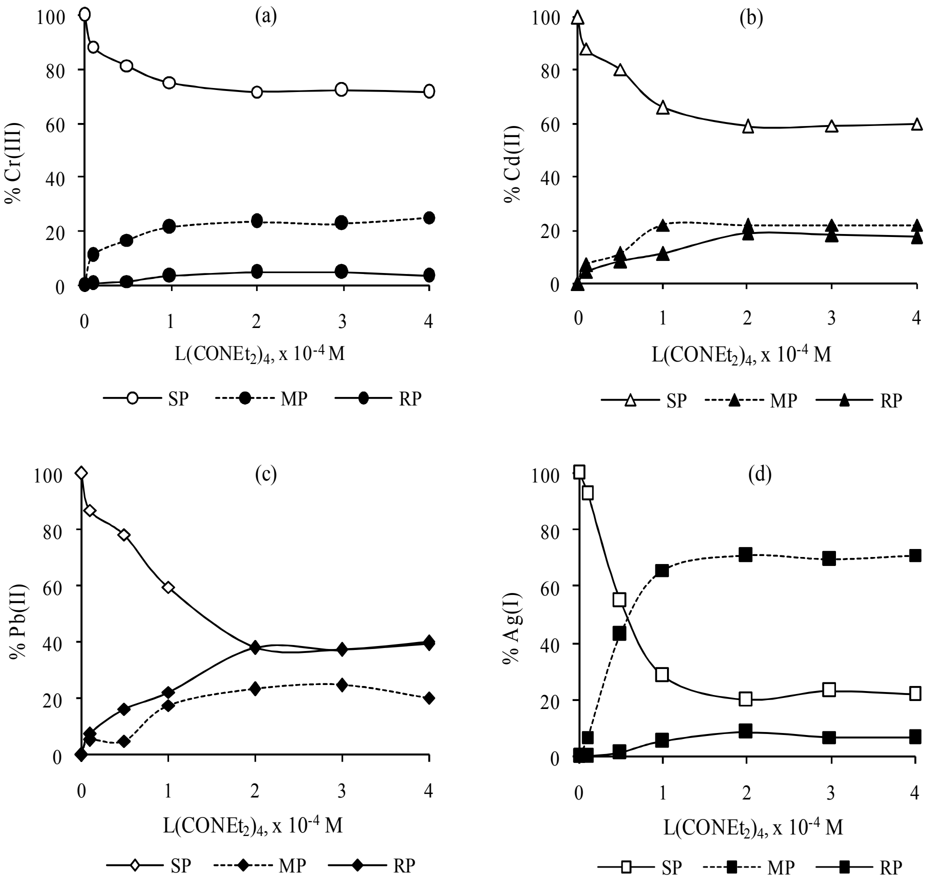

Fig 3. Concentration effects of L(CONEt$_2$)$_4$ in chloroform membrane on transport of Cr(III) (a), Cd(II) (b), Pb(II) (c), and Ag(I) (d) ions (SP, source phase; MP, membrane phase; RP, receiving phase)

source phase decreased with an increasing of pH of source phase up to the optimum pH. The results revealed that the optimum transports of those metal ions occur at pH 4.2 – 5.5, except on transport of Ag(I) which was transported in two optimum pH, i.e. 0.0 and 5.5. These facts relate to the hardness of the metal ions and transport mechanism. That is, the hardness of the metal ions was Cr(III)>Pb(II)>Cd(II)>Ag(I) and the optimum pH of the metal ions was Cr(III)<Pb(II)<Cd(II)<Ag(I). Ag(I) was transported as ionic pair of complex anion with carrier protonated in low pH of source phase (about pH 0,0), while the metal ion was transported in moderate pH of source phase as a simple salt.

In order to suggest a mechanism of the metal ions transport, the pH of both source and receiving phase were measured before and after metal ion transport processes. The change of pH in source and receiving phase after transport processes were not significant showing that the mechanism is *symport* transport, where the metal ions are transported by the ion carrier (L(CONEt$_2$)$_4$) in salt form. The decrease of source pH after metal ions transport processes due to the proton transport by both diffusion and carrier facilitated mechanisms.

Effect of the Concentration of Ion Carrier in Membrane Phase

Fig 3 shows the influence of the concentration of L(CONEt$_2$)$_4$ in membrane phase on transport efficiency of Cr(III), Cd(II), Pb(II), and Ag(I) ions under the optimum pH. Concentrations of L(CONEt$_2$)$_4$ in the range of 0.5 – 4.0 × 10^{-4} mol L^{-1} in chloroform were used. It is obvious that, the percent transport of the metals raise with an increases carrier concentration in membrane phase and becomes constant after the optimum concentration. The optimum transport of Cr(III), Cd(II), Pb(II), and Ag(I) occurred at 2.0, 1.0, 3.0, and 2.0 × 10^{-4} mol L^{-1} of L(CONEt$_2$)$_4$ respectively. These optimum concentrations were chosen for further study.

Effect of the Nature of Decomplexant Agent in Receiving Phase

The transport of Cr(III), Cd(II), Pb(II), and Ag(I) ions in the presence of different compounds in receiving phase was studied, the results are given in Table 1, 2, 3 and 4. It was observed that the nature and concentration of decomplexant agent in receiving

Table 1. Effects of HNO_3 in receiving phase on transport efficiency of Cr(III), Cd(II), Pb(II), and Ag(I) ions

Concentrations of HNO_3, mol L^{-1}	Percentages of metal ions in source phase				Percentages of metal ions in receiving phase			
	Cr(III)	Cd(II)	Pb(II)	Ag(I)	Cr(III)	Cd(II)	Pb(II)	Ag(I)
0.1	80.6	58.1	72.0	18.6	5.2	18.3	26.2	2.7
1.0	79.4	61.4	55.3	30.9	5.8	16.2	36.1	13.4
2.0	81.9	67.2	65.3	28.7	3.3	7.4	30.3	35.3
3.0	82.7	64.3	70.6	28.8	3.6	4.1	33.8	9.4

Table 2. Effects of HCl in receiving phase on transport efficiency of Cr(III) , Cd(II), Pb(II), and Ag(I) ions

Concentrations Of HCl, mol L^{-1}	Percentages of metal ions in source phase				Percentages of metal ions in receiving phase			
	Cr(III)	Cd(II)	Pb(II)	Ag(I)	Cr(III)	Cd(II)	Pb(II)	Ag(I)
0.1	79.4	97.3	74.8	5.7	0.0	2.3	6.5	2.4
1.0	80.5	97.6	78.7	11.7	0.0	1.2	14.8	4.4
2.0	79.9	96.4	92.9	10.9	0.0	0.8	7.8	6.3
3.0	80.7	94.4	96.2	11.2	0.0	1.1	2.6	12.9

Table 3. Effects of H_2SO_4 in receiving phase on transport efficiency of Cr(III) , Cd(II), Pb(II), and Ag(I) ions

Concentrations of H_2SO_4, mol L^{-1}	Percentages of metal ions in source phase				Percentages of metal ions in receiving phase			
	Cr(III)	Cd(II)	Pb(II)	Ag(I)	Cr(III)	Cd(II)	Pb(II)	Ag(I)
0.1	78.7	71.8	76.8	73.8	0.0	18.9	3.2	0.7
1.0	79.9	76.2	75.6	46.6	0.0	16.3	2.6	41.0
2.0	80.0	82.9	68.4	14.3	0.0	3.2	3.9	37.3
3.0	80.7	89.1	64.3	8.9	0.0	0.2	8.3	10.2

Table 4. Concentration effects of $Na_2S_2O_3$ in receiving phase on transport efficiency of Ag(I) ion

Concentration of $Na_2S_2O_3$,mol L^{-1}	Percentages of Ag(I) in source phase	Percentages of Ag(I) in receiving phase
0.00	10.3	10.0
0.01	30.1	39.5
0.05	27.9	11.3
0.10	46.0	10.0

Experimental conditions (Table 1 – 4): metal ions, 5 mL of 1.0 × 10^{-4} mol L^{-1}, ; ion carrier, 6 mL of 1.0 × 10^{-4} mol L^{-1} (for Cr(III), Cd(II), and Pb(II) transport) and 2.0 × 10^{-4} mol L^{-1} (for Ag(I) transport); source phase pH: 4.3 (Cr(III)), 5.2 (Cd(II), 4.5 Pb(II)), and 5.5 (Ag(I)); transport time, 24 hours; stirring 150 rpm in speed; source, membrane, and receiving phase volume were 5, 6, and 5 mL respectively; temperature, 29 ± 1 °C.

phase, were found to have a significant influence on the transport of those metal ions. The complex of Cr(III) ion can be decomplexed only by 1.0 mol L^{-1} HNO_3 in receiving phase with very low transport efficiency (5.8%). Cd(II) can be transported effectively by using either 1,0 mol L^{-1} HCl or H_2SO_4, with transport efficiency of 18.3 and 18.9% respectively. Optimum condition for decomplexation of complex of Pb(II) in receiving phase is in 1.0 mol L^{-1} HNO_3 with 36.1% in efficiency. Ag(I) was the most efficient to be transported where 1,0 M mol L^{-1} H_2SO_4 or 0.01 mol L^{-1} $Na_2S_2O_3$ was used as decomplexant. Transport efficiency of the both condition was about 41.0 and 39.5% respectively. The differences in the transport efficiency of Cr(III), Cd(II), Pb(II), and Ag(I) were probably due to the effects of competition in stability of their complex, solubility of their salt in acid decomplexant, anion affinity in receiving phase, and ability of acid-base interaction [3-5, 16].

Effect of Time

Fig 4 shows the time dependence of Cr(III), Cd(II), Pb(II), and Ag(I) transport through the liquid membrane under optimum experimental condition. It is obvious that, an increasing in time caused to increase the percentage of transport metal ions to the receiving phase and to decrease the percentage of remaining metals in sources phase. The percentage of Cr(III), Cd(II), Pb(II), Ag(I) (d1), and Ag(I)(d2) transported across liquid membrane per optimum time was about 11.6%/48h, 25.5%/32h, 39.5%/24h, 42.1%/32h, and 40.9%/16h respectively. Whereas, the order of

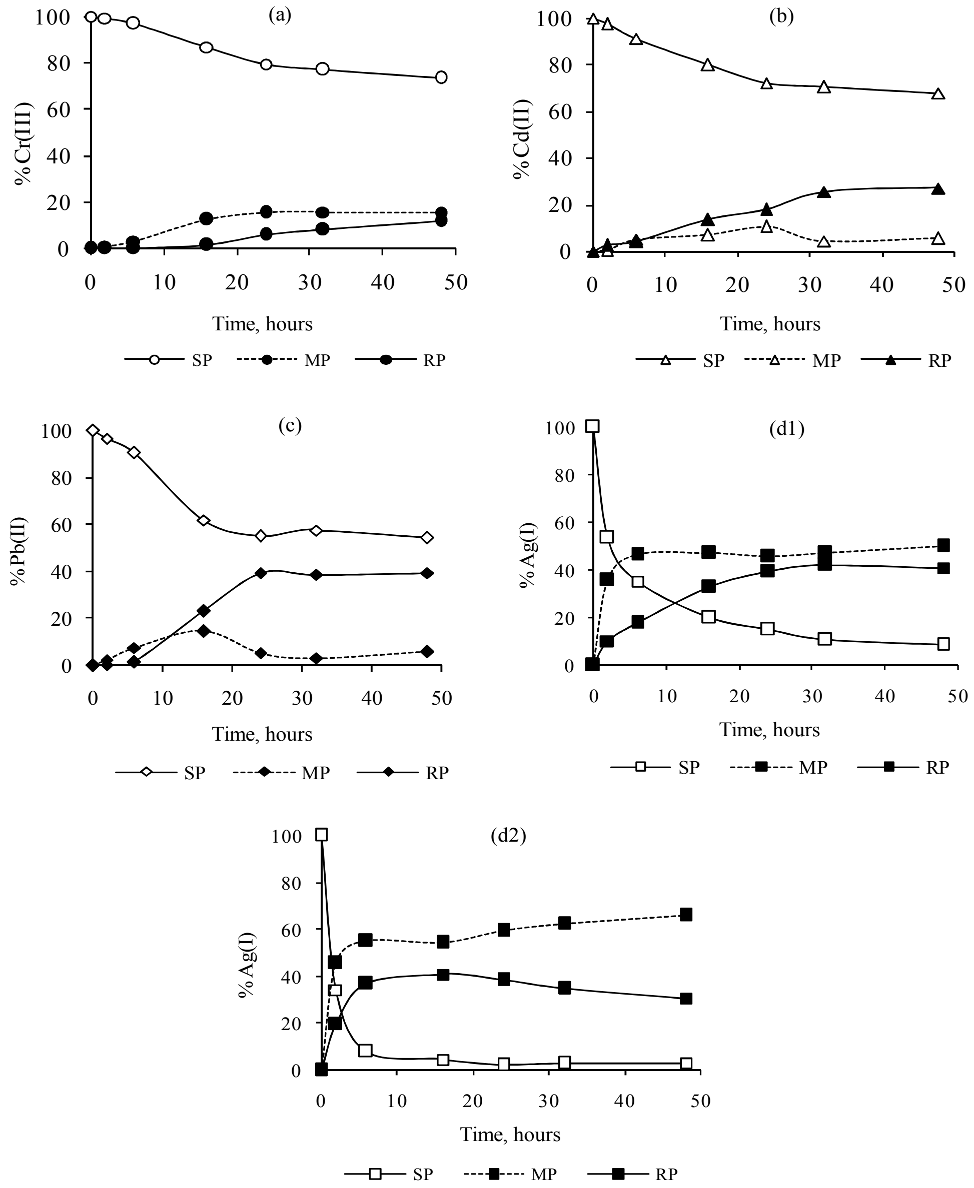

Fig 4. The time effects on transport efficiency of Cr(III) (a), Cd(II) (b), Pb(II) (c), and Ag(I) ions (d1, SP pH = 5.5 and d2, SP pH = 0.0) by L(CONEt$_2$)$_4$ (SP. source phase; MP membrane phase; RP, receiving phase)

Table 5. Transport selectivity of Cd(II), Pb(II), and Ag(I) ions by L(CONEt$_2$)$_4$

Metal Ions	Transport percentages and selectivity (β)			
	Opt. cond. of Cd(II)	Opt. cond. of Pb(II)	Opt. cond. of Ag(I)(d1)	Opt. cond. of Ag(I)(d2)
Cr(III)	0.0 (~)	0.0 (~)	0.0 (~)	0.0 (~)
Cd(II)	19.5	3.0 (3.0)	9.1 (3.8)	0.0 (~)
Pb(II)	2.8 (7.0)	9.1	16.7(2.1)	0.0 (~)
Ag(I)	13.7(1.40)	7.8 (1.2)	34.7	43.0

Experimental conditions : metal ions, 5 mL of 0.4 × 10^{-4} mol L^{-1}; transport experiments were done in their optimum condition for each metal ions; stirring 150 rpm in speed; temperature experiment, 29 ± 1 °C; (d1), SP pH = 5.5 and (d2), SP pH = 0.0).

transport rate was Ag(I)(d2) > Pb(II) > Ag(I)(d1) > Cd(II) > Cr(III) % h^{-1}. After these optimum time, concentration of the metal ions in aquous phases was relatively constant by increasing the transport time, except Cr(III), which was not transported completely by that time. The differences of rate transport of the metal ions were probably due to the difference of both lability of cations and diffusity of their complexes. Therefore, the differences of transport efficiency were probably due to stability, polarity, and decomplexation ability of complex in receiving phase. The maximum percentages of the metal ion transported are so low probably due to its transport mechanism, which is an equilibrium system. In this process, the driving force of transport is concentration gradient of the metal ion.

Selectivity

In order to investigate the transport selectivity of ion carrier to the metal ions, equimolar mixture of the metal ions (4.0×10^{-5} mol L^{-1}) was placed in source phase. Then, the transport process was conducted under the optimum condition of individual ion. A comparison of the results in Table 5 depicts that the ion carrier of $L(CONEt_2)_4$ was selective for Cd(II), Pb(II), and Ag(I) when the transport was carried out under optimum condition of each ion. The ion carrier is remarkably selective to Ag(I) where the transport was carried out under source phase media in high acid concentration. The highest transport selectivity of Ag(I) is probably due to the transport mechanism of that is transported as anion complex in case the other metal ion can not to form it. The higher transport efficiency of Ag(I) rather than the other metals probably is due to the nature of $S_2O_3^{2-}$ decomplexant (soft base) which is prefer to soft acid like Ag(I) and the polarity of Ag(I) complex which is relatively low [16]. Thus, the results suggested the fact that the selectivity of these transport system depends on the nature of decomplexant agent and stability of metal ion complexes.

CONCLUSION

Transport behavior of Cr(III), Cd(II), Pb(II), and Ag(I) ions through a bulk-liquid membrane containing *p-tert*-butylcalix[4]arene-tetradiethylacetamide as ion carrier was studied. Transport efficiency of the metals depends on source phase pH, concentration of ions carrier in membrane, nature and concentration of decomplexant agent in receiving phase, and transport time. The ion carrier is selective for Cd(II), Pb(II), Ag(I), and strongly depends on nature of decomplexant agent as well as transport mechanism. The remarkable selectivity was shown by the ion carrier to Ag(I) when the transport process was carried out under the source phase media in high concentration of acid.

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