

Simultaneous transport of seven heavy metal cations using phosphoric tri-(4-chloro aniline) carrier by bulk liquid membrane technique and the complexation of a numeral ions by conductometry

S. Akbari ^a, R.S. Khoshnood* ^a, M. Pourayoubi^b

^aDepartment of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

^bDepartment of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Azadi squ., Khorasan Razavi, Mashhad, Iran

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The fluxes and selectivity for competitive of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} and Pb^{2+} metal cations transport across bulk liquid membranes by phosphoric tri(4-chloro aniline) ligand were determined using some organic solvents as membranes. The membrane solvents include chloroform (CHCl_3), dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE) and nitrobenzene (NB). The transport process was driven by a back flux of protons maintained by the buffering the source and receiving phase with pH 4.9 and 3.0, respectively. The selectivity order and the transport rates for competitive bulk liquid membrane transport of the studied seven heavy metal cations are strongly sensitive to the nature and also the type of the organic membrane phases. The obtained results show that, among the used organic solvents as liquid membranes, the most transport rate was dedicated to DCM organic solvent for all of the seven studied metal cations by tri(4-chloro aniline) ligand. The competitive transport rate of Zn^{2+} metal cation was also studied in DCM at different times and showed that optimum time is 18 hour. Also, the effect of fatty acids as surfactant on the transfer percent of Zn^{2+} cations were studied in presence of the several fatty acids such as: palmitic acid (P.A), stearic acid (S.A), terephthalic acid (T.A) and fumaric acid (F.A) in DCM organic solvents. In addition to, the complexation reaction between a numeral these metal cations with phosphoric tri(4-chloro aniline) were studied in pure acetonitrile (AN) at different temperatures of 15°C, 25°C, 35°C and 45°C using the conductometric method. The conductance data show that the complexes with stoichiometry of 1:1 (L:M) were formed between phosphoric tri(4-chloro aniline) ligand and these metal cations. Also, the values of complex formation constants and thermodynamic parameters (ΔG_c° , ΔH_c° , ΔS_c°) for these complexes in pure AN solvent were obtained from temperature dependence of stability constants.

Key words: Phosphoric tri(4-chloro aniline) carrier, Bulk liquid membrane technique, Heavy metal cations, Simultaneous transport, Conductometry

INTRODUCTION

According to the daily industry that produced large amounts of waste containing metal cations such as zinc, cadmium, lead and copper that are harmful for human and nature health. The development of techniques that can be used to help restore and reuse the metals in the production cycle is very important. Separation of metal cations by bulk liquid membranes is powerful technique for transition metal ions in the world. This way is useful for separation of materials with low concentrations of dissolved them in the same way very simple and cheap [1]. Today, many separation processes and concentrate such as deposition, ion exchange or solvent extraction [2-5] that have been previously used replaced by processes that are based on synthetic membranes. Compared to conventional separation processes, the membrane separation methods with lower investment costs, high efficiency energy and large penetration rate has attracted a lot of attention.

In recent years liquid membranes are widely for the transfer ion with a concentration gradient be used

[6-11]. The transfer ions from the liquid membrane plays an essential role in the large number of successful studies especially in the field of chemical and biochemical processes and has many useful practical applications in separation science [12-14].

In the present study, the application of phosphoric tri(4-chloro aniline) carrier for the competitive transmission between a set of seven metal cations consist of Co(II), Cd(II), Ag(I), Pb(II), Ni(II), Cu(II) and Zn(II) by bulk liquid membranes have been reported. Fig 1 shows the used carrier in this project. The aim of this study was improve transmission by investigation of the effect of the nature of the cations, ligand and the type of solvent for the competitive transition metal cations. Also, the effect of number of different long-chain fatty acids such as palmitic acid(P.A), stearic acid (S.A), terephthalic acid (T.A) and fumaric acid (F.A) on the competitive transport of mentioned cations by liquid membranes containing of chloroform (CHCl_3), dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE) and nitrobenzene (NB) were employed. We also, investigated the effect of time on competitive transport of the mentioned ions from a source phase to receiving phase across a membrane phase

To whom all correspondence should
E-mail: rskhoshnood@yahoo.com

including ligand I in dichloromethane as the optimum solvent. Complex formation was placed strongly influenced by the reaction medium (solvent) [15] and also the complex stability constant depends on Gibbs free energy (ΔG_c°) that it is so, function of enthalpy and entropy Standard (ΔH_c° , ΔS_c°). Therefore, enthalpy and entropy changes are important factors in determining the stability of complexes [16, 17]

For this purpose, in this work, the potential of this ligand for the complex formation with several metal ions using conductometry method will be proved.

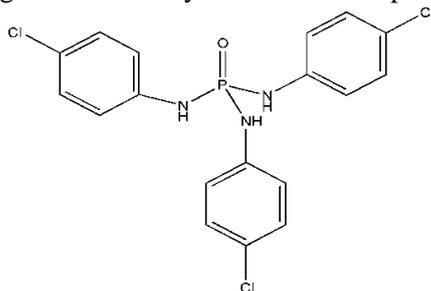


Fig 1. Structure of phosphoric tri(4-chloro aniline) carrier (I)

EXPERIMENTAL SECTION

Chemicals and devices used

The materials chemicals and solvents that were used in this work were all purchased from Aldrich or Merck companies. This materials due to high analytical purity were used without further purification. Distilled water three times to prepare all the solutions were applied.

Devices that were applied in this project include: atomic absorption spectrometer (Hitachi Z-2000) for measuring the concentrations of cations after transition process, digital conductivity apparatus (Metrohm 712) to obtain the formation constant of ligand I with several metal cation and the pH determinations were so carried out using a Metrohm Instruments(MI 691pH meter) with a glass electrode. The transport experiments were carried out in double-walled cylindrical cells (a water jacket) and connected to a thermostated system to keeping constant temperature at 25°C, the modelling based on a supported liquid membrane cell design described by Izatt et al [18]. Details of the construction of the bulk liquid membrane were shown in Fig 2. Also the electrolytic conductance by using a cell consisting of two platinum electrodes (With a distance of 1 cm) and the cell constant of 0.95 in a water bath thermostated were performed. In this study, all the samples were shaken on a shaker (stuart CB-162) by a certain speed.

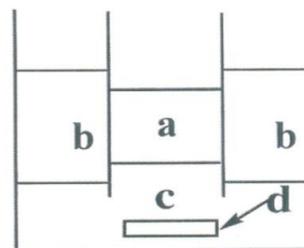


Fig 2. The scheme of BLM cell. The volumes of each source phases (a), receiving phase (b) and membrane phase (c), were 50, 30 and 10 mL, respectively and membrane phase stirred by a magnetic magnetic (d)

Experiments of competitive transition of heavy metal cations

All the metal ion competitive transition experiments discussed in this work were undertaken under similar conditions. The mixture solution of seven salt from studied cations by distilled water three times with a concentration of 0.2 M to each of the cations were prepared. Then by a buffer solution of sodium acetate and acetic acid in pH = 4.9 were diluted to achieve a concentration of 0.01M and eventually was used as the ultimate source phase. The organic phase contained the ionophore at 0.001M and fatty acids were also present at a concentration of 0.004 M. To prepare the aqueous recipient phase also was used of the buffer solution includes formic acid/sodium formate at pH=3.

The transport with the use of the standardized concentric cells were carried out in a 25°C water bath. The organic phase was shaken with a constant speed of 60 cycles per minute with the aid of magnetic magnet. Then the both aqueous phases were sampled with caution by micropipette after each experiment to control the seven metal cation concentration, using atomic absorption spectrophotometer. We enabled also with this concentration achieve to amount of the metal cations in the organic membrane phase. The analyses solutions were made up in a 0.1 M nitric acid matrix and the average of triplicate runs were reported for each data in a certain time period of 24 h.

Complex formation of ligand and several metal cations in AN solvent

Before the experiment, all glass containers with 10% nitric acid and distilled water were washed and dried by acetone. For the study of complex formation between ion-ligand, the salt solution of studied cations was provided at 1.00×10^{-4} M and ligand at 2.00×10^{-3} M concentrations in pure AN solvent. Then certain volume of I ligand was added to the salt solution inside the cell by a pipette and then increase each time and establishing a balance, solution conductivity at constant and certain temperatures

such as: 15°C , 25°C , 35°C and 45°C were recorded, that the conductivity change can be paid to the study of complex formation reactions [19].

RESULTS AND DISCUSSION

The selectivity and fluxes of the metal cations are strongly influenced by the nature of the ligand such as the kind of donor atoms and substituting groups present in the ionophore [20-22]. The macrocycles containing sulfur atoms have been known to preferentially bind whit metal ions such as Ag(I) over many other heavy metals [23], however macrocycles containing phosphor atoms have been less studied. Over the past years, a range of mixed oxygen-nitrogen donor macrocycles that include single ring and double ring systems have been synthesized and the interaction of many of these species with particular transition and post-transition metal ions has also been investigated [24, 25].

In view of this, it was of interest to employ the *o*-donor ligand as the carrier for transport of seven metal ions in order to determine the transport rate for these heavy metals by this hard ligand system. Therefore, with employment a suitable synthetic carrier we studied the competitive transport of Co(II), Cd(II), Ag(I), Pb(II), Ni(II), Cu(II) and Zn(II) cations from the aqueous source phase by four organic liquid membrane chloroform (CHCl₃), dichloromethane (DCM), nitrobenzene (NB) and 1,2-dichloroethane (1,2-DCE) comprising the I ligand within aqueous receiver phase. Simultaneous separation results and comparison of transfer rate for a set of seven metal ions were provided in Table1. The results show that, most of the studied cations moved through organic liquid membrane by a competitive basis.

Table 1. Data for seven metal cations competitive transport across organic solvents as bulk liquid membrane with ligand I

Solvent	Co(II)	Cd(II)	Ag(I)	Pb(II)	Ni(II)	Cu(II)	Zn(II)
Chloroform							
%(Receiving) ^a	-	0.07	0.01	-	-	0.06	0.07
%(Membrane) ^b	8.3	38.53	8.45	92.68	25.97	15.66	28.04
J(mol per 24 h) ^c	-	0.09	0.01	-	-	0.08	0.09
Nitrobenzene							
%(Receiving) ^a	-	0.04	0.04	-	-	0.04	0.12
%(Membrane) ^b	3.33	37.07	0.14	91.91	31.30	8.41	25.91
J(mol per 24 h) ^c	-	0.06	0.05	-	-	0.05	0.15
1,2-Dichloroethan							
%(Receiving) ^a	-	0.05	0.03	-	-	0.05	0.07
%(Membrane) ^b	6.43	37.74	5.37	92.31	19.95	11.85	27.31
J(mol per 24 h) ^c	-	0.07	0.04	-	-	0.06	0.09
Dichloromethane							
%(Receiving) ^a	0.03	0.15	0.05	-	0.01	0.09	0.14
%(Membrane) ^b	4.40	37.40	12.37	92.61	16.88	10.03	26.41
J(mol per 24 h) ^c	0.04	0.18	0.06	-	0.01	0.11	0.18

^a Percent of total metal cations in the receiving phase after 24 h; ^b Percent of total metal cations in the membrane phase after 24 h; ^c All values are $\times 10^{-7}$; ^d The hyphenated symbols mean that values about zero.

The compare speeds for the metal cations in different solvent systems such as: chloroform (CHCl₃), dichloromethane (DCM), nitrobenzene (NB) and 1, 2-dichloroethane (1,2-DCE) in order to evaluate the effect of solvent on transport efficiency, have been so plotted in Fig 3 (A comparison of these

solvent systems). As expected, the transfer is very impressive by the type of solvent accusing were changed ligand selectivity to cations, as far as the by changing the organic membrane, the transfer of cations due to changing the physical and chemical properties of the organic phase be changed [26].

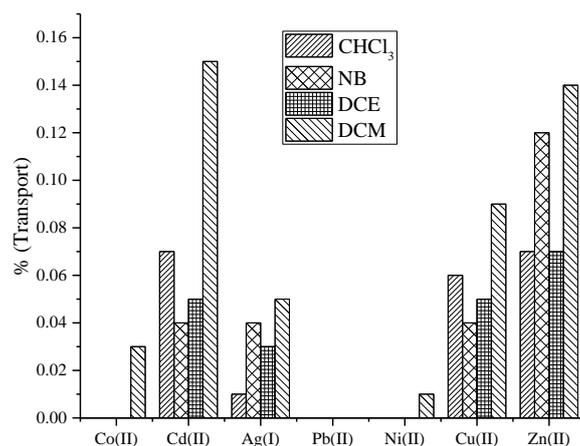


Fig 3. Comparison of the results of metal ions transport (water/organic solvent/water) studies for ligand I. Source phase: pH 4.9 ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) containing metal ions at 0.01M (10ml). Membrane phase: contains ligand I (0.001M) (50ml). Receiving phase: pH 3.0 (NaOH/HCOOH), (30ml) stirred for 24h.

It is noted that Zn^{2+} , Cd^{2+} and Cu^{2+} cations shows the highest percent transport, especially in DCM compared with others solvents. Compare the percentage of transfer for the $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Cu}(\text{II})$ metal cations in various organic solvents according to the obtained results is as:

$\text{Zn}(\text{II})$: $\text{DCM} > \text{NB} > \text{CHCl}_3 > 1,2\text{-DCE}$

$\text{Cd}(\text{II})$: $\text{DCM} > \text{CHCl}_3 > 1,2\text{-DCE} > \text{NB}$

$\text{Cu}(\text{II})$: $\text{DCM} > \text{CHCl}_3 > 1,2\text{-DCE} > \text{NB}$

As you can see, among the organic solvents involving chloroform (CHCl_3), dichloromethane (DCM), nitrobenzene (NB) and 1,2-dichloroethane (1,2-DCE), which were used as liquid membrane, the most transport percent was obtained for DCM in all of the cations.

According to, being different of the physical and chemical properties of solvents, this result may be attributed to the lower viscosity of dichloromethane ($\eta=0.39$) than the chloroform ($\eta=0.58$), 1,2-dichloroethane ($\eta=0.73$) and nitrobenzene ($\eta=1.63$) organic solvents. So, the ligand more quickly moves in along the dichloromethane membrane and transfer rate of cations increased in compared to other solvents [27].

The complex formation of $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Cu}(\text{II})$ metal cations with I ligand in AN system were studied at different temperatures. The molar conductance of the nitrate salts of $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Cu}(\text{II})$ metal cations in acetonitrile solvent was monitored as a function of the ligand I to metal ion mole ratio. The curves at the different temperatures is shown in Fig 4 for each of cations. It is clear that the slope of each curve changes at the point, where the ligand-cation mole ratio is about 1, which is an evidence for formation of a 1:1 $[\text{M}:\text{L}]$ complex. As is seen in these curves, with increase the proportion of ligand to cation, the molar conductivity grows which, indicates of the more mobile studied complexes than free solvated cations only [28-31].

Also in order to achievement of stability constants of complexes, variation of molar conductivity are plots as a function of molar ratio of $[\text{ligand}]_i / [\text{M}^{2+}]_i$, were calculated using a GENPLOT software and the details of calculation of stability constants of complexes have been described in reference [32]. The resulting $\log K_f$ for I- $\text{Zn}(\text{II})$, I- $\text{Cd}(\text{II})$ and I- $\text{Cu}(\text{II})$ complexes at different temperatures in AN system are listed in Table 2.

Table 2. Formation constants for different M^{n+} -ligand I complexes in AN using conductometry

Cations (Ionic radius A°) ^a	Log $K_f \pm \text{SD}^b$			
	15 °C	25 °C	35 °C	45 °C
$\text{Zn}^{2+}(0.75)$	2.44±0.35	2.44±0.34	2.44±0.35	2.48±0.32
$\text{Cd}^{2+}(0.95)$	2.51±0.27	2.55±0.18	2.46±0.28	2.49±0.24
$\text{Cu}^{2+}(0.73)$	3.31±0.04	3.53±0.05	3.68±0.06	4.02±0.09

^aRef. [33]. ^b SD= Standard deviation

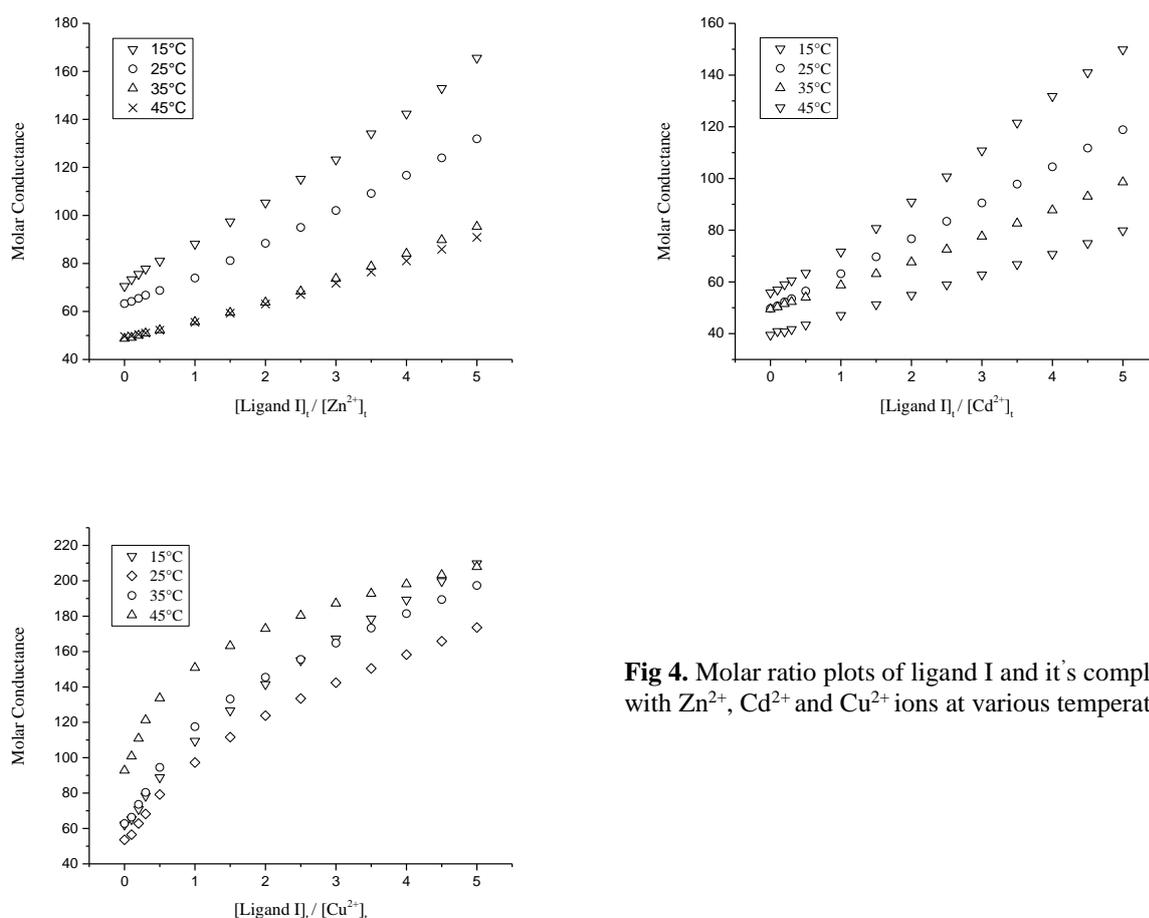


Fig 4. Molar ratio plots of ligand I and its complexes with Zn^{2+} , Cd^{2+} and Cu^{2+} ions at various temperatures.

The $\log k_f$ values for the $Zn(II)$, $Cd(II)$ and $Cu(II)$ ions in $25^\circ C$ are 2.44, 2.55, 3.53, respectively. The sequence of stabilities of these complexes in pure AN at all temperatures is as:



The stability constants for these systems indicates that $Cu(II)$ were complexed the most strong than two other ions with phosphoric tri(4-chloro aniline) ionophore, this is probably due that the ionic radius of $Cu^{2+}(r=0.73 \text{ \AA})$ is smaller than the $Zn^{2+}(r=0.75 \text{ \AA})$ and $Cd^{2+}(r=0.95 \text{ \AA})$ cations. Furthermore, because the softness of $Cu^{2+}(\sigma=0.38)$ into the $Zn^{2+}(\sigma=0.35)$ and $Cd^{2+}(\sigma=0.58)$ cations is lower, based on the concept of hard and soft acid-base, the strong interaction between Cu^{2+} cation and oxygen atom of ligand were created and forms a stable complex [34].

The thermodynamic data for complexation processes between phosphoric tri(4-chloro aniline) ligand and the studied cations, are summarized in table 3. The data in table 3, show that the values of

standard entropy changes (ΔS_C°) for all of complexes are positive, therefore, the complexation reactions between ligand I and the Zn^{2+} , Cd^{2+} and Cu^{2+} cations from entropy view point are stabilized. The value of standard enthalpy change (ΔH_C°) for Cu^{2+} ion is positive (a endothermic reaction), therefore, the complexation reactions between ligand I and Cu^{2+} cation is unfavorable in terms of enthalpy.

In order to achieve the most amount transport of Zn^{2+} ions in the shortest possible time and saving time, the effect of time on the competitive transport of this cation was examined at 4, 6, 12, 18 and 24 h in DCM solvent. It was observed that equilibrium is reached within 18 hour and after 24 hour; the % transport for Zn^{2+} cations were decreased (see Fig 5). We also investigated to effects of different fatty acids (palmitic acid, stearic acid, terphthalic acid and fumaric acid) on the competitive transport of this metal ion in DCM solvent at the optimum time of 18 h. The results are shown in Table 4.

Table 3. Thermodynamic parameters for ligand I, in AN

Cations (Ionic radius Å ^o) ^a	$\Delta G_c^\circ \pm$ SD^b (KJ/m ol)	$\Delta H_c^\circ \pm SD^b$ (kJ/mol)	$\Delta S_c^\circ \pm SD^b$ (J/mol. K)
Zn ²⁺ (0.74)	- 13.93± 1.97	c	57.42±2.41
Cd ²⁺ (0.97)	- 14.56± 1.05	c	55.12±1.57
Cu ²⁺ (0.73)	- 20.15± 0.27	39.53±5.06	200.15±16.95

^a Ref. [33]; ^b SD= Standard deviation; ^c With high uncertainty

Table 4. Effect of surfactants on Zn(II) ion transport across organic solvents systems as bulk membrane with ligand I

Solvent	Fatty acid	% (Receiving) ^a	% (Membrane) ^b	J (mol per 18 h) ^c
DCM	No acid	0.16	33.66	0.2
	Stearic acid	0.17	15.76	0.29
	Palmitic acid	0.15	13.72	0.26
	Terephthalic acid	0.11	13.88	0.18
	Fumaric acid	0.11	13.64	0.19
CHCl ₃	No acid	0.02	39.78	0.04
	Stearic acid	0.02	17.45	0.03
	Palmitic acid	0.02	19.89	0.03
	Terephthalic acid	0.03	19.68	0.05
	Fumaric acid	0.02	20.22	0.03
NB	No acid	0.08	40.85	0.14
	Stearic acid	0.22	5.14	0.37
	Palmitic acid	0.20	0.34	0.34
	Terephthalic acid	0.21	1.91	0.35
	Fumaric acid	0.17	12.24	0.28
1,2-DCE	No acid	0.03	38.63	0.05
	Stearic acid	0.05	17.82	0.09
	Palmitic acid	0.08	18.59	0.13
	Terephthalic acid	0.04	16.89	0.07
	Fumaric acid	0.05	14.53	0.09

^a Percent of total metal cations in the receiving phase after 18 h; ^b Percent of total metal cations in the membrane phase after 18 h; ^c All values are $\times 10^{-7}$; ^d The hyphenated symbols mean that values about zero.

As can be seen, percent transfer of Zn²⁺ ion in NB solvent increased in the presence of these fatty acids. Because the fatty acids aid to the transport process by providing a lipophilic counter ion in the organic phase on proton loss to the aqueous source phase, giving rise to charge neutralization of the cation being transported through ion pairing or adduct formation [35]. The transmission speed for the Zn²⁺ cation in NB solvent by different fatty acids is as follows:

Stearic acid > terephthalic acid > palmitic acid > fumaric acid.

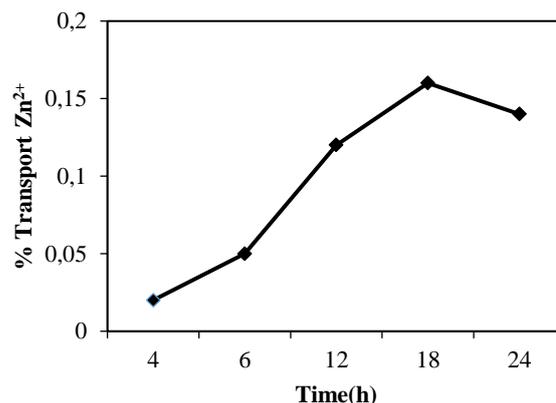


Fig 5. The changes of Zn²⁺ ion transport with time

As is evident from above results, it was found that the fatty acids play a major role via the contribute to the transport process by increasing in lipophilicity of formed complex which can facilitate the cation transport [36] from the organic membrane phase to receiving aqueous phases.

CONCLUSION

The heavy metal transport behavior under the employed conditions in this study, shows that the % of transport is strongly influenced by the nature of ligand, type of organic solvents and the fatty acid. This ligand showed a fully competitive transport for Zn²⁺ cation in often the membrane solvents and also

it confirmed that the nature and the kind of the organic membrane solvents can be effective upon the ion selectivity. The maximum transport for these heavy metal cations was obtained in the dichloromethane organic solvent membrane at 18 hour. The fatty acids exhibited additive behavior for Zn²⁺ transport in NB organic solvent. In other membrane solvents, the Zn²⁺ transport behavior may reflect the operation of different transport

mechanisms. For example, has also proposed by Lamb [37], it appear that the diffusion of the transported species through the LBM may control the transport rate in some (or all) of the membrane experiments. The conductometric investigations have established that the stoichiometry of the formed complexes between phosphoric tri(4-chloro aniline) ligand and Zn²⁺, Cd²⁺ and Cu²⁺ cations in AN is 1:1 at different temperatures.

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