



**SELECTIVE REMOVAL OF Cu(II), Co(II), Zn(II), AND Ni(II)
WITH IONIZABLE DIBENZO-16-CROWN-5 AND DIBENZO-
19-CROWN-6 LARIAT ETHERS AS ION CARRIERS
IN POLYMER INCLUSION MEMBRANE TRANSPORT**

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ABSTRACT

A selective removal of transition metal cations, i.e. Cu(II), Co(II), Zn(II), and Ni(II), with ionizable dibenzo-16-crown-5 and dibenzo-19-crown-6 lariat ethers as ionic carriers in transport across polymer inclusion membrane has been presented. The competitive transport from aqueous nitrate solutions containing metal ions at concentrations of 0.0010 M at pH 4.0 and 7.0 through the cellulose triacetate membrane with 0.5 M lariat ether **1** and **2** (based on a plasticizer) as the ion carrier and *o*-nitrophenyl pentyl ether (ONPPE) as the plasticizer into 0.5 M hydrochloric solution was performed. For pH = 4.0 and 7.0 of source aqueous phases the selectivity orders were as follows: Cu(II) > Co(II) > Zn(II) > Ni(II), and Cu(II) > Zn(II), Ni(II), Co(II), respectively. The semi-empirical equation was used for calculations of enthalpy formation for complexes of lariat ethers studied with transition metal cations. The two possibilities of metal cation-lariat ether coordination were assumed, i.e. via the crown ether cavity or ionizable carboxylic group. We found that for the both lariat ethers studied at pH 4.0 of source phase the transport rate linearly decreases with the enthalpy of formation increase. This correlation confirms that the observed behavior is connected with the stability of complexes formed by interaction of the lariat ether ring and the transition metal cations studied.

Keywords: Polymer inclusion membranes, Competitive transport, Copper(II), Cobalt(II), Zinc(II), Nickel(II), Enthalpy of formation, Derivatives of dibenzo-16-crown-5 and dibenzo-19-crown-6

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INTRODUCTION

One of the novel types of liquid membrane systems are polymer inclusion membranes (PIMs), which provide metal ions transport with high selectivity, as well as easy setup and operation. The review which provides a summary of the current knowledge of PIMs for transport of various metal ions and small organic solutes has recently been published [1]. The PIMs are formed by casting the base polymers (mostly cellulose triacetate - CTA) from an organic solution to the form of a thin film. The casting solution also contains an ionic carrier and a membrane plasticizer (mostly *o*-nitrophenyl alkyl ether). The membrane is used to separate the aqueous source and the receiving phase, but does not utilize an organic solvent to maintain this transport.

The transport on PIMs is accomplished by the ionic carrier, which is a complexing agent or an ion-exchanger. One of the most prospective ionic carriers are crown ethers as well as their derivatives (lariat ethers). They are well known examples of metal ions receptors in host-guest chemistry systems. Due to high selectivity of crown ethers, they have been extensively used as extractants in solvent extraction and as ion carriers in transport across liquid membranes [2].

First macrocycles introduced were neutral crown ethers. Gardner et al. [3] described the potassium cations transport across a series of new cellulose-based PIMs containing bis-*tert*-butylcyclohexano-18-crown-6 and compared their properties to those made of CTA. A competitive transport of trace radionuclides, *i.e.* Cs-137, Sr-90, and Co-60 from NaNO₃ aqueous solutions through polymer inclusion membranes containing a mixture of dibenzo-21-crown-7 and dinonylnaphthalenesulfonic acid provided the selectivity order: Cs(I) > Sr(II) > Co(II) [4].

The importance of crown ethers as the next generation of ion carriers was markedly enhanced by the introduction of crown ethers which bear pendant proton-ionizable groups such as carboxylic ones. These crown ethers were first introduced by Bartsch et al. who applied the highly lipophilic ionizable dibenzocrown ethers with carboxylic and phosphonic proton-ionizable groups as extractants in the solvent extraction process [5-7]. The competitive alkali metal cations transport across PIMs containing *sym*-(alkyl)dibenzo-16-crown-5-oxyacetic acid carriers shows an excellent selectivity for Na⁺ transport with total fluxes being strongly influenced by the length of the alkyl chain geminally attached to the functional side arm in the lariat ether molecule [8]. Mostly, the ionizable lariat ethers were used for alkali and alkaline earth metal cations as well as lead(II) cations selective removal [1]. On the other hand, there are only very few papers which deal with transition metal cations removal with lariat ethers [1].

Now, we present the transition metal cations selective removal by the competitive transport of Zn(II), Ni(II), Cu(II), and Cd(II) through PIM with decyl derivatives of the ionizable crown ethers, *i.e.* *sym*-(decyl)dibenzo-16-crown-5-oxyacetic acid and *sym*-(decyl)dibenzo-19-crown-6-oxyacetic acid.

This work shows the correlation between the facilitated ions transport through PIMs containing a lariat ether with the calculations results of the theoretical enthalpy of formation for carrier complexes with the transition metal cations studied.

EXPERIMENTAL SECTION

Chemicals

Dichloromethane, *o*-nitrophenyl pentyl ether (ONPPE), and cellulose triacetate (CTA), zinc(II), nickel(II), copper(II) and cadmium(II) nitrates, and hydrochloric acid as analytical grade reagents were purchased from Fluka and used without further purification. The methods of synthesis of lariat ether **1** and **2** have been published previously [5, 9].

Preparation of membranes

An organic solution of the support (cellulose triacetate), the ion carrier (lariat ether), and the plasticizer (*o*-nitrophenyl pentyl ether) in dichloromethane was prepared. The structures of lariat ethers investigated in the present work are shown in Fig 1.

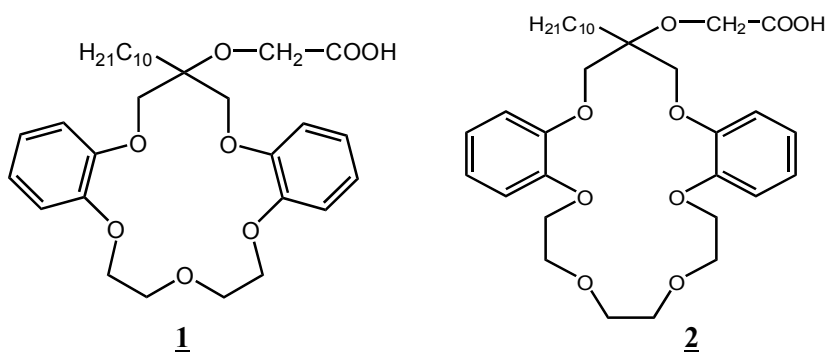


Fig. 1. Structures of the proton ionizable dibenzo lariat ethers.

A portion of an organic solution was poured into a membrane mold comprised of 9.0 cm glass ring attached to the glass plate with CTA - dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion in cold water. The membrane was soaked in the aqueous solution of 0.10 M HCl for 12 hours and stored in distilled water.

Transport studies

Transport experiments were carried out in a permeation cell, in which the membrane film was tightly clamped between two cell compartments. The average CTA membrane thickness was 28 μm which was measured with a digital ultra-meter of A 2002M type from Inco-Veritas with 0.1 μm standard deviation over four readings. The effective surface area of the

membrane was 7.0 cm². Both, the source and receiving aqueous phases (45 ml each) were stirred at 600 rpm with synchronous motors. The PIM transport experiments were conducted at room temperature (22-24 °C). Samples of the aqueous source phase were removed periodically via a sampling port with a syringe and analyzed to determine the metal ions concentration. To determine the metal ions concentration a capillary electrophoresis system with UV detector (Capel-105, Russia) was used. The electrophoretic buffer (pH 4.25, at voltage 25 kV) composed of 15 mM lactic acid, 8 mM 4-methylbenzylamine, and 5% methanol (Fluka).

The transport across PIMs was described according to the kinetics of a first-order reaction:

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (1)$$

where c is the concentration of metal ions in the source aqueous phase at time t (M), c_i is the initial concentration of metal ions in the source phase (M), k is the rate constant (s⁻¹), and t is time of transport (s).

To calculate the k values, the plots of $\ln(c/c_i)$ vs. time were prepared. The relationship of $\ln(c/c_i)$ vs. time was found to be linear, which was confirmed by high values of determination coefficients (r^2), *i.e.* ≥ 0.98 . The permeability coefficient (P) was calculated as follows:

$$P = -(V / A) \cdot k \quad (2)$$

where V is the volume of the aqueous source phase, and A is the area of the effective membrane.

The initial flux (J_i) was determined as:

$$J_i = P \cdot c_i \quad (3)$$

Computations

The computations of the enthalpy of formation were carried out using the SCF LCAO MO ZINDO-1 method with the Cache 4.4. program (evaluation version). In these calculations, we assumed that ligands coordination numbers for Cu(II), Zn(II), and Ni(II) were equal to 4, whereas for Co(II), it was equal to 6.

RESULTS AND DISCUSSION

Transport of transition metal ions by sym(decyl) dibenzo-16-crown-5-oxyacetic acid and sym(decyl)dibenzo-19-crown-6-oxyacetic acid

The competitive transport of Zn(II), Ni(II), Co(II), and Cu(II) from aqueous nitrate solutions containing those metal ions at concentrations of 0.0010 M through PIM with 0.5 M lariat ether 1 or 2 (based on the

plasticizer) as the ion carrier and ONPPE as the plasticizer into 0.5 M HCl receiving phase was investigated. The initial fluxes data (see Table 1) obtained for pH = 4.0 show a preferable Cu(II) transport over other the metal cations studied for **1** and **2**, with the selectivity order equal to: Cu(II) > Co(II) > Zn(II) > Ni(II). At pH 4.0, the both lariat ether carboxylic acids are protonated and serve as hosts forming an assembly with metal cations into the cavity (number of structures: 1 and 3). On the other hand, for pH 7.0 the ionizable group of a lariat ether is deprotonated and interacts with metal cations, especially with Cu(II), forming stable structure (number of structures: 2 and 4). The observed selectivity order Cu(II) > Zn(II), Ni(II), Co(II) is in accordance with the solvent extraction behavior for a typical carboxylic acid, such as Versatic 10 [10, 11]

Table 1. Zn(II), Ni(II), Co(II), and Cu(II) initial flux values for transport from source aqueous phase at pH 4.0 and 7.0 across PIM with lariat ether; receiving phase: 0.5 M HCl. Membrane phase: 0.5 M lariat ether, 4 cm³ ONPPE/1 g CTA

Carriers	Metal ions	Initial fluxes, $\mu\text{mol}/\text{m}^2\text{s}$	
		pH = 4.0	pH = 7.0
1	Zn(II)	1.00	0.75
	Ni(II)	0.41	0.65
	Co(II)	1.43	0.60
	Cu(II)	2.31	3.41
2	Zn(II)	0.92	1.11
	Ni(II)	0.59	0.80
	Co(II)	2.12	0.72
	Cu(II)	2.42	3.40

Correlation of transition metal cations fluxes versus enthalpy formation

In Table 2 a comparison between metal cations diameters and crown ether cavity diameters is shown. Cations diameters are almost the same, since they range from 1.38 to 1.48 Å and are much smaller than crown ether cavity diameters for 16-crown-5 and 18-crown-6. Is not possible to explain the preferential flux of Cu(II) by simple fitting of metal cations into cavities of crown ethers.

Table 2. Comparison of diameters for transition metal cations and crown ether cavities

Cation	Ionic diameter, Å [12]	Crown ether cavity	Cavity diameter, Å [13]
Ni ²⁺	1.38	16-crown-5	2.0 - 2.4
Cu ²⁺	1.46	18-crown-6	2.6 - 3.2
Zn ²⁺	1.48	19-crown-6	3.0 - 3.5
Co ²⁺	1.48	21-crown-7	3.4 - 4.3

This was the reason why we decided to try to correlate our results for the competitive transport of transition metal cations with the enthalpy formation for the lariat ethers **1** and **2** with the metal cations studied. The semi-empirical method using Cache program SCF LCAO MO ZINDO-1 was used for these calculations. The two possibilities of metal cation-lariat ether coordination were assumed, i.e. via crown ether cavity or ionizable carboxylic group. The results of the calculations are summarized in Table 3.

Table 3. The enthalpy of formation (in kJ/mol) values for complexes of lariat ethers **1** and **2** with transition metal cations for structures 1-4

No. of structure	Structure	Co(II)	Cu(II)	Ni(II)	Zn(II)
1	 $C_{10}H_{21}$ O-CH ₂ -COOH	-153.72	-185.46	-142.89	-165.97
2	 $C_{10}H_{21}$ O-CH ₂ -C	-136.43	-154.82	-136.26	-137.22
3	 $H_{21}C_{10}$ O-CH ₂ -COOH	-285.41	-298.76	-199.12	-214.53
4	 $H_{21}C_{10}$ O-CH ₂ -C	-117.91	-149.32	-146.72	-142.24

The highest values for the enthalpy of formations were found for copper(II) cations; for other metal cations values of enthalpy formations were smaller or similar. On the other hand, for coordination via a crown ether the enthalpy of formation values were much higher than for coordination via the carboxylic group.

The correlation for the initial metal cations fluxes transported from the source aqueous phase at pH= 4.0 vs. enthalpy formation for complexes of lariat ethers **1** and **2** with metal cations is shown in Fig. 2. As it comes from this figure, for the both lariat ethers studied the transport rate linearly decreases with the enthalpy of formation increase. This correlation confirms that the observed behavior is connected with the stability of complexes formed by interaction of the lariat ether ring and the metal cations. A comparison of the enthalpy of formation in the case of coordination via the ionizable carboxylic group with the initial fluxes indicates that an analogical correlation as previously is not observed (see Fig. 2).

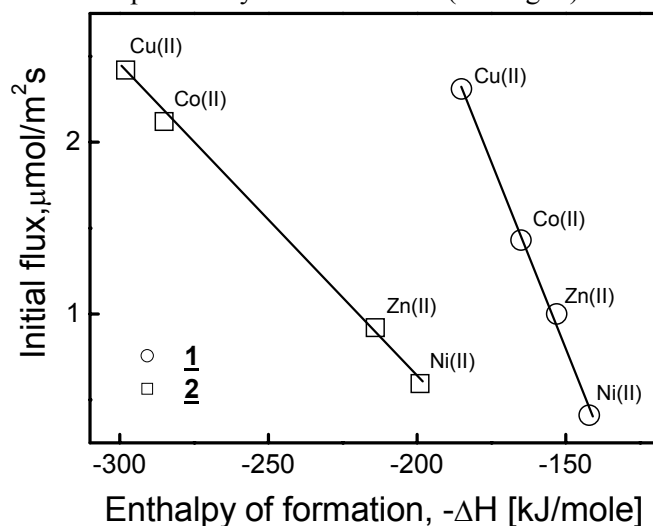


Fig. 2. The initial fluxes of metal ions as a function of the enthalpy of formation for complexes of lariat ethers **1** and **2** with metal cations obtained for the host-guest assembly by calculations. pH of source phase 4.0.

CONCLUSIONS

The competitive transport of Cu(II), Co(II), Zn(II), and Ni(II) cations, from aqueous nitrate solutions containing the metal ions at concentrations of 0.0010 M (each) at pH 4.0 and 7.0 through the cellulose triacetate membrane with 0.5 M dibenzo-16-crown-5 and dibenzo-19-crown-6 (based on the plasticizer) as the ion carriers and *o*-nitrophenyl pentyl ether (ONPPE) as the plasticizer into 0.5 M hydrochloric solution show the

selectivity orders as follows: Cu(II) > Co(II) > Zn(II) > Ni(II) (pH=4.0), and Cu(II) > Zn(II), Ni(II), Co(II) (pH= 7.0), respectively. The semi-empirical equation allowed calculating the enthalpy of formation for the complexes of the lariat ethers studied with transition metal cations. The two possibilities of the metal cation-lariat ether coordination were assumed, i.e. via the crown ether cavity or the ionizable carboxylic group. We found that for the both lariat ethers studied at pH 4.0, the transport rate linearly decreases with an increase in the enthalpy of formation. This correlation confirms that the observed behavior is connected with the stability of complexes formed by interaction of the lariat ether ring and the transition metal cations studied. For pH 7.0 of the source aqueous phase, the ionizable group of the lariat ether is deprotonated and interacts with metal cations, especially with Cu(II), forming a stable structure, which is in accordance with the solvent extraction behavior of a typical carboxylic acid, such as Versatic 10.

ACKNOWLEDGEMENT

Financial support of this work was provided by the Polish Science Foundation (grant No. 3T09C3230).

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