Review Paper:

Review on Complexation-Decomplexation of Guest Encapsulated in Dynamic Cavity of Host

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Abstract

Technology for separation has improved significantly with the use of dynamic cavity of non-cyclic ionophores in bulk liquid membranes to transport metal ions. Due to their flexible and adaptive designs, these non-cyclic ionophores may selectively form complexes with metal ions which make transport across liquid membranes more efficient. Non-cyclic dynamic cavity of ionophores has special structural characteristics that enable the creation of temporary cavities that are suited to hold particular metal ions according to size and coordination chemistry. Target ions can be effectively extracted and transported by means of selective binding which is facilitated by concentration gradients or electrical potentials.

Examining these ionophores' selectivity, stability and transport kinetics, the study highlights their benefits and applications. This technique has several uses such as the purification of metals in metallurgy and mining, the elimination of hazardous ions in environmental remediation and analytical uses in ion-selective electrodes. This technology might lead to additional advancements in membrane and ion transport technologies as well as improvements in industrial separation processes, environmental protection initiatives and analytical procedures.

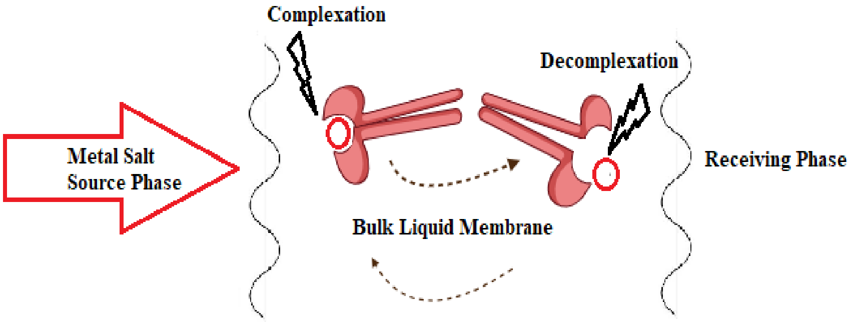
Keywords: Dynamic cavity, flexible, separation, environment, analytical.

Introduction

With applications in hydrometallurgy, analytical chemistry[8,10] and environmental cleaning, the movement of metal ions over bulk liquid membranes is a fundamental method in separation research. Two aqueous phases are separated by a liquid membrane phase using carriers or facilitators to increase efficiency and selectivity and results in the transfer of metal ions from the source phase to the receiving phase in a selective manner[18]. Macrocyclic effect on the stability of Cu complex was investigated by Cabbiness et al[6] in 1969. It is a desirable alternative for industrial and laboratory applications due to its ease of setup and capacity to handle a broad variety of metal ions. Various features of this approach including the types of carriers utilized, the characteristics of the liquid membrane and the operational circumstances, have been the subject of research throughout the years.

The technology of liquid membranes has its roots in the early 1960s. In order to determine the fundamentals of diffusion and partitioning, which control ion transport across liquid membranes. Early research showed the significance of parameters like membrane composition and thickness in affecting transport efficiency and they mostly used basic organic solvents to generate the liquid membrane. In short, a bulk liquid membrane functions as a selective barrier, letting certain ions through while keeping others out. For applications where the separation of certain metal ions from complicated mixtures is necessary, this selectivity is essential. The mechanism works on the basis of diffusion and assisted transport[3,17] in which ion mobility is determined by the gradients of their chemical potential and by their interactions with carrier molecules in the membrane phase[26].

The development of carrier molecules improving the selective transport of metal ions, was an important breakthrough in the discipline. In order for carrier molecules to function, certain metal ions must first form complexes with them in the source phase, diffuse across the liquid membrane and then release the ions into the receiving phase.



Graphical Abstract

The transport method is more selective and efficient[19]. These substances could attach to particular metal ions with selectivity, which made it easier for those ions to pass through the membrane. This finding had a key role in increasing the functionality and applicability of liquid membranes. Izatt et al[12]'s introduction of artificial and natural ligands as carriers in 1985 resulted in further developments. Better selectivity and stability were offered by these ligands, which were crucial for real-world uses. The field is still undergoing research, with current efforts concentrated on creating carriers that are both economical and ecologically benign.

Several operating factors including pH[5,25], temperature[11] and the concentration of metal ions and carriers, affect the effectiveness of metal ion transport via liquid membranes. Since pH has an impact on the ionization state of the carriers and metal ions, it is imperative to maintain an ideal pH range. Matsumoto et al[16] emphasized the need of maintaining a pH balance to optimize transport efficiency. By improving diffusion and decreasing membrane phase viscosity, higher temperatures often result in higher transport rates. A balanced strategy is necessary since high temperatures have the potential to deteriorate membrane materials and carriers. Chen et al[9] showed that obtaining high transfer efficiency without jeopardizing the integrity of the membrane system requires preserving an ideal temperature range.

Further close attention is required to be paid to the concentration of metal ions and carriers. A carrier concentration that is too high, might cause aggregation and can decreased efficiency whereas an ideal concentration guarantees efficient complexation and transport of metal ions. In order to maximize the performance of bulk liquid membranes, researchers are still examining the interaction between these characteristics.

Many industrial and environmental activities can benefit from bulk liquid membrane transport. The removal of heavy metals from wastewater is one such application. Lead, cadmium and mercury may all be effectively removed from industrial effluents using liquid membranes, as shown by Kislik study[14]. It is economically appealing to adopt this approach because it not only offers great removal efficiency but also permits the recovery and reuse of important metals.

Non-cyclic ionophores make it easier for ions to pass through bulk liquid membranes[22]. Because of their capacity to transport and bind ions selectively, these materials are essential to many industrial and scientific operations[13]. Examining their functions in chemical analysis, sensor technologies and separation processes is necessary to comprehend their applications in bulk liquid membrane transport. In contrast to their cyclic relatives, non-cyclic ionophores do not have a ring structure. Rather, they are made up of branching or linear molecules that can combine to create complexes with certain species[24]. Selective ion transport across liquid membranes is made possible by these ionophores which are made to identify and bind ions according to their size, charge and coordination chemistry.

Mechanism of Action: The creation of a complex between the ionophore and the target ion is the fundamental idea behind ion transport by non-cyclic ionophores. Next, this complex can be propelled by concentration gradients, electrical potentials, or other forces across a liquid membrane. The ion is released when it reaches the other side of the membrane, allowing the ionophore to go back to its starting point and repeat the process.

Table 1
Transport of cation (ppm) by podands using different metal salts *via* 1,2- dichloroethane, chloroform and carbon tetrachloride

	DCE				$CHCl_3$				CCl_4			
Metal salt	I_1	I_2	I_3	I_4	I_1	I_2	I_3	I_4	I_1	I_2	I_3	I_4
Na.Pic	0.80	1.40	0.92	0.07	4.00	0.80	0.31	0.09	2.00	1.10	1.16	0.98
Na.Dnp	0.70	0.79	0.38	1.30	0.80	0.65	0.47	1.05	2.00	0.57	0.27	0.65
Na.Onp	0.20	0.60	0.23	0.07	0.20	0.20	0.25	0.04	0.20	0.50	0.30	0.04
K.Pic	0.40	0.70	0.25	0.03	0.50	0.70	0.18	0.05	1.00	0.70	0.09	0.37
K.Dnp	0.02	0.00	0.11	0.01	0.02	0.01	0.07	0.01	0.02	0.01	0.06	0.08
K.Onp	0.08	0.50	0.07	0.05	0.03	0.23	0.02	0.21	0.25	0.20	0.01	0.05
LiPic	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00
Li.Dnp	0.07	0.02	0.00	0.00	0.02	0.02	0.00	0.00	0.02	0.02	0.00	0.00
LiOnp	0.02	0.02	0.00	0.00	0.02	0.02	0.00	0.00	0.02	0.02	0.00	0.00
$Mg(Pic)_2$	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
$Mg(Dnp)_2$	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.00
$Mg(Onp)_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$Ca(Pic)_2$	3.74	2.98	1.58	1.61	2.98	2.18	1.45	1.61	2.20	2.18	1.39	1.61
$Ca(Dnp)_2$	2.32	2.46	1.05	0.80	2.31	2.92	0.97	0.91	2.31	2.46	0.45	1.06
$Ca(Onp)_2$	1.71	1.68	0.54	0.92	2.46	2.46	0.43	1.02	1.65	1.64	0.42	0.92

Transport experiments were carried out for Li, Na, K, Mg and Ca salts by using different podands (I_1-I_4) [Fig. 1-4] in 1,2-dichlorothane (DCE), chloroform and carbon tetrachloride (Table 1)[1,2,15]. The results reveal that transport of Na and Ca metal ions is more amount *via* dynamic cavity of I_1 in $CHCl_3$ and DCE membrane respectively [Fig. 5-7] from picrate salts.

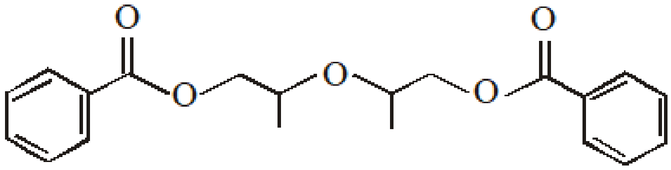


Fig. 1: [$(C_6H_5CO_2C_3H_6)_2O$] [I_1]

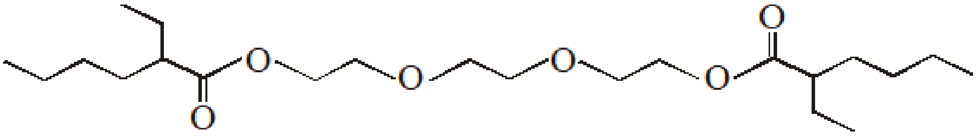


Fig. 2: [$C_{22}H_{42}O_6$] [I_2]

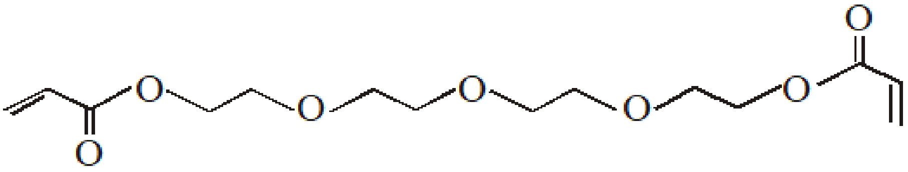


Fig. 3: [$C_{14}H_{22}O_7$] [I_3]

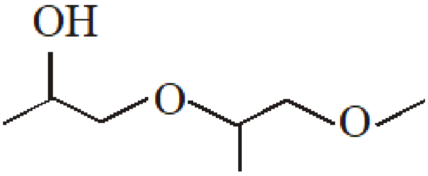


Fig. 4: [$C_7H_{16}O_3$] [I_4]

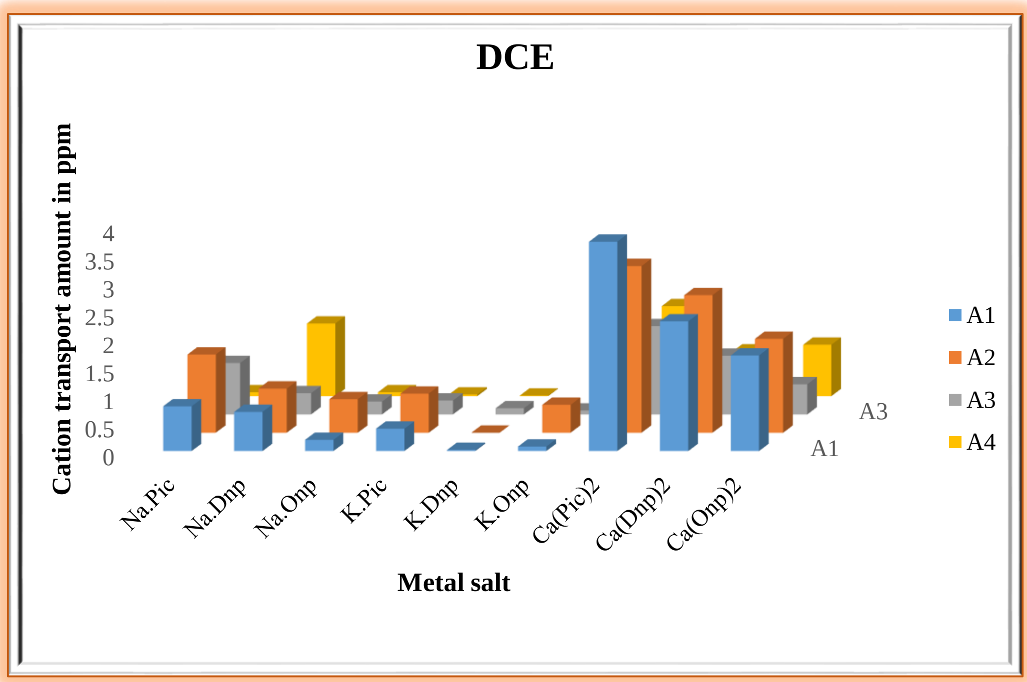


Fig. 5: Transport of metal ion by podand using different salts *via* 1,2- dichloroethane

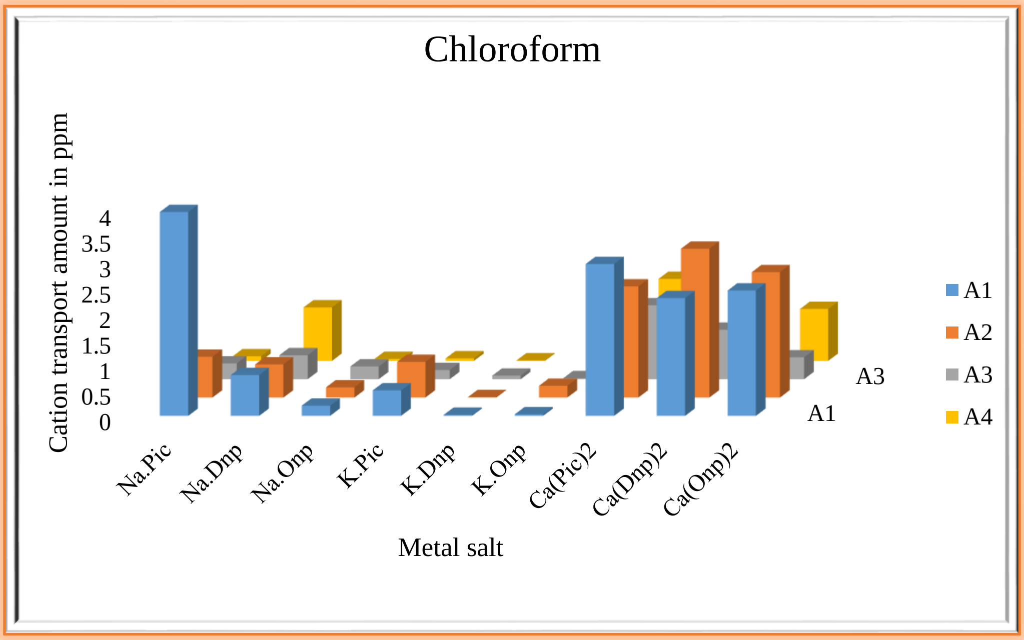


Fig. 6: Transport of metal ion by podand using different salts *via* chloroform

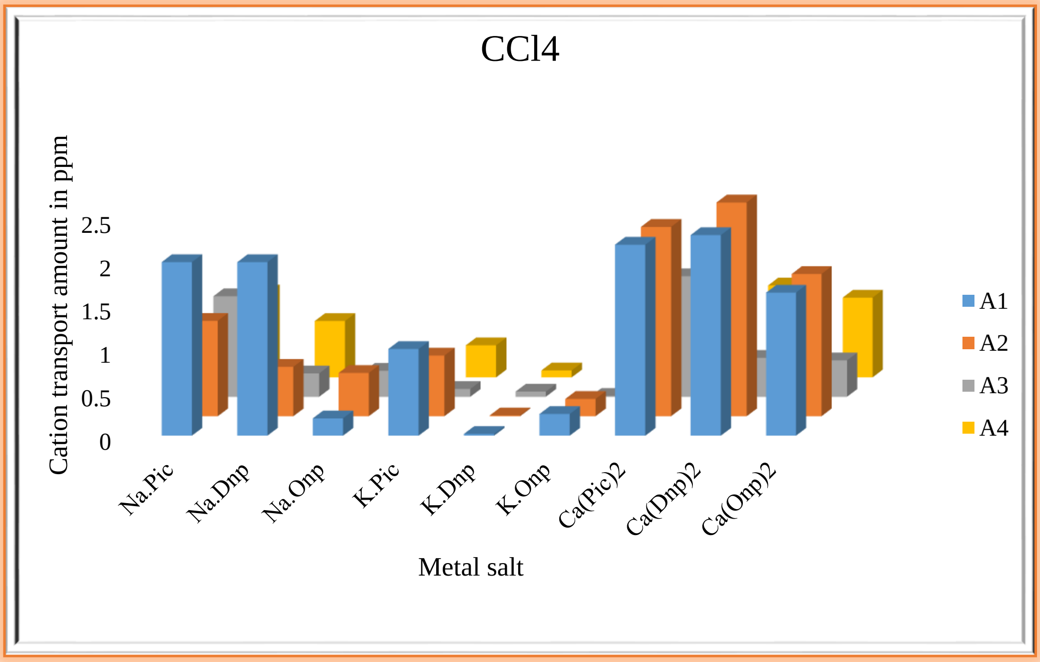


Fig. 7: Transport of metal ion by podand using different salts *via* carbon tetrachloride

Applications of bulk liquid membrane transport using podand

1. Separation Processes: The removal of certain ions from mixtures is one of the main uses of non-cyclic ionophores in bulk liquid membrane transport. This capacity is useful in fields like mining and metallurgy, where it is crucial to extract and purify metals like nickel, copper and zinc. These metal ions can be transported across a membrane selectively by non-cyclic ionophores, keeping them apart from undesirable impurities e.g. transporting zinc ions from an aqueous solution into an organic phase can be facilitated by the use of a non-cyclic ionophore such as di(2-ethylhexyl) phosphoric acid (D2EHPA)[21]. The extracted metal's purity is increased by this effective separation method which may be customized to meet certain industrial requirements.

2. Chemical Analysis: In analytical chemistry, non-cyclic ionophores are also used to identify and measure ions in a variety of substances. The use of non-cyclic ionophores in ion-selective electrodes (ISEs) is widespread for high-sensitivity and specificity ion concentration measurement. These electrodes are essential for industrial quality control, clinical diagnostics and environmental monitoring e.g. the measurement of Cu(II) levels in blood samples using non-cyclic ionophores in ISEs. Calcium ions are specifically bound by the ionophore, enabling the electrode to produce a potential difference proportionate to the ion concentration[20]. This approach is a staple in medical laboratories since it is fast and dependable.

3. Environmental Applications: Toxic ions from water sources must frequently be removed as part of environmental restoration[4,27]. By selectively moving dangerous ions like lead, cadmium and mercury across liquid membranes, non-cyclic ionophores can be very helpful in this process of cleansing the water. Non-cyclic ionophores can be added to membrane systems in wastewater treatment to eliminate heavy metals. The target metal ion helped to move from the polluted water into the clean phase, where it may be collected or disposed of safely by the ionophore's complexation with the metal ion.

4. Sensor Technologies: The special qualities of non-cyclic ionophores are also advantageous for the development of cutting-edge sensor technologies. These substances are utilized in sensors that identify certain ions in a range of settings, giving real-time information essential for industrial operations, environmental tracking and healthcare diagnostics e.g. solid-state ion-selective field-effect transistors[23] are made of non-cyclic ionophores (ISFETs). These sensors are helpful in biomedical applications for tracking ion levels in bodily fluids as well as in agricultural applications for soil analysis. Hence, these ionophores have a number of benefits, including selectivity, adaptability, efficiency and cost-effectiveness, which allow for precise separation and detection in industrial and analytical applications and make them commercially feasible for large-scale applications.

Conclusion

The complexation-decomplexation action-based bulk liquid membrane transport phenomena of metal ions is a well-proven method with great promise for a range of applications. Improvements in carrier molecules, membrane composition and operating parameters have continuously raised this process's effectiveness and selectivity. To reach its full potential, issues like scalability and membrane stability must be resolved. In order to overcome these challenges and to increase the range of real-world uses for this technology, ongoing research and development initiatives including the combination of nanotechnology, sustainable materials and computational tools will be essential. It is still important to build host molecules with improved selectivity and specificity for newly emerging contaminants which call for a thorough comprehension of the fundamentals of molecular recognition.

Technological developments in artificial intelligence and computer modelling can help with the logical design of host-guest systems, enhancing their predictive power and performance. The creation of dynamic systems that can adjust to shifting environmental conditions, may result from further research into nanomaterials and the integration of responsive components into host molecules. Translation of basic findings into useful applications will be aided by collaboration amongst fields including materials science, environmental engineering and chemistry.

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