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Submitted to

Journal of Membrane Science

Jan 2006

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ABSTRACT

The stability of polymer inclusion membranes (PIMs) relative to other liquid membranes is amongst the major reasons for the recent rejuvenation of interest in carrier-mediated transport for selective separation and recovery of metal ions as well as numerous organic solutes. This is reflected by an increasing number of PIM investigations reported in the literature over the last two decades. Given the outstanding performance of PIMs compared to other types of liquid membranes particularly in terms of membrane lifetime, it has been predicted that practical industrial applications of PIMs will be realized in the near future. This review provides a comprehensive summary of the current knowledge relevant to PIMs for the extraction and transport of various metal ions and small organic solutes. PIM studies reported to date are systematically summarised and outlined accordingly to the type of carriers used, i.e. basic, acidic and chelating, neutral or solvating, and macrocyclic and macromolecular. The paper reviews the various factors that control the transport rate, selectivity and stability of PIMs. The transport phenomena observed by various authors are related to the membrane characteristics, physicochemical properties of the target solutes as well as the chemistry of the aqueous solutions making up the source and receiving phases. The results from these studies reveal an intricate relationship between the above factors. Furthermore, while the interfacial transport mechanisms in PIMs are thought to be similar to those in supported liquid membranes (SLMs), the bulk diffusion mechanisms in PIMs governing their permeability and selectivity requires better understanding. This review also delineates two mathematical modeling approaches widely used in PIM literature: one uses a set of assumptions that allow the derivation of analytical solutions valid under steady state conditions only; the other takes into account the accumulation of the target species in the membrane during the initial transport state and therefore can also be applied under non-steady state conditions. The latter is essential when the interfacial complexation reaction kinetics is slow. It involves more complex mathematics and requires the application of numerical techniques. The studies included in this review highlight the potential of PIMs for various niche applications on a practical scale. The discussions provided, however, also emphasize the need for more fundamental research before any such practical applications of PIMs can be realised. This is specifically important for small organic compounds because to date scientific investigation involving the extraction and transport of these compounds remains

limited. Transport mechanisms of small organic compounds are less well understood and are likely to be more complex than those observed with the transport of metal ions.

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1 INTRODUCTION

In recent years, membrane-based processes have attracted considerable attention as a valuable technology for many industries. This significant gain in momentum is driven in part by spectacular advances in membrane development, wider acceptance of the technology as opposed to conventional separation processes, increased environmental awareness and most of all stricter environmental regulations and legislation. However, despite a recent market boom in all other membrane sectors including membrane filtration and electrodialysis, practical applications of liquid membranes remain largely limited. This includes bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs) and supported liquid membrane (SLMs). BLMs have low interfacial surface areas and mass transfer rates while emulsion breakage is the main problem associated with ELMs. A major drawback associated with SLMs is poor stability. These factors have severely rendered liquid membranes mostly impractical for many large scale applications [1, 2].

Nevertheless, given the essential need for metal ion recovery as well as for the extraction of numerous small organic compounds over the last two decades in hydrometallurgy, biotechnology and in the treatment of industrial wastewater, significant scientific effort has been expended to understand [3] and improve [4] the stability of liquid membranes. The number of scientific investigations devoted to this topic has been rising steadily [1]. Such dedicated works have resulted in a novel type of liquid membranes, commonly called polymer inclusion membranes (PIMs) [5], although a number of other names are also being used such as polymer liquid [6, 7], gelled liquid [8], polymeric plasticized [9-11], fixed site carrier [12-14] or solvent polymeric [15, 16] membranes. PIMs are formed by casting a solution containing an extractant, plasticizer and a base polymer such as cellulose triacetate (CTA) or poly(vinyl chloride) (PVC) to form a thin, flexible and stable film. The resulting self-supporting membrane can be used to selectively separate the solutes of interest in a similar fashion to that of SLMs. In several studies [8, 17, 18], PVC has been used to simply gel the liquid phase of an SLM to stabilize it within the pores of an inert support. In these cases, the PVC concentration of the membrane was much lower than that used for a self-supporting membrane.

PIMs retain most of the advantages of SLMs while exhibiting excellent stability and versatility. The lower diffusion coefficients often encountered in PIMs can be easily offset by creating a much thinner membrane in comparison to its traditional SLM counterpart. In several cases, PIMs with higher fluxes than those of SLMs have been reported [5, 19, 20]. In contrast to SLMs, it is possible to prepare a PIM with negligible carrier loss during the membrane extracting process [5, 11, 19, 20]. In addition, the amount of carrier reagent can be greatly reduced, hence creating the possibility of using more expensive extractants, which in the past could only be used for high value metals or organics. This will no doubt create a wider range of applications for PIMs. It is also noteworthy that the mechanical properties of PIMs are quite similar to those of filtration membranes. The technological advancements achieved with filtration membranes for manufacturing, module design and process configuration will be particularly useful for the large scale practical realization of PIMs [21]. Consequently, this will enable PIM based systems to exhibit many advantages such as ease of operation, minimum use of hazardous chemicals and flexibility in membrane composition to achieve the desired selectivity as well as separation efficiency.

It is interesting to note that PIMs have been used in chemical sensing for more than 30 years in the form of polymer membrane ion-selective electrodes (ISEs) [22]. In 1970 [23], it was demonstrated that the organic liquid of a calcium selective liquid membrane ISE could be immobilized into PVC to produce a polymer film with identical calcium sensing properties and selectivity as the organic liquid itself. Since that time there have been numerous PVC-based membranes developed for the potentiometric sensing of various cations and anions. Such membranes for use in potentiometry have also been termed "gelled liquid membranes" and "entangled liquid membranes" [22].

About the same time as this first reported use in ISEs, Bloch *et al.* [21] demonstrated that PVC-based membranes could also be used for metal ion separation although the requirements for the membrane characteristics were somewhat different for the two applications [21, 22]. In sensing, fast ion-exchange or metal ion complexation is required at the sample solution/membrane interface to rapidly establish the interfacial electrical potential difference but there should be negligible transport of the metal containing species through the membrane within the timescale of the measurement. In separation, fast interfacial reactions are required but in this case, high

diffusion coefficients of the metal containing species within the membrane are also desirable in order to achieve mass transport from the source to the receiving phase within a reasonable timeframe.

This review aims at providing a comprehensive summary of the current knowledge relevant to PIMs for the extraction of various metal ions and small organic solutes. Membrane stability, selectivity and transport rates are discussed in relation to the physicochemical properties of the base polymers, carriers and plasticizers as well as the characteristics of the target metal ions or the organic solutes. Transport mechanisms and their mathematical models are also delineated. It should be emphasized that all the research on PIMs carried out so far has been conducted on a laboratory scale and the transition of this research to a pilot or full scale application presents a major challenge for the future.

2 BASE POLYMERS FOR MEMBRANE PREPARATION

The base polymers play a crucial role in providing mechanical strength to the membranes. Despite a vast number of polymers currently used for many engineering purposes, it is surprising that PVC and CTA have been the only two major polymers used for most of the PIM investigations conducted so far. Although the feasibility of several cellulose derivatives (i.e. cellulose acetate propionate (CAP) and cellulose tributyrate (CTB)) as base polymers for PIMs has recently been studied [24], a large number of polymers that can possibly be used for PIMs remains unexplored. To some extent, this is because both PVC and CTA can be used to prepare a thin film with a relatively simple procedure based on dissolution in an organic solvent. Another factor is the dearth of information regarding the role of base polymers in mechanically supporting the membranes, enhancing the membrane stability and at the same time creating a minimal hindrance to the transport of metal ions and small organic compounds within the membranes.

Polymers that make up the skeleton of a PIM are thermoplastic [25]. They consist of linear polymer strands and because there are no cross-links between these strands, they can be dissolved in a suitable organic solvent, where the polymer strands become separated. The mechanical strength of a thermoplastic thin film membrane is a combination of intermolecular forces and the process of entanglement [26]. The former determines the flexibility of the material with high intermolecular forces resulting in a rigid membrane. The latter is the result of random diffusion

of the flexible polymer strands in a sol as the solvent evaporates [26]. Consequently, a very stable thin film can be formed, despite the absence of any intermolecular covalent bonds even though it should be noted that there is a disentanglement process occurring over a very long time scale. It is, however, essential that the molecular weight (MW) of the polymer used is larger than the critical entanglement molecular weight (MW_c) of that polymer. MW_c values together with the glass transition temperature (T_g) or the melting temperature (T_m) of several base polymers which have been used in PIMs are presented in Table 1. It is noteworthy that most, if not all, of the PIM studies available in the literature have used base polymers with a MW much higher than the corresponding MW_c values. Above these MW_c values, variation in the base polymer MW is speculated to exert a negligible influence on the membrane mechanical strength and performance as experimentally illustrated by Rais *et al.* [27].

[TALBE 1]

Although both PVC and CTA have been widely used to prepare PIMs, understanding the effect of the properties of these polymers on the performance of PIMs is still limited. CTA is a polar polymer with a number of hydroxyl and acetyl groups that are capable of forming highly oriented hydrogen bonding. In contrast, the C-Cl functional group in PVC is relatively polar and non-specific dispersion forces dominate the intermolecular interactions. Consequently, PVC is an amorphorous polymer with a small degree of crystallinity whereas CTA is often highly crystalline [28]. Furthermore, while CTA can be slightly hydrated [29], PVC is virtually not. This hydration characteristic of CTA and other cellulose derivatives makes them prone to hydrolysis, particularly in an acidic environment [24, 30]. The polarity and crystalline nature of the CTA polymer may render it incompatible with high concentrations of hydrophobic non-polar carriers. For example, Gherrou *et al.* [13] reported the formation of crystalline layers of crown ether within the CTA domain at a sufficiently high crown ether concentration. As a result, metal ion transport at such a high carrier concentration becomes ineffective [13]. However, it is noteworthy that the excellent mechanical strength of CTA is mostly attributed to its crystalline domain [28]. In addition, cellulose-based polymers are highly infusible [28], which makes them particularly useful for PIM applications.

While the base polymers merely provide mechanical support to the membrane, their bulk properties appear to be an important factor in governing metal ion transport through the

membrane. To date, it is not possible to accurately predict the bulk properties of a polymer based on a finite set of physical parameters. However, the glass transition temperature (T_g) for an amorphorous polymer or the melting temperature (T_m) for a crystalline polymer are often used to characterise the inherent polymer flexibility and its microstructural characteristics. It should be pointed out that both amorphorous and crystalline domains exist in any thermoplastic polymer. Below the glass transition temperature (T_g), the polymer is rigid and glassy and individual polymer strands are unable to change their conformations. Since this condition is thought to be unfavorable for metal ion transport in membranes, plasticizers are often added to the polymer to lower its T_g value and create more flexible and less brittle membranes. In fact, in a pure polymer without a plasticizer, the T_g or T_m value is usually much higher then room temperature (Table 1). Consequently, all PIMs reported in the literature contain some form of plasticizer unless the carrier itself can also act as a plasticizer. The significance of plasticizers in enhancing metal ion fluxes is discussed in Section 4.

3   CARRIERS

Transport in PIMs is accomplished by a carrier that is essentially a complexing agent or an ion-exchanger. The complex or ion pair formed between the metal ion and the carrier is solubilized in the membrane and facilitates metal ion transport across the membrane. The well known classes of solvent extraction reagents namely basic, acidic and chelating, neutral or solvating, and macrocyclic and macromolecular have all been studied in PIMs. The types of carriers used in PIM research as reported in the literature along with the target metal ions or organic solutes are summarized in Table 2.

[TABLE 2]

Much of the research on PIMs has been conducted using commercially available solvent extraction reagents as carriers although some papers report on the use of newly synthesized reagents. However, in most cases the physicochemical properties of these new compounds are not well documented. The chemical reactions that are involved in the extraction and stripping of target solutes using PIMs are essentially the same as for the corresponding solvent extraction systems. However, the essential difference between the two systems is associated with the transport of the target solutes through the membrane and it is this aspect that has formed the focus

of much of the research on PIMs. The main objective of PIM research is to maximize the membrane fluxes whilst retaining the extraction efficiency and selectivity of the corresponding solvent extraction system.

The actual transport phenomena in PIMs and SLMs are, however, quite complex and can be strongly influenced by both the physicochemical properties of the carrier and the target solute and to a lesser extent by the chemical composition of the membrane phase as well as the source and receiving solutions. Although several dedicated investigations have discussed the significance of these physicochemical properties [31-34], more research is still needed to elucidate the intricate relationships between these factors and the membrane permeability and selectivity. Understanding these relationships is particularly important given the diversity of carriers being studied which have significant differences in their physicochemical properties and transport modes. It is noteworthy that while there are a number of commercial carriers available, there are many more that are being synthesized and reported. Basic, acidic and solvating carriers are common reagents in solvent extraction and have been extensively studied and used on a large industrial scale in many hydrometallurgy applications [35-37]. Macrocyclic and macromolecular compounds are also of particular interest to many PIM researchers due to their specific host-guest complexation regimes which often result in excellent separation selectivity [38]. They can, however, be quite expensive for large scale applications and their environmental implications as well as many other characteristics remain unknown at this stage. Carriers in this group have been used in almost half of the PIM investigations reported to date in the literature (Table 2). Furthermore, macrocyclic and macromolecular compounds, unlike other carriers, have been shown to be useful for the separation of the alkali metals.

In addition to membrane selectivity, transport efficiency is another critical consideration for PIMs. It can be expected that the molecular structure of the carrier can markedly influence the rate of transport of the target solutes across the membrane. Walkowiak *et al.* [33] studied the transport of alkali metal cations across PIMs containing a sym-(alkyl)-dibenzo-16-crown-5-oxyacetic acid with side arms of different alkyl chain lengths geminally attached to the lariat ether as the carrier. Maximal flux was found when the alkyl side arm contained 9 carbon atoms with considerably lower transport efficiency when the alkyl chain was longer or shorter [33]. In another study, Aguilar *et al.* [32] demonstrated that both membrane selectivity and transport

efficiency could be optimised by designing a macrocyclic carrier with a careful combination of ring size and substituent groups.

Due to the lack of experimental data, it is currently not possible to correlate in a systematic way the selectivity and transport efficiency with the carrier properties, although some important observations have been established. For example, basic carriers with a lower basicity constant have been reported to have a poorer selectivity but higher transport efficiency [39]. It is noteworthy that different types of carriers are expected to exhibit considerably different transport efficiencies because of differences in their complexation mechanisms.

The carrier molecular structure and the chemistry involved in the complexation and transport processes are amongst the most important factors governing the membrane selectivity. It has been shown that the carrier molecular structures can be tailored to achieve a specific selectivity. For example, hydrophilic diazadibenzocrown ether was reported to have a higher selectivity for Pb(II) over Cd(II) and Zn(II) than a more hydrophobic derivative [32]. Basic carriers with a higher basicity constant were also reported to have a better selectivity for Cr(VI) over Zn(II) and Cd(II) [39]. Basic and neutral carriers often exhibit low selectivity for metals. The corresponding selectivity constants varies within only about two orders of magnitude [33, 39]. The metal ion reacts with the former via an ion-pair mechanism and with the latter via a solvating mechanism [40]. Both of these mechanisms are governed by electrostatic interactions and are non-specific in nature. The selectivity of acidic carriers is also relatively low and is normally controlled by pH [41, 42]. In contrast, certain chelating carriers can offer a much better selectivity due to their specific and conformational interactions with metal ions [42, 43]. PIMs using chelating agents as the carrier can selectively transport the target metal ions [41, 43] whilst the flux of other metal ions is virtually zero. Generally, excellent selectivity can be achieved with macrocyclic and macromolecular carriers, although it may vary significantly depending on their chemical structures [38].

4   PLASTICIZERS

4.1 The role of plasticizers

Strong intermolecular forces between polar groups of the polymer molecules often result in a brittle and rigid thin film, unsuitable for membrane extraction applications. This is because the

individual molecular chains are held together by a combination of various types of attractive forces. Amongst them, van der Waals forces are abundant but are weak and non-specific, while polar interactions are much stronger but can only occur at polar centers of the molecule [44]. The latter often result in a rigid non-flexible thin film with a 3-dimensional structure within its polymeric matrix [28, 44]. This 3-dimensional structure rigidity is, however, unfavourable for a diffusive flux of material within the polymer matrix [28]. Consequently, plasticizers are often used to increase the metal species flux as well as the membrane softness and flexibility. The role of a plasticizer is to penetrate between polymer molecules and "neutralize" the polar groups of the polymer with its own polar groups or to merely increase the distance between the polymer molecules and hence reduce the strength of the intermolecular forces [44].

While there is a large number of commercially available plasticizers, few of them have been tested for applications in PIMs. Amongst them, 2-nitrophenyl octyl ether (2-NPOE) and 2-nitrophenyl pentyl ether (2-NPPE) have been used in the majority of successful PIM studies currently available. The molecular structures of several examples of plasticizers commonly studied with PIMs are shown in Figure 1. Most of these plasticizers seem to have been chosen because of their application in ISE membranes rather than because of their commercial availability at low cost or because of their potential industrial applications.

[FIGURE 1]

As can be seen in Figure 1, plasticizers are generally organic compounds containing a hydrophobic alkyl backbone with one or several highly solvating polar groups. The former governs the compatibility of the plasticizer with the membrane while the latter interact with the polar groups of the base polymer and hence "neutralize" them. Therefore, a balance between the polar and non-polar portions of the plasticizer molecule is an important factor as has been illustrated in an early study by Sugiura [45]. In this study, lanthanide ion flux was evaluated with membranes made with polyoxyethylene alkyl ethers of different alkyl chain length and different numbers of polar oxyethylene groups. The results indicate that the optimum number of carbon atoms in the alkyl chain is 12 and that of the polar groups is 2 or 3 in this homologous series. An increase in the length of the alkyl chain results in a more hydrophobic, viscous plasticizer that eventually suppresses the polar properties of the plasticizer. In contrast, an increase in the

number of polar groups decreases the viscosity and increases the hydrophilicity of the plasticizer, which eventually renders it unusable.

Given their vital role in the plastics industry, plasticizers have been the subject of extensive scientific investigations for many decades [44]. Although findings resulting from such investigations may also to some extent be applicable to PIMs, many aspects of the plasticization process remain poorly understood. The relationship between the membrane performance and plasticizer concentration as well as the physicochemical characteristics of the plasticizers is complex and to a large part remains poorly understood. This is further complicated by the large number of essential properties often required of a plasticizer. Notable amongst these are a good compatibility with the base polymer, low volatility, low viscosity, high dielectric constant, good resistance to migration from the base polymer, low cost and low toxicity. Nevertheless, considerable effort has been made to elucidate the influence of the plasticizer on the membrane performance. Results reported in such studies underline the vital role of the plasticizer as a key ingredient of PIMs. It is noteworthy that several carriers such as quaternary ammonium salts and phosphoric acid esters can also play the role of a plasticizer. Consequently in such cases, no additional plasticizers may be necessary [6, 7, 21, 46, 47]. The influence of the plasticizer concentration and physicochemical characteristics on membrane performance is discussed below.

4.2 Plasticizer concentration

Low plasticizer concentration is undesirable since it may cause the membrane to become more rigid and brittle due to a phenomenon commonly referred to as the "anti-plasticizing" effect [44]. The minimum plasticizer concentration varies widely depending on both the plasticizer and the base polymer. For PVC, this concentration can be in a range of up to 20% (w/w). In a pioneering paper, Barshtein and Kotlyarevskii [48, 49] suggested that it was possible to determine for a given plasticizer the amount necessary for all polar groups on the polymer backbone to be neutralized or shielded from each other by a monolayer of the plasticizer. This later became a commonly used parameter in the plastics industry, often denoted as phr_{min} (parts of plasticizer per 100 parts of polymer by mass). The phr_{min} depends on the molecular weight (MW) of the plasticizer and the molecular weight of one helical unit of the polymer. For a PVC membrane, the molecular weight of one helical unit is 875 g/mol and phr_{min} can be calculated as:

$$phr_{\min} = \frac{MW \quad of \quad plasticizer}{875} \times 100 \qquad (1)$$

This expression is particularly useful to determine a suitable plasticizer concentration for ISE membranes using PVC as the base polymer. In a series of investigations, where the mechanical properties and dielectric characteristics of plasticized PVC electrode membranes were systematically examined using several plasticizers, Gibbons and Kusy [50-52] demonstrated that membrane performance could indeed be improved by using a plasticizer concentration closer to its $phr_{\min}$ value. This is much smaller than the empirical amount (2 parts plasticizer per one part polymer) commonly used in ISE membranes, which has been proven to be rather excessive.

In fact, excessive plasticizer concentration is problematic because the excess plasticizer could migrate or exude to the membrane/aqueous interface and form a film on the membrane surface, which would create an additional barrier to the transport of metal ions across the membrane. Exudation depends on the compatibility between the plasticizer and the base polymer and above the compatible concentration level exudation becomes more severe [29]. Furthermore, excessive plasticizer can significantly reduce the thin film mechanical strength, hence rendering it unusable in a practical situation. Several studies reported an increase in metal ion transport as the plasticizer concentration increased [10, 53, 54]. However, when considering a wider concentration range, it appears that there exists an optimum plasticizer concentration at which a maximum metal ion flux occurs and beyond that, the flux starts to decrease. In an early investigation, Sugiura [45] observed that the lanthanide ion flux through a CTA membrane increased to an optimum value then decreased as the plasticizer concentration increased from 0 to 2 M. Although a plausible explanation for this observation was not given, it is consistent with similar observations in recent studies by Fontas *et al.* [9] and de Gyves *et al.* [43]. In the latter study, the permeability of Cu(II) as a function of the plasticizer tri-n-butoxyethyl phosphate (TBEP) concentration follows a similar trend (Figure 2) to the curve reported by Sugiura [45]. The authors speculated that the decrease in Cu(II) permeability as the plasticizer concentration exceeded the optimum point was attributed to an increase in viscosity, which was unfavorable for the transport of Cu(II) [43]. This explanation, however, contradicts the fact that beyond the anti-plasticizing range, plasticizer addition always results in a lower T_g and hence a less viscous medium.

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[FIGURE 2]

4.3 Plasticizer viscosity

Metal ion transport through PIMs is accomplished by diffusion, which follows the Stokes-Einstein relationship [55]. It is therefore not surprising that the viscosity of the plasticizer is an important parameter, governing the rate of transport in PIMs. Kozlowski and Walkowiak [39] reported a linear correlation between the plasticizer viscosity and the chromium ion flux through both PVC and CTA membranes containing tri-n-octylamine (TOA) as the carrier. This is consistent with the observation by Scindia *et al.* [55] who also investigated the chromium ion flux as a function of plasticizer viscosity. These results are presented in Figure 3. A similar correlation can also be inferred from a study by Sugiura [56], where the fluxes of zinc across CTA membranes prepared from twelve different plasticizers were reported. However, it is notable from Figure 3b that the use of 2-NPOE results in a higher chromium flux than that of the other plasticizers even though one of them, tris(2-ethylhexyl)phosphate (T2EHP), has a similar viscosity. On the basis of the Stokes-Einstein relationship alone this is an unexpected result and the authors point to the fact that these two plasticizers have a considerable difference in their dielectric constants. The dielectric constants are 24 and 4.8 for 2-NPOE and T2EHP, respectively. This argument is supported by an independent study by Mohapatra *et al.* [54] who also investigated the influence of these two plasticizers on Sr(II) transport through CTA membranes.

[FIGURE 3]

4.4 Dielectric constant

It appears in addition to the viscosity that the dielectric constant of the plasticizer plays an important role in the diffusion process. In fact, the dependence of copper ion transport on plasticizer concentration as reported in Figure 2 can possibly be explained by the dielectric constant effect. In high dielectric constant media, ion pairs can dissociate more readily [57]. The individual ions have a higher diffusion coefficient than a neutral and bulky ion pair consisting of the target solute and the carrier [57]. In addition, this could also allow for ions to relocate more readily between active sites of the neighbouring fixed (or partially mobile) carriers. The detail of this fixed site jumping mechanism is discussed in Section 7.2. Kozlowski and Walkowiak [58]

have reported a characteristic correlation between the chromium ion flux and the dielectric constant of the plasticizer. Furthermore, the curve reported previously in Figure 2 resembles very well the dependence of the thin film dielectric constant on the plasticizer concentration, which also takes the shape of a convex curve [29, 44]. Several other researchers have also attributed the success of nitrophenyl alkyl ether plasticizers in PIMs to their high dielectric constants in addition to their relatively low viscosities [9, 54, 56].

5 MEMBRANE CHARACTERISTICS

5.1 Morphology

One important aspect of PIMs is the microstructure of the membrane materials, which determines the distribution of carriers in the polymer matrix and ultimately affects the membrane transport efficiency. Consequently, considerable research effort has been devoted to clarifying this issue. While a variety of surface characterization techniques have been employed in these studies, scanning electron microscopy (SEM) and atomic force microscopy (AFM) have been the most frequently used. Results obtained from SEM and AFM studies consistently indicate a remarkable influence of the polymeric composition on the membrane morphology.

Arous *et al.* [14] reported distinct differences between pure CTA membranes, plasticized CTA membranes without any carriers and plasticized CTA membranes with different macrocyclic carriers (Figure 4). SEM pictures of a pure CTA membrane revealed a highly porous polymer matrix with a relatively uniform pore size in the sub-micrometer range, typical of that for filtration membranes made of cellulose acetate. These pores vanished and a dense membrane was formed as the plasticizer 2-NPOE was added. The addition of macrocyclic carriers resulted in a thin film with distinctive separate layers. In the case of dibenzo 18-crown-6 (DB18C6) as the carrier, a well orientated fibrous structure of sub-micrometer size was clearly visible in the SEM image. The formation of multilayers at high crown ether concentrations has also been reported by other researchers who have observed poor metal ion transport associated with this morphology [10, 13]. This effect was attributed to the discrete distribution of carriers within the membrane polymer matrix [10, 13, 14]. This possibly reflects the high degree of crystallization of both CTA and crown ethers as discussed previously in Section 2.

[FIGURE 4]

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Xu *et al.* [59] studied the morphology of PVC/Aliquat 336 membranes at various Aliquat 336 concentrations. In contrast to the phenomena reported above, PVC membranes with a low concentration of the Aliquat 336 carrier were characterized as dense thin films with no apparent porosity. As the concentration of Aliquat 336 increased above 40% (w/w), the authors [59] reported a clear porous membrane structure with irregular shape pores and pore sizes of a few micrometers or less. It was speculated that this transformation in the interior structure could explain the apparent increase in metal ion transport through the membranes reported by several other studies [6, 60] when the Aliquat 336 concentration reached 40% (w/w). The authors, however, cautioned that these SEM results did not provide direct evidence as to whether these micro pores were previously filled with Aliquat 336 nor did they provide any evidence of the existence of micro channels of Aliquat 336 within the membrane polymer matrix [59]. It is noteworthy that membrane samples must be dry and coated with a thin layer of conductive material such as gold, chromium or carbon prior to SEM analysis. Moreover, due to a relatively low resolution, it is often difficult to discern features at the nanometer scale or smaller. For this reason, AFM is often employed in conjunction with SEM to improve resolution.

Several studies using AFM have been reported and the results are in good agreement with those obtained in SEM studies. Because PIMs are usually cast on a glass surface, the morphology of the membrane surface on the glass side can be quite different to that of the membrane surface exposed to air. Wang *et al.* [6] reported a smoother surface at the glass interface when they examined the surface morphology of PVC/Aliquat 336 membranes. This difference is however alleviated as the concentration of Aliquat 336 increases above 50% (w/w). Given that Aliquat 336 can play the role of a plasticizer and the fact that Aliquat 336 preferentially migrates to the membrane/air surface, results reported in their studies suggest a possible influence of the plasticizer on the membrane surface roughness. This is consistent with studies by Walkowiak *et al.* [33] and Kozlowski and Walkowiak [58], in which a marked difference was shown in the surface roughness of CTA/TOA membranes with and without a plasticizer. A combination of CTA and TOA resulted in a relatively smooth membrane surface while addition of the plasticizer 2-NPPE dramatically increased the membrane surface roughness. In another study, Wang and Shen [61] examined the surface topography of PVC/Aliquat 366 membranes before and after extraction experiments with Cu(II) as the target metal ion. Based on AFM images, they reported a slight increase in the membrane surface roughness after a 2 week exposure to a Cu(II) solution.

The authors attributed this to the redistribution of the carrier within the membrane polymer matrix. However, values of the surface roughness were not reported in this study.

Although both SEM and AFM techniques are versatile and can provide good visual confirmation of the membrane surface and to some degree the membrane interior structure, to date, studies employing these techniques have not been able to clearly elucidate the distribution of carrier and plasticizer within the membrane. Consequently, more advanced material characterization techniques have been attempted. Tripathi *et al.* [62] examined the distribution of carrier within the membrane by pre-extracting Cs^+ and Ag(I) into the membrane and then mapping the distribution of these high atomic mass metal ions using the Rutherford backscattering spectrometry (RBS) technique. Their results suggested a uniform distribution of organic carrier at a microscopic scale. Although this conclusion is in contradiction to the hypothesis about micro channels filled with carrier outlined above, it is prudent to note that evidence available to date remains too limited to conclusively eliminate this speculation.

5.2 Permeability

The rate of metal ion transport through PIMs is arguably a decisive factor influencing the commercialization of this technology. Not surprisingly, most of the PIM studies available to date have reported on this crucial parameter, although often not in a consistent form. While permeate fluxes up to several μmol m^{-2} s^{-1} can be commonly found in studies cited in this review, a permeate flux as high as 45 μmol m^{-2} s^{-1} for Cr(VI) through a CTA membrane containing TOA and plasticized with 2-NPPE ether has been reported [39]. In most cases, the permeate flux for PIMs is marginally lower than that for SLMs. Although the actual transport mechanisms can be quite different, transport in both PIMs and SLMs is governed by a number of factors including the membrane morphology, membrane composition, solution chemistry in the source and receiving phases as well as the temperature. Because many aspects of PIMs remain unclear at this stage, interpretation and comparison of the current literature data will require a careful consideration of the experimental conditions involved. As we delineate in the section below, a comprehensive understanding of the influence of these factors on the membrane transport rate is particularly important for the design and implementation of PIMs.

PIMs and SLMs are distinctively different in their interior structures as well as in their surface morphologies. Because SLMs consist of a porous supporting layer impregnated with carrier and diluent, metal ions can be transported through a network of fluid-filled micro channels. Consequently, transport is subject to the tortuosity of this network and is limited by the available surface area. In contrast, PIMs can be viewed as non-porous and as discussed in the previous section, there is no convincing evidence of a micro channel network in which metal ion transport can take place. As a result, the whole membrane is available for transport. Although the diffusion coefficients of the target solutes in PIMs are generally one or two orders of magnitude lower than those in SLMs, several cases of comparable [9, 11, 55] or even higher diffusion coefficient values [5, 19, 20] in PIMs have been reported when both types of membranes have been investigated under similar extraction conditions. Taking account of the fact that transport can be further improved by preparing a much thinner membrane, PIMs have the potential to offer a very competitive transport rates.

Transport through PIMs can be strongly influenced by the membrane morphology. In certain cases, a high concentration of a crown ether carrier may result in a crystalline thin film characterized by distinctively separate layers [10, 13, 14]. This morphology was found to be unfavourable for transport in PIMs and was often associated with poor target solute fluxes [10, 13, 14]. The membrane surface roughness is also an important morphology parameter. Wang *et al.* [6] reported a slight but discernible increase in metal ion transport when the rougher side of the PIMs was exposed to the source solution. This is consistent with other studies, where a positive correlation between metal ion permeability and the membrane surface roughness was also observed [55, 58]. However, it should be noted that an increase in surface roughness can be attributed to the addition of a plasticizer and therefore the membrane surface roughness can also be related to the membrane composition.

Results from several PIM studies indicate a considerable influence of the membrane composition on the transport rate of the target solutes. However, the data remain quite scattered and the variation in permeate flux following any changes in the membrane composition depends quite substantially on the characteristics of each constituent involved. As discussed previously, there exists an optimum concentration of plasticizer concentration at which a maximum rate of transport is achieved. Similar observations for the carrier concentration have also been reported

for several macrocyclic carriers [10, 13, 14, 63], which is possibly due to their high hydrophobicity and crystallization capacity. In contrast, other researchers reported an increase in the permeate flux with increasing concentration of TOA [64], lasalocid [11] and Aliquat 336 [9] in CTA-based membrane. In the first two cases, the permeate flux approached a plateau value, while in the latter case, a linear increase in permeate flux was reported. In another study, Kozlowski and Walkowiak [58] compared the transport efficiency between CTA-based and PVC-based membranes containing a relatively high TOA concentration in the range from 0.9 to 1.45 M (based on plasticizer volume) and plasticized with 2-NPPE. At 0.9 M TOA, the CTA-based membrane produced a higher permeate flux than that of PVC. However, the Cr(VI) permeate flux of the PVC-based membrane increased at a considerably higher rate than that of CTA as the TOA concentration in the membrane increased. Consequently, at a TOA concentration of 1.45 M, the permeate flux of both membranes was quite comparable. The authors attributed this to the hydrophobicity difference between CTA and PVC and argued that a high concentration of carrier was needed for a high degree of compatibility within the membrane polymer matrix. The results summarized here emphasize the significance and complexity of this issue, which will remain an important topic for further research in the years to come.

The driving force in a PIM system is principally the concentration gradient across the membrane of either the metallic species itself or another species known as the coupled-transport ion [12, 58, 65-68]. Consequently, the ionic compositions of both the source and the stripping solutions play a vital role in governing the metal ion transport process. Kozlowski and Walkowiak [58] studied the effect of the source solution pH on Cr(VI) transport across a CTA-based membrane containing TOA and 2-NPPE as plasticizer. They observed that the Cr(VI) permeate flux increased as the pH of the source phase decreased. In this particular case, the difference in pH between the source and receiving solutions produces a proton concentration gradient across the membrane and consequently, the transport of protons through the membrane results in an uphill transport of $HCrO_4^-$ in order to maintain electroneutrality in both liquid phases.

The driving force in a PIM system can also be influenced by the mobility of the coupled transport ion within the organic phase of the membrane [68]. In general, the efficiency of the coupled transport ions increases in the opposite order of their hydrated radii as follows:

$$F^- < Cl^- < Br^- < NO_3^- < SCN^- < I^- < IO_4^- < ClO_4^- < picrate^-$$

This is evidenced in several studies where transport experiments were carried out with several different coupled transport ions under a similar concentration gradient [12, 65-68]. In these studies, better transport of the target metal ion was consistently reported when lower hydrated energy ions were employed as the driving ion. Ions are hydrated in aqueous solutions and because the membrane phase is hydrophobic, transport of such hydrated ions is thought to be restricted, depending on their hydration energy or the number of attached water molecules [12]. Similarly, Levitskaia *et al.* [68] demonstrated that permeability can be predicted based on the Gibbs energy of ion partitioning between the source and membrane phases, which is essentially related to the hydrated energy of the ion. However, it must be emphasized that most if not all of the coupled transport ions can act as complexing agents. Consequently, the phenomena discussed here are further complicated by the fact that the types of metallic species present are often concentration dependent [69]. In addition, transport of the target metal ion may also be influenced by the competition with other ions present in the aqueous phase. Wionczyk *et al.* [70] found that the effect of H_2SO_4 concentration in the source solution on Cr(VI) transport across a CTA-based membrane containing a basic carrier and plasticized with 2-NPOE can be described by a convex parabolic relationship. This appears to contradict the observation reported by Kozlowski and Walkowiak [58] discussed previously because the driving force is also the proton concentration gradient. However, according to Wionczyk *et al.* [70] the sulfate ion competed with the chromate ion for transport and as a result Cr(VI) transport started to decrease at a sufficiently high sulfate ion concentration.

5.3 Selectivity

Selectivity is undoubtedly an important issue in the implementation of PIMs for a number of reasons. In environmental applications, the concentration of the target metal ions can be quite low and reasonably high selectivity is essential for an effective treatment. In hydrometallurgical applications, purity is a key factor in determining the commodity price of a given metal, particularly for those of high value [71]. Impurities can also affect downstream processing such as electrowinning operations where only a certain level of impurity can be tolerated [72].

In a solvent extraction process, because the selectivity between two metal ions depends almost entirely on the difference in lipophilicity of the metal complexes provided that complexation can be formed with both ions. Consequently, the selectivity is usually low and numerous extraction

stages are often required to increase the selectivity [73]. This flexibility in process design is, however, not available in membrane extraction systems. Fortunately, data available in the SLM and PIM literature consistently indicate that a membrane extraction process can achieve an appreciably higher selectivity than that encountered in solvent extraction although the underlying mechanisms for this phenomenon have not been adequately studied to date. The discussion below is restricted to selectivity amongst metal ions involving the same complexation mechanisms with the carriers used.

It is important to point out two fundamental differences between solvent extraction and PIMs as well as other liquid membranes used for separation [41, 69]. Firstly, while there can be an excess of extractant in solvent extraction, reactive sites or the availability of carrier in a PIM are restricted. Secondly, extraction and back-extraction in PIMs occur simultaneously as opposed to their consecutive arrangement in solvent extraction. In fact, it would be wrong to view the mass transfer phenomena in PIMs (or in fact membrane extraction in general) as analogs of those in solvent extraction [69]. In a recent study by Gyves et $al.$ [43] only Cu(II) transport was observed with a PIM prepared with LIX$^{®}$ 84-I, CTA, and tris(2-n-butoxyethyl) phosphate when the source solution contained a tenfold excess of Fe(III) and Zn(II). The source solution in this experiment was adjusted to pH 5.0, at which pH considerable extraction of Fe(III) and Zn(II) would occur based on the extraction isotherm for LIX$^{®}$ 84-I which can be found in the solvent extraction literature. This is consistent with observations reported in two separate investigations by Ulewicz et $al.$ [42] and Aquilar et $al.$ [41]. In the former study, the selectivity for Pb(II) over Cd(II) was 140 with PIMs using Kelex 100, significantly higher than the theoretical selectivity (c.a. threefold) obtained in a single stage solvent extraction process at the same extraction pH. In the latter study [41], when employing PIMs consisting of CTA, 2-NPOE, and di(2-ethylhexyl) phosphoric acid (D2EHPA), the selectivity for Zn(II), Cu(II) and Co(II) was considerably different despite the fact that solvent extraction isotherms indicated that their extraction coefficients would be comparable at the same pH used in the PIM extraction experiments. Further data showing similar trends have also been reported, although it is not possible to make a direct comparison to a corresponding solvent extraction process in these studies [32, 33, 39, 74, 75]. Such data underscore fundamental differences in transport mechanisms between solvent and membrane extraction processes. Aquilar et $al.$ [41] suggested a direct competition for active transport sites in PIMs due to their limited availability. However, to date, no attempts have been

made to relate complexation stability constants and selectivities amongst competing metal ions. Furthermore, it has also been proposed that the high selectivity observed in PIMs could possibly be attributed to differences in complexation kinetics [69]. Given the difference in structure between PIMs and SLMs, they are expected to exhibit different selectivities under similar experimental conditions. For example, PIMs were reported to have a better selectivity for Pt(IV) over Pd(II) than that of SLMs when exposed to identical source and receiving solution conditions [9]. Unfortunately, further data from the literature to substantiate this premise are not available at this stage. It is prudent to note that the discussion presented here remains quite speculative because of the lack of comprehensive data related to these important issues. However, this fact clearly highlights the need for further fundamental research to fully understand the transport phenomena observed with PIMs.

5.4 Stability

A major reason for the limited use of SLMs on a large industrial scale is the membrane stability or lifetime, which, in general, is far too low for commercial applications [1, 2, 76-78]. This is possibly a major motivation for the development of PIMs. In SLMs, the capillary force or interfacial tension is responsible for the binding of the membrane liquid phase to the supporting pores [76, 77]. This form of adhesive force is, however, weak and membrane breakdown can easily occur via several destabilizing mechanisms including lateral shear forces, emulsion formation and leaching of the membrane liquid phase to the aqueous phase, which can be worsened by an osmotic flow [76, 77]. In contrast, in PIMs, as we have discussed previously, the carrier, plasticizer and base membrane are well integrated into a relatively homogeneous thin film. Although several FTIR studies [10, 13, 14] have revealed no signs of covalent bond formation between the carrier, plasticizer and the base membrane skeleton, it is most likely that they are bound to one another by a form of secondary bonding such as hydrophobic, Van der Waals or hydrogen bonds. These secondary bonds are much stronger than interfacial tension or capillary forces. Consequently, PIMs are considerably more stable than SLMs as clearly evidenced in the PIM studies discussed in this review, where a comparison of the stability between these two types of membranes has been a focus of the work [11, 19, 20, 55]. Kim *et al.* [19, 20] have investigated the stability of PIMs and SLMs under similar experimental conditions. They reported no flux decline or evidence of material losses within 15 days of continuous

transport experiments with PIMs containing CTA, 2-NPOE and macrocyclic carriers. In contrast, leakage of the organic material became clearly evident in the SLM counterparts after 48 hours agitation in aqueous solutions. The superior stability of PIMs over SLMs has also been reported for membranes using Aliquat 336 as carrier [55]. Under similar experimental conditions, stable performance of PIMs for 30 days was recorded while organic material leakage from SLMs was reported after only 7 days. Table 3 summarizes the results from several PIM studies, in which membrane lifetimes have been reported. It is noteworthy that while leakage of the membrane liquid is usually used to assess the stability of a SLM, the membrane lifetime reported in Table 3 for PIMs was evaluated using flux stability because no carrier or plasticizer losses could be observed in most of these studies.

In general, PIMs are highly resistant to carrier and plasticizer leakage. This has probably prompted a recent investigation focusing instead on the hydrolysis of base polymers under extreme conditions. Gardner *et al.* [24] have studied the stability of PIMs prepared from a crown ether, 2-NPOE and various cellulose polymer derivatives including cellulose triacetate (CTA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB) and cellulose tributyrate (CTB). The authors have consistently demonstrated that durability of the base polymer increases as longer alkyl chains are added to the cellulose glucoside backbone units. However, the membrane permeability was found to decrease proportionally. Furthermore, they reported that the membranes broke down quickly under caustic conditions (3 M KOH) while a much longer lifetime was reported under acidic conditions (3 M HNO_3). Hydrolysis of the CTA based membrane occurred within 2.9 days under caustic conditions. Under acidic conditions, the CTA based membrane was stable for 12.3 days. In another study [30], it has also been reported that the CTA based membranes quickly decomposed when the source phase contained 1 M LiOH. Stability of PVC-based PIMs has not been systematically studied. However, on the basis of its polymeric structure, PVC based membranes are expected to be more resistant to hydrolysis under extreme caustic or acidic conditions.

[TABLE 3]

Nevertheless, it is necessary to emphasize that carrier loss from PIMs under certain conditions has been reported in several studies [7, 31, 79]. Although PIMs are typically solid thin films, the carriers remain in a quasi-liquid state and are in contact with the aqueous phase on both the

source and receiving sides. Consequently, hydrophobicity and water solubility are probably amongst the most critical parameters governing the carrier leaching behavior [7, 30, 32]. Nazarenko and Lamb [31] reported a noticeable loss of the DC18C6 carrier from their CTA/2-NPOE-DNNS membranes. However, this problem was resolved by using a more hydrophobic carrier (t-buDC18C6) and the membranes remained stable after several weeks of experimentation [31]. Similarly, while a CTA based membrane containing 2-NPOE and 1,3 calix[4]arene-biscrown-6 became unstable after a few repetitive transport experiments, membrane lifetime under continuous operation of over a month was reported when the carrier was substituted with 1,3 bis(dodecyloxy)calix[4]arene-crown-6, which is more hydrophobic due to the addition of two dodecyl chains [30]. In fact, most of the leaching problems are associated with hydrophilic carriers with an octanol-water partitioning coefficient (log K_{ow}) of less than 5 [30, 32]. The hydrophobicity of the carrier and its water solubility can be strongly influenced by the solution chemistry of the aqueous phase. For example, β-diketone loss at a high source solution pH has been reported [79]. This is because β-diketones can dissociate at high pH and therefore become much more soluble in water [79]. Similarly, Argiropoulos *et al.* [7] reported considerable Aliquat 336 loss from a PVC-based membrane when the membrane was submerged in distilled water for 10 days. However, negligible Aliquat 336 loss (within 2.5% in 10 days) was observed when a 2.5 M HCl solution was used. The evidence reported in this study indicates a possible influence of the solution pH on the water solubility of Aliquat 336 and subsequently on the stability of the membranes using this carrier.

Of particular note is that macrocyclic and macromolecular carriers were used in all but one of the studies reported in Table 3. Further studies will be needed to evaluate the lifetime of membranes involving the use of other types of carriers, particularly those that are currently commercially available. While there is no universal benchmark for a satisfactory membrane lifetime, it is clear that lifetimes of PIMs will continue to be extended as additional base polymers, carriers and plasticizers are being investigated and as the operating conditions and the membrane composition are being optimized. Nevertheless, even with the current expected lifetime, it has been predicted that PIMs would be commercially useful in a range of niche applications in the near future [78].

6 EXTRACTION AND TRANSPORT STUDIES IN PIMs

To date, all research on PIMs has been conducted on a laboratory scale. For extraction studies, beaker experiments have been used where the PIM is immersed in a solution of the target species and samples of the solution are taken at various time intervals for analysis. Some extraction experiments have also been carried out in a two-compartment transport cell of a similar design to that used in a typical SLM experiment (Figure 5). However, this type of cell is more commonly used in transport studies. The transport process across PIMs involves essentially the exchanging of ionic species between these two compartments via the membrane phase which separates them. The overall transport process is quite similar for all four types of carriers. Uphill transport of the target solute across the membrane can be achieved with a suitable ionic composition in the source and receiving compartments. However, because of different complexation mechanisms involved, the transport characteristics and choices of the ionic compositions for both the source and receiving phases with respect to each type of carriers are distinctively different. This is evident in the following sections where the PIM studies reported to date are systematically reviewed and discussed on the basis of the carrier type.

[FIGURE 5]

6.1 Basic carriers

Basic carriers include high molecular mass amines, e.g. tri-n-octylamine (TOA). In addition, some weakly basic compounds such as alkyl derivatives of pyridine N oxides also belong to this group e.g. 4-(1'-n-tridecyl)pyridine N-oxide (TDPNO). A number of researchers [80-82] have classified fully substituted quaternary ammonium compounds (e.g. Aliquat 336) as basic carriers though they do not have a lone electron pair at the nitrogen atom. The reason for this classification, which is also used in the current review, is based on the similarity in the extraction mechanism involving amines and fully substituted quaternary ammonium compounds. Chemical structures of these basic carriers are shown in Figure 6.

[FIGURE 6]

In the case of fully substituted quaternary ammonium compounds, ~~which of course are not truly basic because there is not a lone pair of electrons on the nitrogen atom,~~ the carrier in the PIM

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reacts as an anion exchanger forming an ion-pair with a metal anion complex from the aqueous phase. While in the case of amines and the weak bases mentioned above, the carrier must be protonated first to react with the metal anion complex or react directly with a protonated metal anion complex [40]. In addition, amines can be used to extract simple mineral and organic acids as well as small saccharides [83-85]. With the exception of the saccharides that can form hydrogen bonds with the carrier via their hydroxyl groups, the extraction of the other solutes with amines takes place at a source solution pH below the pK_b value of the carrier.

Basic carriers have been used quite extensively in PIMs studies for the extraction and transport of precious and heavy metals (Table 2). The majority of these studies make use of the fact that such metals readily form anionic complexes with the chloride ion. While no PIMs containing basic carriers have been reported to date for the separation of actinides such as uranium and plutonium, it is noteworthy that these carrier reagents have been used quite extensively in solvent extraction for the separation of these metals [86].

Argiropoulos *et al.* [7] have studied the extraction of Au(III) from hydrochloric acid solutions using a PVC membrane containing Aliquat 336 chloride ($R_4N^+Cl^-$). For a membrane containing 50% (w/w) Aliquat 336, gold was completely extracted from a 2.5 M HCl solution containing 100 μg/l of gold within 75 h. The following reaction mechanism was proposed:

$$R_4N^+Cl^-_{mem} + AuCl^-_{4aq} \rightleftharpoons R_4N^+AuCl^-_{4mem} + Cl^-_{aq} \tag{2}$$
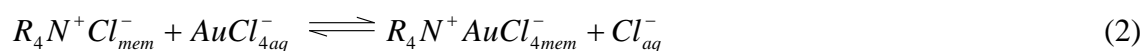
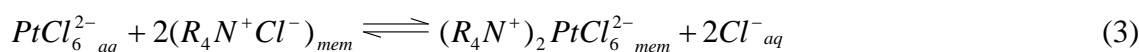where mem and aq refer to the membrane and aqueous phases, respectively.

Transport studies were carried out on this system using a two compartment cell with a solution of thiourea as the receiving phase. However, it was found that thiourea was transported to the source phase thus stopping the gold transport after 50% had been transported. The transport of thiourea using this membrane has been the subject of a separate study [87].

This system was aimed at the recovery of gold from electronic scrap and was tested on a sample of scrap containing 96% (w/w) copper, 0.13% (w/w) gold and a low concentration of iron. This was dissolved in Aqua Regia and the resulting solution diluted to give a HCl concentration of 2.5
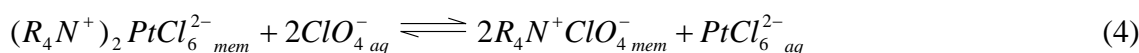
M. It was found that all the gold could be extracted by the membrane with a selectivity factor of 5×10^5 for gold over copper.

The transport of platinum(IV) has been studied by Fontas *et al.* [9] using a CTA membrane containing Aliquat 336 and 2-NPOE as plasticizer. The source phase consisted of Pt(IV) in 0.5 M NaCl at pH 2 and the receiving phase was 0.5 M NaClO$_4$ at pH 2. The authors proposed the following transport mechanism:

Source phase:

$$PtCl_6^{2-}{}_{aq} + 2(R_4N^+Cl^-)_{mem} \rightleftharpoons (R_4N^+)_2 PtCl_6^{2-}{}_{mem} + 2Cl^-{}_{aq} \tag{3}$$

Receiving phase:

$$(R_4N^+)_2 PtCl_6^{2-}{}_{mem} + 2ClO_4^-{}_{aq} \rightleftharpoons 2R_4N^+ClO_4^-{}_{mem} + PtCl_6^{2-}{}_{aq} \tag{4}$$

A suggestion was made that the driving force for the transport of Pt(IV) was provided by the high ClO$_4^-$ concentration gradient. However, this was not verified by analyzing the source solution for the perchlorate ion.

The authors also conducted a comparison between the PIM and the corresponding SLM. It was found that the flux of Pt(IV) for the PIM system exceeded that of the SLM when a certain threshold concentration (250 mM) of the carrier was reached in the PIM [9]. Further, in the case of the SLM there was no difference in selectivity between Pt(IV) and Pd(II) while the PIM showed higher selectivity for Pt(IV). This was explained on the basis of the higher hydrophobicity of the Pt complex compared to the Pd complex making the transport faster for Pt than for Pd in the PIM.

The extraction of Pd(II) from hydrochloric acid solutions has been studied by Kolev *et al.* [47] using PVC membranes containing up to 50% (w/w) Aliquat 336. It was found that the extraction equilibrium constant (K$_{ex}$) values for 40 and 50% (w/w) Aliquat 336 membranes were of the same order of magnitude as for the corresponding solvent extraction systems. Pd(II) was extracted faster than Au(III) and was preferentially extracted over Au(III), Cd(II) and Cu(II). At high Pd(II) loadings a brown precipitate formed at the membrane surface.

Wang *et al.* [6] have studied the extraction of Cd(II) and Cu(II) from 2 M hydrochloric acid solutions using a PVC-based membrane containing 30, 40 and 50% (w/w) Aliquat 336. The extraction of Cd(II) was found to be much higher than that for Cu(II) and the authors suggested this was because the $CdCl_3^-$ species was involved, which was present in higher concentrations than the $CuCl_3^-$ species. In 2 M HCl solution Cu(II) exists mainly as $CuCl_4^{2-}$. An important observation the authors made for this system was that the K_{ex} values for 30 and 40% (w/w) Aliquat 336 membranes were close to each other whereas for a 50% (w/w) membrane the K_{ex} value was more than double. They suggested that the properties of the membrane had altered when the Aliquat 336 concentration exceeded 40% (w/w). This effect is the subject of another paper by Xu *et al.* [59] and is discussed in Section 5.1 of this review. Wang *et al.* [6] have also studied the transport of Cd(II) and Cu(II) from HCl solutions to a receiving phase containing a much lower HCl concentration using a two compartment cell and have found that transport is faster for Cd(II) than for Cu(II) in keeping with the higher extraction constant for Cd(II).

Similar results showing the preferential transport of Cd(II) over Zn(II) from acid chloride solutions have been reported by Walkowiak *et al.* [33] and Kozlowski *et al.* [34, 88] for CTA-based PIMs containing TOA and the plasticizer 2-NPPE. They have also shown that the selectivity coefficients decrease as the HCl concentration in the source phase is increased. In these cases, ammonium or sodium acetate was used in the receiving phase. In one of these papers mentioned above [34], the initial fluxes for Cd(II) and Zn(II) have been calculated using the membrane containing TOA and another membrane containing the carrier 4-(1'-n-tridecyl)pyridine N-oxide (TDPNO). It was shown that the initial fluxes for TDPNO were higher than for TOA whereas the selectivity coefficients were higher for TOA.

The competitive transport of Cd(II) and Pb(II) using a CTA/NPOE–based PIM containing trioctylmethylammonium chloride (TOMAC) as carrier has been described by Hayashita [89]. This work reported that the selectivity depended on the membrane surface area. For a small surface area (0.8 cm^2), Cd(II) was transported preferentially, however for a large surface area (15 cm^2) this was reversed. Hayashita [89] explained this on the basis of accumulation of Cd(II) in the small surface area membrane that consumed most of the carrier thus inhibiting the transport of Pb(II). For the large surface area membrane containing a much larger amount of carrier, this did not occur and preferential transport of Pb(II) was observed.

Extensive research has been reported on the use of PIMs for the extraction and transport of Cr(VI) which is extremely toxic. Consequently, new methods for its removal from natural waters and from industrial effluents arising from electroplating and mining are of considerable interest. Cr(VI) in aqueous solutions at pH 2 exists as $HCrO_4^-$ and as $Cr_2O_7^{2-}$ at pH 8 and most papers on this subject involve the extraction and transport of the $HCrO_4^-$ species using basic extractants as discussed below.

Walkowiak *et al.* [33] have studied the transport of Cr(VI) through CTA-based membranes plasticized with 2-NPPE using a series of tertiary amines and Aliquat 336 as carriers. The source phase for this work was HCl at pH 2 and the receiving phase 0.1 M NaOH. It was found the flux decreased with an increase in the hydrocarbon chain length of the amines used with the highest flux being obtained for TOA. This was further confirmed by Kozlowski and Walkowiak [58] who showed that the flux decreased linearly with an increase in the log K_{ow} values of the tertiary amines. They reported that the flux for a similar PVC-based PIM was lower than for the CTA-based membrane and could be attributed to the fact that PVC was more hydrophobic than CTA. In their study, Walkowiak *et al.* [33] also investigated the competitive transport between Cr(VI) and Cr(III) using acidic chloride and sulfate solutions and the selectivity coefficient was found to be considerably higher for chloride than for sulfate.

Kozlowski and Walkowiak [64] have also proposed a method based on the use of a PIM of composition 41% (w/w) CTA, 23% (w/w) TOA and 36% (w/w) 2-NPPE for the removal of Cr(VI) from acidic chloride solutions according to the following reaction:

$$TOA_{mem} + H_{aq}^+ + HCrO_{4\ aq}^- \rightleftharpoons TOAH^+ HCrO_{4\ mem}^- \tag{5}$$

In another study Wionczyk *et al.* [70] have described the transport of Cr(VI) from a sulfuric acid solution into 0.1 M NaOH using a PIM similar to that used by Walkowiak *et al.* [33] but containing 4-(1'-n-tridecyl)pyridine N-oxide as the carrier. The actual membrane composition was 20% (w/w) CTA, 70% (w/w) 2-NPPE and 10% (w/w) TDPNO (0.5 M based on the plasticizer volume). It was found that the initial flux reached a maximum for 0.3 M sulfuric acid. They proposed the following transport mechanism, where both $HCrO_4^-$ and H^+ were concurrently transported to the receiving phase:

Source phase:

$$TDPNO_{mem} + HCrO_{4\ aq}^{-} + H_{aq}^{+} \rightleftharpoons TDPNOH^{+}HCrO_{4\ mem}^{-} \qquad (6)$$

Receiving phase:

$$TDPNOH^{+}HCrO_{4\ mem}^{-} + 2OH_{aq}^{-} \rightleftharpoons TDPNO_{mem} + CrO_{4\ aq}^{2-} + 2H_2O_{aq} \qquad (7)$$

Kozlowski *et al.* [34] have compared the Cr(VI) fluxes for CTA-based PIMs containing TOA and TDPNO with a source phase containing 0.5 M HCl and a receiving phase of 0.5 M sodium acetate (pH 8.0) and found a much larger flux for TDPNO (16.01 μmol m^{-2} s^{-1}) than for TOA (6.62 μmol m^{-2} s^{-1}). However, selectivity coefficients for Cr(VI) with respect to species such as Cd(II) and Zn(II) tend to be higher for TOA. The authors have suggested that the reason for this was associated with the higher basicity of TOA.

A recent paper by Scindia *et al.* [55] examined three types of membranes for Cr(VI) transport, a SLM, a pore-filled membrane (PFM) and CTA-based PIMs. Aliquat 336 was used as the carrier and various plasticizers were studied for the PIM. In this study, source phases at pH 2 (HCrO$_4^-$ transport) and pH 8 (Cr$_2$O$_7^{2-}$ transport) with 1 M sodium nitrate as the receiving phase were investigated. Coupled-diffusion with Cr(VI) being transported to the receiving phase and the nitrate ion to the source phase has been proposed as the transport mechanism. The authors presented IR spectral evidence that the HCrO$_4^-$ ion dimerizes to Cr$_2$O$_7^{2-}$ in the membrane phase. They suggested the PIM was effective for the recovery of Cr(VI) from municipal water and seawater.

Promising results have also been reported on the use of PIMs for the extraction and transport of organic species. Basic carriers were used in most of these studies. Smith and co-workers [83, 84] have investigated the facilitated non-competitive transport of glucose, fructose and sucrose by PIMs containing 20% (w/w) CTA, 40% (w/w) plasticizer (2-NPOE or TBEP) and 40% (w/w) carrier (various tetraalkylammonium salts). Permeate flux of the disaccharide sucrose was significantly lower than that of the monosaccharide glucose. The PVC/2-NPOE/TOMAC membrane also exhibited ~~a considerable~~ selectivity for fructose over glucose. When both the source and receiving solutions were buffered at pH 7.3 by using 100 mM sodium phosphate and

the source solution contained 300 mM saccharide, the permeate fluxes for fructose and glucose were reported to be 10 and 5.7 μmol m^{-2} s^{-1}, respectively. An improved fructose flux of 31.8 μmol m^{-2} s^{-1} was noted when using TBEP as plasticizer. Various anionic salts of TOMAC and other tetraalkylammonium salts were also investigated as likely carriers in alternate membranes [83]. Anion exchange was used to prepare the bromide, tetraphenylborate, 4-toluensulfonate, bis(2-ethylhexyl)phosphonate, 4-methylbenzoate and diphenylphosphinate salts of TOMAC [84]. The authors reported that the bromide salt outperformed the others, but still only returned a fructose flux of two-thirds of that for TOMAC chloride indicating that the carrier size played an important role in the rate of mass transfer. Of the other tetraalkylammonium salts tested, tetrahexylammonium chloride performed significantly better than tetrabutylammonium chloride, tridodecylmethylammonium chloride or tetraoctylphosphonium bromide, but, the fructose flux was still only one-third of that for TOMAC chloride. Notably, all alternate membranes tested exhibited a significant decline in fructose flux. Some combinations of carrier and plasticizer did not form a stable plastic membrane. All the original and alternate membranes tested exhibited a markedly better flux when TBEP was used, compared to 2-NPOE, as plasticizer, although, no explanation was offered for this observation. A fixed-site jumping mechanism was proposed for the facilitated membrane transport where the hydroxyl groups of the neutral carbohydrate were attracted to the "fixed" chloride ions of TOMAC [84]. This mechanism is explained in more detail in Section 7.2. Evidence to support this mechanism came from experiments that showed negligible transport at a carrier concentration of less that 20% (w/w). Transport rates increased exponentially above this value, referred to as the percolation threshold, as the carrier concentration was increased to a maximum of 50%. Carrier percolation thresholds were consistently observed for all the saccharides and carriers tested [83]. The decrease in carrier percolation threshold from 20% to 17% (w/w) TOMAC for the transport of sucrose compared to fructose was explained on the basis of solute size. Sucrose is the larger molecule it does not need the same extent of "close packing" of carrier molecules to initiate a solute jumping transport mechanism.

White *et al.* [83] have also studied the effect of the carrier structure on the transport mechanism. The cation content of the carrier was varied by changing the length of the alkyl chain from C_8H_{17} in TOMAC to $C_{12}H_{25}$ in tridodecylmethylammonium chloride (TDMAC). The anion content was further changed by preparing various phosphate and carboxylate analogues of TOMAC. An order

of magnitude decrease in glucose diffusion and flux resulted when TDMAC was used rather than TOMAC, with diffusion coefficients of 6×10^{-12} and 0.6×10^{-12} m^2 s^{-1} and flux values of 188 and 16 µmol m^{-2} s^{-1}, respectively [83]. These results indicate that saccharide diffusion is faster with a smaller carrier and imply that diffusion of the carrier is involved in the rate determining transport step [83].

All carriers examined gave similar extraction constants but substantially different diffusion coefficients for glucose and sucrose [83]. For example, when using TOMAC, extraction constants of 0.2 and 0.5 M^{-1} and diffusion coefficients of 6×10^{-12} and 0.7×10^{-12} m^2 s^{-1} for glucose and sucrose, respectively, were calculated [83]. The order of magnitude lower diffusion coefficients for the larger disaccharide sucrose compared to glucose, a monosaccharide, is consistent with diffusion of the saccharide being involved in the rate determining step in the membrane transport process.

The effect on saccharide diffusion by varying the size of the saccharide and of the cation and anion of the carrier indicates that the ion-pair carrier is mobile throughout the membrane. On the basis of these results, the authors proposed a mobile-site jumping transport mechanism [83]. A diffusion only transport mechanism of the saccharide-ion pair complex or of the saccharide ion does not take into account the observed percolation threshold at higher carrier concentration. Alternatively, a fixed-site transport mechanism involving the carrier ion-pair fixed and the saccharide jumping, or the carrier cation fixed and the saccharide-anion complex jumping would not be significantly affected by diffusion of either the anion or cation of the carrier. The experiments did not indicate the form in which the saccharide was transported, that is, whether the saccharide jumped to a carrier anion, or if a saccharide-anion complex jumped to a carrier cation. The authors proposed that saccharide molecules and carrier anions formed hydrogen bonded complexes that were then weakly associated with the carrier cations [83].

Using the same CTA/2-NPOE/TOMAC PIMs with 20, 40, and 40 % (w/w) carrier, respectively, Munro and Smith [85] have studied the facilitated non-competitive transport of several amino acids including L-phenylalanine, L-leucine, L-alanine and dopamine. In this investigation, the source solution contained 100 mM of the individual target solute and both the source and receiving solutions were buffered at pH 7.3 using 100 mM sodium phosphate. While negligible

transport occurred in the absence of carrier, at 40% TOMAC (w/w) the authors observed considerable selectivity amongst these amino acids and reported permeate fluxes for L-phenylalanine, L-leucine, L-alanine and dopamine to be 15.9, 5.2, 2.9 and 0.25 μmol m^{-2} s^{-1}, respectively. A fixed-site jumping transport mechanism was proposed as the flux was minimal at less than 20% (w/w) carrier and increased dramatically, in a non-linear manner, at values above this concentration. The authors suggested that the 20% (w/w) carrier concentration represented a percolation threshold for this system. Flux results were compared to those for similar SLM experiments using a microporous polypropylene support of Celgard 2500™ and a liquid membrane phase of TOMAC in NPOE [85]. The SLM results indicated a small, but linear L-phenylalanine flux up to 40% (w/w) carrier concentration, and then a substantial non-linear increase in the flux as the carrier concentration was raised. The 40% (w/w) carrier concentration represents a percolation threshold for the SLM system. Below this value, transport is slow and linear and occurs by a carrier-diffusion mechanism that is favoured by the lower viscosity of the polymer free liquid membrane phase. Above the percolation threshold, the transport is significantly enhanced by contributions from a fixed-site jumping mechanism. At pH 7.3 all the amino acids studied are significantly ionised and fixed-site jumping of the amino acid anions occurs by attraction to the "fixed" carrier cation. Although not mentioned by the authors, the low dopamine flux observed could be due to its significantly higher pK_a of 8.9 [90] that limits the amount of ionised dopamine available. Further evidence to support the transport of ionised species came from L-phenylalanine flux studies at different pH. The flux increased as the pH was raised from 5.5 to 10 and was five times greater at pH 10 than at pH 7.3. Altering the carrier counter-anion also affected the flux. Changing from chloride to phosphate reduced the flux by 30%. The lipophilic bis(2-ethylhexyl)phosphate anion resulted in a complete absence of L-phenylalanine transport.

Matsumoto *et al.* [91] have investigated the potential of PIMs for commercial applications using a 20% (w/w) CTA, 40% (w/w) 2-NPOE and 40% (w/w) TOMAC membrane for the separation of lactic acid from a source solution containing some NaCl at pH 6 to a receiving solution of 3 M NaCl. The authors reported permeabilities of the same order of magnitude as those for similar SLM experiments. They proposed a carrier-diffusion transport mechanism where at pH 6 the lactic acid was ionised and transported as the trioctylmethylammonium/lactate ion pair [91]. TOMAC leakage from the membrane was identified as an important criterion for accessing the

viability of further development of an *in situ* separation method. TOMAC is known to be toxic to the microbe *Lactobacillus rhamnosus* used in the production of lactic acid by fermentation. Addition of free TOMAC to the fermentation mixture resulted in zero lactate production. A 70% decline in lactate production was consistently observed for PIMs containing 6, 12, 40 and 57% (v/v) TOMAC. This suggested that leakage of TOMAC from the membranes reached a steady state value independent of membrane composition. Areas that were highlighted as requiring further investigation before a commercial PIM extraction system for lactate could be considered were the design of a membrane separator to improve diffusion of lactate from the source solution, and selectivity experiments to determine any co-extracted species.

6.2 Acidic and chelating carriers

There are several types of compounds in solvent extraction chemistry that are classified as acidic carriers. These include phosphorus and thiophosphorus acid esters, carboxylic acids and sulfonic acids. Examples of the phosphorus group are phosphoric, phosphonic and phosphinic acids such as di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and di(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302). Examples of carboxylic acids are Naphthenic and Versatic acids while 5,8-dinonylnaphthalenesulfonic acid (DNNSA) is an example of a sulfonic acid carrier.

In addition to the above acidic carriers, there is another group of compounds that are also acidic but, in addition, show strong chelating properties. These are the α-hydroxyoximes and the β-hydroxyaryloximes (LIX reagents), quinolines (Kelex 100) and β-diketones. Of course, in many circumstances the phosphorus acids, particularly D2EHPA, can also act as bidentate chelating agents.

Of the above list of acidic carriers, some of the commercial carriers that have been used in PIMs to date are LIX® 84-I, Kelex 100 and D2EHPA (Table 2). This limited use is surprising as acidic reagents have proven to be of particular importance for the separation of a wide range of metals including transition metals, rare earth metals and the actinides in solvent extraction. Molecular structures of these carriers are shown in Figure 7.
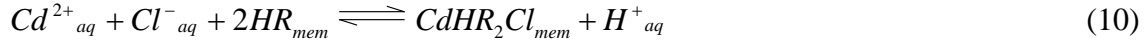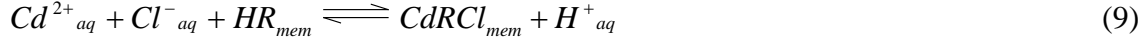
[FIGURE 7]

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Extraction and transport of a metal cation by an acidic carrier is governed by the exchange of the metal ion for protons of the carrier. Consequently, counter-transport of protons is the driving force and is achieved by maintaining a suitable pH difference between the source and receiving solutions. In addition, careful pH control in the source solution can result in good selectivity as is the case in solvent extraction systems using acidic reagents.

Most studies with PIMs using acidic carriers have involved the transport of heavy metals such as Pb(II), Cd(II), Zn(II), Cu(II), Ag(I) and Hg(II) (Table 2) and the focus of much of the work has been on the clean-up of process effluent streams (e.g. the electroplating industry).

Salazar-Alvarez *et al.* [92] have studied the transport of Pb(II) using a CTA-based membrane containing D2EHPA with a source phase containing 10 mM NaNO$_3$ at a pH between 2.85 and 3.45 and a 1.5 M nitric acid receiving phase. This system produced a high Pb(II) flux of 3.5 μmol m^{-2} s^{-1} which was of the same order of magnitude as reported for the analogous SLM system by these authors. The stoichiometry of the transported complex in the PIM system was reported to be PbR$_2$.2HR. The authors found that if the pH of the source phase was greater than pH 3.45, the permeability decreased and suggested that D2EHPA micelle formation was involved. Membrane stability was a problem in this system and Pb(II) transport decreased by about 30% after 5 cycles of 3 hours each. However, membrane stability improved after addition of ethanol to the membrane casting solution although no ethanol was found in the membrane by FT-IR. The mechanism of how ethanol interacts with the CTA membrane is unclear.

A highly selective PIM for the transport of Pb(II) in the presence of Cd(II) (separation factor of 140) has been reported by Aguilar *et al.* [41] using Kelex 100 as the carrier. Selectivity was achieved through pH control of the source solution. Transport was studied using a source phase containing 0.1 M NaCl at pH 6.0 for Pb(II) and pH 8.5 for Cd(II) and a receiving phase of 0.1 M NaCl at pH 3.0. The CTA-based membrane contained 17% (w/w) CTA, 48% (w/w) 2-NPOE and 2.25 M Kelex 100. Comparison of the PIM with the analogous SLM indicated a metal ion permeability about half of that for the SLM. In the Pb(II) case, it is suggested the transport mechanism involves the formation of a single complex in the membrane (Eq. (8)) but for Cd(II), two complexes are involved Eqs. (9) and (10).

$$Pb^{2+}{}_{aq} + 2HR_{mem} \rightleftharpoons PbR_{2\ mem} + 2H^{+}{}_{aq} \tag{8}$$

$$Cd^{2+}{}_{aq} + Cl^-{}_{aq} + HR_{mem} \rightleftharpoons CdRCl_{mem} + H^+{}_{aq} \tag{9}$$

$$Cd^{2+}{}_{aq} + Cl^-{}_{aq} + 2HR_{mem} \rightleftharpoons CdHR_2Cl_{mem} + H^+{}_{aq} \tag{10}$$

The transport of Pb(II) has also been studied by Lee *et al.* [93] using a synthesized lipophilic acyclic polyether dicarboxylic acid as the carrier of structure similar to the antibiotic monensin. The membrane composition was 76% (w/w) 2-NPOE, 18% (w/w) CTA and 6% (w/w) carrier. Using a source phase at pH 4.5 to 5.5, 100% of the Pb(II) could be transported to a 0.1 M nitric acid receiving phase with little transport of Cu(II) and no transport of Zn(II), Co(II) and Ni(II). Negligible decrease of the permeability properties of the membrane was observed over 10 repeated experiments.

Copper transport using a CTA membrane has been studied by de Gyves *et al.* [43]. The other components of the membrane were LIX® 84-I (optimum mass percentage of 50-60% (w/w)) and TBEP (optimum mass percentage of 30% (w/w)) as plasticizer. The source phase contained copper(II) sulfate or chloride at pH 4-6 in acetate buffer with 1 M H_2SO_4 or 1 M HCl as the receiving phase. Maximum permeability for Cu(II) was obtained at pH 5 with no difference between sulfate and chloride for the source phase. However, higher permeability was obtained using H_2SO_4 in the receiving phase rather than HCl. This is most likely due to the higher concentration of H^+ in 1 M H_2SO_4 compared to 1 M HCl. There was a considerable decrease in membrane permeability within only a few runs but some improvement was obtained by adding ethanol to the casting solution. The authors used 'slope analysis' in membrane extraction experiments to determine the complex stoichiometry as $CuR_2.2HR$. They also obtained satisfactory separation of Cu(II) in the presence of a 10-fold excess of Zn(II) and Fe(III).

A comparison between carrier-facilitated transport of Cu(II) in a CTA-based PIM and a SLM has been reported by Paugam and Buffle [94]. The carrier used was lauric acid with TBEP acting as plasticizer for the PIM and as the diluent for the SLM. The source phase was buffered to pH 6.0 using N-morpholinoethane and the receiving phase was 5×10^{-4} M cyclohexanediaminetetraacetic acid (CDTA) at pH 6.4. The authors suggested a stoichiometry for the extracted complex of CuR_2. They found that after normalization by correcting for membrane porosity and tortuosity, the diffusion coefficient was 22 times lower for the PIM than for the SLM.

The transport of Cd(II) across a CTA-based membrane using Lasalocid A (Figure 8) as the carrier has been described by Tayeb *et al.* [11]. The chemical structure of this carrier is shown below.

[FIGURE 8]

The membrane also contained 2-NPOE as plasticizer and transport in this system was compared with the analogous SLM system. The source phase was buffered to pH 8 and the receiving phase contained HCl at pH 2. The authors found the PIM (or polymeric plasticized membrane, PPM, as they termed it) was more efficient for Cd(II) transport at high carrier concentration in the membrane than the SLM system and had good long term stability. Again, as others have observed [13, 65, 83, 84], these authors found that transport in the PIM did not occur until the carrier concentration reached a threshold value (0.031 mg per 1 cm^2 of membrane) which was close to the carrier concentration necessary to reach maximum Cd(II) flux for the SLM.

The selective removal of Zn(II) from other transition metal ions such as Co(II), Ni(II), Cu(II) and Cd(II) using PIMs has been studied by Ulewicz *et al.* [42]. Their system used a CTA membrane containing D2EHPA and 2-NPOE as plasticizer. Separation was achieved by pH control of the source phase with 1.0 M HCl as the receiving phase. Best selectivity for Zn(II) was achieved using the source phase at pH < 2, which was in accordance with the solvent extraction properties of D2EHPA for these metal ions [95]. In another study Baba *et al.* [96] have also demonstrated that Cu(II) can be preferentially transported in the presence of Pd(II) across a PVC-based PIM using D2EHPA as the carrier and plasticizer from a source phase at pH 3-4 (acetate buffer) to a receiving phase of 1.0 M HCl.

Some work on membrane transport used PVC as a gelling agent in an attempt to stabilize SLMs. For example, Bromberg *et al.* [8] used a tetrahydrofuran (THF) solution containing PVC (up to 10% (w/w)), di(2-ethylhexyl)dithiophosphoric acid (D2EHDTPA) and 2-NPOE to impregnate a Celgard 2400 support membrane. On evaporation of the THF, a membrane film formed within the pores of the support phase. This membrane was used to study the transport of Ag(I), Hg(II), Zn(II), Cd(II), Ni(II) and Fe(III). For Ag(I) and Hg(II), thiourea in 1 M H_2SO_4 was used in the receiving phase, while stripping of Zn(II), Cd(II) and Ni(II) required 10 M HCl. Fe(III) could only be stripped using 1 M oxalic acid.

Sugiura *et al.* [79] have studied the transport of rare earth metal ions through CTA-based membranes containing a series of β-diketones as carriers and with 2-NPOE and TBEP as plasticizers. Selectivity was controlled by the pH of the source phase and they found that Sc(III) was transported at a lower pH than both Y(III) and La(III) which was most likely due to the difference in ionic radii. At pH values 5.1 and 6.1, high fluxes were obtained but there was no significant difference in transport amongst the rare earth metal ions except for Sc(III). Also, the solubility of the β-diketones in the aqueous phase increased with increase in pH. In general, fluxes were around 0.6 μmol m^{-2} s^{-1}, which was of a similar order of magnitude to values reported for other CTA-based PIM studies as discussed previously in Section 5.2.

Sigiura has published two further papers [45, 67] on the PIM transport of lanthanides using Hinokitiol and Flavonol as carriers. The membranes were CTA-based and contained 2-NPOE and TBEP as plasticizers. Hinokitiol (β-isotropolone, HIPT) is a derivative of the seven membered ring compound cyclohepta-2,4,6-trien-1-one with an isopropyl- group in the 4-position in the ring and a hydroxo- group in the 2-position. In the first study, Sigiura [67] reported on the effect of the anion and pH of the source phase on the hydrogen ion-coupled transport. Fluxes for the series of lanthanides from Sm(III) to Lu(III) were higher than for La(III) to Nd(III). Also, the addition of perchlorate or thiocyanate ions to the source phase increased the lanthanide flux. In the second study, Sugiura [45] reported on the effect of adding polyoxyethylene n-alkyl ethers (POEs) of different alkyl chain lengths to the membrane mixture. In general, the POEs increased the fluxes of the lanthanides for the series from Sm(III) to Lu(III) but extremely low fluxes were obtained for the series from La(III) to Nd(III).

In an extension to this research on Hinokitiol using POEs in the membrane, Sugiura [97] reported on the effect on the lanthanide flux when two pyrazolone derivatives were used as carriers instead of HIPT. The two carriers were 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (BMPP) and 4-trifluoroacetyl-3-methyl-1-phenyl-5-pyrazolone (TMPP) and were used under the same conditions as HIPT. The fluxes for the lanthanides were found to be higher for BMPP than for TMPP but there was no differentiation between the various lanthanides. Sugiura [97] then replaced the POEs with a series of quaternary ammonium bromides with C_{12} to C_6 alkyl chains and again found higher fluxes for BMPP than for TMPP and the fluxes were much higher for the quaternary ammonium bromides with higher MW.

Rais *et al.* [27] have studied the use of the chlorinated organoboron compound cobalt dicarbollide (bis(dicarbollyl)cobaltate) in a PVC-based membrane for the extraction of ^{137}Cs and ^{90}Sr from high ionic strength solutions containing nitric acid or sodium hydroxide. The plasticizer used was 2-NPOE. The authors claimed the use of this PIM was an improvement on the solvent extraction system for these radioactive elements, which used nitrobenzene as the diluent, even though the PIM extraction was slower. The PVC-based PIM also contained polyethylene glycol as an effective synergistic reagent.

A very recent and novel development in PIM systems has been described by Resina *et al.* [98]. These workers have developed a hybrid membrane using sol-gel technology combined with the procedure for making CTA-based membranes. They have carried this out by mixing a CTA matrix with polysiloxanes containing plasticizers and extractants, mixing vigorously and curing the mixture at 80°C for 20 hours. One aim of this work was to improve the stability of PIMs. Membranes made by this method have been studied for the transport of Zn(II), Cd(II) and Cu(II) with D2EHPA and D2EHDTPA as carriers. The transport properties of the hybrid membranes were compared with normal PIMs and with Activated Composite Membranes (ACMs). In all cases, the source phase was 0.5 M NaCl and the receiving phase was 0.5 M HCl. Flux values of the order of 3.4 - 6.2 μmol m^{-2} s^{-1} were found for all three membrane types although slightly higher values were obtained for the hybrid membrane. Using mixtures of Zn(II), Cd(II) and Cu(II), it was found that with D2EHPA Zn(II) was transported but the membrane was impermeable to Cd(II) and Cu(II). With D2EHDTPA, Cu(II) was extracted preferentially but could not be stripped because of strong complexation within the membrane and this accumulation of Cu(II) within the membrane impeded the transport of Zn(II) and Cd(II). The use of a 5:1 mixture of D2EHPA and D2EHDTPA in the membrane resulted in high transport of Zn(II), no transport of Cd(II) and a limited transport of Cu(II).

6.3 *Neutral or solvating carriers*

Most commercially available neutral or solvating carriers are phosphorus based extraction reagents such as tri-n-butyl phosphate (TBP), tri-n-octyl phosphine oxide (TOPO), and dibutyl butyl phosphonate (DBBP) (Figure 9). However, this group can include other neutral organic reagents with a strong solvating capacity due to Lewis acidic centers or hydrogen bonding (e.g. amides). Solvating reagents such as TBP and TOPO have been used extensively in solvent

extraction for the processing of actinides such as uranium and lanthanides as well as for cerium and other metal ions commonly found in low radioactivity level wastewaters [86]. As mentioned in the introduction section of this review, the use of PIMs can be dated back to almost 40 years ago, when Bloch *et al.* [21] reported on a pioneering attempt to use PIMs containing TBP as a carrier for uranium recovery. However, probably because the use of neutral carriers is largely restricted to radioactive metal ions, only a few PIM studies using this type of carrier have been reported since then.

[FIGURE 9]

The membranes used by Bloch *et al.* [21, 69] were prepared by casting a thin film consisting of 25% (w/w) PVC and 75% (w/w) TBP on paper of high wet strength or on a glass plate. Cyclohexanone was used as the solvent and the membranes were cured at 140°C for 60 seconds. The thickness of the resulting thin film was reported to be 40 μm. By varying the nitrate concentration in the source solution, the authors [21, 69] demonstrated that the permeate flux closely correlated with the distribution ratio of uranyl nitrate between the aqueous phase and the TBP/PVC membrane. In these experiments, the receiving solution was pure water and the source solution contained 0.02 M $UO_2(NO_3)_2$ with the concentration of HNO_3 varying in the range from 2 M to 8 M. Bloch [69] observed that the use of an anion, which can permeate across the membrane such as nitrate might be an inherent disadvantage for PIMs using solvating carriers. A rather unexpected phenomenon occurred where the uranyl ion was transported from the source to the receiving solution and then transported back to the source as nitrate continued to diffuse through the membrane until an equal concentration of nitrate and the uranyl ion in both compartments was attained. This was explained by the fact that nitrate permeated through the membrane not only in association with UO_2^{2+} but also in association with a proton in the form of HNO_3. Because of the high initial concentration of nitrate in the source solution, the uranyl ion was transported to the receiving solution. As long as the nitrate concentration in the receiving solution remained low, this transport process continued even when the uranyl ion concentration in the receiving solution was higher than in the source solution. Then, when a sufficient amount of nitrate had been transported to the receiving solution, back diffusion of uranium occurred until the system reached equilibrium. To confirm this explanation, Bloch *et al.* [21] showed that the permeation of nitrate through the membrane was insignificant when nitrate was introduced to the

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source solution in the form of a suitable nitrate salt such as sodium nitrate instead of nitric acid. However, the authors also reported that a small but discernible passage of nitrate occurred when ferric or aluminum salts were used. This was attributed to a decrease in pH in the source solution due to the hydrolysis of these salts [21].
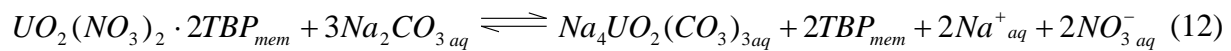
Bloch [69] also emphasized that the rate of complex formation and dissociation could, in certain circumstances, govern the membrane selectivity. Using a membrane prepared with an immobilized chelating agent known to complex slowly with Fe(III), namely, thenoyl trifluoroacetone, the author demonstrated that there was a significant difference in permeability between Fe(III) and Cu(II). The membrane selectivity factor was 200 times for Cu(II) over Fe(III), which was much higher than expected based purely on the distribution ratio differences between these two metals in solvent extraction. Bloch [69] compared this result with observations often encountered in biological systems where the differences in dissociation rates when translated into membrane permeabilities yielded extraordinarily high selectivities.

Matsuoka *et al.* [46] have studied the transport of uranyl nitrate using a CTA-based membrane containing 0.5 mL of TBB for every 0.3 g of the base polymer CTA. The authors reported an uphill transport of uranyl nitrate from a source solution containing 3.5 mM of UO_2^{2+} and 1 M HNO_3 to a receiving solution containing an initially equal concentration of UO_2^{2+} (i.e. 3.5 mM) and 1 M Na_2CO_3 [46]. The transport mechanism is represented by Eqs. (11) and (12).

Source phase:

$$UO_2^{2+}{}_{aq} + 2NO_3^-{}_{aq} + 2TBP_{mem} \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP_{mem} \tag{11}$$

Receiving phase:

$$UO_2(NO_3)_2 \cdot 2TBP_{mem} + 3Na_2CO_3{}_{aq} \rightleftharpoons Na_4UO_2(CO_3)_{3aq} + 2TBP_{mem} + 2Na^+{}_{aq} + 2NO_3^-{}_{aq} \tag{12}$$
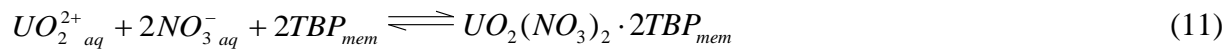
In contrast, they did not observe any uranyl transport when the source solution containing 3.5 mM UO_2^{2+} and 1 M of Na_2CO_3 and the receiving solution contained 1 M HNO_3. This was explained by the formation of the bulky sodium uranyl carbonate complex, which could not effectively be extracted into the membrane.

It should also be noted here that the authors observed a severe leakage of TBP from their membranes and the aqueous phases were saturated with TBP in all of their experiments to prevent carrier loss.

Kusumocahyo *et al.* [53] have developed PIMs consisting of CTA as the base polymer, 2-NPOE as the plasticizer and two novel solvating carriers namely octyl(phenyl)-N,N-diisobutylbarbamoylmethyl phosphine oxide and *N,N,N,N*-tetraoctyl-3-oxapentanediamide denoted as CMPO and TODGA, respectively, for the removal of $Ce(NO_3)_3$ from low radioactivity wastewater. The source solution used in their experiments contained 200 mg/L $Ce(NO_3)_3$, 0.05 M HNO_3, and 2.95 M $NaNO_3$ and the receiving solution was pure water. The distribution ratios for Ce(III) between an aqueous phase of the same composition as the source solution and the membrane containing CMPO or TODGA were reported to be 550 and 28, respectively. By examining the variation of the distribution ratio as a function of the carrier concentration in the membrane, Kusumocahyo *et al.* [53] have successfully determined the stoichiometry of the carrier/cerium nitrate complex to be 2:1. Complete transport of Ce(III) from the source to the receiving solution could be achieved within 60 minutes or more depending on the actual membrane composition and experimental conditions. The authors also presented several sets of data relating to the diffusion of the cerium nitrate complex across the membrane. The transport rate was reported to increase as the plasticizer or carrier concentration increased to certain levels. In addition, this transport rate was also found to correlate well with the membrane thickness and with the reciprocal of the temperature.

Lamb and Nazarenko [66] have examined the influence of the counterion on the sorption and transport processes for Pb(II) using CTA-based PIMs containing TOPO and 2-NPOE. Four different anions (i.e. I^-, SCN^-, Br^- and NO_3^-) were investigated. They reported a correlation between the Pb(II) transport and the hydrophobicity or the hydration energy of the counterion. The permeability increased in the order $NO_3^- \leq Br^- < SCN^- \leq I^-$. This also agrees well with the extraction constant of membranes containing TOPO when these anions have been used in the solution matrix [66]. The authors, however, did not report data relating to the transport of sodium or the counterions.

The transport of the arsenate ion (AsO_4^{3-}) by a solvating carrier has been investigated by Ballinas *et al.* [99] using a PIM based on CTA and dibutyl butyl phosphonate (DBBP) as the carrier.

Passive transport was almost complete after 6 hours when the source solution contained 2800 mg/L AsO_4^{3-} and the receiving solution contained 2 M LiCl. The authors suggested that AsO_4^{3-} was transported through the membrane in the form of $H_3AsO_4[DBBP]_2$. However, when the source solution also contained 2.2 M H_2SO_4, the arsenate transport rate was dramatically reduced and almost 27 hours were needed for the complete transport of AsO_4^{3-} while complete transport of the HSO_4^- ion was achieved within 6 hours in both cases. The authors speculated that this was due to the formation of the additional complex, $H_3AsO_4[DBBP]H_2SO_4$, in a coupling phenomenon in the presence of a sufficient concentration of H_2SO_4 [99]. The same explanation was also used to describe the uphill transport of 10% of the AsO_4^{3-} observed after 5 hours when the source phase contained 2800 mg/L AsO_4^{3-} and 2 M H_2SO_4 and the receiving solution contained an equal concentration of AsO_4^{3-} and 2M LiCl [99]. The authors did not explain the mechanisms for the formation of the $H_3AsO_4[DBBP]_2$ and $H_3AsO_4[DBBP]H_2SO_4$ species.

6.4 Macrocyclic and macromolecular carriers

A considerable amount of the research reported to date on PIMs has used macrocyclic and macromolecular carriers such as crown ethers as the extracting reagents in PIMs. This is likely due to their high complexing selectivity for metal ions as a result of the presence of specifically tailored encapsulating coordination sites in their structures and their low solubility in aqueous solutions. In addition, the use of expensive macrocyclic reagents in membranes is more feasible than in traditional solvent extraction because of the considerably smaller reagent inventory required. The large number of macrocyclic carriers that has been studied are summarized in Table 4. Even though crown ethers and similar macrocyclic ligands have traditionally been used in the complexation of the alkali and alkaline earth metal ions, a large number of PIM studies are related to the transport of heavy metal ions. This is possibly due to the strong interest in the use of membrane separation in the treatment of nuclear wastes and contaminated waters and toxic sludge. The potential to selectively extract and recover organic ions using macrocyclic carriers has also been demonstrated in an early PIM study [15]. In PIMs using macrocyclic and macromolecular carriers, transport is facilitated and the mechanism involves the co-transport of the target cation along with an associated anion and generally water is used as the receiving phase.

[TABLE 4]

Lamb *et al.* [100] have studied the transport of Ag(I) through CTA/2-NPOE membranes containing a series of pyridino- and bipyridino- podands (A, Table 4). These carriers have hydrophilic palmitoyl tails making them insoluble in aqueous solutions and highly soluble in the membranes thus conveying excellent homogeneity and stability. These podands have three pyridine nitrogen atoms in tridentate coordinating positions and have strong binding properties for the Ag(I) ion. Thus, only Ag(I) transport from a perchlorate solution in the presence of Cd(II), Zn(II), Co(II), Ni(II), Pb(II) and Cu(II) to a water receiving phase was observed.

A similarly high transport selectivity for Ag(I) compared to Pb(II) and Cd(II) has been observed by Kim *et al.* [101] for a series of calix[4]azacrown ether derivatives (B, Table 4) immobilized in a CTA-based PIM plasticized with 2-NPOE and TBEP. In another study, Kim *et al.* [20] also investigated the transport of Ag(I) in PIMs and SLMs using acyclic polyether ligands having diamide and diamine end-groups (C, Table 4). They found again highly selective transport of Ag(I) in the presence of Cd(II), Zn(II), Co(II), Ni(II), Pb(II), and Cu(II). In addition, the transport of Ag(I) was considerably faster in PIMs than in SLMs. Only one carrier (the amide where R=H (C, Table 4)) showed some transport of a metal ion (i.e. Pb(II)) other than Ag(I).

A study [102] has been reported on the complexation of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II) with a series of N-benzylated macrocycles incorporating O_2N_2-, O_3N_2- and O_2N_3- donor sets. Part of this work has involved testing these macrocycles in solvent extraction and membrane systems. One macrocycle (D, Table 4) showed high selectivity for Ag(I) in a CTA/2-NPOE based PIM.

A comparison of Ag(I) and Cu(II) facilitated transport has been reported by Arous *et al.* [14] using a series of macrocyclic polyether cryptands (E, Table 4) in CTA/2-NPOE based PIMs. Transport experiments showed a seven-fold higher flux for the PIMs compared to analogous SLMs. The main focus of the study was on the structure of the PIMs using FTIR, X-ray diffraction, differential scanning calorimetry and SEM. The term used by the authors for these polymer membranes was "fixed sites membranes (FSMs)" although they are PIMs according to the definition used in this review. Similar studies [10, 13] were reported on the use of 18-crown-6 ether derivatives (F, G, Table 4) in CTA/2-NPOE based membranes for the transport of Ag(I), Cu(II), and Au(III). These studies were aimed at providing an understanding of the factors that controlled the membrane properties.

The transport of Pb(II) has been studied by Aguilar *et al.* [32]. They synthesized a series of diazadibenzocrown ethers and found two of these (H, Table 4) had high selectivity for Pb(II) over Cd(II) and Zn(II) using a CTA/2-NPOE membrane of composition (w/w) 22.0% CTA, 71.6% 2-NPOE and 6.4% carrier.

Ulewicz *et al.* [103] have reported on the transport of Zn(II), Cd(II) and Cu(II) using CTA-based membranes containing complex diphosphaza-16-crown-6 derivatives as carriers (I, Table 4). In this work they studied the effect of the acidity of the source phase on the selectivity.

A new type of macrocyclic carriers has been reported by Kozlowski *et al.* [104]. This was based on the polymerization of β-cyclodextrin with alkenyl(nonenyl and dodecenyl)succinic anhydride derivatives (J, Table 4). Several cyclic oligomers were synthesized and studied in CTA/2-NPPE membranes for the competitive transport of Cu(II), Co(II), Ni(II) and Zn(II) and gave a transport order that increased from Cu(II) to Zn(II). The authors suggested that transport involved the formation of ion-pairs between hydroxyl groups on the polymer and the metal ion. The addition of 3,7-dinonyl-naphthalene-1-sulfonic acid to the membrane produced a synergistic effect that was used effectively for the removal of Cr(VI), Cu(II) and Cd(II) from industrial wastewaters and municipal sludge.

Sugiura [15] has studied the transport Zn(II) and Cu(II) using CTA membranes plasticized with p-nitrophenyl-n-heptyl ether (NPHE) that contained the carriers bathophenanthroline (for Zn(II)) or bathocuproine (for Cu(II)) (K, Table 4). Transport of Zn(II) against its concentration gradient was observed for solutions containing nitrate and chloride whereas Cu(II) transported in the presence of chloride but not nitrate. An additional study in this paper involved the transport of the picrate ion using dibenzo-18-crown-6 as carrier.

The transport of Sr(II) has been studied by Mohapatra *et al.* [54] using several cyclohexano-18-crown-6 derivatives in CTA/2-NPOE PIMs. They found that t-BuDC18C6 (L, Table 4) provided selective transport of Sr(II) from synthetic nuclear waste solutions containing 1 M and 2 M nitric acid and a large number of other metal ions. At 3 M nitric acid hydrolysis of CTA was observed.
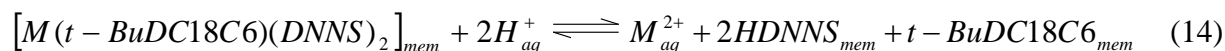
Nazarenko and Lamb [31] have studied the transport of Sr(II) along with Pb(II) from synthetic nuclear waste solutions using DC18C6 and t-BuDC18C6 in CTA/2-NPOE membranes. In their

initial experiments, they added dialkyl-naphthalene-sulfonic acid to the membrane containing DC18C6 and obtained excellent recovery of Sr(II), however, the membrane performance deteriorated due to loss of the carrier to the aqueous phase. This problem was solved by using the more hydrophobic carrier t-BuDC18C6. In this mixed carrier system, the mechanism involved counter-transport as illustrated by the following equations and the receiving phase had to be acidic.

Source phase

$$M_{aq}^{2+} + 2HDNNS_{mem} + t - BuDC18C6_{mem} \rightleftharpoons [M(t-BuDC18C6)(DNNS)_2]_{mem} + 2H_{aq}^+ \quad (13)$$

Receiving phase

$$[M(t-BuDC18C6)(DNNS)_2]_{mem} + 2H_{aq}^+ \rightleftharpoons M_{aq}^{2+} + 2HDNNS_{mem} + t - BuDC18C6_{mem} \quad (14)$$
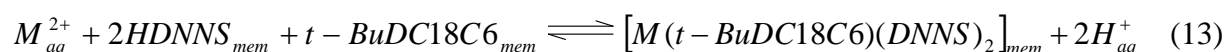
Nazarenko and Lamb [31] also found that the use of t-BuDC18C6 on its own in the membrane gave excellent selectivity for Pb(II). In this case, the mechanism was facilitated transport and water could be used as the receiving phase.

Elshani *et al.* [105] synthesized some di-[N-(X)sulfonyl carbamoyl] polyethers (M, Table 4) and studied them in CTA/PVC/2-NPOE membranes as carriers for the alkaline earth metal ions. They also studied the solvent extraction properties of these new carriers in chloroform. The competitive PIM transport experiments showed high Ba(II) transport compared to the other alkaline earth metal ions with an order for the carriers (compound $1 > 2 > 4 > 3$, (see M, Table 4)) that was associated with the type of the X group attached to the compound backbone molecule.

Kim *et al.* [106] have also reported on a new carrier with high transport selectivity for Ba(II). Amongst several calix[6]arenes having both carboxylic acid and carboxamide groups studied by these authors, 1,3,5-tricarboxylic acid-2,4,6-tricarboxamide-p-tert-butylcalix[6]arene (N, Table 4) exhibit the highest selectivity ratio for Ba(II) over Mg(II) (i.e. 40:1). Much lower selectivities ration for Ba(II) over Mg(II) were reported for the other compounds.

Levitskaia *et al.* [30] have employed some synthesized calix[4]arene-crown-6 carriers (O, Table 4) in CTA/2-NPOE membranes and have reported highly efficient and selective transport of Cs^+.

Of the 17 different metal ions present in a synthetic nuclear wastewater sample containing a high nitric acid concentration only K^+ and UO_2^{2+} were transported along with Cs^+. In a separate study, Levitskaia *et al.* [68] have examined the fundamental thermodynamic parameters that underpin transport in PIMs using these Cs^+ selective carriers.

PIMs transport of Cs^+ has also been investigated by Kim *et al.* [19] using calix[4]arene-crown-6, calix[4]arene-crown-7 and calix[4]arene-crown-8 in CTA/2-NPOE/TBEP membranes. They found that the calix[4]arene-crown-6 compound gave an excellent selectivity and transport rate for Cs^+ compared to the other alkali metal ions and attributed this to the close matching of the sizes of the crown ring cavity and the Cs^+ ion. The authors suggested this PIM system might be useful for separating Cs^+ from radioactive wastewaters [19].

In another report on the use of PIMs for selective Cs^+ transport, Lee *et al.* [63] have demonstrated that a self-assembled isoguanosine structure can be used in a CTA/2-NPOE membrane to separate Cs^+ from Na^+ which is also present in most nuclear waste solutions. The authors have shown that IsoG 1 (5'-(tert-butyldimethylsilyl)-2',3'-O-isopropylene isoguanosine, see P, Table 4) self assembles into a decamer sandwich in the presence of Cs^+. The Cs^+/IsoG 1 decamer dissociates at the receiving phase/membrane interface in the presence of acid and, accordingly, the transport of Cs^+ has been found to increase with decreasing pH of the receiving phase. In the absence of Cs^+ in the solution, the membrane produced high selectivity for Ba(II).

Walkowiak *et al.* [33] have studied a series of sym-(alkyl)dibenzo-16-crown-5-oxyacetic acid carriers (Q, Table 4) in the competitive transport of alkali metal ions. The membranes used were CTA-based and were plasticized by either 2-NPOE or 2-NPPE. The source phase contained 0.2 M of the alkali metal ion studied and the receiving phase was 0.1 M HCl. Due to the presence of the acetic acid functionality in these carriers, the mechanism involved proton-coupled metal ion transport and the flux depended on the chain length of the alkyl chain. These workers found that maximum flux was obtained for the C_9 alkyl chain and that this carrier was very selective for Na^+ with practically no transport of the other alkali metal ions.

An important study of alkali metal ion transport using PIMs has been reported by Lacan *et al.* [65]. They used a hybrid organic-inorganic membrane derived from a sol-gel process. Such heteropolysiloxane membranes are relatively easy to prepare and can contain a covalently bound

carrier. In this paper the carrier was 4'-N-butylcarboxamidobenzo-15-crown-5 (R, Table 4) and the membrane gave good selectivity for Na^+ over Li^+ and high diffusion rates. The presence of the picrate ion in the membrane was found to increase the transport rate and the authors suggested that the transport mechanism involved cation exchange between the picrate ion and carrier sites.

The extraction of the organic picrate ion was studied in an early work by Sugiura [15]. In this study, the membranes consisted of PVC as the base polymer, NPHE as the plasticizer and DC18C6 as the carrier. A concentration gradient of potassium ions across the membrane was used to transport picrate against its concentration gradient with an initial flux of 5.7×10^{-2} μmol m^{-2} s^{-1}. Optimum transport was reported when both the source and receiving solutions contained 10^{-4} M potassium picrate and buffered at pH 8.3 using 0.01 M Tris-H_2SO_4. Additionally, the source and receiving solutions contained 0.5 M potassium sulfate and 0.5 M lithium sulfate, respectively. The author postulated that an ion-pair was transported through the membrane and in this case potassium acted as a counter-ion for the transport of picrate anion across the membrane [15].

A most recent paper [107] that appeared just as this review was in the final stages of completion describes the application of PIMs containing some macrocyclic metal complexes and various plasticizers for the transport of anions. The carriers were essentially bis(pyridylmethyl)amine compounds coordinated to the transition metals ions Fe(III), Cu(II) and Zn(II). One carrier was based on a resorcinarene bonded to four bis(pyridylmethyl)amines. Because of the presence of the metals in the carrier complex, some deviation from the 'Hofmeister' sequence of anions was observed. The PIMs showed excellent selectivity for the ReO_4^- ion and the suggestion was made that they might also show high selectivity for the TcO_4^- ion [107].

7 TRANSPORT MECHANISMS

7.1 *Interfacial transport mechanisms*

Both SLMs and PIMs involve the selective transport of a target solute from one aqueous solution to another via the membrane that separates them as can be seen in Figure 5 [1]. This overall transport consists of two processes, namely the transfer of the target solute across the two interfaces and diffusion through the membrane. The former process is similar for both types of membranes, however, because PIMs are distinctively different from SLMs in their composition and morphology, the actual bulk diffusion mechanisms within the membrane phase can be quite

different. Consequently, the overall transport mechanisms of SLMs and PIMs are not identical. Nevertheless, fundamental findings obtained from SLM studies, which have been comprehensively reviewed by several authors [1, 2, 108], can be particularly useful to elucidate the transport mechanisms observed with PIMs. This section discusses the interfacial transport mechanisms with a focus on the chemistry of the aqueous phase and phenomena observed at the membrane-aqueous interface. The bulk diffusion mechanisms occurring within the membrane phase are delineated in the next section (Section 7.2).

Danesi [108] describes the permeation of the target solute through an SLM as a single-stage extraction in simultaneous combination with a back extraction stage. The transport, therefore, occurs under non-equilibrium conditions. Gyves and de San Miguel [2] provide a more detailed analysis taking into account the diffusion of the target solute through a stagnant layer at the membrane/aqueous solution interface and also consider for the transport of co- or counter- ions. However, these authors note that when suitable hydrodynamic conditions are maintained near the membrane/aqueous solution interface by constant agitation or tangential flow, the diffusion process through this aqueous stagnant layer is relatively fast and can be ignored. Consequently, the interfacial transport description proposed by Gyves and de San Miguel [2] for a typical membrane extraction system is quite similar to that described by Danesi [108]. On the basis of these reviews, the three major steps which characterize the transport of a target solute from the source to the receiving solution in PIMs are schematically illustrated in Figures 10a-d. These figures depict uphill metal transport which will occur in the final stages of the separation process. In the first step, the target solute after diffusing through the aqueous stagnant layer at the source solution/membrane interface, reacts with the carrier at this interface to form a complex, which is then transported across this interface and replaced by another molecule of the carrier. In the second step, the target solute diffuses across the membrane toward the receiving solution. The detailed nature of this bulk diffusion process is discussed in the next section. Finally, at the membrane/receiving solution interface, the target solute is released into the receiving solution, which is essentially the reverse of the process occurring at the source solution/membrane interface. While Figures 10a-d are representative of most PIM systems encountered in the literature, they do not provide any information about the speciation processes occurring in the aqueous phases. Consequently, the aqueous phase metal ion concentration is its total analytical

concentration which is the sum of the concentrations of all metal ions containing chemical species.

[FIGURE 10]

It is obvious that the distribution ratio (often referred to as the partition constant or coefficient, K_p) of the target solute/carrier complex between the organic phase of the membrane and the aqueous solution, K_p^s (superscript s representing the source solution), must be as high as possible to favor the extraction process. In contrast, K_p^r (superscript r representing the receiving solution) at the receiving site must be sufficiently low to favor back extraction of the target solute from the membrane phase. Consequently, within the membrane phase, there is a concentration gradient of the target solute/carrier complex or ion pair acting as a driving force for its transport across the membrane, despite the fact that the total analytical concentration of the target solute in the source solution can be substantially lower than in the receiving solution. In other words, uphill transport only takes place with respect to the total analytical concentration of the solute, while in the membrane phase it is actually downhill transport regarding the actual chemical species diffusing across the membrane. In practice, such a difference in K_p between the source and receiving solutions can be maintained with a suitable chemical composition of these solutions. For example, a strong complexing reagent is often used in the receiving solution to strip the target ion from the membrane. Amongst several studies in which observations in support of this interfacial transport mechanism have been reported, those by Bloch *et al.* [21] and Matsuoka *et al.* [46] can be used as examples. The former argued that permeate flow continues until $K_p^s \cdot C_i^s = K_p^r \cdot C_i^r$ (where C_i is concentration of the target solute in the aqueous solution), that is until the concentration gradients within the membrane have vanished. This is also consistent with the work of the latter authors [46], who examined the transport of the uranyl ion through a CTA/TPB membrane and reported a K_p^s/K_p^r ratio of 10^4 between the source and receiving solutions containing 1 M $NaNO_3$ and 1 M Na_2CO_3, respectively. Consequently, a nearly complete uphill transport of the uranyl ion has been observed with this system.

Another driving force for the uphill transport phenomenon is the potential gradient of a coupled transport ion across the membrane. In a typical PIM process, the target solute is transported in association with this ion to maintain electroneutrality. This is known as the coupled transport phenomenon, which can be counter-transport (Figures 10 b&c) or co-transport (Figures 10 a&d),

depending on the transport direction of the coupled transport ion with respect to that of the target solute. Typical examples for this can be seen by considering PIM systems using acidic or chelating carriers [41, 42, 92]. In such cases, the potential gradient of protons maintained by adjusting the solution pH can be seen as the driving force for the uphill transport of a metal cation across the membrane. In fact, studies involving the use of acidic and chelating carriers have consistently revealed a characteristic correlation between permeability and the pH difference between the source and receiving solutions [41, 42, 92]. However, it should be noted that the distribution ratio of the target solute between the aqueous solution and the membrane phase is also related to the solution pH. While K_p values at various pH values are not usually reported in PIM literature, it is well known in solvent extraction that the distribution ratio by an acidic or chelating extractant is strongly pH dependent.

In practice, these two driving forces outlined above cannot be distinguished. This is partly due to the complexity of the speciation involved at both sides of the membrane as well as within the membrane itself. In essence, usually they are both integral parts of a complex interfacial transport mechanism. One emphasizes the distribution ratio (K_P) difference and the other emphasizes the potential gradient of the coupled transport ion across the membrane. It is probably more convenient to use the former to describe the interfacial transport process in PIMs using solvating carriers such as TBP. The latter presents a more suitable description for membranes carrying fixed charged groups within the polymer matrix, in other words, PIMs prepared with basic, acidic or chelating carriers. Some authors have related such Donnan behavior to a characteristic correlation between permeability and the dielectric constant of the carriers and plasticizers, which has been widely observed by several researchers [9, 58].

7.2 Bulk transport mechanisms

As discussed in the previous section, facilitated transport across a membrane from a source to a receiving phase involves also diffusion of the carrier/target complex through the bulk membrane in addition to transport across the two solution/membrane interfaces [1, 2, 78, 109]. In the case of a bulk liquid membrane, the carrier, which is assumed to be able to move freely within the membrane, plays the role of a shuttle [78]. However, facilitated transport can also occur in ion–exchange and other types of membranes, in which the reactive functional group (or carrier) is covalently bound to the polymeric backbone structure [55]. In this case, the carrier is

immobilized and it is assumed that the bulk diffusion of the target solute takes place via successive relocations from one reactive site to another [78, 109]. For a typical PIM, as discussed in Section 5.1, although the carrier is not covalently bound to the base polymer, the membrane is essentially a quasi-solid homogeneous thin film and it is not a true liquid phase [110]. Because, the carriers are often bulky (Figures 6-9 and Table 4), their mobilities in PIMs are much more restricted compared to SLMs. Consequently, although the actual mechanisms are still a subject of stimulating discussion in the literature, the bulk diffusion processes in PIMs are thought to be different from those in SLMs and other types of liquid membranes [78, 109].

In a pioneering work, Cussler *et al.* [109] proposed the "chained carrier" theory to describe the facilitated transport process in a solid membrane where mobility of the carrier is restricted. The authors developed a mathematical model to compare the mobile carrier diffusion and the chained carrier mechanisms. Their model explicitly indicates that there are several circumstances where the permeate flux of an immobilized carrier membrane can be comparable to that of a mobile carrier membrane. This is consistent with the results reported in several studies [9, 11, 55] where the permeate fluxes between PIMs and SLMs have been found to be comparable, although such observations are uncommon and it is unclear whether the conditions described by Cussler *et al.* [109] and those of the studies mentioned above were indeed similar. More importantly, the model demonstrates that membranes with immobilized carriers may show a percolation threshold, i.e. the carrier concentration must be sufficiently high so that a continuous chain across the membranes can be formed. It is noteworthy that this concept of a percolation threshold has later become the foundation for other PIM studies on the bulk diffusion mechanism within the membrane phase [13, 65, 83, 84, 110, 111]. The model also indicates that facilitated transport can occur only when the carriers themselves have some local mobility. On the basis of their model, Cussler *et al.* [109] have postulated that the apparent diffusion coefficient (or the apparent rate of transport of the target solute) in immobilized carrier membranes does not reflect the diffusion process but rather the chemical kinetics of the complexation reaction. This is consistent with the theory by Bloch [69] discussed earlier in Section 6.3 that selectivity in PIMs may also be governed by the rate of complex formation and dissociation.

Although the model of Cussler *et al.* [109] provides a clear mechanistic insight for the understanding of the diffusion process in PIMs, later experimental results appear to deviate from

this model [83, 110, 111]. In fact, as has been carefully discussed by Cussler *et al.* [109], a limitation of their model is the assumption that free uncomplexed solute cannot enter the membrane and the carrier sites must be within reach of one another so that the transfer of the target solute can take place. Plate *et al.* [110] investigated the transport of Co(II) using TOA as the carrier and found that the percolation threshold also depended on the initial concentration of the target solute.   In another study, White *et al.* [83] reported a higher percolation threshold for fructose as compared to the disaccharide sucrose in a PIM investigation using CTA and TOA as the base polymer and carrier, respectively. It was concluded that the larger disaccharide species did not require the carrier molecules to be as close together for transport to occur as in the case of smaller monosaccharides. The authors also proposed an extended bulk diffusion model, which was essentially an improvement of the model by Cussler *et al.* [109]. In addition to the requirement for locally mobile carrier species, this new model assumed that the target solute can jump from one carrier to another [83]. However, physical conditions for this model were not clearly postulated and a mathematical derivation was not provided.

Unlike the mobile carrier diffusion mechanism, which assumes that complexation formation and dissociation occur only at the solution/membrane interface, the fixed site jumping mechanism explicitly includes the complexation reaction between the carrier and target solute as an integral part of the bulk membrane transport. Both of these mechanisms follow a Fickian diffusion pattern and therefore the overall transport process is similar. However, knowledge of the actual bulk transport mechanism kinetics underlines the significance of the complexation kinetics, which in addition to the complexation thermodynamic, may also be a crucial factor governing both permeability and selectivity in PIMs. Nevertheless, experimental results to support this premise remain limited in the PIM literature.   This is partly due to experimental difficulties in distinguishing between the two mechanisms outlined above. To date, the fixed site jumping mechanism was postulated almost exclusively on the basis of a percolation threshold [13, 65, 83, 84]. However, an increase in the carrier concentration can lead to a variation in the membrane morphology as pointed out by some researchers [6, 59, 60], which may ultimately influence the nature of the diffusion process. In fact, because the carrier is not covalently bound to the base polymer, it may be assumed that the actual diffusion mechanism is intermediate between mobile carrier diffusion and fixed site jumping.

8 MATHEMATICAL MODELING

The development of mathematical models to adequately describe the extraction and transport processes is fundamental for PIM investigations. Mathematical modeling is a vital tool for an in-depth understanding of the relevant physicochemical and transport processes, determining their thermodynamic and kinetic constants as well as optimizing the corresponding membrane separation systems (e.g. membrane and solution composition and system dimensions). Not surprisingly, a considerable number of PIM studies have addressed this subject.

The stoichiometry of the transported complex across PIMs has been determined in a number of studies [43, 53, 92] following the standard approach used in solvent extraction. Kusumocahyo *et al.* [53] fitted Eq. 15a to experimental distribution data to determine the stoichiometry of complexation between Ce(NO$_3$)$_3$ and the carrier N,N,N',N'-tetraoctyl-3-oxapentanediamide (TOGA) immobilized in CTA-based PIMs (Eq. 15b).

$$\log K_P = \log K_{ex} + a \log[L]_{mem} + 3\log[NO_3^-]_{aq} \tag{15a}$$

$$Ce_{aq}^{3+} + aL_{mem} + 3NO_{3\ aq}^- \rightleftharpoons CeL_a(NO_3)_{3\ mem} \tag{15b}$$

where K$_{ex}$ is the extraction equilibrium constant, K$_p$ is the partition constant (K$_p$ =[CeL$_a$(NO$_3^-$)$_3$]$_{PIM}$ / [Ce^{3+}]) and L represents the carrier.

Using a similar approach, Salazar-Alvarez *et al.* (Eq. 16a) [92] and de Gyves *et al.* (Eq. 17a) [43] determined the stoichiometry of the extraction of Pb(II) (Eq. 16b) and Cu(II) (Eq. 17b) into CTA PIMs incorporating the carriers D2EHPA or LIX® 84-I, respectively.

$$\log K_P = \log K_{ex} + \tfrac{1}{2}(2+a)\log[(HL)_2]_{mem} + 2\,pH \tag{16a}$$

$$Pb_{aq}^{2+} + \tfrac{1}{2}(2+a)\{(HL)_2\}_{mem} \rightleftharpoons \{PbL_2aHL\}_{mem} + 2H_{aq}^+ \tag{16b}$$

$$\log K_P = \log K_{ex} + a \log[(HL)_2]_{mem} + 2\,pH \tag{17a}$$

$$Cu_{aq}^{2+} + a\{(HL)_2\}_{mem} \rightleftharpoons \{CuL_2(2a-2)HL\}_{mem} + 2H_{aq}^+ \tag{17b}$$

where $(HL)_2$ is the dimeric form of D2EHPA or LIX$^®$ 84-I.

There have been a number of attempts to mathematically model PIM extraction and transport behaviour [6, 30, 41, 43, 47, 60, 66, 68, 87, 92, 94]. The mathematical models developed can be divided into two main groups according to the simplifying assumptions used. The first group incorporates simple steady-state transport (permeation) models involving metal ions (e.g. Cs^+, Rb^+, K^+, Na^+, Cu(II), Cd(II) and Pb(II)). The majority of these models are based on the following six simplifying assumptions [30, 41, 43, 66, 68, 92, 94]:

(i)   Interfacial and bulk phase reactions are very fast leading to instantaneous establishment of chemical equilibria in the system studied.

(ii)   The metal concentration in the membrane phase is negligible with regard to the carrier concentration in the membrane, thus resulting in constant free carrier concentration within the membrane.

(iii)   The concentration of the metal-carrier complex at the membrane/receiving phase interface is negligible relative to its concentration at the membrane/source phase interface. This assumption will be valid if the concentration of the metal in the receiving phase remains virtually zero.

(iv)   Mass transport within the membrane is the result of Fickian diffusion only and the concentration gradient of the metal-carrier complex is linear.

(v)   The diffusion in the aqueous stagnant layer at the membrane/source phase interface is either much faster than the diffusion of the metal-carrier complex across the membrane or is characterized by a linear concentration gradient.

(vi)   Both the source and receiving phases are ideally mixed.

According to assumptions (ii)-(vi) the depletion of the metal ion in the source phase can be described by differential equation (18) with initial condition (18a) while its transport across the membrane can be described by Eq. (19).

$$AJ_s = -V_s \frac{d[M]_s}{dt} \tag{18}$$

$$[M]_s = [M]_s^0 \text{ at } t = 0 \tag{18a}$$

$$J_s = P_s [M]_s \tag{19}$$

where A is the membrane area, V is the phase volume, t is the time, J is the flux, and [M] and $[M]^0$ refer to the transient and initial concentrations of the metal ion in the source phase, respectively. P is the cation permeability coefficient which can be used to characterize PIM transport efficiency. Subscript s refers to the source phase.

The simultaneous solution of Eqs. (18) and (19) gives:

$$\ln([M]_s/[M]_s^0) = - (A/V_s) P_s t \tag{20}$$

Lamb and Nazarenko [66] applied Eq. (20) to describe Pb(II) transport through a CTA PIM incorporating TOPO as the carrier. After substituting P_s with Eq. (21) they were able to estimate the diffusion coefficients of the $PbX_2 \cdot nTOPO$ complexes ($X = I^-$, SCN^-, Br^- or NO_3^-) in the PIMs studied. All values were of the order of $10^{-12} \text{ m}^2 \text{ s}^{-1}$.

$$P_s = (D/\delta) K_P \tag{21}$$

where D is the apparent diffusion coefficient of $PbX_2 \cdot nTOPO$, δ is the membrane thickness and $K_P = [PbX_2 \cdot nTOPO]_{PIM}/[PbX_2]_s$.

The plot of logP vs $log[TOPO]_{PIM}$ revealed that n in the $PbX_2 \cdot nTOPO$ complexes was at least 2.

Paugam and Buffle [94] compared the transport of Cu(II) through SLMs and PIMs containing various concentrations of lauric acid as the carrier. The polymeric supports used were Celgard 2500 polypropylene for the SLMs and CTA for the PIMs. Assuming a linear concentration gradient in the source phase stagnant layer and 1:2 complexation between Cu(II) and lauric acid (Eq. (22)), the authors derived an equation for the flux (Eq. (19)) which was subsequently fitted to both SLM and PIM experimental flux data calculated by Eq. (18). The PIM apparent diffusion

coefficient was found to be an order of magnitude lower than the SLM apparent diffusion coefficient under the assumption that the PIM and SLM extraction constants were similar.

$$Cu_{aq}^{2+} + 2HL_{mem} \rightleftharpoons CuL_{2\ mem} + 2H_{aq}^{+} \tag{22}$$

Aguilar *et al.* [41] described mathematically the extraction and transport of Cd(II) and Pb(II) in SLM and PIM systems based on Eq. 20. Solvent extraction data regarding the stoichiometry of the corresponding extraction equilibria involving Kelex 100 in Kerosene as the carrier (Eqs. (23)-(25)) were also used [41].

$$Cd_{aq}^{2+} + Cl_{aq}^{-} + HL_{mem} \rightleftharpoons CdL^{+}Cl^{-}_{mem} + H_{aq}^{+} \tag{23}$$

$$Cd_{aq}^{2+} + Cl_{aq}^{-} + 2HL_{mem} \rightleftharpoons CdHL_{2}^{+}Cl^{-}_{mem} + H_{aq}^{+} \tag{24}$$

$$Pb_{aq}^{2+} + 2HL_{mem} \rightleftharpoons PbL_{2\,mem} + 2H_{aq}^{+} \tag{25}$$
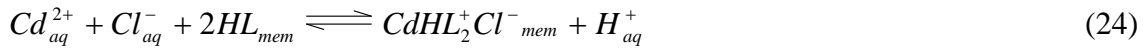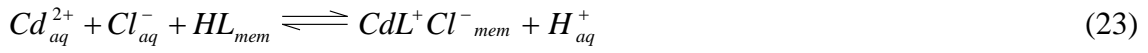
Polyvinylidene fluoride (PVDF) was the polymeric support for the SLMs studied while CTA was used for the PIMs [41]. The model takes into account the transport of the metal species across the aqueous boundary layer at the membrane/source phase interface. Expressions for the permeability coefficients for both Cd(II) and Pb(II) were derived and the model was fitted to experimental data to determine the numerical values of the corresponding apparent membrane diffusion coefficients. The diffusion coefficients of the Cd(II) and Pb(II) complexes within the PIMs studied were determined to be of the order of 10^{-12} m^{2}s^{-1} similar to those obtained by Lamb and Nazarenko [66] while the corresponding SLM values were three orders of magnitude higher.

Salazar-Alvarez *et al.* [92] followed the modeling approach of Aguilar *et al.* [41] to describe the transport characteristics (i.e., maximum flux, thickness and resistance of the boundary layers, the apparent activation energy for the facilitated diffusion of Pb(II) across the membrane) of a CTA-based PIM system used for the extraction of Pb(II) with D2EHPA. The diffusion coefficient found for the transport of the Pb(II)-D2EHPA complex across the PIMs studied (1.5×10^{-11} m^{2}s^{-1}) was similar to the diffusion coefficient values reported earlier for other Pb(II)/PIM systems [41, 92].

de Gyves *et al.* [43] evaluated both the source phase (Eq. (20)) and receiving phase (Eq. (26)) permeability of CTA-based PIMs incorporating LIX® 84-I during the transport of Cu(II) from chloride and sulfate containing source phases.

$$\ln\{1-[M]_r/[M]_r^\infty\} = - (A/V_r)\, P_r\, t \tag{26}$$

where $[M]_r^\infty$ is the equilibrium metal ion concentration in the receiving phase at $t\rightarrow\infty$.

The results obtained showed evidence of metal accumulation in the membrane in the case of the chloride containing source phase. An expression for the permeability coefficient based on Assumptions (i) – (vi) was derived and fitted to experimental data obtained for PIMs with different LIX® 84-I concentrations. The value of the apparent diffusion coefficient of the copper LIX® 84-I complex was estimated as $10^{-12.2}$ m^2 s^{-1}. This value is in good agreement with those reported for the other PIM systems mentioned earlier [43, 66, 92].

Levitskaia *et al.* [30, 68] developed a model for the transport of monovalent metal ions, denoted here as M(I), across CTA membranes incorporating calixarene-crown ethers (B) as carriers which formed 1:1 metal-carrier complexes (MB$^+$, Eq. (27)) in the membrane.

$$M_{aq}^+ + X_{aq}^- + B_{mem} \rightleftharpoons MB_{mem}^+ + X_{mem}^- \tag{27}$$
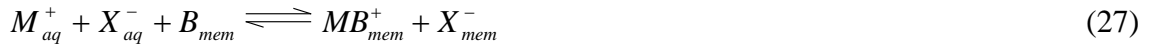
where X$^-$ is the anion in the metal salt dissolved in the source phase.

When a single salt (MX) was present in the source phase, the equation for the transient source phase metal concentration was identical to Eq. (20) where the cation permeability coefficient was defined by Eq. (28).

$$P_f = (K'_{ex}[B]_{PIM})^{1/2}\, D/\delta \tag{28}$$

where K'_{ex} is the formal equilibrium constant of the complexation reaction described by Eq. (27).

The equation for the transient metal concentration derived (Eq. (29)) when the anion concentration was constant differed substantially from Eq. (20) [66].

$$-[M^+]_s^{1/2} = - ([M^+]_s^0)^{1/2} + \tfrac{1}{2}(A/V_s)\, P_s\, [X^-]_s^{1/2}\, t \tag{29}$$

where P_s is defined by Eq. (28).

Eq. (29) is also valid when more than one cation is simultaneously transported across the membrane with one of these ions being preferentially transported.

The validity of the model outlined above (i.e. Eqs. (20), (28) and (29)) was successfully verified using experimental transport data [68]. This model for the case of constant anion concentration (Eq. (29)) was subsequently applied by the same authors [30] to characterize the performance of PIMs in the processing of complex acidic nuclear wastes when different calixarene-crown ether carriers were used and the composition of the source phase was varied.

The steady-state models outlined above are generally valid only for the initial stages of most membrane transport processes when the ratio between the free carrier concentration and the concentration of the metal-carrier complex in the PIM is sufficiently high. These models are, however, not applicable in the cases of slow interfacial kinetics or when metal accumulation in the membrane takes place.

A more general modeling approach overcoming most of the disadvantages of the steady-state PIM models mentioned above was proposed by Kolev *et al.* [60]. The models based on this approach and developed by the same research group [6, 47, 60, 87] involve more complex mathematics requiring the application of numerical techniques. They were successfully used to describe mathematically the extraction and transport of Au(III) [60], Pd(II) [47], Cd(II) [6] and Cu(II) [6] across PVC membranes incorporating Aliquat 336 chloride as the carrier. These models are based on assumptions (iv) – (vi) regarding the Fickian nature of the membrane mass transfer and the rapid mass transport in both the bulk and the stagnant layers of the source and receiving phases. The latter assumption is justified in the case of efficient stirring when the bulk and interface concentrations are almost identical. These models, unlike the steady-state models outlined above, can be used to describe membrane extraction and transport involving metal accumulation in the membrane and slow interfacial complexation reactions. In those cases the diffusion of both the metal-carrier complex and the free complex within the membrane must be taken into account. To simplify the mathematical description in such cases, it has been assumed that the diffusion coefficients of the complexed and uncomplexed carrier are equal. This means that the total concentration of the carrier in the membrane is uniform and constant and it is

sufficient to describe the diffusion of either the uncomplexed or the complexed carrier only. These models have been applied to PIM systems operating in 'extraction mode' only, i.e. both sides of the membrane are in contact with the same source solution only. If the two compartments of the transport cell are identical, the transport cell can be considered as symmetrical with respect to the membrane. This simplifies the development of the mathematical model as only half the transport cell (Figure 11), consisting of one compartment and half of the membrane adjacent to it, must be considered. If the source phase contains a negatively charged metal chloride complex the following interfacial ion-pair formation process can take place:

$$MCl_{m}^{n-}{}_{aq} + nRCl_{mem} \overset{k_{+1}}{\underset{k_{-1}}{\rightleftharpoons}} (MCl_{m}R_{n})_{mem} + nCl_{aq}^{-} \tag{30}$$
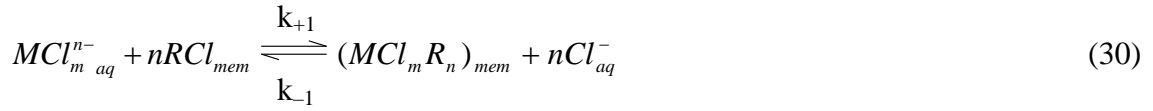
where k_{+1} and k_{-1} are the forward and the backward kinetic rate constants and RCl represents the Aliquat 336 chloride.

Due to steric and viscosity related restrictions n is usually 1 [6, 47, 60]. If the chloride ion is in excess, which is usually the case, the transient interfacial concentration of MCl_{m}^{n-} ($x = \delta$, Figure 11) can be described by Eq. (31).

$$V \frac{d[MCl_{m}{}^{n-}]_{aq}}{dt} = -A\left\{ k_{+1}[RCl]_{mem}^{n}[MCl_{m}{}^{n-}]_{aq} - k_{-1}[MCl_{m}R_{n}]_{mem} \right\} \tag{31}$$

This concentration is identical to the bulk concentration of this chemical species under the assumption of ideal mixing in the aqueous phases.

[FIGURE 11]

The mass transfer of the free Aliquat 336 chloride within the membrane can be described by the Fick's second law (Eq. (32)) with initial and boundary conditions expressed by Eqs. (32a)-(32d), respectively.

$$\frac{\partial [RCl]_{mem}}{\partial t} = D \frac{\partial^{2}[RCl]_{mem}}{\partial x^{2}} \tag{32}$$

$$[RCl]_{mem}(0, x) = [RCl]_{mem}^{0} \tag{32a}$$

$$\left(\frac{\partial \, [RCl]_{mem}}{\partial x} \right)_{x=0} = 0 \tag{32b}$$

$$V \frac{d[MCl_m^{\,n-}]}{dt} = -\frac{AD}{n} \left(\frac{\partial \, [RCl]_{mem}}{\partial x} \right)_{x=\delta} \tag{32c}$$

$$[MCl_m^{\,n-}]_{x=0} = [MCl_m^{\,n-}]^0 \tag{32d}$$

where x is the axial distance and D is the diffusion coefficient of RCl_{mem} which was assumed to be equal to that of $\{MCl_mR_n\}_{mem}$.

The concentration of the ion-pair $\{MCl_mR_n\}_{mem}$ can be determined as:

$$[MCl_mR_n]_{mem} = \frac{[RCl]_{mem}^0 - [RCl]_{mem}}{n} \tag{33}$$

Eqs (31)-(33) cannot be solved analytically because of the non-linearity of Eq. (31) with respect to the dependent variables $[RCl]_{mem}$ and $[MCl_m^{\,n-}]_{aq}$. The implicit finite-difference method [60] was used for the simultaneous solution of Eqs. (31)-(33).

After converting Eqs. (31) and (32) at n = 1 into equations in dimensionless quantities and variables it was shown that the overall membrane extraction process can be characterized by two dimensionless groups (Eqs. (34) and (35)) [60].

$$\alpha = \frac{k_{-1}\delta}{D} \frac{\delta}{L} \frac{[RCl]_{mem}^0}{[MCl_m^{\,-}]_{aq}^0} \tag{34}$$

$$\beta = K_{ex}[MCl_m^{\,-}]_{aq}^0 \tag{35}$$

where L = V/A is the characteristic length of the aqueous (source) phase.

The numerical values of these two dimensionless groups determine whether the extraction process is under diffusion, kinetic or mixed diffusion-kinetic control (Figure 12) [60]. It is possible to estimate whether for a particular extraction system, variations in the value of the diffusion coefficient and the kinetic constants will influence its performance.

[FIGURE 12]

The model outlined above was fitted to experimental extraction data using a simplex optimization algorithm to determine the values of the kinetic rate constants, the extraction constant and the diffusion coefficient in the extraction of Au(III) [60], Pd(II) [47] and Cd(II) [6] from their hydrochloric acid solutions into PVC/Aliquat 336 chloride membranes of different thickness and containing 20 – 50% (w/w) Aliquat 336 chloride. The diffusion coefficient values obtained were of the order of 10^{-13} m^2s^{-1}, similar to the values obtained by fitting the steady-state transport models outlined above to the initial stages of PIM transport experiments [41, 43, 66, 92]. As expected, the diffusion coefficients increased with increasing Aliquat 336 chloride concentration in the PIMs studied. An order of magnitude higher diffusion coefficient values for 50% membranes compared to lower concentration membranes indicated possible structural changes in the membrane occurring at Aliquat 336 chloride concentrations higher than 40%.

The modeling approach outlined above was also applied to the 'non-facilitated' transport of thiourea across PVC/Aliquat 336 chloride PIMs separating acidic source and receiving phases where thiourea was partially protonated [87]. It was assumed that molecular thiourea was only transported across the PIMs and that its interfacial PIM concentration was determined by the corresponding partition constant. By fitting the model to the experimental PIM extraction data an empirical expression for calculating the diffusion coefficient of thiourea in PVC/Aliquat 336 chloride membranes was derived (Eq. (36)) [87].

$$D = 2.43 \times 10^{-18} C^{3.627} \tag{36}$$

where C is the percentage membrane concentration of Aliquat 336 chloride. Eq. 36 is valid for C between 30% and 50% (w/w).

9 THE FUTURE OF PIM RESEARCH

One of the main goals of this review is to provide deeper insight into the factors that control the transport rate, selectivity and stability of PIMs by collating the transport phenomena observed by various authors and relating these to the membrane properties. As discussed in the various sections, a number of factors have been found to influence the performance of PIMs with the most important amongst them being: (1) the membrane composition, (2) the properties of the base

polymers, the carriers and the plasticizers, (3) the morphology of the membrane and (4) the chemistry of the aqueous solutions making up the source and receiving phases. It has been observed that there is an intricate relationship between these factors and so it is essential to take them into account in any holistic approach to the transport mechanisms in PIMs.

As we have documented, there is a respectable number of published papers on PIMs and this number is increasing steadily. One factor stands out in the majority of these papers and this is the need to achieve a balance in membrane composition with respect to the three major constituents of the membrane, namely, the base polymer, the carrier and the plasticizer. While the carrier is essential for the transport of the target solute in PIMs, excessive amounts of carrier can result in carrier aggregation in some cases and exudation in others. Also, excessive amount of plasticizer can lead to "bleeding" from the membrane, whereas insufficient plasticizer can lead to very low permeabilities.

The base polymers have often been thought to merely provide mechanical support for the other constituents in order to give stability to the membrane, however, research has indicated that the bulk properties of the polymers can be important factors governing the transport of target solutes. Thus the optimum composition for a PIM depends quite strongly on the physicochemical properties of each constituent of the membrane as well as on their compatibilities. At the present time, the rule of thumb for a PIM composition appears to be 40% (w/w) base polymer, 40% (w/w) carrier and 20% (w/w) plasticizer although not all researchers have used this composition. There is also some evidence that this composition may not result in the best PIM performance in all cases. Considerable effort can be expected in future PIMs research to study these effects and to develop a model that can be used in the prediction of the optimum composition for a given set of constituents. Although a large number of carriers has been studied in PIMs so far, there is an apparent lack of focus on carriers with high practicality. As we have shown in this review, the number of PIM investigations using commercially available carriers remains limited. Furthermore, only a handful of plasticizers have been investigated to date. Most of these plasticizers seem to have been chosen not because of their commercial availability at low cost or clear industrial application but rather because of their application in ISE membranes. It is also interesting to note that CTA and PVC have been used as the base polymers in most if not all of the PIMs studied so far with CTA predominating. It can be expected that future research will

expand the number of commercially available carriers, plasticizers as well as base polymers that can be used.

Given the demonstrated superior stability of PIMs over the various other types of liquid membranes (e.g. SLMs) and the adequate permeability in practical sense and selectivity of PIMs for industrial applications, Cussler [78] has predicted (with caution about speculation with regard the timeline) a decline in fundamental research on SLMs and an increased interest in PIMs research in the near future and as a result of this, practical applications will emerge (see Figure 13). In fact, this prediction is already becoming reality if one considers the increasing number of papers being published on PIMs. However, we do not believe PIM systems will replace traditional solvent extraction systems, and certainly not in the near future, but will find a role in niche areas such as amino acid separation in biotechnology, fructose enrichment in food processing technology, precious metal recovery from electronic scrap and catalytic converters, the treatment of radioactive waste streams and in environmental cleanup of contaminated waters.

[FIGURE 13]

10 ACKNOWLEDGEMENTS

11 GLOSSARY

2-NPOE	2-nitrophenyl octyl ether
2-NPPE	2-nitrophenyl pentyl ether
ACMs	Activated composite membranes
AFM	Atomic force microscopy
BLMs	Bulk liquid membranes
BMPP	4-benzoyl-3-methyl-1-phenyl-5-pyrazolone
t-BuDC18C6	Di-tert-butylcyclohexano-18-crown-6
CAP	Cellulose acetate propionate
CMPO	Octyl(phenyl)-N,N-diisobutyl carbamoylmethyl phosphine oxide
CTA	Cellulose triacetate
CTB	Cellulose tributyrate
D2EHDTPA	Di(2-ethylhexyl) dithiophosphoric acid

D2EHPA	Di(2-ethylhexyl) phosphoric acid
DBBP	Dibutyl butyl phosphonate
DC18C6	Dicyclohexano-18-crown-6
DNNS	Dinonylnaphthalenesulfonic acid
DOA	Bis(2-ethylhexyl) adipate
DOP	Dioctylphthalate
DOS	Dioctylsecacate
DOTP	Bis(2-ethylhexyl)terephthalate
ELMs	Emulsion liquid membranes
FSMs	Fixed site membranes
FTIR	Fourier transform infrared spectrometry
ISE	Ion selective electrode
Kelex 100	7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline
LIX® 84-I	2-hydro-5-nonylacetophenone oxime
MW_c	Critical entanglement molecular weight
NPHE	p-nitrophenyl-n-heptyl ether
PIMs	Polymer inclusion membranes
POEs	Polyoxyethylene n-alkyl ethers
PVC	Poly(vinyl chloride)
RBS	Rutherford backscattering spectrometry
SEM	Scanning electron microscopy
SLMs	Supported liquid membranes
T2EHP	Tris(2-ethylhexyl)phosphate
TBEP	Tri(butoxyethyl)phosphate
TBP	Tri-n-butyl phosphate
TCP	Tricresyl phosphate
TDMAC	Tridodecylmethylammonium chloride
TDPNO	4-(1'-n-tridecyl)pyridine N-oxide
T_g	Glass transition temperature
THF	Tetrahydrofuran
T_m	Melting temperature
TMPP	4-trifluoroacetyl-3-methyl-1-phenyl-5-pyrazolone
TOA	Tri-n-octyl amine
TODGA	N,N,N,N-tetraoctyl-3-oxapentanediamide
TOMAC	Trioctylmethylammonium chloride
TOPO	Tri-n-octyl phosphine oxide

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Table 1: Physical properties of three polymers most frequently used in PIMs.

Polymer	MW used in PIMs (kDa)	MW_c (kDa)	T_g (°C)	T_m (°C)	Polymeric characteristics
Poly(vinyl chloride) (PVC)	90-180 [a]	12.7 [c]	80 [d]	na	Slightly crystalline, mostly amorphorous [d]
Cellulose triacetate (CTA)	72-74 [b]	17.3 [c]	na	302 [e]	Infusible, high degree of crystallinity, excellent strength [d]
Cellulose tributyrate (CTB)	120 [b]	47.4 [c]	na	207 [d]	Infusible, high degree of crystallinity, excellent strength [d]

[a] Ref [59].
[b] Ref [24].
[c] Ref [112].
[d] Ref [28].
[e] Ref [25].
na: not available.
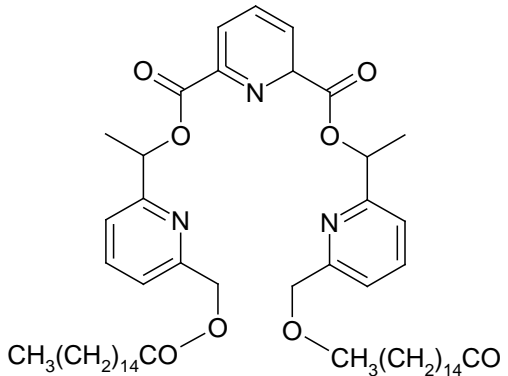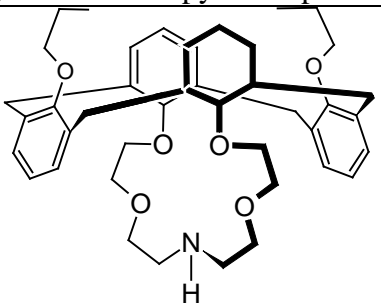
Table 2: Examples of PIM carriers reported in the literature and their typical target solutes (All abbreviations are explained in the Glossary).

	Type of carriers	Examples	Target solutes	Refs
Basic	Quaternary amines	Aliquat 336	As(V), Au(III), Cd(II), Cr(VI), Cu(II), Pd(II), Pt(IV) , small saccharides, amino acids, lactic acid	[6, 7, 9, 33, 47, 55, 59, 83-85, 91, 99]
	Tertiary amines	TOA Other tri-alkyl amines	Cr(VI), Zn(II), Cd(II), Pb(II)	[33, 39, 58, 64, 88, 89]
	Pyridine & derivatives	TDPNO	Ag(I), Cr(VI), Zn(II), Cd(II)	[34, 70, 100]
Acidic and chelating	Hydroxyoximes	LIX® 84-I	Cu(II)	[43]
	Hydroxyquinoline	Kelex 100	Cd(II), Pb(II)	[41]
	β-diketones	Benzoylacetone Dibenzoylacetone Benzoyltrifluoracetone	Sc(III), Y(III), La(III), Pr(III), Sm(III), Tb(III), Er(III), Lu(III)	[79]
	Alkyl phosphoric acids	D2EHPA D2EHDTPA	Pb(II), Ag(I), Hg(II), Cd(II), Zn(II), Ni(II), Fe(III), Cu(II)	[8, 42, 92, 98]
	Carboxylic acids	Lauric acid Lasalocid A	Pb(II), Cu(II), Cd(II)	[11, 93, 94]
Neutral or solvating	Phosphoric acid esters	TBP	U(VI)	[21, 46, 69]
	Phosphonic acid esters	DBBP	As(V)	[99]
	Others	CMPO, TODGA, TOPO, Polyethylene glycol	Pb(II), Cd(III), Cs$^+$, Sr(II)	[27, 53, 66]
Macrocyclic and macromolecular	Crown ethers and Calix arenes	DC18C6 BuDC18C6	Na$^+$, K$^+$, Li$^+$, Cs$^+$, Ba(II), Sr(II), Pb(II), Sr(II), Cu(II), Co(II), Ni(II), Zn(II), Ag(I), Au(III), Cd(II), Zn(II), picrate	[10, 13-15, 19, 20, 30-33, 54, 65, 68, 93, 101, 103-106, 113]
	Others	Bathophenanthroline Bathocuproine	Lanthanides	[15, 45, 67, 97, 114]

Table 3: Reported PIM lifetimes under continuous operation.

Membranes	Reported lifetime and membrane performance	Refs
CTA/Calix[6]arene/2-NPOE	Small flux decline after 30 days	[106]
CTA/Lasalocid A/2-NPOE	No sign of flux decline or carrier and plasticizer losses after 10 days. Stable after 10 months storage in air	[11]
CTA/Acyclic polyether bearing amide/2-NPOE-TBEP	Small flux decline after 15 days but no evidence of carrier and plasticizer loss	[20]
CTA/Calix[4]arene/2-NPOE	Small flux decline after 20 days but no evidence of carrier and plasticizer loss	[19]
CTA/Calix[4]arene/2-NPOE	Stable flux after one month	[30]
CTA/DC18C6/2-NPOE, TBEP	Flux decline began slowly after 100 days but no evidence of carrier and plasticizer loss	[5]
CTA/Aliquat 336/2-NPOE, DOS, DOTP, or DOP	Flux decline and carrier/plasticizer loss began after 30 days	[55]
CTA/Aliquat 336/T2EHP	Flux decline began after 18 days	[55]
CTA/t-buDC18C6/2-NPOE-DNNS	Stable for several weeks	[31]

Table 4: Reported PIM studies using macrocyclic and macromolecular carriers.

	Macrocyclic Carriers	Target species	Base polymer/Plasticizer	Refs
A	 Pyridino- and bipyridino-podands	Ag(I)	CTA/2-NPOE	[100]
B	 Calix[4]arene	Ag(I)	CTA/2-NPOE and TBEP	[101]
C		Ag(I)	CTA/2-NPOE-TBEP	[20]
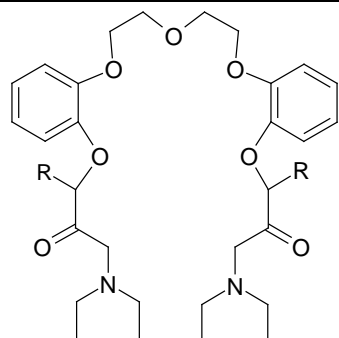
	Acyclic polyether diamide (R = H or $C_{14}H_{29}$)	Acyclic polyether diamine		
D	N-benzylated macrocyclic	Ag(I)	CTA/2-NPOE	[102]
E	4, 7, 13, 16, 21, 24 hexaoxa 1, 10 diazabicyclo [8.8.8] Hexacosane 4, 7, 13, 16, 21 pentaoxa 1, 10 diazabicyclo [8.8.5] Tricosane Dibenzo 18-crown-6 (DB18C6)	Ag(I), Cu(II)	CTA/2-NPOE	[14]
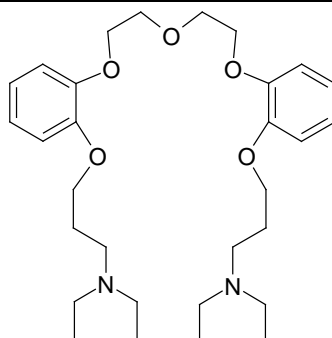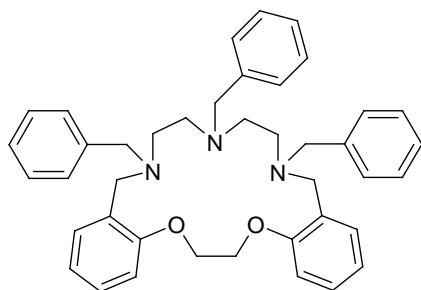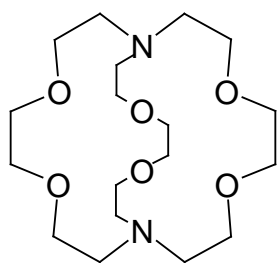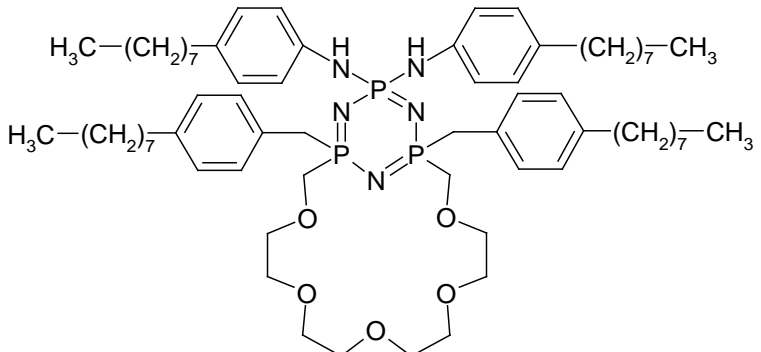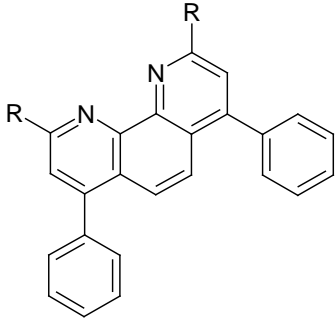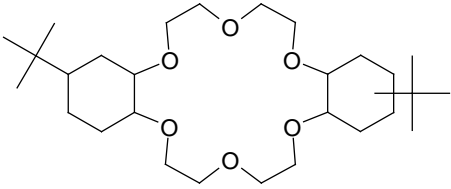
F	Dibenzo-18-crown-6 (DB18C6)	Cu(II)	CTA/2-NPOE	[10]
G	Dibenzo-18-crown-6 (DB18C6) Hexathiol-18-crown-6 (HT18C6) Diaza-18-crown-6 (DA18C6) Hexaza-18-crown-6 (HA18C6)	Ag(I), Cu(II), Au(III)	CTA/2-NPOE	[13]

H	 Diazadibenzocrown ethers		1	2	Pb(II)	CTA/2-NPOE	[32]

Inner table for H:

	1	2
R'	t-Bu	H
R	H	$CH_2CO_2C_2H_5$

I		Zn(II), Cd(II), Cu(II)	CTA/2-NPOE	[103]

Diphosphaza-16-Crown-6 Derivatives

J	β-cyclodextrin (β-CD) polymers	Cu(II), Co(II), Ni(II), Zn(II)	CTA/2-NPPE	[104]
K	 Bathophenanthroline: R = H Bathocuproine: R = CH$_3$	Zn(II), Cu(II), picrate	CTA/Various plasticizers	[15, 56]
L	 di-tert-butylcyclohexano-18-crown-6 (BuDC18C6)	Sr(II)	CTA/2-NPOE	[31, 54]

M

Ligand	X
1	CF$_3$
2	C$_6$H$_4$-4-NO$_2$
3	C$_6$H$_5$
4	CH$_3$

acyclic polyether di[N-(X)sulfonyl carboxamides] | Ba(II) | CTA/PVC/NPOE | [105] |
| N |

1,3,5-Trimethyl-2,4,6-tricarboxamide-p-tert-butylcalix[6]arene
(R=CH$_2$CO$_2$H and R'=CH$_2$CONEt$_2$) | Ba(II) | CTA/NPOE-TBEP | [106] |
| O |

1,3-bis(dodecyloxy) calix[4]arene-crown-6   1,3-calix[4]-arene-biscrown-6 | Cs$^+$ | CTA/2-NPOE | [30, 68] |
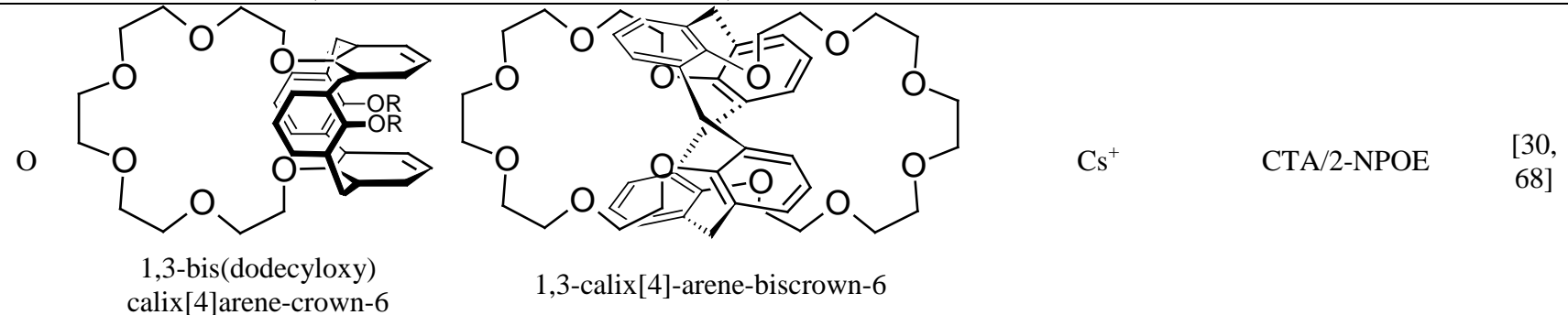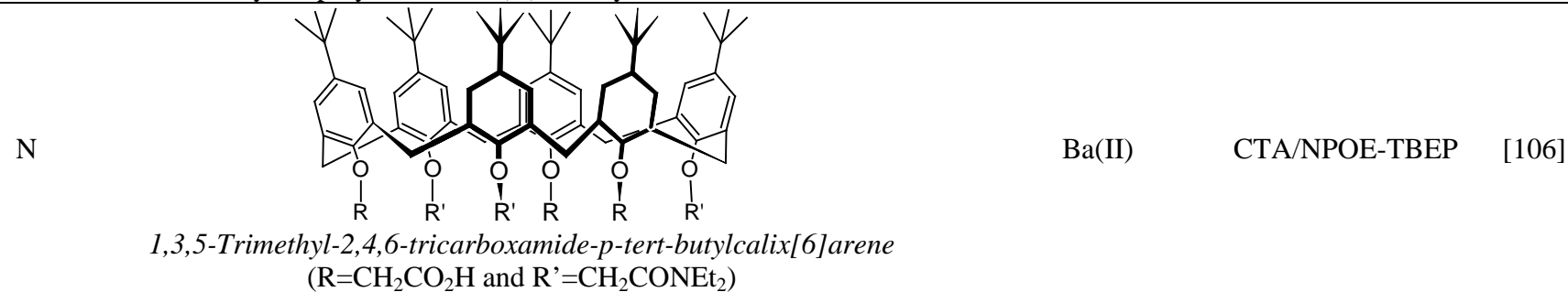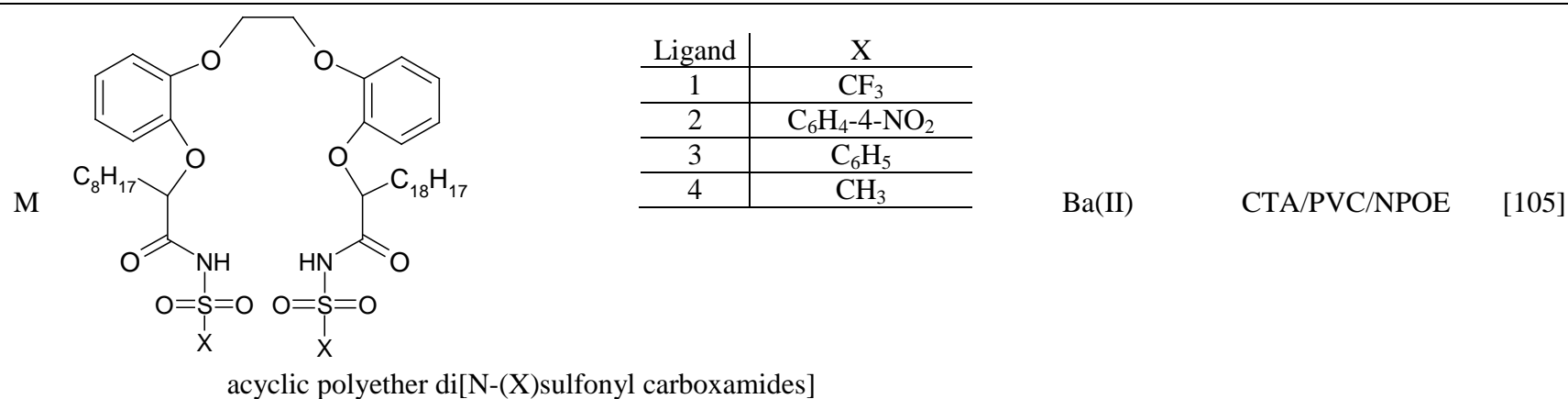
P	5'-(Tert-butyldimethylsilyl)-2',3'-O-isopropylidene isoguanosine (isoG 1)	Cs^+, Pb(II)	CTA/2-NPOE	[63]
Q	R = $C_3 - C_{16}$ alkyl chains Sym-(alkyl)dibenzo-16-crown-5-oxyacetic acids	Na^+	CTA/2-NPOE or 2-NPPE	[33]
R	4'-N-butylcarboxamidobenzo- 15-crown-5	K^+, Li^+	Sol-gel	[65]

FIGURE CAPTIONS

Figure 1: Chemical structures of plasticizers commonly used in PIMs.

Figure 2: Permeability of Cu(II) as a function of the plasticizer TBEP concentration in CTA membranes containing LIX® 84-I as the carrier. Source phase: 20 mg/L Cu(II), 0.025 M AcH/AcNa, pH 5.0; receiving phase: 1 M H_2SO_4. (Reproduced with permission from ref [43]. Copyright 2005 Elsevier Science.)

Figure 3: The effect of plasticizer viscosity on Cr(VI) transport through CTA and PVC membranes. (a) The membranes contained 1.0 M TOA (based on plasticizer volume). Source phase: 2×10^{-2} M Cr(VI), 1.0 M HCl; receiving phase: 0.1 M NaOH. (b) The membranes contained 20% (w/w) Aliquat 336, 40% (w/w) plasticizer. Source phase: 1.8 x 10^{-6} M Cr(VI), pH 2; receiving phase: 1 M $NaNO_3$. See the glossary list for the plasticizer names. (Reproduced with permission from ref [55], copyright 2005 Elsevier Science and from ref [39], copyright 2004 Taylor & Francis.)

Figure 4: Morphology of the thin films with various membrane constituents. The thin films consist of A: pure CTA; B: CTA and 2-NPOE; and C: CTA, 2-NPOE, and DB18C6. (Reproduced with permission from ref [14]. Copyright 2004 Elsevier Science.)

Figure 5: A typical PIM or SLM experimental set up.

Figure 6: Chemical structures of several basic carriers. Note: Aliquat 336 consists of a mixture of up to 5 quaternary ammonium compounds with alkyl chains (R) varying from C8 to C10 [115]. In the following discussion, we are using $R_4N^+Cl^-$ to represent Aliquat 336 for simplicity. It should be noted that some researchers refer to Aliquat 336 simply as tri-n-octylmethyl ammonium chloride (TOMAC).

Figure 7: Chemical structures of some acidic carriers. Note: In the discussion in the text HR and R are used to represent the neutral and deprotonated forms of the carrier, respectively.

Figure 8: Chemical structure of Lasalocid A.

Figure 9: Chemical structures of several neutral carriers.

Figure 10: Schematic description of coupled transport of a positively charged (M^+) or negatively charged (M^-) species through a PIM. C represents the carrier and X is an aqueous soluble coupled transport ion. $[M^+]$, $[M^-]$, $[X^-]$ and $[X^+]$ represent the total analytical concentrations of the respective solute in the bulk aqueous phases. (a): The target solute is a cation and is concurrently transported with a coupled transport anion; (b): the target solute is a cation and is counter-currently transported with a coupled transport cation; (c): the target solute is an anion and is counter-currently transported with a coupled transport anion; (d): the target solute is an anion and is concurrently transported with a couple transport cation.

Figure 11: Schematic diagram of the membrane extraction system where only half of the transport cell is considered. (δ is half the membrane thickness).

Figure 12: Influence of the kinetic and diffusion parameters on the character of the extraction process. (Reproduced with permission from ref [60]. Copyright 1997 Elsevier Science.)

Figure 13: Historical and future development of liquid membranes and PIMs. The width of the bars represents the amount of effort merited. (Adapted from Cussler [78].)

2-Nitrophenyl octyl ether (2-NPOE)
(1-nitro-2-octyloxybenzene)

Dioctyl phthalate
(DOP)

Polyoxyethylene n-alkyl ethers
(POEs) ($R = C_nH_{2n+1}$)

Bis(2-ethylhexyl) adipate (DOA)
(Dioctyl adipate)

Tris(2-ethylhexyl) phosphate
(T2EHP)

FIGURE 1

FIGURE 2

FIGURE 3

A

Pure CTA (cross section)

Pure CTA (surface)

B

CTA + 2-NPOE (cross section)

CTA + 2-NPOE (surface)

C

CTA + 2-NPOE + DB18C6 (cross section)

CTA + 2-NPOE + DB18C6 (surface)

FIGURE 4

**Membrane separating
the two aqueous phases**

FIGURE 5

Quaternary ammonium chloride (Aliquat 336)

Tri-n-octylamine (TOA)

4-(1'-n-tridecyl)pyridine N-oxide (TDPNO)
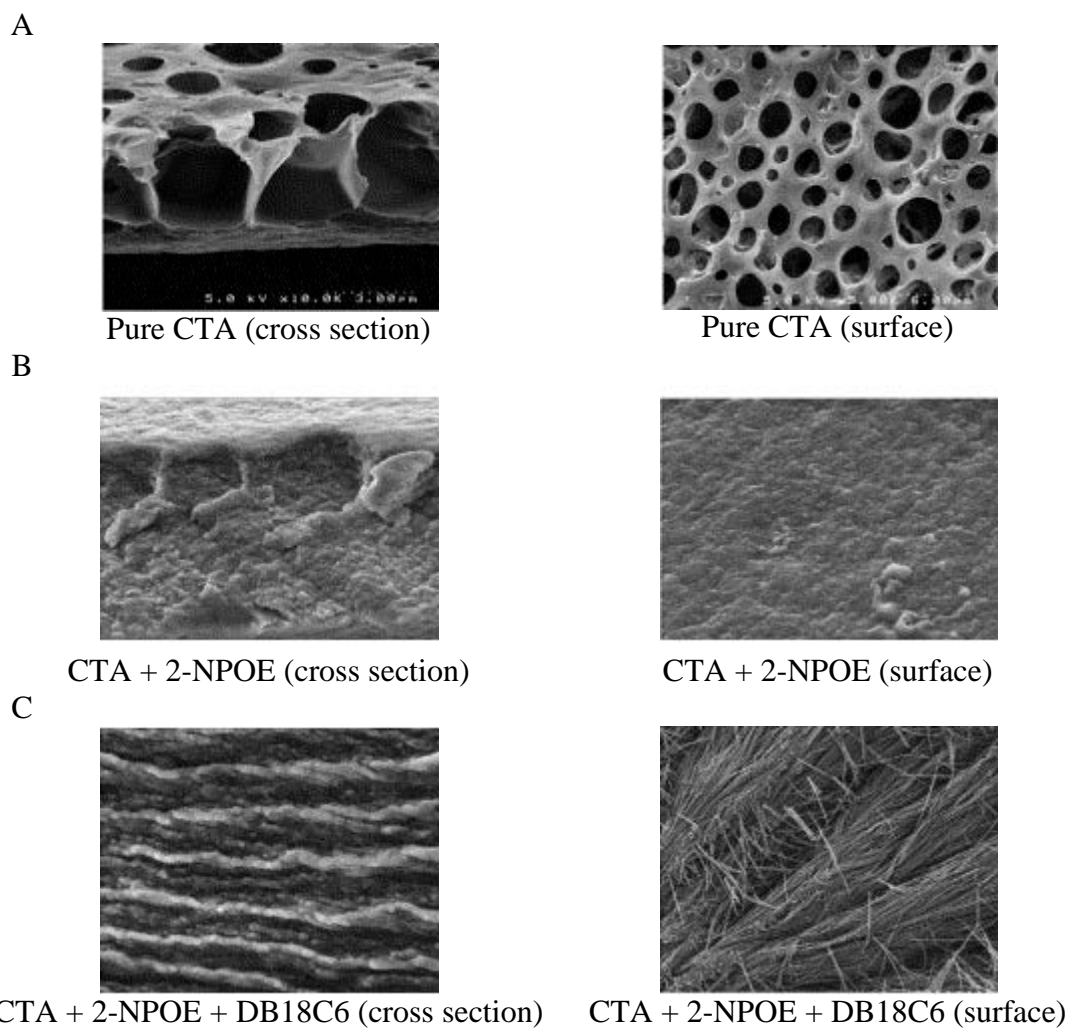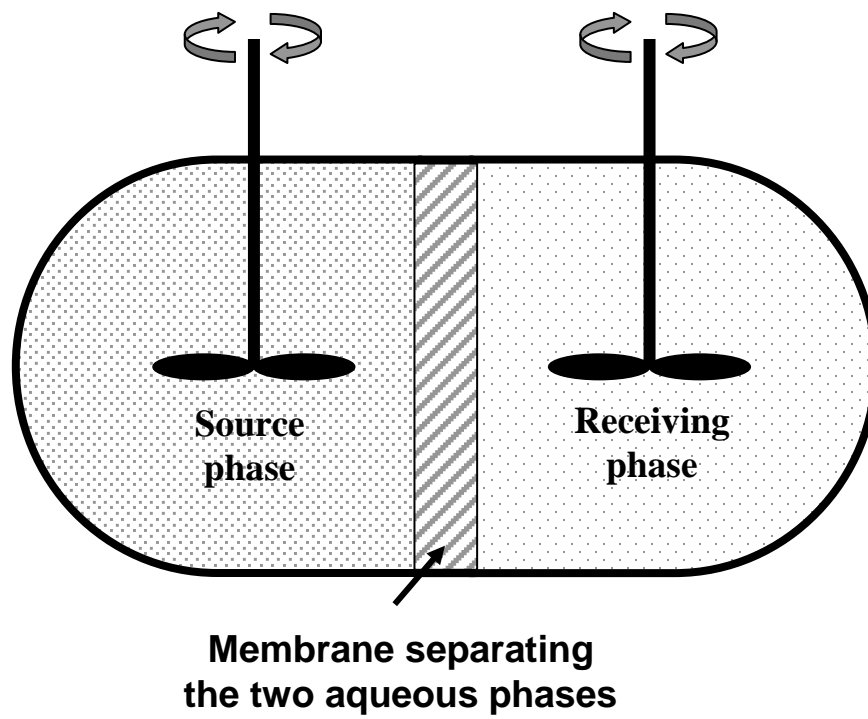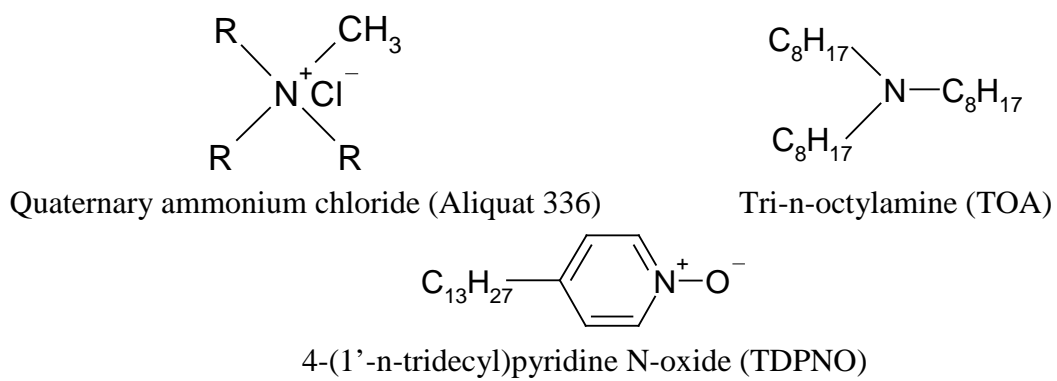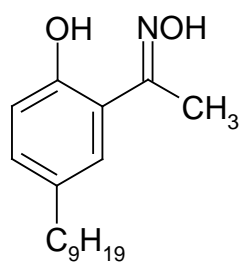
FIGURE 6

2-hydroxy-5-nonylacetophenone
oxime
(LIX® 84)
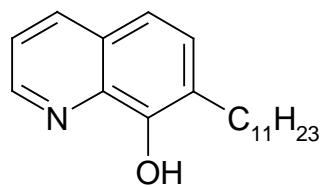
7-(4-ethyl-1-methyloctyl)-8-
hydroxyquinoline
(Kelex 100)
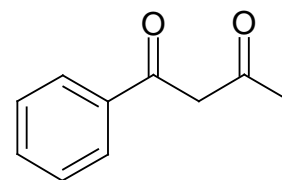
Benzoylacetone

FIGURE 7

FIGURE 8

Tri-n-butyl phosphate (TBP)

Dibutyl butyl phosphonate (DBBP)

Tri-n-octyl phosphine oxide (TOPO)
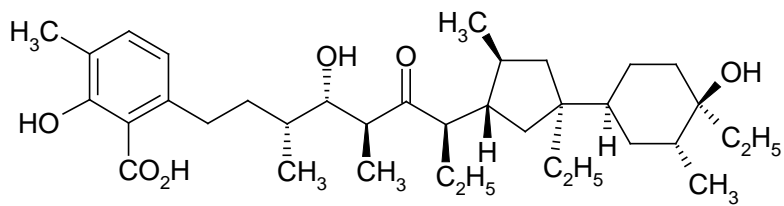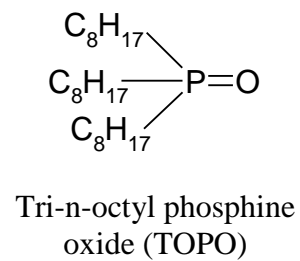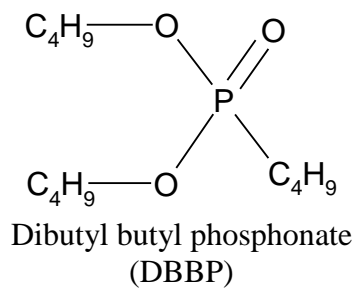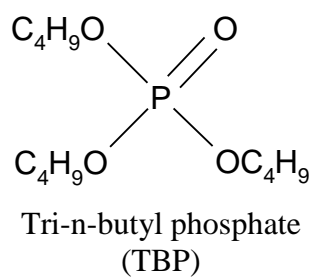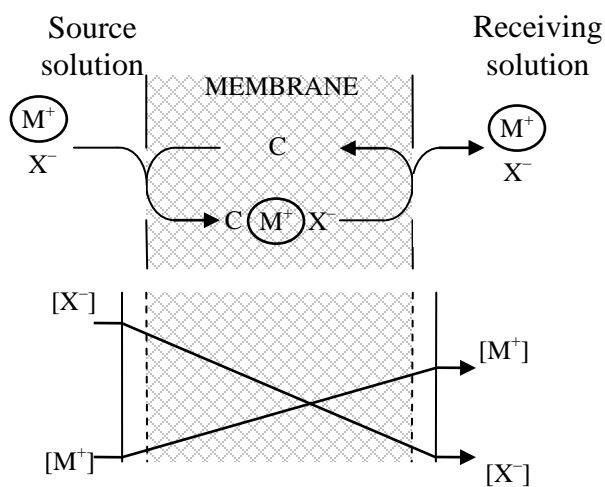
FIGURE 9

(a) Co-transport of a cation
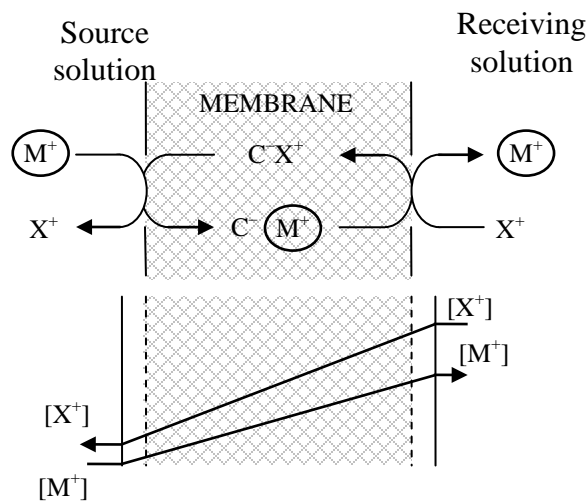
(b) Counter-transport of a cation
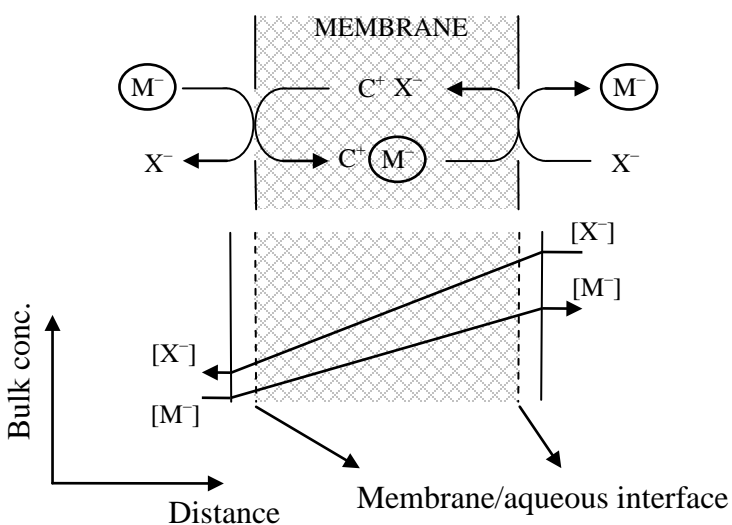
(c) Counter-transport of an anion

(d) Co-transport of an anion

FIGURE 10

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FIGURE 11

FIGURE 12

FIGURE 13