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– *Reviews* –

The Extraction and Transport of Organic Molecules Using Polymer Inclusion Membranes

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Polymer Inclusion Membranes (PIMs) have the potential of providing an attractive alternative to traditional solvent extraction since they drastically reduce the use of volatile, flammable and often toxic diluents. In addition, they also allow the extraction and back-extraction steps to proceed simultaneously and in a continuous fashion. The great majority of the PIM studies have been directed towards metal separation which may suggest that PIMs are less suitable for the separation of organic compounds. However, the present review shows how successfully PIMs can be applied to the separation of various organic compounds of industrial and environmental importance.

1. Introduction

Solvent extraction constitutes one of the most widely applied technologies in industrial separation [1]. While amenable to large scale applications, large volumes of diluents (*e.g.*, kerosene) are required and these can present problems associated with safety and cost and can have a negative environmental impact. Membrane extraction is a viable alternative to traditional solvent extraction with significant advantages including reduced reagent and diluent use [2]. The use of membranes for transport purposes has largely been dominated by metal species due to commercial interests, particularly in the mining and nuclear processing industries [3-6]. However, membranes for the extraction and transport of organic compounds have gained wider acceptance through passive sampling devices [7-10] and electrodialysis [11,12]. This review examines the application of membranes and in particular, Polymer Inclusion Membranes (PIMs), for the extraction and transport of organic molecules.

In membrane extraction, the membrane acts as the organic phase, where the extracted species is stored in the membrane to be removed for later processing. In this form membrane extraction is equivalent to solid phase extraction. However, extracting membranes are also capable of facilitated transport, which allows both extraction and back-extraction to proceed simultaneously at opposite sides of the membrane [13]. By incorporating

selective reagents (carriers), membranes can achieve facilitated rather than passive transport of selected species. Membrane transport offers the potential for substantial improvements to the overall speed of a separation process and to a reduction of its complexity.

The main types of liquid extracting membranes are; Bulk Liquid Membranes (BLMs), Emulsion Liquid Membranes (ELMs), Supported Liquid Membranes (SLMs) and Polymer Inclusion Membranes (PIMs) [14].

BLMs consist of a liquid phase partitioned between an aqueous feed phase and a receiver phase (Fig. 1a). Mechanical stirring of the different phases is used to enhance mass transfer processes, creating added mechanical complexity to the procedure. However, BLMs are superior to traditional solvent extraction methods in the sense that BLMs require smaller quantities of carriers and diluents [2]. BLMs have low interfacial surface areas and mass transfer rates, and are not scalable to industrial levels [13]. An example of BLM use is in solvent-based cellulose membrane passive sampling devices for monitoring of herbicides in environmental waters [10]. Such devices can be as simple as dialysis tubing containing a suitable solvent to enable passive transport.

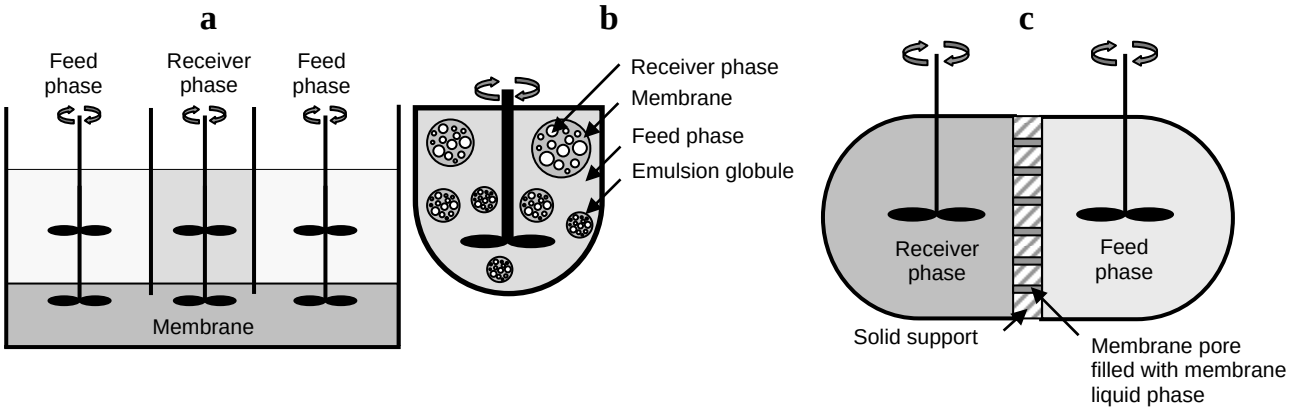

Fig. 1. Schematic diagrams of a BLM (**a**), ELM (**b**) and SLM (**c**) (Preprinted from Ref. [2] with permission from Elsevier.).

ELMs consist of emulsion globules which are a mixture of the receiver solution and the organic membrane liquid phase (Fig. 1b) [2]. Stabilization of the emulsion globules is by a surfactant, which allows the globules to be dispersed in the feed solution. The double emulsion is characterized by a large interfacial surface area between the emulsion globules and the receiver phase, which enables fast mass transfer. After equilibrium has been reached, the aqueous phase is separated from the emulsion globules, which are subsequently broken down into an organic liquid membrane layer and an aqueous receiver solution. The main difficulties with ELM's separation are linked to the formation and breakdown of the emulsion itself, thus limiting the commercial uptake of ELMs [2].

SLMs are prepared by filling the pores of a porous hydrophobic membrane (*e.g.*, PTFE, poly(tetrafluroethylene) or polypropylene) with an organic liquid (Fig. 1c) [2]. The hydrophobic membrane acts as a solid support for the liquid phase retained inside its pores by capillary force. However, over time the liquid phase leaches into the receiver and feed solutions [2].

The above types of membrane systems have been applied to the extraction and transport of organic compounds and these are summarized in Table 1.

Table 1. Applications of BLMs, ELMs and SLMs for the separation of organic compounds.

Membrane Type	Organic Compound	Carrier	Ref.
ELM	Phenol	Dibenzo-18-crown-6/ Aliquat 336	[15]
BLM	Fructose, mannose, galactose, glucose	Phenylboronic acid / TOMA-Cl	[16]
BLM	Uridine	Phenyl boric acid / TOMA-Cl	[17]
BLM	Lactic acid	TOMA-Cl	[18]
BLM	Nucleosides	N-methylpyridiniumboronic acid	[19]
BLM	Catecholamines	Crown boronic acids/ boronic acids	[20]
SLM	Phenol	Dibenzo-18-crown-6	[21]
BLM	Ribose, glucose, fructose	Reversed micelle (Tween 85, Span 60, AOT[1], CTAB[2], DHDMAB[3])	[22]
BLM	Fructose, glucose, sucrose	Aryl boron acid / TOMA-Cl	[23]
SLM	Fructose	Aliquat 336 / boronic acid	[24]
SLM	Cephalosporin antibiotics	Aliquat 336	[25]
SLM	Sodium phenolate	Dibenzo-18-crown-6 / Aliquat 336	[26]
SLM	Sorbose, fructose, glucose, mannose, arabinose, ribose, xylose	Resorcinarene	[27]
SLM	Sialic acid derivatives	Boronic acid / Aliquat 336	[28]
SLM	Fructose, glucose, lactose	Aminomethyl-phenyl boric acid/Aliquat 336	[29]
SLM	Lactic acid	IL-104 (phosphonium ionic liquid)	[30]
SLM	Penicillin G	Amberlite resin / Aliquat 336	[31]

[1]Aerosol-OT; [2]cetyltrimethylammonium bromide; [2]dihexadecyldimethylammonium bromide

2. Polymer Inclusion Membranes

Polymer Inclusion Membranes (PIMs) are homogeneous, transparent and flexible membranes that usually consist of a base polymer, carrier and plasticizer [14]. In some cases the carrier can also act as the plasticizer. The polymer provides mechanical support to the membrane, while the plasticizer increases its flexibility and target solute permeability.

The two polymers poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) are commonly used for making PIMs. PVC is used as a polymer backbone in membranes because of its strength, inertness and compatibility with a variety of plasticisers [32]. It is a non-flammable, lightweight, durable polymer formed from a vinyl chloride monomer. The intermolecular interactions which dominate the C-Cl functional groups in PVC are non-specific dispersion forces, which result in an amorphous structure.

CTA is a polar polymer with a number of acetyl and hydroxyl moieties that are capable of forming highly orientated hydrogen bonding, giving CTA a crystalline structure [14]. CTA is formed by the acetylation of cellulose acetate, which occurs to varying degrees (43-46 % (w/w)). This variation in the degree of hydrogen bonding can lead to high errors associated with membrane measurements depending upon the % (w/w) of non-acetylated hydroxyl groups in the polymer. CTA membranes have good stability and show no evidence of diminished performance after weeks of use [33]. Similar studies with a 0.1 M nitric acid solution have shown no deterioration of the polymer after

100 days of use [13]. However, CTA decomposes when used in strongly acidic and basic solutions [14].

PIMs are formed by dissolving the membrane components in a suitable solvent, *e.g.*, tetrahydrofuran for PVC and chloroform or dichloromethane for CTA; pouring the solution into a mould on a flat surface (*e.g.*, glass plate); and allowing the solvent to evaporate [14]. Successful membranes should be homogeneous, flexible and mechanically strong. The important physicochemical properties of a carrier to obtain useful membranes without the need for an additional plasticizer are lipophilicity, hydrogen bonding capacity, ability to participate in dipole-dipole interactions and its liquid state at room temperature [34].

A comprehensive review on the preparation and physicochemical properties of PIMs and their use in extraction and transport of various species has been published by us and demonstrates that research on PIMs has been largely focused on metallic rather than non-metallic species [14]. This is undoubtedly due to the importance of extraction based separation processes in the metallurgical processing of minerals and in the cleanup of metals from polluted natural waters and industrial and domestic wastewaters.

It should be noted that polymer membranes which fall into the definition of PIMs have been used extensively for many years as the sensing membranes of ion-selective electrodes [35]. Generally, for this application the amount of carrier in the membrane is around 1% (w/w), whereas membranes used for extraction and transport typically contain 20% (w/w) or higher concentrations of carrier. The membrane performance in separation processes is strongly influenced by the membrane diffusion coefficient of the target chemical species, while membranes used for sensing require fast ion-exchange or complexation at the membrane/solution interface to quickly establish the electrical potential difference across the membrane [35].

In the literature, PIMs are also known as polymer liquid, gelled liquid, polymeric plasticized, fixed-site carrier and solvent polymeric membranes [14]. PIMs are generally more stable than SLMs because mainly of the reduceded carrier loss to the aqueous phase, but they can suffer from lower fluxes as a result of their lower diffusion coefficients. However, this can be offset to some extent by using thinner membranes to increase the flux of the targeted species. In a number of cases, it has been observed that at carrier concentrations lower than 20% (w/w) the membrane transport has been negligible , but the transport rates increase exponentially above this value, referred to as the percolation threshold, as the carrier concentration is increased to a maximum of around 50% (w/w) [14].

3. Extraction and transport of organic compounds using PIMs

The solvent extraction of organic compounds is well known in conjunction with phase transfer agents such as Aliquat 336 (a mixture of quaternary ammonium chlorides, predominately trioctylmethylammonium chloride, TOMA-Cl) to facilitate the extraction of polar organic compounds including carboxylic acids [36-40], phenylalanine [41,42] and phenols [43]. While, as seen in Table 1, a number of studies have been conducted on BLMs, ELMs and SLMs for the extraction and transport of organic compounds, there are only a few such studies involving PIMs, which are limited mainly to carbohydrates (Table 2). These studies are discussed briefly in the subsequent paragraphs.

Table 2. The use of PIMs for the transport of organic compounds.

Polymer	Plasticizer	Organic Compound	Carrier	Feed Phase	Receiver Phase	Ref.
CTA	2-NPOE[1] or TBEP[2]	Fructose, glucose, sucrose	TOMA-Cl	0.1 M Sodium phosphate, 0.1 M Target species	0.1 M Sodium phosphate	[33]
CTA	2-NPOE	Phenylalanine, leucine, alanine, dopamine	TOMA-Cl	0.1 M Sodium phosphate, 0.1 M Target species	0.1 M Sodium phosphate	[44]
PVC	2-NPOE	Thiourea	TOMA-Cl	0.29 M HCl, 0.25 M thiourea	0.29 M HCl	[45]
CTA	2-NPOE	Lactic acid	TOMA-Cl	Lactate and NaCl	3 M NaCl	[46]
CTA	2-NPOE	Glucose, sucrose	TOMA-Cl TDMA-Cl TOMA-DHP[3] TOMA-DBP[4]	0.1 M Sodium phosphate, target species	0.1 M Sodium phosphate	[47]

[1]2-nitrophenyloctyl ether; [2]tris(2-butoxyethyl) phosphate; [3]TOMA-dihexadecyl phosphate; [4]TOMA-dibutyl phosphate

Thiourea. The authors have studied the transport of gold(III) from hydrochloric acid solutions using a PVC-based PIM containing Aliquat 336 as the carrier [3,48]. To accelerate and to achieve complete transport, thiourea was added to the receiver solution as a stripping reagent for gold(III). However, thiourea was found to transport through the membrane from the receiver phase to the feed phase where it complexed with gold(III) thus preventing further gold transport. A detailed study of the transport of thiourea through the Aliquat 336/PVC PIM using 0.29 M HCl in both the feed and receiver phases was carried out. A mathematical model of this system was developed and fitted to the experimental transport data thus allowing the determination of the diffusion coefficient of thiourea in the membrane for different concentrations of Aliquat 336 [45]. This is an example of the extraction and transport of a neutral molecule by means of hydrogen bonding with the chloride anion of Aliquat 336 to form a heteroconjugate anion. It could be expected that other organic molecules with the ability to form hydrogen bonds will also be extracted and transported using PIMs containing quaternary ammonium salts as carriers. Other examples of this extraction mechanism are discussed below and they involve the extraction and transport of saccharides (Table 2).

Lactic acid. Matsumoto et al. investigated the transport of lactic acid using a PIM consisting of 20% (w/w) CTA, 40% (w/w) 2-NPOE and 40% (w/w) TOMA-Cl [46]. This membrane was used to remove lactic acid *in situ* during fermentation to increase end product yields. In this example, the use of a PIM was more successful than traditional solvent extraction since, with the latter technique, problems were encountered with microbial decomposition due to contamination of the fermentation liquor by the extracting reagent. The PIM was able to provide a high flux of lactic acid with the same order of magnitude as for an SLM. Matsumoto et al. observed little difference in the flux between 1 M and 0.01 M NaCl in the receiver phase [46]. The pH of the receiver phase was 6 and so lactic acid (pK_a = 3.85) was assumed to be fully dissociated, thus leading to the conclusion that the membrane transport of the lactate ion was based on an anion exchange mechanism.

Saccharides. The extraction and transport of saccharides by membranes has not been studied extensively because of the difficulty in finding carriers that form complexes with sugars. However, Riggs and Smith discovered that PIMs containing TOMA-Cl have the ability to extract and transport saccharides [33]. They used a PIM of composition 20% (w/w) CTA, 40% (w/w) TBEP or 2-NPOE and 40% (w/w) TOMA-Cl to compare the non-

competitive fluxes of glucose, fructose and sucrose as neutral molecules [33]. The flux values are shown in Table 3 and are of the same order of magnitude as those for SLMs. Riggs and Smith attempted to explain the differences in the flux values for the three sugars studied in terms of their molecular size. However, while sucrose, a disaccharide, was the largest of the sugars and had the lowest flux, the other two sugars were monosaccharides and had similar sizes, but quite different fluxes. The explanation for this phenomenon was suggested to be related to steric effects.

Table 3. Non-competitive fluxes for sugars across PIMs. [33].

Membrane	Non-competitive Flux (10^{-8} mol m^{-2} s^{-1})		
	Glucose	Fructose	Sucrose
CTA / 2-NPOE / TOMA-Cl	572	1000	300
CTA / 2-NPOE / TOMA-Br		460	
CTA / 2-NPOE / TOMA-DPP[1]		105	
CTA / TBEP/ TOMA-Cl		3180	
CTA / TBEP/ TOMA-Br		2340	
CTA / TBEP/ THA-Cl[2]		1260	
CTA / TBEP/ TOMA-DPP		600	

[1]TOMA-diphenylphosphinate; [2]trihexylammonium chloride

Riggs and Smith also determined the fluxes for fructose across PIMs containing TOMA salts with different counter anions and different membrane plasticizers (Table 3) [33]. Sugars have a strong ability to form hydrogen bonds and so it is reasonable to assume that the extraction and transport processes involve the formation of heteroconjugate anions between the sugar molecule and the counter anion of the carrier. This would account to some extent for the differences in the flux values between the membranes containing different counter anions characterized by different hydrogen bonding accepting strengths. Also, the plasticizer used would have an effect on the transport. The idea of TOMA salts forming heteroconjugate anions with saccharides through hydrogen bonding has been confirmed by the study of White et al., discussed below [47].

Riggs and Smith proposed that the mechanism for saccharide transport involved fixed-site jumping as shown in Fig. 2 [33].

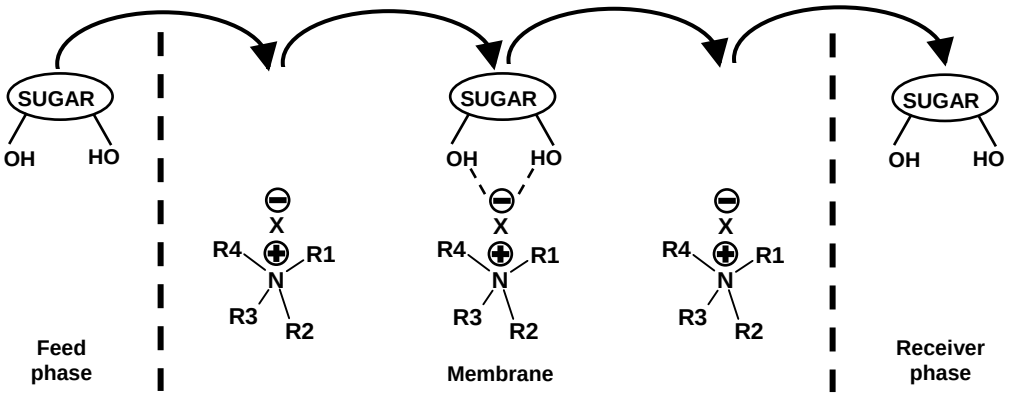

Figure 2. Schematic of a fixed-site jumping mechanism [33].

The rationale for the fixed-site jumping mechanism was based largely on the observation of a "percolation" threshold of carrier concentration (20% (w/w)) in the membrane before any transport was observed. Riggs and Smith calculated that this concentration translated to approximately a distance of 14 Å between adjacent TOMA-Cl ion-pairs. They postulated that the ion-pairs acted like "stepping stones" in the saccharide transport across the membrane.

An extension to the study by Riggs and Smith [33] outlined above has been conducted by White et al. [47]. In this study, a range of carriers was prepared with structures shown in Fig. 3. All these carriers contained the trioctylmethylammonium or tridodecylmethylammonium cation and the chloride, organophosphate or carboxylate anion. The membrane compositions consisted of 100 mg CTA, 200 mg 2-NPOE and different amounts of carrier. The saccharides were sucrose and glucose and the factors investigated were membrane thickness; membrane structure and composition; and sizes of the sugar and the carrier cations and anions. The flux data are summarized in Table 4 and in addition, diffusion coefficients and extraction constants were also determined [47].

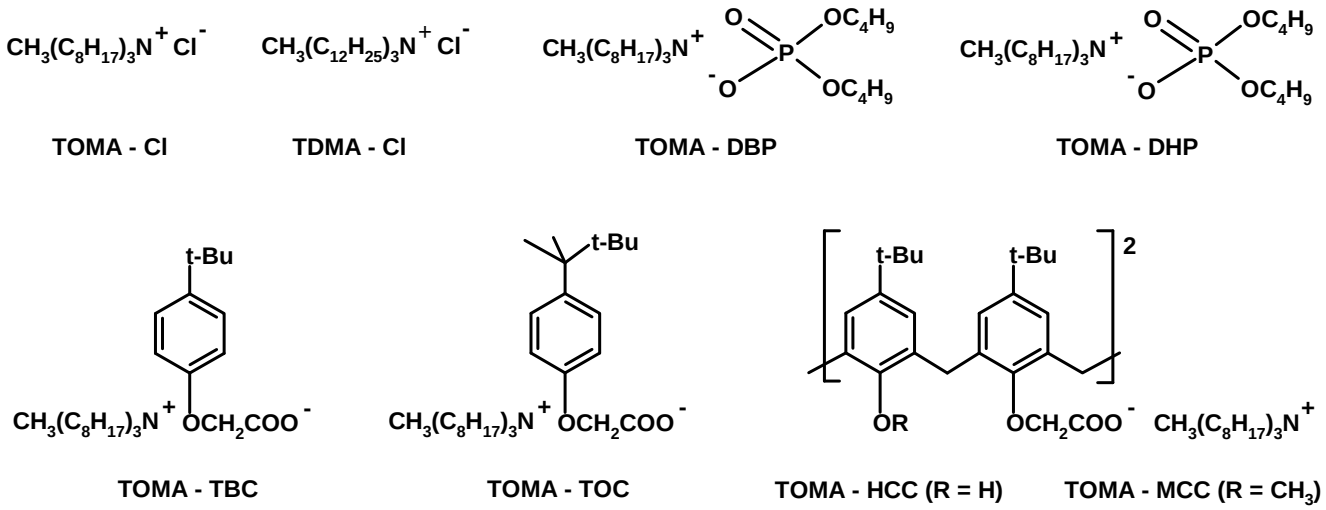

Figure 3. Structures of the carriers investigated [47].

Table 4. Maximum flux for saccharide transport through CTA membranes [47].

Carrier*	Maximum Flux (10^{-8} mol m^{-2} s^{-1})	
	Glucose	Sucrose
TOMA-Cl	18800	2600
TOMA-DBP	2500	1800
TDMA-Cl	1600	500
TOMA-TBC	1080	680
TOMA-HCC	1060	100
TOMA-TOC	340	240
TOMA-DHP	300	80
TOMA-MCC	24	

*See Fig. 3 for the abbreviations used.

Based on the non-linear plot for the flux of sucrose versus the concentration of TOMA-Cl in the membrane, White et al. [47] concluded that the transport mechanism was not based on carrier diffusion alone but was more in agreement with a jumping transport mechanism similar to the one proposed by Riggs and Smith [33]. In addition, they found that the percolation threshold for sucrose was 17% (w/w) of carrier in the membrane which was slightly lower than the 20% (w/w) found previously for fructose. White et al. concluded that this fact implied that the larger size sucrose molecule did not need the carrier molecules to be in as close proximity to each other to allow transport as compared to the case of the smaller fructose molecule. The results in Table 4 indicate that the maximum flux decreases with increase in the size of either the sachharide or the ions of the carrier ion-pair [47]. This information enabled White et al. [47] to refine the fixed-site jumping idea of Riggs and Smith [33]. They proposed a mobile-site jumping mechanism, as depicted in Fig. 4, which was in better agreement with their experimental observations. In this mechanism, the anion-pair of the saccharide heteroconjugate anion and the carrier cation is locally mobile and when it comes in close proximity with a neighbouring carrier ion-pair the saccharide molecule jumps across forming a new heteroconjugate anion. This process results in the saccharide transport through the membrane.

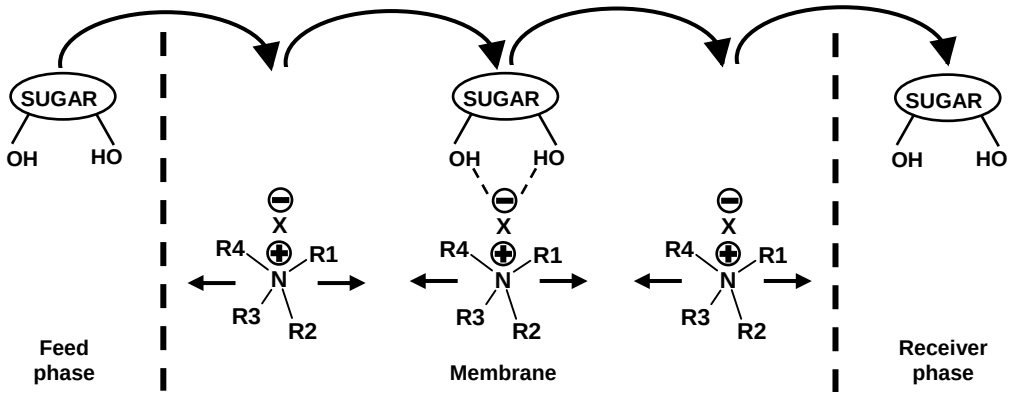

Figure 4. Schematic of a mobile-site jumping mechanism [47].

Amino acids. Munro and Smith have investigated the non-competitive transport of several amino acids including L-phenylalanine, L-leucine, L-analine and dopamine using a PIM of composition 20% (w/w) CTA, 40% (w/w) 2-NPOE and 40% (w/w) TOMA-Cl and the fluxes obtained are shown in Table 5 [44]. Again, the values were of the same order of magnitude as those for SLMs [14].

Table 5. Non-competitive fluxes for amino acids and dopamine in the case of the CTA / 2-NPOE /TOMA-Cl PIM studied [44].

Non competitive Flux (10^{-8} mol m^{-2} s^{-1})			
L-phenylalanine	**L-leucine**	**L-alanine**	**Dopamine**
1590	520	290	25

Munro and Smith established that the flux was linearly dependent on the membrane thickness which was considered as evidence that the rate determining step was the mass transfer through the membrane and not the chemical reaction occurring at the membrane/feed phase interface [44].

With amino acids there are two possibilities for the extraction and transport mechanism, *i.e.*, anion exchange or the formation of heteroconjugate anions. The mechanism operating under a particular set of conditions depends on the pH of the feed phase. If the pH is high and the amino acid is ionized, then the anion-exchange mechanism will predominate. On the other hand, at lower pH values where the amino acid is not ionized then the hydrogen bonded heteroconjugate anion mechanism will predominate. It appears that in the work of Munro and Smith the anion exchange transport mechanism has been the predominant one since for phenylalanine the flux has increased after the isoelectric point of pH 5.5 and it has been five times higher at pH 10 compared to pH 7.3 [44].

Munro and Smith found a 30 % drop in the flux when the chloride anion in TOMA-Cl was replaced with phosphate. However, when the counter ion was changed to the lipophilic bis(2-ethylhexyl)phosphate, phenylalanine transport no longer occurred [44]. These results are consistent with the research on saccharides, discussed above, in which smaller TOMA counter anions have produced higher fluxes. The percolation threshold of 20% (w/w) TOMA-Cl found in this study was similar to that for saccharides [33]. The authors noted that below this concentration the separation between the ammonium sites was too large for the jumping of the amino acid to occur [44].

Xu et al. have explained changes in PIM mass transfer kinetics associated with the amount of carrier in PVC/Aliquat 336 membranes with structural changes in the membrane [49]. At low carrier concentrations (30% (w/w) and below), no micro-pores were evident in the PVC membrane structure and the percolation threshold was explained by structural changes rather than by fixed- or mobile-site jumping. This highlights the need for extensive studies on the microstructure of PIMs in order to fully understand the mechanisms for extraction and transport.

4. Conclusions

PIMs are a relatively new and promising type of membranes for the extraction and transport of selected species. As mentioned in this review, most PIM systems studied to date involve the extraction and transport of metal species [14], however, the small amount of research carried out on organic compounds shows considerable promise.

From the examples discussed, it can be seen that the chemical reactions involved with PIM extraction and transport of organic compounds are either anion exchange or the formation of hydrogen bonded heteroconjugate anions. Since many organic compounds possess the ability to form hydrogen bonds, the formation of heteroconjugate anions with a suitable carrier is particularly attractive. Of course, for this to occur, it is necessary to have a carrier consisting of a lipophilic cation and a hydrogen bond acceptor anion. Aliquat 336, which is well known as a commercial solvent extraction reagent, is an ionic liquid that satisfies all the requirements for use as a carrier in PIMs and can also act as a plasticizer. Thus, it can be expected that we will see many new applications in the future for carriers like Aliquat 336 in PIM extraction and transport of organic compounds. One area of research for which PIMs may be useful and that has only been the subject of limited number of studies is the removal of pesticide residues from contaminated waters.

Another area in which there will be increased research activity is in the study of the microstructure of PIMs and the mechanisms of PIM extraction and transport. As seen in this review, the transport of saccharides is suggested to occur by fixed- or mobile-site jumping and that a percolation threshold arises when the sites are not close enough for the target species to jump from one site to another. Such mechanisms have also been proposed for the transport of metal ion species and may have considerable merit [14]. However, there are other possible transport mechanisms for PIMs, one of which is diffusion through micro-channels or micro-pores in the membrane structure that contain a liquid phase [48-50]. For this mechanism, a percolation threshold could arise simply through a structural change in the membrane.

Support for the presence of micro- or even nano-channels in PIMs is obtained from the work of Qingshan et al. who have studied the structure of PVC-based plasticized membranes using Small-Angle Neutron Scattering (SANS) and have explained their data on the basis of a polydisperse hard-sphere model for the PVC with a mean particle diameter of 6 nm [51]. It may well be that micro- or nano-channels containing a liquid phase are intertwined between these PVC spheres in which carrier and carrier/target species are mobile.

These questions can only be answered by a full understanding of the PIM micro-structure and will lead to the development and formulation of new membranes which are based on scientific principles rather than the “trial and error” methods in use at present.

Most of the research carried out to date on PIMs has involved small scale laboratory equipment similar to the transport cell with an SLM shown in Fig. 1c. However, it is anticipated that as PIM systems become commercially viable, future work will focus on the transfer of the technology to a commercial scale. For this, techniques such as those required for the production of PIM hollow fibres will evolve [52].

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