27 Polymer Inclusion Membranes

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27.1 INTRODUCTION

27.1.1 LIQUID MEMBRANES

The liquid membrane (LM) concept combines solvent extraction (SX) and membrane-based technologies, enabling both extraction and back-extraction in a single step with reduced consumption of extractants and diluents. For these reasons, separation based on LMs can be viewed as a promising alternative to traditional SX. The LM separation approach involves mass transfer of a target chemical species between two solutions (i.e., feed and receiver solutions) separated by an immiscible LM [1]. The main types of LMs are bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs), supported liquid membranes (SLMs), and polymer inclusion membranes (PIMs).

A BLM consists of an organic liquid phase partitioned between an aqueous feed phase and a receiver phase, and the mass transfer is enhanced by mechanical stirring of one or both phases (Figure 27.1a). A low interfacial surface area and mass transfer rate are the main disadvantages of this type of membranes.

Emulsion globules composed of the receiver aqueous solution and an organic liquid phase dispersed into the feed aqueous phase form a typical ELM (Figure 27.1b). A surfactant is usually used to disperse the emulsion globules in the feed solution. After equilibrium has been reached, the feed aqueous phase is separated from the emulsion globules, which are subsequently demulsified to form an organic liquid layer and an aqueous receiver solution containing the separated and preconcentrated target chemical species. Unlike BLMs, ELMs are characterized by a large interfacial surface area between the emulsion globules and the receiver phase on one hand and between the organic liquid phase and the feed aqueous phase on the other. This configuration enables fast mass transfer between the two aqueous phases. The main difficulties in conducting the separation process in this case are related to the formation and breakdown of the emulsion itself, which limits the commercial applications of ELMs.

SLMs are composed of a porous hydrophobic membrane acting as a solid support for the organic liquid phase (Figure 27.1c). The liquid phase, retained inside the membrane pores by capillary forces, leaches slowly into the receiver and feed aqueous solutions. Thus, insufficient long-term stability is the main disadvantage of SLMs that prevents the widespread adoption of these otherwise easy-to-use LMs in industry.

PIMs on the other hand retain most of the advantages of SLMs while exhibiting greater stability and versatility.

27.1.2 POLYMER INCLUSION MEMBRANES

Polymer-based LMs have been known for over 40 years and have been used as the sensing membranes of ion-selective electrodes (ISEs) and optodes where they have been usually referred to as plasticized membranes. However, separation
based on this type of membranes, mostly known in such applications as PIMs, has been proposed as a possible alternative to conventional SX [2,3]. The interest in PIM-focused research has been growing exponentially in the past few years (Figure 27.2). It should be pointed out that the membranes used for sensing and separation differ substantially with regard to their transport properties. In the first case, fast ion-exchange at the membrane/sample solution interface combined with an extremely low transport rate of the ion of interest across the membrane is required. For separation purposes, both fast ion-exchange and transport rates are required, which is only possible if membranes with high concentrations of extractants (>30% m/m) are used as opposed to the low concentrations (~1%–2% m/m) of extractants involved in sensing applications [2–4].

PIMs are usually composed of an extractant (carrier), a base polymer (commonly Polyvinylchloride [PVC] or cellulose triacetate [CTA]), and a plasticizer. In some cases, the carrier also acts as a plasticizer, and so an additional plasticizer is not necessary. Also, a modifier is occasionally added to the membrane composition to improve the solubility of the extracted species in the membrane liquid phase. To prepare a PIM, the membrane components are normally weighed into a beaker and dissolved in a small volume of an appropriate solvent (tetrahydrofuran [THF] if PVC is used as the base polymer or dichloromethane [DCM] for CTA-based PIMs). The mixture is stirred using a magnetic stirrer until all the components are dissolved, and the solution is then poured into a glass ring positioned on a glass plate. The ring is covered with a filter paper in order to allow slow evaporation of the solvent. The membrane formed after the complete evaporation of the solvent is then peeled from the glass plate. Successful membranes are normally transparent, homogeneous, flexible, and mechanically strong (Figure 27.3).
27.2 BASE POLYMERS

The base polymer provides the membrane with mechanical strength. PVC and CTA have been the most widely used base polymers in PIMs since these polymers provide membranes with a high mechanical strength and are compatible with a large range of carriers, plasticizers, and modifiers [5].

CTA is a polar polymer with a number of hydroxyl and acetyl groups that are capable of forming highly orientated hydrogen bonding, which gives CTA a crystalline structure [2]. The polarity and crystalline nature of the CTA polymer may render it incompatible with high concentrations of hydrophobic nonpolar carriers. Moreover, CTA can be slightly hydrated and, thus, susceptible to acid hydrolysis [6]. Gardner et al. studied different cellulose derivatives (i.e., cellulose acetate propionate [CAP], cellulose acetate butyrate [CAB], and cellulose tributyrate [CTB]) in order to assess the durability of PIMs against hydrolysis under alkaline and acidic conditions [7]. The membranes contained bis-tert-butylcyclohexano-18-crown-6 as the carrier. It was observed that the resistance to hydrolysis increased with increase in the alkyl chain length, although the rate of ion transport across the membrane decreased. CAP and CAB together with cellulose acetate hydrogen phthalate (CAH) were also used in attempting to manufacture PIMs with dinonylnaphthalene sulfonic acid (DNNS) and dinonylnaphthalene disulfonic acid (DNNDS) as carriers, and only some of these compositions produced membranes that were found to be fragile [8]. However, cellulose acetate (CA) has been successfully used without a plasticizer to produce PIMs with macrocyclic carriers [9,10].

PVC is a nonflammable and durable polymer formed from a vinyl chloride monomer. The C–Cl functional group in PVC is relatively polar, and nonspecific dispersion forces dominate the intermolecular interactions [2]. Consequently, PVC has an amorphous structure with a small degree of crystallinity. PVC is used as the polymer backbone in membranes because of its strength, inertness, and compatibility with a variety of carriers and plasticizers. Unlike CTA, PVC is also resistant to acid solutions since it is not prone to acid hydrolysis.

Studies involving the use of PVC with different molecular weight (MW) have been reported. It was observed that the nature of the base polymer had only a small influence on the membrane transport properties, although membranes formed with PVC with low MW (e.g., 80,000 g mol\(^{-1}\)) were found to be less fragile [11]. It was noticed that PIMs prepared with PVC with MW of 233,000 g mol\(^{-1}\) were more difficult to dissolve in THF [12].

Poly(vinylidene fluoride) (PVDF) has been recently tested as the base polymer in ionic liquid (IL)-based PIMs [13–15]. PVDF is a thermoplastic fluoropolymer with high hydrophobicity, good chemical resistance, and excellent thermal and mechanical stability making it attractive as a base polymer for PIMs.

27.3 CARRIERS

The carrier (extractant) is usually a complexing agent or an ion-exchanger responsible for binding the species of interest thus facilitating their extraction into the PIM. The transport process across the membrane is driven by the concentration gradient of the extracted species/carrer complex or ion-pair within the membrane. Several classes of SX reagents have been incorporated into PIMs, namely, basic, acidic, and chelating, neutral or solvating, and macrocyclic and macromolecular. Structures of some of these carriers are presented in Figure 27.4, and examples of carriers according to classification outlined previously are presented in Tables 27.1 through 27.3, along with the chemical species they have been applied to.

![FIGURE 27.3 Photographic image of a typical PIM.](image)

![FIGURE 27.4 Chemical structures of examples of basic (Aliquat 336), acidic (D2EHPA, DNNS), and neutral (TBP) carriers.](image)
### TABLE 27.1
**Examples of Basic, Acidic, and Chelating Carriers Used in PIMs and Chemical Species They Have Been Applied To**

<table>
<thead>
<tr>
<th>Type of Carrier</th>
<th>Examples of Carriers</th>
<th>Target Species</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Basic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quaternary amines</td>
<td>Aliquat 336/Capriquat</td>
<td>Anions (e.g., [33]), AuNPs (e.g., [21]), 1-butanol [13], heavy metals (e.g., [18]), organic compounds (e.g., [22])</td>
</tr>
<tr>
<td>Tertiary amines</td>
<td>TBA, THA, TIOA, TOA</td>
<td>Heavy metals (e.g., [48]), ReO$_4^-$ [49]</td>
</tr>
<tr>
<td>Pyridine and its derivatives</td>
<td>TDPNO</td>
<td>Heavy metals (e.g., [50])</td>
</tr>
<tr>
<td>Thiadiazine derivatives</td>
<td>FFAT</td>
<td>Cr(VI) [51]</td>
</tr>
<tr>
<td><strong>Acidic and chelating</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkyl phosphoric acids</td>
<td>D2EHPA, D2EHDTMP, Cyanex</td>
<td>Am(III) (e.g., [52]), Co-60 [53], gases [54], heavy metals (e.g., [23]), In(III) (e.g., [55])</td>
</tr>
<tr>
<td>Sulfonic acids</td>
<td>DNNS, DNNDs</td>
<td>Co-60, Cs-137, Sr-90 (e.g., [56]), H$^+$ [8]</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>Lauric acid, Lasalocid A, r-DAPA</td>
<td>Heavy metals (e.g., [29,57])</td>
</tr>
<tr>
<td>Hydroxycarboxylic acids</td>
<td>LIX$^®$ 84-1/984/54-100</td>
<td>Cu(II) [58]</td>
</tr>
<tr>
<td>Hydroxyquinoline</td>
<td>Kelex 100</td>
<td>Au(III) [59], Cd(II), Pb(II) [60]</td>
</tr>
<tr>
<td>β-Diketones</td>
<td>HBA, HBM, HBT, HTTA, HTFA, HPBI</td>
<td>Cu(II) [61], trivalent rare earth ions [62]</td>
</tr>
</tbody>
</table>

**Note:** All abbreviations are defined in the Glossary.

### TABLE 27.2
**Examples of Neutral or Solvating Carriers Used in PIMs and Chemical Species They Have Been Applied To**

<table>
<thead>
<tr>
<th>Type of Carrier</th>
<th>Examples of Carriers</th>
<th>Target Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphonic acid esters</td>
<td>TBP</td>
<td>Cdf(II), Pb(II) [63], U(VI) [64]</td>
</tr>
<tr>
<td>Phosphoric acid esters</td>
<td>DBBP</td>
<td>As(V) [65]</td>
</tr>
<tr>
<td>ILs</td>
<td>Cyphos IL 101/102/104, Bif-ILEs</td>
<td>1-Butanol [13], Cr(VI) (e.g., [15]), Zn(II) (e.g., [66])</td>
</tr>
<tr>
<td>Others</td>
<td>CMPO, TODGA, TOPO, TETDS, LSI, polyethylene glycol</td>
<td>Mor(VI) [67], Pb(II) [68], Sr(II), lanthanides (e.g., [69])</td>
</tr>
</tbody>
</table>

**Note:** All abbreviations are defined in the Glossary.

### TABLE 27.3
**Examples of Macrocyclic and Macromolecular Carriers Used in PIMs and Chemical Species They Have Been Applied To**

<table>
<thead>
<tr>
<th>Type of Carrier</th>
<th>Examples of Carriers</th>
<th>Target Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crown ethers</td>
<td>Dicyclohexano-18-crown-6, di-tert-butylcyclonxano-18-crown-6, dibenzo-18-crown-6, undecyl-aza-18-crown-6, imidazole azothia crown ethers, imidazole azocrown ethers</td>
<td>Alkaline metals (e.g., [70]), Cs-137 [71], heavy metals (e.g., [72]), pircrate (e.g., [73]), ReO$_4^-$ [31]</td>
</tr>
<tr>
<td>Ionizable lariat ethers</td>
<td>PNP-lariat ethers</td>
<td>Heavy metals [26]</td>
</tr>
<tr>
<td>Cryptands</td>
<td>4,7,13,18-Tetraoxa-1,10-diazabicyclo</td>
<td>Ag(I), Cu(II) [75]</td>
</tr>
<tr>
<td>Calix crowns</td>
<td>Calix[4]-crown-6</td>
<td>Heavy metals (e.g., [76])</td>
</tr>
<tr>
<td>Cyclodextrins</td>
<td>β-Cyclodextrin</td>
<td>Heavy metals (e.g., [27])</td>
</tr>
<tr>
<td>Others</td>
<td>Bathophenanthrolne, bathocuproine, 1-alkylimidazole, 1-decylimidazole, 1-decyl-2-methylimidazol, o-thiocaprolactam, PVP, BPA, thioether donor macrocycles, lipophilic acyclic polyethers</td>
<td>Anions [77], Ba(II) [78], heavy metals (e.g., [79]), I$_2$ [80], lanthanides (e.g., [81])</td>
</tr>
</tbody>
</table>

**Note:** All abbreviations are defined in the Glossary.
27.3.1 Basic Carriers

Basic carriers (Table 27.1) consist mainly of amine-based compounds such as quaternary ammonium salts (e.g., Aliquat 336), tertiary amines (e.g., tri-n-octylamine [TOA], tri-isooctylamine [TIOA]), weakly basic compounds (e.g., alkyl derivatives of pyridine N oxides), and thia diazine derivatives (e.g., 5-(4-phenoxyphenyl)-6H-1,3,4-thiadiazin-2-amine [FFAT]). The reason for this classification is related to the similarity in the extraction mechanism involving the carriers discussed. In the case of fully substituted quaternary ammonium compounds (e.g., Aliquat 336), the carrier reacts as an anion exchanger forming an ion-pair with another anion from the feed phase, which can be a complex metal anion. In the case of amine and other weak bases mentioned earlier, the carrier must be protonated first in order to allow anion exchange with another anion from the feed phase or with a complex metal anion. Alternatively, the carrier may react directly with a protonated complex metal anion [16].

Aliquat 336 is a commercially available extractant, extensively applied as a carrier in PIMs, which also has plasticizing properties. For this reason, it is frequently used in the manufacturing of PIMs without the addition of a separate plasticizer [17,18]. Aliquat 336–based PIMs have been applied to the extraction and/or transport of anionic complexes of mainly heavy metals (e.g., As(V), Au(III), Cd(II), Co(II), Cr(VI), Cu(II), Ni(II), Pd(II), Pt(IV), Re(VII)), common anions (e.g., F-, SCN-), and organic compounds (e.g., small saccharides, amino acids, lactic acid, thiourea) [2,3]. Moreover, it has been recently employed in a PVC-based template for the preparation of Au nanoparticles (AuNPs). The nanoparticles were formed either in the bulk of the PIM or as a layer on the PIM surface by loading the membrane with AuCl₄⁻ by anion-exchange, followed by in situ reduction with BH₄⁻ or EDTA [21]. Capriquat is another liquid anion-exchanger similar in composition to Aliquat 336 with the major component being trioctylmethylammonium (TOMA) chloride [22].

27.3.2 Acidic and Chelating Carriers

The compounds frequently applied in PIMs that come under the classification of acidic carriers include organophosphorus acids, sulfonic acids, and carboxylic acids. Moreover, there is another group of compounds that have not only acidic but also chelating properties, namely, hydroxoximes, quinolines, and β-diketones. Examples of these carriers are given in Table 27.1. Acidic carriers are usually used in PIMs for the extraction and transport of metal cations, which involve the exchange of the metal ion with hydrogen ions from the carrier, while maintaining a suitable difference in the concentration of the hydrogen ion in the feed and receiver solutions [2].

Among the acidic carriers, di-(2-ethylhexyl) phosphoric acid (D2EHPA) has been the most commonly used in PIM studies. D2EHPA is a commercially available extractant that also has the ability to act as a plasticizer [23,24]. It has been applied mostly for the extraction and transport of heavy metals (viz., Zn(II), U(VI), Pb(II), Cd(II), Cr(III), Fe(III)) [2,3]. PIMs incorporating PVC and D2EHPA were successfully coated with Ag nanoparticles after reducing the extracted Ag⁺ at the membrane surface with L-ascorbic acid [21].

DNNS is another commercially available acidic carrier used in PIM studies, which is normally supplied as a 50% solution in n-heptane. This means that a purification step may be required before use in order to eliminate the n-heptane and other impurities [25]. To the best of our knowledge, no purification step has been used so far prior to its application in the manufacturing of PIMs. It has been shown that the addition of DNNS to PIMs prepared with macrocyclic compounds as carriers (e.g., bis-PNP-lariar ether, β-cyclodextrin) produces a synergistic effect toward the target analyte [26,27].

N-6-(t-Dodecylamido)-2-pyridinecarboxylic acid (t-DAPA) is a newly synthesized carrier, proposed as an alternative to LIX® reagents (known to be very selective toward Cu(II)) to overcome problems related to their cost and poor physicochemical stability. However, the fact that t-DAPA is not commercially available and very little is known about its stability raises the question whether it will become an attractive alternative to LIX reagents [28,29]. Its high selectivity for Cu(II), Zn(II), and Ni(II) can be explained by the high affinity of the carboxylic group and the pyridine moiety for these metals, although it is more selective for Cu(II) at low pH values.

The extraction mechanisms for PIMs containing various carriers normally mimic those of the corresponding SX systems. A number of these are described in our previous reviews on PIMs [2,3].

27.3.3 Neutral or Solvating Carriers

Neutral or solvating carriers are commercially available phosphorus-based extractants with high selectivity toward actinides and lanthanides. Examples are presented in Table 27.2, together with the species they have been applied to.

Tri-n-butylphosphate (TBP) and dibutyl butyl phosphate (DBBP) are examples of neutral phosphoric and phosphonic acid esters, respectively, which have been applied in PIMs for the extraction of Cd(II), Pb(II), U(VI), and As(V) [2,3]. Another important group of neutral carriers are ILs, which consist of salts in the liquid state and have the ability to exchange their anion or cation. Aliquat 336, which is categorized as a basic extractant, also has properties associated with an IL. It is thus possible to design different ILs according to particular applications. Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), trihexyl(tetradecyl)phosphonium bromide (Cyphos IL 102), and trihexyl(tetradecyl)phosphonium-(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) are commercially available phosphonium-based ILs that have been investigated recently as carriers in PIMs. Cyphos IL 104 is particularly interesting since it acts as a bifunctional extractant that can extract both cations and anions simultaneously and has been used to extract HNO₃ and Y(III) from nitrate solutions [30] and H₂CrO₄ [14].
27.3.4 MACROCYCLIC AND MACROMOLECULAR CARRIERS

Macroyclic and macromolecular carriers are compounds such as crown ethers, ionizable lariat ethers, calixarenes, calix crowns, and cyclodextrins. Table 27.3 provides examples of such carriers as well as the target chemical species.

A considerable number of research papers have described PIMs using macrocyclic and macromolecular carriers [2,3]. The main reason for selecting these carriers is related to their high complexing selectivity toward metal ions. Due to the fact that their structures can be tailored to a selected metal ion and they exhibit low solubility in aqueous solutions, these carriers have attracted considerable interest, although the majority of them are still not commercially available. Their synthesis is often expensive, and this may affect the economic viability of their utilization in large-scale separation systems. However, only a relatively small amount of a carrier is required for the preparation of a membrane compared to the amount required in traditional SX, which possibly makes their industrial applications more feasible. Moreover, it is possible to redissolve the PIM after use and reform the membrane for subsequent use thus recycling the expensive carrier [31].

27.4 PLASTICIZERS AND MODIFIERS

As mentioned earlier, unless the carrier also has plasticizing properties (e.g., Aliquat 336, D2EHPA, and TBP), a plasticizer or modifier is additionally incorporated into the membrane preparation. The polymer chains of the base polymer are under the influence of weak and nonspecific van der Waals forces and stronger polar interactions resulting in the formation of a rigid 3D membrane structure. Such a structure produces very poor diffusive fluxes for species introduced into the polymer. Consequently, a plasticizer may be required to be added to the PIM composition to penetrate between the polymer chains and reduce the intermolecular forces [5]. This leads to a decrease in the polymer glass transition temperature and an increase in the membrane softness and flexibility. The most common plasticizers used in PIMs are 2-nitrophenyloctyl ether (NPOE) and 2-nitrophenylpentyl ether (NPPE) [2,3]. Others, such as bis(2-ethylhexyl) adipate (DEHA), dibutylphthalate (DBP), or dibutylsebacate (DBS), have also been tested. These plasticizers contain a hydrophobic alkyl backbone and one or more polar groups that neutralize the polar groups of the polymer. A balance between the nonpolar and polar groups is necessary. A longer alkyl chain results in higher hydrophobicity and viscosity and lower polarity of the plasticizer while an increase in the number of polar groups usually decreases viscosity and increases the hydrophilicity, thus leading to loss of the plasticizer to the aqueous phase(s).

The concentration of plasticizer is important since too low a concentration results in rigid and brittle membranes. This is termed the antiplasticization effect, and the minimum plasticizer concentration required is dependent on the plasticizer type and the base polymer used. For example, for PVC PIMs, this concentration is around 20 wt%. If the plasticizer concentration is too high, then excess plasticizer can exude to the PIM surface and the thin film formed can inhibit transport across the membrane. Also, such PIMs are normally mechanically weak and difficult to use.

Higher initial flux values for the extracted species are usually obtained when PIMs incorporate high-polarity and low-viscosity plasticizers such as NPOE and NPPE, and this has led to the conclusion that the initial flux values increase with an increasing dielectric constant and decreasing viscosity of the plasticizer. However, it should be noted that most of the plasticizers used in PIMs have similar viscosity values (Table 27.4), and moreover, the dielectric constant of the membrane liquid phase is also dependent on the dielectric constants of the carrier and the base polymer [32].

---

### TABLE 27.4

<table>
<thead>
<tr>
<th>Plasticizer/Modifier</th>
<th>Dielectric Constant (ε)</th>
<th>Water Solubility (g/kg H₂O)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPOE</td>
<td>24 (25°C) [82]</td>
<td>—</td>
<td>11.1 (25°C) [82]</td>
</tr>
<tr>
<td>NPPE</td>
<td>24 (na) [83]</td>
<td>—</td>
<td>7.58 (na) [72,76]</td>
</tr>
<tr>
<td>DEHA</td>
<td>5 (na) [83]</td>
<td>—</td>
<td>13.7 (na) [72,76]</td>
</tr>
<tr>
<td>DBP</td>
<td>6.58 (20°C) [84]</td>
<td>0.0112 (25°C) [84]</td>
<td>16.6 (25°C) [84]</td>
</tr>
<tr>
<td>TEHP</td>
<td>4.8 (25°C) [82]</td>
<td>—</td>
<td>13.1 (25°C) [82]</td>
</tr>
<tr>
<td>DBS</td>
<td>4.54 (20°C) [84]</td>
<td>0.04 (20°C) [84]</td>
<td>9.5 (na) [85]</td>
</tr>
<tr>
<td>TBP</td>
<td>8.7 (na) [55]</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DOP</td>
<td>5.22 (20°C) [84]</td>
<td>0.000027 (25°C) [84]</td>
<td>40.4 (na) [86]</td>
</tr>
<tr>
<td>TBP</td>
<td>8.34 (20°C) [84]</td>
<td>0.39 (25°C) [84]</td>
<td>3.32 (na) [71]</td>
</tr>
<tr>
<td>EB</td>
<td>6.20 (20°C) [84]</td>
<td>0.83 (25°C) [84]</td>
<td>—</td>
</tr>
<tr>
<td>1-Dodecanol</td>
<td>5.82 (30°C) [84]</td>
<td>0.004 (25°C) [84]</td>
<td>—</td>
</tr>
<tr>
<td>1-Tetradecanol</td>
<td>4.42 (45°C) [84]</td>
<td>0.00031 (25°C) [84]</td>
<td>—</td>
</tr>
</tbody>
</table>

Notes: na, temperature not available. All other abbreviations are available in the Glossary.
Thus, a degree of caution is necessary when attempting to correlate initial PIM flux values with the dielectric constant and viscosity of the plasticizer.

Modifiers are common in SX processes to solubilize extracted species in the organic phase and hence overcome third-phase formation. Long-chain alkyl alcohols, namely, 1-dodecanol and 1-tetradecanol, are examples of modifiers that have been recently tested in PIMs by Cho et al. [33]. The same study has shown that membranes prepared with a range of long-chain alkyl alcohols (C_{10}-C_{14}) as modifiers have exhibited similar transport rates and degrees of extraction when first used. However, when used again, only the PIMs containing 1-dodecanol and 1-tetradecanol have shown no evidence of deterioration in their performance. The fact that these modifiers have the lowest water solubility values (Table 27.4), in comparison to the other modifiers, suggests a direct relationship between membrane stability and water solubility of the modifier.

### 27.5 STRUCTURE, STABILITY, AND LIFETIME

Successful PIMs should be transparent and homogeneous, and most studies involving this type of membranes make this evaluation through observation with the naked eye or under an optical microscope. Nevertheless, such evaluation is rather subjective. For instance, SLMs also look transparent and homogeneous to the naked eye, although they have a microporous structure. Hence, several advanced and sophisticated techniques have been employed in the study of the morphology and structure of PIMs in order to determine the distribution and interaction of the various membrane components and ultimately assess how that affects the membrane transport efficiency.

Such techniques can be used either alone or in conjunction with each other and among them are scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, and transmission infrared mapping microscopy (TIMM) [3]. These techniques are often used in surface morphology studies and have been used with PIMs to provide information on how the carrier and the plasticizer are distributed within the base polymer. Moreover, other techniques have been applied. FTIR has been used to study the type of interactions between PIM constituents, while TIMM has been used to provide a distribution profile of the membrane components. High-resolution, synchrotron-based FTIR spectroscopy was recently used to study the PIM homogeneity [34]. PVC-based PIMs containing D2EHPA or Aliquat 336 as carriers and CTA-based PIMs with Aliquat 336 as the carrier were shown to be homogeneous on the micrometer scale. This study has also included proton-induced x-ray emission microspectrometry (μ-PIXE) measurements that have revealed a homogeneous distribution of the membrane components both on the surface and in the interior of the membrane. On the other hand, PIMs that cannot be produced reproducibly, such as those containing Cyanex 272 and PVC, have been found to lack homogeneity.

PIMs’ homogeneity is considered to be responsible for their better stability in comparison with other LMs. In SLMs, capillary forces or interfacial tension are responsible for the retention of the liquid phase within the membrane pores. However, because of the weakness of these forces, membrane breakdown can easily occur as a result of lateral shear forces, emulsion formation, or leaching of the membrane liquid phase to the adjacent aqueous phase(s). In contrast, in PIMs, the carrier, plasticizer, and base polymer are most likely bound together by a form of secondary bonding as discussed in Section 27.4, which includes weak and nonspecific van der Waals forces and stronger polar interactions such as hydrogen bonding. These interactions are much stronger than interfacial tension or capillary forces and are thought to provide PIMs with considerably more stability than SLMs.

Several authors have studied the stability of PIMs and their reusability by performing repeated transport experiments with the same membrane, which involved renewing both the feed and receiver solutions each time. In general, the stability of PIMs has been proven to be quite good with flux or permeability values varying only slightly within the first several cycles and with no signs of structural weakening of the membrane. In some cases, particularly when very low-ionic-strength aqueous phases are used, there can be considerable leaching of the membrane liquid phase (plasticizer, modifier, and carrier) into the aqueous phase. However, recent work has shown that an equilibrium condition is eventually reached and negligible further leaching occurs [35]. Thus, it is suggested that PIMs need to be conditioned in solutions of similar ionic strength to those to be employed in the actual extraction and transport systems. Although there is little doubt that the stability of PIMs is greater than that of SLMs, lower initial flux values or permeability coefficients are frequently reported for PIMs in comparison with those reported for SLMs.

### 27.6 TRANSPORT MECHANISMS

The overall transport mechanism across a typical PIM can be viewed as consisting of the following three steps [2]:

1. The extracted species diffuses across the stagnant diffusion layer at the membrane/feed solution interface where it reacts with the carrier, and the reacted carrier species is replaced by another carrier species from the bulk of the membrane.

2. The product of the reaction between the extracted species and the carrier, which is usually a complex or an ion-pair, is transported toward the membrane/receiver phase interface along the corresponding concentration gradient.

3. At the membrane/receiver solution interface, the extracted species is released into the receiver solution. This process can be facilitated by a suitable stripping reagent. The liberated in this process carrier species is transported back to the membrane/feed solution interface.
The PIM mass transfer process is often referred to as *facilitated transport*, and it allows transport of the extracted species from a feed solution with a lower concentration to a receiver solution with a higher concentration. Thus, it is possible to transfer quantitatively the extracted species from the feed to the receiver solution without using an external force (e.g., pressure, electrical field). It should be pointed out that despite the uphill character of the overall transport between the feed and receiver solutions, the transport of the complex or ion-pair of the extracted species within the membrane is always downhill, that is, along the corresponding concentration gradient.

When the extracted species forms a complex with the carrier, the receiver solution usually contains a stripping reagent (e.g., a water-soluble complexing reagent). The role of this reagent is to facilitate the dissociation of the carrier-extracted species complex at the membrane/receiver solution interface and to subsequently form a water-soluble complex with the extracted species. In fact, the extracted species is present in the receiver solution due to the stripping complexation reaction as a different chemical species. The driving force in this case is the difference between the concentration of the carrier-extracted species complex at the membrane/feed solution interface and the practically zero concentration of the complex at the membrane/receiver solution interface. In the case of extracted ionic species, the driving force for the uphill transport can be the potential gradient generated by the coupled transport of another ionic species across the membrane. The extracted ionic species, in this case, is transported to satisfy the electroneutrality condition within the membrane system. This coupled transport process can be countertransported (Figure 27.5b,c) and cotransported (Figure 27.5a,d) with respect to the extracted ionic species.

A possible mechanism for the transport of the extracted species across the membrane can be based on Fickian diffusion of its complex or ion pair with the carrier through the membrane liquid phase. Another mechanism that can be responsible for the bulk membrane transport of the extracted species is the so-called *chained carrier* mechanism proposed by Cussler et al. [36]. This mechanism applies to ion-exchange membranes with ionic sites covalently bound to

*FIGURE 27.5* 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 countercurrently transported with a coupled transport cation; (c) the target solute is an anion and is countercurrently transported with a coupled transport anion; and (d) the target solute is an anion and is concurrently transported with a coupled transport cation. (Reprinted from *J. Membr. Sci.*, 281, Nghiem, L.D., Mornane, P., Potter, I.D., Perera, J.M., Cattrall, R.W., and Kolev, S.D., Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs), 7–41, Copyright 2006, with permission from Elsevier.)
Polymer Inclusion Membranes

The polymeric backbone (e.g., Nafion). Very often, the carriers used in PIMs are bulky chemical species, and their mobility within the membrane liquid phase is so low that for all practical purposes, these carriers can be considered as immobile and the membrane transport of the extracted species can be viewed as taking place via successive relocations from one carrier to another. Riggs and Smith [37] used this mechanism to explain the transport of sugars across PIMs containing different TOMA salts as carriers. Sugars have a strong ability to form hydrogen bonds, and the transport process in this case is most probably due to the formation of heteroconjugate anions between the sugar molecule and the TOMA anion. The chained carrier mechanism explains the percolation threshold of PIMs where a certain minimum amount of carrier is required to form a continuous chain across the membrane to allow the uninterrupted transport of the extracted species from the feed to the receiver solution [32,37]. The percolation threshold, which determines the average distance between the carrier molecules, has been found to depend on the size of the extracted species; that is, larger extracted species can be transported even when carrier molecules are not in close proximity to each other. For example, White et al. [38] established that the threshold for the disaccharide sucrose was lower than that for the monosaccharide fructose. The same authors suggested that a local mobility of the carrier particles could facilitate the bulk transport across the membrane. In this case, the extracted species can jump between two neighboring carrier particles when as a result of their local mobility, they come in close proximity. Figure 27.6 illustrates the chained carrier mechanism of transport of a sugar across a PIM containing a TOMA salt as the carrier in the case of fixed and locally mobile carrier ion pairs [39].

It can be expected that often the bulk transport mechanism is a combination of the mechanisms outlined earlier.

27.7 EXTRACTION AND STOICHIOMETRY

SX and ion-exchange are extremely important techniques for the separation of numerous species from aqueous solutions and have been used extensively in separation science and in industrial processes. It has often been said that PIMs mimic the extraction properties of the organic phase in SX systems and the solid phase in ion-exchange systems but have the advantage that both extraction and back-extraction processes can take place in a single step by using the PIM in transport mode (i.e., a PIM separates the feed and receiver phases). Also, PIM-based separation minimizes and even eliminates the use of often highly flammable, toxic, and volatile diluents.

The majority of PIM studies up to date have been concerned with the examination of various carrier/plasticizer/modifier compositions for preparing successful flat-sheet membranes to extract and transport the chemical species of interest such as metallic and organic ions or molecules. Extraction studies can be carried out by simply agitating an
aqueous solution of the species of interest and incorporating the PIM studied. The depletion of the extracted species in the aqueous solution is monitored in time until the extraction equilibrium between the membrane and the solution is reached. Alternatively, a two-compartment transport cell can be used where both compartments contain the same feed solution. Once extraction equilibrium has been established, the extraction constant can be calculated, provided that the carrier in the membrane is not completely reacted.

The molar concentrations of the membrane components can be calculated if the membrane volume is known. It can be determined by measuring the membrane geometric dimensions or by using the membrane density determined independently and knowing the membrane mass. In PIM extraction and transport studies, emphasis is placed on achieving high extraction constants and transport rates and separation from other species present in the aqueous phase.

In a number of studies, attempts have been made to determine the stoichiometry of the extracted complex of the species of interest and the carrier and to elucidate the extraction mechanism. In an SX system, a common approach for determining the stoichiometry of the extracted complex is based on the so-called slope analysis method [16]. This involves carrying out a series of extraction experiments using different concentrations of the extractant in the organic phase. Let us consider a generic extraction reaction described by the following stoichiometric equation:

\[ A_{aq} + nE_{mem} \rightleftharpoons AE_{n\,mem} \quad (27.1) \]

where

- \( A \) is the chemical species of interest
- \( E \) is the extractant
- subscripts \( aq \) and \( mem \) refer to the aqueous and membrane phases, respectively

The extraction constant of this process \( (K_{ex}) \) is described by the following equation:

\[ K_{ex} = \frac{[AE_{n\\,mem}]}{[A_{aq}][E_{mem}^n]} \quad (27.2) \]

All concentrations in this equation are the corresponding equilibrium concentrations.

Taking into account that the distribution ratio \( (D) \) is defined by Equation 27.3, and Equation 27.2 can be converted to Equation 27.4,

\[ D = \frac{[AE_{n\\,mem}]}{[A_{aq}]} \quad (27.3) \]

\[ \log D = \log K_{ex} + n \log [E_{mem}^n] \quad (27.4) \]

If the volumes of the two phases are equal and the initial extractant concentration in the organic phase is selected to be much higher than the initial concentration of the extracted species in the aqueous phase, its equilibrium value can be assumed to be practically equal to its initial value. Under such conditions, the slope of the relationship \( \log D \) versus \( \log [E_{mem}^n] \), where \( [E_{mem}^n] \) is the initial extractant concentration in the organic phase, will be equal to the stoichiometric coefficient \( n \) of the extracted complex \( (AE_n) \).

Another simpler method involves fully reacting the extractant in the organic phase with the extracted species using a high initial aqueous concentration of the extracted species and analyzing the organic phase to determine the extractant: extracted species ratio \( n \) (Equation 27.1).

In the case of a PIM, the latter method can be used by ensuring a sufficiently high initial concentration of the extracted species in the aqueous phase. However, the complex stoichiometry obtained may be different from the stoichiometry of the complex formed when the membrane is not saturated with the extracted species.

On the other hand, the slope analysis method is not readily applicable to PIMs since it is more difficult to prepare a range of membranes with the same volume but with sufficiently different carrier concentrations. Also, it is not possible to fulfill the requirement that the carrier concentration in the membrane remains essentially constant during the extraction process.

A novel method for determining the stoichiometry in PIM systems has recently been proposed by St John et al. [24]. This approach has been applied to the extraction of uranium(VI) from sulfate solutions using a PIM containing D2EHPA as the carrier and involves equilibrating segments of the PIM of the same composition (40 wt% D2EHPA) but with varying masses with the aqueous phase. This enables different equilibrium concentrations of uncomplexed D2EHPA in the membrane to be obtained. At constant acidity in the aqueous phase, the relationship between the distribution ratio \( (D) \) and the concentration of uncomplexed D2EHPA in the PIM can be described by Equation 27.4, and the uncomplexed D2EHPA concentration can be determined by the following equation:

\[ [E_{mem}^0] = [E_{mem}^n] - n[A_{ex}] \quad (27.5) \]

where \( E \) and \( A \) refer to D2EHPA and the uranyl cation \( (UO_2^{\text{2+}}) \) in the membrane, respectively, while superscript 0 refers to initial concentration.

The parameters \( n \) and \( n' \) should have the same value. The method for determining this value involves varying \( n' \) in Equation 27.5 in the range where the true value is expected to be, that is, between 1 and 10, and calculating the uncomplicated equilibrium D2EHPA concentration \( ([E_{mem}^0]) \) for each \( n' \) value. This concentration is then used in determining \( n \) by using Equation 27.4. The function \( n - n' \) is plotted versus \( n' \) (Figure 27.7) and the \( n' \) intercept where \( (n - n') = 0 \) (i.e., \( n = n' \)) corresponds to the true value of \( n \) and gives the number of D2EHPA units in the U(VI)-D2EHPA complex. The value of 4 was obtained, which, along with the fact that two hydrogen ions were exchanged for each uranyl cation.
suggested that the extraction reaction can be described by the following equation:

\[
\text{UO}_2^{2+}(aq) + 2(B\text{H})_{2(\text{mem})} \rightleftharpoons \text{UO}_2\text{B}_2(\text{HB})_{2(\text{mem})} + 2\text{H}^{+}(aq)
\]  

(27.6)

where \((\text{HB})_2\) refers to the dimeric form of D2EHPA and B refers to its conjugate base.

### 27.8 MEMBRANE CONFIGURATION

As mentioned earlier, the common method used for fundamental studies of PIMs involves casting flat-sheet membranes; however, the ability to prepare PIMs in other configurations is of considerable importance, particularly if they are to be applied to large-scale industrial separation problems. Membrane separation on a large scale requires a high membrane surface area to solution volume ratio in order to process large volumes of feed solutions. Separation modules in which the PIM is sandwiched between two meander-shaped flow channels (Figure 27.8) containing the feed and receiver solutions, respectively, provide a longer flow path length and hence a higher contact surface area than is possible with a simple two-compartment cell used in the transport studies outlined earlier. However, the application of such modular approach is limited by the size of the flat-sheet membrane that can be cast and by the number of modules required to achieve the necessary membrane surface area to volume ratio.

The application of membranes to industrial-scale separation problems is a mature technology as demonstrated by the success of processes like reverse osmosis (RO) for desalination and wastewater treatment. Therefore, it can be anticipated that some of the methods for making large surface area membrane modules for these processes could be applicable to PIMs. One such method involves producing spiral wound membrane modules containing a number of individual flat-sheet membranes wound around a central core. A spiral wound module has a very high membrane surface area to volume ratio and is fairly easy to manufacture and replace. Although PIMs have considerable mechanical strength, it may be necessary to use an inert membrane backing material similar to that used in RO membranes to provide additional stability. An example of a spiral wound module incorporating an SLM is shown in Figure 27.9 [40]. This module could easily accommodate a PIM.

Another common method for making large surface area membrane modules can be based on the hollow-fiber (HF) membrane technology. HFs are manufactured by spinning...
techniques involving polymer solutions or melts. A polymer solution is pumped through a spinnerette consisting of an orifice with a central inlet tube that forms the HF shape followed by immersion in a coagulation bath.

In industrial-scale separation, an HF module consists of a bundle of hundreds of individual fibers that provide the required high membrane surface area to volume ratio. In such a module, one aqueous phase flows through the lumen of the fibers while the other phase flows co- or countercurrently on the outside of the fibers.

HFs have been used successfully for preconcentration in chemical analysis. One technique termed hollow-fiber liquid-phase microextraction (HF-LPME) involves filling the pores of an inert HF material (commonly polypropylene) with an organic phase containing a carrier in a similar way to the manufacturing of SLMs. The fiber is then dipped into an aqueous sample solution, and the analyte is transported across the HF to a small volume of receiver phase in the lumen of the HF that is subsequently analyzed [41,42].

It is possible to use HFs with pores filled with a PIM. However, the real challenge is to prepare HFs made of PIM alone, and Kusumocahyo et al. have attempted to produce such HFs for Ce(III) separation using commercially available CTA HFs that have been immersed in a chloroform solution containing \(N,N,N',N'-\text{tetraoctyl-3-oxapentanediame} (\text{TODGA})\) as the carrier and NPOE as the plasticizer [43]. The solution penetrates the CTA HFs and dissolves some of the CTA and, after drying, produces what is essentially PIM HFs.

A PIM can be used as a solid-phase extractant and, as such, mimics the behavior of an ion-exchange resin. Thus, it is of interest to produce PIMs in the form of beads. An apparatus for producing plasticized PVC microspheres has been reported by Tsagkatakis et al. and is shown in Figure 27.10 [44]. The PIM solution passes through an orifice where droplets are formed and these are collected in water where the organic solvent dissipates producing uniform beads. The size of the beads can be controlled by the size of the orifice and the flow rate of the PIM solution. An alternative approach might be based on coating glass or plastic beads with a PIM using a dip-coating procedure.

### 27.9 Applications, Conclusions, and Future Trends

The steady increase in research on PIMs will lead to a wide range of laboratory- and industry-based separation applications. Their attraction for use in industry is based on the fact that PIMs can be formulated using most of the commercially available SX reagents and they do not require a large inventory of diluents. In addition, losses of PIM components to the corresponding aqueous phases are small compared to those in SX systems, and PIMs have the advantage of allowing extraction and back-extraction to be conducted in a single step. Most research on PIMs has been focused on flat-sheet membranes; however, industrial applications will require very high surface area to solution volume ratios, and so other membrane configurations such as HFs or spiral wound modules will be required to achieve this aim.

In spite of their promise for use in separation science, there are still a few improvements to be made before PIM-based separation is fully accepted as a viable alternative to mature separation techniques such as SX, ion-exchange, and SLM-based separation. These problems are highlighted in previous sections of this chapter and are mostly associated with membrane stability and the relatively low membrane diffusion coefficients. It has already been demonstrated that PIMs have considerably lower losses of components to the aqueous phase than SLMs, and recent research has shown that even these losses can become negligible if the membranes are preconditioned in the aqueous phase before use [45]. Also, the incorporation of highly hydrophobic ILs into the membrane composition as carriers, plasticizers or modifiers will further minimize such losses.

The common base polymers used in PIMs are PVC and CTA, and each of these has some limitations such as instability caused by acidity or alkalinity of the aqueous phase. CTA suffers from hydrolysis reactions in strongly acidic solutions, and PVC undergoes dehydrochlorination under alkaline conditions and gradually turns brittle and black. Thus, alternative base polymers may be of use, and one such example is PVDF and its copolymers that are relatively inert under most conditions.

The problem of low diffusion coefficients is more difficult to overcome, and both physical and chemical approaches can be used to improve transport rates. Reduction in the
membrane thickness will have a dramatic effect on the transport rate, and the manufacturing of membranes as thin as 20 μm has been reported that still retain acceptable mechanical strength [35]. Also, the use of an inert porous backing material should allow even thinner membranes to be produced.

An increase in temperature increases the diffusion coefficients in PIMs, and the membranes have been shown to be stable up to around 50°C [35].

The application of sonication to PIM systems increases the transport rate that has been suggested to be due to a reduction in the thickness of the stagnant diffusion aqueous layer at the aqueous phase/membrane interface [46]. However, it is also possible that sonication provides some internal mixing of the liquid phase within the PIM.

The chemical approach to increasing transport rates involves the manipulation of the PIM composition. It has been observed that some PIM compositions provide much higher transport rates than their SLM counterparts, but the reasons for this phenomenon remain unclear. In order to understand the chemical processes occurring in PIMs, a number of researchers have investigated the structure of PIMs with a view to obtaining information regarding the way the carrier and other membrane components interact and the mechanisms for mass transport within the membrane. It is anticipated that once there is a better understanding of the structure of PIMs, it will be possible to better formulate the composition to provide optimum transport rates.

Another area in which PIMs show considerable promise is chemical analysis. The use of PIMs in the construction of ISEs and optodes is well established, but their potential use in analytical separation is only starting to be explored. PIMs are particularly useful in solid-phase extraction (SPE) for preconcentration of analytes [17,18]. Also, Fontáš et al. have used a PIM containing Aliquat 336 as the carrier for preconcentration of Cr(VI) prior to its determination using ISEs and optodes [19,20].

PIMs have shown considerable potential for passive sampling of specific contaminants in waters [87]. In this application, low membrane diffusion coefficients can be an advantage. Passive samplers are generally left immersed in a river, lake, or contaminated water site for several days, and a PIM can slowly and selectively accumulate and transport the analyte to the receiver phase within the passive sampler.

The use of HF-LPME is expected to make an important contribution to analytical separation. Recent research has demonstrated that PIMs can be used either as templates for the production of metallic nanoparticles imbedded within the PIM [19,20] or as a layer on the surface [21]. Such nanoparticles may find use in catalysis and in chemical sensing.

**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>AuNPs</td>
<td>Au nanoparticles</td>
</tr>
<tr>
<td>Bif-ILEs</td>
<td>Bifunctional ionic liquid extractants</td>
</tr>
<tr>
<td>BLM</td>
<td>Bulk liquid membrane</td>
</tr>
<tr>
<td>BPA</td>
<td>Bis(pyridylmethyl)amine</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>CAB</td>
<td>Cellulose acetate butyrate</td>
</tr>
<tr>
<td>CAH</td>
<td>Cellulose acetate hydrophosphate</td>
</tr>
<tr>
<td>Calix[4]pyrrole</td>
<td>Meso-octamethylporphyrinogen</td>
</tr>
<tr>
<td>CAP</td>
<td>Cellulose acetate propionate</td>
</tr>
<tr>
<td>CMPO</td>
<td>Octyl(phenyl)-N,N-diisobutyl carbamoylethyl phosphine oxide</td>
</tr>
<tr>
<td>CTA</td>
<td>Cellulose triacetate</td>
</tr>
<tr>
<td>CTB</td>
<td>Cellulose tributyrate</td>
</tr>
<tr>
<td>Cyanex 272</td>
<td>Bis(2,4,4-trimethylpentyl)phosphonic acid</td>
</tr>
<tr>
<td>Cyanex 301</td>
<td>Bis(2,4,4-trimethylpentyl)dithiophosphinic acid</td>
</tr>
<tr>
<td>Cyanex 302</td>
<td>Bis(2,4,4-trimethylpentyl)monothiophosphinic acid</td>
</tr>
<tr>
<td>Cyanex 471X</td>
<td>Tri-isobutylphosphine sulfoxide</td>
</tr>
<tr>
<td>Cyphos IL 101</td>
<td>Trihexyl(tetradecyl)phosphonium chloride</td>
</tr>
<tr>
<td>Cyphos IL 102</td>
<td>Trihexyl(tetradecyl)phosphonium bromide</td>
</tr>
<tr>
<td>Cyphos IL 104</td>
<td>Trihexyl(tetradecyl)phosphonium-(2,4,4-trimethylpentyl)phosphinate</td>
</tr>
<tr>
<td>t-DAPA</td>
<td>N-6-(t-Dodecylamido)-2-pyrindinocarboxylic acid</td>
</tr>
<tr>
<td>DBBP</td>
<td>Dibutyl butyl phosphonate</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutylphthalate</td>
</tr>
<tr>
<td>DBS</td>
<td>Dibutylsebacate</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DEHA</td>
<td>Bis(2-ethylhexyl) adipate</td>
</tr>
<tr>
<td>D2EHDTPA</td>
<td>Di(2-ethylhexyl) dithiophosphoric acid</td>
</tr>
<tr>
<td>D2EHPA</td>
<td>Di(2-ethylhexyl) phosphoric acid</td>
</tr>
<tr>
<td>DNNDs</td>
<td>Dinonylnaphthalene disulfonic acid</td>
</tr>
<tr>
<td>DNNS</td>
<td>Dinonylnaphthalene sulfonic acid</td>
</tr>
<tr>
<td>DOP</td>
<td>Dioctylphthalate</td>
</tr>
<tr>
<td>EB</td>
<td>Ethyl benzoate</td>
</tr>
<tr>
<td>ELM</td>
<td>Emulsion liquid membrane</td>
</tr>
<tr>
<td>FFAT</td>
<td>5-(4-Phenoxophenyl)-6H-1,3,4-thiadiazin-2-amine</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HBA</td>
<td>Benzoylaceton</td>
</tr>
<tr>
<td>HBM</td>
<td>Dibenzoylethene</td>
</tr>
<tr>
<td>HBTA</td>
<td>Benzoyltrifluoroacetone</td>
</tr>
<tr>
<td>HF</td>
<td>Hollow fiber</td>
</tr>
<tr>
<td>HF-LPME</td>
<td>HF liquid-phase microextraction</td>
</tr>
<tr>
<td>HFTA</td>
<td>Furoyltrifluoroacetone</td>
</tr>
<tr>
<td>HPBI</td>
<td>3-Phenyl-4-benzyloisoxazol-5-one</td>
</tr>
<tr>
<td>HTTA</td>
<td>Thenoyltrifluoroacetone</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
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REFERENCES


