Int. J. Electrochem. Sci., 8 **(2013)** 4955 - 4969

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Dynamic Potential Response and SEM-EDX Studies of Polymeric Inclusion Membranes Based on Ionic Liquids

Francisca Tomás-Alonso[1], *Aurora M. Rubio*[1], *Rodrigo Álvarez*[1], *Joaquín A. Ortuño*[2,*]

[1] Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus de Espinardo, 30100 Murcia, Spain
[2] Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, Campus de Espinardo, 30100 Murcia, Spain
[*]E-mail: jortuno@um.es

Received: 22 January 2013 / *Accepted:* 8 March 2013 / *Published:* 1 April 2013

In this work, the dynamic potential response of ion-selective electrodes constructed with polymeric inclusion membranes (PIM) based on ionic liquids to the inorganic anions chloride, nitrate and thiocyanate was studied. Scanning electron-microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis was used to morphologically and chemically characterize the fresh and used membranes. The membranes were prepared by casting using PVC and the ionic liquids 1-butyl-3-methylilidazolium hexafluorophosphate [bmim$^+$][PF$_6^-$] and trihexyltetradecylphosphonium chloride [thtdP$^+$][Cl$^-$]. The membranes based on [bmim$^+$][PF$_6^-$] showed little or no response, depending on the percentage of IL in the membrane (20 % wt. and 67 % wt., respectively). The membrane based on [thtdP$^+$][Cl$^-$] (20 % wt.) showed a strong response to the abovementioned anions which followed the Hofmeister series. The dynamic response study showed that while a stationary state was attained for the chloride anion, nitrate and thiocyanate did not attain total stabilization of the potential values. When the response of this membrane towards the ibuprofen organic anion was studied, high reproducibility was obtained in both the dynamic and calibration studies.

Keywords: ion-selective electrodes; ionic liquids; polymeric inclusion membranes; scanning electron-microscopy.

1. INTRODUCTION

The science and technology of membranes prepared with ionic liquids has grown in importance throughout the world, due to the large number of applications that they offer in analytical and industrial applications such as separation and purification processes [1]. Traditionally, ionic liquid membranes are prepared in the form of supported ionic liquid membranes (SILMs), which consist of porous supports whose pores are impregnated with ionic liquids [2]. These types of membrane have been exhaustively characterized and applied [3-16].

Several challenges arise from the use of ionic liquids-based membranes, including how to increase membrane stability and find the relationship between the material structure and operation performance [17]. In this sense, SILMs present difficulties for industrial application because of their lack of long term stability. However, these difficulties can be partly overcome by using polymer-based liquid membranes (more recently called polymer inclusion membranes, PIM), whose application for the extraction and transport of metal ions has been recently reviewed [18]. This type of membrane has long been used in the construction of ion-selective electrodes, although they are usually known in this field as solvent or plasticized polymeric membranes. Polymer inclusion membranes exhibit excellent stability and versatility, and they have been applied successfully for the selective extraction and recovery of ions [19-23]. Polymer inclusion membranes based on ionic liquids have also been characterized [24-26] and used for selective extraction and transport [27].

Potentiometry with Ion-Selective Electrodes (ISEs) is an accurate, rapid, cheap and well-established analytical technique, since these electrodes allow the determination of ionic species at relatively low concentrations with reasonable selectivity [28, 29]. The basis of this technique concerning recognition and extraction principles [30, 31] enables it to be used in clinical determinations and food control, among others tasks [32-35]. Many ISEs are made of a PIM composed by a poly(vinyl chloride) (PVC) matrix plasticized with external plasticizers that increase the elasticity of the polymeric membrane and provide a lipophilic environment inside the membrane in order to improve the solubility of other components, such as ionophores and lipophilic ion-exchangers [28, 36-41].

In this paper we focus on anion-selective electrodes since no ionic liquids constituted by an easily exchangeable cation have been reported up to now. The relative tendency of an anion to enter the membrane is measured in terms of force equilibrium between the anion-water and the anion-membrane affinities [42]. The higher the second term, the better the potentiometric electrode response to the selected anion. A selectivity sequence can be established in terms of the relative anion partition coefficients between water and the PVC membrane, which follows the order of the Hofmeister series. In light of this, a very poor response can be expected for hydrophilic anions. Nevertheless, there is currently no agreement on the influence exerted on the Hofmeister series by ion-water interactions [43]. In order to facilitate the determination of hydrophilic anions, ionophores that form strong complexes with anions are introduced into carrier-based anion-selective electrodes. Additionally, a lipophilic anion-exchanger can also be incorporated to modulate the sensor response by varying its concentration. In this way, the hydrophilic counter ion of this lipophilic additive is exchanged with the primary anion. Common anion ionophores are the polyazacycloalkanes and organometallic compounds, while tridodecylmethylammonium chloride (TDMACl) is a suitable anion exchanger [28, 29].

The good performance of polymer plasticizers is connected with the interaction forces between them and the polymer of the membrane, phthalates and 2-nitrophenyl octylether (NPOE) being the most used plasticizers for ion-selective membranes. Despite having been widely used for decades [44], there are a number of problems associated with molecular solvents used as plasticizers. The major technical drawback is the leaching and migration of plasticizers from the polymer matrix, forcing the search for alternatives that show better compatibility with polymers.

Since Hurley and Wier [45] in the second half of the twentieth century discovered the ability to synthesize ionic liquids, many papers on their properties and manufacture have been published [44, 46-48], and reviews of their areas of application [31, 49, 50] have been made. The greenness and eco-toxicity of ionic liquids has also been studied [51-54] as well as their recyclability [55]. In fact, the absence of volatility (among other attractive and well-known properties) that they exhibit has proved providential at a time when concerns about the environment are becoming more genuine in all research and application areas. [56-58].

Due to their unique and valuable characteristics, such as their polymer plasticizing properties and anion-exchange capability, some room temperature ionic liquids (RTILs) have been increasingly used as components in polymeric sensing devices with excellent results. These well known properties have led to ILs being used as a convenient alternative to the combined use of molecular plasticizers and lipophilic anion-exchangers in the construction of ion-selective electrode (ISE) membranes [30, 31, 50, 59, 60].

Shvedene et al. [59] tried membranes based on poly(methyl methacrylate) or PVC, plasticized with the ionic liquids 1-butyl-2,3-dimethylimidazolium bistrifluoromethanesulfonimidate and dodecylethyldiphenylphosphomium bistrifluoromethanesulfonimidate, finding a stable potentiometric response for lipophilic cations and anions. Peng et al. [30], tested the potentiometric response of a poly(vinyl chloride) - trihexyltetradecylphosphonium chloride membrane for several inorganic anions and found a good response. The selectivity of this membrane for the more lipophilic anions such as perchlorate was lower compared with the selectivity of a PVC membrane made with 2-nitrophenyloctylether and a classical anion exchanger. Gourishetty et al. [61] made a study of a number of membranes containing different ionic liquids. The membranes constructed with [thtdP$^+$][Cl$^-$] showed potentiometric response for several inorganic anions, although the electrode slope values for chloride and sulfate were lower than those obtained by Peng [30]. Among the explanations they offered for this difference, were the different compositions of the conditioning and internal filling solutions.

In principle, all ionic liquid-based membranes suffer from ion-exchange processes between one of the constituents of the ionic liquid and the assayed ion present in the contacting sample solution. This leads to changes in the membrane composition which may become manifest in a slow dynamic response, potential drifts and lack of reproducibility. For this reason, dynamic and reproducibility studies of the potential response are essential to confirm the suitability of these membranes for practical purposes. Most studies reported with ion-selective electrodes based on ionic liquids do not deal with these aspects.

The first objective of the present work was to study the dynamic response of ion-selective electrodes based on polymer inclusion membranes constructed with PVC and two selected ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim$^+$][PF$_6^-$] and trihexyltetradecylphosphonium chloride [thtdP$^+$][Cl$^-$], to the Cl$^-$, NO$_3^-$, and SCN$^-$ anions. Additionally, the response towards a very interesting pharmaceutical anion, the ibuprofen anion [2-(4-

isobutylphenyl) propionate] was also analyzed. Also, a reproducibility study of the dynamic response and a calibration graph were made.

Another important objective was to accomplish the microscopic characterization of ion-selective electrode membranes. Scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis has proved to be a valuable tool for determining the chemical composition of membranes and the distribution of ILs within them. Incorporation of EDX spectra in the polymeric inclusion membranes characterization represents a major development in our understanding of the ion exchange and transport processes taking place at the interface of electrodes/sample solution.

2. EXPERIMENTAL PART

2.1. Apparatus and electrodes

Potentiometric measurements were recorded using a home-made high-impedance data acquisition 16-channel box connected to a PC by USB. An Orion Ag/AgCl double-junction reference electrode (Orion 90-02) containing 10 % wt. KNO_3 in the outer compartment was used.

2.2. Materials and reagents

All chemicals were of analytical reagent grade and Milli-Q water was used throughout. Potassium nitrate, potassium chloride, potassium sulfate were purchased from Panreac and potassium thiocyanate purchased from Probus. Sodium 2-(4-isobutylphenyl)-propionate (sodium ibuprofen), trihexyltetradecylphosphonium chloride, ([thtdP$^+$][Cl$^-$]) was purchased from Sigma Aldrich, and 1-butyl-3-methylilidazolium hexafluorophosphate, ([bmim $^+$][PF$_6^-$]) from Solvent-Innovation GmbH. Finally, poly(vinyl chloride) (PVC) of high molecular weight and tetrahydrofuran (THF) of selectophore-grade were purchased from Fluka.

2.3. Preparation of plasticized membranes

The selected membranes were prepared by a casting method by dissolving the corresponding weight of the ionic liquid and PVC (shown in Table 1) in 3 mL of THF. This solution was poured into a Fluka glass ring (inner diameter 28 mm, height 30 mm) on a Fluka glass plate, and allowed to settle overnight until total evaporation of THF had occurred, to obtain a thin plastic membrane. A 6-mm-diameter piece was cut out with a cork borer and was incorporated into a Fluka electrode body ISE containing 3M KCl as an internal filling solution. Table 1 shows the prepared membranes and their composition and morphological features.

Table 1. Composition of the membranes and morphological features.

Ionic Liquid	IL (%)	IL (mg)	PVC (mg)	Appearance
$[bmim^+][PF_6^-]$	20	60	240	White and rigid
$[bmim^+][PF_6^-]$	67	200	100	White and rigid
$[bmim^+][PF_6^-]$	80	240	60	Transparent and jelly
$[thtdP^+][Cl^-]$	20	60	240	Transparent and flexible

2.4. Construction, conditioning and calibration of the electrodes

The electrodes prepared were preconditioned by soaking with constant stirring in Milli-Q water. When not in use, the electrodes were kept immersed in the same solution.

The electrodes were calibrated in a dynamically by adding, while stirring, adequate small volumes of the corresponding ion solution in 50 mL of Milli-Q water. The potentials obtained were then plotted *vs.* the logarithmic values of the corresponding concentrations and the calibration parameters were calculated by fitting the calibration data to the equation

$$E = E^{0\prime} + S \log (C + LOD) \qquad (1)$$

where E is the potential of the cell, $E^{0\prime}$ the formal potential, S and LOD are the slope and the limit of detection of the electrode, respectively.

2.5. SEM-EDX characterization

A scanning electron microscope (SEM) ISI DS-130 coupled to a Kevex Si/Li detector and a Sun SparcStation 5 for energy-dispersive X-ray (EDX) analysis was used to study the morphological appearance, the overall chemical composition and the distribution of the chemical elements of interest in the membranes.

3. RESULTS AND DISCUSSION

For characterization purposes, the respective morphologies and spectra of the membranes were studied before and after potentiometric assays, with the aim of accomplishing a semi quantitative comparative study. The EDX study of polymeric membranes was based on selecting characteristic elements of interest in each ionic liquid. The morphological study showed (micrographs not shown), that in general there were no significant differences between the polymeric membranes before and after the potentiometric assays. All the samples studied showed a smooth surface with no topographic contrast.

3.1. SEM-EDX characterization of fresh [bmim $^+$][PF$_6^-$] membranes

Figure 1 shows the EDX spectra of fresh [bmim $^+$][PF$_6^-$] membranes with different percentages of ionic liquid. In these membranes, F and P were the tracer elements, whereas C, H and Cl are common to the ionic liquid and PVC matrix.

All spectra presented the characteristic peaks assigned to the C, F, P and Cl Kα lines, the P and F peaks being particularly evident in the [bmim $^+$][PF$_6^-$] 80 wt.% membrane. The relative heights of the peaks of the tracer elements were closely related to their respective amounts in the membrane, suggesting a good homogeneity in the fresh samples.

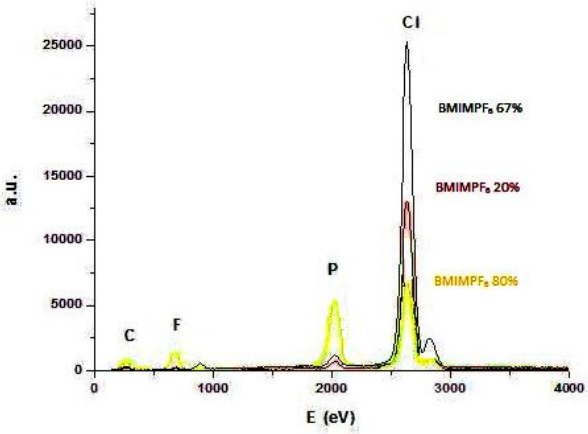

Figure 1. EDX spectra of fresh membranes with [bmim $^+$][PF$_6^-$] 67, 20 and 80 % wt.

3.2. [bmim $^+$][PF$_6^-$] membranes: potentiometric response and SEM-EDX characterization

3.2.1. [bmim $^+$][PF$_6^-$] 20 % wt

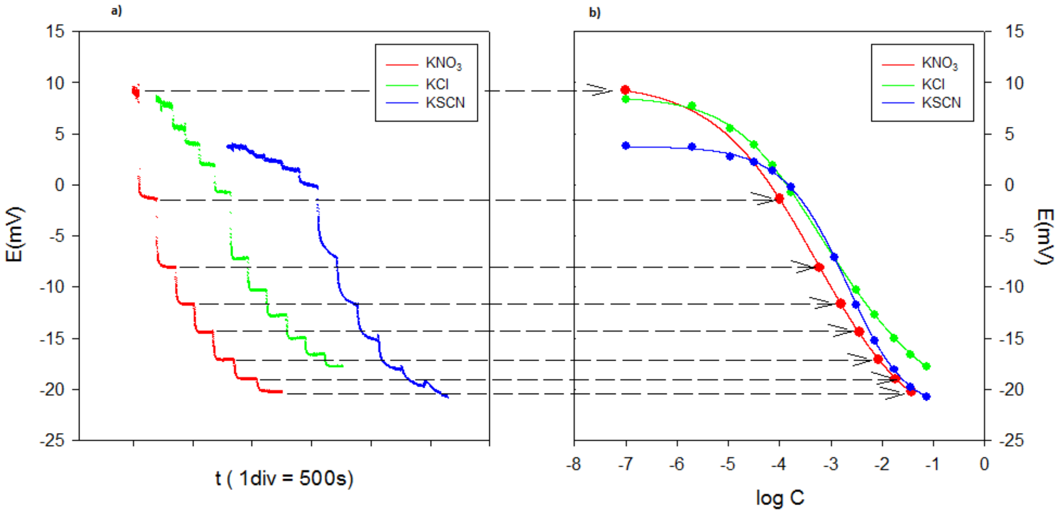

Figure 2. (a) Dynamic response of the [bmim$^+$][PF$_6^-$] (20 % wt.) membrane to increasing concentrations of NO$_3^-$, Cl$^-$ and SCN$^-$ anions. (b) Corresponding calibration graphs for the electrode.

The potentiometric response of a PVC-membrane plasticized with 20 % wt. [bmim $^+$][PF$_6^-$] to nitrate, chloride, and thiocyanate anions in the form of sodium salts, is shown in Figures 2(a) and 2(b).

As can be seen in the dynamic response (Figure 2(a)), the potential for nitrate and chloride decreased rapidly after each concentration increase before finally reaching a constant value. However, in the case of thiocyanate the response was slower and a constant value was never completely reached.

The corresponding calibration graphs (Figure 2(b)) displayed a sigmoid shape. The maximum slope values obtained from the linearization of the central portion were -8.1 mV/dec for nitrate, -4.3 for chloride and -10.3 for thiocyanate, which indicates that, although the responses were markedly sub-Nernstian, they increased in the same order as the Hofmeister series (increasing lipophilicity).

The low potential response obtained to all the anions assayed can be attributed to the low degree of anion exchange between the anion [PF$_6^-$] initially present in the membrane and the corresponding anion present in the aqueous solution. This is a consequence of the higher lipophilicity of [PF$_6^-$] compared with the nitrate, chloride and thiocyanate, as can be concluded from the corresponding standard ion-transfer potential values of the anion between water and organic phase, which is used as a lipophilicity descriptor. Thus, for NPOE as the organic phase, the reported standard ion-transfer potential values were -68 mV for [PF$_6^-$], -260 mV for thiocyanate, -372 mV for nitrate and -521 mV for chloride [62, 63].

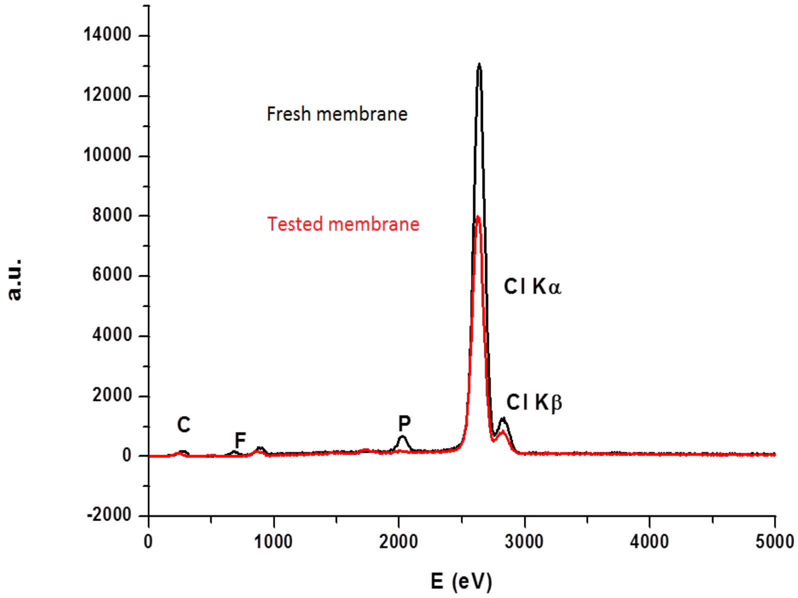

Figure 3. EDX spectra of [bmim$^+$][PF$_6^-$] (20 % wt.) membrane, fresh and after exposure to NO$_3^-$, Cl$^-$ and SCN$^-$ anions.

Figure 3 shows the EDX spectrum of the membrane after potentiometric assays. The fresh membrane spectrum is also included for comparison purposes. The relative peak heights of identical elements in the different membranes are related with the respective concentrations, assuming identical ZAF corrections. The absence of the P and F peaks from the spectrum of the used membrane indicates that the ionic liquid has disappeared from the first layer (ca. 1µm) of the membrane. However, the membrane can retain ionic liquid in the bulk, which could explain why the membrane exhibits a potential response to the studied anions.

It can be concluded that the disappearance of the ionic liquid from the external surface of the membrane is probably due to its progressive lixiviation towards the aqueous phase during exposure.

3.2.2. [bmim$^+$][PF$_6^-$] 67 % wt

The potentiometric response of the electrode with a PVC-membrane plasticized with 67 % wt. [bmim$^+$][PF$_6^-$] to chloride, nitrate and thiocyanate anions in the form of sodium salts, is shown in Figures 4(a) and 4(b).

It is interesting to note that this membrane proved to be very insensitive to the concentration changes of the three anions assayed. Some of the membranes that exhibit this behavior have been proposed as reference electrodes [64]. In our case, the observed potential variation, < 4 mV, over three concentration decades, is lower than previously reported values and so this electrode could be useful as a reference electrode. For this purpose, its potential response towards other anions should be studied. Although the response of this electrode in pure water displays some noise, this noise drastically diminishes in salt solutions.

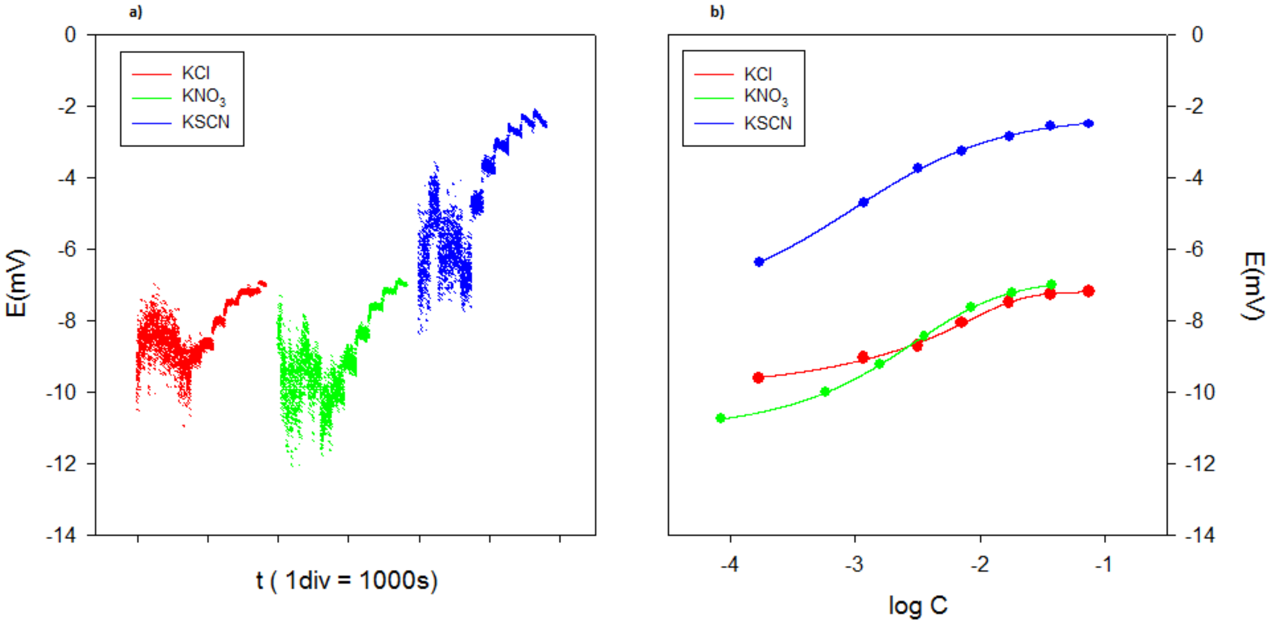

Figure 4. (a) Dynamic response of the [bmim$^+$][PF$_6^-$] (67 % wt.) membrane to increasing concentrations of Cl$^-$, NO$_3^-$ and SCN$^-$ anions. (b) Corresponding calibration graphs for the electrode.

Figure 5 shows the EDX spectrum of the 67 % wt. membrane after the potentiometric assays. The fresh membrane spectrum is also included for comparison purposes. As in the [bmim$^+$][PF$_6^-$] (20 % wt.) membrane. The spectrum for the fresh [bmim$^+$][PF$_6^-$] (67 % wt.) membrane presents the characteristic peaks assigned to the C, F, P and Cl Kα lines, corresponding to the polymeric membrane plasticized with the [bmim$^+$][PF$_6^-$] ionic liquid. From a comparison of the F and P peaks in both membranes it can be concluded that ionic liquid has completely disappeared from the PVC matrix after operation. The decrease in the Cl Kα line was higher than in the above described membrane, indicating a greater reduction in the Cl of the polymeric membrane after potentiometric determinations.

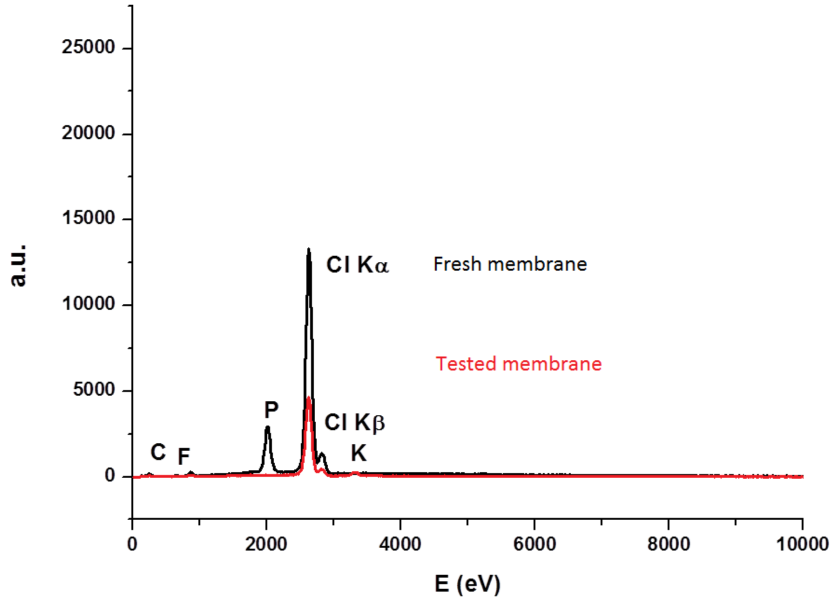

Figure 5. EDX spectra of [bmim$^+$][PF$_6^-$] (67 % wt.) membrane, fresh and after exposure to Cl$^-$, NO$_3^-$ and SCN$^-$ anions.

The [bmim $^+$][PF$_6^-$] 80 % wt. membrane was not subjected to further analysis because of their extreme fragility and handling failure.

3.3. *[thtdP$^+$][Cl$^-$] membranes: SEM-EDX characterization and potentiometric response*

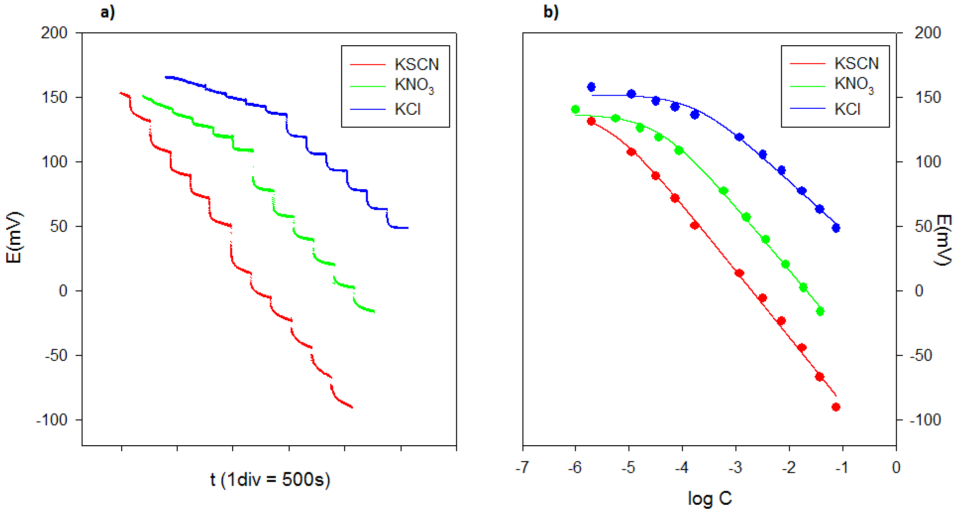

Figure 6. (a) Dynamic response of the [thtdP$^+$][Cl$^-$] (20 % wt.) membrane to increasing concentrations of SCN$^-$, NO$_3^-$, and Cl$^-$ anions. (b) Corresponding calibration graphs for the electrode.

Taking the above results into account we decided to use an ionic liquid containing chloride in order to favor the anion-exchange between the chloride anion and the tested anion present in the sample solution. The ionic liquid [thtdP$^+$][Cl$^-$] was chosen because it contains a very lipophilic cation which prevents cation-exchange processes between the aqueous sample and the membrane and avoids lixiviation of the ionic liquid to the aqueous sample solution. Other authors [30, 61] have also assayed the ionic liquid [thtdP$^+$][Cl$^-$] for the construction of ion-selective electrodes, as mentioned in the Introduction.

The response of PVC-membrane plasticized with 20 % wt. [thtdP$^+$][Cl$^-$] to thiocyanate, nitrate and chloride anions, is shown in Figures 6(a) and 6(b).

Compared with the results shown above for membranes made with the [bmim$^+$][PF$_6^-$] ionic liquid, the membrane made with [thtdP$^+$][Cl$^-$] provided a high potential response towards the three anions assayed, in the sequence $Cl^- < NO_3^- < SCN^-$, which follows the Hofmeister series. The potential changes between the base line and the higher concentration assayed were 114.1, 163.6, and 240.7 mV, respectively. As can be seen in Figure 6(a), the potential response to chloride attained a steady value after each addition in a relatively short time ($t_{95\%}$ = 65 s). However, the potential response in the case of nitrate and thiocyanate did not reach a stable value during the exposure time (3min), which may have been be due to the continuous exchange process between the chloride anion present in the membrane and the nitrate and thiocyanate present in the external sample solution.

In relation to the corresponding calibration graphs shown in Figure 6(b), it has been observed that all anions exhibit sub-Nernstian slope values in the linear range (-38.1, -49.6 and -51.6 for chloride, nitrate and thiocyanate respectively) which increase in the same order as the Hofmeister series.

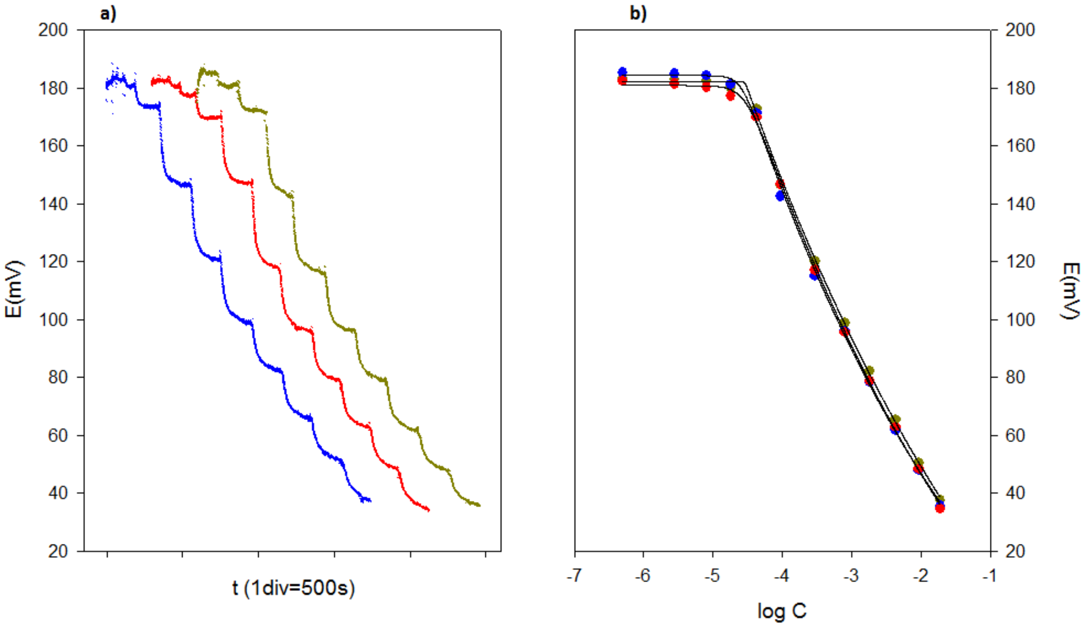

Figure 7. a) Dynamic response of the [thtdP$^+$][Cl$^-$] (20 % wt.) membrane to increasing concentrations of ibuprofen. (b) Corresponding calibration graphs for the electrode.

Since the membrane plasticized with [thtdP$^+$][Cl$^-$] provided the best response for all the inorganic anions assayed, this membrane was selected for further studies, widening the scope of this IL-based membrane to the field of drug analysis. Ibuprofen was used as a typical anionic drug. The dynamic response for the ibuprofen anion and the corresponding calibration graphs obtained (in triplicate) are shown in Figure 7(a) and 7(b), respectively. As can be seen, a very good repeatability was obtained. As for nitrate and thiocyanate, the potential did not completely stabilize in the analyzed period.

The calibration graphs showed a linear response at high concentrations over almost two concentration decades, a super-Nernstian response at intermediate concentrations and no response at low concentrations. The slope of the straight portion was -52.45 ± 0.05 (mV/dec), with a LOD of $1.8 \times 10^{-5} \pm 7.2 \times 10^{-7}$ (M), and a linearity interval of $2.9 \times 10^{-4} \pm 1.8 \times 10^{-2}$ (M).

Between days reproducibility of the electrode was studied by performing calibrations on the first day and after 4 and 5 days. The corresponding calibration graphs are reflected in Figure 8, which shows a slight and gradual loss of the potentiometric response with time for high ibuprofen concentrations. The potential changes between the base line and the higher concentration assayed range from 149.8 mV on the first day, 132.8 mV on the fourth and 125.8 mV on the fifth. With the aim of recovering the initial response, the electrode was immersed in KCl (0.1M) for two days. The new calibration graph is also reflected in Figure 8, showing that only a partial recovery of the membrane response was achieved (139.0 mV).

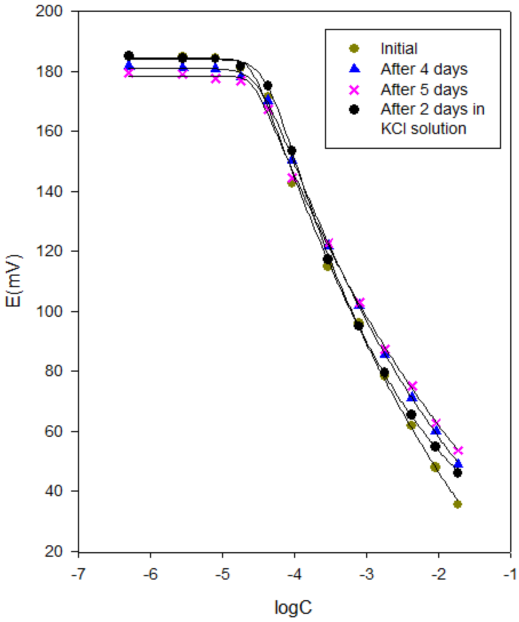

Figure 8. Calibration graphs for the ibuprofen anion response of the [thtdP$^+$][Cl$^-$] (20 % wt.) membrane after 1, 4 and 5 days in water and after 2 days in 0.1M KCl solution.

Figure 9 shows the EDX spectra of fresh membrane and after been subjected to the potentiometric determinations of SCN$^-$, NO$_3^-$, and Cl$^-$ and ibuprofen anions. In all cases, the EDX spectra were taken from the external face of membrane in contact with the sample solution. The tracer P was used to follow the presence of the ionic liquid cation [thtdP$^+$].The P peaks corresponding to the fresh and used membranes were identical, which indicates that no substantial loss of the ionic liquid cation occurred during operation. This is a significant difference with the [bmim $^+$][PF$_6^-$] membranes, in which the ionic liquid was stripped during operation.

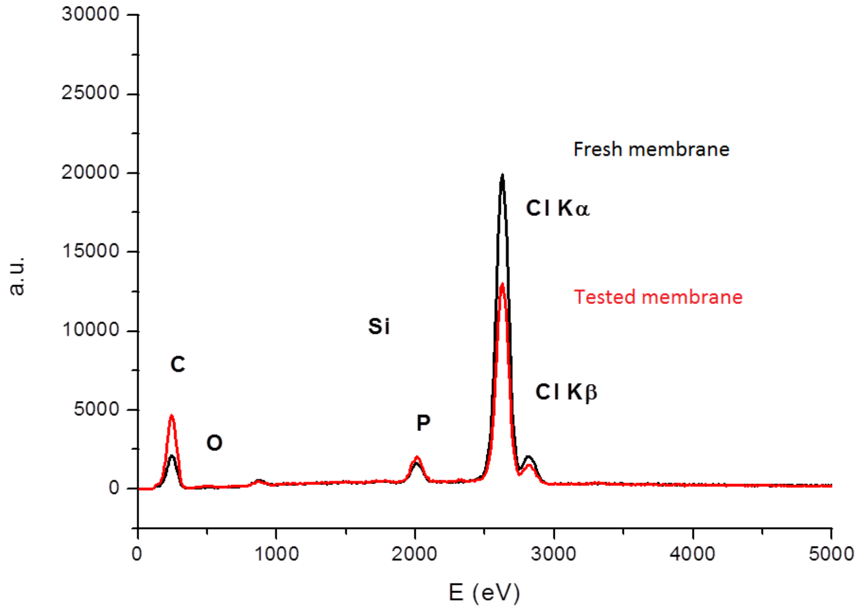

Figure 9. EDX spectra of [thtdP$^+$][Cl$^-$] (20 % wt.) membrane, fresh and after exposure to SCN$^-$, NO$_3^-$, and Cl$^-$ and ibuprofen anions, external side.

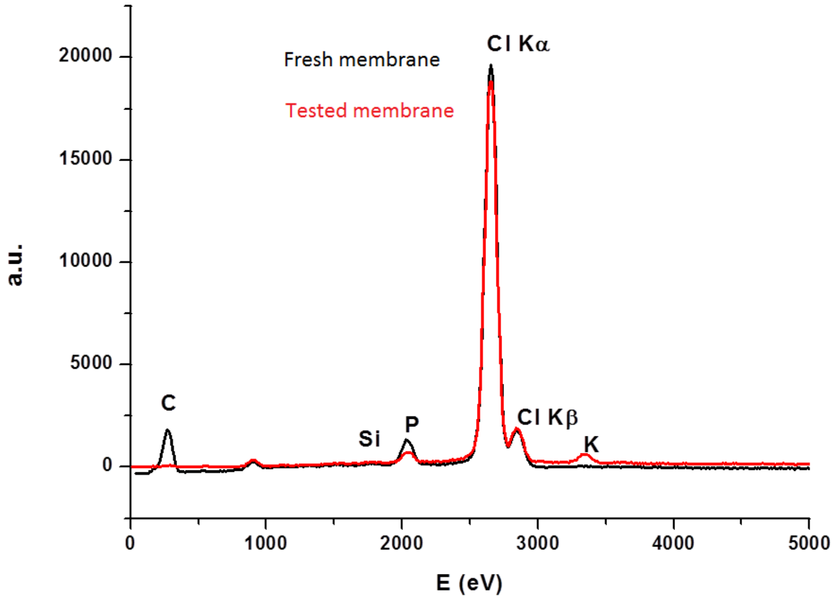

Figure 10. EDX spectra of [thtdP$^+$][Cl$^-$] (20 % wt.) membrane, fresh and after potentiometric responses to SCN$^-$, NO$_3^-$, and Cl$^-$ and ibuprofen anions, internal side.

The relative height of the C peak increased and the corresponding height of Cl Kα diminished substantially, which constitutes clear evidence of anion exchange between the hydrophilic counter ion [Cl^-] present in the membrane and the lipophilic primary anion [$ibuprofen^-$] present in the external aqueous solution. This result is especially relevant, since, to our knowledge, this is the first time that anion exchange has been demonstrated by the EDX technique.

In order to study the exchange processes between the ion-selective membrane and the inner filling solution, an EDX study of the inner face of membrane in contact with 3M KCl solution was made. Figure 10 shows the corresponding spectra for the fresh and used membrane.

Figure 10 shows that the Kα and Kβ Cl peaks are practically superposed in both the fresh and used samples, indicating that no anion exchange between the membrane and the inner solution has occurred. On the other hand, the decrease in the height of the P peak and the simultaneous appearance of a small K peak - no present in Figure 9 - shows that some cation exchange between [$thtdP^+$] from the ionic $liquid^-$ and K^+ from the concentrated inner solution has taken place at the internal interface of the membrane.

4. CONCLUSIONS

Plasticized PVC membranes made with ionic liquids containing no exchangeable anions showed little or no potential response for common inorganic anions, which made them good potential candidates for the construction of reference electrodes. In contrast, ionic liquids containing an easily exchangeable anion, such as chloride, gave membranes with high potential responses for a wide range of anions. EDX studies demonstrated anion exchange processes between the anion initially present in the membrane and those present in the sample solution. Anion exchange processes give rise to potential drifts, which prevents the potential from reaching the steady state. Good reproducibility in the calibration graphs can be achieved by controlling the exposure time to the sample containing the target anion.

ACKNOWLEDGMENTS

The authors acknowledge the Ministerio de Economía y Competitividad, Dirección General de Investigación, Spain (Project CTQ2011-27049). The authors also thank José María Palacios Latasa for the SEM-EDX analytical support in the Institute of Catalysis and Petrochemistry (CSIC) of Madrid.

References

1. J.G. Crespo, J.M. Coelhoso, R.M.C. Viegas, *Encyclopedia of separation processes*, Academic Press, San Diego (2000).
2. L.J. Lozano, C. Godínez, A.P. De Los Ríos, F.J. Hernández-Fernández, S. Sánchez-Segado, F.J. Alguacil, *J. Membr. Sci.*, 376 (2011) 1-14.

3. R. Fortunato, C.A.M. Afonso, J. Benavente, E. Rodriguez-Castellón, J.G. Crespo, *J. Membr. Sci.,* 256 (2005) 216-223.
4. R. Fortunato, C.A.M. Afonso, M.A.M. Reis, J.G. Crespo, *J. Membr. Sci.,* 242 (2004) 197-209.
5. L.C. Branco, J.G. Crespo, C.A.M. Afonso, *Angew Chem. Int. Ed.,* 41 (2002) 2771-2773.
6. P. Luis, L.A. Neves, C.A.M. Afonso, I.M. Coelhoso, J.G. Crespo, A. Garea, A. Irabien, *Desalination,* 245 (2009) 485-493.
7. P. Luis, A. Garea, A. Irabien, *J. Membr. Sci.,* 330 (2009) 80-89.
8. F.J. Hernández-Fernández, A.P. de los Ríos, M. Rubio, F. Tomás-Alonso, D. Gómez, G. Víllora, *J. Membr. Sci.,* 293 (2007) 73-80.
9. A.P. De los Ríos, F.J. Hernández-Fernández, D. Gómez, M. Rubio, F. Tomás-Alonso, G. Víllora, *J. Supercrit. Fluids,* 43 (2007) 303-309.
10. F.J. Hernández-Fernández, A.P. De Los Ríos, F. Tomás-Alonso, J.M. Palacios, G. Víllora, *J. Membr. Sci.,* 341 (2009) 172-177.
11. F.J. Hernández-Fernández, A.P. de los Ríos, F. Tomás-Alonso, J.M. Palacios, G. Víllora, *AICHE J.,* 58 (2012) 583-590.
12. A.P. de los Ríos, F.J. Hernández-Fernández, F. Tomás-Alonso, J.M. Palacios, G. Víllora, *Desalination,* 245 (2009) 776–782.
13. F.J. Hernández-Fernández, A.P. de los Ríos, F. Tomás-Alonso, D. Gómez, G. Víllora, *Desalination,* 244 (2009) 122–129.
14. A.P. de los Ríos, F.J. Hernández-Fernández, H. Presa, D. Gómez, G. Víllora, *J. Membr. Sci.,* 328 (2009) 81–85.
15. A.P. de los Ríos, F.J. Hernández-Fernández, F. Tomás-Alonso, J.M. Palacios, D. Gómez, M. Rubio, G. Víllora, *J. Membr. Sci.,* 300 (2007) 88–94.
16. A.P. de los Ríos, F.J. Hernández-Fernández, F. Tomás-Alonso, J.M. Palacios, D. Gómez, M. Rubio, G. Víllora, *J. Membr. Sci.,* 307 (2008) 233–238.
17. R.D. Noble, D.L. Gin, *J. Membr. Sci.,* 369 (2011) 1-4.
18. M.I.G.S. Almeida, R.W Cattrall, S.D. Kolev, *J. Membr. Sci.,* 415-416 (2012) 9-23.
19. O. Arous, M. Amara, H. Kerdjoudj, *Arab. J. Sci. Eng.,* 35 (2010) 79-93.
20. O. Kebiche-Senhadji, S. Tingry, P. Seta, M. Benamor, *Desalination,* 258 (2010) 59-65.
21. C.A. Kozlowski, T. Girek, W. Walkoviak, J.J. Koziol, *Sep. Purif. Technol.,* 46 (2005) 136-144.
22. J. Kozlowska, C.A. Kozlowski, J.J. Koziol, *Sep. Purif. Technol.,* 57 (2007) 430-434.
23. C.A. Kozlowski, W. Walkoviak, T. Girek, *J. Membr. Sci.,* 310 (2008) 312-320.
24. N. Pereira, A. St John, R.W. Cattrall, J.M. Perera, S.D. Kolev, *Desalination,* 236 (2009) 327-333.
25. J. Schauer, A. Sikora, M. Pliskova, J. Malis, P. Mazur, *J. Membr. Sci.,* 367 (2011) 332-339.
26. N. Gizli, S. Çinarli, M. Demircioglu, *Sep. Purif. Technol.,* 97 (2012) 96-107.
27. D. Kogelnig, A. Regelsberger, A. Stojanovic, F. Jirsa, R. Krachler, B.K. Keppler, *Monatsh. Chem.,* 142 (2011) 769-772.
28. E. Bakker, P. Bühlmann, E. Pretsch, *Chem. Rev.,* 97 (1997) 3083-3132.
29. P. Bühlmann, E. Bakker, E. Pretsch, *Chem. Rev.,* 98 (1998) 1593-1687.
30. B. Peng, J. Zhu, L. Xiaojie, Y. Qin, *Sens. Actuator B-Chem.,* 133 (2008) 308-314.
31. D. Wei, A. Ivaska, *Anal. Chim. Acta,* 607 (2008) 126-135.
32. J.A. Ortuño, M. Cuartero, M.S. García, M.I. Albero, *Electrochim. Acta,* 55 (2010) 5598-5603.
33. M.S. García, J.A. Ortuño, M.I. Albero, M. Cuartero, *Anal. Bioanal. Chem.,* 394 (2009) 1563-1567.
34. M.S. García, J.A. Ortuño, M. Cuartero, M.S. Abuherba, *Sensors,* 11 (2011) 8813-8825.
35. N.V. Shvedene, S.A. Krasnov, M. Yu. Nemilova, A.V. Grigoreva, K.M. Sotnezova, I.V. Pletnev, *J. Anal. Chem.,* 67 (2012) 834-841.
36. F. Faridbod, M.R. Ganjali, R. Dinarvand, P. Norouzi., *Afr. J. Biotechnol.,* 25 (2007) 2960-2987.
37. M. Shamsipur , S. Rouhanib, A. Mohajeri, M.R. Ganjali, P. Rashidi-Ranjbar, *Anal. Chim. Acta,* 418 (2000) 197-203.

38. M.R. Ganjali, M. Emamia, M. Javanbakht, M. Salavati-Niasari, M. Shamsipur, M. Yousefi, *Sens. Actuators B*, 105 (2005) 127–131
39. V.K. Gupta, R.N. Goyal, R.A. Sharma, *Talanta*, 76 (2008) 859-864.
40. V.K. Gupta, L.P. Singh, S. Chandrad, S. Kumare, R. Singhf, B. Sethie, *Talanta*, 85 (2011) 970-974
41. V.K. Gupta, A.K. Jain, M.K. Palc, A.K. Bhartia, *Electrochim. Acta* , 80 (2012) 316-325
42. C. Coll, R.H. Labrador, R. Martínez-Mañez, J. Soto, F. Sancenón, M-J. Seguí, E. Sánchez, *Chem. Commun.*, 24 (2005) 3033-3035.
43. K. Wojciechowski, M. Kuchareka, W. Wróblewskia, P. Warszyński, *J. Electroanal. Chem.*, 638 (2010) 204.
44. H. Rahman, C.S. Brazel, *Polym. Degrad. Stabil.*, 91 (2006) 3371-3382.
45. F.H. Hurley, T.P. Wier, *J. Electrochem. Soc.*, 98 (1951) 203-206.
46. J.L. Anderson, D.W. Amstrong, G.T. Wei, *Anal. Chem.*, 78 (2006) 2892-2902.
47. J.O. Valderrama, R.E. Rojas, *Ind. Eng. Chem. Res.*, 48 (2009) 6890-6900.
48. J.F. Wishart, *Energy Environ. Sci.*, 2 (2009) 956-961.
49. L.J. Lozano, C. Godínez, A.P. De Los Ríos, F.J. Hernández-Fernández, S. Sánchez-Segado, F.J. Alguacil, *J. Membr. Sci.*, 376 (2011) 1-14.
50. D.S. Silvester, *Analyst*, 136 (2011) 4871.
51. S. Zhu, R. Chen, Y. Wu, Q. Chen, X. Zhang, Z. Yu, *Chem. Biochem. Eng. Q.*, 23 (2009) 207-211.
52. M. Petkovic, K.R. Seddon, L.P.N. Rebelo, C.S. Pereira, *Chem. Soc. Rev.*, 40 (2011) 1383-1403.
53. R. Feng, D. Zhao, Y. Guo, *J. Environ. Prot.*, 1 (2010) 95-104.
54. T.P.T. Pham, C-W. Cho, Y.S. Yun, *Water Res.*, 44 (2010) 352-372.
55. B. Wu, W.W. Liu, Y.M. Zang, H.P. Wang, *Chem.-Eur. J.*, 15 (2009) 804-1810.
56. R. Sheldon, *Chem. Commun.*, 23 (2001) 2399-2407.
57. M.J. Earle, K.R. Seddon, *Pure Appl. Chem.*, 72 (2000) 1391-1398.
58. J.F. Brennecke, E.J. Maginn, *AICHE J.*, 47 (2001) 2384-2389.
59. N.V. Shvedene, D.V. Chernyshov, M.G. Khrenova, A.D. Formanovsky, V.E. Baulin, I.V. Pletnev, *Electroanal.*, 18 (2006) 1416-1421.
60. A.V. Kopytin, K.Yu. Zhizhin, Yu.I. Urusov, V. N. Mustyatsa, Yu.V. Kokunova, N.T. Kuznetsov, *J. Anal. Chem.*, 67 (2012) 168–171.
61. R. Gourishetty, A.M. Crabtree, W.M. Sanderson, R.D. Johnson, *Anal. Bioanal. Chem.*, 400 (2011) 3025-3033.
62. A. Molina, J.A. Ortuño, C. Serna, E. Torralba, *Phys. Chem. Chem. Phys.*, 12 (2010) 13296–13303.
63. T. Kakiuchi, Anal. Chem., 79 (2007) 6442–6449.
64. D. Cicmil, S. Anastasova, A. Kavanagh, D. Diamond, U. Mattinen, J. Bobacka, A. Lewenstam, A. Radu, *Electroanal.*, 23 (2011) 1881-1890.