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Characterization and Stability Of CTA-Based Polymer Inclusion Membranes Using 2-NPOE as Plasticizer and $BMIMPF_6$ as Ionic Liquid

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Abstract

The polymer inclusion membranes (PIMs) were prepared by mixing a thermoplastic polymer (cellulose triacetate (CTA)), a plasticizer (2-nitrophenyl octyl ether (2-NPOE)) and an ionic liquid (1-n-Butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$)) to use for the extraction of Cr (VI). These PIMs were characterized using FTIR analysis, the spectra were compared using principal component analysis (PCA) and the interactions between the constituents of prepared PIMs were determined. The stability of membrane was determined by measuring conductivity of the aqueous solution.

Introduction

The polymer inclusion membranes (PIMs) said plasticized polymer membranes (PPMs) [1] have attracted considerable interest during the last few years owing to their advantages over the supported liquid membranes (SLM) in the metal ion transport, such as long term stability, a faster rate of transport, a high selectivity and an easy set up [2]. The large number of reference devoted to PIMs during the last decades reveals the great interest for these membranes [3–5].

The infrared spectroscopy can be used to characterize the PIMs and their constituents. In FTIR spectra, absorbance is measured at thousands of frequencies. In general, the interpretation of spectral data can be significantly favoured by the use of multivariate tools, markedly by Principal Component Analysis (PCA). The use of this method on FTIR spectra, allows a better identification of the spectral differences among the samples.

The new approach in this work is to study the contribution of the ionic liquid $BMIMPF_6$ and the plasticizer 2-NPOE to improve the performance of these membranes, especially relative to their stability and selectivity.

Materials & Methods

The membranes were prepared using a procedure similar to that reported by several researchers, already described in our previous work [4, 5]. In the case of membranes with the ionic liquid, the conventional extractant was replaced by 1-butyl-3-methylimidazolium hexafluorophosphate. Samples of the same mass were cut from the same membrane to monitor their stability.

FTIR spectra were acquired using IR Affnity-1 (Shimadzu) spectrometer and principal component analysis was applied using Matlab (data were mean-centred) to characterize and compare different prepared PIMs.

The stability study was performed at 23°C using a beaker containing distilled water which is cut a piece of the membrane developed and when left under magnetic stirring at 350 rpm for 24 hours, then follows the evolution of the conductivity of the aqueous phase.

Results

In FTIR spectra the main observed bands are those of the individual constituents of the membrane as shown in Table 1. The first three components are significant, the total variance captured by these components is 99.17 %. The scores on PC1, PC2 PC3 (Fig 1) were identical for the membrane FTIR spectra (4, 5, 6) with respectively the addition of their constituents FTIR spectra ((7=1+2), (8=1+3), (9=1+2+3)).

Figure 2 shows that the conductivity of the solution increases quickly during the first 30 minutes of contact and then stabilizes (obtaining a plateau) for the membrane containing the plasticizer. However, with the membranes without plasticizer, the conductivity continues to increase gradually.

Conclusions

PIM systems containing ionic liquid $BMIMPF_6$ as carrier and 2-NPOE as plasticizer CTA membranes were prepared and they are characterized by FTIR. The main observed bands in FTIR spectra of PIMs are those of their individual constituents. This should suggest that there are no chemical reactions between PIMs constituents, there are only weak interactions. These results were confirmed using principal component analysis (PCA).

Recorded conductivities (after 5 hours) are higher for membranes without plasticizer because the ionic liquid is fixed better in the presence of plasticizer. The PIMs show a considerable stability particularly for the membrane with plasticizer.

Table 1: Main identified IR absorption bands in the membrane samples

Membrane	Absorption bands (cm^{-1})	Chemical groups
CTA	3600 - 3200	O-H
	1735	C=O
	1210 - 1035	C-O-C
	2960 - 2850	C-H
	1370	C-H
2-NPOE	1525	NO_2
	1465	$-CH_3$ (octyl)
	2960 - 2850	$-CH_2-$
	1127	C-O-C
	1232	$R-O-CH_2$
	1351	C-N
	720	$-CH_2-$
	730 - 675	C-H
$BMIMPF_6$	756	C-H
	1460	C-N
	2966	C-H

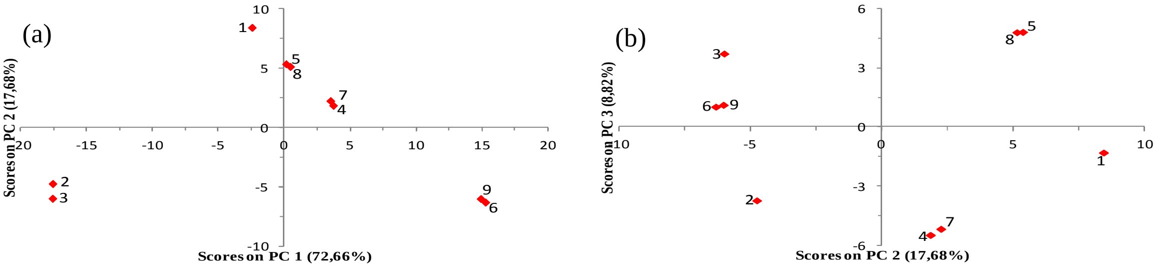

Fig. 1; Scores on: (a) PC2 vs. PC1, (b) PC3 vs. PC2. (1) CTA, (2) 2-NPOE, (3) BMIMPF6, (4) CTA, 2-NPOE, (5) CTA, BMIMPF6, (6) CTA, 2-NPOE, BMIMPF6, (7) spectrum (1+2), (8) spectrum (1+3), (9) spectrum (1+2+3)

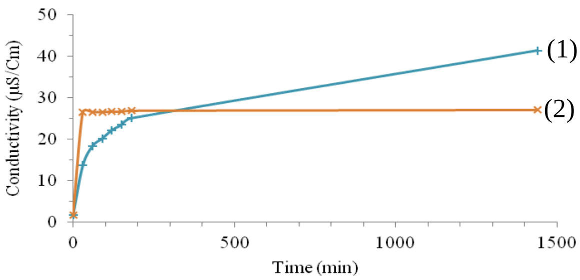

Fig. 2; Conductivity vs. time, (1) CTA, $BMIMPF_6$, (2) CTA, 2-NPOE, $BMIMPF_6$

References

1) A.J.B. Kemperman, H.H.M. Rolevink, D. Bargeman, T.V.D. Boomgaard, H. Strathmann, Stabilization of supported liquid membranes by interfacial polymerization top layers, *J. Membr. Sci.*, 138(1), (1998) 43-55
2) J.S. Kim, S.K. Kim, M.H. Cho, S.H. Lee, J.Y. Kim, S. Kwon, E.H. Lee, Permeation of silver ion through polymeric CTA membrane containing acyclic polyether bearing amide and amine end group, *Bull. Korean Chem. Soc.*, 22(10), (2001) 1076-1080
3) L.D. Nghiem, P. Mornane, I.D. Potter, J.M. Perera, R.W. Cattrall, S.D. Kolev, Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs), *J. Membr. Sci.*, 281(1-2), (2006) 7-41
4) O. Kebiche-Senhadji, L. Mansouri, S. Tingry, P. Seta, M. Benamor, Facilitated Cd(II) transport across CTA polymer inclusion membrane using anion (Aliquat 336) and cation (D2EHPA) metal carriers, *J. Membr. Sci.*, 310(1-2), (2008) 438-445
5) O. Kebiche-Senhadji, S. Bey, G. Clarizia, L. Mansouri, M. Benamor, Gas permeation behavior of CTA polymer inclusion membrane (PIM) containing an acidic carrier for metal recovery (DEHPA), *Sep. Purif. Technol.*, 80(1), (2011) 38-44