Rapid communication

# *In situ* desorption in a $^1$H NMR tube: A simple method for determining membrane sorption selectivity

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## Abstract

Determining membrane sorption selectivity by conventional methods is usually fairly time-consuming and can even become a rather difficult task for membrane materials with low sorption levels. In this case, the amount of the species absorbed by the membrane is indeed so low that large amounts of membrane materials are usually required to determine the composition of the sorbed mixture by a common desorption method with several associated drawbacks (e.g. experimental uncertainty, long sorption and desorption times). The paper describes how performing desorption experiments directly in a $^1$H NMR tube can overcome all the former limitations. The sorption selectivity of new poly(urethane-imide) membranes containing increasing contents in tertiary amine groups was determined for the azeotropic mixture ethanol (20 wt%)/ethyl-*tert*-butyl ether ETBE. Membrane selectivity values given by this method were very close to those obtained by the most common former method, with the advantages of being both very simple and much quicker to implement.
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*Keywords:* Sorption; Method of measurement

## 1. Introduction

Determining membrane sorption selectivity by conventional methods is usually fairly time-consuming and can even become a difficult task for membrane materials with low sorption levels. In this case, the amount of species sorbed by the membrane is indeed so low that large amounts of membrane materials are usually required to determine the composition of the sorbed mixture by the most common desorption method in vacuum with several associated drawbacks (e.g. experimental uncertainty, long sorption and desorption times).

A few papers have already proposed interesting alternative desorption methods for such difficult systems. Hauser et al. have for instance reported the desorption of hydro-organic mixtures from poly(vinyl alcohol) membranes in carbon tetrachloride and the subsequent analysis of the desorbate by infrared spectrometry [1]. Another relevant example is the method developed by Kamaruddin and Koros for analyzing the sorption of methanol/MTBE mixtures in a glassy polyimide. In that case, the sorbed mixture was first extracted by a solution of water containing 5 wt% of a strong polar solvent (*N,N*-dimethyl acetamide) and then analyzed by head-space gas chromatography [2].

This paper reports a new method of direct desorption in a $^1$H NMR tube for determining sorption selectivity in a simple and straightforward way. This method will be compared with the most classical vacuum desorption method for determining the sorption selectivity of a family of poly(urethane-imide)s containing increasing amounts of tertiary amine groups for the isothermal sorption of the azeotropic mixture ethanol (20 wt%)/ethyl-*tert*-butyl ether (ETBE—80 wt%).

## 2. Materials and methods

### 2.1. Solvents and polymer materials

For the preparation of the polymer membranes, chloroform (Carlo Erba) was used as received. For the sorption experiments, ethanol (anhydrous, VWR International) was used as received. Ethyl-*tert*-butyl ether (ETBE) was kindly provided by the Institut Français du Pétrole (IFP—French Petroleum Institute) and was distilled twice over Na prior use. It was then kept in a dark glass bottle under dried argon to avoid peroxide formation.

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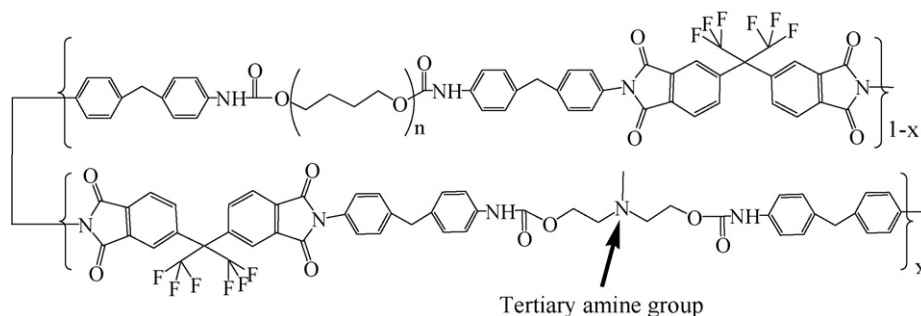*E-mail address:* Anne.Jonquieres@ensic.inpl-nancy.fr (A. Jonquieres).

Fig. 1. Chemical structure of the block copolymers PUI/*x*.

Carbon tetrachloride (spectroscopy grade, Merck) was used as received.

The poly(urethane-imide) block copolymers used in this work (Fig. 1) were obtained from a polytetramethylene oxide diol (PTMO1000), *N*-methyldiethanolamine (MDEA), 4,4′-methylene-bis-phenylisocyanate (MDI) and 4,4′-hexafluoroisopropylidene-bis-phthalic anhydride (6FDA). The synthesis and characterization of these polymers PTMO1000 $(1 - x$ equiv.$) +$ MDEA $(x$ equiv.$)$/MDI (2 equiv.)/6FDA (1 equiv.) have been reported recently [3]. For the sake of simplicity, they will be abbreviated as PUI/*x* in the following text, *x* standing for the number of equivalent of the tertiary amine groups in the poly(urethane-imide) block copolymers. The main originality of these poly(urethane-imide)s is that they contain controlled amounts of tertiary amine groups which can act as Lewis bases and interact with ethanol. These polymers can also be considered as interesting precursors for a wide range of poly(urethane-imide) cationomers which can be obtained by simple quaternization of their tertiary amine groups [4,5].

### 2.2. Polymer membranes and sorption experiments

Polymer membranes were prepared for different block copolymers containing between 0 and 0.7 equiv. of tertiary amine groups. Above this critical content (i.e. for $0.7 < x \leq 1$), the block copolymers were fairly brittle and could not be used for sorption experiments. The typical procedure used for membrane casting follows. Two grams of a given polymer were dissolved in 25 ml of chloroform at ambient temperature for 30 min. The resulting solution was filtered on glass fibbers and cast onto a PTFE plate with a diameter of 78 mm. This plate was then transferred onto a metal support whose horizontality was adjusted with micrometric screws. Due to the high volatility of chloroform, the PTFE plate was partially covered with a glass plate to limit the solvent evaporation rate. The evaporation took place in about 2 h. The sorption membrane was then dried in vacuum during the night at ambient temperature to eliminate the residual solvent. The average thickness of the resulting membrane was ca. 450 μm and slightly depended upon the block copolymer, the density of these polymers increasing linearly with their tertiary amine content as shown earlier [3].

For the sake of comparison, the isothermal sorption experiments were carried out with two different methods for the azeotropic liquid mixture EtOH (20 wt%)/ETBE at 30 °C.

The first one was the most commonly used method in the literature for determining sorption selectivity. After equilibrating a given polymer membrane in the azeotropic feed mixture in a thermostatic oven for 3 days (equilibrium checked by periodic weight measurements of the swollen membrane until constant weight uptake), the sorbed mixture was desorbed by a progressive rise in temperature from 20 to 80 °C for 8 h in vacuum and condensed in a thin glass tube cooled by liquid nitrogen according to a procedure described elsewhere [6]. The validity of the experiment was checked by a simple mass balance. The composition of the desorbate (ca. 0.5 g) was determined by gas chromatography with a Shimadzu GC-8A chromatograph equipped with a Porapak Q column with an error of ±0.005 for the ethanol weight fraction $C_S$. The membrane sorption selectivity $\alpha_S$ was then calculated from the feed and desorbate compositions according to Eq. (1) [7]:

$$\alpha_S = \frac{C_S}{1 - C_S} \times \frac{1 - C}{C} \tag{1}$$

where $C$ is the ethanol weight fraction of the feed mixture (here $C = 0.2$) and $C_S$ is the ethanol weight fraction of the desorbate.

The second method used a thin slice of polymer (ca. 2 mm × 30 mm) which was equilibrated in the azeotropic feed mixture in the same conditions as formerly described. After 3 days of sorption, the thin slice of polymer was inserted into a 5 mm $^1$H NMR tube which contained carbon tetrachloride. A sealed capillary glass tube containing a tiny amount of acetone-$d_6$ was then inserted in the $^1$H NMR tube. The composition of the desorbate was then calculated (Eq. (2)) from the integrated area $I_b$ and $I_e$ of the peaks appearing at 2.53 and 2.84 ppm, respectively, in the $^1$H NMR spectrum (Fig. 2) which was recorded on a Bruker Avance 300 spectrometer:

$$C_S = \frac{I_e M_{EtOH}}{I_e M_{EtOH} + I_b M_{ETBE}} \tag{2}$$

where $M_i$ is the molar weight of species $i$ (g/mol) and $C_S$ is the ethanol weight fraction of the desorbate.

## 3. Results and discussion

Selectivity of poly(urethane-imide)s containing increasing contents of tertiary amine groups (Fig. 1) was determined for the sorption of the azeotropic mixture EtOH/ETBE by two different methods.