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Sorption of single enantiomers and racemic mixture of (+/−)-α-pinene into Nafion membranes

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ABSTRACT

The aim of this work was to elucidate the sorption of α-pinene in the membranes of solution-cast and melt-extruded Nafion. The extruded membrane was Nafion® 115 in H^+ form (DuPont). The cast Nafion membrane was prepared by casting from a 20 wt.% solution of Nafion® (H^+ form) in lower aliphatic alcohols and water. (+)-α-pinene, (−)-α-pinene and racemic mixture sorption isotherms were determined by a gravimetric method using the sorption balance. It was found that the sorption of α-pinene in the Nafion membrane is a stereoselective process. The sorption of α-pinene in cast Nafion is much higher than in extruded Nafion. The sorption of (+)-α-pinene in the extruded Nafion membrane is quite low while the sorption of (−)-α-pinene approaches zero. The sorption of (−)-α-pinene in the cast Nafion membrane is high while the sorption of (+)-α-pinene is low.

Keywords: Sorption; Racemic mixtures; Pinene; Nafion; Isomers

1. Introduction

Enantiomers are pairs of chemical compounds that are mirror images of one another. Their molecules contain one or more chiral carbons (stereo centres). The enantiomers exhibit identical chemical and physical properties in achiral environment, however, due to chiral centres are optically active and they are able to rotate the plane of polarized light in the opposite direction (L and D or (+) and (−) or S and R enantiomers). The racemic mixture contains both enantiomers in equal amounts. The chiral substances include amino acids, proteins, carbohydrates, DNA and others. All of

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these substances are the building blocks of living organisms and they are responsible for all biochemical processes. All amino acids in the human body are present in the L configuration and all of the biochemical processes in the digestion of food are adapted to this configuration [1]. The chiral substances such as alkaloids, terpenes, polysaccharides and flavonoids are used in the food industry. Different tastes, aroma and a nutritional value of food result from L and D configurations of these substances. The most important and also the most problematic applications of chiral substances are in the production of pharmaceuticals. The L and D enantiomers have different and sometimes even antagonistic biological activities [2,3]. Therefore, a great emphasis is placed on the separation and purification of the enantiomers. Some enantiomer drugs can be prepared by a stereoselective synthesis but others must be separated from their racemic mixtures [4]. The techniques used for the separation of enantiomers from their racemic mixtures include column chromatography, diastereometric salt crystallization, kinetic resolution and membrane separation [5,6]. The techniques using membranes are promising methods for chiral separations due to their low cost, simple arrangement, low energy consumption, high capacity and continuous operation [7,8]. The requirements for the membrane are a high-separation efficiency accompanied by high fluxes through the membrane and a good chemical and mechanical stability. The liquid membranes such as supported liquid membranes [9,10], the bulk liquid membranes [11–13] and the emulsion liquid membranes [14] have a low efficiency and stability. More promising are the polymer membranes containing chiral centres [7]. The chiral centres may be situated in a main polymer chain or in a polymer side chain or they may be incorporated into the polymer as stereoselective ligands such as cyclodextrins, crown ethers, antibodies or DNA. The stereoselective membranes also include those prepared from the molecularly imprinted polymers [15] and achiral polymers with a one-handed helical conformation [7,16].

Polymers with a helical conformation include Nafion®, the polymer currently used for manufacture of ion-exchange membranes. Nafion® consists of a hydrophobic tetrafluoroethylene backbone with perfluorinated side chains terminated with hydrophilic sulphonic acid groups, see Fig. 1. Small-angle X-ray scattering (SAXS) and small-angle neutron scattering and also infrared (IR) spectra have shown that Nafion® is a three-phase system consisting of a crystalline phase, ion clusters and an inhomogeneous matrix phase [17–20].

Our preliminary results showed that Nafion® was able to separate α-pinene enantiomers from their racemic mixture. α-Pinene is an alkene with a reactive four-membered ring (Fig. 2). α-Pinene is a component of many essential oils and has anti-inflammatory and antimicrobial properties.

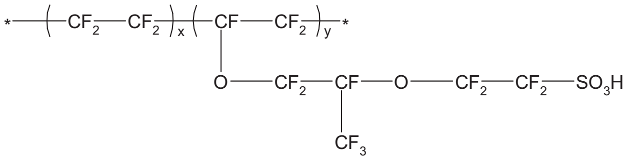
$$*-\!\left(-CF_2-CF_2-\right)_x\!\left(-\underset{\displaystyle O-CF_2-\underset{\displaystyle CF_3}{CF}-O-CF_2-CF_2-SO_3H}{CF}-CF_2-\right)_y\!-*$$

Fig. 1. Chemical formula of Nafion®.

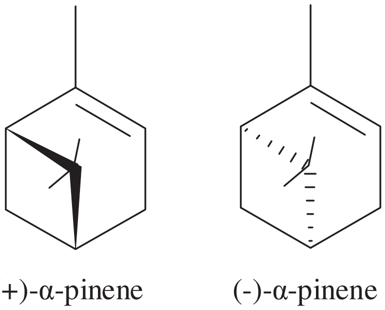

Fig. 2. Chemical formula of (+)-α-pinene and (−)-α-pinene.

The aim of this work is to elucidate the sorption of α-pinene in the membranes of solution-cast and melt-extruded Nafion®.

2. Experimental

2.1. Materials

The extruded membrane was Nafion® 115 in H^+ form (DuPont). Its thickness was 125 μm (dry state) and its equivalent weight was 100 g/eq. Nafion® 115 was used as received. The cast Nafion membrane was prepared from a 20 wt.% solution of Nafion® (H^+ form) in lower aliphatic alcohols and water (Aldrich). 3 ml of 1-propanol was added to 5 g of Nafion solution and the mixture was stirred for 5 h to lower the viscosity of the solution. Then the mixture was poured onto a Teflon plate and the solvents were allowed to evaporate first in a 1-propanol atmosphere (48 h, 25˚C), then in an air atmosphere (24 h, 25˚C). The thickness of cast Nafion membranes was 31–37 μm.

(1R)-(+)-α-pinene (purity ≥ 99%, optical purity ee: 97%) and (1S)-(−)-α-pinene (purity ≥ 99%, optical purity ee: 97%) were purchased from Aldrich. The racemic mixture was obtained by mixing of equimolar amounts of both enantiomers.

2.2. α-Pinene sorption analysis

The α-pinene sorption isotherms were determined by a gravimetric method using the sorption balance

IGA-003 (Hiden Isochema, England). Isothermal static vapour sorption procedure was used for the determination of static vapour sorption isotherms, where the source of α-pinene vapour was liquid α-pinene added to the IGA reservoir. The membrane sample was loaded into the microbalance, weighed and evacuated until constant weight was reached. Dry mass of the sample was then determined. The membrane sample was equilibrated to the temperature of 25°C. In the first sorption run, the pressure of α-pinene vapour was gradually increased in 10 steps until the pressure approached 95% of the saturated α-pinene vapour pressure. Each pressure step took 300 min. The microbalance recorded weight change of the membrane sample. Then, the pressure of α-pinene vapour was gradually decreased in 300 min steps until it reached the zero value (the first desorption run). The second sorption and desorption runs were carried out in the same manner. Amount of adsorbed α-pinene was related to the mass of dry membrane sample. The sorption and desorption isotherms of pure (+)-α-pinene, of pure (−)-α-pinene and their racemic mixture ((+)-α-pinene and (−)-α-pinene 1:1) in extruded Nafion and cast Nafion were determined, respectively.

3. Results and discussion

3.1. *Sorption of (+)-α-pinene, (−)-α-pinene and the racemic mixture in extruded Nafion*

(+)-α-pinene and (−)-α-pinene are sorbed in extruded Nafion to a different extent but their sorption is generally low. Figs. 3 and 4 show sorption isotherms of (+)-α-pinene, (−)-α-pinene and their racemic mixture in extruded Nafion for the first and second sorption runs, respectively. While the sorption of (+)-α-pinene can be detected, the sorption of (−)-α-pinene and also the sorption of racemic mixture are negligible. (+)-α-pinene sorbed in extruded Nafion does not desorb immediately during the following desorption step; its concentration in extruded Nafion even increases a little and at the end of the second desorption run (i.e. after 50 h of desorption time) there is still 3.25 wt.% of (+)-α-pinene in the membrane (Fig. 5). This shows at a very slow establishment of equilibrium in the system. It is plausible that the process is not a sorption of α-pinene but it is the reaction of the α-pinene molecules with the acid groups of Nafion.

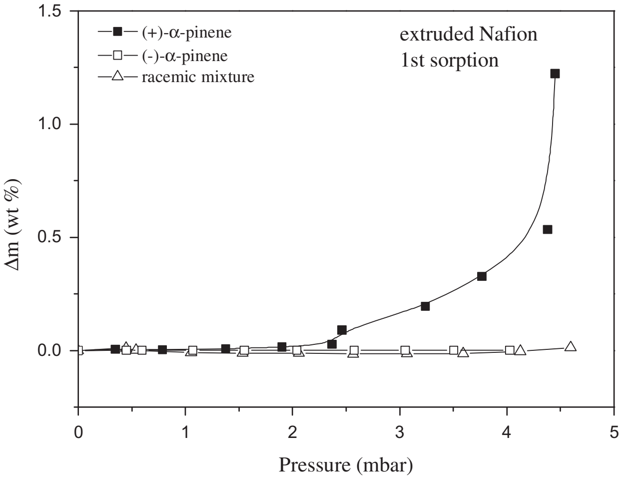

Fig. 3. Sorption isotherms of (+)-α-pinene, (−)-α-pinene and their racemic mixture in extruded Nafion—the first sorption run.

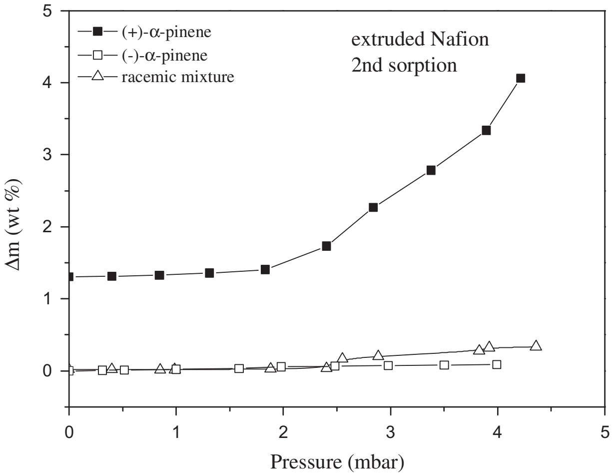

Fig. 4. Sorption isotherms of (+)-α-pinene, (−)-α-pinene and their racemic mixture in extruded Nafion—the second sorption run.

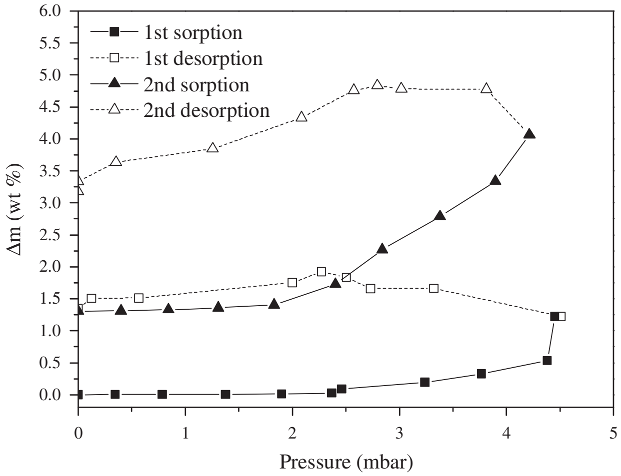

Fig. 5. The first and second sorption and desorption isotherms of (+)-α-pinene in extruded Nafion.

3.2. Sorption of (+)-α-pinene, (−)-α-pinene and the racemic mixture in the cast Nafion

Figs. 6 and 7 show sorption isotherms of (+)-α-pinene, (−)-α-pinene and their racemic mixture in cast Nafion for the first and second sorption runs, respectively. Unlike the sorption in extruded Nafion, the sorption of α-pinene in cast Nafion is rather high and the enantiomers have a reverse affinity for Nafion: (−)-α-pinene sorbs in cast Nafion much more than (+)-α-pinene. Both components in the racemic mixture sorb roughly in the ratio of pure components. Here again, the equilibrium is established rather slowly: sorbed α-pinene does not desorb immediately during the following desorption step; its concentration in cast Nafion remains high at the end of the sorption/desorption cycle (Fig. 8). As mentioned above, this phenomenon can be explained by the chemical reaction of the α-pinene molecules with the acid groups of Nafion.

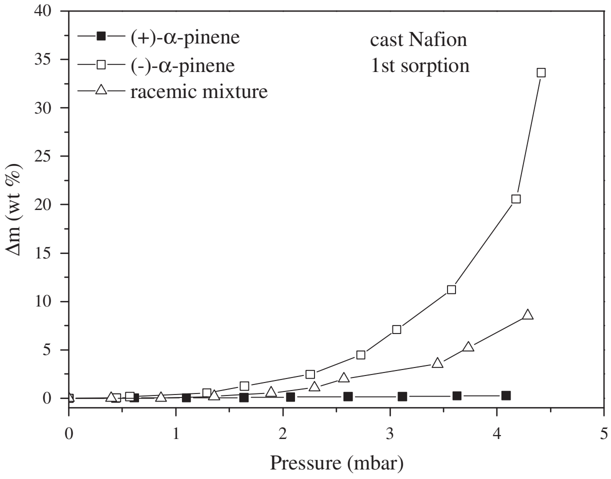

Fig. 6. Sorption isotherms of (+)-α-pinene, (−)-α-pinene and their racemic mixture in cast Nafion—the first sorption run.

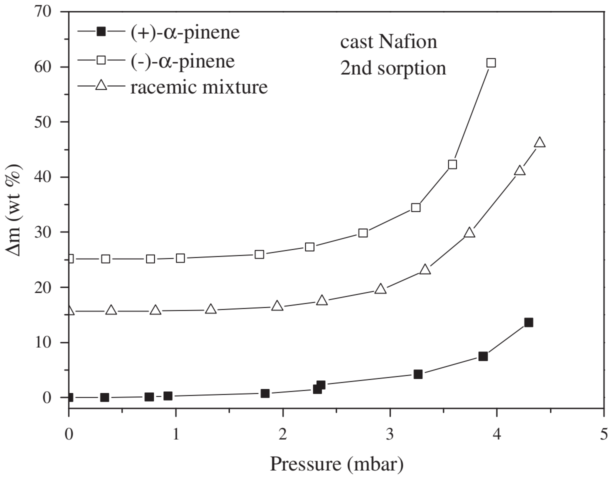

Fig. 7. Sorption isotherms of (+)-α-pinene, (−)-α-pinene and their racemic mixture in cast Nafion—the second sorption run.

3.3. Structure of extruded and of cast Nafion

It is well known [17,21] that Nafion membrane has a heterogeneous structure comprising perfluorocarbon backbone crystalline regions perfluorocarbon backbone amorphous regions, and ionic sulphonic acid group regions, and that the relations between the three regions is strongly dependent on the conditions of Nafion membrane preparation. Suitable tools for the elucidation of polymer morphology are wide-angle X-ray scattering (WAXS)—distinguishing between ordered and disordered sub-nanometre-sized structures—and SAXS—giving information about inhomogeneities from 1 to 100 nm.

WAXS spectra of extruded and cast Nafion show that an extruded membranes exhibit much higher level of crystallinity than a cast membrane (Fig. 9) as expected [21].

SAXS spectra confirm the difference between the morphology of extruded and cast Nafion (Fig. 10). The extruded Nafion spectrum exhibits a well-defined crystalline scattering maximum at low

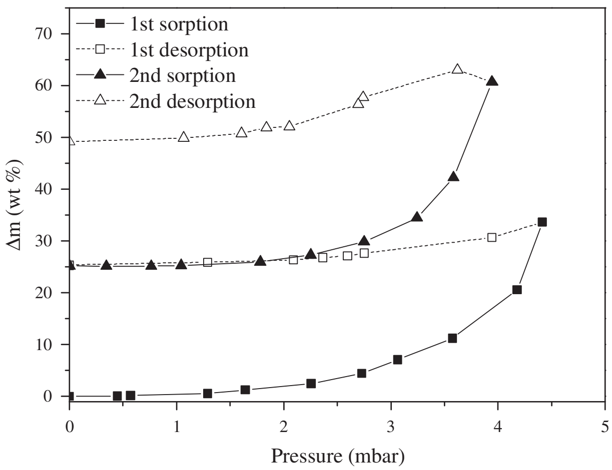

Fig. 8. The first and second sorption and desorption isotherms of (−)-α-pinene in cast Nafion.

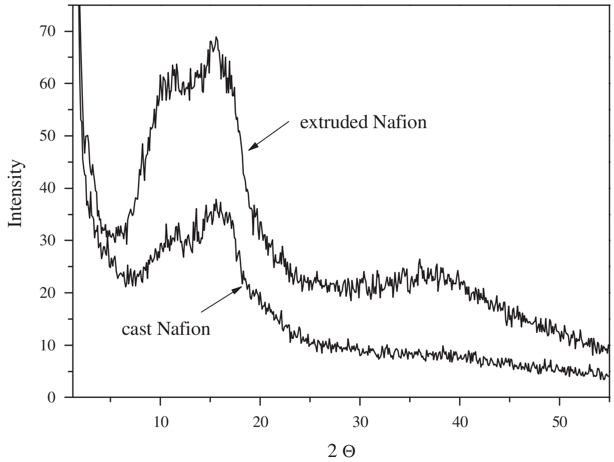

Fig. 9. Extruded Nafion and cast Nafion WAXS spectra.

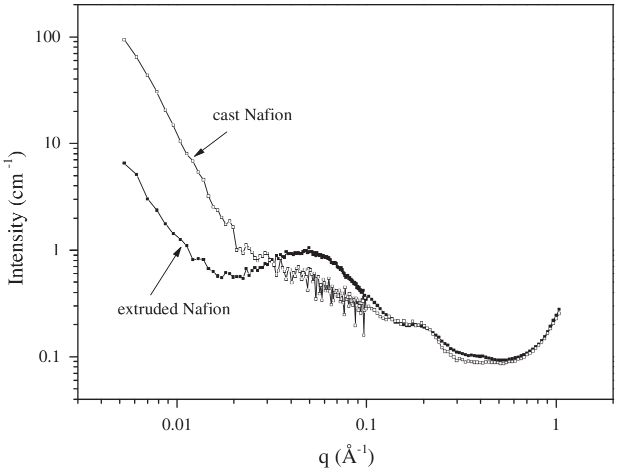

Fig. 10. Extruded Nafion and cast Nafion SAXS spectra.

angles ($q_{\max} = 0.05\,\text{Å}^{-1}$) corresponding to a long period between crystallites while such maximum is hardly discernable for cast Nafion. On the other hand, the ionomer peak (a maximum at $q_{\max} \sim 0.2\,\text{Å}^{-1}$ associated with aggregations of ionic sulphonic acid groups) is equally developed in both curves.

3.4. Possible causes for stereospecific sorption of α-pinene in Nafion membranes

Both Nafion macromolecules and α-Pinene molecules have chiral structures and they can, therefore, participate in stereospecific reaction.

It is already well known [22] that the backbone dihedral angles for the trans-conformation of poly(tetrafluoroethylene) (PTFE) are displaced by about 17° from true trans-state. This distorted state leading to a helical structure, which is not observed in n-alkanes, can be understood as a result of the greater van der Waals radius of the fluorine atoms, the greater bond length for C–F bond relative to the C–H bond, and the highly polar nature of C–F bond, all of which lead to repulsive interactions in a trans-conformation of PTFE. Spectroscopic studies have shown similar structures in Nafion—the fluorocarbon domains of Nafion retain the helical structure of PTFE [23,24].

It is well known [25,26] that in presence of acid catalysts, α-pinene undergoes an isomerization. The isomerization can occur either through a cycle rearrangement (the products are camphene, tricyclene, bornylene and Δ^3-carene) or by means of the rupture of one of the rings (the products are limonene, terpinolene or α- and γ-terpinene). α-Pinene, when treated with acidic catalyst, can also polymerize via a carbocationic mechanism to produce terpene resin with an aliphatic hydrocarbon structure [27].

What products are formed by the α-Pinene stereospecific sorption in the Nafion membranes is under investigation and will be the subject of the next article.

4. Conclusions

The sorption of α-pinene in the Nafion membrane is a stereoselective process and depends on the conditions of Nafion membrane preparation.

The sorption of α-pinene in the extruded Nafion membrane is generally low. The sorption of (+)-α-pinene in the extruded Nafion membrane is quite low while the sorption of (−)-α-pinene approaches zero.

The sorption of α-pinene in the cast Nafion membrane is generally high. The sorption of (−)-α-pinene in the cast Nafion membrane is high while the sorption of (+)-α-pinene is low.

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