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Hydration of α-pinene over molybdophosphoric acid immobilized in hydrophobically modified PVA membranes

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Abstract

A polyvinylalcohol/molybdophosphoric acid (PVA/HPMo) membrane crosslinked with succinic acid was modified by treatment with acetic anhydride in order to improve its hydrophobic properties, and was used as catalyst in the hydration reaction of α-pinene. The increase of membrane hydrophobicity with acetylation is documented not only by the water droplet contact angle but also by the sorption coefficients of α-pinene and water. The introduction of acetyl groups improves the membrane transport properties, as reflected by pinene diffusivity calculated from permeation data.

A kinetic-diffusion model was developed assuming that the reaction product α-terpineol affects the transport of water and α-pinene across the acetylated PVA membranes. When membrane acetylation increases, the model predicted kinetic constants for hydration and isomerization reactions decrease, although the initial water diffusivity increases. These results suggest that the increase of catalytic activity may be due to an improvement of water transport across the membrane.

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Keywords: Polymeric catalytic membranes; Poly(vinyl alcohol); Acetylation; Heteropolyacids; Molybdophosphoric acid; USY; Alpha-pinene hydration

1. Introduction

The hydration of α-pinene yielding α-terpineol, catalysed by polymeric catalytic membranes loaded with molybdophosphoric acid (HPMo) was previously studied with matrices of polydimethylsiloxane (PDMS) and poly(vinyl alcohol) (PVA) crosslinked with succinic acid, in order to test catalytic membranes of opposite hydrophilic/hydrophobic properties [1]. The use of polymeric membranes provided not only a mean for the heteropolyacid heterogenization, but also allowed the tuning of the reactant concentrations in the close vicinity of the catalyst active sites. Particularly, it had been observed that the hydrophobicity of PVA membranes as well as pinene permeation increased with the succinic acid loads. However, the increase of pinene permeation through the crosslinked PVA membranes showed to be limited by crosslinking. Therefore, it would be of interest to find ways of modifying the membrane hydrophilicity and simultaneously improving its transport properties concerning the reactants α-pinene and water.

The modification of poly(vinyl alcohol) in order to obtain materials with improved properties has being thoroughly studied. When PVA is used in aqueous systems such as pervaporative systems or catalytic systems in aqueous media, crosslinking is needed due to the solubility of PVA in water. Crosslinking with carboxylic anhydrides and diglycidyl ethers [2–4], with dicarboxylic acids [1,5], dialdehydes such as glutaraldehydes [6] and low molecular weight polymers [7,8], have being successively performed.

PVA matrices have also been modified in order to modulate their hydrophilic/hydrophobic properties. As examples of modifications aiming to increase the polymer hydrophilicity are crosslinking with sulphur-succinic acid [5] or with low molecular weight poly(acrylic acid) [7,8], as well as grafting with carboxylic anhydrides [2,4] or glycosides [9]. On the other hand, the increase of hydrophobicity can be achieved by ketalization techniques with aldehydes and ketones [10–12] or esterification with fatty acid chlorides [13–15].

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In this work a PVA/HPMo membrane crosslinked with succinic acid was modified by treatment with acetic anhydride in order to improve its hydrophobic properties, and was used as catalyst in the hydration of α-pinene. The effect of acetylation on the membrane transport properties concerning the reactants is discussed and a kinetic-diffusion model is developed.

2. Experimental

2.1. Preparation of the HPMo–PVA membrane

A PVA membrane was prepared according to the technique previously reported [1]. PVA (MERCK, average molecular weight: 72 000), molybdophosphoric acid (Fluka) 10% (w/w) in relation to the PVA amount and succinic acid (Aldrich) 10% (mol/mol) in relation to the amount of PVA hydroxyl groups, were dissolved in dimethylsulfoxide. After 1 h sonication the obtained solution was cast on a Teflon plate and the solvent evaporated at 60 °C, under moderate vacuum (∼300 mbar) during 24 h. Crosslinking was accomplished by heating the membrane to 120 °C for an additional period of 24 h. After curing the membrane for 24 h at 150 °C and ∼0.1 mbar, it was extracted with water in a sohxlet apparatus during 24 h.

2.2. Preparation of PVA/polyvinyl acetate/HPMo membranes

The prepared PVA membrane was divided in four portions, each one of them being refluxed during 6 h with an acetone solution of acetic anhydride. The stoichiometric amounts of acetic anhydride needed for the esterification of 40, 60, 90 and 100% of the PVA OH groups were used. The obtained membranes were denoted by M40, M60, M90 and M100.

Typically 1 g of PVA/HPMo was refluxed with 180 ml of acetic anhydride acetone solution 0.036 M for membrane M40, 0.055 M for M60, 0.082 M for M90 and 0.091 M for M100.

2.3. Membrane characterisation

The sorption coefficients of water and α-pinene in the PVA membranes were determined by equilibrating during 6 h 0.1 g of poly(vinyl alcohol/vinyl acetate), P(VA/VAc), in 3 ml aqueous acetone 1:1 (v/v) for the water sorption coefficient (K_{H_2O}), and 3 ml of 0.06 M α-pinene aqueous acetone 1:1 (v/v) solution for the α-pinene sorption coefficient. The amount of the membrane sorbed α-pinene was evaluated by GC analysis of the pinene aqueous acetone solution. On the other hand the amount of the membrane sorbed water was evaluated by temperature programmed desorption (TPD) carried out in a Micromeritics TPD/TPR 2900 instrument. Membrane samples were cut in small pieces, loaded in a quartz tubular micro-reactor and heated at a temperature rate of 5 °C/min from room temperature until 500 °C under helium flow (25 ml/min, 0.1 MPa). The water evolution was monitored by mass spectrometry with a FISONS MD800 GCMS instrument assembled on-line with the TPD/TPR.

Membrane hydrophobicity was also evaluated through the measurement of the contact angle of water droplets. The amount of HPMo immobilized in the membranes was measured by inductively coupled plasma (ICP)–atomic emission spectroscopy analysis. Pinene permeation data was collected by using a two-chamber apparatus. The two chambers separated by the membrane were both filled with solvent. In one chamber α-pinene was added and the increase of α-pinene concentration in the other chamber was then followed by GC analysis. Diffusivities were calculated using Fick's second law.

FTIR spectra were recorded in a Bio-Rad FTS 155 instrument. ICP analysis was carried out in a Jobin- Yvon ULTIMA instrument. Contact angles were measured with a Goniometer Ramé-Hart Inc. NRL C.A., Model 100-00-230. Table 1 summarizes the membrane characteristics.

2.4. Catalytic tests

Catalytic experiments were carried out in an atmospheric pressure jacketed batch reactor equipped with a stirrer, at 50 °C. In a typical experiment, the reactor was loaded with 114 ml aqueous acetone 1:1 (v/v) and 1.1 g of the membrane cut in small pieces. Reactions were started by adding 7.62 mmol of α-pinene. The stirring speed was kept at 800 min^{-1}. Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m × 0.25 mm DB-1 column.

Table 1
Membrane characteristics

Membrane	Thickness (mm)	HPMo loading (w/w)	K_P	K_{H_2O} ($\times 10^5$)	De_P ($\times 10^{12}$ m^2/s)	α (°)
M40	0.126	0.0939	0.1	19.7	6.14	81.9
M60	0.206	0.0676	49.5	19.4	10.00	108.3
M90	0.061	0.0537	50.3	4.3	12.36	116.0
M100	0.113	0.0331	113.5	4.6	14.97	118.1

HPMo loadings as evaluated by ICP analysis. K_P, K_{H_2O}—sorption coefficients for α-pinene and water, respectively, calculated as the concentration ratio between the membrane and the liquid phase. De_P—α-pinene diffusivity calculated from data collected in the two-chamber apparatus, by applying the second Fick's law. α—contact angle of water drop.

3. Results and discussion

3.1. Characterisation of the HPMo–AcPVA membranes

The HPMo–PVA membranes were prepared by entrapping dodecamolybdophosphoric acid in a crosslinked PVA matrix according to the technique described in a previous work [1]. The polymer crosslinking is accomplished by heating PVA with the dicarboxylic acid succinic acid, in order to esterify hydroxyl groups in two neighbour PVA chains. The crosslinked PVA matrix loaded with HPMo was finally treated with acetic anhydride in order to attach acetate groups to the polymer chains. The ultimate purpose of this treatment is to increase the membrane hydrophobicity by inhibiting the hydrogen bridging capabilities of the polymer. The obtained membranes were denoted by M*x*, where *x* represents the mole percentage of acetic anhydride used in relation to the total number of PVA OH groups.

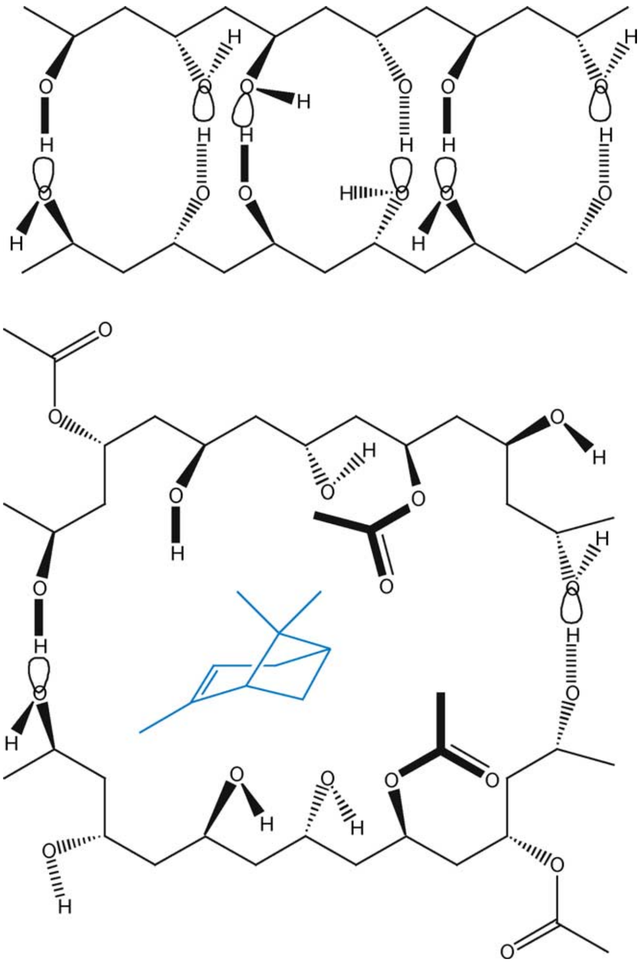
Table 1 shows the results of membrane characterisation. The sorption coefficients of α-pinene and water, respectively K_P and K_{H_2O}, were calculated as the concentration ratios between the membrane and the liquid phase. Pinene diffusivities were calculated from permeation data by using the second Fick's law. Finally the membrane hydrophobicity was measured by the contact angle to water.

In all cases K_P is several orders of magnitude higher than K_{H_2O}, meaning that in the membrane phase water seems to be the limiting reactant, although in the liquid phase it is in very large excess. As expected K_P increases and K_{H_2O} decreases when the membrane acetylation (*x*) increases from membrane M40 to membrane M100. Simultaneously the contact angle to water (α) also increases, reflecting the increase in membrane hydrophobicity.

An increase of α-pinene diffusivity is also observed with membrane acetylation (*x*), meaning that the transport of pinene through the membrane phase becomes easier with increasing amounts of acetate groups. Possibly, the membrane acetylation inhibits not only the hydrogen bridging with water molecules but also the inter-chain hydrogen bridging. At low acetylation levels (M40), the inter-chain hydrogen bridging keeps the PVA chains linked in a very tight way (Scheme 1) restraining the transport of α-pinene across the membrane and leading to a low diffusivity. When *x* increases, the acetate groups inhibit the inter-chain hydrogen bridging. Possibly, there are zones where, due to steric hindrance, the polymer chains are kept away from each other, opening "holes" and enabling the flow of pinene (and water) molecules (Scheme 1). Consequently the diffusivity increases.

3.2. Catalytic tests

Similarly to previous work with polymeric catalytic membranes or other heterogeneous or homogeneous catalysts [16], the main product of α-pinene hydration is α-terpineol, while a number of minor components, namely limonene, terpinolene, α- and γ-terpinenes, β-fenchol, isoborneol and, at high α-pinene conversion, 1,8-terpine are also obtained.



Scheme 1. Illustration of α-pinene diffusion between the acetylated polymer chains.

Fig. 1 shows the concentration profiles of reactants and products obtained with the membranes M40-M100. "H" lumps the group of minor components, which are, however, dominated by the terpenic hydrocarbons limonene, terpinolene, α- and γ-terpinenes.

A distinctive feature of these kinetic curves is the initial induction period. This induction period is particularly pronounced for the reaction performed over membrane M40, as visible from all the kinetic curves. With the increase of membrane acetylation in the order M60, M90 and M100, the induction period decreases and is only found in the curves corresponding to α-pinene and α-terpineol, in these last three cases. A possible explanation for the above observations is the interaction between the α-terpineol molecules formed in the chemical reaction and the polymer chains, similarly to what was previously described for PDMS and PVA catalytic membranes [16,17]. In the case of PVA matrices these interactions are expected to be more intense than in the case of PDMS matrices, due to the strong

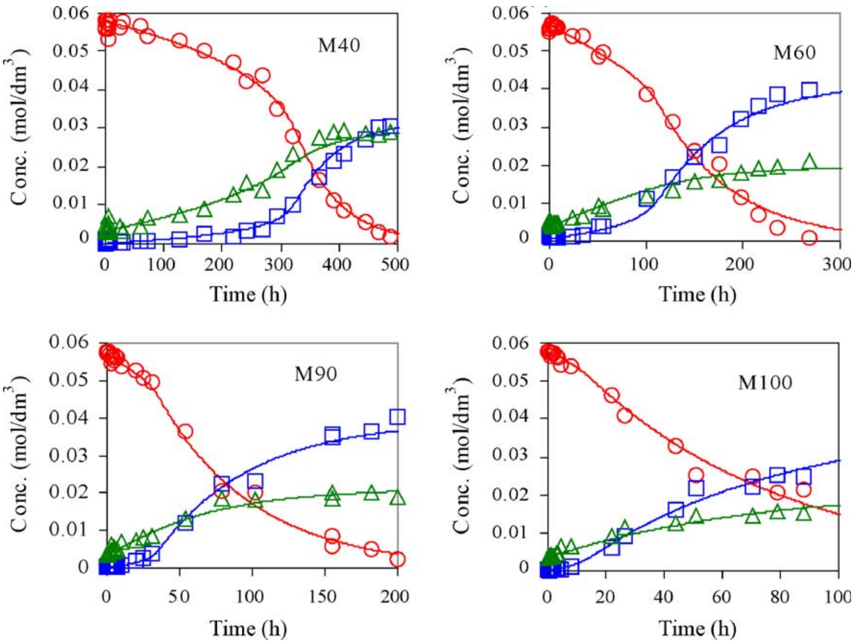


Fig. 1. α-Pinene hydration over HPMo/AcPVA membranes in a batch reactor. Concentration vs. time. (○) α-Pinene; (□) α-terpineol; (△) H-lumps all the minor components. The solid lines represent the model fitted to the data points.

hydrogen bridging between the hydroxyl groups of α-terpineol and PVA. The voluminous α-terpineol molecules attached to the PVA chains block the inter-chain hydrogen bridging and keep the polymer chains away from each other, allowing the passage of water and α-pinene molecules. Consequently, the observed reaction rate increases when the concentration of α-terpineol achieves some critical value, which gives to the kinetic curves the appearance of an initial induction period.

The initial activity of membranes M40–M100, taken as the maximum observed reaction rate, increases with membrane acetylation (Fig. 2) probably due to the increase of α-pinene concentration near the active sites and to the improvement of the membrane transport properties as discussed above.

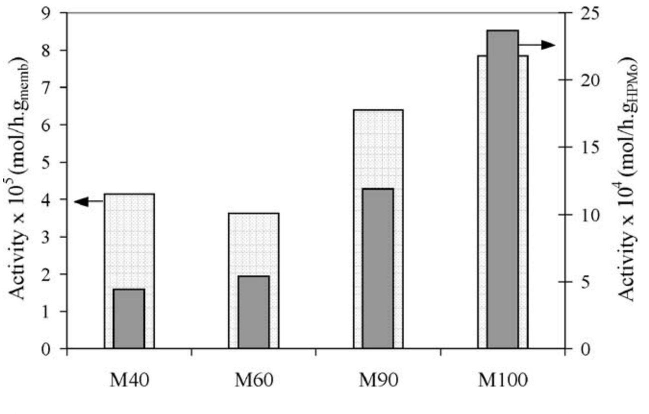


Fig. 2. Initial activity of the acetylated membranes calculated from the maximum slope of the α-pinene kinetic curves, referred to the weight of HPMo (light bars) and to the weight of the membrane (dark bars).

The worst selectivity to α-terpineol is obtained with membrane M40 (Fig. 3). This is a paradoxical result, because membrane M40 is the most hydrophilic one. Consequently, one would expect to obtain the best selectivity to alcohols with this membrane. A possible explanation is the highest hydrogen bonding capability expected for this less acetylated membrane, which would lead to a higher retention of α-terpineol molecules in the membrane M40 than in the other membranes. The higher concentration of α-terpineol in the membrane would lead to dehydration of this alcohol to a higher extent and therefore to lower selectivity.

Fig. 4 compares the activity (also taken as the maximum observed reaction rate) in three consecutive experiments for the four membranes tested. After each experiment the same membrane sample is separated from the reaction mixture, washed with acetone and used in the following experiment. The loss of activity observed for membranes M100 and M90 is expectable and is in agreement with the observed leaching of HPMo (Table 2). Surprisingly, although the highest losses of HPMo from one run to another are observed for membranes M40 and M60 (Table 2), an increase of activity is observed with the re-use of theses membranes. These apparently contradictory observations may also be explained on the basis of the higher hydrogen bonding capabilities of the less acetylated membranes. Probably, in each run a residual amount of α-terpineol that remains irreversibly sorbed is accumulated. Therefore, the transport properties of the membranes would be improved from run to run, due to the blocking of the inter-chain hydrogen bonding by these sorbed α-terpineol molecules, as discussed above. The acid strength of the heteropolyacid (HPA) itself is also likely to

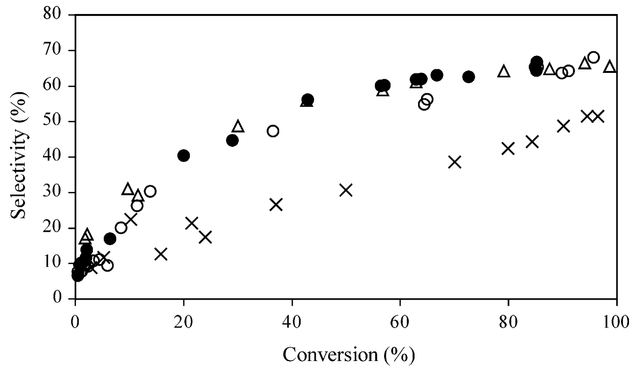


Fig. 3. α-Pinene hydration over HPMo/AcPVA membranes in a batch reactor. Selectivity vs. conversion. (×) M40; (△) M60; (○) M90; (●) M100.

be affected. In fact, the dependence of the HPAs acid strength on the interactions with supports surface groups has been reported [18–20]. Namely, in a recent work [20] Pizzio et al. report the decrease in the acid strength of tungstophosphoric acid (TPA) with the increase of the interactions with the support surface groups (Si-MCM-41). The same authors also report the lowering of the total number of acid sites for TPA supported in poly(vinyl alcohol)–polyethyleneglycol beds in relation to bulk TPA.

3.3. Membrane modelling

3.3.1. Basic assumptions

In order to seek some support for the hypothesis formulated above, a kinetic-diffusion-reaction model was established based on the following assumptions, similar to those in a previous work [17] as well as by other authors [21–23]:

Table 2
Stability tests. HPMo loadings (w/w) before each run

		M40	M60	M90	M100
First	Run	0.0939	0.0676	0.0536	0.0331
Second	Run	0.0829	0.0457	0.0234	0.0319
Third	Run	0.0532	0.0149	0.0232	0.0316

- Isothermal and isobaric reaction conditions.
- Pseudo-steady-state conditions for diffusion and reaction in the membrane.
- Unidirectional diffusion.
- Homogeneous and isotropic membrane macrostructure.
- Fickian transport across the membrane.
- Linear sorption equilibrium isotherm between the bulk liquid phase and the membrane.
- There is zero transport resistance for α-pinene and H_2O from the aqueous acetone bulk phase to the membrane surface.
- Diffusivities of α-pinene and water are independent of α-pinene concentration over the range of values used. However they depend on α-terpineol concentration, according to the generally accepted [24] empirical equations,

$$\mathrm{De}_{\mathrm{H_2O}} = \mathrm{De}^0_{\mathrm{H_2O}}\, e^{\alpha C_{\mathrm{T\,liq}}} \tag{1}$$

$$\mathrm{De}_{\mathrm{P}} = \mathrm{De}^0_{\mathrm{P}}\, e^{\beta C_{\mathrm{T\,liq}}} \tag{2}$$

where $\mathrm{De}^0_{\mathrm{H_2O}}$ and $\mathrm{De}^0_{\mathrm{P}}$ are the initial diffusivities for water and α-pinene, respectively, $C_{\mathrm{T\,liq}}$ is the concentration of

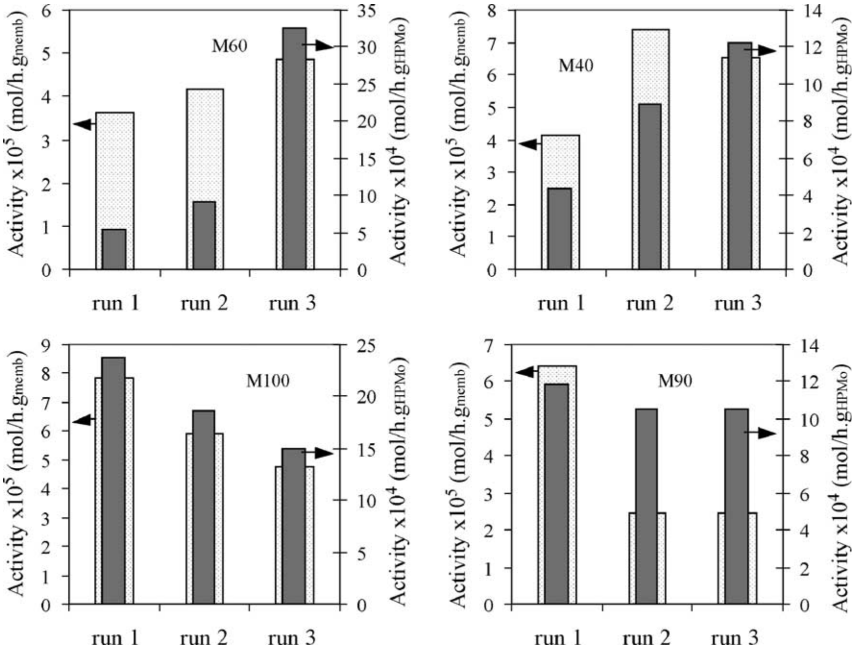


Fig. 4. Activity of the acetylated membranes calculated from the maximum slope of the α-pinene kinetic curves in the membrane re-use experiments, related to the weight of HPMo (light bars) and to the weight of the membrane (dark bars).

α-terpineol in the liquid phase and α and β are diffusivity-enhancing factors for water and α-pinene, respectively, translating the effects of the interactions between α-terpineol and the polymer chains.

3.3.2. Reaction network and reaction rate equations

The hydration/isomerization of α-pinene proceeds via a complex mechanism involving several intermediate carbenium ions [25–30]. α-Pinene transformation occurs by two main pathways: hydration, leading to terpenic alcohols, namely α-terpineol, and isomerization giving raise to terpenic hydrocarbons. Under the reaction conditions those products suffer further reaction, leading to mixtures of increasing complexity. Particularly, α-terpineol may be dehydrated to also yield terpenic hydrocarbons, or rehydrated to give 1,8-terpine. Kinetic models taking into account these transformations have been developed in the past, aiming the fitting of data obtained under homogeneous or heterogeneous catalytic conditions [31,32]. In the present case, the main purpose of the model is only to give some support to the hypothesis in which α-terpineol or membrane acetylation has strong effects on the PVA membrane transport and sorption properties. Since the clarification of the detailed reaction network is behind the model scope, the simple parallel reaction network depicted in Scheme 2 may be assumed, in order to keep the number of model parameters as low as possible. In this scheme W stands for water, P for α-pinene, T for α-terpineol and H lumps all the minor products dominated by the monoterpene hydrocarbons limonene, terpinolene, α- and γ-terpinenes, mainly resulting from the α-pinene isomerization.

The absolute local rates of these two pseudo elementary reactions are expressed as:

$$r_1 = k_1 C_{H_2O} C_P \tag{3}$$

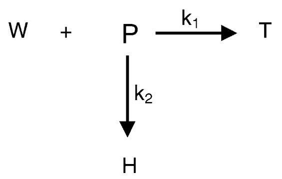
$$r_2 = k_2 C_P \tag{4}$$

where k_1 and k_2 are the kinetic constants of reactions 1 and 2, respectively.

3.3.3. Mole balances to the membrane

The mole balance of component i over a differential element of depth dz in pseudo-steady-state conditions may be written as:

$$\frac{d^2 C_i}{dz^2} + \frac{\rho_{HPMo}}{De_i} r_i = 0 \tag{5}$$



Scheme 2. Reaction network used for modelling purposes. P: α-pinene; T: α-terpineol; W: water; H: assemblage of the minor components dominated by terpene hydrocarbons.

where De$_i$ is the diffusivity of reactant i, as defined above; z the distance within the membrane thickness; ρ_{HPMo} the concentration of HPMo in the membrane (mass of HPMo/volume of membrane); r_i the rate of consumption of component i related to the mass of HPMo. For the two reactants, water and α-pinene, Eq. (5) yields the following equation system:

$$\frac{d^2 C_{H_2O}}{dz^2} - \frac{\rho_{HPMo}}{De_{H_2O}} k_1 C_{H_2O} C_P = 0 \tag{6}$$

$$\frac{d^2 C_P}{dz^2} - \frac{\rho_{HPMo}}{De_P} (k_1 C_{H_2O} C_P + k_2 C_P) = 0 \tag{7}$$

3.3.4. Mole balances to the reactor

For the batch reactor the mole balance equations may be written as:

$$\frac{dC_{H_2O\,liq}}{dt} = -\frac{W}{V} Robs_1 \tag{8}$$

$$\frac{dC_{P\,liq}}{dt} = -\frac{W}{V} (Robs_1 + Robs_2) \tag{9}$$

$$\frac{dC_{T\,liq}}{dt} = +\frac{W}{V} Robs_1 \tag{10}$$

$$\frac{dC_{H\,liq}}{dt} = +\frac{W}{V} Robs_2 \tag{11}$$

where $C_{i\,liq}$ is the concentration of component i in the liquid phase; W the weight of HPMo used in the reaction (as determined by ICP analysis) and V the volume of the reaction mixture. Robs$_j$ are the absolute observed reaction rates defined as:

$$Robs_j = \frac{\int_0^L r_i\, dz}{L} \tag{12}$$

where L is the membrane half thickness.

3.3.5. Definition of boundary conditions

The concentrations of H_2O and α-pinene (P) on the membrane surfaces ($z = \pm L$) are obtained from (see Table 1):

$$C_{H_2O} = K_{H_2O} C_{H_2O\,liq} \tag{13}$$

$$C_P = K_P C_{P\,liq} \tag{14}$$

On the other hand in the membrane centre ($z = 0$) the reactant concentrations achieve a minimum value:

$$\frac{dC_{H_2O}}{dz} = 0 \tag{15}$$

$$\frac{dC_P}{dz} = 0 \tag{16}$$

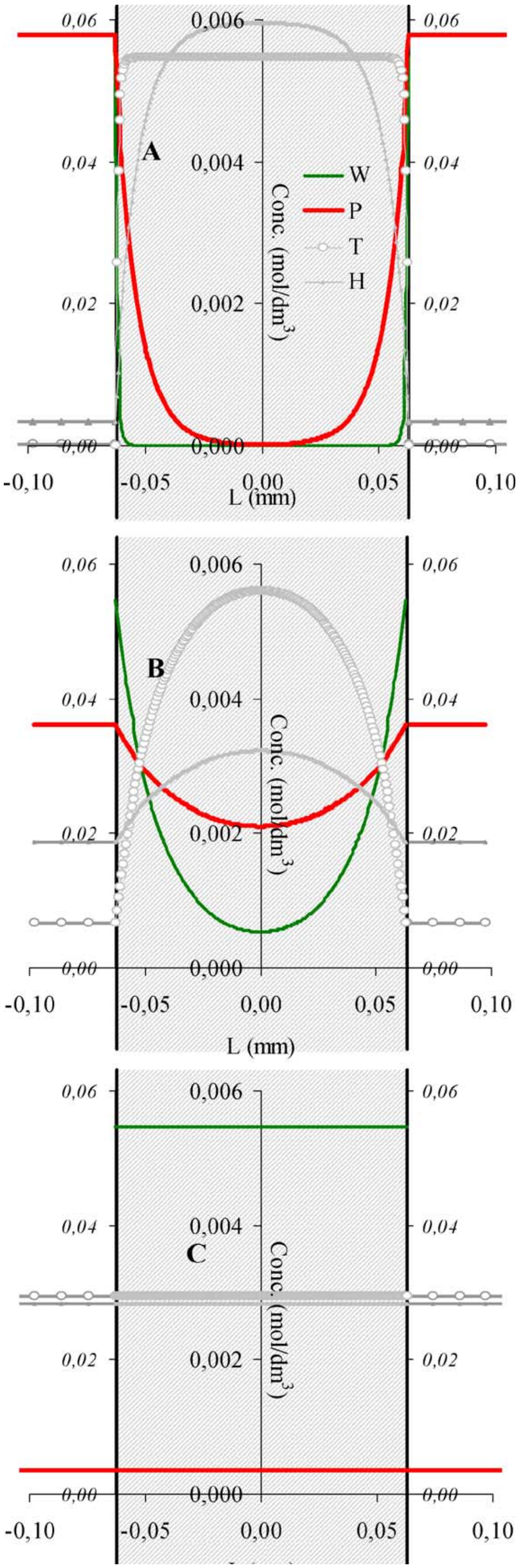


Fig. 5. Model predicted concentration profiles within the membrane M40 at 0 h (A), 298 h (B) and 478 h (C) of reaction time compared to the bulk concentrations. W: water, P: α-pinene, T: α-terpineol, H: terpenic hydrocarbons. T and H profiles are simulated assuming equal diffusivities for the pairs W/T and P/H, as well as the same value of the sorption coefficient for all terpenes (P, T and H).

3.3.6. Model parameters

The model was fitted to the data points shown in Fig. 1 by changing the parameters k_1, k_2, $De^0_{H_2O}$, De^0_P, α and β, for membrane M40. For the other membranes no initial induction period is perceivable in the kinetic curve of H. Therefore, for membranes M60, M90 and M100 transport limitations for pinene were assumed to be absent. Consequently, for De^0_P the values of De_P from Table 1 were used and β was considered to be zero. The variable parameters were, therefore, k_1, k_2, $De^0_{H_2O}$ and α in these three cases.

3.3.7. Modelling calculations

A MATLAB^{TM} program was developed for solving numerically the differential equations (6)–(11) with the boundary conditions (13)–(16) and for estimating the unknown parameters k_1, k_2, $De^0_{H_2O}$, De^0_P, α and β. The parameter estimation algorithm consisted of a standard minimisation of the sum of squared errors employing the Levenberg–Marquardt optimisation algorithm. The integration of the reactor mole balance equations (8)–(11) was performed using the Euler method due to the high CPU requirements. The process dynamics are slow and it was verified that the final results were relatively insensitive to the magnitude of the integration step. Even so the optimal solutions were confirmed with a more accurate fourth/fifth-order Runge–Kutta integration method. The calculation of the observed kinetic rates $Robs_1$ and $Robs_2$ requires the integration of the membrane material balance equations (6) and (7). This second integration over the spatial coordinate 'z' is embedded in the first time integration of Eqs. (8)–(11) resulting in a computationally intensive algorithm. The numerical solution of Eqs. (6) and (7) with the boundary conditions (13)–(16) is classified as a boundary value problem (BVP) because the conditions are formulated at both sides of the membrane, i.e. for $z = 0$ and for $z = L$. For solving this problem the bvp4c MATLAB^{TM} routine was used, which is based on a finite difference method implementing the three-stage Lobatto IIIa formula [33].

3.3.8. Modelling calculation results

The model fit to the data points is shown in Fig. 1, where solid lines represent the calculated concentrations. Fig. 5 shows the concentration profiles of reactants and products within the membrane, predicted by the model for membrane M40, at $t = 0$ h (A), $t = 298$ h (B) and $t = 498$ h (C). The concentration profiles of products (T and H) are simulated assuming equal diffusivities for the pairs W/T and P/H, as well as equal values for the sorption coefficients of all terpenic compounds.

These results show clearly that the assumption of a change of the global process control from reactant diffusion

Table 3
Model parameters obtained by fitting the model to experimental data

Membrane	k_1 (dm^6/mol h g)	k_2 ($\times 10^5$dm^3/h g)	$De^0_{H_2O}$ ($\times 10^{12}$ m^2/s)	De^0_P ($\times 10^{12}$ m^2/s)	α (dm^3/mol)	β (dm^3/mol)
M40	36.20	740.81	0.0047	0.17	802	602
M60	0.08	0.78	0.0928	10.00[a]	571	–
M90	0.38	1.45	0.0417	12.36[a]	1500	–
M100	0.14	0.73	0.7747	14.97[a]	1319	–

[a] Calculated from permeation experiments (Table 1).

(both in the particular case of M40 and only H_2O for the other membranes) to kinetics is consistent with the experimental data. Initially there are strong diffusion limitations for both reactants (A), when the slope of the kinetic curves suffers a strong increment, there is a decrease of diffusion limitations (B), and near the end of the reaction kinetic control (C) takes over. Initially (A) H_2O is the limiting reactant within the membrane, but at the end (C) α-pinene is the limiting reactant.

The calculated model parameters are shown in Table 3. From these results some general trends may be identified:

- The initial diffusivity of water is in all cases several orders of magnitude lower than that of α-pinene. This result is expected, since the intense hydrogen bonding capabilities of the PVA chains are expected to strongly restrict the mobility of the water molecules.
- The value of the initial diffusivity of water increases with membrane acetylation. The explanation is the same as given above for α-pinene diffusivity: the decrease of inter-chain hydrogen bonding due to substitution of PVA hydroxyl groups by acetyl groups.
- Although the highest catalytic activity is obtained with the most acetylated membrane, M100 (Fig. 2), the kinetic constants for both hydration and isomerization decrease when membrane acetylation increases.
- The diffusivity-enhancing factor of water, α, shows a strong increase from the less acetylated membranes M40 and M60 to the most acetylated membranes M90 and M100. In the membranes M40 and M60 there is still a number of free hydroxyl groups capable of inter-chain hydrogen bonding. Therefore, the number of α-terpineol molecules needed to block that inter-chain hydrogen bonding is relatively high and a relatively low diffusivity-enhancing factor is obtained. For the membranes M90 and M100, with sparse hydroxyl groups, the amount of α-terpineol needed to get the same effect is expected to be much lower, leading to high α values.
- Finally, membrane M60 seems to be an exception, possibly due to its highest thickness. Probably the membrane acetylation took place under strong diffusion limitations, leading to a heterogeneous distribution of acetyl groups: they would be preferentially located near the membrane surface. As a consequence the membrane properties would be drastically affected, namely in what concerns the kinetic constants and the diffusivity of water.
- The value of the initial pinene diffusivity predicted by the model is almost two orders of magnitude lower than the one obtained from permeation data (Table 1), showing that there are other factors affecting the initial induction period of the kinetic curves that were not taken into account. Namely, the blocking of PVA OH groups by α-terpineol molecules is likely to lead to a decrease of interactions between those groups and HPMo molecules and, therefore, to a change of the HPA acid strength, as discussed above.

4. Conclusion

The transport and sorption properties of polymeric catalytic membranes consisting of HPMo entrapped in PVA crosslinked with succinic acid can be modified by treatment with acetic anhydride. The increase of membrane hydrophobicity with acetylation is documented not only by the contact angle to water but also by the sorption coefficients of α-pinene and water. Membrane acetylation improves the transport properties as reflected by pinene diffusivity.

The catalytic activity of the PVA membranes concerning the hydration reaction of α-pinene is strongly affected by membrane acetylation and increases with the degree of acetylation. In spite of the increase of hydrophobicity with acetylation, also the selectivity to the desired product α-terpineol achieves its maximum value for the most acetylated membrane M100.

A kinetic-diffusion model was developed assuming that the product α-terpineol also affects the transport properties of PVA membranes concerning water and α-pinene. Namely, exponential dependencies between water and pinene diffusivity and terpineol concentration were assumed, in such a way that the whole process starts under diffusion control and finishes under kinetic control. The good fit of the experimental data supports these assumptions.

The increase of catalytic activity with membrane acetylation is mainly due to the improvement of the membrane transport properties for water. We arrive at this conclusion because although the model predicted kinetic constants for both hydration and isomerization reactions decrease, the initial diffusivity of water increases when membrane acetylation increases. Except for membrane M40 there are apparently no diffusion limitations for α-pinene.

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