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Esterification of acetic acid with isopropanol coupled with pervaporation Part I: Kinetics and pervaporation studies

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Abstract

Reaction–pervaporation hybrid processes can be an alternative to classical chemical processes to enhance the conversion of equilibrium-limited reactions such as esterification and trans-esterification. In this work, the esterification of acetic acid with isopropanol coupled with pervaporation has been investigated. First, the synthesis and hydrolysis of isopropyl acetate have been studied using the commercial ion exchange resin Amberlyst 15. The influence of different operating parameters such as reaction temperature, initial molar reactant ratio and amount of catalyst has been examined. Additionally, the performance of the commercial polymeric membrane PERVAP® 2201 has been studied. The influence of temperature and feed composition on the permeation characteristics of the membrane was analyzed, whereby preferential water permeation from the quaternary mixture involved in the esterification of acetic acid with isopropanol has been observed under the experimental conditions considered in this work.

Keywords: Esterification; Isopropyl acetate; Pervaporation; PERVAP®

1. Introduction

Esterification reactions are of industrial importance. Esters are widely used as solvents, extractants and diluents [1]. Esterification reactions are equilibrium-limited reactions and different possibilities exist to achieve higher conversions. By using a large excess of one of the reactants, usually the alcohol, the reaction yield of the other compound can be enhanced. But, because of the presence of the large excess of one of the reactants, the recovery of the product becomes more expensive. By using a hybrid process this limitation can be overcome. In the last years, reactive distillation has gained increasing interest to obtain higher conversions and selectivities for this type of reactions. By removing directly the products from the reactive section of the column, higher conversions can be obtained. This technique has been successfully applied in our research group for esterification reactions [2–4] as well as trans-esterification reactions [5].

Often pervaporation separation processes are applied for the separation of azeotropic mixtures or systems with separation factors close to unity [6]. The combination of pervaporation with the chemical reaction has gained growing attention in the last years [7,8]. The integration of pervaporation into conventional esterification processes is attractive because a pervaporation separation process with dense membranes is based on the differences in solubilities and transport rates [9]. In a pervaporation process the separation is based on the transport of the components through the membrane, which is determined by the solubility and diffusivity of the components to be separated. Selective permeation of one or more reaction products through the membrane from the reacting mixture can be an alternative way to reach higher conversions for equilibrium limited reactions such as esterification and trans-esterification reactions.

In this work the esterification reaction of acetic acid with isopropanol has been investigated. By using selective membranes, the water formed in the esterification reaction can be selectively removed obtaining higher conversions. The membrane used in this work was the highly cross-linked commercial hydrophilic membrane, PERVAP® 2201, supplied by Sulzer Chemtech. This membrane has already been used for the dehydration of isopropanol in our research group [10]. The same membrane has also successfully been applied by other authors [11] for the synthesis of methyl acetate from methanol and acetic acid in a pervaporation membrane reactor.

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Nomenclature

A	membrane area (m^2)
a	activity
a_{ij}, b_{ij}, c_{ij}	parameters used in Eq. (2)
D_i	diffusion coefficient (m^2/h)
$D'_{i,o}$	apparent diffusion coefficient ($kg\,h^{-1}\,m^{-2}$)
E	apparent activation energy ($kJ\,mol^{-1}$)
J	permeate flux ($kg\,h^{-1}\,m^{-2}$)
k^o	pre-exponential Arrhenius factor ($mol\,min^{-1}\,g^{-1}$)
n	number of experimental data
O.F.	objective function
p	total permeate mass (kg)
R	general gas constant ($J\,mol^{-1}\,K^{-1}$)
r	reaction rate ($mol\,min^{-1}\,g^{-1}$)
T	absolute temperature (K)
t	reaction (min); pervaporation time (h)
Δu_{ij}	UNIQUAC parameters
w	weight fraction
x	mole fraction

Greek letters

γ	activity coefficient
ν	stoichiometric coefficient
τ	plasticizing coefficient

Subscript letters

calc	calculated value
e	esterification reaction
exp	experimental value
f	feed side
h	hydrolysis reaction
HOAc	acetic acid
i, j	components
IPA	isopropanol
*i*PrOAc	isopropyl acetate
p	permeate side
w	water

For a reliable design of a membrane reactor, information on the reaction kinetics as well as on the permeation performance is required. In this work the reaction kinetics and the pervaporation performance have been studied separately to obtain the required permeation and kinetic parameters, which are necessary to simulate the performance of a esterification–pervaporation reactor. The heterogeneously catalyzed esterification of acetic acid with isopropanol and the backward reaction were performed in a stirred batch reactor. As heterogeneous catalyst, the strongly acid ion exchange resin Amberlyst 15 was used. Amberlyst 15 has already successfully been used as catalyst for other esterification reactions [12,13]. Several experiments have been carried out to analyze the influence of the amount of catalyst, the initial molar reactant ratio and the temperature on the forward and the backward reaction. The experimental reaction rates were correlated by using the pseudo-homogeneous model (PH) to obtain a general kinetic equation. The pervaporation performance of the membrane PERVAP® 2201 was studied for the quaternary mixture involved in the esterification of acetic acid with isopropanol, whereby the influence of the feed temperature and feed composition on the permeate flux and composition were considered.

2. Theory

2.1. Kinetics

Different kinetic models have been used to describe the esterification reaction catalyzed by ion exchange resins. The pseudo-homogeneous model assumes complete swelling of the polymeric catalyst in contact with polar solvents, leading to an easy access of the reactants to the active sites. This model has successfully been used for the description of esterification and transesterification reactions catalyzed by ion-exchange resins [5,13,14]. In this work the pseudo-homogeneous model has been used to describe the synthesis and hydrolysis of isopropyl acetate catalyzed by Amberlyst 15. The pseudo-homogeneous model can be written as:

$$r = \frac{1}{m_{\mathrm{cat}}}\frac{1}{\nu_i}\frac{\mathrm{d}n_i}{\mathrm{d}t} = k_{\mathrm{e}}a_{\mathrm{HOAc}}a_{\mathrm{IPA}} - k_{\mathrm{h}}a_{i\mathrm{PrOAc}}a_{\mathrm{w}} \tag{1}$$

with $a_i = x_i\gamma_i$, where x_i is the mole fraction of component i, γ_i its activity coefficient and a_i the activity. In this work the activity coefficients of the components in the liquid phase were calculated by using the UNIQUAC equation, whereby temperature-dependent interaction parameters Δu_{ij} were used:

$$\Delta u_{ij} = a_{ij} + b_{ij}T + c_{ij}T^2 \tag{2}$$

The required van der Waals properties r_i and q_i were taken from the Dortmund Data Bank (DDB) [15] and are listed in Table 1. Interaction parameters were fitted simultaneously to different kind of phase equilibrium data and excess properties (VLE, azeotropic data, activity coefficients at infinite dilution (γ^{∞}), heats of mixing (h^E)), which were also obtained from the Dortmund Data Bank. The resulting interaction parameters are given in Table 2.

An Arrhenius-type temperature dependence for the forward and backward reaction was used:

$$k_i = k_i^{\mathrm{o}} \exp\left(\frac{-E_{\mathrm{A},i}}{RT}\right) \tag{3}$$

and the kinetic parameters k_i^{o} and $E_{\mathrm{A},i}$ of the pseudo-homogeneous model were fitted by minimizing the following

Table 1
UNIQUAC r_i and q_i values

Component	r_i	q_i
Acetic acid	2.2024	2.0720
Isopropanol	2.7791	2.5080
Isopropyl acetate	4.1522	3.6520
Water	0.9200	1.4000

Table 2
UNIQUAC parameters used for the calculation of activity coefficients (Eq. (2))

Component 1	Component 2	i	j	a_{ij} (K)	b_{ij}	c_{ij} (K^{-1})
Acetic acid	Isopropanol	1	2	54.943	−0.20222	
		2	1	27.680	−0.13058	
	Isopropyl acetate	1	2	−73.648	−0.28105	
		2	1	172.21	0.48862	
Isopropanol	Isopropyl acetate	1	2	41.8205	−0.29509	
		2	1	300.9506	−0.39534	
	Water	1	2	1417.50	−4.7263	2.9334×10^{-3}
		2	1	−216.88	−1.1186	5.5673×10^{-3}
Acetic acid	Water	1	2	422.38	−0.051007	-2.4019×10^{-4}
		2	1	−98.120	−0.29355	-7.6741×10^{-5}
Isopropyl acetate	Water	1	2	115.31		
		2	1	433.92		

objective function:

$$\text{O.F.} = \frac{\sum_{i}^{\text{all samples}} \left|(x_{i\text{PrOAc,exp}} - x_{i\text{PrOAc,calc}})/x_{i\text{PrOAc,exp}}\right|}{n_{\text{samples}}} \times 100\% \quad (4)$$

by using the Simplex–Nelder–Mead method.

2.2. Pervaporation

For the study of the pervaporation performance of the membrane PERVAP® 2201 a quaternary mixture has to be considered. In the case of quaternary systems, the transport through the membrane is a very complex phenomenon with interactions between the components and the components with the membrane. To solve this problem some simplifications can be made for mixtures containing only a low amount of water. Many authors supposed that water is the only permeating component through the membrane from the reaction mixture [16,17].

The most widely accepted transport model through the membrane is the solution/diffusion model. Based on this model, the permeation performance is determined by the solubility and diffusivity of each component through the membrane. The diffusion of the components permeating through the membrane can be assumed to occur according to Fick's first law for the components:

$$J_i = -D_i \frac{\mathrm{d}w_i}{\mathrm{d}z} \quad (5)$$

The diffusion coefficient, D_i, is normally dependent on the concentration of the components in the membrane. An exponentially dependency is used by most of the researchers [18]:

$$D_i = D_{i,\text{o}} \exp(\tau_{i,i} w_i^m + \sum_{j \neq i} \tau_{i,j} w_j^m) \quad (6)$$

where τ are the plasticization coefficients. In the case of water, the most strongly permeating component, the permeation rate can be considered to be independent on the presence of the other organic components in the membrane. With this assumption the plasticization coefficients of these compounds in Eq. (6) can be neglected ($\tau_{\text{w},j} = 0$). After combining Eqs. (5) and (6) and integration across the membrane, the water flux can be described by the following relation:

$$J_\text{w} = \frac{D_{\text{w,o}}}{\tau_{\text{w,w}}} [\exp(\tau_{\text{w,w}} w_\text{w}^{m(z=0)}) - \exp(\tau_{\text{w,w}} w_\text{w}^{m(z=\delta)})] \quad (7)$$

For low permeate pressure, the concentration at the downstream side membrane interface can be considered as zero [6].

Assuming an ideal sorption process, the concentration of a component i in the membrane can be considered linearly proportional to the concentration of this component in the feed mixture and the water flux can be expressed as a function of the feed composition [18]. Assuming that the temperature dependency of the diffusion coefficient follows an Arrhenius type law [19]:

$$D = D_\text{o} \exp\left(\frac{-E_D}{RT}\right) \quad (8)$$

the following expression for the water flow can be obtained:

$$J_\text{w} = D'_{\text{w,o}} \exp\left(\frac{-E_\text{w}}{RT}\right) [\exp(\tau'_{\text{w,w}} w_{\text{w,feed}}) - 1] \quad (9)$$

For the other components permeating through the membrane the following expression is obtained to describe their flow:

$$J_i = D'_i \exp\left(\frac{-E_i}{RT}\right) \exp(\tau_{\text{w},i} w_{\text{w,feed}}) [\exp(\tau_{i,i} w_{i,\text{feed}}) - 1] \quad (10)$$

The model parameters, $D'_{i,\text{o}}$, E_i, $\tau_{\text{w},i}$, $\tau_{i,i}$ for the different partial permeate fluxes were obtained by minimizing the following objective function O.F.:

$$\text{O.F.} = \sum^{\text{all samples}} (J_{i,\text{calc}} - J_{i,\text{exp}})^2 \quad (11)$$

by using the Simplex–Nelder–Mead method.

3. Experimental

3.1. Materials

The membrane used for the pervaporation studies was a commercial hydrophilic membrane, PERVAP® 2201, supplied by Sulzer Chemtech with a maximum long term operating temperature of 100 °C. The strongly acidic ion-exchange resin Amberlyst 15 with an exchange capacity of 4.75 meq of H^+ g^{-1} of dry catalyst (Rohm & Haas) was used as catalyst. The resin was washed several times with distilled water and dried at 353.15 K under vacuum until the mass remained constant. The chemicals used for the kinetic and pervaporation experiments showed a purity higher than 99%. No further purification was carried out but the chemicals were dried over molecular sieve.

3.2. Kinetic measurements

The equipment used for the measurement of the kinetic data as well as the operation procedure have already been described in detail elsewhere [12]. The experiments were conducted in a thermostated stirred glass reactor with a volume of 500 cm^3 with an attached reflux condenser to avoid any loss of volatile components. For the esterification, isopropanol and the resin were charged into the reactor and heated to the desired temperature. Acetic acid, was heated separately to the desired temperature and fed to the reactor. This time was considered to be the starting time of the reaction. In the case of the hydrolysis reaction, a mixture of water and isopropanol were heated together with the catalyst in order to avoid a miscibility gap between water and isopropyl acetate. Isopropyl acetate was heated separately. After reaching the reaction temperature isopropyl acetate was added to the reactor. The temperature inside the reactor was kept constant within ±0.5 K. The reaction was followed by withdrawing samples in regular time intervals, which were analyzed by gas chromatography.

3.3. Pervaporation studies

The experimental set-up used in this work has already been used by the authors for different pervaporation studies [5,10]. The effective membrane area in the pervaporation cell was 100 cm^2. The temperature of the feed mixture was kept constant by using a thermostat. The feed flow rate to the membrane module was set to 16.6 kg/h, high enough to avoid concentration polarization effects. On the permeate side, vacuum was maintained below 1 mbar and the permeate was condensed on a glass cold trap filled with liquid nitrogen. The total flow through the membrane was determined by weighing the amount of permeate in a certain time. The membrane was kept in the membrane module overnight together with the feed mixture and a slight vacuum on the permeate side to reach the steady state faster.

3.4. Sample analysis

All kinetic and pervaporation samples were analyzed by gas chromatography using a HP 6890 equipped with a thermal conductivity detector (TCD). The GC column was a HP-FFAP. The injector and detectors were kept at 503.15 and 523.15 K, respectively. The oven temperature was controlled from 348.15 to 483.15 K. Helium was used as the carrier gas with a purity higher than 99.99 wt.%.

4. Results and discussion

4.1. Reaction kinetics

The results of the reaction kinetics for the heterogeneously catalyzed synthesis and hydrolysis of isopropyl acetate are presented in this section. The effect of catalyst loading, initial molar ratio of reactants and temperature on the esterification and hydrolysis kinetics was analyzed.

4.1.1. Effect of temperature

Kinetic measurements were performed in a temperature range from 329.15 to 353.85 K for the esterification reaction and from 332.15 and 350.90 K for the hydrolysis reaction. Typical results are shown in Fig. 1. It can be seen that the reaction rate increases with increasing reaction temperature. Activation energies of

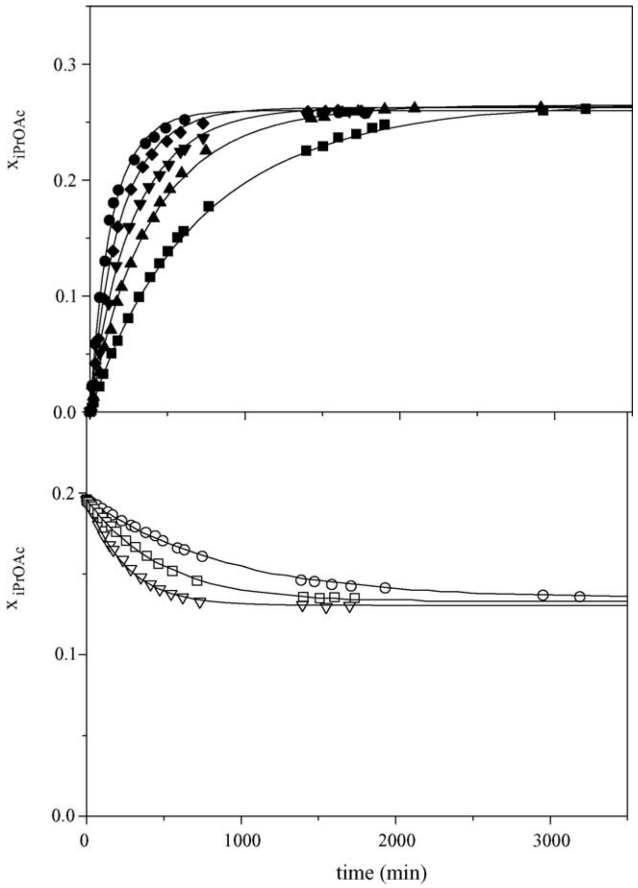

Fig. 1. Isopropyl acetate mole fraction vs. time at different temperatures for the esterification reaction (catalyst = 6 wt.%, $n_{IPA}/n_{HOAc} = 2$): (■) 329.15 K; (▲) 337.65 K; (▼) 343.15 K; (♦), 348.40 K; (●) 353.85 K and for the hydrolysis reaction (catalyst = 6 wt.%, $n_w/n_{iPrOAc} = 2.5$): (○) 332.65 K; (□) 341.40 K; (▽) 350.90. The continuous lines represent the results of the pseudo-homogeneous model.

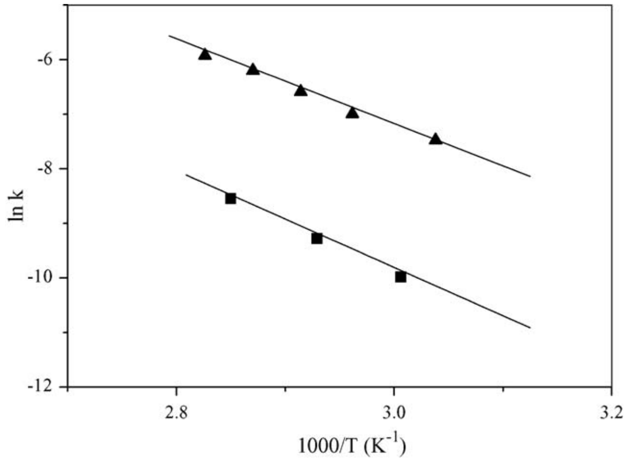

Fig. 2. Arrhenius plot for the isopropyl acetate synthesis (▲) and its hydrolysis (■). The lines represent the results of the pseudo-homogeneous model.

64.59 and 73.63 kJ mol^{-1} for the pseudo-homogeneous model were obtained for the esterification and hydrolysis reactions, respectively, in the fitting procedure. Fig. 2 shows the Arrhenius plot of the reaction rate constants.

4.1.2. *Effect of amount of catalyst*

The catalyst concentration was varied between 2 and 13 wt.% for the esterification reaction and from 3.5 to 10 wt.% for the hydrolysis reaction. As expected, an increase of the catalyst amount leads to an increase of the reaction rate. Consequently the equilibrium is reached faster with increasing catalyst concentration (Fig. 3). Fig. 4 shows a linear relationship between the initial reaction rate, expressed as moles per minute, and the amount of catalyst employed.

4.1.3. *Effect of initial molar reactant ratio*

The initial molar ratio of isopropanol to acetic acid ($n_{\mathrm{IPA}}/n_{\mathrm{HOAc}}$) was varied from 1 to 2 for the esterification reaction. For the hydrolysis reaction the initial molar ratio of water to isopropyl acetate ($n_{\mathrm{w}}/n_{i\mathrm{PrOAc}}$) was varied from 1.5 to 3.5. From Fig. 5 it can be seen that the equilibrium conversion of the limiting compound increases from 66% for a $n_{\mathrm{IPA}}/n_{\mathrm{HOAc}} = 1$ up to a value of 78% for a $n_{\mathrm{IPA}}/n_{\mathrm{HOAc}} = 2$.

4.1.4. *Modeling*

The kinetic data of the esterification and the hydrolysis reaction were simultaneously correlated by means of the pseudo-homogeneous model. The four adjustable kinetic parameters obtained in the fitting procedure (k_e^{o}, k_h^{o}, $E_{A,e}$, $E_{A,h}$) are given in Table 3 together with the value of the objective function. The continuous lines in Figs. 1–5 represent the results obtained with the pseudo-homogeneous model. As can be seen, the results

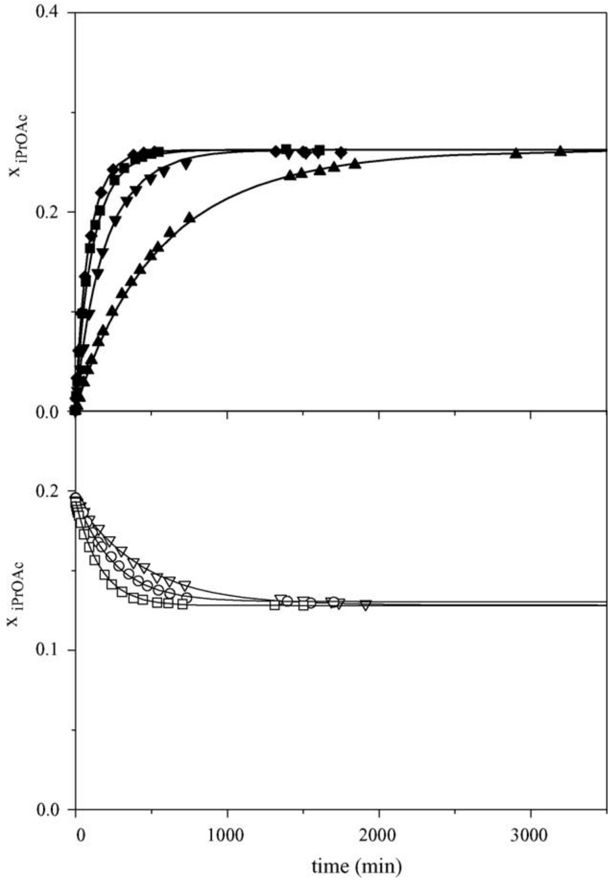

Fig. 3. Isopropyl acetate mole fraction vs. time at different catalyst loading for the esterification reaction ($T = 348.40$ K, $n_{\mathrm{IPA}}/n_{\mathrm{HOAc}} = 2$): (▲) 2 wt.%; (▼) 6 wt.%; (■) 10 wt.%; (♦) 13 wt.% and for the hydrolysis reaction ($T = 350.90$ K, $n_{\mathrm{w}}/n_{i\mathrm{PrOAc}} = 2.5$): (▽) 3.5 wt.%; (○) 6.0 wt.%; (□) 10 wt.%. The continuous lines represent the results of the pseudo-homogeneous model.

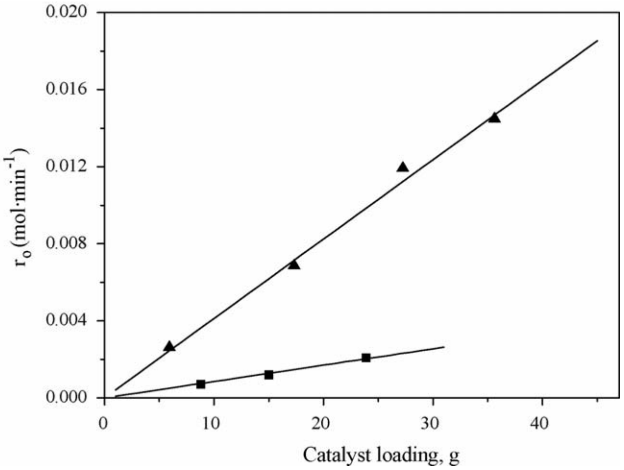

Fig. 4. Initial reaction rate vs. catalyst loading for the synthesis of isopropyl acetate (▲) and its hydrolysis (■). The lines represent the results of the pseudo-homogeneous model.

Table 3
Kinetic parameters for the pseudo-homogeneous kinetic model

Parameter	$k_{\mathrm{e}}^{\mathrm{o}}$ (mol g^{-1} min^{-1})	$E_{\mathrm{A,e}}$ (kJ mol^{-1})	$k_{\mathrm{h}}^{\mathrm{o}}$ (mol g^{-1} min^{-1})	$E_{\mathrm{A,h}}$ (kJ mol^{-1})	O.F.
Value	1.017×10^7	64.59	1.904×10^7	73.63	3.97

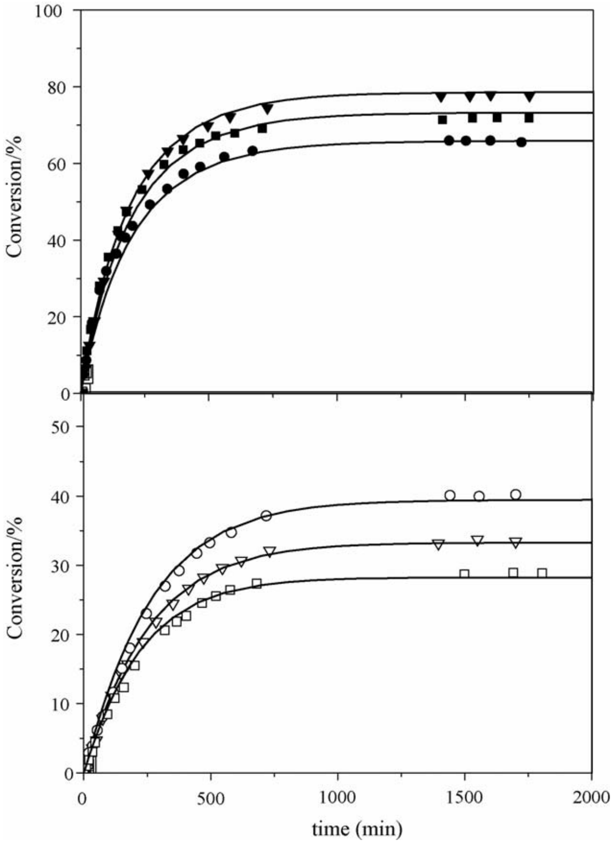

Fig. 5. Conversion of the limiting reactant (acetic acid in the esterification and the ester in the case of the hydrolysis) vs. time for different initial reactant molar ratios of the reactants (n_{IPA}/n_{HOAc}) for the esterification reaction (T = 348.40 K, catalyst = 6 wt.%): (●) 1; (■) 1.5; (▼) 2 and for the hydrolysis reaction (n_w/n_{iPrOAc}) (T = 350.90 K, catalyst = 6 wt.%): (□) 1.5; (▽) 2.5; (◯) 3.5. The continuous lines represent the results of the pseudo-homogeneous model.

of the model are in good agreement with the experimental data.

4.2. Sorption experiments

Sorption experiments for the membrane PERVAP® 2201 were carried out for all pure components at room temperature. The separation layer of the membrane was removed from the PAN support and immersed in a closed bottle containing either water, IPA, isopropyl acetate or acetic acid. After sorption equilibrium was reached, the weight increase corresponds to the liquid sorbed by the membrane. Sorption is mainly influenced by differences of the molar volumes of the penetrants, affinity towards the membrane and mutual affinity. Taking into account only the difference in molar volume, the component with the smallest molar volume should be sorbed preferentially. The effect of the molar volume is especially important in cases where water is one of the components. Due to its small volume, water will be the component sorbed preferentially [20]. In the system investigated, it was also observed that the degree of sorption increases with decreasing liquid molar volume (Fig. 6). The membrane exhibited the best sorption for the preferentially permeating component, water. High sorption was also observed for acetic acid.

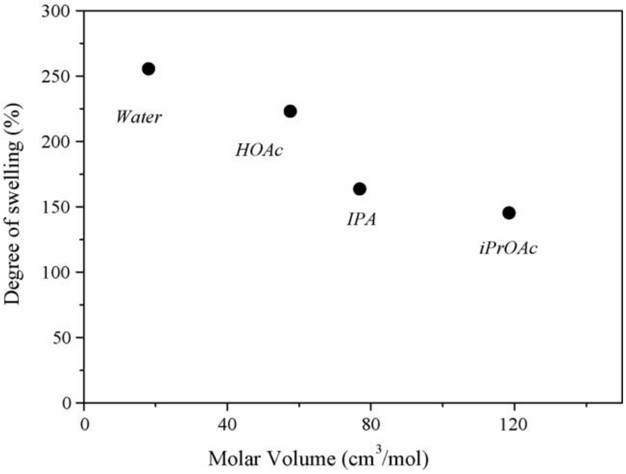

Fig. 6. Degree of swelling of the membrane PERVAP® 2201 at room temperature for water, isopropanol (IPA), isopropyl acetate (*i*PrOAc) and acetic acid (HOAc).

4.3. Pervaporation experiments

The effect of temperature and feed composition on the separation performance for the quaternary mixture by using the membrane PERVAP® 2201 is presented in this section. The partial flux of the components through the membrane was calculated by the following expression:

$$J_i = w_i^{\mathrm{p}} J_T = w_i^{\mathrm{p}} \frac{p}{\Delta t A} \tag{12}$$

where p is the total permeate mass, A the effective membrane area, Δt the period of time, and w_i^{p} the corresponding permeate weight fraction.

Qualitatively, the pervaporation characteristics of the membrane PERVAP® 2201 for the quaternary mixture is similar to the performance observed for the binary system water/IPA during the study of the dehydration of isopropanol by pervaporation [10]. In all pervaporation experiments, the membrane showed a high selectivity towards water.

4.3.1. Effect of feed composition

The water feed composition was varied between 2 and 20 wt.%. The composition range for the other components in the feed solution was as follows: isopropanol 30–50 wt.%, isopropyl acetate 21–51 wt.% and acetic acid 2–20 wt.%.

In Fig. 7, the experimental water permeate flux is plotted as function of water weight fraction in the feed at different operating temperatures. For each operating temperature the flux increased with water feed composition due to a higher swelling of the membrane. The flux of the other organic components also increased with the water content in the mixture, probably caused by the coupled transport with water.

In the composition range investigated in this work, the water flux was always much higher than the fluxes of the other components and close to the values of the total permeate flux. In Fig. 8 the water composition in the permeate is plotted against the water weight fraction in the feed at 321.15 K. It can be seen that the membrane selected in this work, PERVAP® 2201, shows

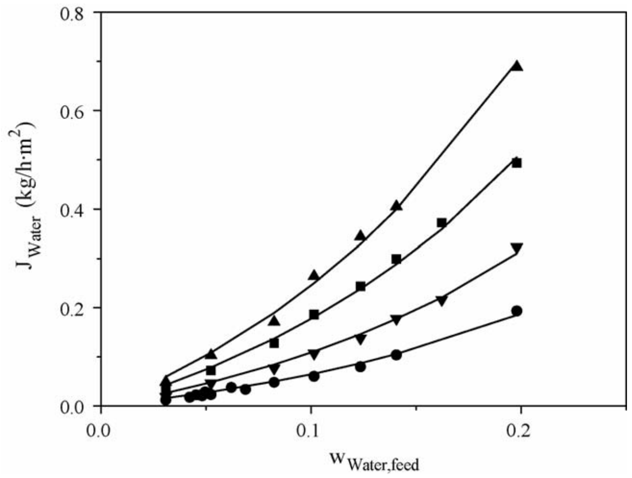

Fig. 7. Water permeate flux vs. water weight fraction in the feed at different feed temperatures ((●) 321.15 K; (▼) 331.15 K; (■) 341.15 K; (▲) 348.15 K). The solid lines represent the results of the model.

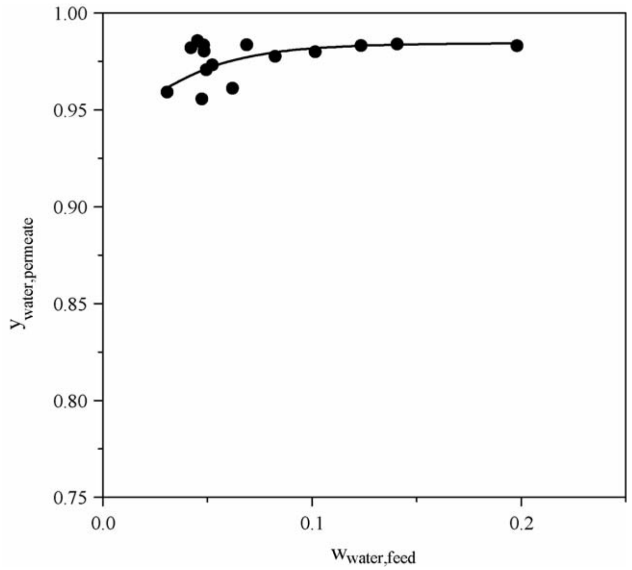

Fig. 8. Permeate water weight fraction vs. water weight fraction in the feed at 321.15 K.

a high selectivity for water. Even at low water concentration in the feed, the water composition in the permeate is about 96 wt.%. It can be concluded that the membrane considered in this work, PERVAP® 2201, can be used to remove selectively the water from the quaternary mixture. Similar behavior was observed for other polyvinyl alcohol composite membrane allowing selective permeation of water independent of the composition of the reaction mixture [21].

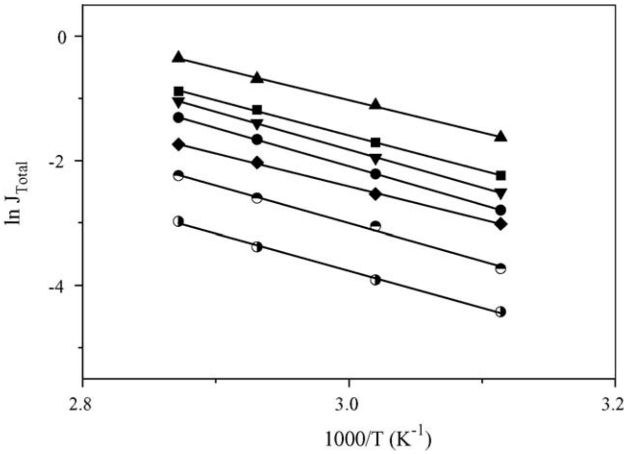

Fig. 9. Temperature dependence of total permeate flux at various water compositions ((▲) 19.8 wt.%; (■) 14.1 wt.%; (▼) 12.4 wt.%; (●) 10.2 wt.%; (♦) 8.2 wt.%; (◓) 5.2 wt.%; (◑) 3.1 wt.%). The continuous lines represent the results of the Arrhenius fit.

4.3.2. *Effect of the temperature*

The effect of the temperature was studied in the range from 321.15 to 348.15 K. The operating temperature influences the driving force for mass transport in pervaporation processes. With increasing temperature, the diffusion of the permeating species is improved, leading to an increase in the total permeation rate (Fig. 7). Empirically, the temperature dependence of the permeation rate, J_{total}, can be expressed by an Arrhenius-type relation [18]:

$$J_{\mathrm{total}} = J_{\mathrm{o}} \exp\left(\frac{-E_{\mathrm{P}}}{RT}\right) \tag{13}$$

where E_{P} is the apparent activation energy of permeation, J_{o} the pre-exponential factor, and T the absolute temperature. The activation energy can be calculated from the slope of the logarithm of the overall pervaporation fluxes versus the reverse absolute temperature at different feed compositions (Fig. 9). The average value determined from the slopes was 48.1 kJ/mol. With increasing temperature only a very small decrease of the selectivity of the membrane towards water has been observed.

4.3.3. *Modeling*

The parameters for the expressions of the partial permeate flux are listed in Table 4 together with the mean relative deviation calculated as followed:

$$\mathrm{MRD} = \frac{\sum^{\text{all samples}} |(J_{i,\mathrm{calc}} - J_{i,\mathrm{exp}})/J_{i,\mathrm{exp}}|}{n_{\mathrm{samples}}} \times 100\% \tag{14}$$

Table 4
Pervaporation parameters for the isopropyl acetate system through the membrane PERVAP® 2201

Component	$D'_{i,\mathrm{o}}$ (kg h^{-1} m^{-2})	$E_{\mathrm{A,P}}$ (kJ mol$^{-1)}$	$\tau_{\mathrm{w},i}$	$\tau_{i,i}$	MRD
Water	2.0×10^6	45.8	–	6.5	1.38
Isopropanol	8.1×10^7	47.5	10.1	3.3×10^{-4}	3.57
Isopropyl acetate	1.9×10^9	58.5	10.1	6.7×10^{-4}	4.07
Acetic acid	2.8×10^9	56.0	12.3	3.8×10^{-4}	2.70

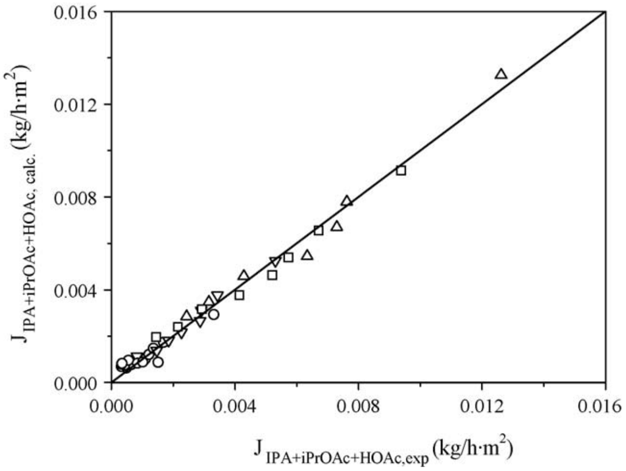

Fig. 10. Calculated permeate flow for IPA, isopropyl acetate and acetic acid vs. the calculated ones at different feed temperatures ((○) 321.15 K; (▽) 331.15 K; (□) 341.15 K; (△) 348.15 K).

The continuous lines in Figs. 7 and 8 represent the results using the parameters from the fitting procedure. In Fig. 10, the sum of the calculated permeate fluxes for isopropanol, isopropyl acetate and acetic acid is plotted against the sum of the experimental fluxes. As can be seen a good agreement between experimental and calculated fluxes is also observed for the hardly permeating compounds. In future studies a more accurate model should be investigated. The ideal sorption assumption is a simplification since in pervaporation, interactions between the polymer and the penetrants are strong, and the sorption of a component is influenced by the presence of the other components.

5. Conclusions

The design of a pervaporation reactor requires information on reaction kinetics and pervaporation performance of the membrane. In this work, the heterogeneously catalyzed synthesis and hydrolysis of isopropyl acetate by Amberlyst 15 have been studied. A kinetic expression was obtained by fitting simultaneously the kinetic results of the esterification and the hydrolysis reactions. The pseudo-homogeneous model gives a good representation of the reaction rate for the isopropyl acetate system with only four adjustable parameters.

In addition, the separation of the quaternary mixture by pervaporation using the commercial polymeric membrane PERVAP® 2201 has been investigated in this work. The permeate flux was found to increase with the water content in the feed and the temperature. The membrane showed a high selectivity towards water in the composition and temperature range studied in this work. Based on these results it can be concluded that the membrane PERVAP® 2201can be used to remove selectively the water formed in the esterification reaction to obtain higher conversions by using membrane reactors.

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