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Pervaporative dehydration of organic mixtures using a commercial silica membrane
Determination of kinetic parameters

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Abstract

In this work, the performance of a pervaporation commercial silica membrane referenced as PVP (supplied by Pervatech BV, The Netherlands), has been studied. The solvent mixtures used in the experiments were: (i) a synthetic water–isopropanol mixture with 15–20 wt.% inital water content and (ii) an industrial mixture containing about 25 wt.% water–75 wt.% acetone, coming from a reaction process devoted to the manufacture of rubber antioxidants. In both systems the flux of water through the membrane was obtained at different water concentrations in the feed, as dehydration proceeded. The effect of temperature was studied in the range 40–90 °C. It was found that for the range of conditions investigated, water fluxes through the PVP membrane were larger than those previously reported through the Pervap SMS commercial membrane (supplied by Sulzer Chemtech). Water flux data were fitted to a semi-empirical correlation that expresses water flux as an exponential function of the water activity in the feed mixture, $\mathrm{Ln}(J_{\mathrm{w,mass}}) = (\mathrm{Ln}\, J_{00,\mathrm{w}} - E_{\mathrm{act}}/RT) + \zeta a_{\mathrm{w}}^{\mathrm{f}}$. The values of the characteristic mass transfer parameters corresponding to the Pervatech PVP membrane, ζ, E_{act} and $\mathrm{Ln}\, J_{00,\mathrm{w}}$, were obtained, as required for design purposes.

Keywords: Pervaporation; Silica membrane; Modelling water flux; Isopropanol; Acetone

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1. Introduction

Pervaporation is a membrane separation process where the liquid mixture to be separated (feed) is placed in contact with one side of a membrane and the permeated product (permeate) is removed as a low-pressure vapour from the other side [1]. The separation is based on the selective solution and diffusion, i.e., the physical-chemical interactions between the membrane material and the permeating molecules. Therefore, on one hand, pervaporation is commonly considered to complement distillation for the separation of azeotropic and close-boiling mixtures, because of its high separation efficiency, together with potential savings in energy cost [2].

On the other hand, the use of pervaporation as a separation technique in multi-purpose equipment seems very attractive. The broad applicability of the membrane, e.g. in the dehydration of various solvents, is the main criteria to be used. Currently several commercial pervaporation units based on inorganic membranes are used at industrial level able to dehydrate routinely a variety of solvents, as reported by Martin [3], using an amorphous silica membrane and Kita [4] and Morigami et al. [5] using a zeolite NaA membrane.

Extensive research has been done in the field of membranes for the pervaporation process, focused on finding the optimised membrane material having selective interaction with a certain component in the feed mixture to maximise the performance in terms of separation factor, flux and stability [6].

Polymeric membranes have shown some limitations regarding their thermal and chemical stability [7-9], giving place to the interest on development of more stable multipurpose membranes. In particular, porous inorganic membranes (e.g. ceramic membranes) exhibit high permeabilities

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Nomenclature

a_w	water activity (mole fraction)
A	effective membrane area (m^2)
c_{w}	mass concentration of water (kg/m^3)
C_{w}	concentration of water in the feed (wt.%)
$C_{\mathrm{w},0}$	initial concentration of water in the feed (wt.%)
D	diffusion coefficient in the membrane (m^2/s)
D_0	intrinsic diffusion coefficient (m^2/s)
D_{T}	thermodynamic diffusion coefficient (m^2/s)
E_{act}	apparent activation energy (cal/mol)
J	flux through the membrane (kg/m^2h)
J_0	parameter of the model in Eq. (3) (kg/m^2h)
m	mass of permeate (kg)
R	ideal gas constant
t	time
T	operating temperature (K)
V_{w}	velocity of species water (m/s)
W	mass fraction

Greek letters

δ	selective layer thickness (m)
μ	chemical potential (J/mol)
ρ	mass density (kg/m^3)
τ	exponential parameter of diffusivity in the membrane
ζ	model parameter in Eq. (2)

Superscripts

f	feed solution
m	membrane phase
p	permeate

Subscripts

w	water

relative to dense membranes and high thermal stability relative to organic membranes [10,11]. In general, inorganic membranes allow working at elevated temperatures, which can be of the utmost importance, for example, in order to enhance the yield of an esterification reaction by coupling a pervaporation unit. [12]. Inorganic membranes, with the active pervaporation layer made of amorphous silica and having narrow pore size distribution have become commercially available [13,14].

In this work, the performance of a commercial microporous silica membrane referenced as Pervatech PVP, regarding its ability to dehydrate different solvents is characterised in terms of the pervaporation flux. This has been done for the separation of a prepared water/isopropyl alcohol mixture and an industrial water/acetone mixture. In both systems the effect of varying the concentration of water in the feed and the operation temperature has been studied. Also, a methodology for the determination of the mass transfer parameters that predict the water flux across the Pervatech PVP silica membrane is presented, that is needed for design purposes.

2. Theory

The performance of a pervaporation membrane is usually characterized in terms of the flux and selectivity. These features are commonly given as a function of temperature, downstream pressure and concentration of the permeating component in the feed mixture. In this work, it will be shown the relationship of the flux with the driving force for transport, i.e., the chemical potential gradient, which can be expressed in terms of the activity of the permeating compound in the liquid feed mixture and of the operation temperature.

Thus, in the case of dehydration of solvents, the flux of water through the pervaporation membrane can be written as

$$J_{\mathrm{w,mass}} = v_{\mathrm{w}} c_{\mathrm{w}}^{\mathrm{m}} = -D_{\mathrm{T,w}}(c_{\mathrm{w}}^{\mathrm{m}}) c_{\mathrm{w}}^{\mathrm{m}} \left(\frac{\mathrm{d}\,\mathrm{Ln}\, a_{\mathrm{w}}^{\mathrm{m}}}{\mathrm{d}z} \right) \tag{1}$$

according to the description of flux in terms of friction [15], being the chemical potential gradient the driving force, and considering negligible variation of temperature and pressure within the pervaporation separation process. This expression has been developed by the authors in a previous work [16] in order to demonstrate its applicability to predict the flux through both polymeric and inorganic hydrophilic pervaporation membranes, for a wide range of solvent mixtures.

Assuming zero downstream pressure, equilibrium at the membrane surface, an exponential concentration dependence of diffusion coefficient [15,17] and, above all, a linear sorption isotherm of the penetrant, i.e. water in the cases analysed within this work, into the membrane surface, integration of Eq. (1) becomes,

$$\mathrm{Ln}(J_{\mathrm{w,mass}}) = \mathrm{Ln}(J_{0,\mathrm{w}}(T)) + \zeta a_{\mathrm{w}}^{\mathrm{f}} \tag{2}$$

with

$$J_{0,\mathrm{w}}(T) = \frac{\rho^{m} D_{\mathrm{w},0}}{\delta \tau} \tag{3}$$

where $J_{0,\mathrm{w}}(T)$ follows the Arrhenius law as

$$\mathrm{Ln}\, J_{0,\mathrm{w}}(T) = \mathrm{Ln}\, J_{00,\mathrm{w}} - \frac{E_{\mathrm{act}}}{RT} \tag{4}$$

In Eqs. (2)–(4) the mass transfer parameters that must be determined empirically are ζ, $J_{00,\mathrm{w}}$ and E_{act}. The first one, ζ, is related to the adsorption of the permeating species onto the membrane since it contains the influence of the adsorption equilibrium parameter. Secondly, $J_{0,\mathrm{w}}$ depends proportionally on the density and the intrinsic diffusion coefficient of the permeating species in the feed solution, being inversely