Tesi doctoral presentada per En/Na

Marc PERA TITUS

amb el títol

"Preparation, characterization and modeling of zeolite NaA membranes for the pervaporation dehydration of alcohol mixtures"

per a l'obtenció del títol de Doctor/a en

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Departament d'Enginyeria Química

UNIVERSITAT DE BARCELONA

A: Work of adsorption according to Eq. I.12 [J mol^{-1}]; Parameter in Eq. III.2 [mol m^{-2} s^{-1} Pa^{-1}]; Area drawn by breakthrough curves in Eqs. III.4 and A.1-A.2 [s^{-1}]; Parameter in the Antoine Equation; Pre-exponential factor in Eq. I.40 and VIII.45

A_{12}, A_{21}: Parameters of the Van Laar model (Eq. VII.35)

A_b: Bed cross section [m^2]

a: Activity [-]

a_m: Packing factor [m^2 m^{-3}]

B: Parameter in Eq. III.2 [mol m^{-2} s^{-1} Pa^{-2}]; Parameter in the Antoine Equation

B_{ij}^S: Factor defined according to Eq. I.45 [s m^{-2}]

C: Concentration

d or d_p: Pore size [m]

$\overline{d}_i$: Mean pores of the function $\varepsilon(d)$ [m] defined by Eq. VI.3

$\overline{d}_p$: Mean pore size [m]

$d_{m,i}$: Kinetic diameter of the species **i** [m]

$\langle d^n \rangle$: n^{th} moment of the function $\varepsilon(d)$ [m^n]

D: Fick or transport diffusivity [m^2 s^{-1}]

D^*: Self-diffusivity [m^2 s^{-1}]

D_o: Pre-exponential factor according to Eq. I.34

D_b: Bed diameter [m]

D_{ij}: Molecular diffusivity between species **i** and **j**

D_L Viscous diffusivity [m^2 s^{-1}]

D_p: Particle size [m]

D_∞: Solute diffusion in an environment without interaction with the pore walls

$D_\pm$: Electrolyte diffusion in an environment without interaction with the pore walls

$Đ_i^S$: Maxwell-Stefan surface or "jump" diffusivity of species **i** [m^2 s^{-1}]

$Đ_{ij}^S$: Maxwell-Stefan counterexchange diffusivity of species **i** and **j** [m^2 s^{-1}]

E: Surface energy in Eqs. I.4 and VII.27 [J mol^{-1}]

E_D: Activation energy for diffusion [J mol^{-1}]

E^S_{eff}: Effective activation energy [J mol^{-1}]

E^o: Characteristic energy in the Dubinin-Astakhov isotherm (Eqs. I.14 and VII.16)

$E(d^*)$: Cumulative pore size function

f: Fugacity [kPa]

Fo: Fourier number [-]

$\overline{G}$: Gibbs free energy [J kg^{-1}]

G^o: Dimensionless integral free energy at molar saturation loading in Eq. 15 [-]

He: Henry coefficient [mol kg^{-1} kPa^{-1}],

IEP: Isoelectrical point [-]

j_D: Colburn factor [-]

k: Parameter of the Potential Thermodynamic Isotherm (Eq. VII.15)

k_B: Boltzmann's constant [1.38×10^{-23} J K^{-1}]

k_G External mass transfer coefficient [m s^{-1}]

ℓ : Membrane thickness [m, μm]

L_b: Bed length [m]

M: Molecular weight [kg mol^{-1}]

$\overline{M}$: Mean molecular weight [kg mol^{-1}]

m: Weight [kg]; Exponent in the Potential Thermodynamic Isotherm (Eq. VII.15)

MWCO: Molecular weight cutoff [kg mol^{-1}]

n: Exponent of the Freundlich isotherm (Eq. I.8) [-]; Number of mols [mol]

N: Flux [kg m^{-2} h^{-1}; mol m^{-2} s^{-1}]; Permeance [mol m^{-2} s^{-1} Pa^{-1}]; Number of finite elements [-]

N_A: Avogadro Number [6.023×10^{23} mol^{-1}]

N_{Pe}: Peclet Number [-]

N_{Sc}: Schmidt Number [-]

N_{Sh}: Sherwood Number [-]

P: Pressure [Pa]

P_m: Mean pressure [Pa]

P^o: Saturation vapor pressure [Pa]

P^S: Pressure at the active layer / support surface [kPa]

q: Molar loading [mol kg^{-1}]

q_M; Molar saturation loading [mol kg^{-1}]

q_T; Total molar loading [mol kg^{-1}]

Q: Permeance [mol m^{-2} s^{-1} Pa^{-1}] or permeability [kg m^{-2} h^{-1}]

$Q_{G,1}$: Parameter defined by Eq. VI.40 [mol m^{-2} s^{-1} Pa^{-1}]

$Q_{G,2}$: Parameter defined by Eq. VI.41[m^{-1} Pa^{-1}]

r: Reaction rate [mol s^{-1} kg^{-1}]; Radius [m]

R: Constant of gases [8.314 Pa m^3 mol^{-1} K^{-1}]; Radius [m]; Resistance offered by the membrane according to Eqs. VI.22-VI.24.

Re_p: Particle Reynolds number [-]

S: Surface [m^2]

$\bar{S}$: Specific entropy [J mol^{-1} K^{-1}]

S_{ext}: External specific surface of a particle [m^2 g^{-1}]; External surface [m^2]

S_{in}: Internal surface [m^2]

S_r^2 : Residual mean squares according to Eq. F.13

S_e^2 : Error mean squares according to Eq. F.14

$S_{\overline{Y}i}^2$: Estimated variance of variable $\overline{Y}_i$

SWG: Seeding weight gain [mg cm^{-2}]

t: Time [s]

T: Temperature [K]

T_b: Boling point [K]

T^*: Characteristic temperature in Eq. E.4

T_M: Mean temperature of an experimental series [K]

u_o: Surface velocity [m s^{-1}]

U: Internal energy [J]

$\overline{U}$: Specific internal energy [J kg^{-1}]

V: Volume [m^3]

$\overline{V}$: Molar volume [m^3 mol^{-1}] or specific volume [m^3 kg^{-1}]

$\overline{V}_b$: Molar volume at boiling point [m^3 mol^{-1}]

w: Molar flow [mol s^{-1}]

W: Weight of zeolite NaA powder [kg]

X: Weight fraction in the liquid phase [-]; Reaction conversion [-]

x: Molar fraction in the liquid phase or in the adsorbate in Eq. I.30 [-]

Y: Weight fraction in the gas phase [-]; Integral free energy relative to saturation loading [J kg^{-1}]

y: Molar fraction in the gas phase [-]; Variable defined by Eqs. I.5 and VII.28

z: Number of nearest neighbor sites [-]

Z: Variable defined in Eq. VII.15

z_L Length of capillary filled with liquid [m]

Greek symbols:

α: Characteristic parameter in a log-normal distribution [-] (Eq. VI.25); Exponent of the Dubinin-Astakhov isotherm (Eqs. I.14 and VII.16) [-]; Dimensionless flux (Eq. VIII.26) [-]

$\alpha_{i,j}$: Selectivity towards the separation of species **i** from **j** [-]

β: Parameter defined in the generalized Langmuir isotherm (Eqs. I.5 and VII.28) [-]; Molecular volume in Eq. I.11 [m^3]; Characteristic parameter in a log-normal distribution [-] (Eq. VI.25)

$\chi(E)$: Distribution function of adsorption energies in Eqs. I.4 and VII.27 [-]

δ: Parameter defined in the generalized Langmuir isotherm (Eqs. I.5 and I.6 and VII.28) [-].

δ_i: Parameter defined in Eq. E.5

Δ: Increment [-]

$\Delta\overline{G}^a$: Integral free energy of the adsorbed phase [J kg^{-1}]

$\Delta\overline{g}^a$: Differential free energy of the adsorbed phase [J mol^{-1}]

ΔH^o: Adsorption enthalpy [J mol^{-1}]

ΔS^o: Adsorption entropy [J mol^{-1} K^{-1}]

ε: Porosity [-]

$\varepsilon(d)$: Pore size density function

ε_i: Parameter defined in Eq. E.6

ϕ_v: Volumetric gas flow [cm^3 (STP) min^{-1}]

Φ: Surface potential in the zeolite pores [J kg^{-1}]; Parameter defined in Eq. VI.11 [mol m^{-4} s^{-1} Pa^{-1}]

γ: Activity coefficient [-]; Shear rate [s^{-1}]

γ_i^{∞}: Activity coefficient at infinite dilution

Γ: Gamma function [-]

Γ_{ij}: Thermodynamic factors between species **i** and **j** according to Eq. I.43

η: Dimensionless z-coordinate [-]

φ: Origin ordinate in Eq. VI.71 [mol m^{-2} s^{-1} Pa^{-1}],

K: Adsorption constant [Pa^{-1}]

K_f: Constant in Freundlich isotherm in Eqs. I.8

K_∞: Pre-exponential factor in Eqs. I.6

λ: Mean-free path of the molecules [m]; Displacement of an adsorbed molecule in Eq. I.36 [m]; Slope in Eq. VI.70 [mol m^{-2} s^{-1} Pa^{-2}]

μ: Chemical potential of the adsorbate [J mol^{-1}]; Viscosity [kg m^{-1} s^{-1}]

μ': Chemical potential of the adsorbent [J kg^{-1}]

μ_D: Dipole moment [debbye]

ν: Jump frequency [s^{-1}]; Exponent in Eq. VI.14; Relative frequency [-]

π: Spreading pressure [N m^{-1}]

Π: Reduced pressure [-]

θ: Fractional occupancy [-]; Contact angle [º]; Time lag [s]

$\bar{\theta}$: Mean fractional occupancy in a particle [-]

$\bar{\bar{\theta}}$: Mean fractional occupancy in a bed of particles [-]

ρ: Density [kg m^{-3}]

σ: Surface tension [N m^{-1}]

σ_i: Parameter defined in Eq. E.7 [Å]

τ: Tortuosity [-]; Shear stress [Pa]

Ω_D: Collision integral [-]

ξ: Variable defined in Eq. E.12

Ψ: Parameter defined in Eq. VI.10 [mol m^{-3} s^{-1} Pa^{-1}]; Integral free energy relative to saturation loading (Eq. VII.15) [J mol^{-1}]

∇: Nabla operator [m^{-1}]

Subscripts:

ads: Adsorption

b: Bed

bl: Blank

bulk: Bulk

C: Capillary

DNPE:	Di-n-pentylether
E:	Ethanol
eff:	Effective
eq:	Equilibrium
G:	Gas
in:	Inner
inter:	Intercrystalline
Kn:	Knudsen
L:	Liquid
M:	Membrane layer
m:	Mean; Molecule; Mixture
min:	Minimum
max:	Maximum
o:	Feed in a membrane module; Inlet
p:	Particle
1-pent:	1-pentanol
S:	Support or solid
surf:	Surface
T:	Total
v:	Vapor
w:	Water
V:	Vacancy
ZA:	Zeolite A

Superscripts:

a:	Adsorbate
C:	Capillary
D:	Diffusion
E:	Ethanol
in:	Inlet of the packed bed
Kn:	Knudsen
L:	Langmuir
m:	Molecule / solute
max:	Maximum
min:	Minimum
o:	Standard state or unary isotherm
out:	Outlet of the packed bed
P:	Permeate
R:	Retentate

S: Surface or support
T: Total
V: Viscous
W: Water

Acronyms

AFM: Atomic force microscopy
BET: Brunauer-Emmett-Teller isotherm
C: Continuous
CF: Centrifugal field
D: Dialysis
DNPE: Di-n-pentyl ether
DSC: Differential scanning calorimetry
ED: Electrodialysis
EDS: Energy dispersive spectroscopy
EMD: Equilibrium molecular dynamics
EMT: External mass transfer
ESR: Electron spin resonance
FESEM: Field energy electron microscopy
GF: Generalized Freundlich isotherm
GS: Gas separation
GMS: Generalized Maxwell-Stefan
HPLC: High performance liquid chromatography
IAST: Ideal Adsorbed Solution Theory
IMT: Internal mass transfer
INN: Inner-side membrane
LF: Langmuir-Freundlich isotherm
LG: Generalized Langmuir isotherm
MF: Microfiltration
MS: Maxwell-Stefan
NF : Nanofiltration
NEMD: Non-equilibrium molecular dynamics
NSE: Neutron spin-echo
NMR: Nuclear magnetic resonance
OBMC: Orientational-Bias Monte Carlo
OUT: Outer-side membrane
PCS: Photon correlation spectroscopy
PFG-NMR: Pulse field gradient nuclear magnetic resonance
PRAST: Predictive Real Adsorbed Solution Theory

PSD :	Pore size distribution
PTI:	Potential Thermodynamic Isotherm
PV:	Pervaporation
QENS:	Quasi-elastic neutron scattering
RAST:	Real Adsorbed Solution Theory
RO:	Reverse osmosis
SAC:	Steam-Assisted crystallization
SANS:	Small-angle neutron scattering
SBU:	Secondary building unit
SC:	Semi-continuous
SDA:	Structure directing agent
SEM:	Scanning electron microscopy
SGPV:	Sweep gas pervaporation
SQ:	Sum of squares
SSU:	Structural subunit
T:	Tóth isotherm
TEM:	Transmission electron microscopy
TEOM:	Tapered oscillating microbalance measurements
TGA:	Thermogravimetric analyzer
UF:	Ultrafiltration
UFDR:	Ultrasonic frequency domain reflectometry
VLE:	Vapor-liquid equilibrium
VP:	Vapor permeation
VPT:	Vapor Phase Transport
VPV:	Vacuum pervaporation
XRD:	X-ray diffraction
XRF:	X-ray fluorescence