



# Single and binary surface diffusion permeation through zeolite membranes using new Maxwell-Stefan factors for Dubinin-type isotherms and occupancy-dependent kinetics



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## ABSTRACT

The development of accurate mass transfer models is essential to describe and, most importantly, to predict the dynamic behavior of separation and reaction processes. In this work, the Maxwell-Stefan (MS) thermodynamic factors for Dubinin-Astakhov (DA) and Dubinin-Radushkevich (DR) isotherms are derived for the first time, with the objective to model the permeation of pure and mixed gases through zeolite membranes, which implies reliable kinetic and equilibrium data/equations. The new MS expressions are validated using equilibrium and permeation data for (methane, ethane)/silicalite-1 systems according to the following procedure: (i) the best modeling approaches for single DA and DR isotherms are determined; (ii) the binary DA and DR isotherms are then predicted from pure gas data; (iii) the influence of surface loading on the diffusivity of permeating species is carefully assessed; (iv) the diffusion parameters of each gas are obtained from unary permeation data; (v) the MS counter-sorption diffusivities are then predicted using the Vignes correlation; finally (vi) the separation of methane/ethane mixtures in the silicalite-1 membrane is totally predicted using the new MS thermodynamic factors combined with the binary isotherms. The results achieved for the permeation of pure methane, pure ethane, and methane/ethane mixtures reveal that the new MS factors are able to correlate data of single gases and accurately predict binary permeation through silicalite-1 membrane, particularly if DA is selected. The calculated root mean square deviations are only  $8.75 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$  in the first case and  $1.55 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$  for prediction.

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## 1. Introduction

Membrane-based processes provide significant alternatives for energy-intensive thermally driven separation techniques such as those found in petrochemical and commodity chemical industries. Despite the high level of maturity of these industries, in some cases, energy consumption can be reduced by one order of magnitude using membranes for long term operation [1,2]. In particular, gas separation membranes are attracting increasing interest due to lower industrial costs and their contribution to attenuate environmental impact associated to growing energy demands. For instance, membranes are fit for concentration/purification of hydrogen (alternative fuel) and for carbon dioxide capture [3–5].

Polymeric membranes are the most utilized for gas separation due to their low production costs, high fluxes and mechanical

flexibility. Nonetheless, in general they experience short lifetimes due to low thermal and chemical stabilities, and are affected by the limiting trade-off between permeability and selectivity [6] as illustrated by the well-known Robeson's upper bound [7]. Microporous inorganic zeolites and zeotype materials have attracted great attention in the last years, due to the wide range of possible applications as membranes, catalysts, ion exchangers, adsorbents, chemical sensors, electrodes, optoelectronic devices, low dielectric constant materials for insulation and protection layers [2,8–11]. Their well-documented properties make them suitable and highly desirable for gas separation. One may cite, for instance, the uniform pore size distribution, high thermal and chemical stabilities, high internal surface area, and ease of regeneration by thermal, pressure or other swing adsorption approaches [12]. The separation mechanisms in zeotype materials rely on molecular sieving, chemical affinity between solutes and surface, and intraparticle kinetic features of the system, which allow the fractionation of non-

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## Nomenclature

$a$	parameter in DA and DR isotherms ( $\text{mol kg}^{-1}$ ) – Eq. (13)	$\mathfrak{R}$	universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$A, B$	parameter in Eqs. (28)–(31)	$S$	membrane surface area ( $\text{m}^2$ )
$[B^s]$	matrix of inverted MS diffusivities ( $\text{m}^{-2} \text{s}$ )	SCS	strong confinement scenario
$b_k$	adsorption equilibrium/affinity constant ( $\text{Pa}^{-1}$ ); $k = \text{Langmuir or Nitta}$	$T$	absolute temperature (K)
$b$	parameter in DA and DR isotherms ( $\text{mol kg}^{-1} \text{K}^{-1}$ ) – Eq. (13)	$T_b^0$	normal boiling point
$c$	parameter in DA and DR isotherms ( $\text{J mol}^{-1}$ ) – Eq. (14)	$U_i, V_{ij}, W_{ij}$	parameters of Eqs. (36)–(38)
$C$	parameter in Eq. (24)	$V_m$	liquid molar volume ( $\text{m}^3 \text{mol}^{-1}$ ) – Eq. (15)
$d$	parameter in DA and DR isotherms ( $\text{J mol}^{-1} \text{K}^{-1}$ ) – Eq. (14)	$W_0$	micropore volume ( $\text{m}^3$ ) – Eq. (15)
$Det$	parameter in Eqs. (26) and (27)	WCS	weak confinement scenario
$D^s$	Fick surface diffusivity ( $\text{m}^2 \text{s}^{-1}$ )	$x$	adjustable parameter – Eq. (18)
$\mathfrak{D}^s$	MS surface diffusivity ( $\text{m}^2 \text{s}^{-1}$ )	<i>Greek letters</i>	
$\mathfrak{D}_0^s$	pre-exponential term of MS surface diffusivity ( $\text{m}^2 \text{s}^{-1}$ ) – Eqs. (4) and (35)	$\delta$	thickness (m)
DA	Dubinin-Astakhov	$\varepsilon$	porosity
DR	Dubinin-Radushkevich	$\phi$	adsorption potential in DA and DR isotherms ( $\text{J mol}^{-1}$ )
$E$	adsorption energy ( $\text{J mol}^{-1}$ )	$\Gamma$	thermodynamic factor of Maxwell-Stefan model
$E_a^s$	activation energy for surface diffusion ( $\text{J mol}^{-1}$ ) – Eqs. (4) and (35)	$\theta$	fractional occupancy in the solid
$d_p$	average pore diameter (m)	$\rho_p$	density of zeolite top layer ( $\text{kg m}^{-3}$ )
$f$	fugacity (Pa)	$\chi$	parameter – Eq. (9)
$m$	adjustable parameter – Eq. (35)	$\nabla$	gradient operator ( $\text{m}^{-1}$ )
MS	Maxwell-Stefan	<i>Subscripts</i>	
$N^s$	molar flux by surface diffusion ( $\text{mol m}^{-2} \text{s}^{-1}$ )	0	reference condition; relative to pre-exponential variable
NC	number of components in a mixture	b	relative to boiling point
$n_{\text{Nit}}$	parameter of Nitta isotherm	c	critical
$n$	heterogeneity parameter of DA isotherm	feed	feed
NDAT	number of data points	ij	species $i$ and $j$
$P$	total pressure (Pa)	interf	interface
$P^\sigma$	pseudo-saturation pressure (Pa)	L	Langmuir
$p_i$	partial pressure of species $i$ (Pa)	Nit	Nitta
$Q_{\text{He}}$	helium (sweep gas) molar flow rate ( $\text{mol s}^{-1}$ )	perm	permeate
$Q_{\text{st}}$	isosteric heat of adsorption (Langmuir model) or heat of adsorption (Nitta model) ( $\text{J mol}^{-1}$ )	sat	saturation
$q$	molar concentration of adsorbed species in the solid ( $\text{mol kg}^{-1}$ )	supp	support
$R^2$	coefficient of determination	zeol	zeolite
$R_{\text{adj}}^2$	adjusted coefficient of determination	<i>Superscripts</i>	
RMSD	root mean square deviation	calc	calculated value
		exp	experimental value
		s	relative to surface diffusion mechanism
		$\sigma$	relative to saturation condition

condensable inorganic and/or condensable organic gases such as, for example,  $\text{H}_2/\text{CH}_4$  [13,14],  $\text{H}_2/\text{CO}_2$  [15,16] and  $\text{CO}_2/\text{CH}_4$  [17,18].

The transport mechanisms behind gas permeation in porous membranes are intimately connected with average pore size diameter ( $d_p$ ). When  $d_p > 50$  nm (macropores) viscous flow dominates and the fluid moves as a whole. For smaller diameters,  $2 < d_p < 50$  nm (mesopores), collisions between molecules and pore walls prevail and thus transport falls in the Knudsen diffusion regime [19]. In micropores,  $d_p < 2$  nm, the influence of the force field inside the pore is dominant over the molecules, therefore diffusion becomes an activated process with two possible mechanisms: activated gaseous diffusion or, if the interaction potential is so strong that molecules may lose their gaseous identity, surface diffusion [19,20].

Modeling of adsorption-based surface diffusion is currently described in the literature by three approaches: the Fick's law, the Onsager theory of irreversible thermodynamics, and the generalized Maxwell-Stefan (MS) theory [21]. Fick's law assumes the concentration gradients are the driving forces for mass transfer and ignores friction forces between distinct diffusing species, thus being suitable only for single component systems. The Onsager theory contemplates the non-idealities by adopting chemical potential gradients; the cross-coefficients of its  $[L]$  matrix portray

the coupling between species diffusion. However, this theory provides no fundamental guidelines for estimating  $[L]$  from unary transport data, which means it is only appropriate for multicomponent systems with negligible interactions between permeating molecules. The generalized Maxwell-Stefan (MS) approach is totally consistent with the theory of irreversible thermodynamics, and considers both non-idealities and frictions forces. It extends the well-known Dusty Gas Model [22,23] to surface diffusion, being generally preferred for multicomponent transport [19,24]. Both Fick and Onsager matrices may be estimated from the knowledge of MS diffusivities for pure components.

For permeating molecules in micropores, the surface MS flux can be expressed in matrix form as [67]:

$$(N^s) = -\rho_p [q_{\text{sat}}] [B^s]^{-1} [\Gamma] (\nabla \theta) \quad (1)$$

$$B_{ij}^s = \frac{1}{\mathfrak{D}_i^s} \sum_{j=1, j \neq i}^n \frac{\theta_j}{\mathfrak{D}_{ij}^s}, \quad B_{ij}^s = -\frac{\theta_i}{\mathfrak{D}_{ij}^s}, \quad [q_{\text{sat}}] = \begin{bmatrix} q_{\text{sat},i} & 0 \\ 0 & q_{\text{sat},j} \end{bmatrix} \quad (2)$$

where superscript  $s$  denotes surface, subscripts  $i$  and  $j$  represent generic components of the gas mixture,  $\rho_p$  is the solid density,

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