

The Generalized Maxwell-Stefan Model Coupled with Vacancy Solution Theory of Adsorption for Diffusion in Zeolites

Seyyed Milad Salehi^{1*} and Mahmood Reza Rahimi²

¹ Department of Chemical Engineering, Masjed-Soleiman Branch, Islamic Azad University, Masjed Soleiman, Iran

² Department of Chemical Engineering, Yasuj University, Yasuj, Iran

Received: October 05, 2013; revised: November 03, 2013; accepted: November 27, 2013

Abstract

It seems using the Maxwell-Stefan (M-S) diffusion model in combination with the vacancy solution theory (VST) and the single-component adsorption data provides a superior, qualitative, and quantitative prediction of diffusion in zeolites. In the M-S formulation, thermodynamic factor (T) is an essential parameter which must be estimated by an adsorption isotherm. Researchers usually utilize the simplest form of adsorption isotherms such as Langmuir or improved dual-site Langmuir, which eventually cannot predict the real behavior of mixture diffusion particularly at high concentrations of adsorbates because of ignoring nonideality in the adsorbed phase. An isotherm model with regard to the real behavior of the adsorbed phase, which is based on the vacancy solution theory (VST) and considers adsorbate-adsorbent interactions, is employed. The objective of this study is applying vacancy solution theory to pure component data, calculating thermodynamic factor (T), and finally evaluating the simulation results by comparison with literature. Vacancy solution theory obviously predicts thermodynamic factor better than simple models such as dual-site Langmuir.

Keywords: Adsorption, Maxwell-Stefan, Thermodynamic Factor, Vacancy Solution Theory

1. Introduction

With an increase in adsorbent and catalyst applications, the proper description of intracrystalline diffusion has become more important due to its influence on the selectivity of separations and reactions (Ruthven, 1984). The Maxwell-Stefan (M-S) equations are widely used to describe mixture diffusion in zeolites only by pure adsorption isotherm data (Kazemimoghadam and Mohammadi, 2011; Krishna and Van Baten, 2005; Kangas et al., 2013):

$$-\nabla\mu_i = RT \sum_{\substack{j=1 \\ j \neq i}}^n \theta_j \frac{u_i - u_j}{D_{ij}^s} + RT \frac{u_i}{D_i^s}, \quad i = 1, 2, \dots, n \quad (1)$$

where, $-\nabla\mu_i$ is the force acting on species i tending to move along the surface with a velocity of u_i (chemical potential gradients). D_{ij}^s and D_i^s represent the corresponding Maxwell-Stefan surface diffusivities and $\theta = q_i/q_i^{sat}$ is fractional coverage. The chemical potential gradients can be expressed in terms of the gradients of the occupancies by the introduction of thermodynamic factor (T) (Equation 5). Therefore, a model for the estimation of thermodynamic factor is necessary. It is noted

* Corresponding Author:
Email: milad.salehi@iaumis.ac.ir

that thermodynamic factor (Γ) can be obtained by choosing an adsorption isotherm to relate the bulk fluid phase pressure and the fractional loading of components. This adsorption isotherm should be valid for the whole range of adsorption. Vanden Broeke and Krishna (1995) used Langmuir isotherm to obtain Γ ; Kapteijn et al. (2000) used ideal adsorbed solution (IAS) to estimate thermodynamic factor. Krishna et al. (2004) employed dual-site Langmuir model, while Li et al. (2007) utilized statistical thermodynamics to calculate thermodynamic factor. Patricia et al. (2011) used Toth and Langmuir–Freundlich isotherms to predict thermodynamic factor. However, none of these isotherm models has been confirmed to be the most precise model for the prediction of the thermodynamic factor of M-S equation. Langmuir, Toth, and dual-site Langmuir isotherms or ideal adsorbed solution theory are too simple for the accurate prediction of thermodynamic factor especially at high concentrations of adsorbates. Equations of statistical thermodynamics are not easy to handle either. However, it seems vacancy solution theory can predict thermodynamic factor better than those models due to considering nonideality in the adsorbed phase. In this study, VST was used to calculate thermodynamic factor by pure component parameters and eventually the results were compared with other simulation data and dual-site Langmuir model.

2. Theory

The fractional coverage is converted into flux using Equation 2:

$$N_i \equiv \rho q_i^{sat} \theta_i u_i = \rho q_i u_i \quad (2)$$

By dropping the superscripts for the surface diffusivities in the M-S expression for convenience (Equation 1) and multiplying both sides by θ_i/RT , Equation 1 reforms into:

$$-\frac{\theta_i}{RT} \nabla \mu_i = \sum_{j=1}^n \theta_i \theta_j \frac{u_i - u_j}{D_{ij}} + \frac{\theta_i u_i}{D_i} = \sum_{j=1}^n q_i q_j \frac{u_i - u_j}{q_i^{sat} q_j^{sat} D_{ij}} + \frac{q_i u_i}{q_i^{sat} D_i}, \quad i=1,2,\dots,n \quad (3)$$

Using the definition of the flux, Equation 2 leads to:

$$-\rho \frac{\theta_i}{RT} \nabla \mu_i = \sum_{j=1}^n \frac{q_j N_i - q_i N_j}{q_i^{sat} q_j^{sat} D_{ij}} + \frac{N_i}{q_i^{sat} D_i}, \quad i=1,2,\dots,n \quad (4)$$

The gradient of the thermodynamic potential can be expressed in terms of thermodynamic factors (Krishna, 1993):

$$\frac{\theta_i}{RT} \nabla \mu_i = \sum_{j=1}^n \Gamma_{ij} \nabla \theta_j, \quad \Gamma_{ij} \equiv \frac{\theta_i}{p_i} \frac{\partial p_i}{\partial \theta_j} = \theta_i \frac{\partial \ln p_i}{\partial \theta_j}, \quad i,j=1,2,\dots,n \quad (5)$$

An isotherm model with regard to the real behavior of the adsorbed phase is based on the vacancy solution theory (Suwanayuen and Danner, 1980). By using Wilson equation for expressing the nonideality of the adsorbed phase, the general form of the model for the adsorption of pure component is given by:

$$p = \left[\frac{q_i^{sat}}{b_i} \frac{\theta}{1-\theta} \right] \left[\frac{\Lambda_{iv} (1 - (1 - \Lambda_{vi}) \theta)}{\Lambda_{iv} + (1 - \Lambda_{iv}) \theta} \right] \exp \left[- \frac{\Lambda_{vi} (1 - \Lambda_{vi}) \theta}{1 - (1 - \Lambda_{vi}) \theta} - \frac{(1 - \Lambda_{iv}) \theta}{\Lambda_{iv} + (1 - \Lambda_{iv}) \theta} \right] \quad (6)$$

where, subscript i refers to the adsorbate and v stands for the vacancy. p , q_i^{sat} , b_i , and θ represent the equilibrium pressure, the limiting adsorption amount, Henry's constant, and the fractional coverage respectively. Λ_{iv} and Λ_{vi} are the Wilson parameters. Thus the vacancy solution theory has four parameters, namely q_i^{sat} , b_i , Λ_{iv} , and Λ_{vi} , which can be obtained by a nonlinear regression if isotherm data are available. These parameters for vacancy solution theory are determined by a nonlinear

regression using the least squares method. The nonlinear least squares programs were solved using Levenberg-Marquardt or Gauss-Newton algorithms. A computational program written in Matlab (Constantinides and Mostoufi, 1999) was used to determine the adsorption parameters of each adsorption isotherm by minimizing the following objective function:

$$\Theta = \frac{1}{2} \sum_i^{NPTS} (q_i^{cal} - q_i^{expt})^2 \quad (7)$$

where, q_i^{cal} and q_i^{expt} are the calculated and experimental amounts of adsorbed components respectively, and $NPTS$ is the number of experimental points.

3. Results and discussion

3.1. Pure adsorption isotherm

The adsorption isotherms of pure CF_4 and CH_4 in MFI (298 K) and FAU (300 K) are respectively presented in Figures 1 and 2, which are obtained by GCMC simulation (Skoulidas and Sholl, 2001-2002) and are correlated by the vacancy solution theory (VST). The correlated parameters are given in Table 1. According to the Brunauer classification of isotherms, methane and carbon tetra fluoride isotherms closely resemble to the type I isotherms. Therefore, the pore size of zeolite particles is not much larger than the molecular diameter of the adsorbate (Yang, 1986). This shows that the adsorbate-adsorbent interactions are more significant than adsorbate-adsorbate interactions and hence the former cannot be ignored. Consequently, an isotherm model considering these interactions should be advantageous. The VST model take these interactions into account (parameters A_{iv} and A_{vi} in Table 1).

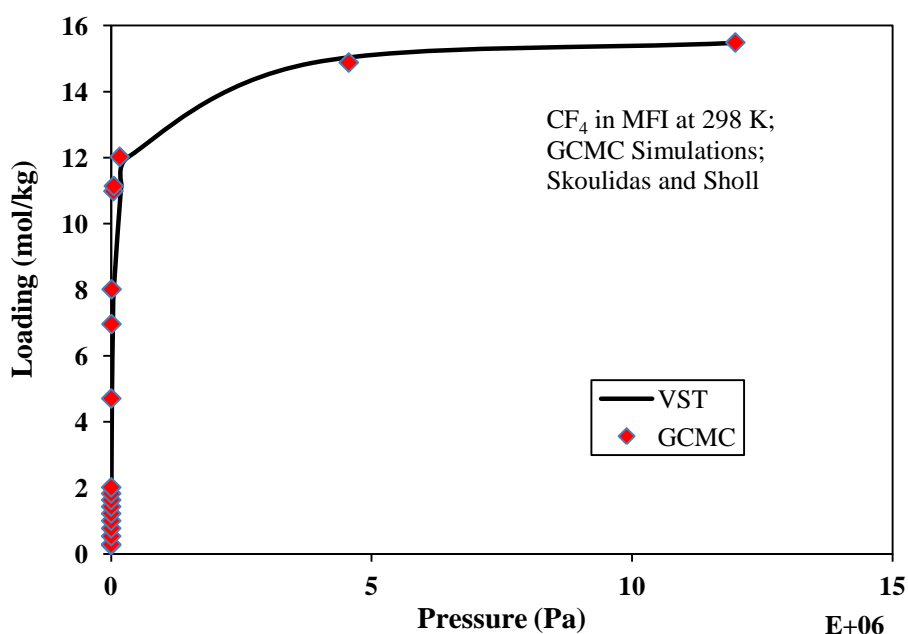
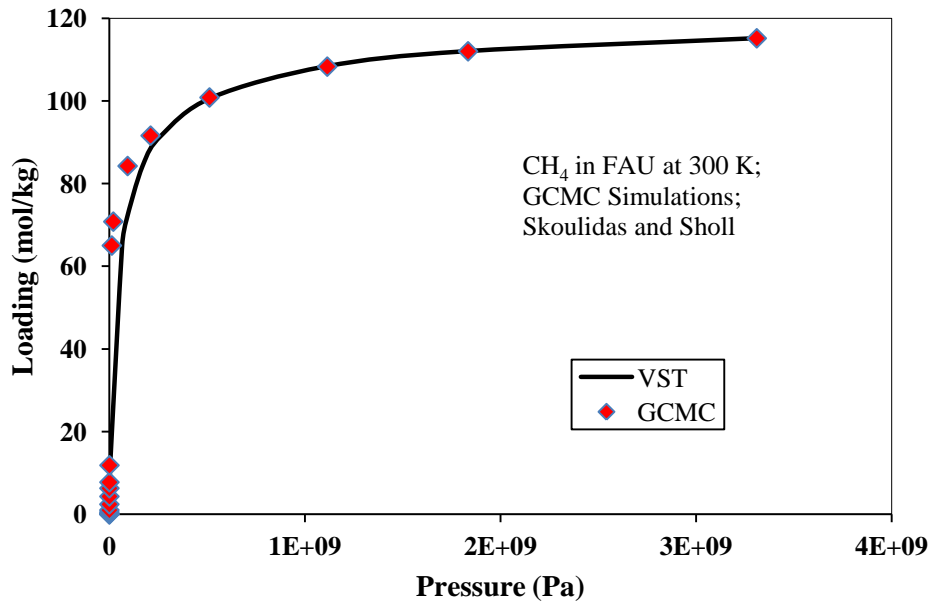


Figure 1

The adsorption isotherm of CF_4 in MFI at 298 K; the symbols represent the GCMC simulations (Skoulidas and Sholl, 2001-2002) and the continuous line represents the VST fit of the isotherm with the parameters specified in Table 1.

**Figure 2**

The adsorption isotherm of CH_4 in FAU at 300 K; the symbols represent the GCMC simulations (Skoulidas and Sholl, 2001-2002) and the continuous line represents the VST fit of the isotherm with the parameters specified in Table 1.

Table 1

Regression results of pure adsorption on zeolite MFI and FAU by using vacancy solution theory.

Adsorbent	Molecule	Temperature(K)	$q_i^{sat,\infty} (\frac{mol}{kg})$	$b_i (\frac{mol}{kg.Pa})$	A_{iv}	A_{vi}
MFI- Zeolite	CF_4	298	15.99	$7.07\text{E-}5$	3.41	0.78
FAU-Zeolite	CH_4	300	120.10	$3.45\text{E-}6$	4.10	0.11

3.2. Model Analysis

Thermodynamic factor (I) was calculated by using Equations 5 and 6 and the parameters tabulated in Table 1. The results were compared with dual-site Langmuir fit and GCMC simulation (Skoulidas and Sholl, 2001-2002). The thermodynamic factor (I) is a measure of the nonideality of a system. For ideal systems or very low adsorbate loadings, the thermodynamic factor (I) is close to 1 and the Fick and Maxwell-Stefan diffusivity are the same. The results of the model are shown in Figures 3 and 4. As can be seen, increasing adsorbate loading raises thermodynamic factor. Therefore, system approaches a nonideal behavior and adsorbate-adsorbent interactions cannot be ignored. Consequently, by increasing adsorbate loading the results of the VST model (which considers adsorbate-adsorbent interactions) are closer to the simulation data than dual-site Langmuir fit.

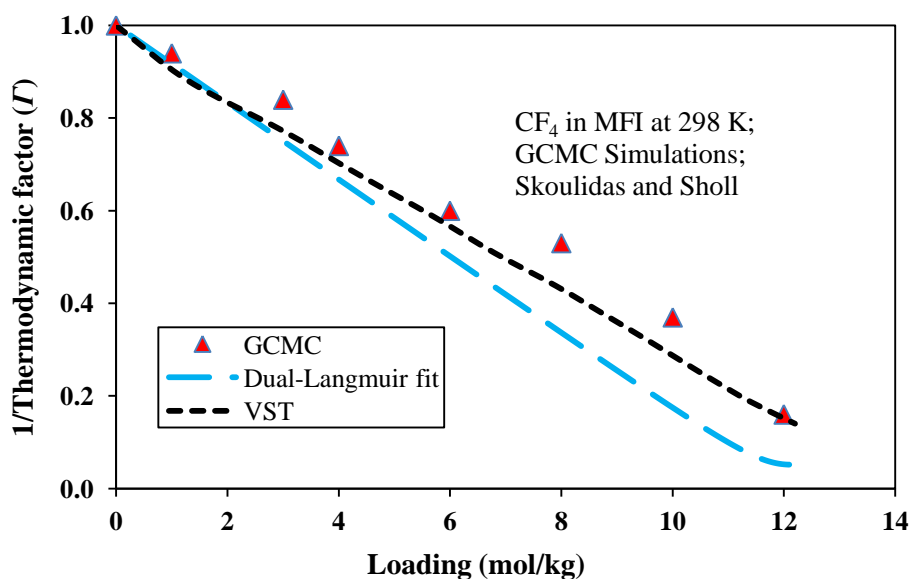


Figure 3

Comparison of VST and dual-site Langmuir fit with the simulation data (Skoulidas and Sholl, 2001-2002) for CF_4 in MFI zeolite at 298 K.

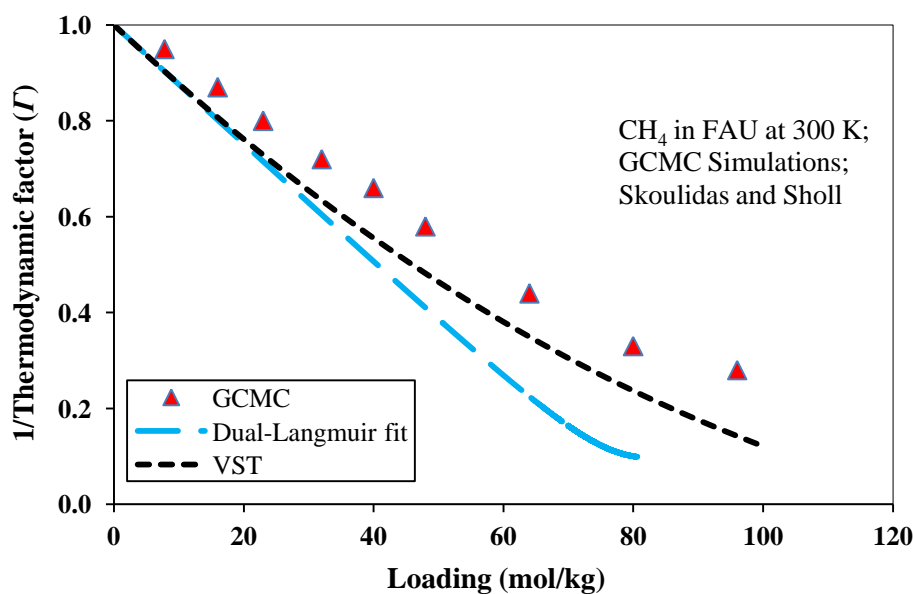


Figure 4

Comparison of VST and dual-site Langmuir fit with the simulation data (Skoulidas and Sholl, 2001-2002) for CF_4 in MFI zeolite at 298 K.

4. Conclusions

According to the Maxwell-Stefan diffusion formula, thermodynamic factor is a parameter for explaining the nonideality of a system. At low concentrations of adsorbate, simple models such as Langmuir predict thermodynamic factor fairly well but by increasing the concentration of adsorbate deviations become more evident. As a result, it seems necessary to consider adsorbate-adsorbent interactions at high concentrations of adsorbate. Hence, to obtain thermodynamic factor, vacancy solution theory with four parameters was applied. The results were obviously better than models such

as dual-site Langmuir because of considering adsorbate-adsorbent interactions in terms of A_{iv} and A_{vi} in the VST model.

Nomenclature

b_i	: Henry's constant ($\text{mol. kg}^{-1} \cdot \text{Pa}^{-1}$)
D_{ij}^s	: Binary exchange coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)
D_i^s	: Maxwell-Stefan surface diffusivity of species i ($\text{m}^2 \cdot \text{s}^{-1}$)
N_i	: Molar flux of species i across zeolite ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)
p	: The equilibrium pressure (Pa)
p_i	: Partial pressure of i in bulk vapor (Pa)
q_i	: Adsorption amount ($\text{mol} \cdot \text{kg}^{-1}$)
q_i^{sat}	: Limiting adsorption amount ($\text{mol} \cdot \text{kg}^{-1}$)
R	: Gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
T	: Absolute temperature (K)
u_i	: Velocity of species i with respect to zeolite ($\text{m} \cdot \text{s}^{-1}$)
Greek Symbols	
∇	: Delta operator (m^{-1})
μ	: The surface chemical potential ($\text{J} \cdot \text{mol}^{-1}$)
θ	: Fractional coverage (dimensionless)
Γ	: Thermodynamic correction factor (dimensionless)
ρ	: Density of zeolite ($\text{kg} \cdot \text{m}^{-3}$)
A_{iv}, A_{vi}	: Adsorbate-vacancy interaction parameters (dimensionless)
Subscripts and Superscripts	
i, j and n	: Component
sat	: Value at maximum adsorption limit
s	: Refer to surface phase
v	: Vacancy site

Reference

- Constantinides, A., Mostoufi, N., Numerical Methods for Chemical Engineers with MATLAB Applications, Prentice Hall: Upper Saddle River, NJ, 1999.
- Li, S., Falconer, J. L., Noble, R. D., and Krishna, R., Modeling Permeation of CO_2/CH_4 , CO_2/N_2 , and N_2/CH_4 Mixtures Across SAPO-34 Membrane with the Maxwell-Stefan Equations, Ind. Eng. Chem. Res., Vol. 46, p. 3904-3911, 2007.
- Kangas, J., Sandstrom, L., Malinen, I., Hedlund, J., and Tanskanen, J., Maxwell-Stefan Modeling of the Separation of H_2 and CO_2 at High Pressure in an MFI Membrane, Journal of Membrane Science., Vol. 435, p. 186-206, 2013.
- Kapteijn, F., Moulijn, J. A., and Krishna, R., The Generalized Maxwell-Stefan Model for Diffusion in Zeolites: Sorbate Molecules with Different Saturation Loadings, Chemical Engineering Science, Vol. 55, p. 2923-2930, 2000.
- Kazemimoghadam, M. and Mohammadi, T., A Modeling Approach Based on the Maxwell-Stefan Theory for Pervaporation Using Homemade Nanopore NaA Zeolite Membranes, Desalination, Vol. 281, p. 298-305, 2011.
- Krishna, R. and Van Baten, J. M., Diffusion of Alkane Mixtures in Zeolites: Validating the Maxwell-Stefan Formulation Using MD Simulations, Journal of Physical Chemical Chemistry. B., Vol. 109, p. 6386-6396, 2005.
- Krishna, R., A Unified Approach to the Modeling of Intraparticle Diffusion in Adsorption Processes, Gas Separation and Purification, Vol. 7, p. 91-104, 1993.

- Krishna, R., Van Baten, J. M., and Dubbeldam, D., On the Inflection in the Concentration Dependence of the Maxwell-Stefan Diffusivity of CF_4 in MFI Zeolite, *Journal of Physical Chemical Chemistry. B*, Vol. 108, p. 14820-14822, 2004.
- Patrícia, F., L., Ana, S., S., Simão, P. C., Bruno, R. F., and Carlos, M. S., New Expressions for Single and Binary Permeation through Zeolite Membranes for Different Isotherm Models, *Journal of Membrane Science*, Vol. 367, No. 2, p. 21-32, 2011.
- Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, First Ed., John Wiley, New York, 1984.
- Skoulidas, A. I., and Sholl, D. S., Direct Tests of the Darken Approximation for Molecular Diffusion in Zeolites Using Equilibrium Molecular Dynamics, *Journal of Physical Chemical Chemistry. B.*, Vol. 105, p. 3151-3154, 2001.
- Skoulidas, A. I., and Sholl, D. S., Transport Diffusivities of CH_4 , C_2H_6 , He, Ne, Ar, Xe, and SF_6 in Silicalite from Atomistic Simulations, *Journal of Physical Chemical Chemistry. B.*, Vol. 106, p. 5058-5067, 2002.
- Suwanayuen, S. and Danner, R. P., A Gas Adsorption Isotherm Equation Based on Vacancy Solution Theory, *AIChE Journal*, Vol. 26, p. 68-75, 1980.
- Van den broeke, L. J. P. and Krishna, R., Experimental Verification of the Maxwell-Stefan Theory for Micropore Diffusion, *Chemical Engineering Science*, Vol. 50, p. 2507-2522, 1995.
- Yang, R. T., *Gas Separation by Adsorption Processes*, First Ed., Butterwoths, Boston, 1986.