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Reactive vacancy solution theory for correlation and prediction of adsorption equilibria for physical and chemical adsorptions

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ABSTRACT

An isotherm equation was developed in the framework of the vacancy solution theory. In the model, vacancies in the adsorbed phase are dealt with as a kind of reactive entity, which leads to more flexible adsorption isotherm equations. The model can be called as reactive vacancy solution theory (RVST). Practical RVST equations for single-component and binary-component adsorption systems were derived by using Wilson, NRTL and UNIQUAC equations for activity coefficients. The RVST equations were found to coincide with the Langmuir–Freundlich equation when the effect of activity coefficients is assumed to be negligible. Furthermore, it was also found that the RVST model conforms to several simple-theoretical or empirical isotherm equations when the model is simplified. Therefore, it can be stated that the reactive vacancy solution theory can be regarded as more universal and general mathematical description of adsorption equilibria. Validity of the RVST equations for single-component adsorption was tested. The results reveal that the RVST-W and RVST-N equations can appropriately correlate non-ideal adsorption equilibrium data.

1. Introduction

The vacancy solution theory (VST) was first proposed by Suwanayen and Danner [1,2]. They revealed that the theory provides accurate correlation and predictions of adsorption equilibria. A particularly appealing aspect of the vacancy solution theory is its ability to predict highly non-ideal adsorption equilibria. Recently, Munakata derived a vacancy solution theory based on the NRTL equations for activity coefficients [3] and revealed its applicability for correlation of adsorption isotherms [4,5]. The vacancy solution theory was somewhat refined by other authors as well [6,7]. In this work, the author proposes a methodology to deal with vacancies in adsorption phases as a sort of reactive entity and derives more flexible adsorption isotherm equations based on rigid thermo-dynamical consideration. Furthermore, the validity of the equations for single-component adsorption was tested using experimental data.

2. Theory

2.1. Governing equations

We often encounter experimental adsorption isotherms that do not conform to the Henry law even if the partial pressure of an adsorbate is small. Then, it is not known whether the adsorption system conforms to the Henry law in the infinitesimal dilution of the adsorbate of interest, since there are detection limits of experimental apparatus. This type of isotherms is also observed in the case of chemisorptions or adsorption on heterogeneous sorption sites, which takes place via chemical dissociation of adsorbates or formation of clusters of adsorbates in adsorption phases [8]. Fig. 1 shows visual examples of adsorption phenomena. The stoichiometry of the adsorptions can be generally expressed as

$$\nu \mathrm{A} + \sigma \rightleftarrows (\nu \mathrm{A} \cdot \sigma) \tag{1}$$

where A, ν and σ represent adsorbate molecule, stoichiometry factor and adsorption site, respectively. The above equation indicates that

$0 < \nu < 1$: dissociative adsorption
$\nu = 1$: purely physical adsorption
$\nu > 1$: cluster formation in adsorption.

The theoretical consideration is directly started from the viewpoint of multi-component adsorption based on the vacancy solution theory proposed by Suwanayen and Danner [2] but the derivation of equations progresses in a different way. With regard to the expression of the chemical potential of a component in the surface phase, the author uses the methodology given by Lucassen–Reynders [9]. The chemical potential of component i ($i = 0$: vacancy, $i \neq 0$: adsorbate) in the surface phase is given by

$$\mu_i^s = \mu_i^{s,0} + RT\ln\left(\gamma_i^s x_i^s\right) + \pi\bar{a}_i. \tag{2}$$

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Nomenclature

$\overline{a}_i$	partial molar surface area [m^2/mol]
A	surface area of adsorbent [m^2/g]
b_i	temperature dependent constant for each sorbate-adsorbent system [mol/(g Pa$^{-\nu i}$)]
$b_{0,i}$	temperature independent constant for each sorbate-adsorbent system [mol/(g Pa)]
E_i	energy terms related to b_i [J/mol]
g_{ij}	pair interaction energy between i and j molecules for NRTL model [J/mol]
ΔG_i^0	standard Gibbs energy for adsorption [J/mol]
n_i^s	number of moles in surface phase [mol/g]
$n_i^{s,\infty}$	maximum number of moles in surface phase [mol/g]
N	total number of adsorbate
P	total pressure [Pa]
p_i	partial pressure of i in vapor phase [Pa]
r_i	UNIQUAC structural parameter [−]
R	gas constant (=8.31) [J/mol K]
q_i	UNIQUAC structural parameter [−]
T	temperature [K]
u_{ij}	pair interaction energy between i and j molecules for UNIQUAC model [J/mol]
V_i^L	molar liquid volume (m^3/mol)
x_i	molar fraction in vacancy-free adsorbed phase [−]
y_i	molar fraction of vacancy-free vapor phase [−]
z	coordination number in UNIQUAC model [−]
α_{ij}	NRTL parameter [−]
λ_{ij}	pair interaction energy between i and j molecules for Wilson model [J/mol]
μ_i^g	chemical potential of i in gas phase [J/mol]
$\mu_i^{g,0}$	standard chemical potential of i in gas phase [J/mol]
μ_s^g	chemical potential of i in surface phase [J/mol]
$\mu_i^{s,0}$	standard chemical potential of i in surface phase [J/mol]
θ_i	fractional coverage of i ($=n_i^s/n_i^{s,\infty}$) [−]
γ_i^s	activity coefficient in adsorbed phase [−]
ν_i	stoichiometric factor for adsorption of i
Λ_{ij}	Wilson parameters for interaction between i and j [−]
ϕ_i	fugacity coefficient in gas phase [−]
π_i	spreading pressure [N/m]

Subscript

i	number of component ($i=0$: vacancy, $i\neq0$: number of adsorbate)

The chemical potential of component i in the gas phase is

$$\mu_i^g=\mu_i^{g,0}+RT\ln(P\phi_i y_i). \tag{3}$$

When the system is in equilibrium, both chemical potentials have to be equal. As far as purely physical adsorption is concerned, the equilibrium leads to

$$\mu_i^g=\mu_i^s. \tag{4}$$

However, in more general cases shown as Eq. (1), consideration of stoichiometry in adsorption results in

$$\nu_i\mu_i^g=\mu_i^s. \tag{5}$$

In the above equation, the vacancy in the adsorption phase is regarded as a sort of reactive entity on the surface of adsorbents. An equilibrium equation governing the distribution of an adsorbate between the adsorbed and gas phase is obtained by inserting Eqs. (2) and (3) to Eq. (5).

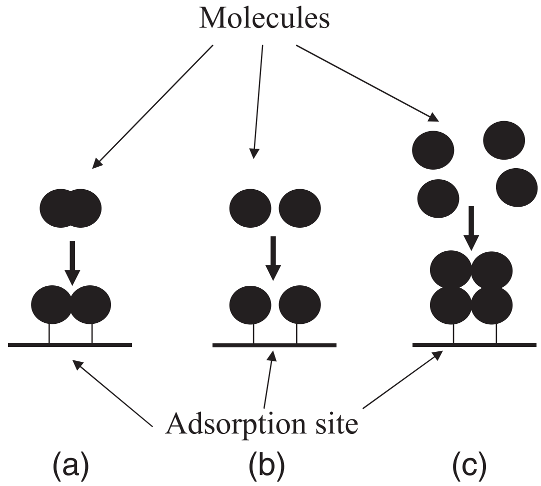

Fig. 1. Visual images of several types of adsorption. (a) Dissociative adsorption. (b) Purely physical adsorption. (c) Adsorption via cluster formation.

$$\nu_i\left[\mu_i^{g,0}+RT\ln(P\phi_i y_i)\right]=\mu_i^{s,0}+RT\ln\left(\gamma_i^s x_i^s\right)+\pi\overline{a}_i. \tag{6}$$

The above equation is rearranged as

$$\left(P\phi_i^g y_i\right)^{\nu_i}=\gamma_i^s x_i^s\exp\left(\frac{\Delta G_i^0}{RT}\right)\exp\left(\frac{\pi\overline{a}_i}{RT}\right) \tag{7}$$

$$\Delta G_i^0=\mu_i^{s,0}-\nu_i\mu_i^{g,0}. \tag{8}$$

In the original vacancy solution theory [2], the following approximation was assumed.

$$\overline{a}_0=\overline{a}_i \tag{9}$$

However, in this work, the partial molar area of adsorbates is considered to be unequal to the partial molar area of vacancy.

$$\overline{a}_0\neq\overline{a}_i. \tag{10}$$

The spreading pressure expressed in terms of vacancy [2] is given by

$$\pi=-\frac{RT}{\overline{a}_0}\ln\left(\gamma_0 x_0^s\right). \tag{11}$$

Inserting Eqs. (11) and (7) leads to

$$\left(P\phi_i^g y_i\right)^{\nu_i}\exp\left(-\frac{\Delta G_i^0}{RT}\right)=\frac{\gamma_i x_i^s}{\left(\gamma_0 x_0^s\right)^{\overline{a}_i/\overline{a}_0}}. \tag{12}$$

The surface coverage of component i is defined as

$$\theta_i=\frac{n_i^s}{n_i^{s,\infty}}. \tag{13}$$

The molar surface areas are given as

$$\overline{a}_i n_i^{s,\infty}=A. \tag{14}$$