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A Modified Peng-Robinson Equation State for Prediction of Gas Adsorption Isotherm

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Abstract This research proposes a modified two-dimensional Peng-Robinson equation model to predict adsorption isotherm in adsorbate-adsorbent systems. The parameters of the proposed model are calculated by using the optimization of experimental data for the different single gas adsorption systems at various temperatures. The experimental adsorption equilibrium data of adsorbate-adsorbent systems was compared with the calculated results in our proposed model and the two-dimensional Hill-deBoer equation model. The proposed model as indicated in the results shows a better prediction of the experimental results compared with two others.

Keywords gas adsorption isotherm, Peng-Robinson equation state

1 INTRODUCTION

Man was aware of adsorption phenomena for a very long time and used it in an increasing way to perform desired bulk separation or purification purposes. A porous solid medium is usually core to the adsorption process. In describing single component of the adsorption equilibrium it is undoubtedly necessary to use a suitable isotherm equation so as to represent adsorption kinetics [1].

Such fluids as gas and liquid adsorbed on the solid surface are actually distributed on the solid surface un-uniformly and are inhomogeneous, *i.e.*, their density is a function of the distance from the solid surface. In this case, the modern density functional theory [2, 3] is a powerful tool to describe this adsorption equilibrium. However, density functional theory needs the integral equations to be solved by the numerical iterations so as to obtain density profiles of the fluids in the first place. Therefore some simplified models appear to be simple enough for real gas adsorption. This requires that the surface layer be treated as a third homogeneous phase, as done in the Flowler-Guggenheim and Langmuir models.

There are several simplified models for adsorption isotherm. Langmuir model [4] is the primary theory in adsorption; Langmuir suggested a model for adsorption of gases onto a flat surface based on a kinetic viewpoint. It is clear that Langmuir's approach is kinetic by nature, but adsorption equilibria can also be explained by the thermodynamic approach. In Gibbs approach the classical thermodynamic, in the bulk phase of the volume concept and gas pressure is replaced by the area and spreading pressure, respectively. Using Gibbs equation, a number of two dimensional isotherm equations were derived such as the Volmer isotherm [5] and the Hill-deBoor isotherm [6, 7]. Volmer used imperfect gas low-effect of covolume term in ideal equation state and Hill-deBoor obtained his model on the basis of the van der Wall's equation state. In other approach it was assumed that the surface of an adsorbent can be treated as a solvent and the adsorption process as the formation of the solution between the adsorbate and adsorbent; this model is called the vacancy solution model (VSM). Suwanayuen and Danner [8] used Wilson activity equation while Cochran *et al.* [9] used the Flory-Huggins equation that leads to one lower parameter in comparison with the original vacancy solution model. Based on the vacancy solution theory (VST) and using the non-random two liquid model (NRTL) activity coefficient model, recently Haghtalab and *et al.* [10] developed a new adsorption isotherm. Basic knowledge of classic adsorption isotherm equations as mentioned above is discussed in article of Terzyk *et al* [11].

Generally speaking, in the thermodynamic representation of adsorption equilibrium, there are two methods to describe the adsorbate-adsorbent system, either a two-dimensional gas or as a solution which is composed of adsorbate and vacancies. In this research, we followed the two-dimensional approach to develop a new isotherm using the Peng-Robinson and our proposed modified Peng-Robinson equation state. Comparison between the pressure deviation in the modified Peng-Robinson equation state and the results from this and Hill-deBoer equation model shows that the former works much better than the others.

2 THE MODIFIED TWO-DIMENSIONAL PENG-ROBINSON EQUATION MODEL

The study of gas-liquid equilibria plays an important role in solution thermodynamics. It resembles very much the study of gas-solid adsorption equilibria. Van Ness [12] considered the actual interfacial region as transformable into an imaginary mathematical surface in which the properties of the gas phase imagined to be the same until it reaches this surface which is treated as a two-dimensional phase with its own thermodynamic properties.

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According to Do [5] when the adsorbed phase is treated as a two-dimensional surface, the fundamental equations in classical thermodynamics can still be applied. Thus, the Gibbs-Duhem equation at constant temperature for a planar surface is as follows [5]

$$-A\mathrm{d}\pi + \sum_i n_i \mathrm{d}\mu_i = 0 \tag{1}$$

where A is the surface area of an adsorbent, n_i is the mole amount of species i, π is the spreading pressure, playing the same role as the pressure in the bulk phase, and μ_i is the surface chemical potential of species i. In a two-dimensional approach we have only one component (*i.e.*, an adsorbate). If this component is shown by the subscript "1," Eq. (1) can take the form below:

$$-A\mathrm{d}\pi + n_1 \mathrm{d}\mu_1 = 0 \tag{2}$$

At equilibrium, the chemical potential of the adsorbed phase is equal to that of the gas phase, which is supposed to be ideal; *i.e.*, [5]

$$\mu_1 = \mu_{1,\mathrm{g}}^{\Theta} + RT\ln\left(\frac{P}{P^{\Theta}}\right) \tag{3}$$

where P is the pressure of "1" in the gas phase and P^{Θ} is the standard pressure.

Inserting Eq. (3) into Eq. (2), the fundamental Gibbs formula is derived as follows [1],

$$\frac{\mathrm{d}\pi}{\mathrm{d}\ln P} = \frac{RT}{\sigma} = RT\frac{\theta}{\Omega_1} \tag{4}$$

where σ is equal to

$$\sigma = \frac{A}{n_1} \tag{5}$$

Ω_1 and θ represent the surface area occupied by one mole of the adsorbate molecules, and the surface coverage respectively which are as below:

$$\theta = \frac{\Omega_1}{\sigma} \tag{6}$$

Two-dimensional Peng-Robinson equation state is as follows:

$$\pi = \frac{RT}{\sigma - \Omega_1} - \frac{a}{\sigma^2 + 2\sigma\Omega_1 - \Omega_1^2} \tag{7}$$

the a is a characteristic constant, and T is the absolute temperature.

Inserting Eq. (7) into Eq. (4) the following pure-component adsorption isotherm would be resulted:

$$P = k\frac{\theta}{1-\theta}\exp\left\{\frac{\theta}{1-\theta} + C\left[\frac{\theta}{-1-2\theta+\theta^2} - \frac{\sqrt{2}}{2}\tanh^{-1}\left(\frac{\sqrt{2}}{2}(\theta-1)\right) + \frac{\sqrt{2}}{2}\tanh^{-1}\left(\frac{-\sqrt{2}}{2}\right)\right]\right\} \tag{8}$$

The Henry's law constant k in the above equation is defined as:

$$k = \lim_{\theta\to 0}\frac{P}{\theta} \tag{9}$$

where $C\left(=\frac{a}{RT\Omega_1}\right)$ is adjustable parameter.

The modified Two-dimensional Peng-Robinson equation state used in this work is as a result of introducing a parameter m into Eq. (7),

$$\pi = \frac{RT}{\sigma - \Omega_1}\left(1 + m\frac{\Omega_1}{\sigma}\right) - \frac{a}{\sigma^2 + 2\sigma\Omega_1 - \Omega_1^2} \tag{10}$$

Inserting Eq. (10) into Eq. (4) the following pure-component adsorption isotherm would be resulted:

$$P = k\frac{\theta}{(1-\theta)^{m+1}}\exp\left\{\frac{(m+1)\theta}{1-\theta} + C\left[\frac{\theta}{-1-2\theta+\theta^2} - \frac{\sqrt{2}}{2}\tanh^{-1}\left(\frac{\sqrt{2}}{2}(\theta-1)\right) + \frac{\sqrt{2}}{2}\tanh^{-1}\left(\frac{-\sqrt{2}}{2}\right)\right]\right\} \tag{11}$$

As a result, we derived Eq. (8) and then we modified Peng-Robinson equation state and Eq. (11) is derived for the prediction of adsorption isotherm in adsorbate-adsorbent systems.

3 RESULT AND DISCUSSION

The new isotherm model, Eq. (8) and Eq. (11), is tested with pure gas adsorption data for different gases such as CH_4, C_2H_6, C_3H_8, H_2S, CO_2 and water vapor on the diverse adsorbents at three different temperature. Adsorption data for 10 different systems of adsorbate-adsorbent from various sources are collected at different temperature as shown in Table 1.

Table 2 reports the parameters of each Eq. (8), Eq. (11) and Hill-deBoer equation model resulted from the least-square optimization procedure. The new isotherm parameters are as a result of the optimization of the following objective function:

$$\sigma = \sqrt{\sum_{i=1}^{N}\frac{\left(P^{\mathrm{exp}} - P^{\mathrm{cal}}\right)^2}{N}} \tag{12}$$

In the objective function in use, N is the number of experimental data.

The parameters of Hill-deBoer equation model are also optimized here, using both the new models and Hill-deBoer equation model the deviation for the same systems are presented in Table 3. As is observed the results from modified Peng-Robinson equation model is better than those of Peng-Robinson and Hill-deBoer equation models. One of the advantages of the present isotherm is much better correlation between the pressure