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Mixture adsorption on zeolites applying the P_i^{sat} temperature-dependency approach

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HIGHLIGHTS

- ▸ Mixture adsorption on zeolites can be predicted by P_i^{sat} temperature-dependency approach.
- ▸ Prediction is possible based on pure component adsorption data at one temperature.
- ▸ Applying the approach is convenient due to the availability of pure component P_i^{sat} data.
- ▸ Besides vapour adsorption, the approach can be used for liquid mixture adsorption.
- ▸ The approach is a valuable engineering tool when there is a lack of adsorption data.

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ABSTRACT

In this study, the feasibility of the P_i^{sat} temperature-dependency approach in predicting mixture adsorption loadings on zeolites is examined. The presented case examples show that IAST, RAST or extended Langmuir together with the pure component saturated vapour pressure P_i^{sat} to describe the temperature dependency of adsorption, can be used to predict mixture adsorption. The approach makes it possible to predict mixture adsorption in various temperature, pressure and composition conditions by utilizing pure component adsorption data at only one temperature. In addition to vapour phase adsorption, the P_i^{sat} temperature-dependency approach is also found to be applicable in modelling liquid mixture adsorption. The approach is a valuable engineering tool especially in cases where there is a lack of adsorption data. The approach can be used e.g., in zeolite membrane permeation modelling, where the adsorption phenomenon has a considerable significance.

1. Introduction

Adsorption equilibrium data is typically reported for single components, as pure component adsorption measurements are the most reliable and easiest to perform. On the other hand, applications of adsorption usually involve mixtures. Mixture adsorption equilibrium measurements, however, are considerably more complicated, tedious and error-prone than single component measurements (Talu, 2011). Nevertheless, multi-component adsorption data is crucial, but it is challenging to cover experimental mixture adsorption data for a wide range of temperature, pressure and composition conditions (Lamia et al., 2009).

In practice, typically only single component isotherms are determined experimentally, and mixture adsorption is then predicted by adsorption models. Models developed for the purpose include e.g., ideal adsorbed solution theory (IAST), real adsorbed solution theory (RAST) and extended Langmuir-type models. The models are often sufficiently accurate to be used for engineering purposes such as process design and modelling.

In general, pure component adsorption is described using models that incorporate the temperature dependency of adsorption through the adsorption equilibrium parameter. Alternatively, if the temperature dependency is not known, the pure component adsorption data is required at the same temperature where mixture adsorption is to be predicted. Herein this approach is referred to as 'the traditional approach'.

Recently, Leppäjärvi et al. (2012) showed how pure component adsorption could be modelled by using solely P_i^{sat} in describing the temperature dependency of physisorption on zeolites. The application of the P_i^{sat} temperature-dependency approach was found in Leppäjärvi et al. (2012) to be straightforward because equations and parameters to determine pure component saturated vapour pressures are available in various

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textbooks and databanks. In this paper, the application of the P_i^{sat} temperature-dependency approach is extended to mixture adsorption. The feasibility of P_i^{sat} temperature dependency in predicting binary mixture adsorption on zeolites is studied with the help of illustrative example cases.

2. Modelling mixture adsorption

2.1. Extended Langmuir isotherm

For mixtures, the adsorption loadings on a zeolite can be estimated using the extended Langmuir isotherm. It is the simplest mathematical function to account for multi-component adsorption, and is presented as

$$q_i = \frac{q_i^{\mathrm{sat}} b_i p_i}{1+\sum_{j=1}^{N} b_j p_j},\quad i,j = 1, 2,\ldots,N \tag{1}$$

where q_i (mol kg^{-1}) is the adsorbed amount, q_i^{sat} (mol kg^{-1}) is the maximum adsorption loading, b_i (Pa^{-1}) is the adsorption equilibrium parameter obtained from single component isotherms, and p_i (Pa) is the partial pressure of component i. The extended Langmuir isotherm, however, is strictly applicable only when the saturation loadings of the adsorbing species are identical, since otherwise Eq. (1) is not thermodynamically consistent (Krishna, 2001). Thus, for the general case of unequal saturation loadings, it is better to use other models based on e.g., adsorbed solution theory (AST) to describe multi-component adsorption.

2.2. IAST

The thermodynamically consistent Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz (1965) is often applied in the prediction of mixture adsorption on the basis of pure component adsorption equilibrium data. In the model, the energetic homogeneity of adsorption sites is assumed and no interaction between an adsorbate–adsorbate couple is considered (Valenzuela and Myers, 1989). In IAST the relationship between the bulk gas and adsorbed phase is described as

$$y_i P = x_i P_i^0 \tag{2}$$

where y_i is the gas phase mole fraction, P (Pa) is the system pressure, and x_i the adsorbed phase mole fraction of component i. P_i^0(Pa) is the equilibrium pressure of component i adsorbed at the same temperature and spreading pressure, π, as the mixture. IAST is based on the thermodynamic equivalence of each component spreading pressure at equilibrium. Spreading pressure is a thermodynamic variable, which cannot be measured directly. At equilibrium the spreading pressure is constant and can be evaluated from the pure component adsorption isotherms as

$$\frac{\pi A}{RT} = \int_0^{P_1^0} \frac{q_1}{P_1}\,dP_1 = \int_0^{P_2^0} \frac{q_2}{P_2}\,dP_2 = \cdots = \int_0^{P_i^0} \frac{q_i}{P_i}\,dP_i, \tag{3}$$

where A (m^2 kg^{-1}) is the specific surface area of an adsorbent, R (J mol^{-1} K^{-1}) is the gas constant and T (K) is the temperature.

Naturally, the sum of the adsorbed phase mole fractions must be one:

$$\sum_{i=1}^{N} x_i = 1 \tag{4}$$

Based on knowledge of the pure component adsorption behaviour at the given temperature as well as the bulk gas composition and the system pressure, the values of P_i^0 and x_i for each component in the mixture can be determined using Eqs. (2)–(4). The adsorbed amount of each component can be calculated with

$$q_i = x_i q_{\mathrm{tot}}, \tag{5}$$

where q_{tot} (mol kg^{-1}) is the total adsorbed amount calculated as

$$q_{\mathrm{tot}} = \frac{1}{\sum_{i=1}^{N} \frac{x_i}{q_i^0}}, \tag{6}$$

where q_i^0 (mol kg^{-1}) is the amount of component i adsorbed at the same temperature and spreading pressure of the mixture, and is thus obtained with the respective adsorption isotherm applied to P_i^0.

IAST is suitable for components that have unequal saturation loadings. In addition, IAST is not limited to any particular pure component adsorption isotherm. Thus, different isotherm models can be used to fit the adsorption equilibrium data of pure components. In addition, the adsorption model can be selected separately for each component in the mixture. For example, the Langmuir isotherm

$$q_i = \frac{q_i^{\mathrm{sat}} b_i P}{1+b_i P} \tag{7}$$

and the Sips isotherm

$$q_i = \frac{q_i^{\mathrm{sat}} (b_i P)^{1/n}}{1+(b_i P)^{1/n}} \tag{8}$$

are commonly applied with IAST in describing the adsorption equilibrium of pure components on zeolites. In Eq. (8) n is a dimensionless heterogeneity factor; deviations from the value of one indicate that the system is heterogeneous. System heterogeneity can stem from the adsorbent, adsorbate or a combination of both (Do, 1998).

The calculation of the integral presented in Eq. (3) can be performed analytically for the Langmuir isotherm as

$$\frac{\pi A}{RT} = q_i^{\mathrm{sat}} \ln\left(1+b_i P_i^0\right), \tag{9}$$

and for the Sips isotherm as

$$\frac{\pi A}{RT} = n q_i^{\mathrm{sat}} \ln\left(1+\left(b_i P_i^0\right)^{1/n}\right). \tag{10}$$

2.3. RAST

Some mixtures behave non-ideally when adsorbed on a solid surface. In such circumstances, IAST predicts the mixture adsorption unsatisfactorily, since in the theory it is assumed that each of the adsorbates in the adsorbed phase acts independently in the presence of other adsorbates. To tackle the deficiency, Real Adsorbed Solution Theory (RAST) can be applied. RAST is derived from adsorbed solution theory. The main difference between RAST and IAST is that in RAST the deviations of the adsorbed phase from ideal behaviour are taken into account. It is often assumed that the non-ideality is due to adsorbate–adsorbate interactions, but the non-ideal behaviour may result from adsorbate–adsorbent interactions as well (Ghosh et al., 1993). The non-ideality effects in RAST are incorporated by introducing an activity coefficient into Eq. (2)

$$y_i P = \gamma_i^{\mathrm{ads}} x_i P_i^0, \tag{11}$$

where γ_i^{ads} is the activity coefficient of component i in the adsorbed phase.

The activity coefficient γ_i^{ads} is basically a function of temperature, adsorbed phase mole fractions and the spreading pressure. Thus, based on the application of the activity coefficient in Eq. (11) the calculation of the total loading in Eq. (6) is