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Article

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Adsorption of binary hydrocarbon gas mixtures on activated carbon: Theoretical prediction of the binary equilibrium data

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Abstract

Experimental binary equilibrium data for the adsorption of hydrocarbon mixtures on activated carbon at given temperature are presented and discussed. Pure-component adsorption isotherms were fitted by using Langmuir model. Then adsorption isotherms were determined for different binary mixtures. Adsorption isotherms of binary mixtures were calculated using the real adsorbed solution theories, which requires the calculation of the activity coefficients for the components in the adsorbed phase. Activity coefficients are evaluated using Margules activity model and UNIQUAC model. We described the adsorption equilibria using proposed model parameters with taken to be equal to those of VLE. The results show that, except for a few systems, the calculated results were in good agreement with experimental adsorption equilibrium data.

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Keywords: Adsorption equilibria; Real adsorption solution theory; Gas-adsorbed equilibrium

1. Introduction

Adsorption equilibria are required in the design of separation processes containing gas mixtures and in many applications such as upgrading natural gas. In comparison, the calculation of adsorption equilibria of mixtures from pure component data often give a large deviation for real system. Since industrial adsorption operation usually contain more than one adsorbate component, the thermodynamic model for calculating adsorption equilibria of gaseous mixtures is particularly important in the process design for industrial applications. Significant attention has been focused on the adsorption behavior of mixtures since the experimental determination of adsorption is time-consuming and formidable tasks. The adsorption equilibria of mixtures was first theoretically explained by Myers and Prausnitz [1] for a gaseous mixture from the known adsorption isotherms of the pure component. They theoretically applied the adsorbed solution theory (AST) based on the analogy between vapor–liquid and

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vapor-adsorbed phase equilibrium to the multicomponent adsorption behaviors and provided good agreement with experimental data.

Several thermodynamic frameworks exist for interpreting the adsorption equilibria of mixtures in terms of the binary parameters between adsorbed phases. Costa et al. [2] predicted with good accuracy multicomponent adsorption equilibrium using Wilson and UNIQUAC parameters. Sochard et al. [3] also well explained the relationship between binary parameters on adsorption equilibria.

The aim of this study is to present a simple method for calculating multicomponent adsorption equilibria. The adjustable parameters in the resulting adsorption model were determined from vapor adsorbed equilibrium data. Using those parameters, calculated adsorption equilibria were compared with experimental data for hydrocarbon mixtures.

2. Thermodynamic modeling

Adsorption isotherm represents the experimental adsorbed amount as a function of partial pressure. The commonly used isotherm model is Langmuir equation which is useful to describe adsorption equilibria. For this equation (Eq. (1)), the adsorbed amount of component i at equilibrium expresses n_i (moles/g) as a function of the partial pressure of the single solute i in the gaseous phase P_i

$$n_i = \frac{m_i K_i P_i}{1 + K_i P_i} \quad (1)$$

Where m_i is the maximum adsorbed quantity and K_i is Langmuir constant of component i .

2.1. Ideal adsorbed solution theory (IAST)

In the case of AST, the mixture adsorption equilibria are calculated utilizing only pure component isotherms. The basic equation for AST has the following form

$$P y_i = x_i \gamma_i P_i^0(\pi) \quad (2)$$

This equation is analogous with Raoult's law for vapor–liquid equilibria (VLE), but there is the subtle difference in the meaning of P_i^0 . In VLE P_i^0 is the vapor pressure of the pure saturated liquid i at the given temperature of the mixture. Here, $P_i^0(\pi)$ is the adsorbate pressure corresponding to the given temperature and to the spreading pressure π for the adsorption of pure component i . P is the mixture pressure, y_i and x_i are the gas-phase and adsorbed phase mole fractions for component respectively, and γ_i is the activity coefficient in the adsorbed phase depending on temperature. For ISAT, activity coefficient, γ_i , is unity. Relation between the spreading pressure π and the equilibrium pressure of each species P_i can be obtained using Gibbs adsorption isotherm equation:

$$\Pi_i = \frac{A\pi}{RT} = \int_0^{P_i^0} \frac{n_i}{P_i} dP_i \quad (3)$$

Where Π_i is reduced spreading pressure of the mixture, and n_i is related to pure component isotherm. Total adsorbed amount, n_T , and partial adsorbed amounts of the components, n_i , can be obtained using the following equations:

$$\frac{1}{n_T} = \sum_{i=1}^N \frac{x_i}{n_i}, \quad (n_i = x_i n_T) \quad (4)$$

$$\sum_{i=1}^N x_i = 1 \quad (5)$$

Where N is the number of components in the mixture.

2.2. Real adsorbed solution theory (RAST)

Calculations based on the real solution concept was performed using the activity coefficients. There are several methods calculating activity coefficients. In this work, activity coefficients are calculated using two classical

thermodynamic equilibrium models, Margules [4] and UNIQUAC [5] for which only binary parameters are required for binary systems. Activity coefficients estimated using Margules model are expressed as follows

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \quad (6)$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})x_2]x_1^2 \quad (7)$$

Where A_{12} and A_{21} are adjustable parameters for binary mixture.

Activity coefficients estimated using UNIQUAC model are expressed as follows

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (8)$$

UNIQUAC model is consist of a sum of a combinatorial term ($\ln \gamma_i^C$) to account for molecular size and shape differences and a residual term ($\ln \gamma_i^R$) to account for molecular interactions. $\ln \gamma_i^C$ and $\ln \gamma_i^R$ can be expressed as

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2}s_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (9)$$

$$\ln \gamma_i^R = s_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) \right] - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{ki}} \quad (10)$$

with

$$\tau_{ji} = \exp \left(- \left(\frac{u_{ji} - u_{ii}}{RT} \right) \right), \quad (\tau_{jj} = \tau_{ii} = 0) \quad (11)$$

$$l_i = \frac{z}{2} (r_i - s_i) - (r_i - 1) \quad (12)$$

where the average area fraction θ_i and the average segment fraction ϕ_i are defined by

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (13)$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (14)$$

In these equations, s_i and r_i are surface area and volume parameters of component i , z is a coordination number and is taken equal to 10. $u_{ji} - u_{ii}$ ($u_{ij} = u_{ji}$) represents the interaction energy of pairs of non-bonded segments between sites i and j . Here, τ_{ji} is adjustable parameters of UNIQUAC activity model.

One of the approaches to solve the equilibrium compositions is as following:

- (Step 1) Since the experimental data for pure-component adsorption equilibrium data give the value of n_i corresponding to the known values of P_i , the total amount adsorbed, n_T , can be calculated by Eqs. (1) and (3).
- (Step 2) Use Simpson's numerical integral method back calculate P_i^0 and P_j^0 for each component in Eq. (3).
- (Step 3) Form an objective function employing Eq. (5), and use Newton–Raphson iteration method to update the estimate of Eq. (4).

$$F(\Pi) = \sum_{i=1}^N x_i - 1 = 0 \quad (15)$$

- (Step 4) Repeat Step 2 and 3 until convergence. After convergence, the values of and are determined.
- (Step 5) The adsorbed phase is calculated as using Eqs. (2) and (4) ($n_i = n_T x_i$).

3. Result and discussion

Pure component adsorption data for CH_4 , C_2H_4 and C_2H_6 on activated carbon are shown in Fig. 1. The corresponding optimal regression using Langmuir isotherm model are also shown in the figure.

Experimental data are well fitted with Langmuir model as shown on these figures. The fitted parameters for the three components are listed in Table 1.

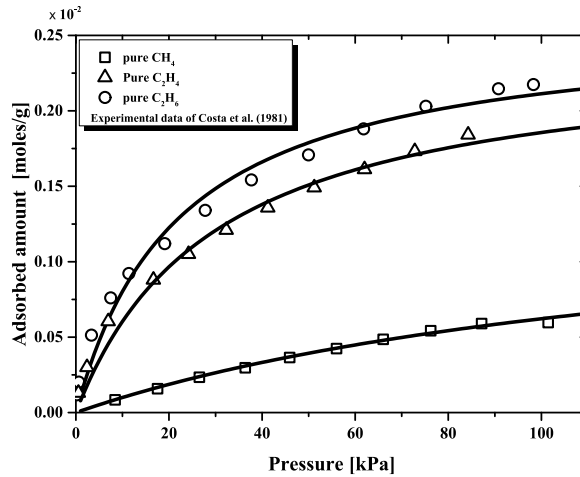


Fig. 1. Pure adsorption isotherms of mixture at 20° C: the solid lines represent the fitted results using Eq. (1).

Table 1. Parameters of pure component isotherms model.

Component <i>i</i>	CH ₄	C ₂ H ₄	C ₂ H ₆
m_i [moles.g ⁻¹]	0.1486	0.2412	0.2582
K_i [kPa ⁻¹]	0.0072	0.0334	0.0451

In Eq. (1) n_i is represents the adsorbed amount and m_i is the maximum number of moles adsorbed per gram of adsorbent and K_i is specific constant. Experimental data are well fitted with Langmuir model as shown on Fig. 1. All parameters of Langmuir equations were determined by using a nonlinear regression method.

In using the RAST, activity coefficients for the components were calculated from experimental data. For calculating the equilibrium composition of adsorption mixtures, Margules and UNIQUAC equations were used. The following calculated values for binary interaction parameters and UNIQUAC structural parameters are given in Table 2.

Table 2. UNIQUAC parameters taken from Poling et al. [6] and adjustable model parameters.

Parameters	CH ₄	C ₂ H ₄	C ₂ H ₆
UNIQUAC			
r_i	1.1278	1.8022	1.5721
q_i	1.156	1.696	1.484
τ_{ij}	CH ₄ (1)-C ₂ H ₆ (2) $\tau_{12} = 0.2092, \tau_{21} = 1.4745$		CH ₄ (1)-C ₂ H ₄ (2) $\tau_{12} = 0.2401, \tau_{21} = 0.8343$
Margules			
A_{ij}	CH ₄ (1)-C ₂ H ₆ (2) $A_{12}=0.4659, A_{21}=1.3587$		CH ₄ (1)-C ₂ H ₄ (2) $A_{12}=0.6679, A_{21}=1.5814$

Determining the binary interaction parameters of activity model may be helpful for predicting the total adsorption capacity. These parameters can be calculated from adsorption equilibrium data. Results are shown in Figs. 2 and 3 for mixtures of CH₄-C₂H₆ and CH₄-C₂H₄, and RAST with binary interaction parameters shows improved results compared to IAST. In addition, the RAST with UNIQUAC model gives more accuracy compared to the RAST with Margules model. These results confirm that IAST cannot describe the real gases behaviors. Therefore, activity parameter must be taken account for real adsorption behaviors of mixtures.

4. Conclusion

Experimental results and theoretical approaches were conducted in order to evaluate the performance of two different activity models to calculate the adsorption of hydrocarbon mixtures. Pure solute adsorption isotherms

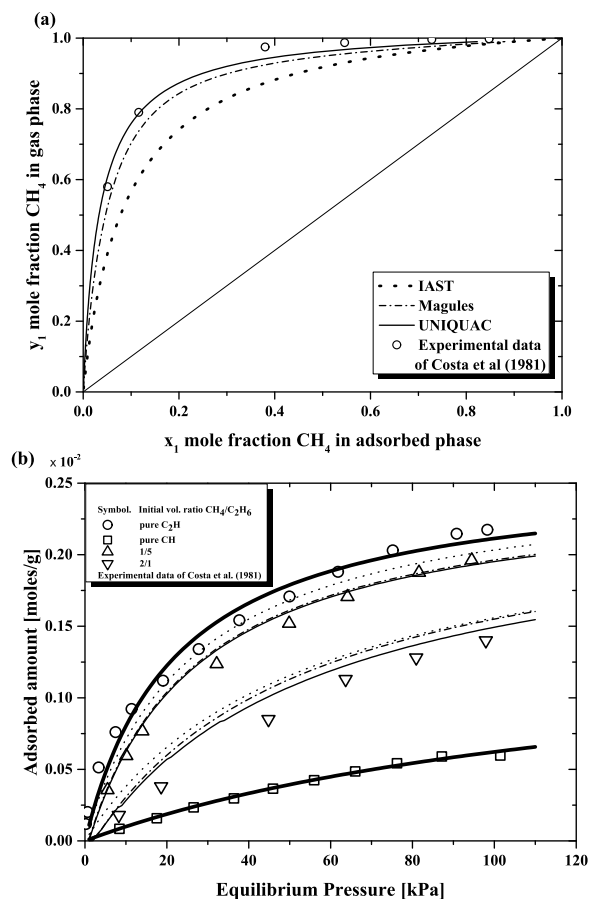


Fig. 2. Calculation of adsorption of $\text{CH}_4\text{-C}_2\text{H}_6$ mixtures at 20°C : (a) calculation of equilibrium gas-adsorbed phase (b) calculation of mixture adsorption equilibria (the bolded line is Langmuir model; the solid line is UNIQUAC model; the dashed-dot line is Margules model; the dotted line is IAST model)

were determined by Langmuir isotherm model with good accuracy. The predetermined activity model parameters from vapor adsorbed equilibrium were used directly to calculate adsorption of mixtures on adsorbent. The use of IAST was not satisfactory to calculate the real behaviors in the adsorbed phase, but use of RAST combined with Margules and UNIQUAC activity models can provide an improvement in the calculation. However, Margules activity model showed deviations lower than 5% for the whole range of adsorbed phase, whereas UNIQUAC activity model showed deviation lower than 3%. The mixtures of hydrocarbon on adsorption equilibrium calculated by UNIQUAC was in more accuracy with those of the experimental data. The proposed theoretical approach can help predict the adsorption of mixed gases using the corresponding equilibrium data, but limitations remained due to the fitting procedure in the calculation of adsorption equilibrium data. For those adsorption isotherms, the calculation results using activity coefficient models were a small deviation from experimental data; however, our approach shows to be useful in calculating without complicated parameters. The advantage of this study follows from its simplicity and a simple approach of RAST with activity model parameters appears to be suitable for predicting the adsorption behavior of the given system.

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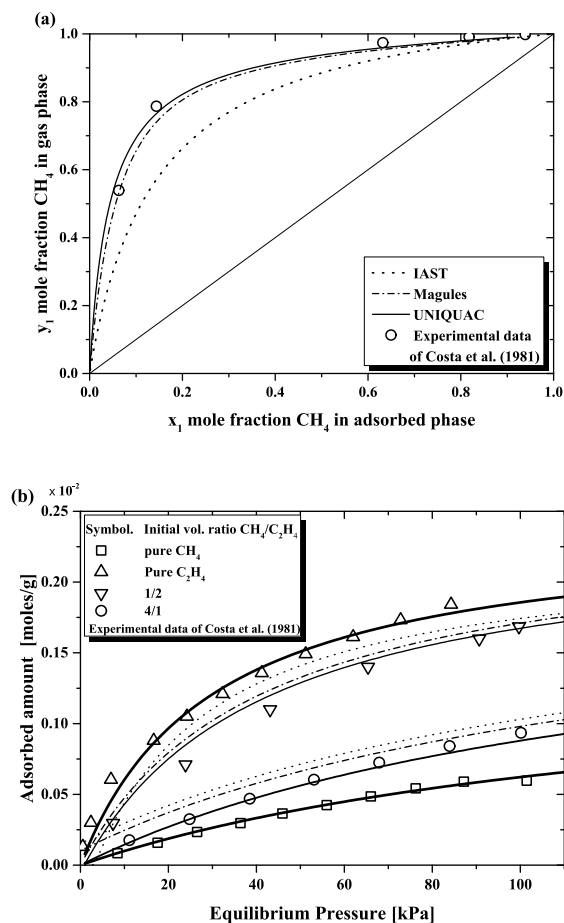


Fig. 3. Calculation of adsorption of CH_4 - C_2H_4 mixtures at 20°C : (a) calculation of equilibrium gas-adsorbed phase (b) calculation of mixture adsorption equilibria (the bolded line is Langmuir model; the solid line is UNIQUAC model; the dashed-dot line is Margules model; the dotted line is IAST model)

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