

The adsorbed solution theory with Wilson's activity.
Adsorption equilibria and calorimetry

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The modified Adsorbed Solution theory is used to describe the calorimetric effects accompanying mixed-gas adsorption equilibria. As the model of non-ideality of adsorbed phase the Wilson's parameters are used. The obtained results were compared with the regular adsorbed solutions theory and the Flory-Huggins activity. The simple way to minimize the number of best-fit parameters in the Wilson's model is presented. Theoretical expressions for phase diagrams and isosteric heats of adsorption are compared with the experimental data.

1. INTRODUCTION

The modern industrial gas separation processes utilize adsorption techniques. It is due to economic reasons: gas separation by adsorption processes occur under relatively low temperatures and pressures in comparison to distillation techniques. For example, it concerns PSA (Pressure Swing Adsorption) or TSA (Temperature Swing Adsorption). These processes require reversible adsorption, so that the preferentially adsorbed species can be removed readily during the regenerative portion of the cycle.

It seems so because adsorption equilibrium is highly sensitive to temperature, the heat effects accompanying mixed-gas adsorption should be taken into account. Although the adsorption phenomena for gas separation processes were theoretically well described, the calorimetric effects accompanying the mixed-gas adsorption are still not well investigated. Only a few papers devoted to calorimetric effects accompanying mixed-gas adsorption can be found in literature. As the example we cite works [1-9].

The present paper is the continuation of the theoretical studies on Adsorbed Solution (AS) approach. Recently [11,12] we showed a simple way to calculate isosteric heats of adsorption for non-ideal systems. As the model of non-ideality of the adsorbed phase we used the Flory-Huggins and “regular adsorbed solution” theories. Here we use the Wilson’s activity as another very popular model of non-ideality. Although the Wilson’s model characterizes a large number of parameters which can be determined only by theoretical analysis of adsorption system, we show the simple way to minimize their number. The results of calculations will be compared with the models studied recently [11,12].

2. THEORY

Adsorption equilibria. As the introduction we show briefly the way to calculate gas adsorption equilibria and accompanying them enthalpic effects in single- and mixed-gas adsorption systems. Rudzinski et al. [10] considered the usage of AS for the two models of surface energetic topography: random (the sites with adsorption energy ε_i are distributed randomly across the surface) and patchwise (the sites with energy ε_i are grouped into ‘patches’). For the case of random topography, the following expression for mole fraction in the adsorbed phase was obtained [10]:

$$X_1^{rand} = p_1 \cdot \left(\frac{\gamma_1^s}{K_1 \exp\{\varepsilon_1^0/kT\}} \left[\exp\left\{ \frac{F_{N_1} kT}{M_1 c_1} (\Pi^* - \Pi^m - M_1 \ln \gamma_3^s) \right\} - 1 \right]^{c_1/kT} \right)^{-1} \quad (1)$$

and for patchwise:

$$X_1^{patch} = \frac{\left\{ \left[\frac{\gamma_2^s (1/\gamma_3^s) \exp\{\Pi^*/M_2\} - 1}{\gamma_1^s (1/\gamma_3^s) \exp\{\Pi^*/M_1\} - 1} \right] \frac{p_1 K_1}{p_2 K_2} \exp\left\{ \frac{\varepsilon_1^0 - \varepsilon_1^0}{kT} \right\} \right\}^{kT/c_1}}{1 + \left\{ \left[\frac{\gamma_2^s (1/\gamma_3^s) \exp\{\Pi^*/M_2\} - 1}{\gamma_1^s (1/\gamma_3^s) \exp\{\Pi^*/M_1\} - 1} \right] \frac{p_1 K_1}{p_2 K_2} \exp\left\{ \frac{\varepsilon_1^0 - \varepsilon_1^0}{kT} \right\} \right\}^{kT/c_1}} \quad (2)$$

where M_i is the maximum adsorbed amount of component i , $K_i \exp\{\varepsilon_i^0/kT\}$ is the Langmuir constant, kT/c_i – the heterogeneity parameter, Π^* – the equilibrium spreading pressure, p_i – the partial pressure and γ_i^s – the activity coefficients. F_{N_i} and Π_i^m are some parameters, which, if infinite limits of

adsorption energies are assumed, disappeared ($F_{N_i} = 1$ and $\Pi_i^m = 0$) [10]. The subscript '3' refers to the Vacancy Solution Theory formalism where the adsorbed mixture is composed of two different gases and the third component called 'vacancy'.

All parameters necessary to calculate X_i can be obtained from the single-gas adsorption data. For example, if the model of 'regular adsorbed solution' theory will be used, the single-gas isotherms should be correlated by:

$$p_i K_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\} = \left(\frac{\theta_{it}}{1-\theta_{it}}\right)^{c_i/kT} \exp\left\{-\frac{\omega_{ii}\theta_{it}}{kT}\right\} \quad (3)$$

Whereas for the model of Flory-Huggins non-ideality:

$$p_i K_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\} = \left(\frac{\theta_{it}}{1-\theta_{it}}\right)^{c_i/kT} \exp\left\{\frac{(a_{i3})^2 \theta_{it}}{1+a_{i3}\theta_{it}}\right\} \quad (4)$$

where θ_{it} is the surface coverage, ω_{ii} and a_{i3} are the interaction parameters.

Let us focus on the case of Wilson's model of non-ideality. In this case the single-gas adsorption isotherm has the following form:

$$p_i K_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\} = \left(\frac{\theta_{it}}{1-\theta_{it}}\right)^{c_i/kT} \left[\Lambda_{i3} \frac{1-(1-\Lambda_{3i})\theta_{it}}{\Lambda_{i3} + (1-\Lambda_{i3})\theta_{it}} \right] \times \exp\left\{-\left(\frac{\Lambda_{3i}(1-\Lambda_{3i})\theta_{it}}{1-(1-\Lambda_{3i})\theta_{it}} + \frac{(1-\Lambda_{i3})\theta_{it}}{\Lambda_{i3} + (1-\Lambda_{i3})\theta_{it}}\right)\right\} \quad (5)$$

where Λ_{i3} and Λ_{3i} are the Wilson's coefficients. Generally they can be treated as two additional best-fit parameters. But, these parameters can be also estimated from an equation analogous to that introduced for a bulk liquid mixture [15]

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\left\{\frac{\lambda_{ii} - \lambda_{ij}}{kT}\right\} \quad (6)$$

where v_j/v_i is the size ratio of mixture components and λ_{ij} is the potential energy of interaction between species i and j .

For the case of gas adsorption eq. (6) becomes:

$$\Lambda_{ij} = \frac{M_i}{M_j} \exp\left\{\frac{\lambda_{ii} - \lambda_{ij}}{kT}\right\} \quad (7)$$

Eq. (7) makes it possible to minimize the number of best-fit parameters used during adjustment eq. (5) to single-gas isotherms. Namely

$$\Lambda_{i3} = \exp\left\{\frac{\lambda_{ii}}{kT}\right\} \text{ and } \Lambda_{3i} = 1 \quad (8)$$

because the interaction energy between the adsorbed molecule and the vacancy is equal to zero.

So, to adjust eq. (5) to the single-gas adsorption isotherms we have the four best-fit parameters: monolayer capacity M_i , heterogeneity parameter c_i/kT , Langmuir constant $K_i \exp\{\varepsilon_i^0/kT\}$ and interaction parameter λ_{ii} .

Calorimetric effects. In our recent studies [11,12] we considered the application of AS theory to theoretical description of the heat effects accompanying non-ideal adsorption systems. To calculate the adsorption phase diagrams we used the general Raoult's law:

$$p_i = p_i^0(\Pi^*) X_i \gamma_i^s \quad (9)$$

The logarithmic form of Raoult's law can be used to calculate the isosteric heats of adsorption by simply differentiating over $(1/T)$ and multiplying by $(-k)$:

$$Q_i^{st} = -k \left(\frac{\partial \ln p_i}{\partial (1/T)} \right)_{\{X_i\}} = -k \left(\frac{\partial \ln p_i^0(\Pi^*)}{\partial (1/T)} \right)_{\{X_i\}} - k \left(\frac{\partial \ln \gamma_i^s}{\partial (1/T)} \right)_{\{X_i\}} \quad (10)$$

The above eq. (10) is the master equation, which makes it possible to calculate the isosteric heat of a given component accompanying the mixed-gas adsorption.

The first term in (10) i.e. $-k \left(\frac{\partial \ln p_i^0}{\partial (1/T)} \right)_{\{X_i\}}$ can be obtained by using (1) and (2). For the case of random topography it has the following form:

$$-k \left(\frac{\partial \ln p_1^0(\Pi^*)}{\partial(1/T)} \right) = q_{01}^{st} + kT \ln \frac{X_1^{rand} \gamma_1^s}{p_1 K_1 \exp\{\varepsilon_1^0/kT\}} \quad (11)$$

and for patchwise topography:

$$-k \left(\frac{\partial \ln p_1^0(\Pi^*)}{\partial(1/T)} \right) = q_{01}^{st} - c_1 \ln \frac{X_1^{patch}}{1 - X_1^{patch}} \quad (12)$$

where $q_{0i}^{st} = k(\partial \ln K_i / \partial(1/T))_{\{X_i\}} + \varepsilon_i^0$ is frequently called 'non-configurational' isosteric heat and can be treated as the additional best-fit parameter. If we use the 'regular adsorbed solutions' (RAS) formalism, q_{01}^{st} can be determined by adjusting the single-gas calorimetric data by [11]:

$$q_i^{st} = q_{i0}^{st} - c_i \ln \frac{\theta_{it}}{1 - \theta_{it}} + \omega_{ii} \theta_{it} \quad (13)$$

whereas for the Flory-Huggins (FH) model [12]:

$$q_i^{st} = q_{i0}^{st} - c_i \ln \frac{\theta_{it}}{1 - \theta_{it}} - \xi_{i3} \frac{2a_{i3} \theta_{it} (1 + a_{i3} \theta_{it}) - (a_{i3} \theta_{it})^2}{(1 - a_{i3} \theta_{it})^2} \quad (14)$$

where

$$\xi_{i3} = k \left(\frac{\partial a_{i3}}{\partial(1/T)} \right)_{\{X_i\}} \quad (15)$$

For the case of Wilson's (W) activity to calculate single-gas isosteric heat of adsorption eq. (5) should be rearranged for $\ln p_i$ and differentiated by $(1/T)$:

$$q_i^{st} = q_{i0}^{st} - c_i \ln \frac{\theta_{it}}{1 - \theta_{it}} + \theta_{it} \left[\frac{(\Lambda_{i3}(\theta_{it} - 2) - \theta_{it}) \zeta_{i3}}{\Lambda_{i3}(\Lambda_{i3} + \theta_{it} - \Lambda_{i3} \theta_{it})^2} - \frac{\Lambda_{3i}(2 + (\Lambda_{3i} - 1)\theta_{it}) \zeta_{3i}}{(1 + (\Lambda_{3i} - 1)\theta_{it})^2} \right] \quad (16)$$

where

$$\zeta_{ij} = k \left(\frac{\partial \Lambda_{ij}}{\partial(1/T)} \right)_{\{X_i\}} \quad (17)$$

In the case of mixed-gas adsorption, there appear the cross-interaction parameters ω_{ij} , a_{ij} and Λ_{ij} , ζ_{ij} . The idea proposed by Cochran et al. [13] can be used to calculate the cross-parameter a_{ij} by using the single-gas adsorption data:

$$a_{ij} = \frac{a_{i3} + 1}{a_{j3} + 1} - 1 \quad (18)$$

Then, differentiating (18) over $(1/T)$ we obtain

$$\xi_{ij} = k \left(\frac{\partial a_{ij}}{\partial (1/T)} \right)_{\{x_i\}} = \frac{\xi_{i3}(a_{j3} + 1) - \xi_{j3}(a_{i3} + 1)}{(a_{j3} + 1)^2} \quad (19)$$

The cross-interaction parameter ω_{ij} is defined by the following equation:

$$W_{ij} = \omega_{ii} + \omega_{jj} - 2\omega_{ij} = 0 \quad (20)$$

where W_{ij} is called the ‘interchange energy’ and the above case refers to ‘ideal solutions’, where W_{ij} vanishes.

The Wilson’s coefficients Λ_{ij} or ζ_{ij} , $i, j = 1, 2$, represent the interactions between the neighbouring adsorbed molecules. Generally, they can be treated as additional best-fit parameters improving the fitting procedure of theoretical curves with the experimental phase diagrams. But eq. (7) gives the possibility to minimize the number of Λ_{ij} . While inserting eq. (7) into (17) ζ_{ij} can be calculated by using the following equation:

$$\zeta_{ij} = \Lambda_{ij} (\lambda_{ii} - \lambda_{jj}) \quad (21)$$

and then $\zeta_{i3} = \Lambda_{i3} \lambda_{ii}$ and $\zeta_{3i} = 0$.

Finally, the cross interaction coefficient λ_{ij} can be assumed to be a geometric mean of the pure component coefficients λ_{ii} and λ_{jj} :

$$\lambda_{ij} = (\lambda_{ii} \lambda_{jj})^{1/2} \quad (22)$$

While summarizing the case of Wilson's coefficients, the use of eq. (7) leads to a simpler form of the single-gas isotherm equation:

$$p_i K_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\} = \left(\frac{\theta_{it}}{1-\theta_{it}}\right)^{c_i/kT} \left[\frac{\Lambda_{i3}}{\Lambda_{i3} + (1-\Lambda_{i3})\theta_{it}}\right] \exp\left\{-\frac{(1-\Lambda_{i3})\theta_{it}}{\Lambda_{i3} + (1-\Lambda_{i3})\theta_{it}}\right\} \quad (23)$$

and for the single-gas isosteric heats of adsorption:

$$q_i^{st} = q_{i0}^{st} - c_i \ln \frac{\theta_{it}}{1-\theta_{it}} + \theta_{it} \left[\frac{(\Lambda_{i3}(\theta_{it} - 2) - \theta_{it})\zeta_{i3}}{\Lambda_{i3}(\Lambda_{i3} + \theta_{it} - \Lambda_{i3}\theta_{it})^2} \right] \quad (24)$$

where ζ_{i3} can be expressed by eq. (21). From the adjustment of eq. (23) to the single-gas adsorption isotherm the values of $K_i \exp\{\varepsilon_i^0/kT\}$, c_i/kT , M_i and Λ_{i3} can be determined. Then, the use of eq. (24) to the experimentally measured isosteric heats accompanying single-gas adsorption gives the possibility to determine the non-configurational isosteric heat q_{i0}^{st} . The cross-interaction parameter λ_{ij} can be calculated by (22) and finally eqs (1), (2), (11) and (12) can be used to calculate adsorption phase diagrams and theoretical isosteric heats accompanying mixed-gas adsorption.

While considering the model of non-ideality of adsorbed phase, the definitions of γ_i^s and $-k(\partial \ln \gamma_i^s / \partial (1/T))_{(x_i)}$ are necessary. As these equations have a very complicated mathematical form, the corresponding expressions for the regular adsorbed solution theory (RAS), the Flory-Huggins (FH) and Wilson's (W) model are presented in the appendix.

2. PREDICTION OF PHASE DIAGRAMS AND ISOSTERIC HEAT OF ADSORPTION

To check the efficiency of the presented model of calculations we need specific experimental data. Namely, all single-gas isotherms, adsorption phase diagrams and the isosteric heats of adsorption should be estimated at the same temperature. It is important to notice that the individual isosteric heats of adsorption of mixed gases are difficult to determine. A special procedure was proposed by Myers' team [14-17]. Here we use the experimental data reported by Siperstein et al. [14] on MFI: SF₆+CH₄. These experiments were performed at a temperature around 23-24⁰C and at the low adsorbate pressures close to

atmospheric conditions. These individual isosteric heats of adsorption were measured as a function of surface coverage.

First we studied the single gas adsorption and calorimetric data. To check the correctness of AS approach with the Wilson's coefficients we compare our present calculations with those made recently [11,12] i.e. for the RAS and FH models of non-ideality. Due to the numerical convenience we adjust single-gas theoretical isotherms (3), (4) and (5) to the experimental data in a linear form. In the case of Wilson's coefficients the linear form of eq. (23) is following:

$$\ln\left(\frac{\theta_{it}}{1-\theta_{it}}\right) + \frac{kT}{c_i} \left[\frac{\Lambda_{i3}}{\Lambda_{i3} + (1-\Lambda_{i3})\theta_{it}} \right] - \frac{kT}{c_i} \left[\frac{(1-\Lambda_{i3})\theta_{it}}{\Lambda_{i3} + (1-\Lambda_{i3})\theta_{it}} \right] = \frac{kT}{c_i} \ln p_i + \frac{kT}{c_i} \ln \left(K_i \exp\left\{ \frac{\varepsilon_i^0}{kT} \right\} \right) \quad (25)$$

While assuming the starting value of kT/c_i , the adsorption capacity M_i and the Wilson coefficient Λ_{i3} are chosen so that the deviation from linearity of the double ln-ln plot will be the smallest. Then new values of kT/c_i and $K_i \exp\{\varepsilon_i^0/kT\}$ are obtained from the tangent of the slope of r.h.s. of eq. (24) plotted against $\ln p_i$. The procedure should be repeated until the value of kT/c_i does not change.

The best-fit parameters obtained from fitting (3), (4) and (5) to the single-gas isotherms and the adjustment of (13), (14) and (16) to the calorimetric data are presented in Tables 1, 2 and 3 and graphically in Figure 1.

Tab. 1. Values of the parameters obtained by applying eq. (3) to the experimental isotherms of SF₆ and CH₄ adsorbed on MFI, reported by Siperstein et al. [14]. In the last but one column the best-fit values obtained from adopting the theoretical equation for heat of adsorption (13) were inserted. We also present the Error values corresponding to fitting quality, defined as the residual sum of squares [11]

Adsorption system	T [°C]	M_i [mmol/g]	$\frac{kT}{c_i}$	$\frac{\omega_{it}}{kT}$	$K_i \exp\left\{ \frac{\varepsilon_i^0}{kT} \right\}$	Linear Regression Error	q_i^{st0} [kJ/mol]
SF ₆	≈24	1.98	0.751	1.265	$1.4 \cdot 10^{-2}$	$4.2 \cdot 10^{-3}$	36.00
CH ₄	≈23	2.35	0.978	0.204	$5.0 \cdot 10^{-4}$	$3.1 \cdot 10^{-5}$	21.50

It is interesting to notice that all three models of non-ideality applied to SF₆ and CH₄ adsorption give similar values of the monolayer capacity M_i (which substantiate the use of a lattice model of adsorbed phase). Also the values of heterogeneity parameters kT/c_i and non-configurational isosteric heats of adsorption q_{0i}^{st} determined for given adsorbate are similar.

Tab. 2. Values of the parameters obtained by applying eq. (4) to the experimental isotherms of SF₆ and CH₄ adsorbed on MFI, reported by Siperstein et al. [14]. In the last two columns the best-fit values obtained by applying the theoretical equation for heat of adsorption (14) to the experimental data were inserted [12]

Adsorption system	T [°C]	M_i [mmol/g]	$\frac{kT}{c_i}$	a_{i3}	$K_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}$	Linear Regression Error	q_i^{st0} [kJ/mol]	ξ_{i3}
SF ₆	≈24	1.95	0.967	0.2	$2.8 \cdot 10^{-2}$	$6.3 \cdot 10^{-4}$	32.41	-20.33
CH ₄	≈23	2.69	0.981	0.1	$4.4 \cdot 10^{-4}$	$3.4 \cdot 10^{-6}$	17.84	-56.19

Tab. 3. Values of the parameters obtained by applying eq. (5) to the experimental isotherms of SF₆ and CH₄ adsorbed on MFI, reported by Siperstein et al. [14]. In the last two columns the best-fit values obtained by applying the theoretical equation for heat of adsorption (16) to the experimental data were inserted

Adsorption system	T [°C]	M_i [mmol/g]	$\frac{kT}{c_i}$	Λ_{i3}	$K_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}$	Linear Regression Error	q_i^{st0} [kJ/mol]
SF ₆	≈24	1.96	0.838	0.7	$1.9 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	35.2
CH ₄	≈23	2.37	0.976	0.9	$5.0 \cdot 10^{-4}$	$2.1 \cdot 10^{-6}$	19.4

While looking in Figure 1 a very good conformity of the single-gas isotherm equations with the experimental data can be seen, the values of linear regression errors in Tables 1, 2 and 3 are small. But, simultaneously, difficulties in the theoretical description of enthalpic effects, accompanying the single-gas adsorption, can be seen. The RAS model of non-ideality fails completely, when used to describe calorimetry. On the other hand, the FH model proves successful for the description of the enthalpic effects of single-gas adsorption. Only moderate conformity of W model with experiment can be stated.

Figure 2 presents the comparison between the theoretical phase diagrams (1) and (2) and the theoretical, individual isosteric heats of adsorption (11) and (12) with the experimental data. The theoretical curves were calculated by using the parameters collected in Tables 1, 2 and 3. The notation used in Figure 2 is following: Y_1 is the mole fraction in the gas phase, and X_1 relates to

the adsorbed phase. The theoretical phase diagrams were calculated with the assumption of infinite limits of adsorption energies i.e. $\Pi^m = 0$ and $F_{N_i} = 1$. As in the case of single-gas adsorption systems, a better agreement of the FH and W models with experiment were obtained. Especially in the case of FH the phase diagram is better correlated by both random eq. (1) and patchwise eq. (2) model. When the Wilson's coefficients are used, the adsorption phase diagram is better correlated by the patchwise type of energetic heterogeneity.

While looking in Figure 2, it can be found that the adjustment of the individual isosteric heats of adsorption by (11) and (12) is not satisfactory. Following down in Figure 2 we observe increasing conformity of theoretical calculations with the experimental calorimetric data. Especially Wilson's model suggests that in experimental adsorption system the patchwise model of energetic heterogeneity occurs. In the case of FH and W a very good agreement with the experimental isosteric heats accompanying CH_4 adsorption was obtained by the patchwise model of topography. But, if we look at Figure 1, part (B), we can see that all theoretical curves (13), (14) and (16) have a similar shape and differ only by shift on the heat axis. That position of heat curves defines the values of q_{0i}^{st} . So, it seems that these values were determined with a certain error. Probably it is caused by almost homogeneous character of adsorption – the values of heterogeneity parameters kT/c_i collected in Tables 1, 2 and 3 are close to one. The values of q_{0i}^{st} determined by eqs (14) and (16) are more accurate than in the case of RAS.

A certain explanation of that problem is the fact that the experimental data by Siperstein et al. [14] were measured in a low range of pressures close to room conditions. In such a range the adsorption occurs like on the homogeneous surface. Although when $p \rightarrow 0$ all isotherm equations must reduce to Henry's law, none of (3), (4) and (5) satisfies this condition. It is caused by the assumption of the infinite energy limits of adsorption energy. Recently we showed a certain solution of that problem [11,12] and it consist in the negligence of the logarithmic term in (13), (14) and (16).

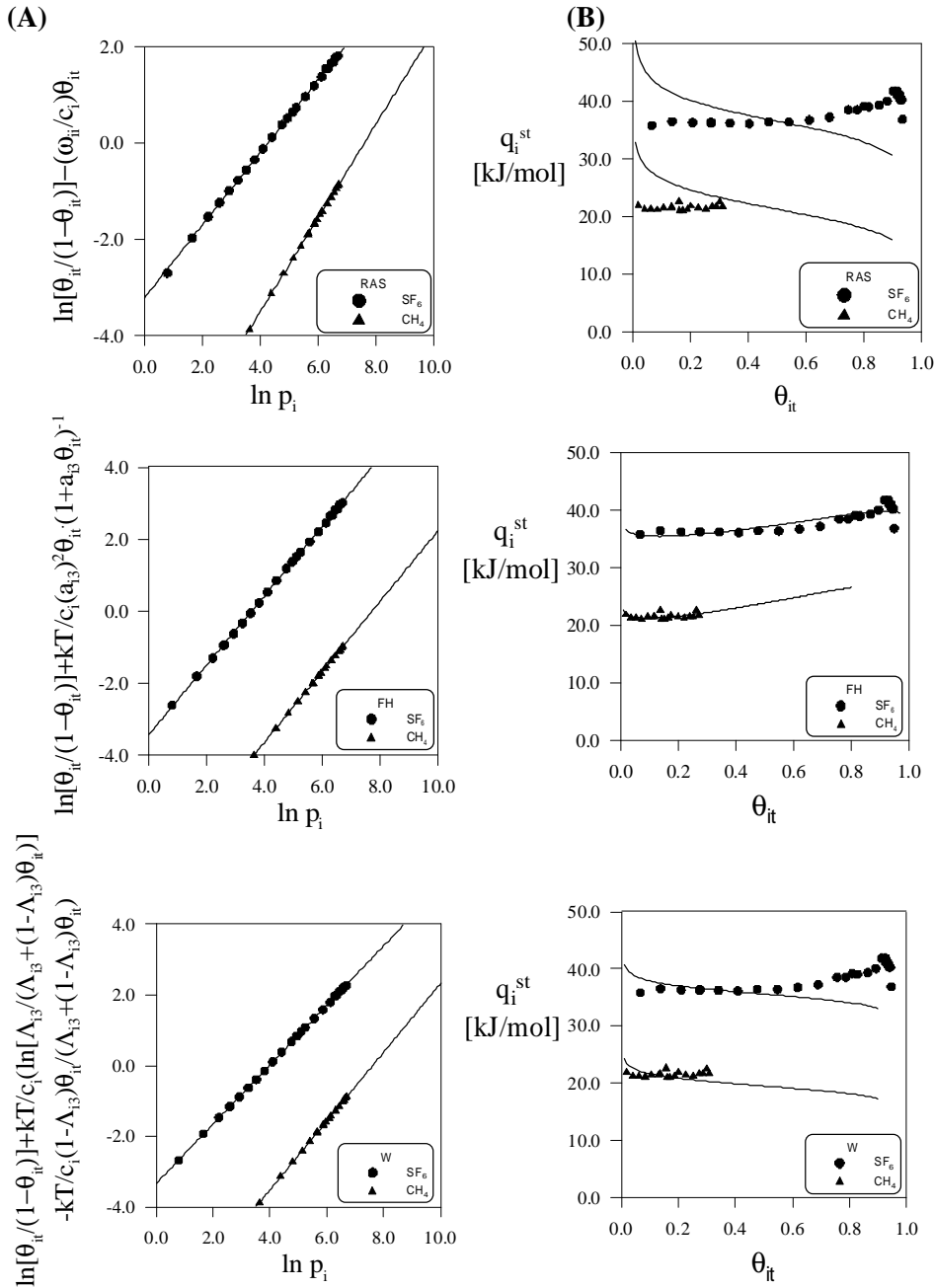


Fig. 1. Part (A): Linear regression by eqs (3), (4) and (5) (solid lines) for the experimental data (●,▲) reported by Siperstein et al. [14]: SF₆ and CH₄ adsorbed on MFI. Part (B): Comparison of the theoretical isosteric heats of adsorption of pure components (13), (14) and (16) (solid lines) with the analyzed experimental data

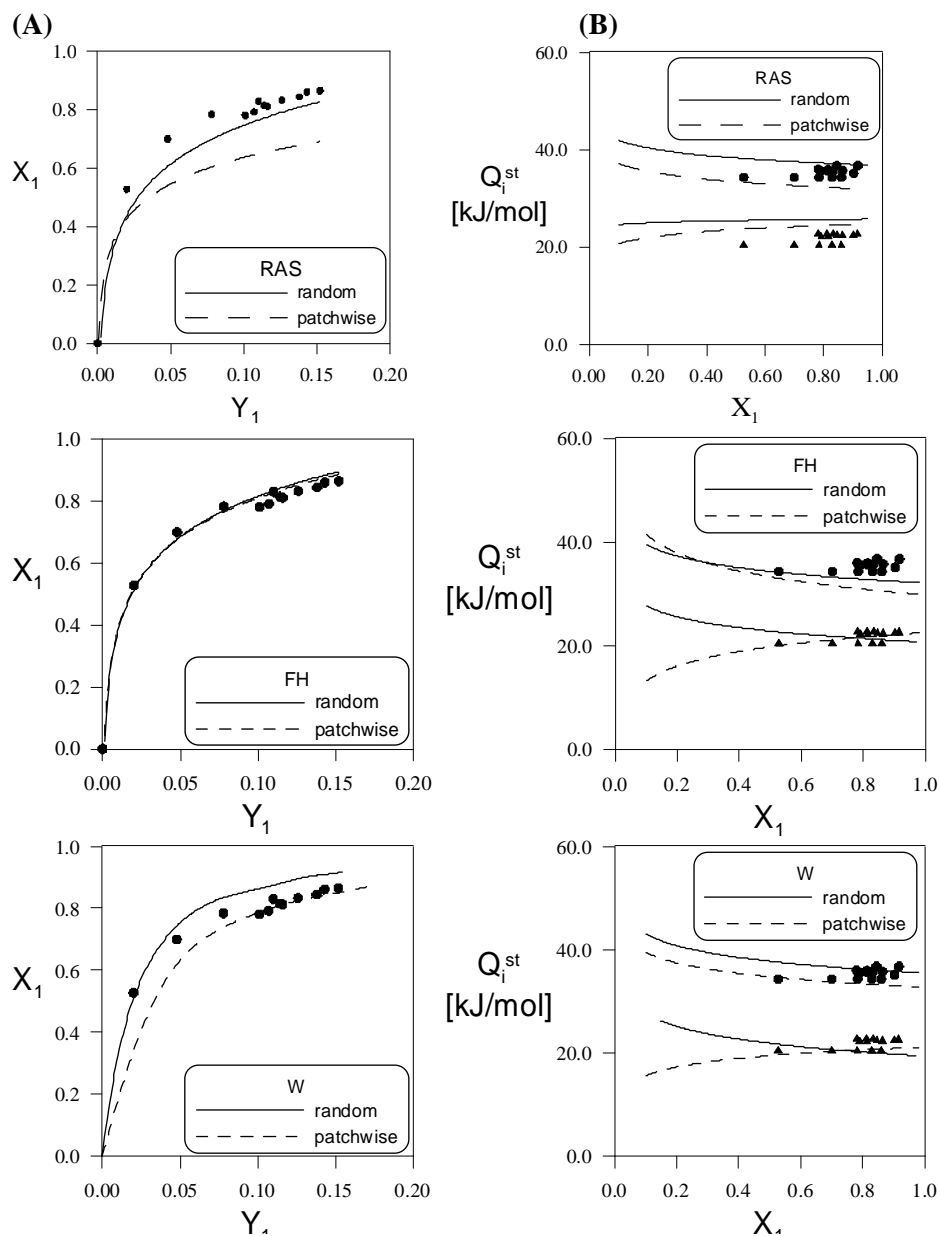


Fig. 2. Part (A): Adsorption from the (SF₆+CH₄) on MFI [14] at the temperature about 21 °C. Comparison with the experiment (●) of the X-Y composition phase diagrams calculated by applying eq. (1) (solid line, random topography) and eq. (2) (dashed line, patchwise topography). Part (B): Comparison of the individual theoretical isosteric heats of adsorption from the gaseous mixtures (● - SF₆, ▲ - CH₄) calculated by using the eqs (10), (11) and (12), respectively. Theoretical curves were calculated by using the parameters collected in Tables 1, 2 and 3

3. CONCLUSIONS

In the previous section we presented a simple way for using the AS approach to determine theoretically the mixed-gas adsorption phase diagrams and individual isosteric heats of adsorption accompanying them. We showed that the application of AS approach for non-ideal adsorption systems requires only the analytical expressions for the activity coefficient. While comparing the models of non-ideality used, it can be stated that the Flory-Huggins and Wilson model works better than RAS. It is probably due to the fact that the FH and W models are more general as they take into account the different size of molecules i.e. entropic effects.

All best-fit parameters necessary to calculate adsorption phase diagrams and isosteric heats of adsorption can be obtained by using the single-gas experimental data. The presented expressions are simple and can be applied for any model of non-ideality. Due to the simplicity of analytical expressions, the calculations are very fast and can be applied industrially.

4. APPENDIX

Regular Adsorbed Solution – RAS [11]

$$kT \ln \gamma_1^s = W_{12} (x_2^s)^2 + W_{13} (x_3^s)^2 + (W_{12} + W_{13} - W_{23}) x_2^s x_3^s \quad (\text{A1})$$

$$kT \ln \gamma_2^s = W_{12} (x_1^s)^2 + W_{23} (x_3^s)^2 + (W_{12} + W_{23} - W_{13}) x_1^s x_3^s \quad (\text{A2})$$

$$kT \ln \gamma_3^s = W_{13} (x_1^s)^2 + W_{23} (x_2^s)^2 + (W_{13} + W_{23} - W_{12}) x_1^s x_2^s \quad (\text{A3})$$

where x_i^s refers to the vacancy solution formalism and $x_1^s = \theta_{1r}$, $x_2^s = \theta_{2r}$, $x_3^s = (1 - \theta_{1r} - \theta_{2r})$. After differentiation over $(1/T)$:

$$k \left(\frac{\partial \ln \gamma_1^s}{\partial (1/T)} \right)_{\{x_i\}} = W_{12} (\theta_{2r})^2 + W_{13} (1 - \theta_{1r} - \theta_{2r})^2 + (W_{12} + W_{13} - W_{23}) \theta_{2r} (1 - \theta_{1r} - \theta_{2r}) \quad (\text{A4})$$

$$k \left(\frac{\partial \ln \gamma_2^s}{\partial (1/T)} \right)_{\{x_i\}} = W_{12} (\theta_{1r})^2 + W_{23} (1 - \theta_{1r} - \theta_{2r})^2 + (W_{12} + W_{23} - W_{13}) \theta_{1r} (1 - \theta_{1r} - \theta_{2r}) \quad (\text{A5})$$

Flory-Huggins model – FH [12]

$$\ln \gamma_1^s = -\ln\left(x_1^s + \frac{x_2^s}{a_{12}+1} + \frac{x_3^s}{a_{13}+1}\right) + \left[1 - \left(x_1^s + \frac{x_2^s}{a_{12}+1} + \frac{x_3^s}{a_{13}+1}\right)^{-1}\right] \quad (\text{A6})$$

$$\ln \gamma_2^s = -\ln\left(\frac{x_1^s}{a_{21}+1} + x_2^s + \frac{x_3^s}{a_{23}+1}\right) + \left[1 - \left(\frac{x_1^s}{a_{21}+1} + x_2^s + \frac{x_3^s}{a_{23}+1}\right)^{-1}\right] \quad (\text{A7})$$

$$\ln \gamma_3^s = -\ln\left(\frac{x_1^s}{a_{31}+1} + \frac{x_2^s}{a_{32}+1} + x_3^s\right) + \left[1 - \left(\frac{x_1^s}{a_{31}+1} + \frac{x_2^s}{a_{32}+1} + x_3^s\right)^{-1}\right] \quad (\text{A8})$$

and,

$$\begin{aligned} \left(\frac{\partial \ln \gamma_1^s}{\partial(1/T)}\right)_{\{x_i\}} &= \left(\frac{x_2^s \xi_{12}}{(a_{12}+1)^2} + \frac{x_3^s \xi_{13}}{(a_{13}+1)^2}\right) \\ &\quad \left[\left(x_1^s + \frac{x_2^s}{a_{12}+1} + \frac{x_3^s}{a_{13}+1}\right)^{-1} - \left(x_1^s + \frac{x_2^s}{a_{12}+1} + \frac{x_3^s}{a_{13}+1}\right)^{-2}\right] \end{aligned} \quad (\text{A9})$$

$$\begin{aligned} \left(\frac{\partial \ln \gamma_2^s}{\partial(1/T)}\right)_{\{x_i\}} &= \left(\frac{x_1^s \xi_{21}}{(a_{21}+1)^2} + \frac{x_3^s \xi_{31}}{(a_{31}+1)^2}\right) \\ &\quad \left[\left(\frac{x_1^s}{a_{21}+1} + x_2^s + \frac{x_3^s}{a_{31}+1}\right)^{-1} - \left(\frac{x_1^s}{a_{21}+1} + x_2^s + \frac{x_3^s}{a_{23}+1}\right)^{-2}\right] \end{aligned} \quad (\text{A10})$$

where

$$x_i^s = N_{it} \left[\frac{N_{1t} + N_{2t}}{N_{1t}M_1 + N_{2t}M_2} \right], \quad i = 1, 2 \quad \text{and} \quad x_3^s = 1 - x_1^s - x_2^s. \quad (\text{A11})$$

Wilson model (W)

$$\ln \gamma_1^s = 1 - \ln [x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13}] - \left[\frac{x_1^s}{x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13}} + \frac{x_2^s \Lambda_{21}}{x_1^s \Lambda_{21} + x_2^s + x_3^s \Lambda_{23}} + \frac{x_3^s \Lambda_{31}}{x_1^s \Lambda_{31} + x_2^s \Lambda_{32} + x_3^s} \right] \quad (\text{A12})$$

$$\ln \gamma_2^s = 1 - \ln [x_1^s \Lambda_{21} + x_2^s + x_3^s \Lambda_{23}] - \left[\frac{x_1^s \Lambda_{12}}{x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13}} + \frac{x_2^s}{x_1^s \Lambda_{21} + x_2^s + x_3^s \Lambda_{23}} + \frac{x_3^s \Lambda_{32}}{x_1^s \Lambda_{31} + x_2^s \Lambda_{32} + x_3^s} \right] \quad (\text{A13})$$

$$\ln \gamma_3^s = 1 - \ln [x_1^s \Lambda_{31} + x_2^s \Lambda_{32} + x_3^s] - \left[\frac{x_1^s \Lambda_{13}}{x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13}} + \frac{x_2^s \Lambda_{23}}{x_1^s \Lambda_{21} + x_2^s + x_3^s \Lambda_{23}} + \frac{x_3^s}{x_1^s \Lambda_{31} + x_2^s \Lambda_{32} + x_3^s} \right] \quad (\text{A14})$$

and

$$\left(\frac{\partial \ln \gamma_1^s}{\partial (1/T)} \right)_{(x_i)} = \frac{x_1^s (x_2^s \zeta_{12} + x_3^s \zeta_{13})}{(x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13})^2} - \frac{x_2^s \zeta_{12} + x_3^s \zeta_{13}}{x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13}} - \frac{x_2^s \zeta_{21}}{x_2^s + x_1^s \Lambda_{21} + x_3^s \Lambda_{23}} + \frac{x_2^s \Lambda_{21} (x_1^s \zeta_{21} + x_3^s \zeta_{23})}{(x_2^s + x_1^s \Lambda_{21} + x_3^s \Lambda_{23})^2} - \frac{x_3^s \zeta_{31}}{x_3^s + x_1^s \Lambda_{31} + x_2^s \Lambda_{32}} + \frac{x_3^s \Lambda_{31} (x_1^s \zeta_{31} + x_2^s \zeta_{32})}{(x_3^s + x_1^s \Lambda_{31} + x_2^s \Lambda_{32})^2} \quad (\text{A15})$$

$$\left(\frac{\partial \ln \gamma_2^s}{\partial (1/T)} \right)_{(x_i)} = - \frac{x_1^s \zeta_{12}}{x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13}} + \frac{x_1^s \Lambda_{12} (x_2^s \zeta_{12} + x_3^s \zeta_{13})}{(x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13})^2} + \frac{x_2^s (x_1^s \zeta_{21} + x_3^s \zeta_{23})}{(x_2^s + x_1^s \Lambda_{21} + x_3^s \Lambda_{23})^2} - \frac{x_1^s \zeta_{21} + x_3^s \zeta_{23}}{x_2^s + x_1^s \Lambda_{21} + x_3^s \Lambda_{23}} - \frac{x_3^s \zeta_{32}}{x_3^s + x_1^s \Lambda_{31} + x_2^s \Lambda_{32}} + \frac{x_3^s \Lambda_{32} (x_1^s \zeta_{31} + x_2^s \zeta_{32})}{(x_3^s + x_1^s \Lambda_{31} + x_2^s \Lambda_{32})^2} \quad (\text{A16})$$

where x_i^s are defined by eq. (A11).

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CURRICULUM VITAE



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