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Unit 5, No. 96, Shohadaye Jandarmery St., 12th Farvardin St.,
Enghelab Ave., Tehran-Iran P.O.Box: 13145-198
Tel: +98 21 66976060 Fax: +98 21 66970742
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Multicomponent Adsorption Equilibria: Effect of Site Matching Correlation in HEL and HIAST Models

M. Niknam Shahrak , A. Ahmadpour*

Chemical Engineering Department, Ferdowsi University of Mashhad, Iran
ahmadpour@um.ac.ir

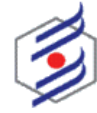
Abstract

In this study, the comparison between Perfect Negative (PN) and Perfect Positive (PP) site matching correlation (SMC) in Heterogeneous Extended Langmuir (HEL) and Heterogeneous Ideal Adsorbed Solution Theory (HIAST) models was done for estimating experimental data of three binary azeotrope mixtures ($C_3H_8-H_2S$, $C_3H_8-CO_2$ and $C_7H_8-C_3H_8O$) and a non-azeotrope mixture ($CH_4-C_2H_6$). The results show that Perfect Negative form of these models predicts the experimental data fairly well when size and polarity differences of adsorbates are large and pore size distribution of adsorbent is extensive.

Keywords: Multicomponent adsorption, Azeotrope, HEL, HIAST, Site matching correlation.

Introduction

Design of equipment and operation of adsorption processes require knowledge of multicomponent equilibria. Experimental equilibrium data for single component adsorption could be determined in a simple way, while measurement of multicomponent adsorption equilibrium data is relatively costly and difficult process. Therefore, implementation of models using only single component adsorption isotherms for estimating multicomponent adsorption equilibrium data could solve this problem. Extended Langmuir (EL), Ideal Adsorbed Solution Theory (IAST), Dual Site Langmuir (DSL), Heterogeneous Extended Langmuir (HEL) and Heterogeneous Ideal Adsorbed Solution Theory (HIAST) are most commonly used multicomponent adsorption models. Unfortunately, most of these models cannot predict azeotropic behavior of adsorbed phase in the multicomponent adsorption process. In these systems, selectivity could be changed from a particular component to another one by gas phase mole fraction variation. Thereby, many efforts have been done to find appropriate models that describe azeotropic behavior of adsorbed phase. In one of these studies by Ritter in 2011 [1], attention was made to choose appropriate form of Site Matching Correlation (SMC; Perfect Negative (PN) or Perfect Positive (PP)) as one of the factors affecting the results of predictive multicomponent adsorption models specially for azeotropic mixtures. HIAST and HEL models were presented on the basis of PP SMC in order to improve IAST and EL models by account adsorption heterogeneity in 1988 and 1990, respectively [2,3]. Simulation results of these models have been published in a few monographs, but none of them used PN SMC [4]. In this study, for the first time, PN form of SMC has been applied in HEL and HIAST models for



various binary mixtures and calculated results have been compared with the experimental data. Also, physical relation between azeotropic behavior and PN SCM has been explained.

Theory

1- Single Component Isotherm. Prediction of multicomponent adsorption equilibrium by HEL and HIAST models need to use Unilan isotherm equilibrium parameters This isotherm was introduced by Honig in 1952 as:

$$n = \frac{n_s}{2s} \ln \left(\frac{1 + b \exp(s)p}{1 + b \exp(-s)p} \right) \quad (1)$$

$$s = \frac{E_{max} - E_{min}}{2RT}; \quad b = b_0 \exp \left(\frac{\bar{E}}{RT} \right); \quad \bar{E} = \frac{E_{max} + E_{min}}{2}$$

Where n_s , b and s denote saturation capacity, affinity constant and system heterogeneity and E_{max} , E_{min} and \bar{E} are maximum, minimum and average energies of adsorption, respectively.

2- Multicomponent Adsorption Isotherm. Calculative algorithm of HIAST and HEL models could be find in detail elsewhere [2,3]. The adsorbed amount of each component is given by Olivier-Ross equation as follow:

$$n_i = \int_0^{\infty} n_i(T, P, y, E_1, E_2, \dots, E_{N_c}) F(E_i) dE_i \quad (2)$$

To apply Eqn. (2) for estimating adsorbed phase concentration of each component, the following must be determined:

a) Specify the local multicomponent adsorption isotherm or $n_i(T, P, y, E)$; EL or IAST.

b) Specify type of energy distribution or $F(E)$; Uniform distribution function in both models.

$$F(E) = \begin{cases} \frac{1}{E_{max} - E_{min}} & E_{min} \leq E \leq E_{max} \\ 0 & E > E_{max} \text{ or } E < E_{min} \end{cases} \quad (2a)$$

c) Specify site matching correlation form (PP or PN); assuming that the adsorbed phase composed of two patches of adsorption sites, the PP and PN SMC are explained as follow.

i. PP SMC occurs when both adsorbates meet patch 1 as a high-energy patch and patch 2 as a low-energy patch. Eqn. (3) describes PP form of SMC between various components.

$$\int_{E_{min,i}}^{E_i} F(E_i) dE_i = \int_{E_{min,j}}^{E_j} F(E_j) dE_j \quad (3)$$

ii. PN SMC occurs when one adsorbate meets patch 1 as a high-energy patch while another component sees patch 1 as a low-energy patch. Eqn. (4) describes PN form of SMC.

$$\int_{E_{min,i}}^{E_i} F(E_i) dE_i = \int_{E_j}^{E_{max,j}} F(E_j) dE_j \quad (4)$$

Results and Discussion

Adsorption equilibria of various gases on H-Mordenite [5], Zeolite DAY13 [6] and Template Carbon [7] were used to achieve HEL and HIAST results. The equilibrium parameters were obtained by fitting Unilan model to the single component experimental data and Average Relative Errors (AREs) are presented in Table 1. ARE is defined as:

$$ARE(\%) = \frac{100}{N_c} \sum_{i=1}^{N_c} \left| \frac{n_p - n_e}{n_e} \right| \quad (5)$$

Where n_p and n_e denotes the predicted and experimental amounts adsorbed, respectively.

Three different binary azeotrope systems including adsorption of C_3H_8 - H_2S and C_3H_8 - CO_2 on H-Mordenite and adsorption of C_7H_8 - C_3H_8O on Zeolite DAY13 have been chosen to compare PP and PN results. Differences between the experimental data and the predicted values of PP



and PN SMC are evaluated as the average relative error with respect to the amount adsorbed for each component (n_i), to the total amount adsorbed (n_{Total}) and the arithmetic mean of n_i 's (n_{Avg}) is named as the general average relative error for the amount adsorbed. These values are presented in Tables 2 and 3 for HEL and HIAST models. The results show that AREs of PN form prediction of HEL and HIAST models are less than PP prediction for the mentioned azeotrope systems. Unlike H₂S, PP-HEL prediction for C₃H₈ is better than PN-HEL prediction in C₃H₈-H₂S binary system. In this situations, appropriate model is specified by n_{Avg} , therefore PN prediction is more accurate than PP correlation for this binary pair. x-y equilibrium diagram of C₇H₈(1)-C₃H₈O(2) mixture is shown in Figure 1. This figure indicates that PN-HEL and PN-HIAST can predict the experimental data or azeotropic behavior of adsorbed phase, but PP prediction is not correct. In fact, weaker component (smaller affinity constant) in azeotropic mixtures is strongly adsorbed on the patches where stronger component is excluded from them. So, PN form can describe azeotropic behavior.

Table 1. Equilibrium parameters of Unilan isotherm for single component adsorption

Adsorbate	T (K)	Adsorbent	n_s (mmol/g)	b_0 (1/Kpa)	E_{min} (J/mol)	E_{max} (J/mol)	ARE (%)
CO ₂	303	H-Mordenite	8.033	8.471×10^{-8}	195.00	40145	7.78
H ₂ S			5.525	2.679×10^{-6}	0.3870	40493	1.03
C ₃ H ₈			1.44	5.678×10^{-7}	19916	42976	6.67
C ₇ H ₈	298	Y-Zeolite	2.249	0.05531	12522	29567	0.25
C ₃ H ₈ O			DAY-13	3.14	0.2252	2485.0	19276
CH ₄	273	Template	44.98	1.031×10^{-7}	163.00	21594	8.38
C ₂ H ₆			Carbon	29.05	2.886×10^{-7}	878.00	26578

Table 2. Average relative errors predicted from PP-HEL and PN-HEL models at indicated conditions

Adsorbent	Binary pair	P (kPa)	T (K)	PP				PN			
				n_1	n_2	n_{Avg}	n_{Total}	n_1	n_2	n_{Avg}	n_{Total}
Mordenite	C ₃ H ₈ (1)+CO ₂ (2)	41	303	11.24	91.06	51.15	33.74	13.71	31.52	22.62	19.41
	C ₃ H ₈ (1)+H ₂ S(2)	8	303	14.09	71.22	42.66	37.19	31.16	9.83	20.50	11.81
DAY-13	C ₇ H ₈ (1)+C ₃ H ₈ O(2)	0.35	298	86.60	80	83.30	9.30	51.23	29.33	40.28	2.65
TC	CH ₄ (1)+C ₂ H ₆ (2)	101.3	273	37.07	3.83	20.45	8.53	11.40	3.87	7.64	3.02

Adsorption of CH₄-C₂H₆ on Template Carbon is another binary system that shows PN-HEL simulated results are more proper than PP-HEL model, as seen from Figure 2 and Table 2. This is not an azeotrope mixture, but due to wide pore size distribution on Template Carbon, smaller micropores are only accessible to CH₄ molecules. So, PN form of SMC occurs in this system. Unfortunately, there is not any theoretical guidelines for developing a correct criterion for site matching correlation. However, using PN form of SMC is reasonable when high discrepancy appears between adsorbates sizes and polarities (and even affinity constants).

Conclusion

The behaviours of PP and PN site matching correlations in HEL and HIAST models were investigated for estimating the experimental data of various binary mixtures. From the results, PN form of SMC in calculative algorithm of HEL and HIAST can predict experimental data more accurately than PP form of SMC when the adsorbate sizes and polarities of the components differ substantially, especially for azeotropic mixtures.



Table 3. Average relative errors predicted from PP-HIAST and PN-HIAST models at indicated conditions

Adsorbent	Binary pair	P (kPa)	T(K)	PP				PN			
				n ₁	n ₂	n _{Avg}	n _{Total}	n ₁	n ₂	n _{Avg}	n _{Total}
Mordenite	C ₃ H ₈ (1)+CO ₂ (2)	41	303	62.43	84.30	73.36	8.74	23.52	21.39	22.45	16.48
	C ₃ H ₈ (1)+H ₂ S(2)	8	303	78.69	68.46	73.58	18.62	61.85	13.85	37.85	9.60
DAY-13	C ₇ H ₈ (1)+C ₃ H ₈ O(2)	0.35	298	65.7	55.9	60.8	2.53	34.19	14.47	24.33	4

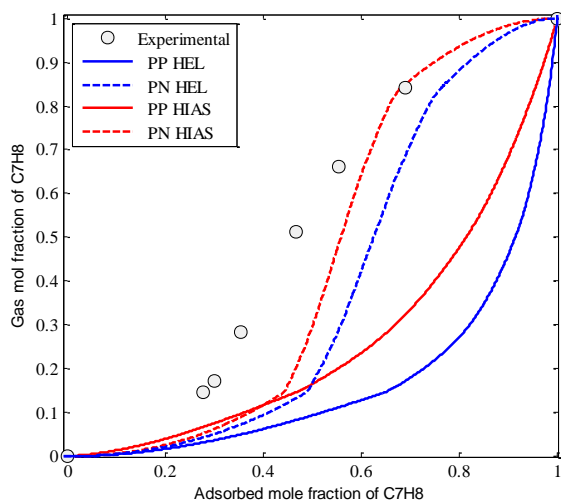


Figure 1. x-y equilibrium diagram of Toluene for Adsorption of Toluene-1, Propanol on zeolite DAY13 at 298 K and 0.35 Kpa.

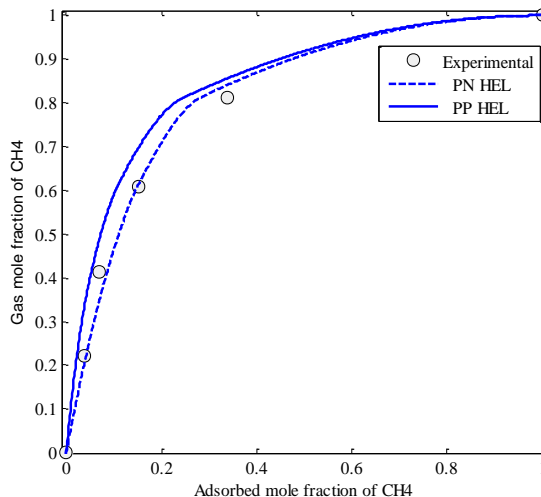


Figure 2. x-y equilibrium diagram of Methane for adsorption of Methane-Ethane on Template Carbon at 273 K and 101.3 Kpa .

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