Adsorbed Solution Theory Models for Multicomponent Adsorption Equilibria

A new approach is developed for applying ideal and real adsorbed solution theory models to the description of multicomponent adsorption equilibria at fixed pressure. This allows ignoring single-component behavior in the Henry's law region, $P \rightarrow 0$, but introduces new parameters that must be evaluated from binary equilibrium data. Comparisons with various sets of experimental data show that the new approach gives results as good as the classical one, but without requiring knowledge of the single component behavior in the Henry's law region; moreover, it removes the sensitivity to the type of model adopted in fitting single-component equilibrium data.

Giuseppe Gamba
Renato Rota
Giuseppe Storti
Sergio Carra
Dipartimento di Chimica Fisica Applicata
Politecnico di Milano
20133 Milano, Italy

Massimo Morbidelli
Dipartimento di Ingegneria Chimica
e Materiali
Universitá di Cagliari
09123 Cagliari, Italy

Introduction

The use of adsorption as a tool for separating multicomponent mixtures makes it necessary to describe multicomponent adsorption equilibria in a rather accurate fashion. The most widely used thermodynamic model is IAST (ideal adsorption solution theory), developed by Myers and Prausnitz (1965), which can be extended to RAST (real adsorption solution theory) when dealing with adsorbed phases exhibiting deviations from ideal behavior. This is done by introducing an activity coefficient for the adsorbed phase, so that the equality between the fugacities of the generic ith component in the two phases in equilibrium can be written as follows:

$$Py_i = p_i^o(\pi, T)\gamma_i x_i \tag{1}$$

where for simplicity ideal behavior for the gaseous phase is assumed. The single-component pressure value $p_i^o(\pi, T)$ in equilibrium, at the same spreading pressure and temperature values as the mixture, is given by the Gibbs isotherm;

$$\psi = \frac{\pi A}{RT} = \int_0^{p_i^o} \Gamma_i^o(P)\, d \ln P \tag{2}$$

where $\Gamma_i^o(P)$ indicates the single-component equilibrium isotherm. Equations 1 and 2 can be used, together with the stoichiometric relationship:

$$\sum_{i=1}^{N} x_i = 1 \tag{3}$$

to compute multicomponent equilibria. In particular, for given temperature, pressure, and gas phase composition, from Eqs. 1–3 the spreading pressure and adsorbed phase composition at equilibrium conditions can be calculated.

The adsorbed amount for each component may be calculated as follows:

$$\Gamma_i = \Gamma_t x_i \tag{4}$$

where:

$$\frac{1}{\Gamma_t} = \sum_{i=1}^{N} \frac{x_i}{\Gamma_i^o(\pi)} + \sum_{i=1}^{N} x_i \left(\frac{\partial \ln \gamma_i}{\partial \psi}\right) \tag{5}$$

The IAST model requires knowledge of single-component adsorption isotherms, $\Gamma_i^o(P)$ in the pressure range $0 \le P \le p_i^o$, and from these predicts multicomponent equilibrium behavior. In the case of nonideal mixtures, the RAST model needs binary equilibrium data as well, so as to estimate the adjustable binary interaction parameters to be used in some suitable model for activity coefficients in multicomponent mixtures. In fact, no thermodynamic model available at the present time can extract such information about intermolecular interactions between two

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Correspondence concerning this paper should be addressed to M. Morbidelli.

different components from single-component equilibrium behavior.

In this work, the Hildebrand model (Hildebrand et al., 1970), originally developed for liquid mixtures in the context of the regular solution theory and suitably modified so as to include the spreading pressure dependence, has been used. In particular, according to the relationship suggested by Myers (1986) for binary systems, the following empirical expressions for multicomponent systems have been derived such that the limiting conditions for $P \to 0$ and $x_i \to 1$ are fulfilled:

$$\ln \gamma_i = \Sigma_j \Sigma_k (A'_{ji} - \tfrac{1}{2} A'_{jk}) \Phi_j \Phi_k \tag{6}$$

$$\Phi_i = \frac{x_i/\Gamma_i^o(p_i^o)}{\Sigma_j x_j/\Gamma_j^o(p_j^o)} \tag{7}$$

$$A'_{jk} = \frac{1 - e^{-C_{jk}\psi}}{\Gamma_i^o(p_i^o)} A_{jk}; \quad A_{jk} = A_{kj}; \quad A_{jj} = 0 \tag{8}$$

where C_{jk} and A_{jk} are adjustable parameters to be evaluated by comparison with experimental binary equilibrium data.

The major difficulty encountered in using either IAST or RAST is in the evaluation of the integral on the righthand side of Eq. 2, which is very sensitive to the value of $\Gamma_i^o(P)$ at low pressure. As a consequence, the value of p_i^o, and then the result of the entire equilibrium calculation, is very sensitive to the accuracy of the single-component isotherm representation in the Henry's law region. Therefore, the IAST or RAST prediction is often dependent upon the type of single-component isotherm used to fit the same set of equilibrium data (Myers, 1987; Rasmuson, 1986).

The obvious solution to this problem is to experimentally investigate the single-component behavior at low pressure values, down to the Henry's law region. Often this is not easily done in practice, and particularly for strongly adsorbable components, whose Henry's law region may be confined to extremely low pressure values. However, besides these experimental difficulties, this procedure is intrinsically not convenient when the goal is to compute the equilibrium behavior at a fixed pressure value P, inasmuch as it requires investigating single-component behavior at much lower pressure values. In such a situation the most active sites of the adsorbent surface, which at the larger pressure value of interest are always covered, enter the adsorption-desorption equilibrium processes. This enhances the effect of surface heterogeneity on the equilibrium behavior.

The aim of this work is to present an alternative way of applying the IAST or RAST model, one that does not require knowledge of the single-component Henry's law region, but introduces new parameters to be determined from binary equilibrium data. It should be noted that we refer to multicomponent equilibria at fixed pressure, since this is the situation prevailing in applications such as fixed-bed adsorbers for bulk separation processes.

New Approach to IAST and RAST

In order to avoid the single-component Henry's law region, Eq. 2 is modified as follows:

$$\psi - \psi_i^* = \Delta\psi - \Delta\psi_i^* = \int_P^{p_i^o} \Gamma_i^o(P)\, d \ln P \tag{9}$$

where the first extreme of integration is not zero, but rather is equal to the pressure value at which the multicomponent equilibrium is to be computed. ψ_i^* is the value corresponding to the spreading pressure at equilibrium conditions for the single ith component; $\Delta\psi_i^* = \psi_i^* - \psi_1^*$ and $\Delta\psi = \psi - \psi_1^*$. The value of $\Delta\psi$ is obtained from Eq. 3, while $\Delta\psi_i^*$, with $i = 1, 2 \,.\,.\, N$, represents $N - 1$ independent parameters ($\Delta\psi_1^* = 0$), which, even though related to single-component behavior, are more conveniently estimated from binary data (at pressure P). The advantage of Eq. 9 over Eq. 2 is that the single-component Henry's law region is not involved any more. It is worthwhile noticing that a similar approach has been suggested before, in a different context, by Myers (1973).

Following the same procedure, the coefficients A'_{jk} in the Hildebrand model as given by Eq. 8 are modified as follows:

$$A'_{jk} = \frac{1 - \eta_{jk} e^{-C_{jk}\Delta\psi}}{\Gamma_i^o(p_i^o)} A_{jk}; \quad A_{jk} = A_{kj}; \quad A_{jj} = 0 \tag{10}$$

where the new parameter η_{jk}, defined as $\eta_{jk} = \exp(-C_{jk}\psi_1^*)$, has been introduced. This is regarded as an adjustable parameter to be evaluated from binary equilibrium data.

In Figure 1 the qualitative behavior of spreading pressure is shown as a function of pressure for two components, whose mixture is assumed not to be azeotropic. Thus, when operating at pressure P and depending upon mixture composition, the mixture equilibrium ψ value lies between ψ_1^* and ψ_2^* (corresponding to the single-component equilibrium at P). Consequently, the value of p_1^o lies between p_{1A}^o and P, and that of p_2^o (relative to the less adsorbable component) between P and p_{2B}^o. These are the pressure ranges where the single-component equilibrium behavior has to be investigated.

It can be noted that it is necessary to investigate pressure values larger than P for the less adsorbable component, and lower than P for the more adsorbable one. These may involve pressure intervals not covered by experimental data, particularly when the two components have largely different adsorptivity, so that p_{1A}^o and p_{2B}^o lie quite apart from P. For the high-pressure region this problem, which also arises in the classical approach, Eq. 2, is much less important, because the integrand in Eq. 2 or Eq. 9 vanishes for increasing pressure values. On the other hand, in the low-pressure region this extrapolation can be a very important source of error. In this case Eq. 9 has the advantage over Eq. 2 that such extrapolation is stopped at p_{1A}^o, rather than at

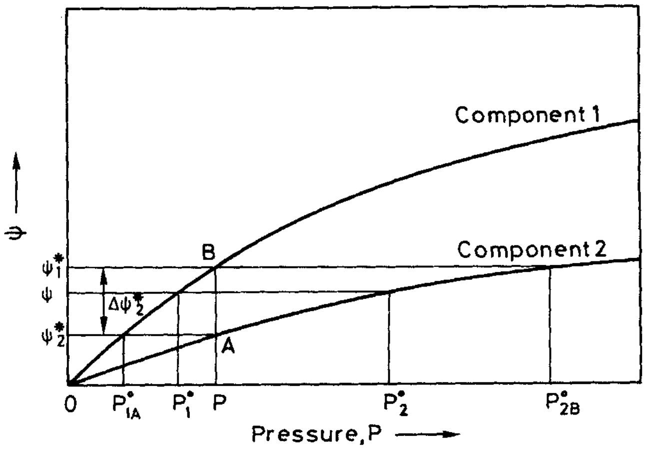

Figure 1. ψ behavior as a function of pressure for two single components.

Table 1. Average % Error in Reproducing Single-Component Equilibrium Data for Ethylene, Propane, and Ethane

	Range of Exp. Data Considered*			
	$\Gamma^\infty/2 < \Gamma < \Gamma^\infty$		$0 < \Gamma < \Gamma^\infty$	
	Langmuir Model	Toth Model	Langmuir Model	Toth Model
C_2H_4	4.89	0.50	12.30	1.82
C_3H_8	4.48	1.76	7.53	3.72
C_2H_6	0.69	0.74	3.39	2.25

*Experimental data of Costa et al. (1984).

Table 2. Parameter Values of Single-Component Equilibrium Models Reported in Table 1

	Range of Exp. Data Considered*			
	$\Gamma^\infty/2 < \Gamma < \Gamma^\infty$		$0 < \Gamma < \Gamma^\infty$	
	Langmuir Model	Toth Model	Langmuir Model	Toth Model
C_2H_4	$K = 52.67$ $\Gamma^\infty = 2.60$ E-3	$A = 4.20$ E-3 $B = 0.11$ $C = 0.23$	$K = 87.02$ $\Gamma^\infty = 2.52$ E-3	$A = 3.45$ E-3 $B = 8.99$ E-2 $C = 0.33$
C_3H_8	$K = 158.19$ $\Gamma^\infty = 1.88$ E-3	$A = 2.35$ E-3 $B = 5.95$ E-2 $C = 0.31$	$K = 188.39$ $\Gamma^\infty = 1.87$ E-3	$A = 2.04$ E-3 $B = 3.25$ E-2 $C = 0.54$
C_2H_6	$K = 7.14$ $\Gamma^\infty = 2.28$ E-3	$A = 2.35$ E-3 $B = 0.15$ $C = 0.92$	$K = 6.80$ $\Gamma^\infty = 2.31$ E-3	$A = 2.22$ E-3 $B = 0.12$ $C = 1.11$

zero. In many situations this means that the Henry's law region of this component can be fully ignored.

In order to confidently apply Eq. 9 without extrapolating the single-component isotherm model to regions not covered by experimental data, it would be necessary to know *a priori* the values of p_{1A}^o and p_{2B}^o. Since this is not possible, a trial and error procedure should be performed. This can be avoided in practice by using, as a rule of thumb, the criterion of investigating single-component equilibria down to about one-half of their saturation coverage, and then relying on the particular isotherm adopted for any possible extrapolation. A useful check of the accuracy of the procedure (besides *a posteriori* computation of p_{1A}^o and p_{2B}^o), is to verify the insensitivity of the results obtained to the type of isotherm adopted for describing single-component equilibria.

Comparison with Experimental Data

In order to investigate the reliability of the proposed approach, a comparison between the results obtained with the modified RAST model using only single-component equilibrium data outside the Henry's law region and the best performance of the classic RAST model using all single-component equilibrium data has been performed.

The experimental data used to compare the two models have been reported by Costa et al. (1984) and refer to the nonideal system ethylene-propane-ethane on zeolite 5Å at $P = 93$ kPa and $T = 293$ K.

In order to show the role of the data in the Henry's law region, let us first consider, for each single component, only equilibrium data corresponding to surface coverage larger than one-half of the saturation value. Obviously, all these data lie well outside the Henry's law region, and thus any equilibrium model adopted for their interpretation will most likely give a very poor representation of such a region. In particular, the following two single-component isotherms are considered:

$$\text{Langmuir} \quad \Gamma_i = \frac{K_i P \Gamma_i^\infty}{1 + K_i P} \tag{11}$$

$$\text{Toth} \quad \Gamma_i = \frac{A_i P}{(B_i + P^{C_i})^{1/C_i}} \tag{12}$$

which include two and three adjustable parameters, respectively. The average percentage errors (with reference to the adsorbed amount) obtained for each model in fitting the experimental data mentioned above are reported in the left half of Table 1, while the corresponding parameter values are summarized in the same portion of Table 2. As expected, the Langmuir model, which includes a lower number of adjustable parameters, is much less accurate than the Toth model.

By means of the single-component isotherms obtained in this way, it is now possible to fit the experimental data relative to the three binary systems and then predict the ternary equilibrium data using the modified RAST model, that is, Eqs. 1, 3–7, 9, and 10. The average percentage errors obtained following this approach are summarized in Table 3 under the heading Modified RAST. The corresponding parameter values are shown in Table 4 under the same heading. It is worth noticing that in the system under examination, the three parameters $\Delta\psi_j^*$, each estimated independently from one set of binary equilibrium data,

Table 3. Average % Error in Reproducing Binary and Ternary Equilibrium Data (Models with Activity Coefficients Depending upon Spreading Pressure)†

	Binary Model					
	Modified RAST		Classic RAST Single-Component Model		Classic RAST	
	Langmuir*	Toth*	Langmuir*	Toth*	Langmuir**	Toth**
C_2H_4–C_3H_8	2.51	1.49	18.33	3.80	11.42	3.49
C_2H_4–C_2H_6	5.05	5.17	20.35	7.69	10.34	5.76
C_3H_8–C_2H_6	3.37	2.94	3.70	18.60	6.96	7.40
C_2H_4–C_3H_8–C_2H_6	5.84	4.09	18.35	11.33	13.96	7.10

*Parameters as in lefthand portion of Table 2.
**Parameters as in righthand portion of Table 2.
†Experimental data of Costa et al. (1984).

Table 4. Parameters of Equilibrium Models Reported in Table 3

	Binary Model					
	Modified RAST		Classic RAST Single-Component Model		Classic RAST	
	Langmuir*	Toth*	Langmuir*	Toth*	Langmuir**	Toth**
C_2H_4–C_3H_8	$\Delta\psi_j^* = -2.33$ E-3 $A_{ij} = -7.24$ E-2 $C_{ij} = 4.85$ $\eta_{ij} = 0.95$	$\Delta\psi_j^* = -2.39$ E-3 $A_{ij} = -2.10$ E-2 $C_{ij} = 5.04$ $\eta_{ij} = 0.81$	$A_{ij} = -2.46$ E-3 $C_{ij} = 3.00$ E + 3	$A_{ij} = -4.43$ E-3 $C_{ij} = 150.95$	$A_{ij} = -2.25$ E-3 $C_{ij} = 3.02$ E + 3	$A_{ij} = -5.59$ E-3 $C_{ij} = 97.46$
C_2H_4–C_2H_6	$\Delta\psi_j^* = -7.42$ E-3 $A_{ij} = -3.00$ E-2 $C_{ij} = 8.54$ $\eta_{ij} = 0.84$	$\Delta\psi_j^* = -7.41$ E-3 $A_{ij} = -7.83$ E-3 $C_{ij} = 79.17$ $\eta_{ij} = 0.39$	$A_{ij} = -3.08$ E-3 $C_{ij} = 3.87$ E + 3	$A_{ij} = -8.57$ E-3 $C_{ij} = 83.74$	$A_{ij} = -3.08$ E-3 $C_{ij} = 3.83$ E + 3	$A_{ij} = -8.30$ E-3 $C_{ij} = 72.06$
C_3H_8–C_2H_6	$\Delta\psi_j^* = -4.69$ E-3 $A_{ij} = -6.00$ E-3 $C_{ij} = 10.88$ $\eta_{ij} = 0.93$	$\Delta\psi_j^* = -4.67$ E-3 $A_{ij} = -5.73$ E-3 $C_{ij} = 29.36$ $\eta_{ij} = 0.89$	$A_{ij} = -1.44$ E-2 $C_{ij} = 3.78$	$A_{ij} = -3.11$ E-3 $C_{ij} = 228.64$	$A_{ij} = -2.49$ E-2 $C_{ij} = 4.30$	$A_{ij} = -3.28$ E-2 $C_{ij} = 4.31$

*Parameters as in lefthand portion of Table 2.
**Parameters as in righthand portion of Table 2.

satisfy the thermodynamic consistency constraint (Syrcar and Myers, 1971):

$$(\psi_1^* - \psi_2^*) + (\psi_2^* - \psi_3^*) + (\psi_3^* - \psi_1^*) = 0 \quad (13)$$

with a reasonably small percentage error.

It should be mentioned that in the above parameter estimation procedure, the objective function has been taken as the sum of the squares of the differences between calculated and experimental values of the amount adsorbed for each component, Γ_i.

The results reported in Table 3 show not only that the errors are small, but also that the modified RAST model is not sensitive to the type of single-component equilibrium model adopted. This is because the Henry's law region, which is where such single-component equilibrium models differ, has now been ruled out. The effect of the proposed modification of RAST becomes evident when considering the results of the classic RAST, Eqs. 1–8, obtained using the same single-component models as above, that is, ignoring the Henry's law region. Such results are summarized in the central portions of Tables 3 and 4 under the heading Classic RAST, and they confirm not only that the accuracy in reproducing the experimental data is poor, but also that the method is very sensitive to the model adopted for describing single-component equilibria.

The only way to obtain the same performance as the modified RAST with the classic RAST model is to investigate experimentally the Henry's law region for each single component. In the case under examination this can be done by considering all the single-component equilibrium data reported by Costa et al. (1984). The errors obtained by fitting such data with the two single-component equilibrium models, Eqs. 11 and 12, are summarized in the right half of Table 1, while the corresponding values of the adjustable parameters are reported in Table 2. The errors and parameter values relative to the fitting of binary systems and the prediction of ternary systems are shown under the heading Classic RAST on the righthand sides of Tables 3 and 4, respectively. It appears that the sensitivity to the type of single-component model adopted is very strong. In particular, when using the Langmuir model both the correlation of binary data and the prediction of the ternary data are poor, since the Langmuir model does not represent appropriately the single-component equilibrium data in the Henry's law region. This is confirmed by the clear improvement encountered when using the more accurate Toth isotherm. However, even in this case the performance of the classic RAST model is never superior to that of the modified RAST model. This is because apparently the available experimental data for single-component equilibria are not sufficient to perfectly cover the Henry's law region.

Table 5. Average % Error in Reproducing Binary and Ternary Equilibrium Data Models with Activity Coefficients Not Depending upon Spreading Pressure†

	Binary Model					
	Modified RAST		Classic RAST Single-Component Model		Classic RAST	
	Langmuir*	Toth*	Langmuir*	Toth*	Langmuir**	Toth**
C_2H_4–C_3H_8	9.39	2.47	18.34	3.21	11.42	4.33
C_2H_4–C_2H_6	8.38	9.32	20.35	10.05	10.34	10.07
C_3H_8–C_2H_6	4.29	4.35	4.80	16.85	7.27	7.08
C_2H_4–C_3H_8–C_2H_6	9.33	7.82	18.58	13.59	13.79	9.71

*Parameters as in lefthand portion of Table 2.
**Parameters as in righthand portion of Table 2.
†Experimental data by Costa et al. (1984).

Table 6. Parameters of Equilibrium Models Reported in Table 5

	Binary Model					
	Modified RAST		Classic RAST		Classic RAST	
	Single-Component Model					
	Langmuir*	Toth*	Langmuir*	Toth*	Langmuir**	Toth**
C_2H_4–C_3H_8	$\Delta\psi_j^* = -2.42$ E-3 $A_{ij} = -3.10$ E-3	$\Delta\psi_j^* = -2.41$ E-3 $A_{ij} = -3.82$ E-3	$A_{ij} = -2.46$ E-3	$A_{ij} = -3.58$ E-3	$A_{ij} = -2.25$ E-3	$A_{ij} = -3.43$ E-3
C_2H_4–C_2H_6	$\Delta\psi_j^* = -7.32$ E-3 $A_{ij} = -3.72$ E-3	$\Delta\psi_j^* = -7.22$ E-3 $A_{ij} = -3.60$ E-3	$A_{ij} = -3.07$ E-3	$A_{ij} = -4.79$ E-3	$A_{ij} = -3.08$ E-3	$A_{ij} = -3.65$ E-3
C_3H_8–C_2H_6	$\Delta\psi_j^* = -4.67$ E-3 $A_{ij} = -2.19$ E-4	$\Delta\psi_j^* = -4.61$ E-3 $A_{ij} = -1.21$ E-4	$A_{ij} = -3.04$ E-3	$A_{ij} = -2.61$ E-3	$A_{ij} = -7.14$ E-4	$A_{ij} = -8.85$ E-4

*Parameters as in lefthand portion of Table 2.
**Parameters as in righthand portion of Table 2.

A closer analysis of the values of the adjustable parameters reported in Table 4, as obtained by the modified RAST, indicate that those parameters representing the nonideal behavior of the system still exhibit a significant sensitivity to the type of model adopted for representing single-component equilibria. The reason is that such parameters (i.e., A_{ij}, C_{ij}, and η_{ij}) are strongly correlated and, in the particular case under examination here, they are redundant since the effect of the spreading pressure on the activity coefficients is actually very small in the range of operating conditions covered by the experimental data at hand. This point is well illustrated by the results shown in Tables 5 and 6, which correspond to the same situations analyzed in Tables 3 and 4, but now neglecting the effect of spreading pressure on the activity coefficients, that is, $C_{jk} = 0$ and $\eta_{jk} = 1$ in Eq. 10. The results obtained indicate that the accuracy in reproducing the experimental data is not significantly decreased, while the values of the adjustable parameters are now independent of the particular single-component equilibrium model adopted. Thus, the parameter sensitivity evidenced in Table 4 is not due to the proposed modification of RAST, but rather is intrinsic to the available experimental data, which do not allow for an unambiguous and quantitative estimation of the effect of the spreading pressure on the activity coefficients. Most likely this would require investigation of a much wider interval of spreading pressure values, such as is usually obtained by exploring a wider range of pressure values (particularly including the limit where $P \rightarrow 0$).

Another example of application of the proposed approach is offered by the data reported by Talu and Zwiebel (1986) relative to the ideal system H_2S-CO_2 on H-mordenite at 16 kPa and 303 K. The single-component equilibrium data reported in the work mentioned above, which also involve the Henry's law region, have been fitted using the isotherm models of Freundlich:

$$\Gamma_i = A_i P^{1/\beta_i} \tag{14}$$

and Langmuir, Eq. 11.

The relative average percentage errors obtained using the modified and classic IAST models are summarized in Table 7. The corresponding parameter values are reported in Table 8. The results of the classic IAST model confirm the conclusion reached by Myers (1987) for this same system: the Freundlich model leads to much larger errors than the Langmuir model due to its intrinsic inability to correctly reproduce the single-component Henry's law region (i.e., as $P \rightarrow 0$, $\Gamma/P \rightarrow \infty$). However, this difficulty is overcome when using the proposed modified IAST model. In particular, the results reported in the lefthand

Table 7. Average % Error in Reproducing Single-Component and Binary Equilibrium Data for Ideal System H_2S–CO_2

	Binary Model			
	Modified IAST		Classic IAST	
	Single-Component Model			
	Langmuir	Freundlich	Langmuir	Freundlich
H_2S	4.86	0.86	7.03	2.21
CO_2	2.33	0.92	16.67	6.47
H_2S–CO_2	15.80	15.10	17.17	40.35

Experimental data of Talu and Zwiebel (1986).

Table 8. Parameters of Equilibrium Models Reported in Table 7

	Single-Component Model			
	Modified IAST		Classic IAST	
	Binary Model			
	Langmuir	Freundlich	Langmuir	Freundlich
H_2S	$K = 69.96$ $\Gamma^\infty = 2.25$ E-3	$A = 2.99$ E-3 $\beta = 5.02$	$K = 103.56$ $\Gamma^\infty = 2.14$ E-3	$A = 3.09$ E-3 $\beta = 4.66$
CO_2	$K = 4.36$ $\Gamma^\infty = 2.70$ E-3	$A = 2.19$ E-3 $\beta = 3.33$	$K = 7.56$ $\Gamma^\infty = 2.41$ E-3	$A = 2.22$ E-3 $\beta = 2.91$
H_2S–CO_2	$\Delta\psi^*_{ij} = -4.32$ E-3	$\Delta\psi^*_{ij} = -4.32$ E-3	—	—

side of Table 7, obtained by considerng only single-component data with surface coverage greater than one-half of the saturation value (thus fully disregarding the Henry's law region), show that the performance of the Freundlich model becomes comparable to that of the Langmuir model. This is because the proposed approach does not depend upon the accuracy of the representation of single-component Henry's law region.

The most important conclusion arising from the comparisons shown in Tables 3 and 7 is that the proposed approach allows one to obtain the same results as with the classic approach, but without requiring knowledge of single-component equilibria in the Henry's law region.

Comparison of RAST and Modified RAST Models

In order to further support the above conclusion, one more comparison between the modified and the classic approaches has been carried out, where a fictitious set of experimental data, generated through a suitable equilibrium model, has been considered. This allows one to disentangle the errors due to the proposed procedure and other errors due to scatter in the experimental data.

Let us consider a fictitious binary mixture whose components, *A* and *B*, when not mixed behave according to the single-component Toth adsorption isotherm, Eq. 12, characterized by the following parameter values:

$$A_A = 0.003 \quad A_B = 0.002$$
$$B_A = 0.05 \quad B_B = 0.1$$
$$C_A = 0.8 \quad C_B = 1.2$$

Using Eq. 12, fictitious single-component equilibrium data in the range $\Gamma_i^\infty/2$ to Γ_i^∞, thus excluding the Henry's law region as discussed above, are generated. Such data have been used for tuning, through a suitable nonlinear regressive analysis, the adjustable parameters of the single-component Langmuir adsorption isotherm, Eq. 11, leading to the following parameter values: $K_A = 28.30$, $\Gamma_A^\infty = 0.00290$, and $K_B = 8.20$, $\Gamma_B^\infty = 0.00207$. The percentage error values obtained are shown in Figure 2 as a function of pressure. The corresponding average values in the pressure interval explored (solid line) are $\epsilon_A = 0.93\%$ and $\epsilon_B = 0.72\%$.

Let us first examine the reliability of the proposed approach in the case of ideal behavior of the adsorbed phase. Using the classic IAST model, together with the single-component Toth equilibrium isotherms, a fictitious set of binary equilibrium data is generated at constant temperature and pressure (i.e., $P = 101$ kPa). According to the proposed approach these data can be reproduced, using the single-component Langmuir equilibrium isotherms obtained above, by adjusting the binary parameter $\Delta\psi_B^*$. The result of the nonlinear regression analysis is $\Delta\psi_B^* = -0.00567$, which leads to the values reported in Table 9. In this case, the average percentage error is $\epsilon = 1.59\%$. This result is quite satisfactory, since this error is comparable to those mentioned above relative to the accuracy of the Langmuir isotherm in reproducing the single-component fictitious data.

Before proceeding with this analysis it is worthwhile to indicate an alternative way of applying the proposed approach, based on the isobaric integral:

$$\Delta\psi_2^* = \int_0^1 \left(\frac{\Gamma_2}{y_2} - \frac{\Gamma_1}{y_1}\right) dy_1 \qquad (15)$$

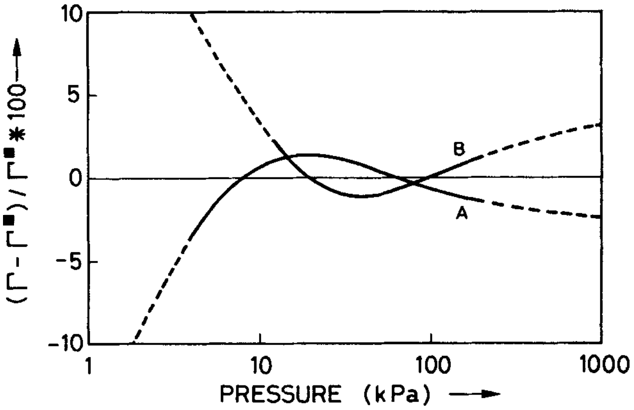

Figure 2. Comparison between calculated (Γ_i) and fictitious experimental ($\Gamma^{\blacksquare}$) adsorbed amount values for single-component systems as a function of pressure.

— Interval covered by fictitious experimental data

whose value can be estimated directly from the fictitious binary equilibrium data, through a suitable quadrature formula. In the case examined above, using eleven fictitious equilibrium data, this procedure leads to $\Delta\psi_B^* = -0.00564$, in good agreement with the value estimated above. It is noticeable that this way of applying the proposed approach, which has the significant advantage over the previous one of avoiding the fitting procedure for estimating $\Delta\psi_B^*$, leads to substantially identical results. However, it is to be noted that the accurate evaluation of the integral, Eq. 15, requires the binary experimental data to be properly distributed over the entire vapor phase composition range.

Let us now consider a binary mixture exhibiting nonideal behavior in the adsorbed phase. The corresponding fictitious equilibrium data are generated using the RAST model together with the single-component Toth isotherms and the Hildebrand model, Eqs. 6–8, with the following parameter values: $A_{AB} = -0.01$, $C_{AB} = 100$. According to the proposed approach and using the Langmuir isotherm for single-component equilibrium behavior, the following parameter values have been estimated:

Table 9. Fictitious Ideal Binary System: Adsorbed Phase Mole Fraction *x* and Adsorbed Amount Γ Calculated with Modified IAST Model

	Fictitious Exp. Values		Modified IAST Model	
y_1	x_1	Γ_t	x_1	Γ_t
0.05	0.3359	2.021 E-3	0.3339	2.038 E-3
0.10	0.5304	2.158 E-3	0.5283	2.184 E-3
0.20	0.7375	2.357 E-3	0.7356	2.387 E-3
0.30	0.8400	2.490 E-3	0.8381	2.516 E-3
0.40	0.8980	2.584 E-3	0.8962	2.603 E-3
0.50	0.9338	2.653 E-3	0.9323	2.663 E-3
0.60	0.9573	2.704 E-3	0.9561	2.708 E-3
0.70	0.9735	2.744 E-3	0.9726	2.741 E-3
0.80	0.9851	2.776 E-3	0.9845	2.767 E-3
0.90	0.9936	2.801 E-3	0.9933	2.787 E-3
0.95	0.9970	2.812 E-3	0.9969	2.796 E-3

Table 10. Fictitious Nonideal Binary System: Adsorbed Phase Mole Fraction x and Adsorbed Amount Γ Calculated with Modified RAST Model

	Fictitious Exp. Values		Modified RAST Model	
y_1	x_1	Γ_t	x_1	Γ_t
0.05	0.4441	2.466 E-3	0.4448	2.458 E-3
0.10	0.5486	2.582 E-3	0.5481	2.583 E-3
0.20	0.6509	2.679 E-3	0.6499	2.686 E-3
0.30	0.7102	2.727 E-3	0.7093	2.735 E-3
0.40	0.7533	2.758 E-3	0.7528	2.764 E-3
0.50	0.7889	2.781 E-3	0.7887	2.784 E-3
0.60	0.8209	2.799 E-3	0.8211	2.799 E-3
0.70	0.8520	2.813 E-3	0.8528	2.809 E-3
0.80	0.8853	2.825 E-3	0.8866	2.816 E-3
0.90	0.9262	2.832 E-3	0.9280	2.818 E-3
0.95	0.9543	2.831 E-3	0.9562	2.816 E-3

$\Delta\psi_B^* = -0.0057$, $A_{AB} = -0.012$, $C_{AB} = 72.20$, and $\eta_{AB} = 0.44$, which agree reasonably with those used to generate the fictitious data. The corresponding values are listed in Table 10. The mean percentage error is $\epsilon = 0.63\%$.

It is worthwhile pointing out that the proposed approach, in the case of nonideal adsorbed phase behavior, requires the estimation of four adjustable parameters by comparison with binary equilibrium data. Since the parameters may be strongly correlated, the fitting process may lead to some difficulties. In this case, the alternative way of directly evaluating $\Delta\psi_2^*$ *a priori* from the isobaric integral according to Eq. 15 may be particularly convenient. Using this approach in the nonideal case examined above, the value $\Delta\psi_B^* = -0.00529$ has been obtained, in good agreement with the corresponding value estimated through the fitting procedure.

Systems Under Saturation Conditions

Many bulk adsorption separation processes are based on the principle of displacement chromatography, which requires operation with the adsorbent very close to saturation conditions. Examples are given by the separation of xylene or chloroaromatic isomer mixtures on various zeolites of types X and Y (Morbidelli et al., 1984, 1985). The absorptivity of these components on zeolites is so strong that it can be safely assumed that the single-component isotherm is at saturation, that is, $\Gamma_i^0 = \Gamma_i^\infty$, for all pressure values in the relevant interval. A similar situation occurs in the case of adsorption of large organic molecules onto activated carbon from aqueous solution (Minka and Myers, 1973).

In these cases the proposed approach reduces to very simple expressions, which have been used in previous work to simulate multicomponent equilibrium data for the system mentioned above (Minka and Myers, 1973; Morbidelli et al., 1987; Paludetto et al., 1987). In fact, the integral in Eq. 9 can be solved analytically, so that Eq. 1 reduces to:

$$x_i = \frac{y_i}{\gamma_i} \exp\left[-\frac{(\Delta\psi - \Delta\psi_i^*)}{\Gamma_i^\infty}\right] \tag{16}$$

which, coupled to Eq. 3, allows one to compute multicomponent equilibria. In the particular case where all components exhibit the same saturation concentration Γ^∞, Eqs. 9 and 16 can be solved analytically, leading to the following explicit form of the multicomponent isotherm:

$$x_i = \frac{y_i/\gamma_i}{\sum_{j=1}^{N} y_j \alpha_{ji}/\gamma_j} \tag{17}$$

where α_{ji} is an adjustable parameter defined as follows:

$$\alpha_{ji} = \exp\left[\frac{(\Delta\psi_j^* - \Delta\psi_i^*)}{\Gamma^\infty}\right] \tag{18}$$

It should be noted that this is the case where the new approach is most convenient, since it requires only the saturation value Γ_i^∞ rather than the entire single-component equilibrium isotherm for all the involved compounds. Moreover, for such systems the experimental analysis of the Henry's law region is particularly difficult, since it requires extremely low concentration values in the fluid phase.

Conclusions

The new approach for using IAST or RAST model consists in replacing Eq. 2 with Eq. 9. This modification allows one to reduce the pressure interval where single-component isotherms have to be known, and, more important, to exclude the region of very low pressure values, that is, the Henry's law region. Accurate knowledge of the single-component Henry's law region constitutes certainly the greatest limitation in the application of the IAST and RAST models according to the classic approach. Once this problem is removed, the sensitivity of these models to the particular model adopted for fitting single-component data, pointed out by several authors, vanishes.

The price to be paid for this advantage is the introduction of two new parameters (or one in the case of ideal behavior), which must be evaluated by comparison with binary experimental data. Thus, the proposed approach does not allow prediction of multicomponent equilibrium data from only single-component data. This limitation is of importance in principle but certainly much less in practice. When dealing with RAST, binary data are needed anyway for estimating the adsorbed phase activity coefficients, independent of whether Eq. 2 or 9 is used. Also for ideal mixtures, that is, IAST, the proposed approach may be more convenient. In fact, two alternatives are possible: either using Eq. 2 and measuring single-component isotherms down to the Henry's law region, or using Eq. 9 and measuring binary equilibrium at constant pressure. From an experimental point of view, the second option is often preferable, particularly when dealing with strongly adsorbable components.

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Notation

A = surface area of adsorbent, m^2/g
A_{ij} = Hildebrand activity coefficient parameter
C_{ij} = parameter, Eqs. 8, 10
K = Henry's constant
P = pressure, kPa

$p_i^o(T, \pi)$ = adsorption equilibrium pressure of single component at T and π identical to that of multicomponent mixture, kPa
R = ideal gas constant, kJ/kmol · K
T = temperature, K
x = adsorbed phase mole fraction
y = vapor phase mole fraction

Greek letters

α_{ij} = parameter, Eq. 18
γ_i = activity coefficient in adsorbed phase
Γ = adsorbed amount, kmol/kg
ϵ = average percentage error in amount adsorbed
π = spreading pressure, N/m
Φ_i = parameter, Eq. 7
η_{ij} = parameter, Eq. 10
$\psi = A\pi/RT$

Superscripts

$*, o$ = single component
∞ = saturation

Subscripts

i, j, k = component
t = total

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