Adsorption Equilibria of Nonideal Multicomponent Systems at Saturation

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The use of adsorption devices for large-scale bulk separations is becoming quite common. Most of such units operate by displacement chromatography, which requires conditions very close to the sorbent saturation. A well known example is provided by the separation of paraxylene from the hydrocarbon fraction C_8, which can be performed by adsorption on zeolites from either liquid or vapor phase. The key problem in the mathematical simulation of adsorption separation units is the evaluation of the multicomponent adsorption equilibria (Paludetto et al., 1987).

When strongly adsorbable compounds are involved, the high surface coverage can induce deviations from ideality in the adsorbed phase. Nonideal behaviors, such as selectivity values depending on the mixture composition, are quite common and cannot be accounted for by simple equilibrium correlations. For instance, the well known multicomponent Langmuir isotherm is not able to reproduce such behaviors. Moreover, for strongly adsorbable compounds, the investigation of the region at very low surface coverages (the so-called Henry region), with the accuracy required by many classical equilibrium models, can be quite difficult and cumbersome due to the very high values of the Henry constants characterizing these compounds. However, for such compounds it is quite easy to measure vapor mixtures equilibrium data at a fixed temperature and pressure by using, for example, the device presented by Paludetto et al. (1987). Thus, when dealing with strongly adsorbable compounds, particularly when the main goal is to evaluate the multicomponent adsorption equilibria at a fixed temperature and pressure (as it is often the case for industrial separations), it is convenient to base the equilibrium model on binary-mixture equilibrium data at fixed temperature and pressure values.

The aim of this paper is to test the reliability of two equilibrium relationships valid at the saturation limit by comparison with two sets of nonideal experimental data, namely toluene/benzene/parachlorotoluene and benzene/parachlorotoluene/chlorobenzene on zeolite K–Ca X at 200°C. Single-component, binary, and ternary-mixture data are reported. The aforementioned models, which originate from the adsorbed solution theory (Myers and Prausnitz, 1965) and the simplified statistical model (Ruthven and Wong, 1985), provide suitable approximations that are reasonable when dealing with strongly adsorbable compounds. They allow us to compute multicomponent equilibria using only information from experiments performed at the same conditions of temperature and pressure, even though they refer to binary, rather than to single-component systems.

Finally, the comparison has been extended to sets of experimental data involving para- and metaxylene, as previously reported in the literature.

Multicomponent Equilibrium Models

The first model considered is the ideal adsorbed solution theory (IAST), which was originally developed by Myers and Prausnitz (1965) and is a widely used macroscopic thermodynamic approach. This can be easily extended to nonideal adsorbed solutions by introducing suitable activity coefficients for the adsorbed phase leading to the so-called real adsorbed solution theory (RAST).

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It is well known that the main limitation of such a powerful theory is its high sensitivity to the low-pressure values of the single-component isotherms (c.f. Richter et al., 1989). This is an intrinsic problem of the model, which requires the accurate knowledge of the single-component equilibria in the Henry region. A new approach to IAST and RAST, which is able to remove this sensitivity, has been recently proposed (Gamba et al., 1989), where, to disregard Henry's region, the integration of the Gibbs isotherm is performed from the pressure value, P, at which the multicomponent equilibria must be evaluated, rather than from zero.

When dealing with strongly adsorbable compounds, this approach is particularly convenient because, as mentioned above, the Henry's region is difficult to investigate, and using the classic method can lead to a poor evaluation of the multicomponent equilibria. Moreover, for such compounds, one can safely assume that the adsorbed load in the entire integration field is constant, which means $\Gamma_i^o(p) = \Gamma_i^\infty$ if $p \in [p_i^0(\psi), P]$, and the Gibbs isotherm integral can be analytically evaluated. In the special case where not only all the components are strongly adsorbable, but also they exhibit the same saturation load, the IAS Theory reduces to (Paludetto et al., 1987):

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

where $\alpha_{ij} = \exp[(\psi_i^* - \psi_j^*)/\Gamma^\infty] = \exp(\Delta\psi_{ij}^*/\Gamma^\infty)$. This is a simple equilibrium model that can be conveniently used when the saturation loads are close to each other by introducing an average value. However, due to the presence of the activity coefficients, Eq. 1 represents a system of nonlinear algebraic equations.

Various models for the activity coefficients can be used; in this work, Hildebrand's model (Hildebrand et al., 1970) has been employed by replacing the original liquid density with the saturation load (Paludetto et al., 1987). As discussed in detail elsewhere (Gamba et al., 1989), such a model can be extended to account for the spreading pressure dependence; this is not necessary for representing the experimental data considered in this study because the spreading pressure ranges in a narrow field.

If one neglects the nonideality of the adsorbed phase, that is, $\gamma_i = 1$ in Eq. 1, it is possible to obtain explicit expressions for the adsorbed-phase mole fractions. Note that in this case, Eq. 1 becomes identical to the classic multicomponent Langmuir isotherm, which, for strongly adsorbable compounds, can be simplified by assuming $\sum_{i=1}^{NC} K_i p_i \gg 1$ to give:

$$x_i = \frac{y_i}{\sum_{j=1}^{NC} \alpha_{ji}^* y_j} \tag{2}$$

where $\alpha_{ij}^* = K_i/K_j$. Equation 2 is often referred to as the constant selectivity equilibrium model.

For a NC–component mixture, the parameters of the modified IAST model (Eq. 1 with $\gamma_i = 1$) are the NC saturation loads, Γ_i^∞, and the NC–1 spreading pressure differences, $\Delta\psi_{i1}^*$. In principle, the latter can be evaluated from single-component experimental data if the entire single-component isotherm from $p = 0$ to the desired pressure value is measured. In the case of strongly adsorbable compounds, it is more convenient to estimate these values from the equilibrium data relative to the binary mixtures arising from the NC different compounds; in this event, only one experimental single-component datum is necessary for each compound: the saturation value. Two different methods are available to evaluate such parameters: the first one regards the $\Delta\psi_{ij}^*$ as adjustable parameters, which can be tuned by fitting the experimental binary data using a nonlinear optimization procedure; the second one involves the binary-mixture isobaric integral:

$$\psi_i^* - \psi_j^* = \Delta\psi_{ij}^* = \int_0^1 \left(\frac{\Gamma_i}{y_i} - \frac{\Gamma_j}{y_j}\right) dy_i \tag{3}$$

which can be evaluated by suitable quadrature formulas directly from the experimental data of the binary mixtures. It should be stressed that the latter approach is possible only when the experimental data are properly distributed over the entire range of the vapor-phase composition. This method, which has the advantage to avoid the fitting procedure for $\Delta\psi_{ij}^*$ has been adopted in this work.

The modified RAST retains the same parameters as the IAST and involves some new parameter characteristics of the activity coefficients model, A_{ij}, which must be tuned by comparing with binary experimental data.

Finally, the amount adsorbed can be easily calculated (Paludetto et al., 1987). Note that if the dependence of the activity coefficients from the spreading pressure is neglected, the excess load due to the nonideality of the adsorbed phase disappears, and the model cannot account for maxima and minima in the curve representing the total adsorbed amount as a function of composition. Actually, strongly nonideal gaseous systems need this correction, or errors as high as 30% can be introduced (c.f. Talu and Zwiebel, 1986). On the other hand, for the compounds considered in this work, the maximum percentage excess of total adsorbed amount never exceeds 6% of the average saturation load, also for highly nonideal systems. Thus, this effect has been neglected.

The simplified statistical model (SSM) proposed by Ruthven and Wong (1985), which results from a microscopic thermodynamic approach, is the second equilibrium model considered in this work. Following the approach of Rota et al. (1988), only the two-body interactions have been considered, and the binary interaction parameter between a molecule of type i and one of type j, R_{ij}, has been calculated from the interaction parameters between like molecules, R_{ii}, by introducing a new parameter δ_{ij}, which accounts for deviations from ideality. Thus, if the Henry constants are very high, the model reduces to:

$$x_i = \frac{y_i \sum_{j=1}^{NC} y_j a_{ji}^\#(1 - \delta_{ij})}{\sum_{k=1}^{NC} y_k a_{ki}^\# \sum_{j=1}^{NC} y_j a_{ji}^\#(1 - \delta_{kj})} \tag{4}$$

where $\alpha_{ij}^\# = K_i/K_j \sqrt{(R_{ii}/R_{jj})}$. Besides δ_{ij}, all the other parameters can be estimated from single-component experimental data, but they can be more conveniently computed by comparison with binary–mixture data.

Note that if we neglect the nonideality of the adsorbed phase

by setting the parameters $\delta_{ij} = 0$, Eq. 4 becomes identical to Eq. 2, that is, for ideal adsorbed solutions with equal saturation loads both the IAST and the ISSM (ideal SSM) degenerate to the multicomponent equilibrium Langmuir equation. This is not suprising because accounting for only two-body interactions implies to assume that the volume (i.e., the saturation load) of all the components is the same, and it is known that for compounds of equal volume ISSM reduces to IAST (Ruthven et al., 1973).

Besides the NC saturation loads, the parameters of the ISSM (Eq. 4 with $\delta_{ij} = 0$) are the NC-1 $\alpha^{\#}_{ij}$, while for the real SSM (RSSM, Eq. 4) there are NC-1 more parameters, δ_{ij}. These parameters can be related to each other by equating the experimental value of the isobaric integral (calculated as discussed above) to that predicted by the model. The predicted value can be evaluated by introducing the RSSM equations in the isobaric integral. The following relation among δ_{ij} and $\alpha^{\#}_{ij}$ is then obtained:

$$\Delta\psi^{*}_{ij} = \int_0^1 \frac{\left[\left(\dfrac{y_i[y_i + y_j\alpha^{\#}_{ji}(1-\delta_{ij})]}{y_i[y_i + y_j\alpha^{\#}_{ji}(1-\delta_{ij})] + y_j\alpha^{\#}_{ji}[y_i(1-\delta_{ij}) + y_j\alpha^{\#}_{ji}]}\right)\left(\dfrac{1}{y_i} + \dfrac{1}{y_j}\right) - \dfrac{1}{y_j}\right]}{\left[\left(\dfrac{y_i[y_i + y_j\alpha^{\#}_{ji}(1-\delta_{ij})]}{y_i[y_i + y_j\alpha^{\#}_{ji}(1-\delta_{ij})] + y_j\alpha^{\#}_{ji}[y_i(1-\delta_{ij}) + y_j\alpha^{\#}_{ji}]}\right)\left(\dfrac{1}{\Gamma^{\infty}_i} - \dfrac{1}{\Gamma^{\infty}_j}\right) + \dfrac{1}{\Gamma^{\infty}_j}\right]} dy_i \tag{5}$$

where $y_j = 1 - y_i$ and the integral is evaluated numerically through suitable quadrature formulae. This relationship represents a constraint which allows to compute $\alpha^{\#}_{ij}$ as a function of δ_{ij} if the experimental value of $\Delta\psi^{*}_{ij}$ is known. It is worth noting that for ISSM with equal saturation loads (i.e., for $\delta_{ij} = 0$, and $\Gamma^{\infty}_j = \Gamma^{\infty}$), Eq. 5 leads to $\alpha^{\#}_{ij} = \exp(\Delta\psi^{*}_{ij}/\Gamma^{\infty})$, which is the same expression found above for the parameter α_{ij} in the IAST.

As previously discussed for IAST and RAST, two possibilities for estimating the parameters $\alpha^{\#}_{ij}$ are available. The former involves a best-fit procedure of the binary experimental data, while the latter involves the isobaric integral, Eq. 5. In this work, the latter approach, which avoids the fitting procedure for $\alpha^{\#}_{ij}$, has been used. However, the parameters δ_{ij} must always be tuned by direct comparison with the experimental data of binary mixtures.

This model has the advantage of leading to explicit mole fraction expressions for nonideal adsorbed solutions. This is quite an interesting feature when dealing with dynamic simulation of adsorption separation units.

Thus, both of the models discussed above need only one single-component experimental datum for each component, the saturation load Γ^{∞}_i, and a few other experimental data, properly distributed in the vapor-phase composition field, for all the binary mixtures arising from the NC components considered. The use of the binary data is twofold: 1. to evaluate the $\Delta\psi^{*}_{ij}$ values by means of the isobaric integral and 2. to tune the adjustable parameters present in any nonideal model, that is, A_{ij} for RAST, and δ_{ij} for RSSM. Using such parameters, one can predict equilibria of mixtures involving any number of components.

Experimental Results and Discussion

Experiments

Four tenary systems and all the binary systems related to them have been considered in this work: toluene/benzene/parachlorotoluene and benzene/parachorotoluene/chlorobenzene both at 200°C on zeolite X exchanged with Ca and K ions; paraxylene/metaxylene/toluene at 150°C and paraxylene/metaxylene/isopropylbenzene at 170°C both on zeolite K–Y. Atmospheric pressure was adopted in all the experimental runs. The first two experimental systems investigated have been selected because of their very strong nonideality in the adsorbed phase, which offers a challenging point of comparison between the models. On the other hand, the last two systems, previously investigated by Paludetto et al. (1987), have been selected because of their industrial relevance in the context of the separation of paraxylene from the hydrocarbon fraction C_8. Toluene and isopropylbenzene are used as desorbent in industrial separation processes operating by displacement chromatography.

The adsorbents have been prepared from commercial zeolites of type CaX and CaY by exchanging Ca ions with K ions. The experimental procedure is illustrated elsewhere (Santacesaria et al., 1985). All the compounds used were reagent grade (Farmitalia Carlo Erba) and were purified by adsorption on zeolites 5A prior to use. All the equilibrium experiments have been performed in a simple apparatus designed to give fast and accurate responses when dealing with strongly adsorbable compounds. By means of such an apparatus, which is described in detail elsewhere (Paludetto et al., 1987), it is easier acquiring multicomponent data at a fixed temperature and pressure than measuring the entire single-component isotherms. Since the same apparatus can also measure the single-component saturation loads, all the requirements of the aforementioned equilibrium models in terms of experimental information can be fulfilled.

Parameter estimation

Following the procedure outlined above, single-component as well as binary-mixture data have been collected. At first, we have experimentally determined the saturation loads, Γ^{∞}_j, for all the components. The obtained values in Table 1 are close to each other, and therefore the models which assume equal saturation loads should be considered for simulating the multicomponent equilibrium data. The binary-mixture data for the two highly nonideal systems investigated experimentally in this work are summarized in Table 2 and Figures 1 to 4. For the two systems involving meta- and paraxylene, we will refer to the original data as reported by Paludetto et al. (1987). As mentioned above,

Table 1. Experimental Values of the Single-Component Adsorbed Amount at Saturation Conditions

Index	Compound	Zeolite	T °C	$\Gamma_i^{\infty} \times 10^3$ mol/g
1	Paraxylene*	K – Y	150	1.96
2	Metaxylene*	K – Y	150	1.91
3	Toluene*	K – Y	150	1.78
4	Paraxylene*	K – Y	170	1.62
5	Isopropylbenzene*	K – Y	170	1.57
6	Metaxylene*	K – Y	170	1.55
7	Toluene	K Ca – X	200	1.63
8	Benzene	K Ca – X	200	1.96
9	Parachlorotoluene	K Ca – X	200	1.63
10	Chlorobenzene	K Ca – X	200	1.89

*Data from Paludetto et al. (1987).

various evidences of nonideal behavior, such as azeotropes and selectivity values changing with composition, have been found.

The second step is the evaluation of the $\Delta\psi_{ij}^*$ values from the isobaric intergral. A cubic spline quadrature routine has been used to numerically calculate the integral in the righthand side

Table 2. Experimental Binary-Mixture Data*

Compounds		Data		
A	B	y_A	x_A	$\Gamma_{tot} \times 10^3$
7	8	0.052	0.074	1.854
		0.097	0.132	1.766
		0.301	0.370	1.684
		0.499	0.578	1.624
		0.707	0.770	1.574
		0.900	0.919	1.581
		0.950	0.958	1.603
7	9	0.057	0.202	1.587
		0.110	0.269	1.573
		0.206	0.361	1.557
		0.501	0.555	1.553
		0.701	0.704	1.584
		0.893	0.879	1.591
		0.949	0.939	1.591
8	9	0.053	0.113	1.640
		0.103	0.187	1.643
		0.299	0.357	1.644
		0.501	0.527	1.708
		0.700	0.699	1.801
		0.900	0.876	1.893
		0.949	0.930	1.926
8	10	0.052	0.133	1.855
		0.100	0.204	1.829
		0.300	0.432	1.761
		0.499	0.608	1.764
		0.698	0.761	1.840
		0.900	0.917	1.922
		0.949	0.956	1.937
9	10	0.050	0.081	1.875
		0.101	0.156	1.858
		0.302	0.398	1.807
		0.450	0.587	1.782
		0.699	0.751	1.735
		0.904	0.926	1.796
		0.949	0.958	1.667

*Compound indices as shown in Table 1.

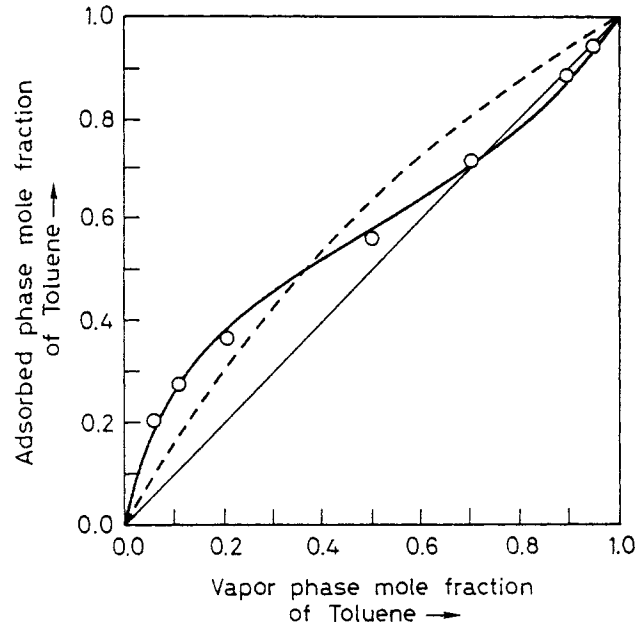

Figure 1. Isothermal (T = 200°C) and isobaric (P = 101 kPa) X-Y diagram for the binary mixture toluene/parachlorotoluene.

O, experimental data; ---, ideal model; ——, RAST and RSSM

of Eq. 3 for each binary system directly from the binary equilibrium experimental data. The obtained results, normalized as discussed below, are reported in Table 3. It is worth mentioning that in a previous work (Paludetto et al., 1987), the $\Delta\psi_{ij}^*$ values for the systems involving the xylene isomers were estimated by directly fitting the experimental data. As expected, the two methods show quite a wide compatibility; the average

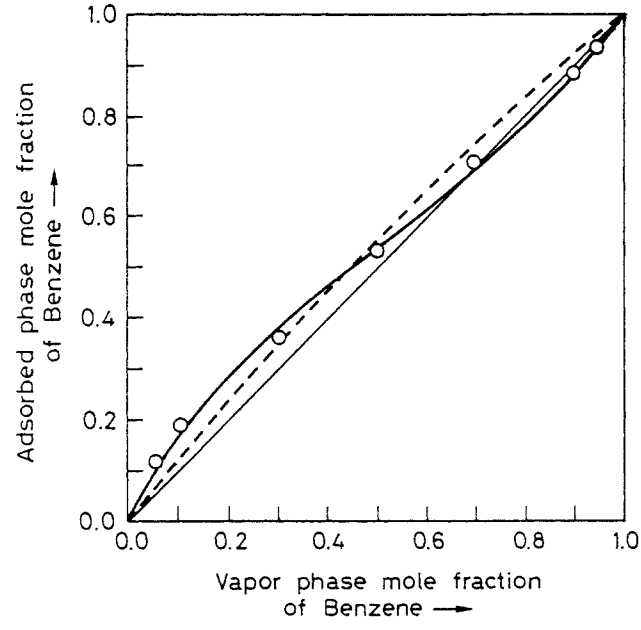

Figure 2. Isothermal (T = 200°C) and isobaric (P = 101 kPa) X-Y diagram for the binary mixture benzene/para-chlorotoluene.

O, experimental data; ---, ideal model; ——, RAST and RSSM

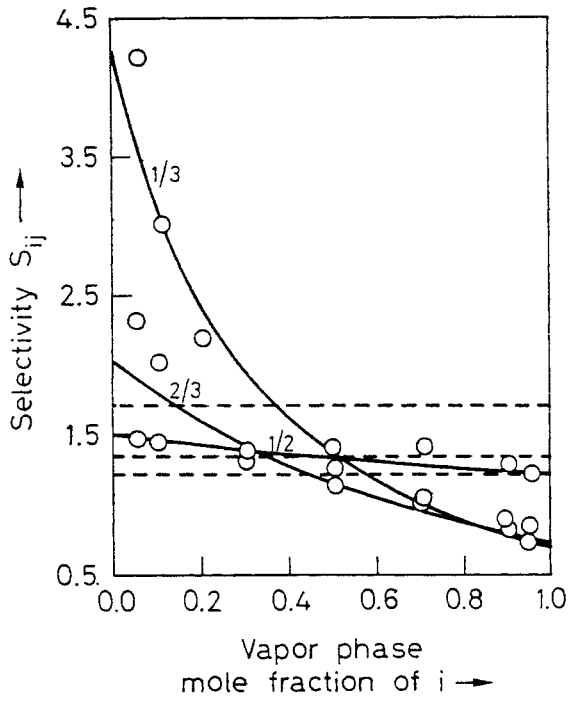

Figure 3. Selectivity values as a function of vapor phase mole fraction for the binary mixtures arising from the system toluene (1)/benzene (2)/parachlorotoluene (3).

O, experimental data; ---, ideal model; ——, RAST and RSSM

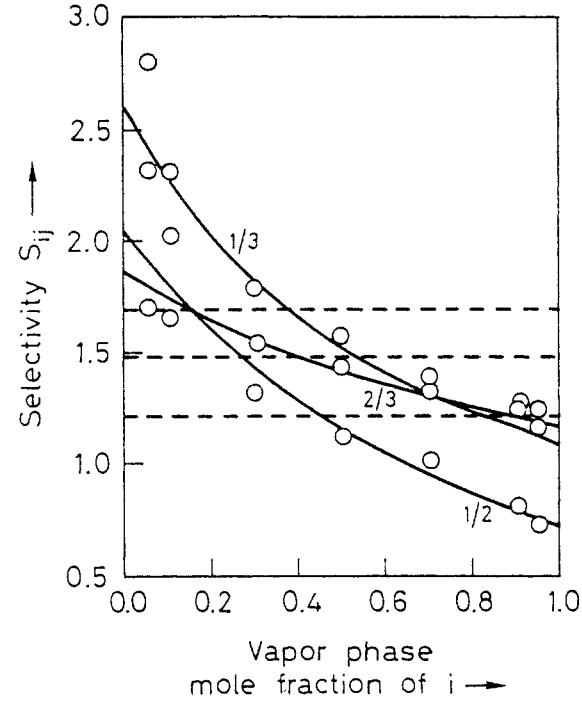

Figure 4. Selectivity values as a function of vapor phase mole fraction for the binary mixtures arising from the system benzene (1)/parachlorotoluene (2)/chlorobenzene (3).

O, experimental data; ---, ideal model; ——, RAST and RSSM

difference between the values calculated by the two methods is in fact less than 3%. Similarly, the RSSM parameters $\alpha_{ij}^{\#}$ for the system paraxylene/metaxylene/toluene were estimated by Rota et al. (1988). In this work, the same parameters are calculated from the $\Delta\psi_{ij}^{*}$ values reported in Table 3 using Eq. 5. The average difference between the values arising from the two approaches is less than 1%.

The parameters Γ_i^{∞} and $\Delta\psi_{ij}^{*}$, whose values are given in Tables 1 and 3, are all that are needed to calculate multicomponent equilibria by Eq. 1 with $\gamma_i = 1$, or Eq. 4 with $\delta_{ij} = 0$. In the following, we will refer to both these models as a single "ideal" model because they become coincident when the adsorbed solution is ideal, as discussed above. If the adsorbed phase is nonideal, the new parameters, A_{ij} for RAST and δ_{ij} for RSSM, have been estimated by comparison with the binary-mixture data. To estimate such parameters, a standard multiresponse nonlinear optimization routine has been used. The objective function was the sum of the squared average relative error on both the total load and the adsorbed mole fraction of the first component. The values of the obtained parameters are summarized in Table 3. Note that the activity coefficients calculated by the RAST parameters are less than unity, which means negative deviations from ideality. This is a common trend in adsorption systems, and it can be explained in terms of energetic heterogeneity of the surface (c.f. Valenzuela et al., 1988).

Comparison with experimental data

Let us first consider the ideal model, which does not involve any adjustable parameter, even though it cannot be regarded as predictive for binary systems because the parameters $\Delta\psi_{ij}^{*}$ are evaluated from such data. The results of the comparison with experimental data for binary mixtures are summarized in the first two columns of Table 4 in terms of average percentage errors of the adsorbed-phase mole fraction and of the total adsorbed amount. A detailed comparison of the model results with the experimental data is shown in Figures 1 to 4 (dotted line). As expected, experiments and model simulations do not agree very well, in particular for the most nonideal systems. It is worth noting, for instance, that at full saturation the ideal model cannot represent the change of selectivity with composition,

Table 3. Values of $\Delta\psi_{ij}^{*}$ Calculated by Cubic Spline Quadrature of the $i - j$ Binary-Mixture Experimental Data and the Nonideal Behavior Parameters for RAST (A_{ij}) and RSSM (δ_{ij})*

System $i - j$	$\Delta\psi_{ij}^{*} \times 10^3$	$A_{ij} \times 10^3$	δ_{ij}
1 – 2	−1.73	−0.4344	−0.2204
1 – 3	−2.30	−0.9961	−0.5124
2 – 3	−0.57	−0.2540	−0.1384
4 – 5	−0.31	−0.3281	−0.2112
4 – 6	−1.54	−0.2226	−0.1199
5 – 6	−1.23	−0.5343	−0.3599
7 – 8	−0.53	−0.0287	−0.1127
7 – 9	−0.87	−1.9319	−1.5236
8 – 9	−0.34	−1.0518	−0.6934
8 – 10	−1.02	−0.9697	−0.5476
9 – 10	−0.68	−0.3931	−0.2618

*Compound indices as shown in Table 1.

Table 4. Average Percentage Errors in Fitting Binary-Mixture and Predicting Ternary-Mixture Equilibrium Data*

	Model					
	Ideal		RAST		RSSM	
System	ϵ_x	$\epsilon_{\Gamma_{tot}}$	ϵ_x	$\epsilon_{\Gamma_{tot}}$	ϵ_x	$\epsilon_{\Gamma_{tot}}$
1 – 2	6.35	0.61	0.97	0.64	1.05	0.64
1 – 3	10.30	3.26	1.16	3.19	1.15	3.18
2 – 3	4.04	0.48	2.59	0.47	2.40	0.46
4 – 5	4.59	4.04	0.38	4.02	0.38	4.02
4 – 6	3.41	0.23	1.01	0.25	1.06	0.25
5 – 6	7.41	4.24	0.41	4.24	0.36	4.24
7 – 8	2.67	6.23	1.24	6.23	1.20	6.22
7 – 9	23.04	3.40	3.65	3.40	3.82	3.40
8 – 9	14.71	2.58	5.35	2.59	4.78	2.53
8 – 10	11.59	4.75	2.06	4.74	2.26	4.74
9 – 10	5.22	1.71	2.11	1.88	1.83	1.89
1 – 2 – 3	7.52	0.67	2.87	0.61	3.17	0.62
4 – 5 – 6	4.93	1.46	1.29	1.50	1.21	1.50
7 – 8 – 9	12.76	3.58	2.10	2.74	2.55	2.78
8 – 9 – 10	8.16	1.24	4.87	1.05	5.83	0.95

*Compound indices as shown in Table 1.

which is a common behavior of all the systems analyzed in this work. A similar conclusion arises from the comparison of model predictions with ternary experimental data, also reported in Table 4. In this case, the model is fully predictive (since it is based only on single and binary equilibrium data), and the errors, which are of the same magnitude of those found for the binary systems, are quite large.

To obtain a good agreement between experiments and model results, some deviations from the ideal behavior of the adsorbed phase must be accounted for. In Table 4, the average errors of the RAST (third and fourth columns) and RSSM (fifth and sixth columns) models in fitting binary experimental data are reported. A significant improvement of the performance of the models is obtained, since the fitting errors are comparable with the experimental ones. Detailed comparisons between experiments and calculated values are shown in Figures 1 to 4, where the continuous lines represent the results of both RAST and RSSM, which are indistinguishable in these plots.

The ability in fitting experimental data is not a proof of the quality of the models. Thus, the predictions of the models have been compared with the four ternary systems investigated experimentally: the obtained relative errors are summarized in Table 4, while the experimental and calculated values are reported in Tables 5 and 6 for the two ternary systems experimentally investigated in this work.

Note that in all cases the errors in predicting ternary data are of the same magnitude as those obtained in fitting binary data. This is a strong evidence of the reliability of such models. Because both RAST and RSSM are equally able to predict multicomponent equilibria, they can be safely used as part of mathematical models simulating industrial separation devices. However, explicit models, such as the RSSM, generally provide better performance in terms of computing time.

Thermodynamic consistency

The first consistency test concerns the continuity between binary-mixture and single-component data, which requires that at a constant temperature and pressure all the multicomponent-mixture total loads approach the single-component saturation load when the corresponding mole fraction goes to one (Talu and Myers, 1988). All the experimental data considered in this work fulfil this constraint. Since the single-component- and the multicomponent-mixture experimental data are collected independently, this is a sensitive test for the accuracy of the experiments. About the models, it can be easily shown that this constraint is also satisified by both the models presented above.

The thermodynamic consistency test proposed by Sircar and Myers (1971) has also been performed. Such a test requires that the sum of the three values of $\Delta\psi^*_{ij}$ independently calculated from three related binary-mixture is equal to zero, that is:

$$\Delta\psi^*_{12} + \Delta\psi^*_{23} + \Delta\psi^*_{31} = 0 \tag{6}$$

Nonzero values of the above sum should be attributed both to experimental errors and inaccuracies in the evaluation of the isobaric integral. The average errors, defined as the sum of the original values of the three integrals divided by their mean value, for all the systems experimentally investigated, are upper-bounded by 10%. It should be noted that the values of the parameters $\Delta\psi^*_{ij}$ adopted in the model calculations, Table 3, have been normalized so as to exactly satisfy Eq. 6. This normalization has been performed by subtracting from each experimental value a weighted fraction of the nonzero residual computed by Eq. 6 proportional to the absolute value of each $\Delta\psi^*_{ij}$.

Table 5. Comparison between Experimental and Calculated Data for the Ternary System Toluene (1)/Benzene (2)/Parachlorotoluene (3) at $T = 200°C$ and $P = 101$ kPa

					Calculated								
Experimental					Ideal			RAST			RSSM		
y_1	y_2	x_1	x_2	$\Gamma_{tot} \times 10^3$	x_1	x_2	$\Gamma_{tot} \times 10^3$	x_1	x_2	$\Gamma_{tot} \times 10^3$	x_1	x_2	$\Gamma_{tot} \times 10^3$
0.100	0.226	0.205	0.231	1.694	0.148	0.247	1.701	0.199	0.235	1.697	0.196	0.243	1.699
0.100	0.450	0.165	0.427	1.693	0.142	0.471	1.770	0.166	0.427	1.756	0.164	0.427	1.756
0.100	0.673	0.145	0.627	1.760	0.136	0.676	1.839	0.144	0.614	1.818	0.146	0.614	1.818
0.198	0.204	0.324	0.174	1.656	0.279	0.211	1.690	0.318	0.183	1.682	0.317	0.187	1.683
0.201	0.399	0.296	0.335	1.671	0.273	0.399	1.747	0.288	0.345	1.730	0.287	0.345	1.730
0.200	0.600	0.282	0.517	1.688	0.262	0.580	1.806	0.264	0.517	1.785	0.266	0.518	1.786
0.400	0.299	0.476	0.225	1.677	0.498	0.274	1.709	0.474	0.230	1.696	0.471	0.231	1.696

Table 6. Comparison between Experimental and Calculated Data for the Ternary System Benzene (1)/Parachlorotoluene (2)/Chlorobenzene (3) at $T = 200°C$ and $P = 101$ kPa

Experimental					Calculated								
					Ideal			RAST			RSSM		
y_1	y_2	x_1	x_2	$\Gamma_{tot} \times 10^3$	x_1	x_2	$\Gamma_{tot} \times 10^3$	x_1	x_2	$\Gamma_{tot} \times 10^3$	x_1	x_2	$\Gamma_{tot} \times 10^3$
0.226	0.672	0.324	0.612	1.732	0.269	0.662	1.724	0.312	0.615	1.739	0.312	0.616	1.739
0.452	0.446	0.524	0.415	1.756	0.514	0.420	1.802	0.514	0.415	1.804	0.504	0.425	1.800
0.670	0.225	0.699	0.235	1.856	0.731	0.203	1.878	0.688	0.235	1.866	0.679	0.243	1.863
0.199	0.602	0.317	0.558	1.757	0.245	0.614	1.735	0.286	0.570	1.749	0.285	0.571	1.749
0.401	0.400	0.501	0.378	1.808	0.473	0.392	1.808	0.476	0.384	1.810	0.469	0.392	1.807
0.599	0.200	0.668	0.207	1.867	0.681	0.189	1.879	0.641	0.212	1.870	0.634	0.219	1.867
0.299	0.299	0.430	0.307	1.778	0.385	0.319	1.822	0.397	0.312	1.825	0.394	0.316	1.824

Acknowledgment

Financial support of E.N.I. group for one of us (RR) is gratefully acknowledged.

Notation

A = surface area of the sorbent
A_{ij} = parameters of Hildebrand's model, Eq. 6
K = Henry's constant
NC = number of components
$p^o(\psi)$ = single-component adsorption equilibrium pressure
P = pressure
R = ideal gas constant
R_{ij} = binary interaction parameters of RSSM
S_{ij} = selectivity, $(x_i/y_i)/(x_j/y_j)$
T = temperature
x = adsorbed phase mole fraction
y = vapor phase mole fraction

Greek letters

α_{ij} = parameter of RAST model, $\exp[\Delta\psi^*_{ij}/\Gamma^\infty]$
α^*_{ij} = parameter of Langmuir's model, K_i/K_j
$\alpha^\#_{ij}$ = parameter of RSSM, K_i/K_j, $\sqrt{(R_{ii}/R_{jj})}$
γ = activity coefficient
Γ_i = adsorbed amount of the ith component
Γ_{tot} = total adsorbed amount
δ_{ij} = empirical coefficient of RSSM
π = spreading pressure
$\psi = \pi A/RT$
ψ^*_i = spreading pressure of the ith pure component at P
$\Delta\psi = \psi - \psi^*_1$
$\Delta\psi^*_{ij} = \psi^*_i - \psi^*_i$

Superscripts

o = single component
∞ = saturation

Subscripts

$1, i, j, k$ = component

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Manuscript received Mar. 28, 1990, and revision received Aug. 9, 1990.