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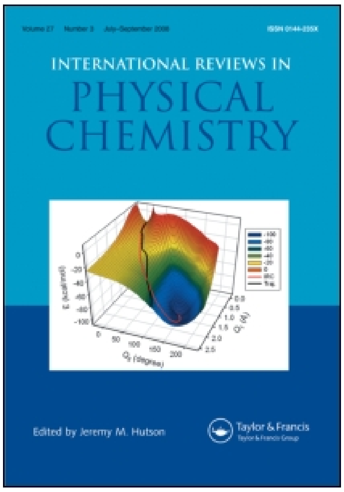

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Thermodynamic aspects of multicomponent adsorption processes on zeolites

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Thermodynamic aspects of multicomponent adsorption processes on zeolites

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The macroscopical thermodynamic approach to the adsorption of gaseous mixtures on zeolites can be developed on the basis of direct or indirect methods. The former method implies the employment of a suitable equation of state for the adsorbed phase, while the latter is based on the equality of the fugacities of each component in the adsorbed and fluid phase, respectively. The presence in zeolites of a regular network of discrete cages interconnected through orifices offers a suitable system for the application of statistical thermodynamics in the description of adsorption phenomena.

Contents

1. Introduction

Zeolites form a family of aluminosilicates with the capacity of adsorbing a large amount of molecules from fluid phases in contact with them. This capability is due to their structure, since they are constituted by porous crystals permeated by networks of channels, connecting a lattice of regular cavities (Barrer 1978). Therefore, zeolites can be likened to crystalline sponges, able to imbibe molecules small enough, or of the 'right' shape, but not others that are too big or of the 'wrong' shape. This feature allows the selective adsorption of particular species and it confers upon them a significant industrial potential for the realization of unusual separation processes (Ruthven 1984, Morbidelli *et al.* 1986).

The understanding of the factors that affect the selectivity of adsorption on zeolites represents an interesting scientific problem in which different physico-chemical aspects, such as intermolecular forces and multicomponent thermodynamics, are involved. A challenging problem is the one connected with the adsorption equilibrium behaviour of a multicomponent fluid phase in contact with a zeolitic material, particularly that concerning the quantitative description of such a complex system by minimizing the amount of experimental data. Some significant aspects of the above-mentioned topics will be reviewed through a comparison of different approaches.

2. Macroscopic thermodynamic approach

Following the classical Gibbs approach, we can postulate the existence of two phases in equilibrium: the fluid phase and the adsorbed phase. The first one is a normal three-dimensional phase (e.g., liquid or gas), its Gibbs free energy is defined as $G = G(T, P, n_i)$, and the various thermodynamic quantities are obtained through well known relationships. On the other hand, the adsorbed phase can be either two-dimensional, when dealing with surface adsorption, or three-dimensional as in the case of microporous adsorbents, like zeolites. In either case the Gibbs free energy is now dependent upon one more variable: the number of moles of the adsorbent, i.e. $G = G(T, P, n_a, n_i)$. This produces one extra term in the expression of the differential of G, which, taking as reference condition the adsorbent surface with no adsorbate, reduces to (Ruthven 1984):

$$\mathrm{d}G = -S\,\mathrm{d}T + V\mathrm{d}P - \Phi\,\mathrm{d}n_a + \Sigma_i \mu_i\,\mathrm{d}n_i \tag{1}$$

where Φ represents the energy change due to the adsorbate spreading, caused by an increase in the adsorbent surface or volume. In order not to introduce an unnecessary new formalism, in the sequel we will adopt that originally developed by Gibbs, which refers to two-dimensional adsorption, where the term $\Phi\,\mathrm{d}n_a$ is replaced by $\pi\,\mathrm{d}A$, where π is the spreading pressure and A is the adsorbent surface area. Besides this formal aspect, the relationships thus obtained can be used, as here, for describing three-dimensional adsorption such as in zeolite.

Noting that the volume of the adsorbed phase is negligible, equation (1) reduces to:

$$\mathrm{d}G = -S\,\mathrm{d}T - \pi\,\mathrm{d}A + \Sigma_i \mu_i\,\mathrm{d}n_i \tag{2}$$

which is identical to the usual expression for three-dimensional phases, but with P and V replaced by π and A, respectively. This similarity is often exploited to directly transfer to two-dimensional phases, relationships originally developed for three-dimensional phases.

Assuming isothermal conditions and, after a few manipulations, equation (2) reduces to:

$$\mathrm{d}\pi = \Sigma_i \Gamma_i\,\mathrm{d}\mu_i \tag{3}$$

where $\Gamma_i = n_i/A$ is the surface concentration in the adsorbed phase.

The adsorption equilibrium condition can now be introduced by equating the chemical potential, of each component in the adsorbed and fluid phases, i.e. $\mu_i = \mu_i^f$. For the sake of simplicity we focus on the case where the fluid phase is a gas at low pressure (so that $\mathrm{d}\mu_i^f = RT\,\mathrm{d}\ln p_i$), and derive from equation (3) the well known Gibbs isotherm:

$$\mathrm{d}\pi = RT \Sigma_i \Gamma_i\,\mathrm{d}\ln p_i \tag{4}$$

In order to obtain a multicomponent equilibrium isotherm, it is necessary to couple one more equation to equation (4), so as to eliminate the spreading pressure and get an expression in terms of the measurable quantities T, p_i and Γ_i. This is where the modelling aspects enter, since this extra equation does not enlarge from formal thermodynamics but has to be derived based on some assumption regarding the adsorbed phase behaviour.

Similarly to the case of vapour–liquid equilibria (which has heavily inspired most developments in adsorption thermodynamics), two approaches can be followed: direct or indirect methods.

2.1. *Direct methods*

The idea is to formulate, on the basis of some suitable assumption, an equation of state for the adsorbed phase, i.e. $\pi = \pi(\Gamma_i, A, T)$. Such an equation, coupled to equation (4), produces directly the desired equilibrium model. Considering, for example, single component adsorption, this has been done in several cases, deriving the equation of state of the adsorbed phase from those known for three-dimensional phases by simply replacing P and V with π and A, respectively.

(*a*) Ideal adsorbed phase: $\pi A = n_i RT$, leads to the Henry isotherm

$$\Gamma_i = Kp_i \tag{5}$$

which applies at very low concentration values, where molecular interactions tend to vanish.

(*b*) Accounting for molecule surface occupation in the ideal adsorbed phase, leads to the equation of state

$$\pi(A - \alpha) = n_i RT \tag{6}$$

which, coupled to equation (4), after some manipulation leads to the Langmuir isotherm model

$$\Gamma_i = \frac{K_i \Gamma_\infty p_i}{1 + K_i p_i} \tag{7}$$

(*c*) The Van der Waals equation of state

$$\Gamma_i = \frac{RT}{A - \beta} - \frac{\alpha}{A^2} \tag{8}$$

leads to the Hill–De Boer isotherm model

$$p_i = \frac{K_i \Gamma_i}{\Gamma_{\infty_i} - \Gamma_i} \exp\left[\frac{\Gamma_i}{\Gamma_{\infty_i} - \Gamma_i} - \frac{2\alpha\Gamma_i}{RT}\right] \tag{9}$$

which can predict, under certain circumstances, some phase transition in the adsorbed phase.

In spite of the simplicity of the examples reported above, direct methods have not been widely applied to the case of multicomponent equilibria, for which indirect methods, to be described next, are in general preferred.

2.2. *Indirect methods*

The general framework for the application of indirect methods has been developed by Myers and Prausnitz (1965). The equilibrium condition is stated by the equality of the fugacities of each component in the adsorbed and fluid phases. Considering this again as an ideal gas phase, the relative fugacity coincides with the component partial pressure, i.e. $f_i^f = p_i$. For the adsorbed phase, a direct extension of the Lewis and Randal equation for three-dimensional phases is applied:

$$f_i(T) = f_i^0(T, \pi) x_i = p_i^0(T, \pi) x_i \tag{10}$$

where p_i^0 is the adsorption equilibrium pressure for the single component at the same temperature and spreading pressure value as the multicomponent mixture.

In conclusion, the equilibrium condition is given by

$$Py_i = p_i^0 x_i \tag{11}$$

where p_i^0 is computed by direct integration of the Gibbs isotherm (equation (4)), written for a single component

$$\frac{\pi}{RT} = \int_0^{p_i^0} \Gamma_i^0 \, \mathrm{d} \ln P \tag{12}$$

and $\Gamma_i^0(P)$ represents the adsorption isotherm of the single component.

A typical problem of multicomponent adsorption equilibrium calculation is as follows: given the temperature, pressure and fluid phase composition, compute the spreading pressure and adsorbed phase composition. The solution is obtained by solving the system formed by equation (11), coupled to equation (12) for p_i^0, and the stoichiometric relationship

$$\Sigma_i x_i = 1 \tag{13}$$

On the whole, equations (11–13) provide a means of predicting multicomponent equilibria based only on single component equilibrium data, i.e. $\Gamma_i^0(P)$. This procedure is called IAST (Ideal Absorbed Solution Theory), due to the ideality assumption implicit in equation (11), and has been shown to provide satisfactory results, particularly in the case of low surface coverage, where intermolecular interactions are usually weak. In many cases of interest in applications (such as bulk adsorption separation processes, where the adsorbent operates at very high coverages according to the principle of displacement chromatography), the system behaviour deviates significantly from ideality, and equation (11) has to be corrected. This is done through the introduction of the adsorbed phase activity coefficient, γ_i so that equation (11) reduces as follows

$$Py_i = p_i^0 x_i \gamma_i \tag{14}$$

The difficulty has then been transferred to the evaluation of the activity coefficient, which is done through its definition (compatible with equation (14)) in terms of the excess Gibbs free energy g^E, as follows

$$RT \ln \gamma_i = \left(\frac{\partial(\Gamma g^E)}{\partial \Gamma_i} \right)_{T, \pi, n_i} \tag{15}$$

It should be noted that g^E is a function of T, π and the adsorbed phase composition. The usual models derived for three-dimensional phases (usually liquid) do not obviously account for the spreading pressure dependence. In principle, this makes all such models inadequate, since they cannot meet the thermodynamic condition that $g^E \to 0$ as $\pi \to 0$. Since in most cases multicomponent equilibrium calculations are performed at fixed T and P, but with variable π, it follows that the activity coefficient model to be used in equation (14) should include such an effect. The only model proposed to date which satisfies this requirement is the one by Talu and Zwiebel (1986), which utilizes the isostheric heats of adsorption of single components to introduce the spreading pressure dependency.

In practical applications, when computing multicomponent equilibria at constant T and P, the usual models for γ_i developed for liquid mixtures (such as Wilson, Hildebrand, Van Laar and others) have been applied. In such a case, single component equilibria data are not sufficient any more, and at least binary equilibrium data are needed to estimate the adjustable parameters of the activity coefficient models. In fact, these are usually based on binary interaction parameters, whose values can be obtained from binary data relative to all the possible couples among the involved components. As an example, we report here the Hildebrand model, whose application will be discussed shortly

$$\ln \gamma_i = \frac{1}{\Gamma_i}\left(\sum_j \sum_k A_{ji} - \frac{1}{2}A_{jk}\right)\phi_j \phi_k \tag{16}$$

where

$$\phi_i = \frac{x_i/\Gamma_i}{\Sigma_j x_j/\Gamma_j}; \qquad A_{jk} = A_{kj}; \qquad A_{jj} = 0$$

The systems studied through this approach are not numerous in the literature; as an example let us consider the equilibrium behaviour of the ternary system; toluene (*a*), ortho-chlorotoluene (*b*) and parachlorotoluene on zeolite CaX at 230°C and 101 KPa (Morbidelli *et al.* 1986). In figures 1 to 3 the model results are compared with the experimental data for each of the binary systems. In each case one parameter has been adjusted according to the Hildebrand model (equation (16)). When used to predict ternary equilibrium data, the so-tuned model exhibits a 5·1% error in the predicted adsorbed amount of each component. This is a satisfactory result, particularly in view

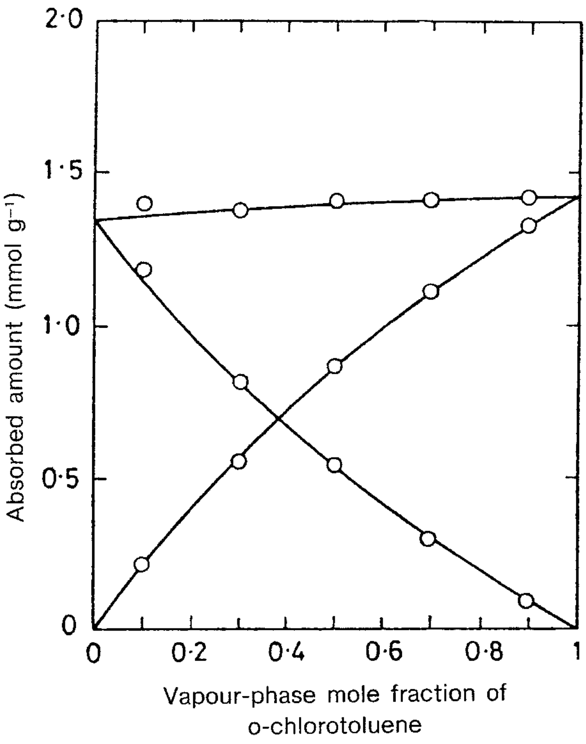

Figure 1. Adsorbed amount, Γ_i as a function of vapour-phase mole fraction for the system o-chlorotoluene, p-chlorotoluene. Experimental point (○).

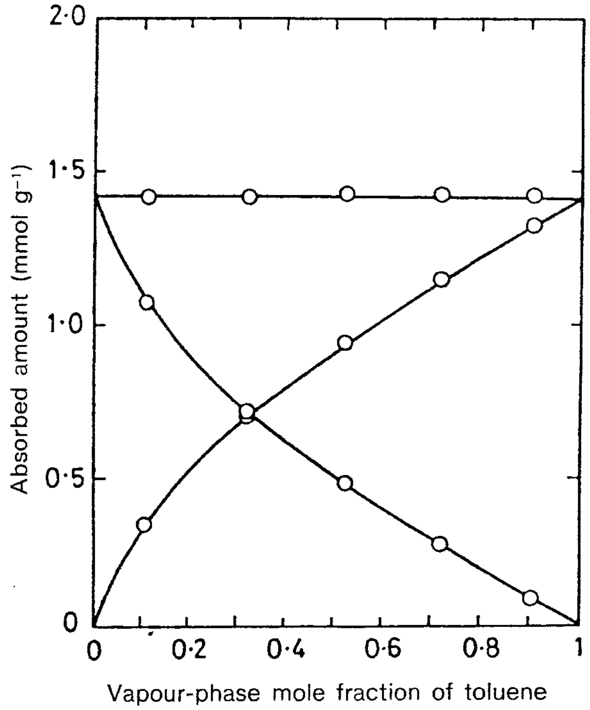

Figure 2. Adsorbed amount, Γ_i as a function of vapour-phase mole fraction for the system toluene, o-chlorotoluene. Experimental point (○).

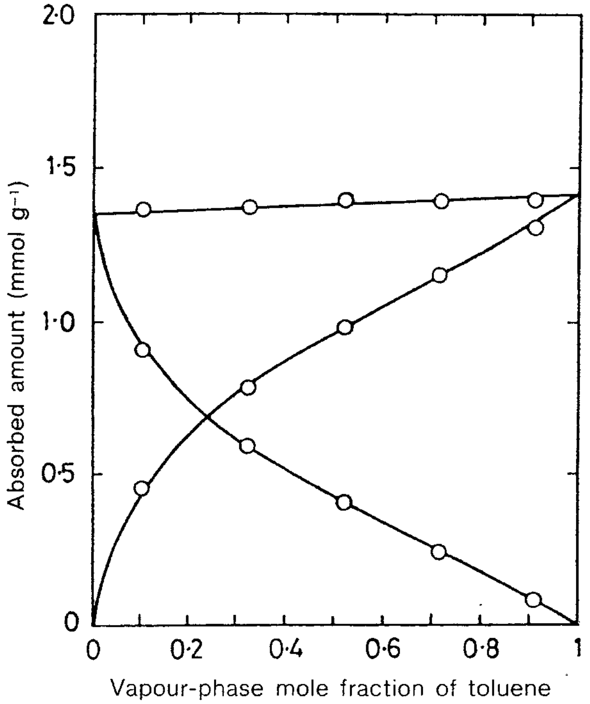

Figure 3. Adsorbed amount, Γ_i as a function of vapour-phase mole fraction for the system toluene, p-chlorotoluene. Experimental point (○).

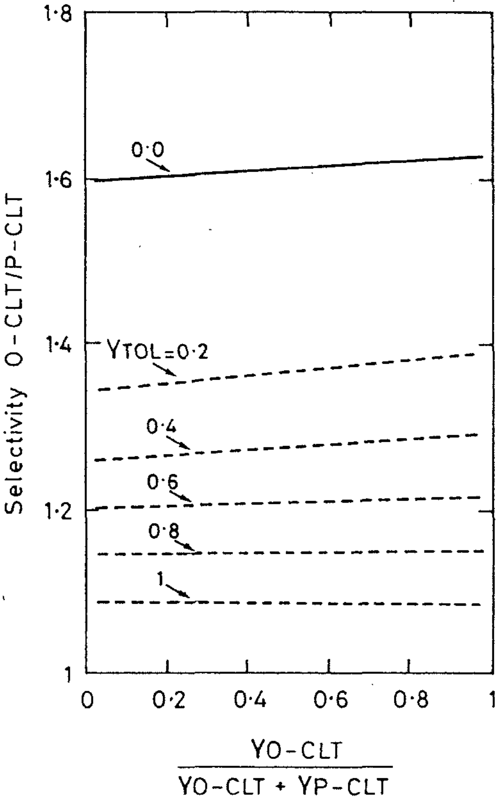

Figure 4. Selectivity between o-chlorotoluene (O-CLT) and p-chlorotoluene (P-CLT) as a function of the relative vapour-phase percentage of the two isomers, for various values of vapour-phase mole fraction of toluene. The solid curve represents the binary system.

of the high non-ideality of this system, which is clearly apparent from the data shown in figure 4. The selectivity between ortho- and para-chlorotoluene (defined as the ratio between the ripartition ratios of each component in the two phases) in the ternary system is plotted as a function of the fluid phase composition. It appears that toluene content has a dramatic effect on selectivity, which is entirely due to non-ideal behaviour of the adsorbed phase, since for $\gamma_i = 1$, in this case, selectivity would be concentration independent. These effects are extremely important in the design of adsorption separators.

It should be pointed out that the accuracy obtained in the case mentioned above using equation (16), which ignores the activity coefficient dependence upon spreading pressure, is probably due to the small variation of spreading pressure with composition, at fixed T and P, registered for the system examined.

The quantity of interest in adsorption calculations is the amount of each component adsorbed per unit mass of adsorbent, Γ_i. Once the adsorbed phase mole fractions are obtained, from the relationships reported above, Γ_i can be readily evaluated as $\Gamma_i = \Gamma_t x_i$, where Γ_t indicates the total loading of the absorbent. This can be obtained as follows

$$\frac{1}{\Gamma_t} = \Sigma_i \frac{x_i}{\Gamma_i^0(\pi)} + \Sigma_i x_i \left(\frac{\partial \ln \gamma_i}{\partial(\pi/RT)} \right)_{T,x} \quad (17)$$

where Γ_i^0 is the single component equilibrium value at π. The last term in equation (17) accounts for changes in the adsorbed surface (or volume) upon mixing.

It is worth noticing that, independently of the activity coefficient model adopted, accounting for deviations from ideality requires single and binary equilibrium data, so that the predictive character of the procedure is confined to mixtures containing three or more components.

One final comment on the use of this approach, as pointed out by several authors (Myers 1986), is its sensitivity to the single component equilibrium isotherm, $\Gamma_i^0(P)$ to be used in the integral appearing in equation (12). This sensitivity arises because the largest contribution to the integral value comes from the very low pressure region, i.e. in the so-called Henry's region ($P \rightarrow 0$), which is also the most difficult one to investigate experimentally. Thus, unless the Henry's region of each single component is very well characterized experimentally, it will be more or less differently predicted depending upon which equilibrium model is used to fit the single component equilibrium data. This will in turn affect the multicomponent equilibrium behaviour predicted by this procedure.

This difficulty may be overcome by avoiding the Henry's region in equation (12), thus modifying it as follows

$$\frac{\pi - \pi_i^*}{RT} = \int_P^{P_i^0} \Gamma_i^0 \, \mathrm{d} \ln P \tag{18}$$

where P is the pressure value at which the multicomponent equilibrium is to be computed, and π_i^* is the single component pressure in equilibrium at P. This is now regarded as an adjustable parameter, and its value can only be estimated from binary data. This is the price to be paid in order to be able to ignore single components behaviour in the Henry's region. This situation may be more convenient in applications, particularly when dealing with non-ideal adsorption, where binary data are needed anyway. Applications of this procedure, as well as comparisons with the classical one, have been reported by Gamba *et al.* (1987).

Before proceeding to other approaches to the modelling of adsorption equilibria, it is worth briefly mentioning the energetic heterogeneity of surfaces. It is well known that the adsorbent surface is constituted by various 'sites', the adsorption characteristics of which are not identical. On the other hand, energy distributions cannot be measured directly and their derivation from adsorption equilibrium data is quite ambiguous. Nevertheless, it has been shown (Myers 1983) that even a very simple heterogeneity (such as that caused by two sites exhibiting two different Langmuir equilibrium constants) produces, when interpreted with a homogeneous model such as that given by equation (14), values of activity coefficients smaller than one. This is a very interesting result since, in most adsorption equilibria studies, negative deviations from the ideal law (equation (11)) have been found, including those systems which in the liquid phase exhibit positive deviations. The possibility of introducing surface heterogeneity has been investigated recently, as discussed by Myers (1986). The approach is to assume a certain shape for the energy distribution, such as a discrete binomial distribution, and then fit its characteristic parameters to some experimental equilibrium data. The results obtained indicate some improvement with respect to the corresponding homogeneous model, for cases in which single or binary data are used in tuning the available adjustable parameters.

3. Statistical approach

The structure of zeolites can be assimilated to a regular network of discrete cages, interconnected through relatively small orifices. As a consequence of this feature, zeolites represent a suitable system for the application of statistical thermodynamics in the description of adsorption phenomena.

In fact, each of the M cavities, of volume v, can be considered as an independent subsystem, containing a different number of adsorbed molecules, up to a maximum value m. The key idea (Hill 1962, Rieckert 1970, Ruthven 1971) is to incorporate the above-mentioned set of equivalent subsystems into a statistical ensemble representative of the macrosystem under examination.

The average number of molecules per subsystem can be evaluated as follows:

$$C = n/M = \lambda\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_T \tag{19}$$

where n is the total number of molecules, and λ the activity, which for an ideal gaseous phase is equal to $P\exp(\mu^0/RT)$, where μ^0 is the standard chemical potential. Ξ is the grand-partition function, for the system under examination; if single component adsorption is considered it can be written as follows:

$$\Xi = \sum_{s=0}^{m} (P/kT)^s (z'_{\mathrm{int}}/z_{\mathrm{int}})^s Q(s) \tag{20}$$

where z_{int} is the molecular partition function corresponding to the internal states of free molecules, and z'_{int} is the corresponding value for hindered molecules in zeolitic cages, where rotational degrees of freedom may be lost. If particular information on the molecular motion is not available the afore-mentioned ratio is assumed to be equal to one.

The preceding equation is consistent with a fluid-like behaviour of the guest molecules as is suggested from NMR and diffusion studies on their intracrystalline mobility. m is the saturation limit (an integer) fixed by the condition $m \leqslant v/b$ and $m > v/b - 1$, where b is the covolume of adsorbed molecules. $Q(s)$ is the configurational integral, corresponding to a zeolite cavity containing s molecules:

$$Q(s) = \frac{1}{s!}\int_v \exp(-U_s(\mathbf{r}^s)/kT)\,d\mathbf{r}_s \tag{21}$$

where $U_s(\mathbf{r}^s)$ is the configurational energy of a cluster of s molecules occluded within a single zeolite cavity. $d\mathbf{r}_s$ is a volume element at a position whose coordinates from any convenient origin are defined by the vector $\mathbf{r}_s$. Of course $Q(0)=1$. By introducing equation (20) into (19) the following expression is derived:

$$C = n/M = \sum_{s=0}^{m} s(P/kT)^s Q(s) \Big/ \sum_{s=0}^{m} (P/kT)^s Q(s) \tag{22}$$

which yields a relationship between the gas phase pressure P and the average concentration in the cage, C under equilibrium conditions.

An approximate evaluation of the configurational integrals (equation (21)) can be performed by assuming that the form of the potential field within a zeolite cavity does not depend on the number of adsorbed molecules. Besides, it can be assumed that molecules move randomly, subjecting each other to an intermolecular potential (Ruthven and Loughlin 1972).

The following equation for the configurational integral can be written:

$$Q(s)=\frac{1}{s!}\rho^{s}\left(1-\frac{sb}{v}\right)^{s}\exp\left(-\langle U_{\mathrm{int},s}\rangle/kT\right) \tag{23}$$

where $b=(2/3)\pi\,\sigma^3$ is the effective Van der Waals covolume of adsorbed molecules. ρ is the configurational integral of a single molecule occluded within a cage, and its evaluation requires accurate knowledge of the interaction energy between adsorbed molecules and the atoms of the zeolite cavity. An approximate evaluation of ρ can be performed by assuming that the negative framework charge is distributed uniformly among all oxygen atoms (Brauer *et al.* 1968). In a more simplified approach the actual potential energy profile is replaced by an energy well of volume v, with vertical sides and flat base of a depth ϕ:

$$\rho=v\exp(-\phi/kT) \tag{24}$$

$\langle U_{\mathrm{int},s}\rangle$ is the average interaction energy between the s molecules present in the same cage. In addition, equation (23) is consistent with the fact that the reduction of the volume available to molecules is an important effect. According to equation (22) the following adsorption isotherm can be written:

$$C=\frac{KP+(KP)^2Q(2)^2+\ldots+((KP)^m/(m-1)!)Q(m)^m}{1+KP+1/2!(KP)^2Q(2)^2+\ldots+((KP)^m/m!)Q(m)^m} \tag{25}$$

where $K=\rho(1-b/v)/kT$ is the Henry constant, while $Q(s)$ can be evaluated through equation (23).

The described model can be extended to multicomponent adsorption systems. In this case the grand partition function can be written as follows:

$$\Xi=\left[\sum_{0\,s_1}^{m}\;\sum_{0\,s_2}^{m-s_1}\;\sum_{0\,s_3}^{m-s_1-s_2}\;\sum_{0\,s_N}^{m-s_1-\ldots s_{N-1}}\;\prod_{1\,i}^{N}\left(\frac{p_i}{kT}\right)^{s_i}\left(\frac{z'_{\mathrm{int},i}}{z_{\mathrm{int},i}}\right)^{s_i}Q(s_1,s_2,\ldots s_N)\right]^{M} \tag{26}$$

where i indicates a generic component, s_i is the number of its molecules present in a cage and N is the number of components.

The summation present in equation (26) must be limited to the values of s_i which satisfy the restriction:

$$\Sigma s_i\leqslant(v/\Sigma s_ib_i) \tag{27}$$

The concentration of component i is given by:

$$C_i=\frac{n_i}{M}=\lambda_i\left(\frac{\partial\ln\Xi}{\partial\lambda_i}\right)_{\lambda_i\neq i,T}$$

$$=\frac{\sum\limits_{0\,s_1}^{m}\;\sum\limits_{0\,s_2}^{m-s_1}\;\sum\limits_{0\,s_3}^{m-s_1-s_2}\cdots\sum\limits_{0\,s_N}^{m-s_1-\ldots s_{N-1}}s_iQ(s_1,s_2,\ldots s_N)\prod_i(p_i/kT)^{s_i}}{\sum\limits_{0\,s_1}^{m}\;\sum\limits_{0\,s_2}^{m-s_1}\;\sum\limits_{0\,s_3}^{m-s_1-s_2}\cdots\sum\limits_{0\,s_N}^{m-s_1-\ldots s_{N-1}}Q(s_1,s_2,\ldots s_N)\prod_i(p_i/kT)^{s_i}} \tag{28}$$

In it:

$$Q(s_1, s_2, \ldots s_N) = \frac{1}{\prod_i s_i!} \prod_i \rho_i^{s_i} \left(1 - \frac{\sum_i s_i b_{ii}}{v}\right)^{s_i} \exp(-\langle U_{\text{int}} \rangle / kT) \tag{29}$$

where:

$$\rho_i = \frac{K_i kT}{(1 - b_{ii}/v)} \tag{30}$$

The average interaction energy $\langle U_{\text{int}} \rangle$ can be evaluated as a function of mean intermolecular potentials as follows:

$$\langle U_{\text{int}} \rangle = \sum_{i=1}^{N} \frac{s_i}{2} \left[(s_i - 1) \langle U_{ii} \rangle + \sum_{j \neq i}^{N} s_j \langle U_{ij} \rangle \right] \tag{31}$$

where $\langle U_{ii} \rangle$ and $\langle U_{ij} \rangle$ are the mean intermolecular potential energies of the couples of molecules *ii* and *ij*. These can be expressed by means of a hard sphere potential with an attractive force. For instance a Sutherland potential may be used:

$$U_{ij} = \begin{cases} \infty, & \text{for } r < \sigma_{ij} \\ -\varepsilon_{ij} \left(\dfrac{\sigma_{ij}}{r} \right)^6, & \text{for } r \geqslant \sigma_{ij} \end{cases} \tag{32}$$

where σ is the sphere diameter and ε the parameter of the attractive force. The values of $\langle U_{ii} \rangle$ and $\langle U_{ij} \rangle$ in equation (31) are averaged over the distance between molecules. Taking as mean distance the radius of the cage r_c, it follows:

$$\langle U_{ij} \rangle = -\varepsilon_{ij} \left(\frac{\sigma_{ij}}{r_c} \right)^6 = -\varepsilon_{ij} \left(\frac{2b_{ij}}{v} \right)^2 \tag{33}$$

and then:

$$\langle U_{\text{int}} \rangle = -\sum_{1^i}^{N} \frac{s^i}{2} \left[(s_i - 1) \varepsilon_{ii} \left(\frac{2b_{ii}}{v} \right)^2 + \sum_{j \neq i}^{N} s_j \varepsilon_{ij} \left(\frac{2b_{ij}}{v} \right)^2 \right] \tag{34}$$

In principle the single component parameters ε_{ii} and b_{ii} can be evaluated from molecular properties. However, in order to obtain better agreement with experimental data it may be convenient to estimate such parameters by direct comparison with single component equilibrium data.

As an example the data reported by Costa *et al.* (1983) for the system ethane (1) propane (2) ethylene (3) on zeolite 5A at $T = 293$ K and $P = 93{\cdot}3$ KPa have been considered. When considering single component equilibria, the model developed above (equation (25)) exhibits four parameters: the Henry constant, K, the energy interaction parameter ε_{ii}, the molecule covolume b_{ii} and the maximum number of molecules per cage, m. The last two parameters have to satisfy the obvious condition

$$\frac{v}{m+1} < b_{ii} \leqslant \frac{v}{m} \tag{35}$$

A convenient way of approaching the best fitting problem is to first fix the value of m and then optimize the remaining adjustable parameters. This is then repeated for

Table 1. Average percentage errors ($\varepsilon\%$) and model parameters in fitting single component equilibrium data (Costa *et al.* 1983), with the statistical model. System: ethane (1), propane (2), ethylene (3). m represents the maximum number of molecules per cage.

System	($\varepsilon\%$)	K (molecules/cage atm.)	σ (Å)	ε/k (K)	m
1	0·9	22·4	4·04	1043·6	5
2	9·6	806·9	4·84	1076·2	3
3	10·8	949·9	4·31	701·1	4

various values of m. The best value of m is then selected, based on the quality of the obtained agreement with experimental data and on considerations about the physical meaning of the obtained value of b_{ii} as compared with its value in usual liquid phases.

Thus, once m is fixed, three adjustable parameters should be estimated by comparison with experimental data. Clearly, due to the physical meaning of such parameters it could be convenient to somehow exploit the well-known values of these molecular parameters derived from measurements other than adsorption equilibria. From amongst various possibilities, we chose to adopt the following relationship between the parameters σ_{ii} and ε_{ii} of the Sutherland potential:

$$\Delta H_w - RT = 4{\cdot}16208\,\rho^1\sigma^3(\varepsilon/k)$$

whose derivation, for the case of the Lennard-Jones potential, has been described in detail by Carrà *et al.* (1980). ΔH_w is the heat of vaporization and ρ^1 the density (molecules per Å^3), of the corresponding liquid. On the whole, two adjustable parameters are left: K_i and b_{ii}, the latter subject to condition (35). In table 1 the average percentage errors are shown for each component together with the values of the model parameters. It is noticeable that using such parameter values, coupled to equations (36), a satisfactory prediction of the adsorption equilibria of binary aliphatic hydrocarbon mixtures, such as: ethane–propane (average percentage error of 6%) can be obtained. Besides the accuracy of the predictions of the model, it can be noted that all parameters exhibit physically meaningful values thus indicating the reliability and consistency of the described approach.

Extension to a multicomponent mixture follows readily from the application of the mixing rules:

$$\left.\begin{aligned}\sigma_{ij} &= (\sigma_{ii}+\sigma_{jj})/2\\ \varepsilon_{ij} &= (\varepsilon_{ii}\varepsilon_{jj})^{1/2}\end{aligned}\right\} \qquad (36)$$

The described approach gives, in principle, a procedure able to predict the multicomponent adsorption isotherm on zeolites in terms of molecular interactions.

In practical applications our lack of knowledge of the interaction energies between non-spherical molecules in zeolitic cavities limits the predictive value of the model. Thus, it is often convenient to adopt an empirical approach based on the following assumption:

(i) the equilibrium constants K_i are evaluated by fitting the single component experimental adsorption data in the low pressure limit (Henry region);

(ii) the configurational integrals are evaluated as follows:

$$Q\left(s_1, s_2 \ldots s_N\right) = \prod_i \frac{\rho_i^{s_i}}{s_i!} R(s_1, s_2, \ldots s_N\Big) \qquad (37)$$

where $R(s_i)$ are taken as adjustable parameters, tuned on single component data according to Ruthven and Wong (1985).

In this case extension to multicomponent mixtures can be performed through the following empirical relationship:

$$R(s_1, s_2 \dots s_N) = [\textstyle\prod_i R(s_i)^{s_i}]^{1/\Sigma s_i} \tag{38}$$

Actually, in the case of strongly non-ideal mixtures it may be necessary to introduce a mixing empirical parameter. In the results to be shown shortly the preceding has been multiplied by $(1-\delta_{ij})$.

4. Comparison with experimental data

In the sequel we report some comparisons between model simulations and experimental data for a few of the multicomponent systems investigated in the literature. The aim is to compare the two approaches described above, and establish their reliability for the prediction of adsorption equilibria. Emphasis is placed on systems at constant pressure, which are those of interest in practical applications, such as in the simulation of fixed-bed adsorbers.

The ternary system ethane (1)–propane (2)–ethylene (3) on zeolite 5A at $T = 293$ K and $P = 93{\cdot}3$ KPa has been investigated by Costa *et al.* (1983). The single component equilibrium isotherms have been fitted with the Langmuir–Freundlich model (*b*)

$$\Gamma_i = \frac{K_i p^{\beta i} \Gamma \infty_i}{1 + K_i p^{\beta i}}$$

and the statistical models (equation (25)) including a maximum of either two (*c*) or three (*d*) molecules per subsystem. The number of adjustable parameters for each model is 2, 3, 3 and 4, respectively. The average percentage deviations summarized in table 2 show that the accuracy of each model is substantially proportional to the number of adjustable parameters involved.

In principle, any of these models could be used in the classical thermodynamic approach to simulate multicomponent equilibria. However, as mentioned above, this approach is sensitive to the accuracy in reproducing single components Henry's region, so that using the most accurate model (*d*) is advisable (or, alternatively, the procedure outlined by equation (18)). In table 3 are summarized the average percentage errors in the IAST model (α) for prediction of binary and ternary data. In the same table the average errors relative to the statistical model (equation (31)) (β), including at most two molecules per subsystem, are also reported. It appears that the two models are

Table 2. Average percentage errors in fitting single component equilibrium data (Costa *et al.* 1983). System: ethane (1), propane (2), ethylene (3). Models: Langmuir (*a*), Langmuir–Freundlich (*b*), Statistical with maximum two molecules per subsystem (*c*), Statistical with maximum three molecules per subsystem (*d*).

	Model			
System	*a*	*b*	*c*	*d*
1	3·39	1·42	3·39	0·39
2	7·53	4·39	2·52	0·65
3	12·30	2·63	4·05	0·36

Table 3. Average percentage differences between experimental (Costa *et al.* 1983) and calculated data. Models: IAST (α), ideal statistical model (β), RAST (γ), real statistical model (δ). Legend as in table 2.

	Model			
System	α	β	γ	δ
1–2	5·18	4·83	5·11	4·83
1–3	31·3	26·6	9·34	11·0
2–3	23·6	25·9	4·09	5·25
1–2–3	33·7	21·3	8·90	10·8

Table 4. Average differences between experimental (Morbidelli *et al.* 1986) and calculated data. System: toluene (1), ortho-chlorotoluene (2), para-chlorotoluene. Models: as in table 3.

	Model	
System	γ	δ
1–2	0·50	0·90
1–3	1·02	3·43
2–3	1·30	2·08
1–2–3	5·09	5·16

substantially equivalent. It should be recalled with this respect that the latter model could be improved by introducing higher-order interaction parameters, according to the procedure proposed by Ruthven and Wong (1985). From the data given in table 3 it also appears that, except for the ethane–propane system, the predictions of these models are certainly inadequate. This is due to the non-ideal behaviour of the systems under consideration. In order to account for deviations from ideality, one has to introduce activity coefficients in the classical thermodynamic approach (i.e. the RAST model (γ), equations (14) and (16)) and the correction parameter δ_{ij} in the cross-coefficients for interactions between unlike molecules, given by equation (38), in the statistical thermodynamic approach (δ)). In both cases the newly-introduced adjustable parameters are estimated by comparison with binary equilibrium data, so that the predictive capability of the models is confined to mixtures containing three or more components. The average percentage deviations for the two models are summarized in table 3. A significant improvement is apparent in both cases, but yet the accuracy of the two approaches is entirely comparable. The success in the prediction of ternary data can be judged considering that the errors in predicting such data are very similar to the errors in fitting the relative binary data.

The conclusion arising from the results reported above is that non-ideal behaviour of adsorption equilibria can be described with reasonable accuracy only using binary equilibrium data. No theory is currently available for predicting non-ideal equilibria based only on single component data. This conclusion is not surprising, since it is substantially the same one reached in the most widely studied field of vapour–liquid equilibria for highly non-ideal mixtures.

The substantial agreement between the two approaches described above can be confirmed by examining the system: toluene (*a*), ortho-chlorotoluene (*b*) and para-chlorotoluene on zeolite CaX, shown in figures 1 to 4 (Morbidelli *et al.* 1986). The two real models, i.e. γ and δ, are considered in this case. The average percentage errors, given in table 4, confirm the validity of both approaches. It should be mentioned that in this case the adsorbent operates very close to saturation conditions, so that both the above mentioned approaches can be highly simplified. Without entering here into the details of this particular aspect, it is sufficient to remark that the data given in table 4 are obtained without using single component equilibrium data. All the parameters in the model are estimated by fitting binary equilibrium data. Ternary data are instead predicted (Gamba *et al.* 1987, Morbidelli *et al.* 1986).

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