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THERMODYNAMIC ASPECTS OF MULTICOMPONENT MIXTURE ADSORPTION EQUILIBRIA ON ZEOLITES *

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ABSTRACT

Adsorption equilibria of single-component and multicomponent mixtures can be studied thermodynamically and statistically.

The macroscopic, thermodynamic approach can be based on direct or indirect methods. The former require formulation of suitable equations of state for the adsorbed phase, while the latter involve explicit representation of the chemical potential of the components in the two phases in equilibrium by the introduction of suitable activity coefficients.

The structure of the zeolites can be described as a regular network of discrete cages. This provides a suitable model of a statistical ensemble representative of the macrosystem under examination.

A comparison with experimental data is reported for both approaches.

INTRODUCTION

The zeolites are a family of aluminium silicates which adsorb a large quantity of molecules from fluid phases [1,2] because they are formed of porous crystals permeated by networks of channels connecting a lattice of regular cavities. This feature allows the selective adsorption of particular species which can be exploited to devise unusual separation processes in industry.

In thermodynamic terms, the adsorption equilibrium behaviour can be described in accordance with the classical Gibbs approach, where it is assumed that:

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(a) there is an interphase where all the variations of all the thermodynamic properties of the two phases are concentrated;

(b) the adsorbent is thermodynamically inert, uninfluenced by temperature, pressure, amount adsorbed or type of the adsorbed compounds; and

(c) the adsorbent surface area is accessible to each adsorbable species [3–5].

Assuming isothermal conditions, the following equation describes the behaviour of the adsorbed phase

$$A\,\mathrm{d}\pi = \sum_i \Gamma_i\,\mathrm{d}\,\mu_i \tag{1}$$

where $\Gamma_i = n_i A$ is the adsorbed amount of the ith component and π is the spreading pressure.

The adsorption equilibrium conditions can be introduced by equating the chemical potential of each component in the adsorbed and in the fluid phase. Assuming ideal behaviour for the fluid phase, the well-known Gibbs isotherm for multicomponent mixtures is obtained

$$A\,\mathrm{d}\pi = RT\sum_i \Gamma_i\,\mathrm{d}\ln P_i \tag{2}$$

Full description of multicomponent systems at equilibrium requires the addition of one more equation to eliminate π and obtain an expression in terms of the measurable quantities T, P and Γ_i.

As in the case of vapour–liquid equilibria, use can be made of either direct methods based on a suitable equation of state or indirect methods based on the introduction of activity coefficients.

In the first approach, an equation of state for the adsorbed phase (usually derived from those known for three-dimensional phases by simply replacing P and V with π and A, respectively [6]) is employed to obtain

$$\pi = \pi(\Gamma_i, A, T) \tag{3}$$

Several single-component equilibrium isotherms can be obtained with this approach, each compatible with the particular properties of the equation of state employed. Some single-component equilibrium isotherms and their equations of state are illustrated in Table 1.

THERMODYNAMIC APPROACH

The use of indirect methods to describe adsorption equilibria is due to Myers and Prausnitz [7], who developed the so-called ideal adsorbed solution theory (IAST).

Assuming ideal behaviour for the vapour phase and using a direct extension of the Lewis and Randal equation to the adsorbed phase, the

TABLE 1

Equations of state for the adsorbed phase and corresponding adsorption isotherms

Equation of state	Single-component equilibrium model
Henry's isotherm	
$\pi A = \Gamma RT$	$\Gamma = KP$
Volmer's isotherm	
$\pi(A-\beta) = \Gamma RT$	$KP = \left[\frac{\theta}{1-\theta}\right] \exp\left[\frac{\theta}{1-\theta}\right]$ where $\theta = \beta/A$
van der Waals' isotherm	
$\left[\pi + \frac{\alpha}{A^2}\right](A-\beta) = \Gamma RT$	$KP = \left[\frac{\theta}{1-\theta}\right] \exp\left[\frac{\theta}{1-\theta}\right] \exp\left[-\frac{\alpha^2\theta}{RT}\right]$

adsorption equilibrium conditions can be expressed as follows

$$Py_i = p_i^{\ominus}(T, \pi)x_i \qquad i = 1, N \tag{4}$$

where the single-component equilibrium pressure value, $p_i^{\ominus}$, in equilibrium at the same spreading pressure and temperature values as the mixture, is given by direct integration of the Gibbs isotherm

$$\frac{A\pi}{RT} = \int_0^{p_i^{\ominus}} \Gamma_i \, \mathrm{d} \ln P \qquad i = 1, N \tag{5}$$

where $\Gamma_i(P)$ represents the single-component equilibrium isotherm.

Equations (4) and (5) can be used, together with the stoichiometric relationship

$$\sum_i x_i = 1 \tag{6}$$

to fully characterise the equilibrium conditions of the system.

A new approach to the IAST model has been proposed by Gamba et al. [8]. This is particularly convenient when experimental investigation of the very low pressure region of the single-component equilibrium isotherm, i.e. inside the so-called Henry region, is difficult.

Because of the mathematical form of the function to be integrated in eqn. (5), the results of the entire equilibrium calculation are very sensitive to the representation of $\Gamma_i(P)$ in this region, i.e. when $P \to 0$ [9]. This feature can be avoided by changing the lower integration limit in eqn. (5), thus going from P to $p_i^{\ominus}$ rather than from 0 to $p_i^{\ominus}$. The single-component Henry region is no longer involved and eqn. (5) reduces to

$$\frac{A}{RT}(\Delta\pi - \Delta\pi_i^{\star}) = \int_P^{p_i^{\ominus}} \Gamma_i \, \mathrm{d} \ln P \qquad i = 1, N \tag{7}$$

where $\Delta\pi_i^{\star} = \pi_i^{\star} - \pi_1^{\star}$ is a parameter to be estimated from binary equilibrium data, $\pi_i^{\star}$ being the ith pure component spreading pressure at the mixture pressure with the first component as the reference. It should be noted that this approach is not based purely on single-component equilibrium data, as it requires binary data for evaluation of $\Delta\pi_i^{\star}$.

Most industrial bulk adsorption separation processes rely on displacement chromatography, where the adsorbent operates very close to saturation [10,11]. In this case, the overall amount adsorbed is almost constant and equal to the saturation value. Thus, assuming $\Gamma_i = \Gamma_i^{\infty}$, the integral on the RHS of eqn. (7) can be solved analytically, so that eqn. (7) reduces to

$$p_i^{\ominus}(T, \pi) = P \exp\left[\frac{A}{RT\Gamma_i^{\infty}}(\Delta\pi - \Delta\pi_i^{\star})\right] \qquad i = 1, N \qquad (8)$$

In many cases of industrial interest, the system behaviour deviates significantly from ideality, and eqn. (4) has to be modified by introduction of the adsorbed-phase activity coefficients, as follows

$$Py_i = p_i^{\ominus}(T, \pi)\gamma_i x_i \qquad i = 1, N \qquad (9)$$

which is usually referred to as the real adsorbed solution theory (RAST). The activity coefficients are functions of the excess free energy g^e through the following relationship [12,13]

$$g^e = RT\sum_i x_i \ln \gamma_i \qquad (10)$$

Several models for γ_i have been derived from suitable expressions for g^e originally developed in the context of liquid mixtures, such as: the Hildebrand model, obtained from the regular solution theory [14]; and the

TABLE 2

Activity coefficient models for the adsorbed phase

Hildebrand
$\ln \gamma_i = \frac{1}{\Gamma_i^{\ominus}(p_i^{\ominus})}\sum_j\sum_k(A_{ij} - 1/2A_{jk})\Phi_j\Phi_k$
$\Phi_j = \frac{x_j/\Gamma_j^{\ominus}(p_j^{\ominus})}{\sum_k x_k/\Gamma_k^{\ominus}(p_k^{\ominus})}$
$A_{jk} = A_{kj}; \qquad A_{jj} = 0$
Wilson
$\ln \gamma_i = 1 - \ln\left[\sum_j x_j\Lambda_{ij}\right] - \sum_k \frac{x_k\Lambda_{ki}}{\sum_j x_j\Lambda_{kj}}$
$\Lambda_{ij} \neq \Lambda_{ji}; \qquad \Lambda_{ii} = 1$

Wilson model, obtained from the local composition theory [15]. Detailed expressions for the activity coefficients are summarised in Table 2.

STATISTICAL THERMODYNAMICS APPROACH

A typical zeolite crystal consists of an ensemble of cages of constant volume and geometry interconnected through relatively narrow channels. This structure makes zeolites particularly suitable for the application of statistical thermodynamics in the description of adsorption equilibria.

In particular, each of the M cavities of volume v can be treated as an independent subsystem that can contain a maximum value of sorbate molecules m. The idea is to regard such a subsystem as a statistical ensemble representative of the macrosystem under examination [16].

The average number of molecules per cavity can be obtained as follows [17]

$$c_i = \frac{M_i}{M} = \lambda_i \left[\frac{\partial \ln \Xi}{\partial \lambda_i} \right]_{T, \lambda_{j \neq i}} \tag{11}$$

where λ_i is the activity which for an ideal vapour phase is given by $P \exp(\mu_i^{\ominus}/RT)$, where $\mu_i^{\ominus}$ is the standard chemical potential. Ξ is the macrocanonical partition function which for a multicomponent system may be written as

$$\Xi = \left[\sum_{s_1=0}^{m} \sum_{s_2=0}^{(m-s_1)} \sum_{s_3=0}^{(m-s_1-s_2)} \cdots \sum_{s_N=0}^{(m-s_1 \ldots -s_{N-1})} \prod_{i=1}^{N} \left[\frac{P_i}{kT} \right]^{s_i} Q(s_1, s_2, \ldots, s_N) \right]^M \tag{12}$$

where s_i is the number of molecules of the ith component present in a cage and N is the number of components. It is worth noting that not all the combinations of s_i values between zero and m are possible in eqn. (12), but only those satisfying the following condition

$$\sum_{i=1}^{N} s_i b_{ii} \leqslant v \tag{13}$$

where b_{ii} represents the effective van der Waals co-volume of the ith species.

The configurational integrals $Q(s_1, s_2, \ldots, s_N)$ in eqn. (12) can be computed as follows

$$Q(s_1, s_2, \ldots, s_N) = \frac{1}{\Pi_i s_i \delta} \Pi_i \rho_i^{s_i} \exp(-\langle U_{\text{int}} \rangle / kT) \left[1 - \frac{\sum_i s_i b_{ii}}{v} \right]^{\Sigma_i s_i} \tag{14}$$

where

$$\rho_i = \frac{K_i(kT)}{(1 - b_{ii}/v)} \tag{15}$$

and K_i is the Henry constant of the ith component. The average interaction energy $\langle U_{\text{int}} \rangle$ between the adsorbed molecules can be evaluated as a function of the molecular diameter σ_{ii} and of the London attractive potential parameter ϵ_{ij}, as follows

$$\langle U_{\text{int}} \rangle = - \sum_{i=1}^{N} \frac{s_i}{2} \left[(s_i - 1)\epsilon_{ii} \left[\frac{2b_{ii}}{v} \right]^2 + \sum_{j \neq i}^{N} s_j \epsilon_{ij} \left[\frac{2b_{ij}}{v} \right]^2 \right] \tag{16}$$

The van der Waals co-volume is related to the molecular diameter by the well-known relationship

$$b_{ii} = \tfrac{2}{3} \Pi \sigma_{ii}^3 \tag{17}$$

A simple relation between ϵ and σ can be obtained from the pure component liquid-phase heat of vaporisation [18], as follows

$$\sigma_{ii}^3 \left[\frac{\epsilon_{ii}}{k} \right] = \frac{(\Delta_{\text{vap}} H - RT)}{4.16208 \rho_1 N_{\text{A}}/\text{MW}} \tag{18}$$

where ρ_1 is the liquid density and MW the molecular weight.

Table 3 shows the average percentage errors and the corresponding parameter values of the model obtained by fitting single-component equilibrium data in the gas phase. It is worth stressing that the parameter values obtained are compatible with the molecular properties of the adsorbed compounds. This is evidence in support of the reliability of this approach [19].

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 points:

TABLE 3

Average percentage errors (ϵ%) and estimated parameter values for the statistical model in the case of single-component equilibria. Systems: 1, ethylene; 2, propane; and 3, ethane on zeolite 5A at 298 K and 92 KPa [23]

System	ϵ%	K (molecules/cage atm)	σ (Å)	ϵ/k (K)	m (molecules/cage)
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

(i) the equilibrium constants K_i are estimated from the single-component experimental data in the Henry region; and

(ii) the configurational integrals are evaluated as follows [20,21]

$$Q(s_1, s_2, \ldots, s_N) = \Pi_i \frac{\rho_i^{s_i}}{s_i \delta} R(s_1, s_2, \ldots, s_N) \tag{19}$$

where the extension to multicomponent mixtures is performed through the following empirical relationship

$$R(s_1, s_2, \ldots, s_N) = \left[\Pi_i R_i^{s_i}\right]^{(1/\Sigma_i s_i)} \tag{20}$$

where R_i are adjustable parameters tuned on single-component equilibrium data.

In the case of highly non-ideal mixtures, it is convenient to introduce an empirical mixing parameter δ_{ij} to be estimated from binary equilibrium data through the following relationship [22]

$$R_{ij} = (R_{ii} R_{jj})^{1/2} (1 - \delta_{ij}) \tag{21}$$

When the adsorbent operates very close to saturation conditions, as in the thermodynamic approach the above equations can be reduced as follows [22]

$$c_i = \frac{2P_i \sum\limits_{j=1}^{NC} \alpha_{ji} P_j (1 - \delta_{ji})}{\sum\limits_{k=1}^{NC} \alpha_{ki} P_k \sum\limits_{j=1}^{NC} \alpha_{ji} P_j (1 - \delta_{ji})} \qquad i = 1,\ N \tag{22}$$

where

$$\alpha_{ij} = \frac{K_i}{K_j} \left(\frac{R_{ii}}{R_{jj}} \right)^{\frac{1}{2}} \tag{23}$$

The value of the adjustable parameters α_{ij} must be estimated by comparison with binary equilibrium data.

COMPARISON WITH EXPERIMENTAL DATA

The experimental system examined was composed of ethylene, propane and ethane on zeolite 5A at 293 K and 93 KPa [23]. The single-component experimental data have been fitted with the Langmuir isotherm

$$\Gamma = \frac{K \Gamma^{\infty} P}{1 + KP} \tag{24}$$

In Table 4, the binary and ternary experimental data are compared with the results of the IAST, RAST, modified RAST and semi-empirical statistical models in terms of their average percentage errors. The activity coeffi-

TABLE 4

Average percentage difference between calculated and experimental values. Models: a, IAST; b, RAST; c, modified RAST; and d, semi-empirical statistical model. Systems: 1, ethylene; 2, propane; and 3, ethane on zeolite 5A at 293 K and 93 KPa

Systems	Models			
	a	b	c	d
1–2	23.57	9.69	7.77	5.25
1–3	29.35	11.65	7.97	11.02
2–3	13.87	6.75	3.82	5.03
1–2–3	28.89	12.25	11.32	10.84

TABLE 5

Average percentage difference between calculated and experimental values; models as in Table 4. Systems: 1, *para*-xylene; 2, *meta*-xylene; and 3, toluene on zeolite KY at 423 K and 101 KPa

Systems	Models		
	a	c	d
1–2	6.22	1.25	2.16
1–3	11.04	3.04	6.90
2–3	5.66	3.81	5.55
1–2–3	7.70	4.04	5.04

cients in the RAST and modified RAST models are evaluated through the Hildebrand relationships reported in Table 2.

To explore the performance of the models at saturation conditions, the system *para*-xylene, *meta*-xylene and toluene on zeolite KY at 423 K and 101 KPa was considered [10]. Here the Henry constants of all the components involved are very high. The percentage errors obtained with the Hildebrand relationships are summarised in Table 5.

CONCLUSIONS

The values in Tables 4 and 5 make it clear that the thermodynamic and the statistical approaches display very similar reliabilities and capabilities in simulating multicomponent adsorption equilibria.

The accuracy obtained in the prediction of ternary equilibrium data is satisfactory, as it involves the same errors encountered in fitting the corresponding binary data.

The conclusion to be drawn from these results is that non-ideal behaviour of adsorption equilibria can only be described with reasonable accuracy by using binary equilibrium data. No theory is currently available for predicting non-ideal equilibria based upon single-component equilibrium data only.

In the case of adsorbents operating very close to saturation conditions, the equilibrium models reduce to very simple relationships that can be conveniently adopted in large simulation models of the dynamic behaviour of adsorption separation units.

LIST OF SYMBOLS

A	specific surface area of adsorbent ($m^2\ g^{-1}$)
A_{ij}	Hildebrand model parameter
b_{ii}	van der Waals co-volume (m^3)
c	concentration in adsorbed phase (molecules/cage)
g	free energy ($J\ mol^{-1}$)
$\Delta_{\text{vap}}H$	heat of vaporisation ($J\ mol^{-1}$)
k	Boltzmann constant ($J\ K^{-1}$)
K	Henry constant
m	maximum number of molecules per cage
M	number of cages
M_i	total number of adsorbed molecules
MW	molecular weight ($g\ mol^{-1}$)
n_i	superficial concentration ($mol\ m^{-2}$)
N	number of components
N_A	Avogadro number ($molecule\ mol^{-1}$)
P	pressure (Pa)
$p_i^{\ominus}$	equilibrium pressure of the ith single component at T and π of the mixture (Pa)
Q	configuration integral
R	gas constant ($J\ K^{-1}\ mol^{-1}$)
R_{ii}	parameter
s_i	number of molecules of the ith component in a cage
T	temperature (K)
$\langle U_{\text{int}} \rangle$	average interaction energy between molecules ($J\ mol^{-1}$)
v	volume of cage (m^3)
x_i	adsorbed-phase mole fraction
y_i	fluid-phase mole fraction

Greek letters

γ	activity coefficient in the adsorbed phase
Γ	adsorbed amount ($mol\ g^{-1}$)

δ	parameter
ϵ	London attractive potential (J)
λ	activity
Λ	parameter of the Wilson model
μ	chemical potential ($J\ mol^{-1}$)
Ξ	macrocanonical partition function
π	spreading pressure ($N\ m^{-1}$)
$\pi_i^\star$	spreading pressure of the pure ith component at T and P of the mixture ($N\ m^{-1}$)
ρ_i	parameter
ρ_l	density of the liquid phase ($mol\ m^{-3}$)
σ	molecular diameter (m)
Φ	volumetric fraction

Superscripts

$\ominus$	standard, pure
e	excess function
∞	saturation value

Subscripts

i, j, k, l	components

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