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Exact statistical thermodynamics of alkane binary mixtures in zeolites: New interpretation of the adsorption preference reversal phenomenon from multisite-occupancy theory

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A B S T R A C T

The rigorous statistical thermodynamics of mixtures of polyatomic species adsorbed on one-dimensional substrates is presented. The thermodynamic functions calculated for a monomer–dimer mixture are applied to describe the adsorption of methane–ethane mixtures in zeolites. The theoretical formalism reproduces the main features of the system, showing that the displacement of ethane by methane at higher pressures, a phenomenon known as Adsorption Preference Reversal, is the result of the difference of size (or number of occupied sites) between the adsorbed species.

1. Introduction

Adsorption of polyatomics ranging from small light molecules to hydrocarbons, macromolecules and polymers is a topic of surface science of considerable practical interest in technological applications as well as it is a challenging for theoretical modelling in both, atomic-level simulations and pure analytical approaches [1–3]. Various singular behaviors of adsorbed polyatomics on regular and non-uniform surfaces have been reported experimentally and from molecular simulations. Amongst them, propane on graphite has been reported to develop orientational reordering at relatively high coverage [4]. Similarly, benzene on zeolites reorients suddenly at high coverages showing an abrupt step in the adsorption isotherm [5]. Desorption of alkanes from highly regular planes of graphite has shown that the entropic contribution of the various adsorption should be accounted for as to interpreting the square-root dependence of the activation energy for desorption on the number of carbon atoms of the adsorbate [6–8]. Peculiar behavior has been found for hexane and heptane on silicalite [9–11].

Adsorption of mixtures is a much demanding problem both experimentally and theoretically. Whereas for pure components the number of adsorbed molecules can be determined accurately by simply measuring the weight increase of the zeolite sample, for mixtures one has to carry out additional experiments to determine the composition inside the zeolite. This is one of the reason for the lack of polyatomic mixture adsorption data.

Nevertheless, some simulation studies have been published on mixtures of hydrocarbons [12–19]. An unusual feature is observed in the case of methane–ethane mixtures [12,13]: at low pressure the adsorbed phase is almost entirely ethane, but at higher pressures methane molecules displace ethane molecules. A similar scenario has been observed for different mixtures of linear hydrocarbons in silicalite [14–19], carbon nanotube bundles [20] and metal-organic frameworks [21]. In all cases, at low (high) pressure the selectivity is toward the larger (smaller) component. This behavior is known as Adsorption Preference Reversal (APR) [22].

From the theoretical point of view, the interpretation of the APR phenomenon is not simple. In this sense, following a scheme in the framework of the theory of adsorption of molecules with single occupancy (each molecule occupies one lattice site), Ayache et al. [22] and Dunne et al. [23] show how the competition between two species in presence of repulsive mutual interactions can lead to the displacement of one species by the other. In Refs. [22,23], the lateral interactions were introduced using mean-field approximation and exact calculations, respectively. However, hydrocarbon molecules adsorbed on solid surfaces should be regarded under the light of a multisite-adsorption model [3], in order to properly account for the effects of configurational entropy (k-mer size and flexibility) on the thermodynamics of the adlayer. Clearly, the dependence of entropy on the molecular size, structure and density it is expected to play a significant role in the thermodynamics of this kind of systems and be responsible for a rich variety of entropy driven phenomena and transitions.

For understanding the role of molecular size and structure on the properties of thermodynamic functions of the adlayer is of fundamental interest in statistical physics and the formulation of descriptions which capture the relevant features of these large set of physical systems is of major interest in the design and optimization of separation process in petrochemical technology. Along this line of thought, an original theory of multicomponent

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adsorption of polyatomic species based upon the foundations of Haldane's statistics have been recently presented [24].

The results in Ref. [24] showed that the effect of the multisite-occupancy adsorption plays a determinant role in the description of the APR phenomenon. This Letter goes a step further, addressing the rigorous statistical thermodynamics of s-mer (particle occupying s lattice sites)–k-mer (particle occupying k lattice sites) mixtures adsorbed on one-dimensional substrates (Section 2). The formalism presented here is, to our knowledge, the first exact model of mixture adsorption in zeolites which allows for multisite-occupancy adsorption. Taking advantage of this new theoretical scheme, we demonstrated that the APR phenomenon is the result of the difference of size (or number of occupied sites) between the adsorbed species (Section 3).

2. One-dimensional lattice model for adsorption of alkane binary mixtures: exact forms of the thermodynamic functions

Let us assume a one-dimensional lattice of M sites with lattice constant a ($M \to \infty$) and periodic boundary conditions. Under this condition all lattice sites are equivalent, hence edge effects will not enter our derivation.

N_s s-mers and N_k k-mers are adsorbed on the surface. A s-mer (k-mer) is assumed to be a linear molecule containing $s(k)$ identical units, with each one occupying a lattice site; hence exactly $s(k)$ sites are occupied by a s-mer (k-mer) when adsorbed. In addition, double site occupancy is not allowed as to represent properties in the monolayer regime. Since different particles do not interact with each other through their ends, all configurations of N_s s-mers and N_k k-mers on M sites are equally probable; henceforth, the canonical partition function $Q(M, N_s, N_k, T)$ equals the total number of configurations, $\Omega(M, N_s, N_k)$, times a Boltzmann factor including the total interaction energy between adparticles and lattice sites, $E(N_s, N_k)$

$$Q(M,N_s,N_k,T) = \Omega(M,N_s,N_k)\exp\left[-\frac{E(N_s,N_k)}{k_BT}\right]. \tag{1}$$

$\Omega(M, N_s, N_k)$ can be readily calculated as the total number of permutations of the N_s indistinguishable s-mers and N_k indistinguishable k-mers out of n_e entities, being n_e

$$\begin{aligned} n_e &= \text{number of } s\text{-mers} + \text{number of } k\text{-mers} \\ &\quad + \text{number of empty sites} \\ &= N_s + N_k + M - sN_s - kN_k = M - (s-1)N_s - (k-1)N_k. \end{aligned} \tag{2}$$

Accordingly,

$$\Omega(M,N_s,N_k) = \frac{[M-(s-1)N_s-(k-1)N_k]!}{N_s!N_k![M-sN_s-kN_k]!}. \tag{3}$$

On the other hand, $E(N_s, N_k)$ can be written as

$$E(N_s,N_k) = \epsilon_s N_s + \epsilon_k N_k, \tag{4}$$

where ϵ_i represents the adsorption energy of a i-mer unit ($i = s, k$).

In the canonical ensemble, the Helmholtz free energy $F(M, N_s, N_k, T)$ relates to $\Omega(M, N_s, N_k)$ through

$$\begin{aligned} \beta F(M,N_s,N_k,T) &= -\ln Q(M,N_s,N_k,T) \\ &= -\ln\Omega(M,N_s,N_k) + \beta\epsilon_s N_s + \beta\epsilon_k N_k, \end{aligned} \tag{5}$$

where $\beta = 1/k_BT$.

The chemical potential of the adsorbed species i, $\mu_{i,ads}$, can be calculated as [25]

$$\mu_{i,ads} = \left(\frac{\partial F}{\partial N_i}\right)_{N_j's} \quad \{i,j = s,k\}. \tag{6}$$

From Eqs. (3)–(6) it follows that

$$\begin{aligned} \beta\mu_{s,ads} &= (s-1)\ln\left[1-\left(\frac{s-1}{s}\right)\theta_s-\left(\frac{k-1}{k}\right)\theta_k\right]+\ln\frac{\theta_s}{s} \\ &\quad - s\ln(1-\theta_s-\theta_k)+\beta\epsilon_s, \end{aligned} \tag{7}$$

and

$$\begin{aligned} \beta\mu_{k,ads} &= (k-1)\ln\left[1-\left(\frac{s-1}{s}\right)\theta_s-\left(\frac{k-1}{k}\right)\theta_k\right]+\ln\frac{\theta_k}{k} \\ &\quad - k\ln(1-\theta_s-\theta_k)+\beta\epsilon_k, \end{aligned} \tag{8}$$

where $\theta_i = iN_i/M$ represents the partial coverage of the species i $\{i = s,k\}$.

At equilibrium, the chemical potential of the adsorbed and gas phase are equal. Then,

$$\mu_{s,ads} = \mu_{s,gas}, \tag{9}$$

and

$$\mu_{k,ads} = \mu_{k,gas}, \tag{10}$$

where $\mu_{s,gas}$ ($\mu_{k,gas}$) corresponds to s-mers (k-mers) in gas phase.

The chemical potential of each kind of molecule in an ideal gas mixture, at temperature T and pressure P, is

$$\beta\mu_{s,gas} = \beta\mu_s^0 + \ln X_s P, \tag{11}$$

and

$$\beta\mu_{k,gas} = \beta\mu_k^0 + \ln X_k P, \tag{12}$$

where μ_s^0 and μ_k^0 (X_s and X_k) are the standard chemical potentials (mole fractions) of s-mers and k-mers, respectively. In addition,

$$\beta\mu_i^0 = -\ln\left[\left(\frac{2\pi m_i k_BT}{h^2}\right)^{3/2} k_BT\right] \quad \{i = s,k\}. \tag{13}$$

Then, equating Eq. (7) with Eqs. (11) and (8) with Eq. (12) we obtain,

$$\begin{aligned} &(s-1)\ln\left[1-\left(\frac{s-1}{s}\right)\theta_s-\left(\frac{k-1}{k}\right)\theta_k\right]+\ln\frac{\theta_s}{s}-s \\ &\quad\times\ln(1-\theta_s-\theta_k)+\beta\Phi_s \\ &\quad= 0, \end{aligned} \tag{14}$$

and

$$\begin{aligned} &(k-1)\ln\left[1-\left(\frac{s-1}{s}\right)\theta_s-\left(\frac{k-1}{k}\right)\theta_k\right]+\ln\frac{\theta_k}{k} \\ &\quad - k\ln(1-\theta_s-\theta_k)+\beta\Phi_k = 0, \end{aligned} \tag{15}$$

where

$$\beta\Phi_i \equiv \beta\epsilon_i - \beta\mu_i^0 - \ln X_iP \quad \{i = s,k\}. \tag{16}$$

3. Applications: interpretation of the adsorption preference reversal phenomenon

Following the line of Ref. [22], we start calculating the parameter $A \equiv \exp[\beta(\Phi_k - \Phi_s)]$, which is obtained from the equilibrium equations (Eqs. (14) and (15)):

$$\begin{aligned} A &= \frac{X_s}{X_k}\exp\left[\beta(\epsilon_k-\epsilon_s)-\beta(\mu_k^0-\mu_s^0)\right] \\ &= \frac{k\theta_s}{s\theta_k}\,\frac{(1-\theta_s-\theta_k)^{k-s}}{\left[1-\left(\frac{s-1}{s}\right)\theta_s-\left(\frac{k-1}{k}\right)\theta_k\right]^{k-s}}. \end{aligned} \tag{17}$$

In order to understand the basic phenomenology, we consider in the first place a monomer–monomer mixture ($s = k = 1$), with equimolar amounts of each kind of molecules in the gas phase ($X_s = X_k$). Under these conditions, Eq. (17) can be written as:

$$A=\exp\left[\beta(\epsilon_k-\epsilon_s)-\beta(\mu_k^0-\mu_s^0)\right]=\frac{\theta_s}{\theta_k}. \tag{18}$$

In this case, $\theta_s/\theta_k = \text{const}$. Accordingly, the partial adsorption isotherms corresponding to the species s and k do not intersect and the APR phenomenon does not occur. This situation is reflected in Fig. 1, where an equimolar monomer–monomer mixture has been studied for $\beta(\epsilon_s-\mu_s^0)=-2$ and $\beta(\epsilon_k-\mu_k^0)=-4$. The inset shows a similar analysis, where the values of the adsorption energies per particle were taken from Ref. [22]: $\beta\epsilon_s=-14.77$ ($\epsilon_s=-5.1\times\ 10^{-20}$ J and T = 250 K) and $\beta\epsilon_k=-21.81$ ($\epsilon_k=-7.875\times10^{-20}$ J and T = 250 K). In addition, the values of $\beta\mu_s^0$ and $\beta\mu_k^0$ were obtained by using Eq. (13) with m_s (m_k) equal to the molecular mass of methane (ethane). Thus, $m_s=16.04$ uma, $m_k=30.07$ uma (where 1 uma = 1.660531×10^{-27} kg) [26] and, consequently, $\beta\mu_k^0=-26.77$ and $\beta\mu_s^0=-25.83$.

The results in Fig. 1 are consistent with previous work on monomer–monomer mixtures [22], where a complex set of lateral interactions is needed to reproduce the phenomenon of APR.

Now, we will analyze the general case of an equimolar s-mer–k-mer mixture. As it is possible to observe from Eq. (17), if $s=k$, the partial isotherms do not cross one another and the shape of curves is similar to the shown in Fig. 1.

On the other hand, if $s\neq k$, different behaviors are expected depending on the value of A and the relation between the size of the species s and the size of the species k. Without any loss of generality, we assume that $s<k$. With respect to A, some physical assumptions have to be made: the heats of adsorption of linear alkanes (1) are attractive and (2) increase (in absolute value) linearly with the chain length. It is important to remark that the conditions (1) and (2) are not pure mathematical constructions. They physically characterize the real energetics of adsorption of alkanes in zeolites and are strongly supported in the literature [27–30].

Under these considerations, the argument of the exponential in Eq. (17) is negative, A varies between 0 and 1 and there exists a value of coverage, θ^* ($0<\theta^*<1$), at which the partial isotherms coincide ($\theta_s=\theta_k=\theta^*$) and, consequently, the APR phenomenon occurs. The value of θ^* can be obtained from Eq. (17) by simple algebra:

$$\theta^*=\frac{1-\left(\frac{sA}{k}\right)^{1/(k-s)}}{2-\left(\frac{k-1}{k}+\frac{s-1}{s}\right)\left(\frac{sA}{k}\right)^{1/(k-s)}}. \tag{19}$$

The crossing point (μ^*,θ^*) separates two adsorption regimes. Thus, for $\mu<\mu^*$, θ_k is larger than θ_s. This tendency is reverted for $\mu>\mu^*$, where θ_s is larger than θ_k. Then, the existence of the point θ^* is directly related to the displacement of the species k by the species s, and, consequently, to the presence of APR phenomenon.

This situation is clearly observed in Fig. 2, where a monomer($s=1$)–dimer($k=2$) mixture, with equimolar amounts of each kind of molecules in the gas phase, has been considered. The values of the parameters $\beta\epsilon_s$, $\beta\epsilon_k$, $\beta\mu_s^0$ and $\beta\mu_k^0$ are as in the inset of Fig. 1. The monomer–dimer case (i) represents the simplest system of adsorption of two species of different size; (ii) contains all the properties of the multisite-occupancy adsorption and (iii) the results can be applied to the study of methane–ethane mixture adsorption in silicalite (as is common in the literature, we adopt a 'bead segment' chain model of the molecules, in which each methyl group is represented as a k-mer unit and coincides in size with one adsorption site on the surface. Under this consideration, we set $s=1$, $k=2$ in fitting data corresponding to $C, C2$, respectively).

Due to the fact that the ethane molecules have greater adsorption energy, they begin to adsorb first. As the pressure is increased, the adsorption of methane starts becoming more favorable and the ethane molecules are displaced. Consequently, the partial adsorption isotherms cross at θ^* and the APR phenomenon is observed. In this case, $\theta^*=0.4998$.

The rigorous results presented here represent an important contribution to the understanding and interpretation of the APR phenomenon, showing that, the APR will appear as a result of the difference of size (or number of occupied sites) between the adsorbed species. In this sense, it is worth emphasizing that a rather artificial model with six fitting parameters (adsorption energy of methane, adsorption energy of ethane, methane–methane interaction, methane–ethane interaction, ethane–ethane interaction and temperature) was necessary to interpret analogous data in the framework of the theory of monomer–monomer mixtures [22]. The high number of parameters needed in such a study results in badly defined parameters leading to only qualitative conclusions as in the case of the analysis reported in Ref. [22]. Note that very small variations of the parameters (much smaller than the typical experimental errors) provide completely different results. As a example, a change of the order of 5% in the adsorption energy of ethane determines the existence or not of APR in the model of Ref. [22].

Reinforcing the arguments above, Eq. (19) shows that, if $s\neq k$, the APR phenomenon occurs even in the extreme case of systems with purely steric interactions ($\beta\epsilon_s=\beta\epsilon_k=\beta\mu_s^0=\beta\mu_k^0=0$ and

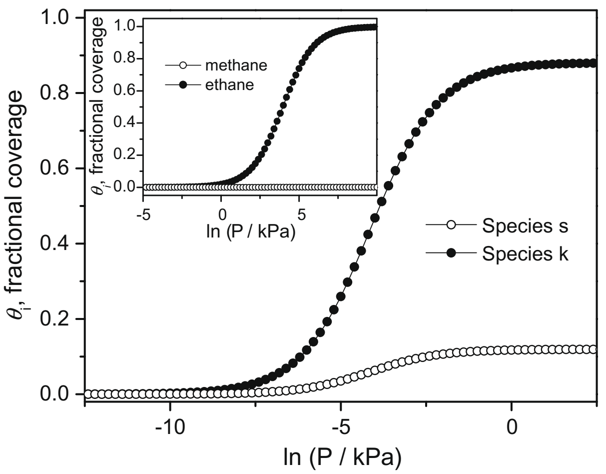

Fig. 1. Partial adsorption isotherms for an equimolar monomer($s=1$)–monomer($k=1$) mixture on an one-dimensional lattice. Parameter values (figure): $\beta(\epsilon_s-\mu_s^0)=-2$ and $\beta(\epsilon_k-\mu_k^0)=-4$. Parameter values (inset): parameter values: $\beta\epsilon_s=-14.77$, $\beta\epsilon_k=-22.81$, $\beta\mu_s^0=-25.83$ and $\beta\mu_k^0=-26.77$.

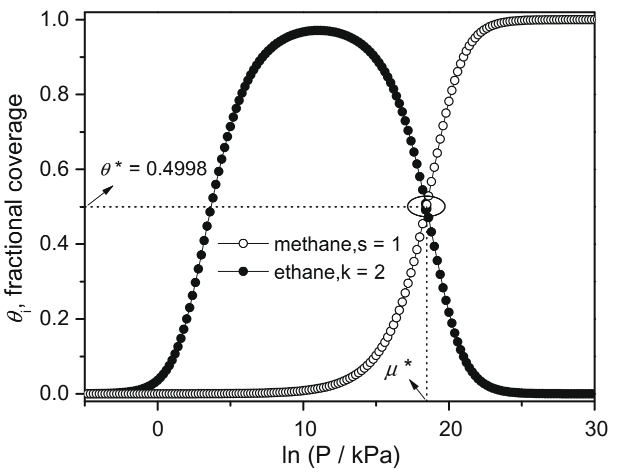

Fig. 2. Partial adsorption isotherms for an equimolar methane($s=1$)–ethane($k=2$) mixture on an one-dimensional lattice. Parameter values: $\beta\epsilon_s=-14.77$, $\beta\epsilon_k=-22.81$, $\beta\mu_s^0=-25.83$ and $\beta\mu_k^0=-26.77$.

$A = 1$). Thus, to introduce a complex set lateral interactions in the adsorbate is a fictitious or effective way of taking into account geometric or steric effects by means of energetic arguments.

In summary, this work provides the first exact model of alkane mixture adsorption in zeolites which allows for multisite-occupancy adsorption. Two main conclusions can be drawn from the present study: (1) the entropic contribution of nonspherical adsorbates is significant in the interpretation of surface phenomena when compared with monoatomic adsorption and (2) a real description of the phenomenon of APR may be severely misunderstood, if the polyatomic character of the adsorbate is not properly incorporated in the thermodynamic functions from which experiments are interpreted.

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