Non-empirical quantum chemical calculation of Henry and separation constants and heats of adsorption for diatomic gases in faujasite

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The Henry and separation constants and heat of adsorption of N_2 and O_2 in faujasite are calculated in a non-empirical way; they show fair agreement with experiment taking into account the extreme sensitivity of the configuration integral to small variations in interaction energy values.

Zeolites are of utmost importance both as catalysts, essentially due to the acidic properties of their bridging hydroxy groups,[1,2] and as adsorbents due to their adsorption properties.[3] Present-day quantum chemistry already allows non-parametrized, highly accurate *ab initio* calculations on the acidic properties using the supermolecule approach yielding interaction energies and spectroscopic properties used as acidity indicator (*e.g.* IR frequency and intensity shifts).[4–6] The calculation of the adsorption behaviour and the thermodynamic quantities associated with it (Henry constant, separation constant, heat of adsorption) was up to now, essentially due to computational reasons, performed using model interaction potentials[7–9] and various models involving adjustable parameters.[10,11]

In this contribution we report the, as far as we know, first *ab initio* calculations of Henry constants, separation constants and heats of adsorption. The methodology is described and applied to the adsorption behaviour of O_2 and N_2 in the large cavities of a faujasite large cavity for which experimental data are available.[12,13] Its extension to less symmetrical cases and cation distributions will be straightforward.

The starting point in the evaluation of the above mentioned properties is the Henry constant expression, based on an evaluation of the ratio of the partition functions of the free and adsorbed gas.[14,15] Neglecting vibrational corrections upon adsorption and applying the ideal gas law for the non-adsorbed gas one arrives at the following expression for the Henry constant K [eqn. (1)], where B is the number of cavities

$$K = \frac{BI}{aRT} \tag{1}$$

in which the adsorption process can take place per mass zeolite, R the ideal gas constant and T the absolute temperature. The factor a‡ = 1 in the case of a monoatomic gas, 4π for a linear molecule and $8\pi^2$ for a non-linear molecule. I is the configuration integral [eqn. (2)], where E represents the interaction

$$I = \int \exp[-E(\boldsymbol{r},\boldsymbol{\phi})/RT]\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{\phi} \tag{2}$$

energy molecule–zeolite cage when the centre of gravity of the molecule is at position $\boldsymbol{r}$ and the molecular orientation characterized by angles gathered in a vector $\boldsymbol{\phi}$. The integration is performed over all positions $\boldsymbol{r}$ in the faujasite cavity and for each position over all orientations.

The cage was chosen as to represent a faujasite Y zeolite, using hydroxy groups as terminators and showing a Si/Al ratio of 3, with bruto-formula $Na_{16}Si_{36}Al_{12}O_{120}H_{48}$.

Four of the 16 Na^+ ions are localized in site II with a tetrahedral orientation towards the centre of the large cavity. The interaction of the molecules (N_2 and O_2) with the cage were calculated using the 'molecule in point charge environment' approach as often used in the study of molecular crystals.[17] The point charges of the cage atoms were obtained with the ChelpG method[18] at an STO 3G[19] level. A scaling procedure was then introduced in order to account for the change in potential when removing the terminating hydroxy groups in order to be able to fully exploit the symmetry of the cage (*vide infra*): all charges were multiplied by a constant yielding the 'correct' potential at the centre of the cage (*i.e.* the potential at the centre of the cavity with the terminating hydroxy groups still present).§ This procedure is based on the idea that the artificial terminators (hydroxy groups) might perturb the real symmetry of the cage due to the presence of the hydrogen atoms.

Being able to fully exploit the cage symmetry, a cubic grid of points in the cage has been created by selecting points at a 0.5 Å distance along x, y and z axis, thereby performing the integration over $\boldsymbol{r}$ in eqn. (2) *via* a numerical procedure of evaluating the interaction energy E of molecules at the centre of each cube, inserting it in the $\exp(-E/RT)$ expression and multiplying it by the elementary volume ΔV of 0.125 Å.^{3} The integration over all orientations is ensured by performing the above-mentioned interaction energy calculation once with the molecule aligned along the x- as (E_x), once along the y-axis (E_y), and once along the z-axis (E_z) and multiplying each contribution $\exp(-E_\alpha/RT)$ ($\alpha = x, y, z$) by $4\pi/3$. Symmetry is exploited by considering only 1/24th part of the zeolite cage (*cf.* ref. 7) using a self-developed algorithm to select those grid points contained in a polyhedron with the following vertices: the centre of the cavity and the position of the cations at S_{II}, S_{III} and S_{IV}.

In this way 321 points were selected and the integral (2) was replaced by the sum given in eqn. (3), where g_i is a weight

$$I \approx \frac{4\pi}{3}\sum_i [\exp(-E_{x,i}/RT) + \exp(-E_{y,i}/RT) + \exp(-E_{z,i}/RT)]\,\Delta V_{gi} \tag{3}$$

factor taking the value 1,4, 12, or 24 for a point at the centre of the cavity, at an edge, on a side, or inside the '1/24' sector.

Moreover those points were rejected for which the distance to the Na^+ ions in the sector is smaller than the sum of the equilibrium distance $Na^+\cdots X_2$ (X = N, O) and half of the equilibrium distance of X_2 (both values being calculated at a 6-31G* level lead to spheres around the Na^+ cation of 2.50 (X = N) and 2.52 Å (X = O) respectively, in order to account for the deficiency in the short-range behaviour of the point charge model. At these distances, the true interaction energy will in most cases be repulsive so that in reality very small terms add to the sum in eqn. (3). We prefer to stick to this approximation rather than introducing a repulsive part in the point-charge potential, which will inevitably lead to some adjustable parameters in the procedure.

All interaction energies were calculated at the HF-631G* level[19] with equilibrium distances for N_2 and O_2 at the same level (1.0784 and 1.1677 Å respectively) using RHF and UHF[19] procedures for N_2 and O_2 respectively.

The configuration integrals I (in m^3) for N_2 and O_2 at 298.15 K resulting from (3) were: 1.937 10^{-23} m^3 for N_2 and 6.335

10^{-25} m^3 for O_2. The larger value for N_2 is in line with 6-31G* calculated stabilization energy for a linear molecule cation complex, taking basis set superposition errors[21] into account ($\Delta E = -6.98$ *vs.* -5.11 kcal mol^{-1}, 1 cal = 4.184 J).

Using eqn. (1) the following values for Henry constants and the separation constant α [$=K(N_2)/K(O_2)$] were obtained at 298.15 K;[¶] $K(N_2) = 37.87 \times 10^{-6}$ mol kg^{-1} Pa^{-1}, $K(O_2) = 7.78 \times 10^{-6}$ mol kg^{-1} Pa^{-1}, $\alpha = 4.87$: the corresponding experimental values, for an NaY zeolite with an Si/Al ratio of 2.43 are,[12,13] 2.58×10^{-6}, 1.01×10^{-6} mol kg^{-1} Pa^{-1} and 2.56, respectively.

The theoretical values reproduce the higher value of the Henry constant for N_2 as compared to O_2 whereas both values are roughly one order of magnitude too large, their ratio (separation constant) being of the correct order.

At this point the extreme sensitivity of K to the interaction energy values appearing in the exponent should be realized. It is easily checked that, assuming a position independent difference between theoretical and experimental values, a difference of only 1.4 kcal mol^{-1} accounts for an order of magnitude difference in K at 298.15. In view of the parameter-free evaluation of K the result is therefore pleasing, certainly when compared with literature results often adjusting interaction potentials to experimental Henry constants.

Moreover, when applying the Van't Hoff's eqn. (4)[15] the

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^\circ}{RT^2} \qquad (4)$$

temperature range 250–310 K, recalculating for each temperature K *via* eqn. (1) and (3) an almost perfect linear plot of ln K *vs.* $1/T$ is found as shown in Fig. 1 for O_2. The resulting heats of adsorption, $-\Delta H^\circ$, are 28.8 and 18.0 kJ mol^{-1} respectively, whose order of magnitude and sequence is in reasonable agreement with the experimental values of 19.5 and 16.5 kJ mol^{-1}.

In view of the fast increase in computational software and hardware, *e.g.* in the application of density functional theory,[22] to problems of charge distribution[23] we consider the results of these first non-parametrized evaluations of thermodynamic quantities describing adsorption in zeolites as highly promising, offering possibilities in developing tailor-made materials (cations, structure, *etc.*) using computer experiments.[24]

P. G. and G. B. wish to thank their colleague Professor R. Schoonheydt (Laboratory for Surface Science and Catalysis, Catholic University of Leuven) for providing the Cartesian coordinates of the zeolite cage and Professor R. Kieboom of the Mathematics Department of the Free University of Brussels for advice in constructing the algorithm for selecting grid points. Dr G. Destree from the Computer Center of the Free University of Brussels is thanked for help in the automation of the interaction energy calculations. F. D. P. and C. V. A. are indebted to the Belgian National Science Foundation (NFWO) for a postdoctoral research fellow (F. D. P.) and Research Director (C. V. A.) position, respectively.

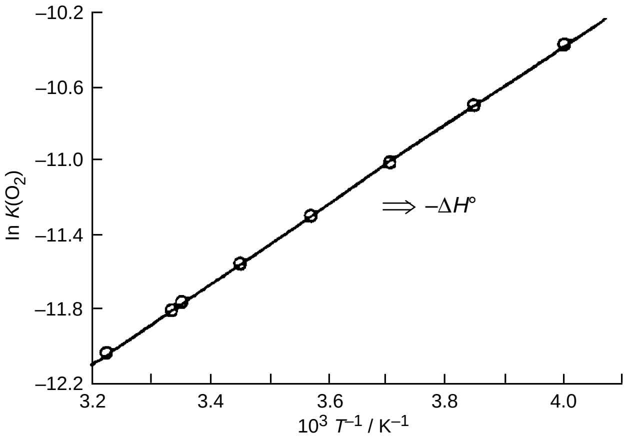

Fig. 1 Plot of ln $K(O_2)$ *vs.* $1/T$ calculated for T in the range 250–310 K

Footnotes

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[‡] Originating from the rotational partition function.

[§] In a later stage the cage charges were recalculated at the 3-21G[19] level, using one of the author's MIA method[20] in order to speed up this 2008 basis functions problem. As the linear correlation coefficient r of STO 3G and 3-21G charges amounts to 0.988, no fundamental difference between each result can be expected.

[¶] The B value was computed starting from the bruto formula of the unit cell [$Na_{48}(AlO_2)_{48}(SiO_2)_{144}$]: taking into account that eight large cavities are present in the unit cell $B = 3.8275 \times 10^{20}$ g^{-1}.

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Received, 28th November 1996; Com. 6/08061H