CALCULATION OF POTENTIAL ENERGY OF ADSORBED MOLECULES ON ZEOLITES

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Application of a semiempirical potential function, based on the Lennard–Jones potential with terms of electrostatic interaction added, to the calculation of adsorption energy of molecules is described. Examples of the adsorption of simple molecules Ar, Kr, Xe, and N_2 serve to discuss the role of various adsorption centers of the Y-type zeolite (faujasite) lattice.

The question of specific adsorption of an adsorbate molecule on various adsorbents is an important task for the theory of adsorption. In the first approximation, one expects that for weak adsorbent–adsorbate interactions this problem may be solved, if one succeeds in characterizing the system adsorbent–adsorbate by such physical parameters which would describe independently the properties of adsorbed molecules on the one hand and of the solid phase on the other hand.

   The basic problem in calculating thermodynamic functions of molecules sorbed on an adsorbent surface is the calculation of the potential energy of an adsorbed molecule in the field of force of the adsorbent. A critical analysis of the state of the adsorption forces theory has been made recently by several authors[1-3].

   Studies of adsorbed molecules of various electronic structure on ionic crystals — zeolites — have provided a series of important results. These data as well as first attempts of their appraisal from the point of view of a primitive theory of adsorption forces give a certain chance that a model of adsorption treating the problem semiempirically can be formulated.

The aim of this communication is to formulate such a model for adsorption on zeolites of the faujasite type which would be in agreement with experimental facts and which would make possible an orientation prediction and evaluation of experimental data.

THEORETICAL

The potential energy Φ of a molecule in the field of force of an adsorbent can be expressed — in the first approximation — as a sum of contributions of dispersion forces Φ_D, polarization forces Φ_P, potential energy of electrostatic moments of an adsorbed molecule in the electrostatic field of an adsorbent Φ_E, and repulsion Φ_R. It holds, therefore, that the potential energy is

$$\Phi = \Phi_D + \Phi_P + \Phi_E + \Phi_R \, . \tag{1}$$

The potential energy of the dispersion forces interaction is described in the atom — atom approximation as a sum of pair interactions of the adsorbed molecule (i) with the corresponding atom of the adsorbate lattice (j)

$$\Phi_D = C_1 \sum_j r_{ij}^{-6} + C_2 \sum_j r_{ij}^{-8} + C_3 \sum_j r_{ij}^{-10} . \tag{2}$$

For the sake of simplicity, only the first term of the expansion is considered here, as contributions of the other terms do not usually exceed 10% of the total value. The separation between the centers of the interacting particles is given by the modulus vector r_{ij}. The constant C_1 was approximated, according to Kirkwood and Miller, by means of electrical polarizabilities α and diamagnetic susceptibilities χ of the interacting particles

$$C_1 = -6mc^2 \frac{\alpha_i \alpha_j}{(\alpha_i/\chi_i) + (\alpha_j/\chi_j)} , \tag{3}$$

where m is the electron mass, c the velocity of light. The constant C_1 expressed in this way provides usually the highest value of all constants usually employed[2].

To calculate the contribution of the induced dipole of the adsorbed molecule in the electrostatic field of intensity **E**, the following expression was used

$$\Phi_P = -\tfrac{1}{2}\alpha_i E^2 . \tag{4}$$

Here, α_i is the polarizability tensor.

The electrostatic field is defined here by

$$\mathbf{E} = -\operatorname{grad} \varphi , \tag{5}$$

$$\varphi = \sum_j e_j/r_j , \tag{6}$$

where φ is the potential of the electrostatic field, e_j is the charge of the ion in the zeolite lattice.

In our calculation only molecules with quadrupole moments will be considered. This is a second-order tensor with components defined by

$$\Theta_{\alpha\beta} = \tfrac{1}{2} \sum_i e_i (3r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta}) . \tag{7}$$

e_i are charges at points with coordinates x_i, y_i, z_i defined by the radius vector components $r_{i\alpha}$, $r_{i\beta}$; $\delta_{\alpha\beta}$ is the Kronecker symbol. The potential energy of this quadrupole

in the electrostatic field is given by

$$\Phi_E = -\tfrac{1}{3}\Theta_{\alpha\beta}E'_{\alpha\beta} = -\tfrac{1}{3}\sum_{\alpha\beta}\Theta_{\alpha\beta}\frac{\partial^2\varphi}{\partial r_\alpha\,\partial r_\beta} \tag{8}$$

in which α, β acquire the meaning of the indices x, y, z, and equation (8) is a shortened transcription of the summation over all combinations of indices α, β.

The repulsive potential was considered to have the following form

$$\Phi_R = B\sum_j r_{ij}^{-12}. \tag{9}$$

The value of the repulsive contant B was obtained from the condition for a local minimum of the potential function, where $(\partial\Phi/\partial r_{ij})_{r=r_0} = 0$. The equilibrium distance r_0 between the adsorbed molecule and the adsorption center was obtained assuming that both the adsorbed molecule and the surface atoms behave as an ensemble of hard spheres.

As the potential energy of non-spherically symmetric molecules depends on their spatial orientation with respect to the adsorption center, the adsorption energy changes with temperature. Therefore, both the maximum potential energy of the molecule at the absolute zero was calculated and its mean value for the temperature $T = 200$ K. For this purpose, the dependence of the potential sum $\Phi_P + \Phi_E$ was calculated on the angles φ and ϑ of the spherical coordinates of the molecule, and the orientation of the molecule for the maximum value of the sum $\Phi_P + \Phi_E$ was determined. The value of this function at $T > 0$ K can be determined from the expression for the mean value

$$\overline{(\Phi_P + \Phi_E)} = \frac{\displaystyle\sum_{\varphi=0}^{2\pi}\sum_{\vartheta=0}^{\pi/2}(\Phi_P + \Phi_E)\exp\left(-\frac{\Phi_P + \Phi_E}{RT}\right)\sin\vartheta}{\displaystyle\sum_{\varphi=0}^{2\pi}\sum_{\vartheta=0}^{\pi/2}\exp\left(-\frac{\Phi_P + \Phi_E}{RT}\right)\sin\vartheta}. \tag{10}$$

The Model of Adsorption

The geometry calculated from roentgen structural data of zeolites Y in the dehydrated form was used[13]. Exchangeable cations Na$^+$ and K$^+$ occupy in the zeolite lattice three types of positions, M_1, M_2, and M_3, as can be seen from Fig. 1. Some positions are not completely occupied: this is expressed in the occupation factor which describes the probability of occupation of a given position.

In the communications so far published, the adsorption center was chosen to lie on the symmetry axes of the faujasite structure[4-12]. In this paper, as an adsorption

center such a molecular position was designated, where a contact with at least three atoms of the zeolite lattice occurs. The geometry of the center was determined from the hard-sphere model, the spheres representing both the surface atoms and the adsorbed molecule. The radii of atoms of the center as well as the radius of the adsorbed molecule are summarized, together with other parameters, in Table I.

TABLE I

Constants Used in Potential Energy Calculations

Particle	Radius Å	$\alpha \cdot 10^{24}$ cm^3	$\chi \cdot 10^{29}$ cm^3
Ar	1·90[a]	1·63[a]	3·22[a]
Kr	2·02[a]	2·48[a]	4·65[a]
Xe	2·20[a]	4·00[a]	7·15[a]
N_2	1·75[b]	1·45[a,h] 2·39[a,i]	1·98[a,h]
Na^+	1·17[c]	0·15[a]	—
$O^{-\delta}$	1·50[e,f]	0·7—1·6[g]	—
Si^{+4}	—	0·052[a]	—
Al^{+3}	—	0·0165[a]	—

[a] See ref.[27]; [b] see ref.[30]; [c] see ref.[25]; [d] see ref.[28]; [e] see ref.[26]; [f] see ref.[14-16]; [g] $\Theta = 1·3 \cdot 10^{-26}$ elst. u. (see ref.[29]); [h] $\alpha_{xx} = \alpha_{yy}$; [i] α_{zz}.
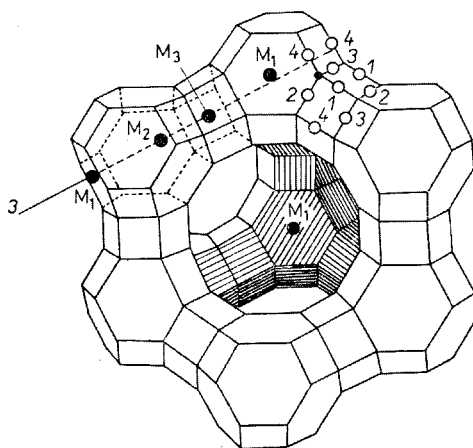

FIG. 1

Structure of Zeolite Y

Within the framework of the atom—atom approximation the solid phase is approximated by an ensemble of quasi-independent atoms or ions. Each particle in the lattice is characterized by its position, electrical polarizability α_γ, diamagnetic susceptibility χ_j, and effective charge e_j; surface atoms are, in addition, characterized by their radii R_j. In view of the difficulties in obtaining the values α_j and e_j for bound states of ions in the zeolite lattice, these quantities were regarded in the calculations as adjustable parameters whose values were chosen in the range of theoretically expected values. In contrast with the other models so far described in the literature, the calculation has taken into consideration also Si and Al atoms. Because the distribution of these particles in the lattice is not known, all their constants were taken as weighted averages according to the ratio Si/Al of the composition of the zeolite under study. The composition of the employed elementary cell of zeolite Y in the dehydrated state was $Na_{34.7}(AlO_2)_{54.7}(SiO_2)_{137.2}$. Diamagnetic polarizabilities were obtained from electrical polarizabilities with the use of the Kirkwood formula.

Several ways have been used to solve the problem of calculating the electrostatic field in zeolites[6,19,20]. In our study the method of direct summations was used without the correction on the internal polarization of the dielectric. Also, the effect of the adsorbed molecule on the dielectric state was neglected, as the polarization of the zeolite lattice is eesential only with molecules of large dipolemoments. As in case of ionic crystals of the NaCl, NaBr, etc. type the full ionicity of ions is not probable (as reported by Suchet[18]), the effect of $Na^{+\delta}$ cation charge on the values $\Phi_p + \Phi_E$ was examined.

The adsorbed molecule is in this approximation characterized by the position of its center x_i, y_i, z_i, its effective radius R_i, its electrical and diamagnetic polarizability, and by its quadrupole-moment.

RESULTS AND DISCUSSION

In view of the well-known difficulties in the convergence of the summation series when calculating the ion crystal lattice energy, the convergence of Φ and of its components was examined for an electroneutral spherical section of the lattice of the radius R, centered in the adsorbed molecule. The total potential Φ forms, with the increasing radius R, an oscillating converging series, mainly due to the oscillating component of the polarization potential Φ_P. A satisfactory value of Φ was reached at $R = 2\cdot1$ which was then used in all calculations (R is expressed in units of the lattice parameter, $d = 24\cdot71$ Å). This result agrees well with the calculation of the electrostatic field convergence as carried out by Lechert[19] who found a satisfactory value for $R = 1\cdot4$.

The effect of charge distribution in the zeolite lattice was further examined on the values of adsorption energies of Ar, Kr, Xe, and N_2. Fig. 2 shows a plot of the total adsorption potential of noble gases on all the three possible (in the above mentioned

sense) adsorption centers $M_1O_2O_4(I)$, $O_1O_1O_4O_4(II)$, and $O_1O_1O_2(III)$ in dependence on the oxygen charge, for a constant Na charge. In case of noble gas molecules, there is no pronounced dependence on the oxygen anion charge. The values of Φ increase at most by 12%. This results from the compensation of the oxygen ion charges by the positive charges of Si and Al in the vicinity of the oxygen ions.

TABLE II

Values of Φ (kcal/mol) for NaY Zeolite with Incomplete Ionic Lattice on Centers I—III in Dependence on α_0

| Center | α_0 | Ion charges $Na^{+0.7}$, $O^{-0.75}$ | | | |
		Ar	Kr	Xe	N_2
I. $M_1O_2O_4$	1·0	2·67	3·14	3·61	4·93
	1·3	3·05	3·64	4·25	5·34
	1·6	3·40	4·11	4·84	5·72
II. $O_1O_1O_4O_4$	1·0	2·67	3·42	4·19	3·56
	1·3	3·20	4·11	5·03	4·13
	1·6	3·68	4·73	5·80	4·66
III. $O_1O_1O_2$	1·0	2·32	3·00	3·72	3·06
	1·3	2·77	3·59	4·46	3·54
	1·6	3·18	4·13	5·14	3·99

TABLE III

Potential Energy (kcal/mol) of Argon and Nitrogen on NaY
Charge distribution: $Na^{+0.7}$, $O^{-0.75}$; $\alpha_0 = 1\cdot3$ Å^3; not corrected on Φ_0.

Adsorption	$-\Phi_D$	$-\Phi_P$	$-\Phi_E$	$+\Phi_R$	$-\Phi$ (0 K)	$-\Phi$ (200 K)
			Argon			
$M_1O_2O_4$	4·08	0·85	—	1·89	3·05	—
$O_1O_1O_4O_4$	5·86	0·57	—	2·66	3·20	—
$O_1O_1O_2$	4·95	0·60	—	2·24	2·77	—
			Nitrogen			
$M_1O_2O_4$	3·98	1·36	2·66	2·63	5·34	4·91
$O_1O_1O_4O_4$	5·86	$4 \cdot 10^{-3}$	1·23	2·97	4·13	3·86
$O_1O_1O_2$	4·88	$9 \cdot 10^{-2}$	1·06	2·48	3·54	3·07

This is also why in the adsorption positions II and III a negligible polarization potential was found (Table III). The value of Φ is substantially more influenced by the magnitude of the cation charge, $Na^{+\delta}$, and by the magnitude of the polarizability coefficient of oxygen, α_0. The calculations carried out for various degrees of the ionicity of the zeolite structure showed that structures with a high ionicity degree were not suitable. The charge distribution Na^+, O^{-2}, Si^{+4}, Al^{+3} gave an unrealistically high value of Φ both for the noble gases and for nitrogen. The values of charges corresponding to an incomplete ionicity proved themselves reasonable, in agreement with the existing general experimental experience. Table II lists the values
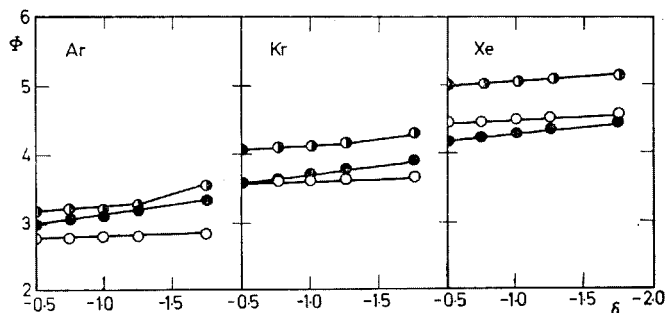

FIG. 2
Dependence of Potential Energy Φ (kcal/mol) of Ar, Kr, and Xe on the Lattice Oxygen Charge
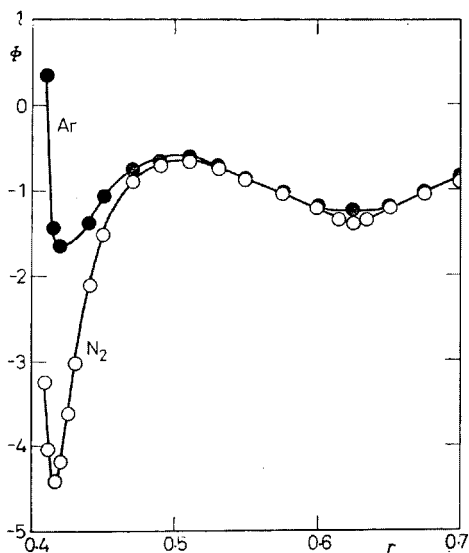

FIG. 3

Potential Curve of Ar and N_2 along the Three-Fold Symmetry Axis in NaY

of the total potential Φ at the absolute zero for the molecules studied on the particular centers I – III. Table III plots the components of the adsorption potential for Ar and N_2 on the centers I – III, and the total potential for $T = 0$ K and 200 K.

One can see by comparing the values of the adsorption potentials for Ar, Kr, Xe in Fig. 2 and Table III that the maximum calculated values of Φ follow the sequence Ar < Kr < Xe which is the sequence found experimentally from isosteric heats. This sequence is almost independent both of the lattice ionicity and of the values of the parameters characterizing Na and O. The sequence is, however, very sensitive to the choice of the van der Waals radii of the adsorbed molecules. It turns out that the best values were obtained for those radii that proved themselves useful in the calculations of the adsorption energy on graphitized carbon black (Ross[21], Kiselev and coworkers[24]). Quite unsuitable were the radii obtained from molecular beam scattering as well as from virial coefficients and from viscosity data[30].

The comparison of the adsorption energies of Ar, Kr, Xe, and N_2 on different adsorption centers I – III (see Table II and Table III) is useful, too. With argon and krypton the difference of the calculated energies does not exceed 500 cal/mol, with xenon it is 800 cal/mol. On the other hand, with nitrogen the difference between the potential energy of the cation position I and non-cation position II is 1 200 cal/mol, and between I and III it is as large as 1 790 cal/mol. Such a difference in adsorption energies must manifest itself in the dependence of the adsorption heat on the adsorbed amount. Indeed, while with Ar, Kr, and Xe the adsorption heats are almost independent of the extent of adsorption over a wide range, with nitrogen a strong decrease of the adsorption heat was found, typical for a sorption on heterogeneous surfaces[22,23].

Fig. 3 provides another illustration of the problem of sorption of molecules with a different electronic structure. In this figure, calculated potential curves for Ar and N_2 along the three-fold symmetry axis of the zeolite are plotted. It can be seen that the potential curves differ substantially in the region very close to the cation center (*i.e.* to the cation M_1). This difference in the region about the minimum is influenced to a certain extent by the difference in the radii of both molecules. However, with nitrogen also a substantial contribution of the quadrupole interaction manifest itself which increases the adsorption energy of N_2 in comparison with Ar (Table II). The quadrupole contribution can be seen also very significantly on the raising part of the potential curve, as here there is no pronounced difference in the dispersion forces contribution in Ar and N_2 (the polarizabilities of both of them are almost the same). In the center of the cavity ($r = 0.5$), both curves are identical as in this region the electrostatic field is weak ($\Phi_p \to 0$), the field inhomogeneity approaches zero ($\Phi_E \to 0$), and the total energy is determined by the value of the potential of dispersion forces. During the passage of the molecule from one cavity to another through the entrance window there is for $r = 0.625$ a secondary minimum which corresponds to narrowing of the cavity.

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