P. BREUER, A. V. KISELEV, A. A. LOPATKIN, S. SHPIGEL

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

P. BREUER, A. V. KISELEV, A. A. LOPATKIN, S. SHPIGEL

INTERACTION ENERGY OF SIMPLE MOLECULES WITH FAUJASITE-TYPE ZEOLITES

(Presented by Academician A. N. Frumkin, 24 IX 1964)

The theoretical calculation of the potential energy of molecules in the field of an adsorbent is important both for the theory of adsorption and for the theory of intermolecular interactions in general. A considerable number of such calculations have been published (see references in [1–5]), concerning adsorption on a nonpolar adsorbent (graphite). Close to this limiting case are cases of adsorption on polar adsorbents of the NaCl [6], MgO [7] type, when, owing to the alternating arrangement of ions on the crystal face, the principal attractive forces are also dispersion forces. More complicated are cases of specific interactions [5,8]. Of great interest is the calculation of the adsorption energy by the porous crystals of zeolites, whose structure is sufficiently well known. It includes Si, Al, and O atoms and cations. In [9] the interaction of an iodine molecule with a significant number of O atoms of the zeolite was considered, while the influence of cations was not taken into account. In [10,11], on the contrary, only interaction with cations was considered. In [12] the interaction was calculated both with oxygen atoms located on the walls of the large cavity and with cations located in this cavity. In the present work an attempt has been made to calculate the interaction energy of simple molecules with the zeolite lattice, taking into account a large number of O atoms of the lattice and one cation*; both the dispersion component and the induction component, caused by polarization of the adsorbate molecules in the electrostatic field of the lattice, were calculated. An idealized model of the zeolite (with higher symmetry) was used.

Basic assumptions. The interaction potential of an adsorbate molecule with an oxygen skeleton of the zeolite, in the approximation adopted, is expressed by the formula:

$$\Phi = -C\sum_i r_i^{-6} + B\sum_i r_i^{-12} + \Phi_{\text{ind}}, \tag{1}$$

where the first two terms represent the Lennard-Jones potential [13] for the set of pair interactions, and Φ_{ind} is the induction component. The summation was carried out over the oxygen atoms of the lattice. A substantial difficulty arises

in calculating the constant of dispersion attraction C. In [9] it was calculated by the Kirkwood-Müller formula:

$$C_{12} = 6mc^2 \frac{\alpha_1 \alpha_2}{\alpha_1/\chi_1 + \alpha_2/\chi_2}, \tag{2}$$

where m is the mass of the electron, c is the speed of light, and α_1 and α_2 and χ_1 and χ_2 are, respectively, the polarizabilities and magnetic susceptibilities of the adsorbate molecule and of the lattice element, for which in [9] the oxygen ion O^{2-} was adopted.

* In doing so, of course, the electroneutrality of the lattice is formally violated. However, since the exact position of some of the remaining cations is unknown, we have introduced the assumption that along the axis of the third order of the chosen cation their total field is zero. A special calculation of the electrostatic field is being carried out by us in a separate work.

However, it is impossible to determine α_2 and χ_2 exactly, and therefore one has to use approximate and insufficiently justified values. The constants C for the interaction of O^{2-} with various adsorbates are given in Table 1. The values of α and χ for O^{2-} were taken from ([9]). Another way of approximately determining the constant C is also possible from the values of the parameters ε and σ of the Lennard-Jones potential, written in the form ([13]):

Table 1

Constants of dispersion attraction
($C_{O-M} \cdot 10^{45}$, kcal/mol)

Adsorbate	According to the Kirkwood-Müller formula	From the second virial coefficient	Mean
Ne	0.492	0.472	0.485
Ar	1.878	1.628	1.753
Kr	2.807	2.248	2.526
Xe	4.553	3.645	4.099
CH_4	2.705	2.545	2.625

$$\Phi = 4\varepsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right]. \tag{3}$$

These parameters are determined from the second virial coefficient and are related to the constant C by the relation ([13]):

$$C = 4\varepsilon\sigma^6. \tag{4}$$

The constant C according to (4) is calculated for pair interactions of identical molecules (C_{11} and C_{22}). For unlike molecules ([2])

$$C_{12} = \sqrt{C_{11} \cdot C_{22}}. \tag{5}$$

The values of C_{12} calculated in this way are also given in Table 1. The first and second methods give close values of the constants C_{12}. For the subsequent calculations, the arithmetic mean was taken.*

The interaction of an adsorbate molecule M with a cation K was calculated separately. The interaction with Si and Al atoms was not taken into account.

Figure 1 shows the part of the geometric model used. The most probable adsorption site was taken to be the six-membered ring opening into the large cavity. The origin of coordinates was placed at the center of this six-membered ring. Various positions of the cation and of the adsorbate molecule were considered on the z-axis passing through the center of the ring perpendicular to its plane. It was also assumed that the cation and the molecule are in contact for all z_j, i.e., the distance between them is:

$$d_{\mathrm{K-M}} = r_{\mathrm{K}} + r_{\mathrm{M}}, \tag{6}$$

Fig. 1. Schematic representation of the six-membered ring leading into the small cavity of the zeolite. Also shown are the relative positions of the cation and adsorbate molecule, and the distances used in the calculation.

where r_{M} is the van der Waals radius of the adsorbate molecule, and r_{K} is the ionic radius of the cation. It was assumed that all cations, upon adsorption of all the molecules considered, lie in the plane of the six-membered ring** (i.e., $d_{\mathrm{K}} = 0$).

In calculating Φ_{ind}, the ordinary polarizability of the adsorbate molecule was used. The electrostatic field of the adsorbent is formed both by cations and by negative charges arising because the positive valence of Al is one unit less than the valence of Si. These negative charges were approximately assumed to be uniformly distributed–

* Strictly speaking, the constant C_{22}, calculated for oxygen from the second virial coefficient, refers to the interaction of molecules, not atoms. However, the main contribution is made by the interaction between two atoms of different O_2 molecules.

** This assumption was verified by a calculation, which is presented separately.

distributed over all O atoms and localized at their centers ([9]). The average charge per O atom for a type X zeolite of composition $0.97\,Na_2O \cdot Al_2O_3 \cdot 2.96\,SiO_2$ ([14]) is $\sim 0.214\,e$, where e is the electron charge.

Calculation of the adsorption energy. The interaction with the 111 nearest O atoms was taken into account, i.e., up to a maximum distance of $\sim$ 10 Å from the center of the adsorbate molecule. The distance from the center of the adsorbate molecule to the center of each O atom was calculated by the formula:

$$L_i = \sqrt{b_i^2 + (z_j - d_i)^2}, \tag{7}$$

where the meaning of the quantities is clear from Fig. 1. The expression for the potential of the adsorption interaction, under the assumptions made, takes the form:

$$\Phi = -C_{\text{O–M}} \sum_{i=1}^{111} L_i^{-6} + B_{\text{O–M}} \sum_{i=1}^{111} L_i^{-12} - C_{\text{K–M}} d_{\text{K–M}}^{-6} + B_{\text{K–M}} d_{\text{K–M}}^{-12} + \Phi_{\text{ind}}. \tag{8}$$

The constant $B_{\text{O–M}}$ was found from the condition of a minimum of Φ at the equilibrium distance, i.e.,

$$(\partial\Phi/\partial z_j)_{z_j = z_{j0}} = 0. \tag{9}$$

For an isolated cation-adsorbate molecule pair, the constant is:

$$B_{\text{K–M}} = \frac{1}{2} C_{\text{K–M}} d_{\text{K–M}}^6, \tag{10}$$

where the constant of dispersion attraction $C_{\text{K–M}}$ is calculated by the Kirkwood-Müller formula.

Two methods were used to calculate the geometric sums for different z_j: an exact one and one using empirical formulas. Both gave very similar results. The exact calculation was based on the fact that, according to (7), L_i is a continuous function of z_j, and therefore, when differentiating expression (8) with respect to z_j (to determine the constant $B_{\text{O–M}}$ from (9)), one can obtain an expression for the derivative as an explicit function of z_j. The second calculation method is based on the use of empirical formulas of the form:

$$\sum_{i=1}^{111} L_i^{-6} \cong 10^{-Az_j + B} \equiv a_j; \qquad \sum_{i=1}^{111} L_i^{-12} \cong 10^{-A' z_j + B'} \equiv b_j, \tag{11}$$

where the coefficients A, B, A', and B' were determined graphically in semilogarithmic coordinates, and also by the method of least squares.

The contribution of the induction component Φ_{ind} was calculated as follows. The energy Φ_{ind} is determined by the formula:

$$\Phi_{\text{ind}} = -\frac{1}{2}\alpha_M = F^2, \tag{12}$$

where F is the absolute value of the resultant vector of the electrostatic field strength at the center of the molecule. The total vector is obtained by adding the projections of each of the partial vectors onto the z-axis. The individual vectors are determined by the positions of the corresponding charges. The expression for the absolute value of the resultant vector can be written as:

$$F = v_{\text{O}} e \sum_{i=1}^{111} \frac{\cos \alpha_i}{L_i^2} + \frac{v_{\text{K}} e}{d_{\text{K-M}}^2}. \tag{13}$$

Since $\cos \alpha_i = (z_j - d_i)/L_i$, then

$$F = v_{\text{O}} e \sum_{i=1}^{111} \frac{z_j - d_i}{L_i^3} + \frac{v_{\text{K}} e}{d_{\text{K-M}}^2}, \tag{14}$$

where v_{O} and v_{K} are the charges on the O atom and on the cation, and e is the electron charge.

The sum entering into (14) can also be represented with the aid of the approximate empirical formula:

$$\sum_{i=1}^{111} \frac{z_j - d_i}{L_i^3} \cong A'' z_j^2 + B'' z_j + C'' \equiv c_j. \tag{15}$$

The coefficients can be chosen so that, in the region of z_j required for the calculation, the approximation is the best possible. Finally, for Φ_{ind} we obtain:

$$\Phi_{\text{ind}} = -\frac{1}{2}\alpha_M e^2 \left[v_0^2 c_j^2 + \frac{2 v_0 v_K}{d_{K-M}^2} c_j + \frac{v_K^2}{d_{K-M}^4} \right]. \tag{16}$$

Introducing the notation:

$$-\frac{1}{2}\alpha_M e^2 v_0^2 = K_1; \quad -\alpha_M e^2 v_0 v_K / d_{K-M}^2 = K_2; \quad -\alpha_M e^2 v_K^2 / K - M = K_3 \tag{17}$$

and taking (11) into account, for the equilibrium distance z_{j0} we obtain:

$$\Phi(z_{j0}) = -C_{O-M} a_j(z_{j0}) + \frac{A}{A'} C_{O-M} a_j(z_{j0}) + \frac{2K_1 C_j(z_{j0}) + K_2}{A' \ln 10} \times$$

$$\times \left(\frac{dc_j(z_j)}{dz_j}\right)_{z_j=z_{j0}} - \frac{1}{2}C_{K-M}d_{K-M}^{-6} + K_1c_j^2(z_{j0}) + K_2c_j(z_{j0}) + K_3. \qquad (18)$$

Using this formula, the interaction energies of the Li-, Na-, K-, Ca-, Sr- and Ba-forms of faujasite with Ne, Ar, Kr, Xe and CH_4 were calculated.

Table 2

Comparison of calculated adsorption energies with experimental heats of adsorption, kcal/mole

Adsorbate	Cationic form of zeolite	Adsorption energy	Heat of adsorption
Ar	Li X	3.44	3.3 [11]
Ar	Na X	3.04	2.8 [11]
Ar	K X	3.20	3.0 [11]
Ar	Ca X	4.73	5.0 [11]
Ar	Sr X	3.90	3.8 [11]
Ar	Ba X	3.22	3.3 [11]
Kr	Li X	4.75	3.8 *
Kr	Na X	4.42	4.4 *
Kr	K X	4.57	4.7 *
Xe	Li X	7.86	4.9–5.4 *
Xe	Na X	7.67	5.5–5.7 *
Xe	K X	7.95	5.4–5.9 *
CH_4	Na–X	4.36	4.3 [15]

* These data were kindly communicated to us by V. Bosachek.

In Table 2 the calculated energies are compared with experimental ones for those cases for which data on heats of adsorption were available. In the case of Ar and CH_4, isosteric heats extrapolated to zero coverage were taken. In the case of Kr and Xe, the isosteric heats refer to a coverage of ~ 0.2, owing to the difficulty of extrapolation. The extrapolated values of the heats given in [11] should be regarded as approximate. Thus, with the approximations made, good agreement is obtained between the calculated values and the experimental ones in all cases, except for the adsorption of Kr on LiX and the adsorption of Xe on the three cationic forms.

Moscow State University
named after M. V. Lomonosov

Received
17 IX 1964

REFERENCES

1. N. N. Avgul' , A. A. Isirikyan et al., *Izv. AN SSSR, OKhN*, 1957, 1314.
2. A. D. Crowell, R. B. Steele, *J. Chem. Phys.*, **34**, 1347 (1961).
3. S. Cross, J. P. Olivier, *Advances in Chem.*, **33**, 309 (1961).
4. J. R. Sams, *Trans. Farad. Soc.*, **60**, 149 (1964).
5. A. V. Kiselev, *ZhFKh*, **38**, 2753 (1964).
6. J. W. Orr, *Trans. Farad. Soc.*, **35**, 1247 (1939).
7. A. V. Kiselev, D. P. Poshkus, *ZhFKh*, **32**, 2824 (1958).
8. Ya. Koutecký, I. Chizhek, *ZhFKh*, **36**, 1508 (1962).
9. R. M. Barrer, S. Wasilewski, *Trans. Farad. Soc.*, **57**, 1140 (1961).
10. R. M. Barrer, G. C. Bratt, *J. Phys. Chem. Solids*, **12**, 130, 146, 154 (1959).
11. R. M. Barrer, W. S. Stuart, *Proc. Roy. Soc.*, A **249**, 464 (1959).
12. R. M. Barrer, R. M. Gibbons, *Trans. Farad. Soc.*, **59**, 2569 (1963).
13. J. Hirschfelder, C. Curtiss, R. Bird, *Molecular Theory of Gases and Liquids*, IL, 1961.
14. A. V. Kiselev, A. A. Lopatkin, *Kinetika i kataliz*, **4**, 786 (1963).
15. R. M. Barrer, J. M. Sutherland, *Proc. Roy. Soc.*, A **237**, 1211 (1956).

Note: Figure translations are in progress. See original paper for figures.