

CHROMSYMP. 221

THEORETICAL AND EXPERIMENTAL STUDY OF THE SORPTION PROCESSES OF GASES ON NaY ZEOLITES

S. MIERTUŠ*

Department of Analytical Chemistry, Slovak Technical University, Jánska 1, 812 37 Bratislava (Czechoslovakia)

and

J. MIERTUŠOVÁ

Department of Experimental Physics, Comenius University, Mlynská dolina F II, 841 25 Bratislava (Czechoslovakia)

SUMMARY

Elementary processes involved in the sorption of gaseous N₂, CO, CO₂, H₂O, CH₄, C₃H₈, *n*-C₄H₁₀, iso-C₄H₁₀, C₂H₄ and C₆H₆ molecules on the surface of zeolite NaY were studied. A theoretical approach based on the method of empirical potentials and experimental determinations of the sorption energies by thermal desorption spectroscopy were used. The calculated sorption energies were compared with isosteric heats of sorption determined by gas chromatography. The nature of the interaction forces can be clearly seen from the profile of the individual energy components during sorption.

INTRODUCTION

Zeolites (molecular sieves) are hetero-ionic adsorption materials widely used in gas chromatography (GC). From the theoretical point of view it is necessary to study the nature of the elementary sorption processes, to determine the stablest positions of sorbed molecules on the surface and to obtain the energy profile along the sorption path. These values can be used to acquire a deeper understanding of the sorption and separation processes.

Theoretical studies of the sorption processes on zeolites are in their infancy. Bezus and co-workers have calculated the interaction energies between NaX zeolites and molecules of rare gases¹, some polar molecules² and selected alkanes³. There have also been attempts to use quantum chemical methods for such approaches⁴.

In this work we studied the sorption processes of N₂, CO, CO₂, H₂O, CH₄, C₃H₈, *n*-C₄H₁₀, iso-C₄H₁₀, C₂H₄ and C₆H₆ with the surface of NaY zeolites by the method of empirical potentials. The theoretical results are compared with the sorption energies determined by thermal desorption spectroscopy and with isosteric heats of sorption determined by GC.

THEORETICAL

The total energy of interaction (sorption energy) can be approximately expressed as a sum of individual contributions of dispersion, repulsion, coulombic (electrostatic) and inductive forces:

$$E = E_D + E_R + E_C + E_I \quad (1)$$

The dispersion term is expressed as⁵

$$E_D = -\sum_i \sum_j C_{ij} r_{ij}^{-6} \quad (2)$$

where C_{ij} is the Kirkwood-Müller constant of dispersion attraction and r_{ij} is the distance between an atom of the sorbent i and an atom of a gas molecule j .

The repulsion term is⁵

$$E_R = \sum_i \sum_j B_{ij} r_{ij}^{-12} \quad (3)$$

The constant B_{ij} is determined by the condition of minimum non-bonded interaction.

The electrostatic part of the sorption energy, E_C , corresponds to interactions between charges distributed on the atoms of zeolites and the charge distribution of sorbed molecules. In this work, for polar molecules we have used the term

$$E_C = \frac{1}{4\pi\epsilon_0} \sum_i \sum_j \frac{q_i q_j}{r_{ij}} \quad (4)$$

where ϵ_0 is the permittivity of a vacuum and q_i and q_j are charges of atoms representing the surface and the gas molecule, respectively.

If the sorbed gas molecule has a permanent quadrupole moment, the electrostatic part of the interaction can be expressed as

$$E_C = \frac{1}{16\pi\epsilon_0} \sum_i \sum_j q_i \theta_j (3 \cos^2 \varphi - 1) r_{ij}^{-3} \quad (5)$$

where the angle φ corresponds to orientation of the quadrupole θ of a molecule *versus* a position vector r_{ij} .

The inductive part of interaction energy is expressed as

$$E_I = \sum_j \frac{\alpha_j}{2} \cdot \epsilon_j^2(r) \quad (6)$$

where α_j is the polarizability of atom j of the gas molecule and $\epsilon_j(r)$ is the intensity of the electrostatic field which creates charges on the atoms in the zeolite. All constants used in eqns. 2-6 are taken from ref. 6.

EXPERIMENTAL

Experimental values of the sorption energy (E_{ads}) were determined by thermal desorption spectroscopy⁷. NaY molecular sieves were placed in a pumped vacuum system and successively heated from the temperature of liquid nitrogen to room temperature. From the desorption spectrum, *i.e.*, the dependence of pressure changes on the temperature of the surface, activation energies of desorption were evaluated. In cases of physical adsorption the activation energy of sorption is equal to the sorption energy.

Isosteric heats of sorption, Q_{is} , of some gases determined by GC were taken from the literature⁸.

RESULTS AND DISCUSSION

The surface of NaY zeolites is represented by ten cubo-octahedrons surrounding a large cavity of zeolite (Fig. 1). Each cubo-octahedron contains 48 atoms of oxygen with negative charges and 14 atoms of sodium with positive charges. A total of 620 atoms of oxygen and sodium were considered. The effect of Al and Si is included in the effective charge on O and Na.

To calculate interaction (sorption) energies, two computer programs were used. Program I finds the stablest position of a gas molecule in the large cavity of the zeolite. This position corresponds to the minimum of an interaction energy curve.

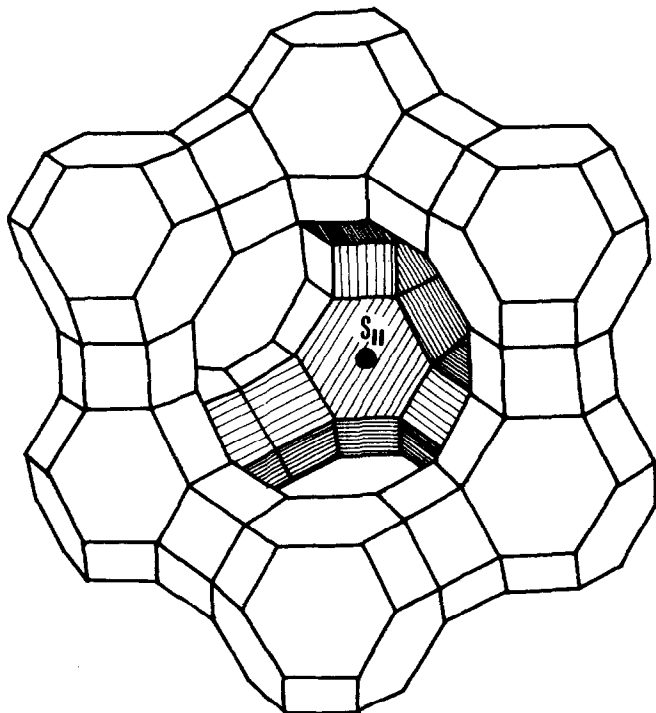


Fig. 1. Model of NaY zeolite.

TABLE I
CALCULATED AND EXPERIMENTAL VALUES OF SORPTION ENERGIES

Molecule	Experimental (kJ mol^{-1})		Calculated (kJ mol^{-1})	
	Q_{is} (GC)	E_{ids}	Program I	Program II
N_2		29.4	23.6	20.2
CO	24.3	31.2	25.6	21.8
CO_2		53.2	48.4	39.5
H_2O		87.4	83.2	81.2
CH_4	18.4		18.8	18.1
C_3H_8	34.1	36.4	33.9	30.3
$n\text{-C}_4\text{H}_{10}$		50.9	48.9	47.5
$\text{iso-C}_4\text{H}_{10}$		65.5	64.2	61.1
C_2H_4	45.7	43.6	40.6	38.5
C_6H_6		88.6	90.2	86.4

Program II calculates the energy of sorption along a three-fold symmetry axis passing through a large cavity window towards the sorption centre S_{II} . The curve of the total interaction energy is the sum of the curves of the dispersion, repulsion, electrostatic and inductive energy components.

The calculated values of the sorption energies of individual gases evaluated by programs I and II are given in Table I, and are compared with experimental values. A qualitative agreement is obtained between the energies E_{ids} and those calculated by program I. The values obtained by program II are generally lower than those obtained by program I. Program I optimizes the position of a sorbed molecule in all

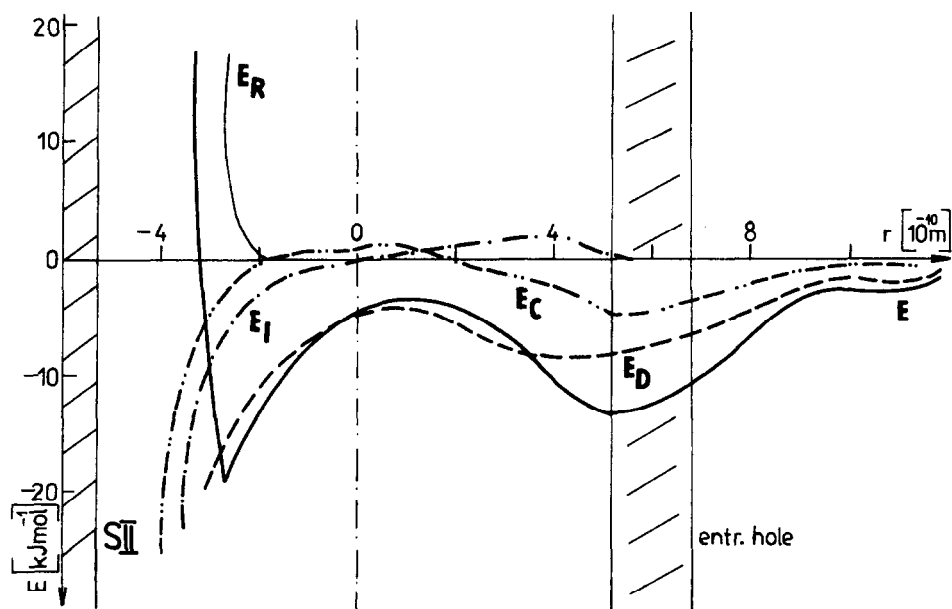


Fig. 2. Curves of the individual energy terms during adsorption of an N_2 molecule.

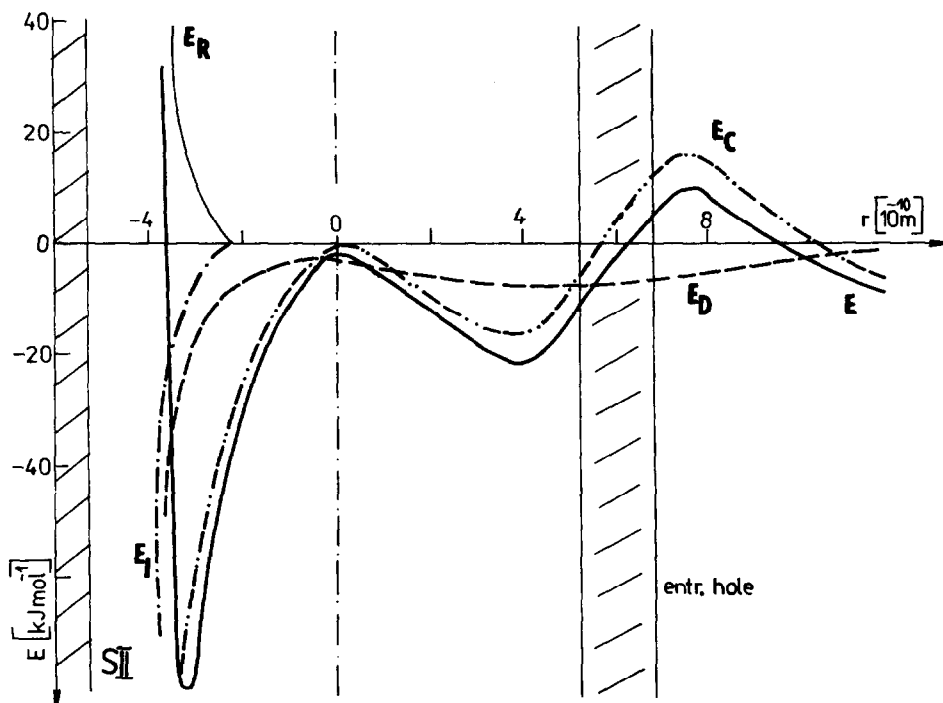


Fig. 3. Curves of the individual energy terms during adsorption of an H_2O molecule.

the space of the large cavity of the zeolite, whereas the values obtained by program II correspond to minima near to sorption centre S_{II} . Although in most instances calculated optimal positions of sorbed molecules are close to the centre S_{II} , the difference between energies calculated by the two programs are small. Values of isosteric heats of sorption Q_{is} , determined by GC are not known for all the gases considered on the NaY zeolites. It should be stressed that a direct comparison with calculated values is possible if the value RT (2.4 kJ mol^{-1} at $300 \text{ }^\circ\text{K}$) is subtracted from Q_{is} .

The nature of the interaction forces acting in sorption and separation processes can be clearly seen from the calculated energy profile. For non-polar molecules (N_2 , CO_2 , alkanes, etc.) the sorption process is governed by the dispersion component of the interaction energy. Fig. 2 shows energy profiles of adsorption of N_2 on NaY zeolites. For slightly polar molecules the coulombic component contributes to total stabilization. For polar molecules such as H_2O the coulombic component is dominant (Fig. 3). The induction component is important, especially for larger molecules such as C_6H_6 (Fig. 4).

The theoretical values obtained by this approach can be used for the calculation of other thermodynamic quantities (H , S , Henry's constant, etc.)¹. This method also enables the model of the surface of zeolites to be modified and necessary changes in the surface to be predicted in order to obtain desirable sorption and separation properties. We shall consider these problems in subsequent papers.

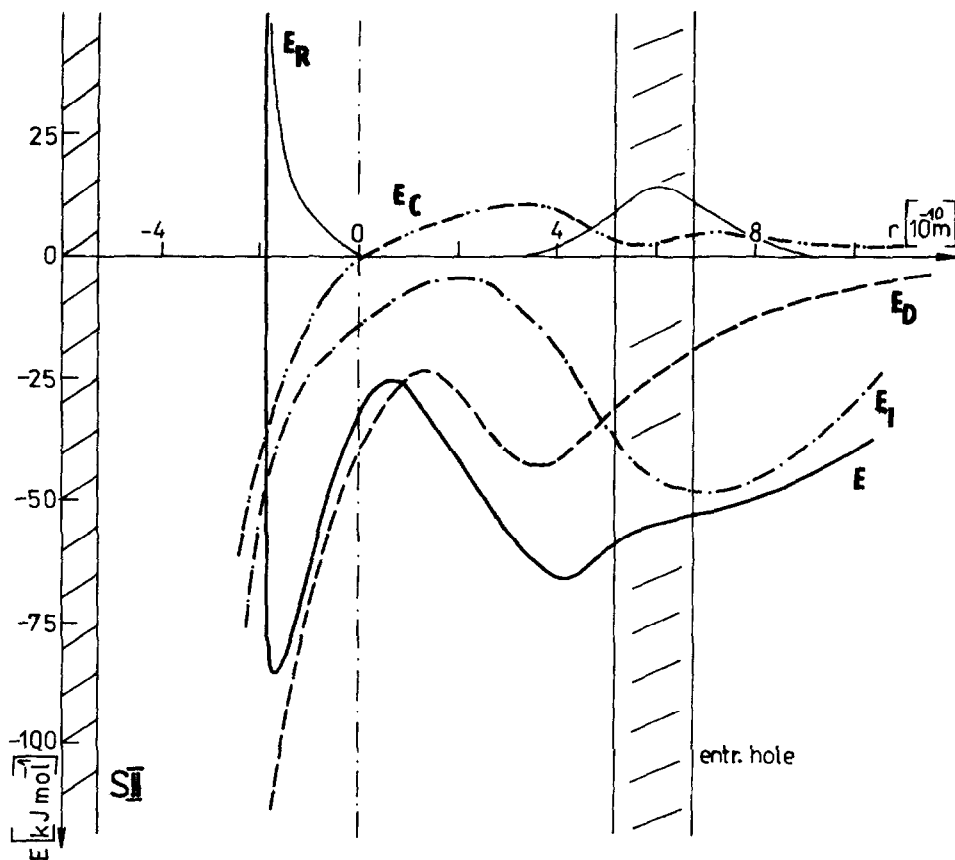


Fig. 4. Curves of the individual energy terms during adsorption of a C_6H_6 molecule.

ACKNOWLEDGEMENT

We are indebted to Dr. A. G. Bezus of the Institute of Physical Chemistry, Prague, For providing computer program I.

REFERENCES

- 1 A. G. Bezus and C. E. Dobrova, *Kolloidn. Zh.*, 37 (1975) 1045.
- 2 A. G. Bezus, A. V. Kiselev and Fam Kuang Zy, *Dokl. Akad. Nauk SSSR*, 237 (1977) 126.
- 3 A. G. Bezus and M. Kočířik, *Adsorption of Hydrocarbons in Zeolites*, Akademie Verlag, Berlin, 1979, p. 56.
- 4 J. Sauer, P. Hobza and R. Zahradník, *J. Phys. Chem.*, in press.
- 5 M. Born and J. E. Mayer, *Z. Phys.*, 75 (1932) 1.
- 6 J. Miertušová, *Thesis*, Comenius University, Bratislava, 1981.
- 7 G. Carter, *Vacuum*, 12 (1962) 245.
- 8 V. Patzelová, *Chem. Zvesti*, 29 (1975) 331.