

# Importance of adsorption kinetics in the separation of N<sub>2</sub> and O<sub>2</sub> on NaA zeolite\*

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In the study of processes which influence the separation efficiency of adsorbents it was proved that the kinetics of adsorption of O<sub>2</sub> and N<sub>2</sub> on NaA zeolite under chromatographic conditions is rather slow.

При изучении процессов, которые влияют на сепарационное действие адсорбентов, было доказано, что адсорбция O<sub>2</sub> и N<sub>2</sub> на NaA цеолите при хроматографических условиях происходит довольно медленно.

From the theory of the equilibrium gas chromatography it follows that in the case of a linear adsorption isotherm the ratio of the retention volumes  $V_R$  of two different gases should be equal to the ratio of the equilibrium constants of adsorption  $K_a$ . This relation may be expressed in the well known form [1]

$$\frac{V_{\text{corrA}}}{V_{\text{corrB}}} = \frac{K_{\text{aA}}}{K_{\text{aB}}} \quad (1)$$

The corrected retention volume  $V_{\text{corr}} = V_{\text{ad}} - V_{\text{H}_2}$ , where  $V_{\text{ad}}$  is the retention volume of adsorbed gas and  $V_{\text{H}_2}$  that of the nonadsorbed gas (hydrogen). The validity of this relation is simultaneously the basic condition for determination of adsorption heats by the chromatographic method [2].

Many authors apply erroneously this relation even in cases of the nonequilibrium dynamics of adsorption [3]. The statistical moments theory of gas chromatography of *Kuera* and *Grubner* [4] also assumes that the position of the centre of gravity of the chromatographic peak which determines the so-called first statistical moment,  $\mu_1$ , does not depend on the kinetic coefficients and consequently on the adsorption kinetics in the chromatographic column.

On the other hand, *Habgood* [5] found that the gas chromatographic retention volumes of O<sub>2</sub> and N<sub>2</sub> agree with the isotherms in the case of zeolite NaX but are significantly lower for AgX. In the present study it was found that the above-mentioned assumptions are not fulfilled for O<sub>2</sub> and N<sub>2</sub> on zeolite NaA either.

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## Experimental

For the gas chromatographic measurements zeolite NaA in pellets was used. This probe prepared in 1963 by V. Y. Nikolinoi (USSR) contains 32.40% SiO<sub>2</sub>, 30.19% Al<sub>2</sub>O<sub>3</sub>, 15.00% Na<sub>2</sub>O, and 22.10% H<sub>2</sub>O.

The gas chromatographic measurements were carried out using a glass column 40 cm long, 5 mm in diameter. The gas sample volume was 0.6 ml. The gas flow rate was 40 ml/min and the retention volumes could be reproduced within  $\pm 1$  ml. The column was activated by heating in flowing helium up to 400°C. As a carrier gas helium was used. The adsorption isotherms measured on this probe gravimetrically by *Arkharov, Bering, Kalinikova, and Serpinski* [6] were used. A table of the experimental data was made available to the authors through the cooperation among the Institutes of Physical Chemistry of the Academies of Sciences of the USSR, GDR and ČSSR.

## Results and discussion

The equilibrium constants of adsorption  $K_a$  were calculated from the adsorption isotherms in low pressure (Henry coverage) region, where the isotherms are linear. This corresponds to the maximal adsorption amount of 0.19 mmole for N<sub>2</sub> and 0.15 mmole for O<sub>2</sub> and maximal pressure of 1 torr at 20°C in both cases. The values of  $K_a = a/p$ , where  $a$  is the adsorbed amount in mmole/g and  $p$  pressure in torr, their ratio and the retention volumes  $V_{ad}$  for O<sub>2</sub> and N<sub>2</sub> on NaA are presented in Table 1.

In the case of an ideal equilibrium chromatography, the separation factor N<sub>2</sub>—O<sub>2</sub> should equal 3 (as follows from Table 1). However, the experimental values of the retention times  $V_{ad}$  of oxygen and nitrogen are equal and do not differ from that of H<sub>2</sub>, which is only weakly adsorbed and was employed for the measurement of the column dead volume. Under the same experimental conditions and the same length of the chromatographic column filled up by zeolite LiX the retention volumes  $V_{ad}$  at 0°C are 12.0, 22.95, and 33.64 cm<sup>3</sup>, respectively.

This result can be explained in the following way: With some systems, especially those with very narrow entrances into pores, a dominant role is played by diffusion kinetics which prevents instantaneous equilibrium establishment. When, on the other hand, substances have sufficiently wide pores, equilibrium is established rela-

Table 1

Equilibrium constants of adsorption  $K_a$  and retention volumes  $V_{ad}$  of N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> on zeolite NaA at 20°C

Adsorbate	$K_a \cdot 10^4$ mmol/g torr	$V_{ad}$ cm <sup>3</sup>
N <sub>2</sub>	5.180	12.0
O <sub>2</sub>	1.713	12.0
H <sub>2</sub>	—	12.0

tively rapidly, in an ideal case almost instantaneously. Here the experimental data agree with the eqn (1). This is the case of argone and krypton on zeolites LiX and KX, as evident from the data presented by Bosáček [7]. Hence, generally it is impossible to assess unambiguously the magnitude of retention times and consequently also the separation factors from the shape of the adsorption isotherms only unless the effect of diffusion kinetics is known.

For the above reasons the applications of the statistical method of gas chromatography and the determination of adsorption heats by the method of gas chromatography on microporous adsorbents cannot be considered as reliable.

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