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# Evaluation of Thermodynamic Data of Adsorption of Carbon Dioxide on NaA, NaX and NaY Zeolites

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Adsorption isotherms of carbon dioxide on NaX and NaY zeolites were measured at 288 K and 298 K and isosteric heat and differential entropy of adsorption were determined. The equilibrium adsorption data were analyzed by means of the theory of volume filling of micropores.

The degree of heterogeneity of the adsorption centres in the zeolites was estimated from the differential distribution of the degree of volume filling of pores with respect to the differential molar work of adsorption. This distribution was determined from the Dubinin-Astakhov equation. Heterogeneity of the adsorption centres is considered in terms of the distribution of sodium ions over various sites in the lattice of zeolites.

The nature of the adsorption interaction is discussed in reference to the isosteric heat and the differential entropy of adsorption.

## INTRODUCTION

The distribution of positive charge on the exchangeable cations and negative charge over the oxygen framework of the zeolites causes a heterogeneous electrostatic field inside each unit cell. This charge distribution leads to specific and nonspecific interactions of the adsorbate molecules with the adsorption centres of zeolites. The Heterogeneity of adsorbate/zeolite interaction is changed as a result of the different sites on which the exchangeable cations are located.

A great number have papers published dealt with the adsorption characteristic of zeolites, but there is less evidence for the degree of heterogeneity of the adsorption centres considered in terms of the adsorption interaction and expressed as a comparable value. The present paper reports an attempt to determine the degree of heterogeneity of the adsorption centres in the NaA, NaX and NaY zeolites. For this purpose, the equilibrium and thermodynamic adsorption data of carbon dioxide have been analyzed. The degree of heterogeneity was estimated from the differential distribution of the degree of volume filling of adsorption space with respect to differential molar work of adsorption. This distribution was determined by means of the Dubinin-Astakhov equation. The nature of the adsorption interaction is considered in terms of the isosteric heat and differential entropy of adsorption.

Carbon dioxide as adsorbate is suitable for characterization of zeolites by the adsorption method because of its large quadrupole moment and relatively large polarizability.

## THEORETICAL PART

The theory of volume filling of micropores, developed by Dubinin and co-workers,[1-4] is a widely used theory for adsorption of gases on microporous adsorbents. The basic equation of the theory of adsorption in micropores, i.e. the theory of volume filling of micropores is the Dubinin-Astakhov equation, expressed in the form

$$W/W_0 = \exp[-(a/\beta E_0)^n] \tag{1}$$

In the equation, $W$ is the volume of pores filled with adsorbate at temperature $T$ and relative pressure $P/P_0$, $W_0$ is the micropore volume, $E_0$ is the characteristic adsorption energy which with $n$ presents equation parameters on the system under investigation, $\beta$ is the affinity coefficient characterizing the adsorbate, and $A$ denotes the differential molar work of adsorption, i.e. the differential free energy of adsorption, $\Delta G$ taken with a minus sign, expressed by the relation

$$A = -\Delta G = RT\ln(P_o/P) \tag{2}$$

Burevski[5,6] has shown that useful information on the nature of adsorption interaction can be provided from the differential distribution of the adsorption with the differential molar work of adsorption. The function which represents the differential distribution of the degree of volume filling micropores, $\theta$ ($\theta = W/W_0$), with respect to the differential molar work of adsorption, $A$, can be obtained from the first derivative of the Dubinin-Astakhov equation, giving

$$\frac{d\theta}{dA} = -\frac{nA^{n-1}}{(\beta E_0)^n}\exp[-(A/\beta E_0)^n] \tag{3}$$

The mean value of differential molar work of adsorption, $A_{mean}$, can be obtained from the expression

$$A_{\text{mean}} = \frac{\int_{0}^{W_0} A\, dW}{W_0} = \int_{0}^{1} A\, d\theta \qquad (4)$$

The substitution of $d\theta$ from expression (3) in the expression (4) gives

$$A_{\text{mean}} = \int_{o}^{\infty} \frac{nA^n}{(\beta E_0)^n} \exp[-(A/\beta E_0)^n]\, dA \qquad (5)$$

hence,

$$A_{\text{mean}} = betaE_0\, \Gamma\, (\frac{1}{n} + 1) \qquad (6)$$

where $\Gamma$ is gamma function.

## EXPERIMENTAL

The zeolite samples were supplied by the VEB Chemiekombinat, Bitterfeld, and had the following composition[7]:

NaA: 0.918 $Na_2O$ $Al_2O_3$ 1.884 $SiO_2$

NaX: 0.957 $Na_2O$ $Al_2O_3$ 2.486 $SiO_2$

NaY: 0.991 $Na_2O$ $Al_2O_3$ 5.033 $SiO_2$

Prior to adsorption experiments, the samples were treated by heating for 5 h at 723 K. The adsorption measurements were carried out by the flow method. The adsorption of carbon dioxide is performed from stream of gas mixture, where nitrogen is used as carrier gas. The partial pressure of carbon dioxide in the gas mixture is calculated from the flow values of the gases. The amount of adsorption is measured gravimetrically. The measured error is less than 3%.

## RESULTS AND DISCUSSION

The adsorption isotherms of carbon dioxide were interpreted by the Dubinin-Astakhov equation expressed in the linear form

$$\ln W = \ln W_0 - \frac{1}{E_0^n} (A/\beta)^n \qquad (7)$$

The Dubinin-Astakhov plots for adsorption of carbon dioxide at 288 K are presented in Figure 1.

The least-squares method was employed to select the n value which gave the best agreement between the experimental adsorption data and theoretical isotherms. There is a very good fit of the experimental data to the Dubinin-Astakhov equation. The difference between the experimental values and the values calculated from the Dubinin-Astakhov equation is within the limits of experimental error. The regression coefficients are not less than 0.9993 for the $P/P_o$ range from 0.0023 to 0.0167. The Equation parametres, n and $E_o$, are given in Table I.

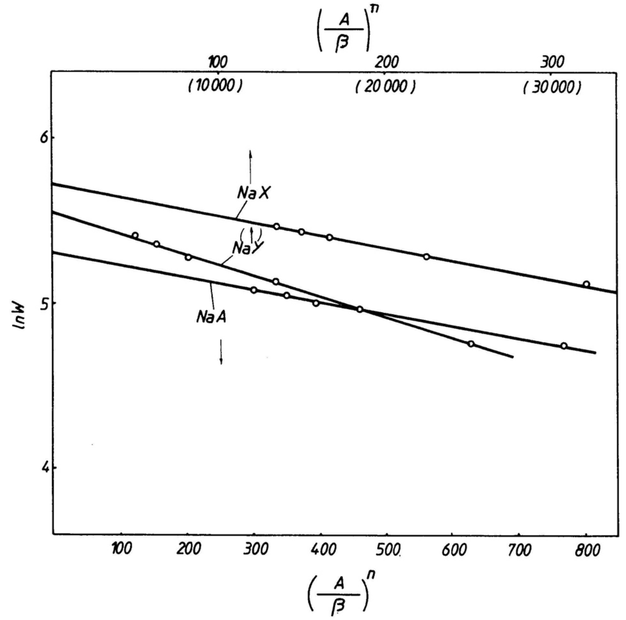

Figure 1. Dubinin-Astakhov plots for adsorption of carbon dioxide at 288 K (W in $cm^3kg^{-1}$, A in kJ $mol^{-1}$)

Considering the fact that the free energy of adsorption, $\Delta G$ is a measure of the affinity of adsorbent for the adsorbate molecules, the differential distribution of the degree of volume filling, $\theta$, with respect to the differential molar work of adsorption, $A$, ($A = -\Delta G$) is concerned with the degree of heterogeneity of the adsorption interaction. It has been shown that this distribution depends on pore distribution[5,8] and surface heterogeneity[6]. For synthetic zeolites, the differential distribution of $\theta$ with $A$ is determined by the porous structure and the nature of adsorption centres. However, for zeolites with similar porous structure, like zeolites NaX and NaY (the dimensions of their large cavities and the openings to the cavities are the same), this distribution can provide quantitative information on the heterogeneity of adsorption centres considered with respect to different affinities for the adsorbate molecules. The differential distribution curves of $\theta$ with $A$, determined from equation (3), are illustrated in Figure 2.

Figure 2 shows that for zeolites NaA and NaX the distribution of $\theta$ with $A$ is wider than for zeolite NaY. This indicates a higher degree of heterogeneity of the adsorption centres contained in the NaA and NaX zeolites. The heterogeneity of the adsorption centres depends mainly on the distribution of exchangeable cations over various sites in the zeolite lattice. Namely, in zeolite NaX the sodium ions, accessible to the carbon dioxide molecules, are located in sites $S_{IIIII}$, whereas in zeolite NaY they are located in site $S_{II}$ only.[9-11] An additional element for a higher degree of heterogeneous interaction in the case of zeolite NaA are the sodium ions located in 8-membered oxygen rings (site $S_{II}$). This oxygen ring is smaller (0.42 nm) than the 12-membered oxygen ring in zeolites NaX and NaY (0.74 nm), which causes a stronger interaction between the carbon dioxide molecules and the cationic adsorption centres ($S_{II}$). The different

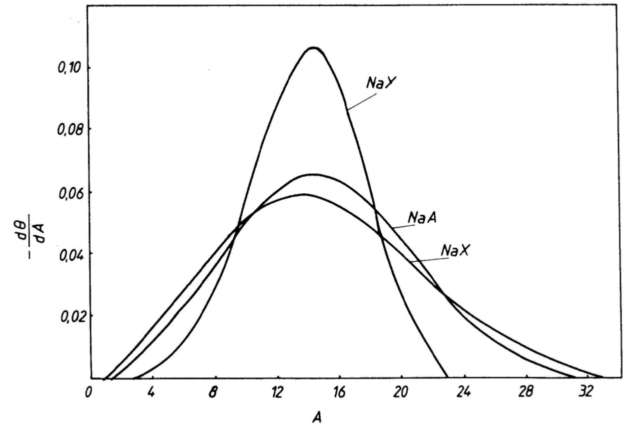

Figure 2. Differential distribution curves of $\theta$ with A (A in kJ mol$^{-1}$)

TABLE I

*Equation parameters n and $E_0$, and the mean values of differentialm olar work of adsorption, $A_{mean}$,*

| Zeolite | $n$ | $E_0$<br>kJ mol $^{-1}$ | $A_{mean}$<br>kJ mol -1 |
|---|---|---|---|
| NaA | 2.9 | 12.27 | 15.05 |
| NaX | 2.5 | 12.33 | 15.04 |
| NaY | 4.3 | 11.14 | 13.95 |

degree of heterogeneity of the adsorption centres, as determined from the differential distribution of $\theta$ with $A$, is attributed to the fact that the sodium ions, located in various sites, have different affinities for the adsorbate molecules.

The mean values of differential molar work of adsorption, $A_{mean}$, calculated from expression (6) are recorded in Table I.

The $A_{mean}$ value is a measure of the average affinity of adsorption centres for the adsorbate molecules, thus being in correlation with the adsorption interaction energy.

The isosteric heat of adsorption of carbon dioxide was determined from the adsorption isotherms obtained at 288 K and 298 K. The error of calculation of the isosteric heat of adsorption from the adsorption isotherms is less than 5%. The dependence of isosteric heats, $q_{st}$, on the molecules of carbon dioxide adsorbed per unit cell of zeolites, $n^s$, is shown in Figure 3.

The relatively high values of isosteric heat of adsorption is mainly due to the specific interaction of the carbon dioxide molecules with the cationic adsorption centres. The lower values of the isosteric heat of adsorption on zeolite NaY are attributed to the following Fact: The sodium ions located in site $S_{II}$ are more firmly bound to the zeolite lattice than the ions located in site $S_{III}$ (zeolite NaX). As the interaction energy of adsorbed molecules with the cationic adsorption centres is in inverse correlation

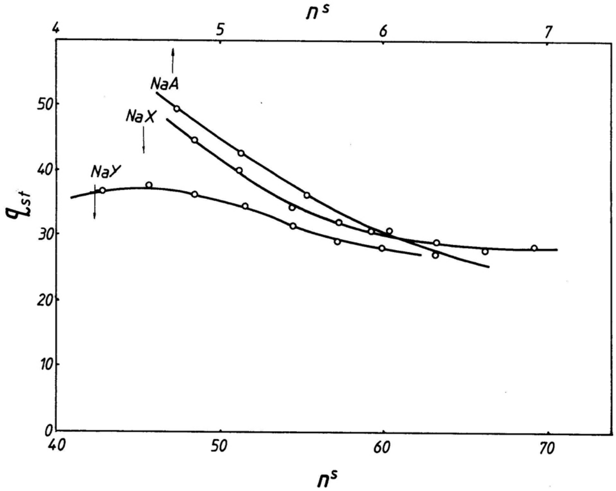

Figure 3. Isosteric heat of adsorption of carbon dioxide in dependence on molecules adsorbed per unit cell ($q_{st}$ in kJ mol$^{-1}$)

with the strength of bonding of the cations in the zeolite lattice, a smaller amount of heat is evolved by adsorption on zeolite NaY.

The state of adsorbed phase is characterized by the differential entropy of adsorption. The values of differential entropy of adsorption, $\Delta S$, of carbon dioxide have been determined from the isosteric heat of adsorption and the equilibrium adsorption data using the equation

$$\Delta S = -g_{\mathrm{st}}/T - R\ln(P/P^0) \tag{8}$$

where $P^{\mathrm{o}}$ is standard pressure. The entropy values are listed in Table II

The values of translational entropy of carbon dioxide in the ideal gas state, ${}_{\mathrm{g}}S_{\mathrm{tr}}$, and in the ideal two-dimensional gas, ${}_{\mathrm{a}}S_{\mathrm{tr}}$, both in standard state, were calculated to be 155.7 J mol$^{-1}$K$^{-1}$ and 106.1 J mol$^{-1}$K$^{-1}$, respectively. A comparison of the $-\Delta S$ values with the ${}_{\mathrm{g}}S_{\mathrm{tr}}$ and ${}_{\mathrm{a}}S_{\mathrm{te}}$ values and with their difference (${}_{\mathrm{g}}S_{\mathrm{tr}} - {}_{\mathrm{a}}S_{\mathrm{tr}} - 49.6$ J mol$^{-1}$K$^{-1}$) shows that the carbon dioxide molecules in the adsorbed phase are in a state of re-

TABLE II

*Differential entropy of adsorption, $-\Delta S$ (J mol$^{-1}$K$^{-1}$) of carbon dioxide*

| NaA | | NaX | | NaY | |
|---|---|---|---|---|---|
| $n^s$ | $-\Delta S$ | $n^s$ | $-\Delta S$ | $n^s$ | $-\Delta S$ |
| 4.8 | 156.4 | 48 | 136.3 | 43 | 113.1 |
| 5.1 | 135.4 | 51 | 122.7 | 46 | 116.7 |
| 5.5 | 115.5 | 54 | 106.2 | 49 | 115.3 |
| 5.9 | 99.7 | 60 | 97.0 | 54 | 102.2 |
| 6.3 | 87.6 | 69 | 93.5 | 60 | 92.3 |

stricted translational freedom of motion. The molecules adsorbed on zeolites NaA and NaX at lower $n^s$ values are more reduced freedom owing to the stronger interaction.

In summary, it can be said that the differential distribution of $\theta$ with $A$ gives information on the degree of heterogeneity of the adsorption centres considered in terms of their affinity for the adsorbate molecules. The finding of the nature of adsorption interaction, obtained from the isosteric heat and the differential entropy of adsorption, confirms the result achieved by this distribution.

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## IZVOD

### Određivanje termodinamičkih vrednosti za adsorpciju ugljik-dioksida na zeolite NaA, NaX I NaY

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Izmjerene su adsorpcijske izoterme ugljik-dioksida na temperaturi od 288 K i 298 K na zeolitima NaA, NaX i NaY te su određene izosterna toplina i diferencijalna entropija adsorpcije. Ravnotežni adsorpcijski podaci analizirani su pomoću teorije volumnog popunjavanja mikropora.

Stupanj heterogenosti adsorpcijskih centara u zeolitima određen je iz diferencijalne distribucije stupnja popunjavanja volumena pora u odnosu na diferencijalni molarni rad adsorpcije. Ova distribucija je određena jednadžbom Dubinin-Astakhova. Heterogenost adsorpcijskih centara promatrana je s obzirom na distribuciju natrijevih iona u strukturi zeolita.

Priroda adsorpcijskog uzajamnog djelovanja diskutirana je s obzirom na izosterne topline i diferencijalne entropije adsorpcije.