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Sorption of *n*-hexane in cation-exchanged Y zeolites: chemical affinities and entropies

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Abstract

The free energies (affinities) and entropies of sorption of *n*-hexane on zeolites of the M_xNa_{56-2x} type (M = Co, Ni, Zn, Cd) were determined from their isosteric sorption heats. From the derived values, the influence of the exchanged cations was analysed and discussed.

INTRODUCTION

Although the sorption of *n*-hexane on synthetic faujasite-type zeolites [1–3] has been extensively investigated, there are practically no data on the sorption behaviour of X and Y zeolites in which the sodium ions are replaced by divalent transition metal cations. In one of our recently published papers [4], the sorption isotherms of *n*-hexane on some highly exchanged X and Y zeolites of the types $M_xNa_{87-2x}X$ and $M_xNa_{56-2x}Y$ (M = Co, Ni, Zn, Cd) were presented and interpreted using the Dubinin–Radishkevich equation. The isosteric sorption heats were also determined in $M_xNa_{87-2x}X$ (M = Co, Ni, Zn, Cd) and presented as a function of the coverage of the surface area of the zeolites [5].

In the present paper, an attempts was made to investigate thermodynamically the nature and strength of the sorbent–sorbate (Y zeolite–*n*-hexane) bond. The isosteric heats of sorption of *n*-hexane in NaY zeolite, where the Na^+ ion was exchanged with cations of transition metals (Co, Ni, Zn, Cd) [6], were used to calculate their free energies (affinities, $-\Delta\mu$) and sorption entropies. The influence of the exchanged cations on the derived values for the thermodynamic properties of free energy and entropy, were analysed.

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EXPERIMENTAL

The experimental procedure for determining isosteric heats of sorption of *n*-hexane on Y zeolites has been described elsewhere [4], together with the method and materials used. The compositions of unit cells of cation-exchanged zeolites are given in Table 1.

RESULTS AND DISCUSSION

A decrease in the chemical affinity $-\Delta\mu$ takes place when a gas is reversibly and isothermally transferred from the gas phase at standard pressure p_0 into an infinitesimally small amount of the sorbent-sorbate mixture, above which the pressure is p. This decrease represents a quantitative measure of the affinity of the sorbate towards the sorbent. Neglecting the non-ideal behaviour of the sorbate, the chemical affinity can be expressed through the equation

$$\Delta\mu = RT \ln(p/p_0) \tag{1}$$

The calculated affinities (chemical potentials), $-\Delta\mu$, at two temperatures (288 and 298 K) for all exchanged Y zeolites are shown in Fig. 1 as a function of the surface coverage θ. It can be observed that the sorption affinities are different for different cation forms of the investigated zeolites, and that they decrease with increasing coverage. This behaviour suggests that the exchanged cations have a pronounced influence on the process of sorption of *n*-hexane on the zeolites. The order of affinity for *n*-hexane at 298 K is as follows:

for $\theta < 1$, NiY = NaY > ZnY > CoY > CdY
for $\theta = 1$, NiY = NaY > ZnY > CoY > CdY
for $\theta = 2$, NiY > ZnY > CoY > NaY > CdY
for $\theta = 3$, NiY > CoY > NaY
for $\theta = 4$, NiY > CoY > NaY

The sorption of *n*-hexane on Y zeolites was analysed only up to the value of their sorption capacities [7]. It has been calculated and confirmed

TABLE 1

Unit cell composition and percentage sodium exchange of zeolites

Symbol	Unit cell composition	Na exchange (%)
NaY	$Na_{56}(AlO_2)_{56}(SiO_2)_{136}$	-
CoY	$Na_{16}Co_{20}(AlO_2)_{56}(SiO_2)_{136}$	67.68
NiY	$Na_{11}Ni_{22}H(AlO_2)_{56}(SiO_2)_{136}$	79.71
ZnY	$Na_{15}Zn_{20}(AlO_2)_{56}(SiO_2)_{136}$	73.41
CdY	$Na_{13}Cd_{21}H(AlO_2)_{56}(SiO_2)_{136}$	76.59

experimentally that one α-cage can accept a maximum of four n-hexane molecules [8].

At every coverage, θ, n-hexane shows the highest affinity for NiY. The results of the chemical analysis of the investigated zeolites (Table 1) show that the extent of exchange of Na^+ ion in the NiY zeolite is the greatest over the whole range of coverage. Accordingly, the effects which are attributed to the cation density in the α-cages are certainly the cause of such behaviour of the NiY zeolite. The smallest affinity for n-hexane was found for CdY. This suggests that the size of the Cd^{2+} cation generates a lower electrostatic field in the α-cages, i.e. it lessens the strength of cation–sorbate interaction. It is observable that the CdY and NaY affinities decrease rapidly with increasing coverage.

ZnY and CoY have lower affinity values, $-\Delta\mu$, for n-hexane than NaY at coverage $\theta \leq 1$. This is probably due to the change in the sites of cations Zn^{2+} and Co^{2+} with migration after dehydration, such that their positions in the lattice are shielded for sorbate molecules [9]. At the same time, the influence of their electrostatic fields in the α-cages is reduced. The consequence of this is that admolecules interact more readily with the residual Na^+ ions in the α-cages than with Co^{2+} and Zn^{2+}. With increasing coverage ($1 < \theta \leqslant 4$), the affinity of n-hexane becomes higher towards CoY and ZnY than towards NaY.

The order of affinity of the investigated zeolites for n-hexane at 288 K remains almost unchanged. NiY shows the highest, and CdY the lowest affinity for n-hexane molecules.

To calculate the sorption entropy changes, $\Delta S^{\ominus}$, of n-hexane with different cation forms of the Y zeolites, the following expression was used:

$$\Delta S^{\ominus} = R \ln(p^{\ominus}/p) + \Delta H^{\ominus}/T \tag{2}$$

where $p^{\ominus}$ is the standard pressure (1 atm = 101.325 kPa), p is the equilibrium pressure at temperature T, at which the isotherm was obtained and $\Delta H^{\ominus}$ is the standard enthalpy change in the process of sorption. For isothermal conditions, neglecting gas imperfections, $\Delta H^{\ominus} = \Delta H$. The enthalpy changes ΔH, i.e. the isosteric heats of sorption q^{st} ($\Delta H = -q^{st}$) derived earlier [4], are given in Table 2 together with the calculated $\Delta S^{\ominus}$ values for the investigated Y zeolite samples.

The entropy change accompanying the sorption ($\Delta S^{\ominus}$) can be expressed as

$$\Delta S^{\ominus} = S_g^{\ominus} - \bar{S}_s \tag{3}$$

where $S_g^{\ominus}$ is the molar entropy of n-hexane vapour at standard pressure $p^{\ominus}$ and temperature T, while $\bar{S}_s$ is the differential molar entropy of the sorbed n-hexane. Using eqn. (3), the values of $\bar{S}_s$ for the cation forms of the Y zeolite at different coverages (θ) were calculated. The values are given in Table 2 and presented in Fig. 2.

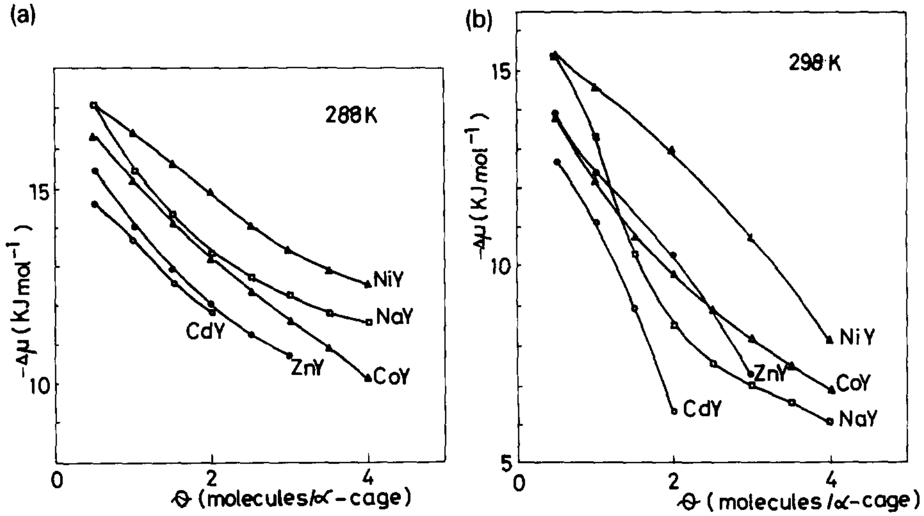

Fig. 1. Chemical affinity for *n*-hexane sorption at 288 and 298 K.

TABLE 2

Thermodynamic data for *n*-hexane adsorption on Na, Co, Ni, Zn and Cd zeolites

Zeolite	θ	$-\Delta H$ (kJ mol^{-1})	$-\Delta G$ (kJ mol^{-1})	$-\Delta S^{\ominus}$ (kJ mol^{-1} K^{-1})	$\bar{S}_s$ (kJ mol^{-1} K^{-1})
NaY	0.5	52	15.4	0.12	0.27
	1	77	13.3	0.21	0.18
	2	148	8.5	0.47	−0.08
	3	164	7.0	0.53	−0.14
	4	164	6.1	0.53	−0.14
CoY	0.5	75	13.7	0.21	0.18
	1	106	12.2	0.32	0.07
	2	122	9.8	0.38	0.01
	3	115	8.2	0.36	0.03
	4	102	6.9	0.32	0.07
NiY	0.5	66	15.4	0.17	0.22
	1	69	14.6	0.18	0.21
	2	70	13.0	0.19	0.20
	3	91	10.7	0.27	0.12
	4	142	8.7	0.45	−0.06
ZnY	0.5	60	13.9	0.15	0.24
	1	60	12.4	0.16	0.23
	2	62	10.3	0.17	0.22
	3	110	7.2	0.34	0.05
CdY	0.5	52	12.7	0.13	0.26
	1	88	11.1	0.26	0.13
	2	171	6.4	0.55	−0.16

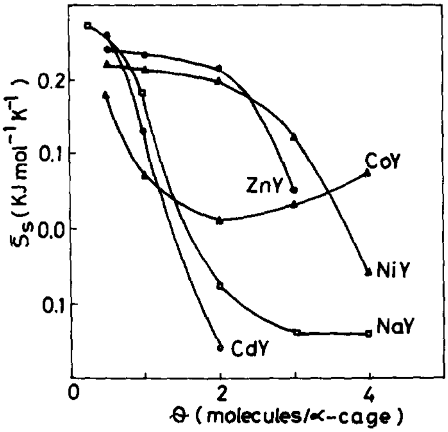

Fig. 2. Differential molar entropies, $\bar{S}_s$, of *n*-hexane sorption.

It can be seen that the differential molar entropies of the sorbed *n*-hexane, $\bar{S}_s$, decrease with increasing sorption in all investigated zeolite samples except for CoY. In the region of lower coverage, $\theta < 2$, NaY and CdY show a sharp decrease in $\bar{S}_s$, which indicates a strong sorbate–sorbate interaction. It is likely that the cations Na^+ and Cd^{2+} obstruct the diffusion of *n*-hexane through the zeolite, which means that the sorbate–sorbate interaction which occur at lower coverage also originate from interactions of *n*-hexane molecules in adjacent α-cages [4]. The values of $\bar{S}_s$ for the first and second molecule of *n*-hexane sorbed in the α-cages of NiY and ZnY are almost the same. The sorption of third *n*-hexane molecule causes a decrease in $\bar{S}_s$, which reflects strong sorbate–sorbate interactions, as a consequence of closer packing of *n*-hexane molecules in the α-cages. The curve of $\bar{S}_s$ versus θ for CoY shows a minimum. In the region of lower coverage ($\theta < 2$), CoY exhibits an initial decrease, and then ($\theta > 2$) an increase in $\bar{S}_s$. This is indicative of both the sorbate–sorbate and cation–sorbate interactions. The minimum in the CoY zeolite curve is the result of the occurrence of new sites of sorption at higher coverage. Possible new sorption sites are $Co(OH)^{2+}$, formed in the process of dehydration of CoY in the presence of the residual OH groups. The entropy of the sorbed phase, $\bar{S}_s$, can be further analysed in the manner originally proposed by Barrer and Sutherland [10]. In this case, $\bar{S}_s$ can be represented by

$$\bar{S}_s = \bar{S}_c + \bar{S}_{th} \qquad (4)$$

where $\bar{S}_c$ and $\bar{S}_{th}$ denote the differential molar configurational and thermal entropies of the adsorbed phase.

When the density of the molecules sorbed in the α-cages of the crystals is high, it is generally assumed that these molecules attempts to pack closely together and take up the walls of the anion framework. With such

TABLE 3

Configurational entropies, $\bar{S}_c$, and thermal entropies, $\bar{S}_{th}$, for different coverages x of the zeolite surface

Zeolite	x (mmol g^{-1})	$\bar{S}_c$ (J mol^{-1} K^{-1})	$\bar{S}_{th}$ (kJ mol^{-1} K^{-1})
NaY	0.32	−16.17	0.29
	0.65	−9.13	0.19
	1.29	0.00	−0.08
	1.94	9.13	−0.13
	2.56	38.18	−0.10
CoY	0.29	−17.37	0.20
	0.55	−11.01	0.08
	1.07	−3.02	0.01
	1.62	34.92	−0.01
	2.14	12.60	−0.06
NiY	0.30	−17.37	0.24
	0.58	−11.01	0.22
	1.16	−2.68	0.20
	1.74	4.42	0.12
	2.32	13.78	−0.07
ZnY	0.30	−14.41	0.25
	0.56	−7.04	0.24
	1.17	3.02	0.22
	1.76	17.37	0.03
CdY	0.29	−9.58	0.27
	0.56	−1.00	0.13
	1.13	22.86	−0.18

an ideally localized sorption process, eqn. (4) can be used. It is also assumed that

$$\bar{S}_c = R \ln x/(1-x) \tag{5}$$

and that

$$\bar{S}_s = \bar{S}_{th} + R \ln x/(1-x) \tag{6}$$

where $x = W/W_0$. Here, W is the amount sorbed at equilibrium pressure p, and W_0 is the total sorption capacity of the zeolites at 298 K [7]. In addition, it is possible to compute the thermal entropy $\bar{S}_{th}$ of the sorbed phase (Table 3). The values of $\bar{S}_{th}$ may be compared with the molar entropy of the liquid n-hexane ($S_1 = 0.30$ kJ mol^{-1} K^{-1} at 298 K). The entropy of the liquid n-hexane is greater than $\bar{S}_{th}$ for n-hexane sorbed in Y zeolites. This suggests that n-hexane has less freedom within the crystal as compared with this molecule in its liquid.

We calculated earlier [4] that the heat of sorption of *n*-hexane at maximum coverage is several times greater than the heat of condensation of *n*-hexane, which is in agreement with the results of Barrer et al. [11]. The high value of the heat of sorption indicates strong sorbate–sorbate interactions, which are the consequence of the increase in *n*-hexane density with respect to the state of the free liquid. At maximum coverage, the highest heat of sorption is found with NaY and CdY, which thus have the lowest values of the differential molar thermal entropy $\bar{S}_{\text{th}}$ of *n*-hexane sorbed in the α-cages (Table 3).

From the derived different values of $\bar{S}_{\text{th}}$ for each cation form of the Y zeolite, it can be said that the state of the sorbed *n*-hexane is determined by the cation-induced dipole, and by specific cation–sorbate and sorbate–sorbate interactions. In the α-cages of the Y faujasite, the molecules of the sorbed *n*-hexane are arranged in a more orderly fashion than in the free liquid.

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