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Influence of Traces of Water on Adsorption and Diffusion of Hydrocarbons in NaX Zeolite

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Abstract. Measurements have been performed on the influence of a small amount of water on adsorption properties of alkanes (C_3 to C_6) and olefins (C_3 and C_4) in NaX zeolite. Adsorption capacity and heat of adsorption have been measured by a Volume Step method. Kinetics has been measured by Thermal Frequency Response method and the results have been compared with the results obtained by PFG-NMR.

It has been found that water reduces the adsorption capacity especially at low adsorbate concentration. The heat of adsorption is slightly reduced by water. The kinetics of alkanes is always reduced by the adsorbed water. On the contrary, the diffusion kinetics of olefins is improved or remains unchanged, depending of the sorbat concentration.

Keywords: adsorption, diffusion, NaX zeolite, paraffins, olefins, water-thermal frequency response, activation energy

Introduction

This study focuses on the influence of a small quantity of water (∼3%) on the thermodynamical and kinetic adsorption properties of paraffins (C_3 to C_6) and olefins (C_3 and C_4) on NaX zeolite (Malka-Edery, 1999).

Most zeolite manufacturers cannot guarantee that their sample are completly anhydrous, but the maximum water amount present in the zeolite is generally less than 3%. For this reason, we performed our study with this amount.

The influence of a small quantity of water on the kinetics of hydrocarbons in NaX zeolite has been already studied by PFG-NMR (Germanus et al., 1984). With this microscopic method, the measurements are made at equilibrium and give the self-diffusion.

Macroscopic methods have been developed at L.I.M.S.I., based on the temperature response of a sample submitted to a pressure perturbation. With these methods, it is possible to measure either sorption capacity and sorption enthalpy (Volume Step Thermal method—VSTM) or kinetics (Thermal Frequency Response method—TFR).

VSTM and TFR Methods

With the methods developed at LIMSI, the adsorbent sample is put in a chamber closed by a bellows which enables the variation of the volume. There is two possibilities of varying the volume:

VSTM: The sample being under in equilibrium conditions (P_0, T_0), the bellows is suddenly compressed increasing suddenly the pressure. Thus adsorption occurs releasing heat which increases the temperature of the sample. The temperature and the pressure at constant volume are recorded after the step, until equilibrium is reached again. It can be shown that VST allows the determination of the parameters involved in the adsorption process, and especially the sorption capacity and the sorption enthalpy (Abdallah et al., to be published). This method can be considered as an

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improvement of the "Single Step Frequency Response method" (Van-Den-Begin et al., 1989) where only the pressure is measured.

TFR: In this method, the volume varies periodically at a given frequency. The pressure and the temperature responses are also periodical functions of time at the same frequency. The complex ratio between temperature and pressure response is a function of the frequency, independent of time. It gives accurate information on heat and mass transfert kinetics. (Bourdin et al., 1996).

Model

For both methods, the relevant equation of the adsorbent-adsorbate system are the same:

Mass Balance.

$$\frac{d}{dt}\left(\frac{PV}{RT}+V_{\mathrm{s}}\bar{q}\right)=0 \tag{1}$$

where V and V_{s} are the volumes of the chamber and the sample respectively and $\bar{q}$ the adsorbate mean concentration. R_e is the gas constant.

The NaX crystals used in the present study may be considered as spherical with a mean diameter smaller than 100 μm. In such small particles, the heat diffusion is very fast (heat diffusion characteristic time less than 1 ms) and the temperature may be considered as uniform. Thus, the heat balance can be written.

Heat Balance.

$$C_{\mathrm{s}}\frac{dT}{dt}+\frac{3h}{R_{\mathrm{c}}}\Delta T=|\Delta H|\frac{d\bar{q}}{dt} \tag{2}$$

where C_{s} is the overall volumetric heat capacity of the sample, R_{c} is the crystal radius, ΔH is the sorption enthalpy and h is the overall heat transfer coefficient from the sample to the surroundings.

Diffusion Equation.

$$\frac{\partial q}{\partial t}=\frac{D_{\mathrm{c}}}{r_{\mathrm{c}}^2}\frac{\partial}{\partial r_{\mathrm{c}}}\left(r_{\mathrm{c}}^2\frac{\partial q}{\partial r_{\mathrm{c}}}\right) \tag{3}$$

where D_{c} is the intracrystalline diffusion coefficient.

Boundary conditions, taking into account a finite mass transfer rate at the adsorbent surface are the following:

$$\left.\frac{\partial q}{\partial r_{\mathrm{c}}}\right|_{r_{\mathrm{c}}=0}=0 \qquad -D_{\mathrm{c}}\left.\frac{\partial q}{\partial r_{\mathrm{c}}}\right|_{r_{\mathrm{c}}=R_{\mathrm{c}}}=k_{\mathrm{s}}\left(q|_{r_{\mathrm{c}}=R_{\mathrm{c}}}-q^*\right) \tag{4}$$

where k_{s} is the surface barrier transfer coefficient.

The following mass transfer characteristic times τ_D and τ_s are associated with the diffusion coefficient and the surface barrier coefficient:

$$\tau_D=\frac{1}{15}\frac{R_{\mathrm{c}}^2}{D_{\mathrm{c}}} \qquad \tau_s=\frac{1}{3}\frac{R_{\mathrm{c}}}{K_{\mathrm{s}}} \tag{5–6}$$

State Equation. The mass adsorbed at equilibrium, $q^*(P,T)$, is given by a linearized state equation around its mean value, q_e:

$$q^*-q_e=K_P\Delta P-K_T\Delta T \tag{7}$$

K_P and K_T are the slope at the equilibrium point of the isotherm and of the isobar respectively.

These equations allow the calculation of the pressure and temperature responses either for VSTM or for TFR methods, when the parameters are known.

The boundary conditions are different in case of VST or TFR method.

VST Method

As noticed previously, in the VSTM method, the chamber volume is suddenly reduced (20 ms) and remains constant afterwards (Grenier et al., 1995). The equations of the model allow the calculation of the pressure and the temperature after the step. For this calculation, the following parameters must be known: the slopes of the isotherm and of the isobar, K_P and K_T respectively, the sorption enthalpy, ΔH, the heat capacity, C_{S}, the heat transfer coefficient, h, and the characteristic times τ_D and τ_s. Conversely, it can be shown (Abdallah et al., 2001) that the treatment of the pressure and the temperature records allows the determination of the overall mass transfer characteristic time τ_m, and the determination of all thermodynamic parameters, especially the sorption enthalpy, ΔH.

TFR Method

This method consists of a periodically variation of the chamber volume which can be expressed as a sum of sinusoidal variations (Sun et al., 1994).

For such a sinusoidal volume variation, the volume can be written,

$$V = V_e(1 - ve^{i\omega t}) \tag{8}$$

where ω is the angular frequency and v is the relative amplitude of the volume variation.

The pressure and the temperature are periodical functions at the same frequency:

$$P = P_e\left[1 + pe^{i(\omega t+\varphi)}\right] \tag{9}$$

$$T = T_e + A_t e^{i(\omega t+\psi)} \tag{10}$$

where p is the relative pressure amplitude, A_T the temperature amplitude and φ, ψ the pressure and temperature phase respectively.

The complex ratio between the temperature response and the presure response is independent of time, but depends on the frequency. This ratio (multiplied by the volume amplitude v), is called the characteristic function. It can be written:

$$\theta^p = \theta^p_{\text{in}} + i\theta^p_{\text{out}} = v\frac{A_T}{p}\, e^{i}(\varphi - \psi) \tag{11}$$

It can be shown that this function gives very accurate and detailed information on the heat and mass transfer kinetic parameters (Bourdin et al., 1996). Figure 1 shows a typical characteristic function. At low frequency, the temperature amplitude is small, due to the heat transfer toward the wall. It increases when frequency increases and tends toward a limit when the heat transfer during a period is negligible (adiabatic regime). When frequency still increases, the mass transfer is no more completed during a period and the temperature amplitude decreases. The imaginary part of the characteristic function (out-of-phase function) passes through a minimum closely related to the mass transfer characteristic time. The diffusion coefficient and the surface barrier coefficient are identified by comparing the experimental function and the theoretical characteristic function calculated from Eqs. (1) to (4) and Eq. (7).

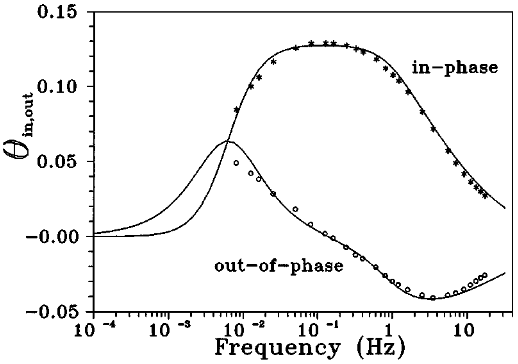

Figure 1. Typical caracteristic function: Anhydrous NaX—butane at 95 Pa and 30°C. ($*$) and ($\circ$): experimentals in-phase and out-of-phase functions, respectively (—): model.

As stated previously, TFR gives the transport diffusivity D_{i}. On the contrary, NMR gives the self-diffusivity D_0. According to Darken's law, it can be written:

$$D_0 = D_{\text{i}}\left[\frac{\partial \ln q}{\partial \ln P}\right]_T \tag{12}$$

The ratio D_{i}/D_0 is called "Darken's factor" and can be written:

$$\frac{D_{\text{i}}}{D_0} = \frac{q}{PK_P} \tag{13}$$

Experimental

The apparatus built at L.I.M.S.I. consists of a 600 cc chamber closed by a bellows (Grenier et al., 1995). This bellows is moved by a cam and a stepper motor at constant frequency, comprised between 1 mHz and 30 Hz. The pressure is recorded by a fast Baratron® gauge and the temperature is measured by infrared detection. The minimum measurable mass transfer characteristic time is 1 ms.

The measurements can be performed only in a definite domain of pressure: at very low pressure, the response is too small because the mass of the gas displaced by the bellows is very small. Thus, no reliable measurement is possible under 4 Pa. On the other hand, at high pressure, a spurious effect of heating of the gas appears, limiting the measurment domain at approximately 1 kPa.

Two sorts of NaX zeolite crystals have been used in the experiments:

- (I): 50 μm diameter, coming from Zdanov's Laboratory, Leningrad, provided by J. Kärger, Leipzig.
- (II): 70–80 μm diameter, coming from Kessler Laboratory, Mulhouse.

The weight of the sample is approximately 0.1 g. In all experiments, the experimental protocol is as follows:

At first, the sample is reactivated overnight: 8 hours heating up to 400°C and 2.5 hours of plateau at 400°C followed by 3 hours cooling. During the reactivation, the chamber is pumped down, and the pressure is approximately 10^{-4} Pa at the end of the process. Then, a small amount of water vapor (approximately 3% by weight of the anhydrous sample) is introduced in the chamber. The pressure decreases dramatically, down to the limit of the pressure measurement possibility (∼0.03 Pa). At such a low pressure, a uniform distribution of water in the crystals is not obtained instantaneously. In fact, experiments have been performed introducing the hydrocarbons either immediatly after the water introduction, or waiting 2 or 4 hours. It has been observed that experiments performed without waiting period gave different results from experiments performed after 2 hours. On the contrary, experiments performed after a waiting period of 2 or 4 hours gave the same results. Thus, it has been concluded that water distribution is practically uniform after 2 hours and this waiting time has been systematically observed for all experiments.

The water pressure being very small in experimental conditions (temperature: 30°C, concentration: 3% by weight), practically all the introduced water is adsorbed and no appreciable amount of water remains in gaseous form. Using a simple coadsorption model (Langmuir), it can be shown that the adsorbed water is not appreciably displaced by introduction of an another gas, up to pressure as large as 10 kPa (Malka-Edery, 1999). Thus, it seems possible to consider that the hydrated sample behaves like a new adsorbent and that it is possible to apply the model developed in case of single component adsorption. The validity of this assumption is confirmed by the good accordance observed between the experimental data and the curves calculated with the single component model.

The apparatus, whose volume is carefully calibrated, has been used also for measuring isotherms of anhydrous and hydrated samples.

Results

The measurements have been performed with sample (I) for olefins and samples (II) for saturated hydrocarbons.

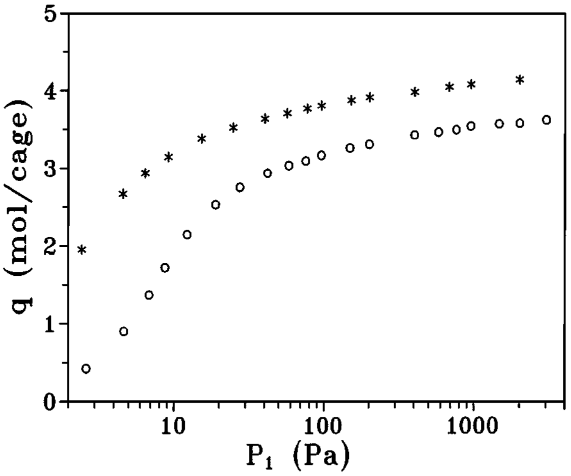

Figure 2. Isotherms NaX—pentane at 30°C. (∗): anhydrous. (○): hydrated (water amount ∼3%).

Thermodynamic

The sorption capacity is always lowered by water. This effect is more pronounced at low pressure. Figure 2 shows a typical result obtained with pentane at 30°C. For the studied species, at high pressure, near saturation, the loss of sorption capacity is comprised between 11% and 15%, as shown in Table 1. This amount corresponds approximately to the volume occupied by water. Thus, at such high pressure, the loss of sorption capacity seems to be exclusively due to volumic effects.

The sorption enthalpy has been measured by VSTM and by isotherms at two temperatures, using the Clausius-Clapeyron equation:

$$\Delta H = R\left[\frac{\partial \ln P}{\partial(1/T)}\right]_q \tag{14}$$

Table 1. Adsorption capacity of anhydrous and hydrated NaX zeolite. Water amount of hydrated sample: ∼3%.

	$q_{\text{Sat, anhydrous}}$ (mol/cage)	$q_{\text{Sat, hydrated}}$ (mol/cage)	Relative loss of adsorption capacity (%)
Propane	6.0	5.2	−13
Butane	4.6	3.9	−15
Pentane	4.3	3.8	−12
Hexane	3.9	3.3	−15
Propene	6.2	5.5	−11
Butene-1	5.6	5.0	−11
Butene-2cis	5.6	5.0	−11

Table 2. Mean sorption heat of anhydrous and hydrated NaX zeolite. Water amount of hydrated sample: ~3%.

	$\Delta H_{\text{anhydrous}}$	$\Delta H_{\text{hydrated}}$	$\Delta H_{\text{anhydrous}}$ (Literature)
Propane	39.6	35.9	40.0[a] 47.9[b]
Butane	55.1	51.7	42.9[a] 60.5[b]
Pentane	66.6	61.1	58.8[a] 70.6[b]
Hexane	71.0	64.0	60.5[a] 84.9[b]
Propene	38.2	35.3	40.7[c]
Buten-1 or -2	53.0	45.6	—

[a,b]Kärger et al. (1980).
[c]Costa et al. (1991).

Measurements at various concentrations show that the concentration has little influence on the sorption enthalpy. Table 2 shows the mean measured sorption enthalpy in case of anhydrous and hydrated sample, and, for comparison, the sorption enthalpy in anhydrous case found in literature. It can be seen that the sorption enthalpy is always reduced by water, but this effect is small, always less than 10%.

Kinetics

1. Saturated Hydrocarbons.

Propane. Table 3 and Fig. 3 contain the results obtained with propane at 30°C. It can be seen that, in studied concentration domain, the kinetics is approximately constant. The kinetics of hydrated sample is approximately half time less than the kinetics of anhydrous sample.

Butane. Butane results are presented Table 4 and Fig. 4. It can be observed that the corrected diffusivity decreases with increasing concentration. In presence of water, the kinetics is slowed down, and this effect is more pronounced at high concentration reaching a factor 7 at 3 mol/cage.

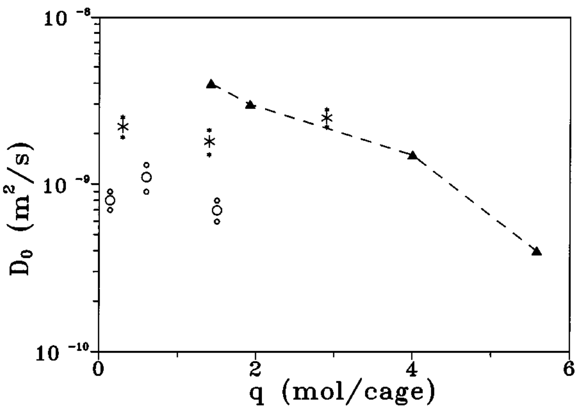

Figure 3. Corrected diffusivity or self-diffusivity of propane in NaX zeolite at 30°C. (∗): TFR, anhydrous sample. (○): TFR, hydrated sample (water amount ~3%). Experimental errors are indicated by small symbols. (▲) NMR, anhydrous sample, [Kärger, 1987].

The comparison in anhydrous case of the corrected diffusivity obtained from TFR measurements with the self-diffusivity given by NMR (Kärger et al., 1980) shows an improtant discrepancy. An error on the Darken's factor induces an error on the corrected diffusivity, but at low pressure the discrepancy is larger than a factor 10 and the Darken's factor is smaller than 2. Thus the discrepancy cannot be attributed to an error on the Darken's factor and remains unexplained. Nevertheless both NMR and TFR show a slowing down of the kinetics in presence of water.

Pentane and Hexane. Isotherms of pentane and hexane are very favorable: but, at low concentration, accurate measurements are not possible since the pressure is very low. Thus, the diffusivity has been measured at high concentration. The results are summarized in Table 5. As for lighter alkanes, the kinetics is slowed down in presence of a small quantity of water.

Table 3. Diffusivity of propane in anhydrous and hydrated NaX zeolite.Water amount of hydrated sample: ~3%; temperature: 30°C.

P(Pa)	q(kg/m^3)	q(mol/cage)	K_P(kg/m^3/Pa)	D_i(10^{-9} m^2/s)	Darken factor	D_0(10^{-9} m^2/s)
95.1 anhydrous	12.7	0.33	0.11	2.6 ± 0.3	1.2	2.2 ± 0.3
94.44 hydrated	5.4	0.14	4.6e-2	1.0 ± 0.1	1.2	0.8 ± 0.1
398.8 anhydrous	54.4	1.4	1.21e-1	2.0 ± 0.3	1.1	1.8 ± 0.3
402.2 hydrated	21.7	0.57	5.52e-2	1.1 ± 0.2	1.0	1.1 ± 0.2
956 anhydrous	110.6	2.9	5.45e-2	5.4 ± 0.7	2.1	2.5 ± 0.3
949 hydrated	55.9	1.5	5.29e-2	1.3 ± 0.2	1.1	1.2 ± 0.2

Table 4. Diffusivity of butane in anhydrous and hydrated NaX zeolite. Water amount of hydrated sample: ~3%; temperature: 30°C.

P(Pa)	q(kg/m^3)	q(mol/cage)	K_P(kg/m^3/Pa)	D_i(10^{-10} m^2/s)	Darken factor	D_0(10^{-10} m^2/s)
39.8 anhydrous	93.8	1.9	1.20	6.0 ± 0.6	2.0	3.0 ± 0.3
39.8 hydrated	33.7	0.7	7.1e-2	3.2 ± 0.5	1.2	2.7 ± 0.4
95.0 anhydrous	145.5	3.0	4.1e-1	9.4 ± 0.2	3.7	2.5 ± 0.5
95.4 hydrated	80.2	1.7	6.4e-2	1.9 ± 0.3	1.3	1.4 ± 0.2
399.4 anhydrous	183.8	3.8	4.5e-2	16.0 ± 2.0	10.1	1.6 ± 0.2
399.4 hydrated	146.5	3.0	6.4e-2	2.0 ± 0.4	5.8	0.35 ± 0.07
949.5 anhydrous	198.9	4.1	1.5e-2	18.0 ± 2.0	13.6	1.3 ± 0.1
953.1 hydrated	164.8	3.4	1.8e-2	2.5 ± 0.3	9.8	0.26 ± 0.03

Table 5. Diffusivity of pentane in anhydrous and hydrated NaX zeolite. Water amount of hydrated sample: ~3%; temperature: 30°C.

P(Pa)	q(kg/m^3)	q(mol/cage)	K_P(kg/m^3/Pa)	D_i(10^{-10} m^2/s)	Darken factor	D_0(10^{-11} m^2/s)
9.3 anhydrous	173.0	2.8	2.6	3.0 ± 0.6	7.1	4.2 ± 0.8
9.2 hydrated	97.8	1.6	2.6	1.2 ± 0.2	4.1	2.9 ± 0.5
39.6 anhydrous	200.8	3.2	3.9e-1	9.0 ± 1.0	13.0	6.9 ± 0.8
39.6 hydrated	157.9	1.0	5.1e-1	1.2 ± 0.3	7.8	1.5 ± 0.4
95.8 anhydrous	212.1	1.3	1.1e-1	1.4 ± 0.2	10.1	1.6 ± 0.2
95.8 hydrated	171.6	1.1	1.5e-1	1.1 ± 0.3	11.9	0.9 ± 0.3
403.0 anhydrous	225.8	1.4	2.2e-2	2.4 ± 0.2	25.5	0.9 ± 0.1
403.0 hydrated	187.2	1.2	3.0e-2	0.8 ± 0.1	15.5	0.5 ± 0.07

The discrepancy between NMR, and TFR observed with butane in anhydrous case, appears also with pentane (Kärger et al., 1980).

Table 6 gives the results obtained by TFR for hexane. Measurements performed by NMR on lighter alkanes, (Kärger et al., 1980) and on heavier alkanes, (Kärger and Ruthven, 1992) show a dramatic decrease of the diffusivity at high concentration, and a rough extrapolation of the data at 303 K and 3 mol/cage gives a diffusivity approximately 10 times larger than the diffusivity obtained by TFR.

Comparison. Figure 5 shows the corrected diffusivity of C_3 to C_6 paraffins at 3 mol/cage. It can be seen

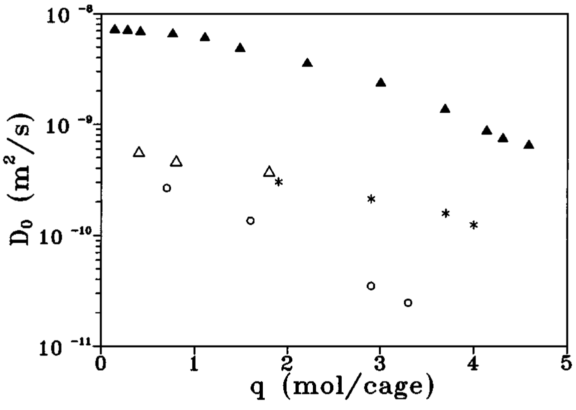

Figure 4. Corrected diffusivity or self-diffusivity of butane in NaX zeolite at 30°C. (∗): TFR, anhydrous sample, (○): TFR, hydrated sample (water amount ~3%). (▲) NMR, anhydrous sample, (△) NMR, hydrated sample (water amount ~4%) [Germanus, 1984].

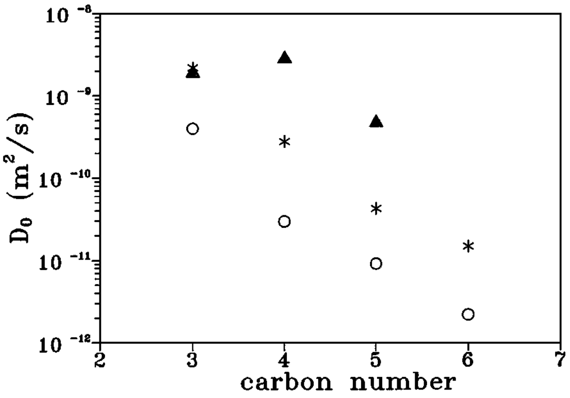

Figure 5. Corrected diffusivity or self-diffusivity of saturated hydrocarbons in NaX zeolite at 30°C and 3 mol/cage. Data of propane in hydrated sample is extrapolated from data at lower concentration. (∗): TFR, anhydrous sample. (○): TFR, hydrated sample (water amount ~3%). (▲) NMR, anhydrous sample, [Kärger et al., 1980].

Table 6. Diffusivity of hexane in anhydrous and hydrated NaX zeolite. Water amount of hydrated sample: ~3%; temperature: 30°C.

P(Pa)	q(kg/m^3)	q(mol/cage)	K_P(kg/m^3/Pa)	D_i(10^{-10} m^2/s)	Darken factor	D_0(10^{-12} m^2/s)
3.99 anhydrous	225.8	3.0	1.96	4.8 ± 0.6	28.9	17.0 ± 2.0
3.99 hydrated	193.0	2.6	4.0	1.2 ± 0.2	12.1	9.9 ± 1.6
9.51 anhydrous	234.8	3.2	1.0	1.8 ± 0.2	24.7	7.3 ± 0.8
9.5 hydrated	203.4	2.7	1.1	0.35 ± 0.03	20.4	1.7 ± 0.15
40.6 anhydrous	247.1	3.3	1.7e-1	4.6 ± 0.7	35.9	12.8 ± 1.9
40.6 hydrated	215.3	2.9	1.74e-1	0.6 ± 0.06	30.4	2.0 ± 0.2
400.0 anhydrous	258.7	3.5	2.1e-2	5.1 ± 1.1	31.1	16.4 ± 0.35
401.7 hydrated	235.4	3.2	2.3e-2	0.7 ± 0.09	25.5	2.8 ± 0.35

that the diffusivity decreases regularly with the carbon number. The water effect is approximately the same for all species at 3 mol/cage: the diffusivity is reduced by a factor 5 to 10.

Morever, as remarked previously, the TFR corrected diffusivities are in good agreement with NMR for propane but a discrepancy is observed for heavier alkanes. Nevertheless that discrepancy (factor about 10) is much less than the discrepancy, (factor 100 to 200) observed between RMN and ZLC for butane and hexane at low concentration and 358 K (Kärger and Ruthven, 1992).

Olefins

Measurements have been performed with propene, 1-butene and 2cis-butene. No noticeable difference between butene isomers appears as well in thermodynamics properties as in kinetics properties.

The results are summarized in Table 7. It can be observed that for both studied olefins the diffusivity increases slightly in presence of water. This results is in accordance with NMR results (Germanus et al., 1984).

The diffusivities of alkanes and olefins witch have the same carbon number are presented in Fig. 6. A decrease of the diffusivity with increasing carbon number can be observed for alkanes as well as for olefins. The influence of the double bonds on the diffusivity appears also clearly. The double bonds, increasing the interaction with the ionic sites, leads to a slower kinetics.

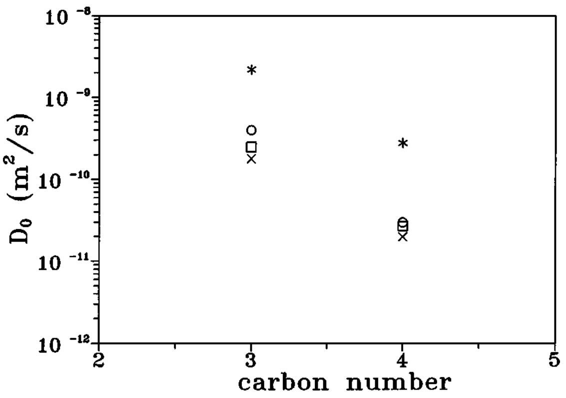

Figure 6. Comparison of corrected diffusivity in NaX zeolite of C_3 and C_4 saturated and unsaturated hydrocarbons at 30°C and 3 mol/cage (excepted butene: 4 mol/cage). (∗): alkanes, sample anhydrous. (○): alkanes, sample hydrated. (×): olefins, sample anhydrous. (□): olefins, sample hydrated.

The influence of water is not the same for alkanes and olefins: in the first case, the kinetics is slowed down by water. For olefins, the reduction of the interaction with the ionic sites by water leads to a kinetics slightly faster.

Table 7. Diffusivity of propene and butene in anhydrous and hydrated NaX zeolite. Water amount of hydrated sample: ~3%; temperature: 30°C. 1-butene and 2cis-butene have very closed diffusivity and are called ≪ butene ≫.

	q(kg/m^3)	q(mol/cage)	K_P(kg/m^3/Pa)	D_i(10^{-10} m^2/s)	Darken factor	$10^{10} D_0$(m^2/s)
Propene anhydrous	114–193	3.1–5.3	0.9–0.06	4.1–20.0	3.0–8.2	1.3–2.4
Propene hydrated	22.0–104	0.6–2.9	0.4–0.11	3.0–6.0	1.4–2.4	2.2–2.5
Butene anhydrous	219–254	4.5–5.2	0.36–0.03	0.22–0.7	15–21	0.14–0.3
Butene hydrated	132–191	2.7–3.9	1.17–0.04	0.12–0.42	20–13	0.06–0.3

Discussion

The influence of water on sorption properties of the studied hydrocarbons can be summarized as follows:

- the sorption capacity is reduced for all species, and this reduction depends on the concentration.
- the sorption enthalpy is slightly reduced for all species.
- water reduces the corrected diffusivity of saturated hydrocarbons whichever the concentration.
- the diffusivity of olefins is increased at medium concentration. NMR measurements indicate a slowing down of the kinetics at high concentration.

To explain these results, it may be proposed the following interpretation:

- at first, water molecules act as a screen between the cationic sites and the hydrocarbon molecules, reducing the interaction potential (screening effect).
- second, water interacts with the cationic sites, and especially the site near the window, creating cation-water complexes reducing the aperture of the window between the zeolite α-cages (blocking effect), (Tezel et al., 1983; Germanus et al., 1984). This is in accordance with the previous assumption on which water remains bounded to the adsorbent.
- third, water reduce the sorption volume (steric effect). The maximum loading of water in NaX is close to 0.33 kg/kg. Thus 3% by weight of water occupy approxymately 9% of the volume of the cage.
- endly, water or cation-water complexes interact directly with hydrocarbon molecules.

The first effect explains the reduction of the adsorption capacity, observed for all species. At low pressure this effect is more effective because the interaction molecule-molecule of the hydrocarbon is negligible. At high pressure, it becomes small and the reduction of the adsorption capacity is due to the reduced sorption volume. The screening effect explains also the reduction of the sorption enthalpy, but it is partially compensated by interaction water molecule-hydrocarbon molecule and this reduction is rather small.

With regard to the kinetics, the screening of the cationic electric field reduces the residence time, increasing the diffusivity. This effect is more pronounced for polar molecules (unsaturated hydrocarbons).

The blocking effect reduces the diffusivity. It is dominant at all concentrations for non polar molecules (saturated hydrocarbons) and thus the diffusivity is always reduced by water for these molecules. On the contrary, for olefins, this blocking effect is dominant at high concentration, but at low concentration the screening effect is dominant.

Nomenclature

A_T	Temperature amplitude (K)
C_s	Sample heat capacity ($\mathrm{J\,m^{-3}\,K^{-1}}$)
D_c	Transport diffusivity ($\mathrm{m^2\,s^{-1}}$)
D_0	Self-diffusivity ($\mathrm{m^2\,s^{-1}}$)
h	Heat transfer coefficient ($\mathrm{W\,m^{-2}\,K^{-1}}$)
K_P	Isotherm derivative vs pressure ($\mathrm{kg\,m^{-3}\,Pa^{-1}}$)
K_T	Isotherm derivative vs temperature ($\mathrm{kg\,m^{-3}\,K^{-1}}$)
k_s	Surface barrier coefficient ($\mathrm{ms^{-1}}$)
P, P_e	Pressure, its mean value (Pa)
p	Relative pressure amplitude
q, q_e	Adsorbed amount, its mean value ($\mathrm{kg\,m^{-3}}$)
q^*	Adsorbed amount at thermodynamic equilibrium ($\mathrm{kg\,m^{-3}}$)
R_e	Gas constant ($\mathrm{J\,kg^{-1}\,K^{-1}}$)
R_c	Crystal radius (m)
T, T_e	Temperature, its mean value (K)
V, V_e	Chamber volume, its mean value ($\mathrm{m^3}$)
V_s	Sample volume ($\mathrm{m^3}$)
v	Relative volume amplitude
ΔH	Sorption Enthalpy ($\mathrm{J\,kg^{-1}}$)
φ	Pressure vs volume phase lag
ψ	Temperature vs volume phase lag
ω	Angular frequency ($\mathrm{s^{-1}}$)

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