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Adsorption of Alkanes and Aromatic Compounds on Various Faujasites in the Henry Domain. 2. Composition Effect in X and Y Zeolites

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Volatile organic compounds (VOCs) released in the atmosphere are responsible for important climate changes on earth, and some may have short- and long-term adverse health effects. Recovery of these VOCs can be a solution to reduce pollution. At low pressure, Henry constants are needed to develop recovery processes. Representative molecules were chosen to determine adsorption data. Nine alkanes (linear, cyclic, and branched molecules with carbon numbers between five and eight) and four aromatic and chlorinated compounds on a series of faujasite zeolites (LiLSX, NaLSX, KLSX, NaX, and two NaY) were studied in the Henry domain at temperatures ranging from (448.15 to 673.15) K using the well-known pulse chromatography technique. The zeolites were characterized to determine the main structural properties such as cell parameters, chemical composition, porous volume, specific surface area, and water adsorption capacity. The Henry constant increases with rising Si/Al ratio and probe molecule carbon number.

Introduction

Faujasite-type zeolites are quite often used in the industry either as catalysts or for recovery and separation of gases. Volatile organic compounds (VOCs) (alkanes, aromatic, chlorinated) released in the atmosphere resulting from human activities may have an important impact on Earth (greenhouse effect, ozone layer depletion, ozone formation) and on human health (eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system; and sometimes cancer). More and more constraining regulations which aim at limiting VOC contents in waste gases are set on an international level. Adsorption is well-known as a method which makes possible the treatment of gas flows containing traces of VOCs. The lack of VOC adsorption data in the low-pressure range in the literature can be a limitation to the development of new adsorption processes for purification of waste gases and recovery of pollutants. Such data are of prime importance not only for process design but also for the development of new adsorbents characterized by high VOC compound adsorption capacities. As far as zeolite adsorbents are concerned, the understanding of the effect of the zeolite structure, the type and number of compensating cations, for example, on its adsorptive performances is a key issue in the adsorbent selection procedure for a specific adsorption application (separation of normal and iso-alkanes, xylene separation, gas purification...).

Some previous work[1−13] provides interesting adsorption data on zeolites. These papers deal with specific adsorptives (nitrogen, argon, water, hydrocarbons, hydrofluorocarbons) and/or zeolites. Some of them aim to provide adsorption data for a specific application: xylene separation,[1,2,9] air purification[6] and separation,[8] HFC separation techniques.[10] Others are focused on physical interpretation of adsorbate−adsorbent behavior.[3−5,7,11−13] It appears that a more general experimental study which would provide extensive results would be an interesting tool for further developments in the understanding of adsorption mechanisms and in predictive modeling.

This paper is the second part of work dealing with the influence of the zeolite structure on the adsorption properties of hydrocarbons in the low partial pressure range (Henry constant). In the first part, the influence of the compensating cation in Y faujasites was studied. This second paper is devoted to the presentation of experimental adsorption data in the low partial pressure domain on monovalent cationic faujasite zeolites LiLSX, NaLSX, KLSX, NaX, and two NaY (with a Si/Al ratio of 2.43 and 3.4) for nine alkanes (linear, cyclic, and branched compounds) and four aromatic and chlorinated compounds used as probe molecules in the temperature ranges from (448.15 to 673.15) K and (448.15 to 623.15) K for alkanes, (523.15 to 673.15) K for aromatic compounds, and (498.15 to 673.15) K for chlorobenzene. Measurements were carried out using the well-known pulse chromatographic method.[3−6,11,12,14−16] With the two complementary papers, one can easily understand the effect of the compensating cation and the influence of the number of compensating cations in faujasites on the adsorption mechanisms of the first molecules in the zeolite cages.

Experimental Section

Experimental Device and Procedure. The column filled with the adsorbent was located in the oven of an HP 5890 chromatograph equipped with a thermal conductivity detector (TCD). A purifier, filled with 3A zeolite, was placed in the system to remove water contained in the carrier gas (nitrogen with a purity higher than 99.999 %). Before any measurement, the temperature was raised to 673.15 K at a rate of 1 K per minute; this temperature was kept constant overnight under a flow of inert gas to regenerate the adsorbent. A mass flow controller was

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Table 1. Column Dimensions (Adsorbent Mass in g and Column Length in cm)

	alkane measurements		aromatic measurements	
	column length	adsorbent mass	column length	adsorbent mass
LiLSX	4.04	0.300	1.15	0.097
KLSX	3.42	0.292	0.99	0.091
NaLSX	3.42	0.278	1.22	0.090
NaX	3.67	0.298	1.31	0.100
NaY 2.4	4.66	0.337	2.29	0.155
NaY 3.4	2.43	0.171	1.17	0.089

Table 2. Adsorbent Characteristics (Chemical Composition, Specific Area, Si/Al Ratio, Cell Parameter "*a*", and Crystal Density)

	chemical composition	specific surface $m^2 \cdot g^{-1}$	Si/Al	*a* nm	crystal density $kg \cdot m^{-3}$
LiLSX 1.0	$Na_1K_7Li_{88}Al_{96}Si_{96}O_{384}$	704	1.0	2.4749	1351.8
KLSX 1.0	$K_{96}Al_{96}Si_{96}O_{384}$	485	1.0	2.5221	1572.3
NaLSX 1.0	$Na_{96}Al_{96}Si_{96}O_{384}$	629	1.0	2.5022	1446.3
NaX 1.2	$Na_{86}Al_{86}Si_{106}O_{384}$	627	1.2	2.4987	1428.3
NaY 2.4	$Na_{56}Al_{56}Si_{136}O_{384}$	621	2.43	2.4691	1405.9
NaY 3.4	$Na_{43.5}Al_{43.5}Si_{148.5}O_{384}$		3.4	[a]	1378.3

[a] The cell parameter used is that of NaY 2.4.

used to regulate the flow of carrier gas (nitrogen). After this regeneration step, the temperature was adjusted to the experimental temperature. The hydrocarbon probe was injected with a syringe in the heated injector, passed through the column where it was adsorbed and desorbed, and passed into the TCD. The VOC concentration profile, $c(t)$, at the column outlet was then recorded on a personal computer as a function of time t.

The mass of adsorbent in the column was determined by weighing the empty column and the column after degassing.

The details of the experimental procedure can be found in our previous work.[17]

Treatment of the Chromatographic Measurements. At the end of the experimental run, the following measurements were provided.

- Volumetric flow of inert carrier gas in the column.

- VOC concentration profile in the carrier gas vs time at the column outlet $c(t)$.

The first moment of this profile is related to the Henry constant by eq 1.[3−5,11−12,17]

$$\mu = \frac{V_{\text{column}}}{Q_{\text{T}}}[\epsilon + (1-\epsilon)\rho_{\text{c}} \cdot RTK'] + \frac{V_{\text{d}}}{Q_{\text{T}}} \qquad (1)$$

with $\epsilon = \epsilon_i + \epsilon_p(1 - \epsilon_i)$ and where μ is the retention time (s); V_{column} is the column volume (m^3); V_d is the dead volume between the injector and the detector (m^3); Q_T is the total volume flow ($m^3 \cdot s^{-1}$); T is the bed temperature (K); R is the ideal gas constant ($J \cdot K^{-1} \cdot mol^{-1}$); ϵ is the total porosity; ϵ_i is the interstitial bed porosity; ϵ_p is the pellet macroporosity; ρ_c is the crystal density ($kg \cdot m^{-3}$); and K' is the Henry constant ($mol \cdot kg^{-1} \cdot Pa^{-1}$).

Equation 1 may be written[17]

$$\mu = \frac{V_{\text{column}}}{Q_{\text{T}}}\left[1 - \frac{m_{\text{pellets}}}{V_{\text{column}} \cdot \rho_{\text{c}}} + \frac{m_{\text{pellets}}}{V_{\text{column}}}RTK'\right] + \frac{V_{\text{d}}}{Q_{\text{T}}} \qquad (2)$$

where m_{pellets} is the pellets mass in the column. μ was determined by the appropriate statistical treatment of $c(t)$. On the basis of our previous study,[17] we take a relative error on the retention time of 5 %. V_{column} and V_d were determined from metric measurements, and ρ_c was calculated for an ideal crystal structure.

Table 3. Micropore Volume ($cm^3 \cdot g^{-1}$), Dehydration Factors, and Adsorption Capacity of Water at Ambient Temperature ($g_{\text{water}}/g_{\text{zeolite}}$) for LiLSX, NaLSX, KLSX, NaX, and NaY

zeolite	pore volume $cm^3 \cdot g^{-1}$	dehydration factor	adsorption capacity ($g_{\text{water}}/g_{\text{zeolite}}$)
LiLSX 1.0	0.395	0.2443	0.323
KLSX 1.0	0.261	0.2022	0.253
NaLSX 1.0	0.342	0.2352	0.308
NaX 1.2		0.2388	0.313
NaY 2.4	0.323	0.2461	0.326
NaY 3.4		0.2561	0.344

The Henry constant K' can be expressed in a dimensionless form, K

$$K = K'\rho_{\text{c}}RT \qquad (3)$$

The physical meaning of the Henry constants determined by this method implies an execution of the measurements in the Henry domain. The Henry domain is characterized by the fact that the retention time is not influenced by the injected volume. This is checked by performing several experimental runs with decreasing injected volumes of adsorbate for which we calculate the retention time. The linear correlation between the retention time and the inverse flow rate also has to be verified: this is done by performing several runs with various gas flow rates. Once the retention time becomes independent of the injected volume and when the linearity between the retention time and the inverse flow rate has been confirmed, the hypothesis of the column working in Henry's domain is valid. Typically, the injected volume is between (0.01 and 0.25) μL.

The van't Hoff plot of the dimensionless form of the Henry constant leads to the adsorption energy, given as

$$K = K_0 \exp\left(\frac{-\Delta U}{RT}\right) \qquad (4)$$

where K_0 is the pre-exponential dimensionless constant and ΔU is the adsorption energy ($J \cdot mol^{-1}$). The maximum relative error in K is 8 % based on the error analysis given elsewhere.[17] The isosteric heat of adsorption at zero coverage, ΔH ($J \cdot mol^{-1}$), is calculated by

$$\Delta H = \Delta U - RT \qquad (5)$$

Column Characteristics. For the measurements, the zeolite samples are pelletized in a press by applying a pressure of around 4.5 MPa. We use the (400 to 800) μm fraction to fill a 1/4 in. (6.35 mm) external diameter stainless steel column with an internal diameter of 4.61 mm. The column lengths were between (1 and 5) cm with an absolute error of 0.01 cm having to be accounted for in the measurement of both the length and the diameter of the column. The adsorbent masses used for the different experimental runs were measured with an accuracy of 0.0005 g. The gas flow rates are between (1 and 2) $Nl \cdot h^{-1}$. The uncertainty in the volumetric flow measurement is 2.7 % (accuracy of the mass flow controller).

With such a column diameter and length, no pressure drop is measured in the apparatus. Table 1 gives the accurate column dimensions for each experimental run.

Adsorbents. All zeolites studied are commercial faujasite zeolites with various compensating cations and various Si/Al ratios: LiLSX, NaLSX, KLSX, NaX, and two NaY (with a Si/Al ratio of 2.43 and 3.4). There are three zeolites with a Si/Al ratio of 1.0 with compensating cations Li^+, Na^+, and K^+, all provided by Tricat GmbH. The four sodium-type faujasites have increasing Si/Al ratio ranging from 1.0 to 3.4. NaX was provided

Table 4. Dimensionless Henry Constant Data for Various VOCs at T = 448.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	3108.8	4573.9	1854.0	1902.9	686.0	604.4
n-pentane	3211.2	3931.5	1984.8	2009.0	1014.7	765.3
cyclohexane	9933.9	17629.6	5089.1	4901.2	1541.1	1446.0
2-methylpentane	15241.5	19028.2	8313.3	8236.7	2194.9	1941.2
3-methylpentane	15446.9	20537.8	8016.7	8104.5	2278.9	1962.5
2,3-dimethylbutane	15138.8	19509.9	7976.5	8306.7	2207.9	1445.8
n-hexane	15035.9	18533.6	8610.1	8478.8	4307.1	2025.5
n-heptane						6353.7

Table 5. Dimensionless Henry Constant Data for Various VOCs at T = 473.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	1770.4	2283.3	1121.5	1050.1	394.5	394.4
n-pentane	1825.3	2095.9	1182.4	1095.4	625.7	455.7
cyclohexane	4893.7	8345.2	2935.2	2753.1	897.5	834.2
2-methylpentane	7189.5	8825.0	4439.1	4407.9	1160.6	1045.8
3-methylpentane	7254.7	9332.2	4462.7	3989.7	1196.1	1078.2
2,3-dimethylbutane	7157.0	8934.4	4440.4	4427.4	1192.8	835.7
n-hexane	7124.3	8553.6	4415.5	4409.0	2050.1	1153.4
n-heptane	32358.8	36100.2	16929.1	15910.5	6256.2	3319.8
2,2,4-trimethylpentane			51452.6	46535.3	12047.2	10892.6

Table 6. Dimensionless Henry Constant Data for Various VOCs at T = 498.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	995.5	1304.7	701.4	635.9	244.9	270.4
n-pentane	1043.1	1125.2	736.4	654.7	412.0	299.7
cyclohexane	2691.1	4423.2	1671.4	1570.0	542.7	498.5
2-methylpentane	4071.3	4648.2	2397.3	2414.4	709.7	598.0
3-methylpentane	4179.5	4884.7	2404.1	2388.4	722.0	624.5
2,3-dimethylbutane	4017.0	4592.1	2392.0	2541.0	718.3	500.2
n-hexane	3963.0	4316.9	2390.5	2302.8	1088.7	693.4
n-heptane	14344.9	16081.7	8081.6	8388.1	3282.4	187.0
2,2,4-trimethylpentane	52186.5	53131.6	21809.6	22627.3	6189.1	5218.9
chlorobenzene					17017.4	9869.6

Table 7. Dimensionless Henry Constant Data for Various VOCs at T = 523.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	621.4	786.8	437.3	429.6	166.9	191.3
n-pentane	628.7	736.8	452.3	437.2	248.1	202.3
cyclohexane	1572.6	2437.3	988.6	930.3	343.0	340.4
2-methylpentane	2135.5	2457.5	1384.5	1376.6	432.3	393.7
3-methylpentane	2133.3	2478.0	1398.8	1210.4	436.8	407.3
2,3-dimethylbutane	2136.6	2401.8	1392.2	1398.0	441.0	340.4
n-hexane	2137.6	2328.1	1370.2	1389.6	697.6	451.1
n-heptane	7491.5	7684.9	4248.5	4164.8	1685.5	1015.0
2,2,4-trimethylpentane	22827.7	22505.2	11047.8	10785.7	3242.9	2597.9
chlorobenzene					8591.2	5263.3
toluene					17895.9	10358.3

Table 8. Dimensionless Henry Constant Data for Various VOCs at T = 548.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	405.7	466.4	305.5	286.5	130.0	142.0
n-pentane	406.4	425.7	301.9	293.9	171.8	143.0
cyclohexane	978.8	1421.9	676.3	654.1	240.4	230.6
2-methylpentane	1261.9	1310.0	871.3	825.6	275.2	263.0
3-methylpentane	1288.4	1373.4	811.7	780.9	278.4	273.4
2,3-dimethylbutane	1248.7	1341.3	807.5	841.8	284.4	230.6
n-hexane	1235.4	1249.6	930.6	835.7	403.7	272.0
n-heptane	4364.1	4381.6	2499.8	2405.2	974.2	641.6
2,2,4-trimethylpentane	12449.1	12548.2	6613.1	5935.3	1851.5	1457.1
chlorobenzene	43464.1		31661.6	32642.2	4567.5	2878.2
toluene	59507.0	23938.5	40651.7	43390.3	9045.3	5522.9
m-xylene						13324.3
p-xylene						14280.3

by Zeolist, and NaY 2.43 was provided by Union Carbide. The dealuminated NaY was obtained by treatment of NH4Y with a (NH4)2SiF6 solution at 363 K for 3 h. The obtained material with a Si/Al ratio equal to 3.4 was further exchanged with NaCl solution (see Part 1) to give the Na^+-exchanged dealuminated Y (NaYd).

Nitrogen adsorption−desorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 instrument. The samples were first degassed under a vacuum at 593.15 K for several hours. The Horvath−Kawazoe[18,19] method was used for the determination of the pore volume. The surface areas were determined using the BET equation in the low-pressure region

Table 9. Dimensionless Henry Constant Data for Various VOCs at T = 573.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	267.9	316.7	218.9	195.1	86.12	107.8
n-pentane	275.3	283.8	223.6	202.6	119.2	104.2
cyclohexane	640.3	879.3	460.1	380.9	167.1	169.2
2-methylpentane	787.7	813.0	546.8	547.3	206.4	187.5
3-methylpentane	793.6	847.1	537.7	475.6	211.8	188.0
2,3-dimethylbutane	784.8	829.9	535.0	553.9	213.4	171.0
n-hexane	781.9	780.3	555.8	541.4	263.2	194.4
n-heptane	2264.6	2243.1	1516.9	1348.5	579.9	395.8
2,2,4-trimethylpentane	5922.9	6441.7	3368.4	3428.4	1125.7	918.6
chlorobenzene	21418.7		15056.8	17012.3	2535.6	1749.0
toluene	31060.5	11590.4	20385.9	23267.6	4747.3	3235.2
m-xylene		25538.9			19672.0	7352.9
p-xylene		35791.9			18647.2	7728.5

Table 10. Dimensionless Henry Constant Data for Various VOCs at T = 598.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	195.4	211.0	156.9	146.3	68.35	81.20
n-pentane	195.8	198.5	160.5	152.0	93.16	78.14
cyclohexane	425.6	573.1	296.3	276.0	121.5	129.9
2-methylpentane	511.4	507.6	367.7	377.7	140.8	143.7
3-methylpentane	513.4	527.9	348.1	337.0	143.2	149.0
2,3-dimethylbutane	510.4	517.6	346.4	376.5	146.9	143.6
n-hexane	509.4	488.2	387.2	351.7	171.6	148.6
n-heptane	1326.3	1309.0	901.7	922.6	396.2	265.2
2,2,4-trimethylpentane	3444.8	3407.1	1903.9	1957.4	733.4	596.7
chlorobenzene	11047.0		8691.0	8398.9	1515.8	1096.4
toluene	15873.9	6595.6	11167.0	13275.7	2710.8	1956.8
m-xylene	57805.6	15409.0	41228.0	43902.1	11597.1	4236.7
p-xylene	58025.5	19579.3	40911.7	44676.4	9766.9	4650.8

Table 11. Dimensionless Henry Constant Data for Various VOCs at T = 623.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	131.6	157.1	107.2	107.4	50.66	65.27
n-pentane	131.9	143.7	114.7	110.0	72.18	60.55
cyclohexane	286.6	384.3	222.7	207.0	96.40	95.75
2-methylpentane	332.8	341.4	254.6	254.6	109.1	105.9
3-methylpentane	339.1	350.3	255.0	238.5	111.0	113.4
2,3-dimethylbutane	329.7	345.8	253.8	255.0	111.8	110.8
n-hexane	326.5	332.9	254.1	257.0	121.6	110.9
n-heptane	807.8	794.9	571.8	632.7	268.6	194.0
2,2,4-trimethylpentane	1913.6	1820.5	1284.9	1179.9	489.7	382.2
chlorobenzene	5933.1		5105.7	4913.8	966.1	676.0
toluene	8468.6	4191.5	6556.2	7331.9	1727.0	1161.3
m-xylene	30677.1	9698.1	22812.5	22781.1	5986.7	2610.1
p-xylene	30818.1	11260.6	22185.2	22660.4	5213.8	2791.2

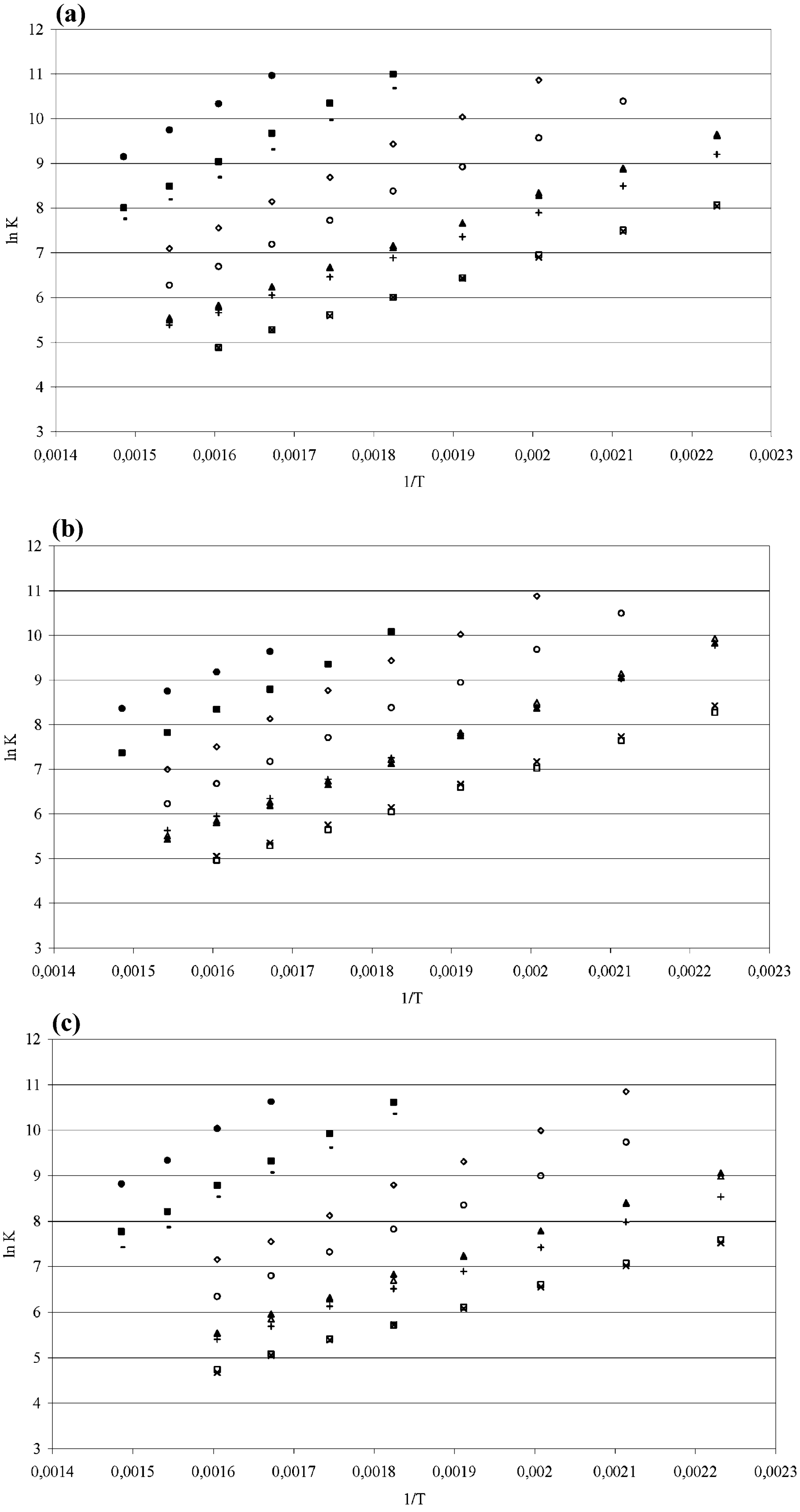
Table 12. Dimensionless Henry Constant Data for Various VOCs at T = 648.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
cyclohexane	218.4	280.7				
2-methylpentane	250.5	238.8				
3-methylpentane	255.6	248.8				
2,3-dimethylbutane	247.9	243.8				
n-hexane	245.3	229.3				
n-heptane	531.2	508.3				
2,2,4-trimethylpentane	1205.7	1094.6				
chlorobenzene	3642.5		2616.9	2912.6	606.9	456.3
toluene	4847.1	2514.6	3697.1	4218.3	1126.0	759.6
m-xylene	17106.4	6335.4	11348.7	12147.4	3260.9	1650.9
p-xylene	17202.9	6769.0	11558.8	11764.6	2881.8	1760.6

(relative pressure between 0.05 and 0.25). The nitrogen adsorption−desorption isotherms, obtained on these materials, are typical of microporous materials with specific surface areas between (485 and 704) $m^2 \cdot g^{-1}$. A decrease in the specific surface area is observed when the Si/Al ratio increases. It is noteworthy that the HK method used can slightly underestimate the pore size opening of the zeolites. More recent methods such as Saito−Foley and NLDFT could be applied for the precise calculation.[20] However, the utilization of the HK method will not change the trend of our present systematic study. Specific surface areas, chemical compositions determined by atomic absorption, and characteristics of all the studied samples are collected in Table 2. Unit cell sizes were determined by X-ray diffraction (experimental error ± 0.0005 nm) at the laboratories of the Institut Français du Pétrole.

Table 13. Dimensionless Henry Constant Data for Various VOCs at T = 673.15 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
chlorobenzene	2340.9		1675.0	1730.3	412.4	312.3
toluene	2990.3	1589.0	2368.0	2670.9	754.2	511.3
m-xylene	9411.7	4277.8	6785.7	7231.3	1898.3	1119.6
p-xylene	9477.8	4231.8	6685.2	7510.6	1715.6	1160.9


(a)
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1/T

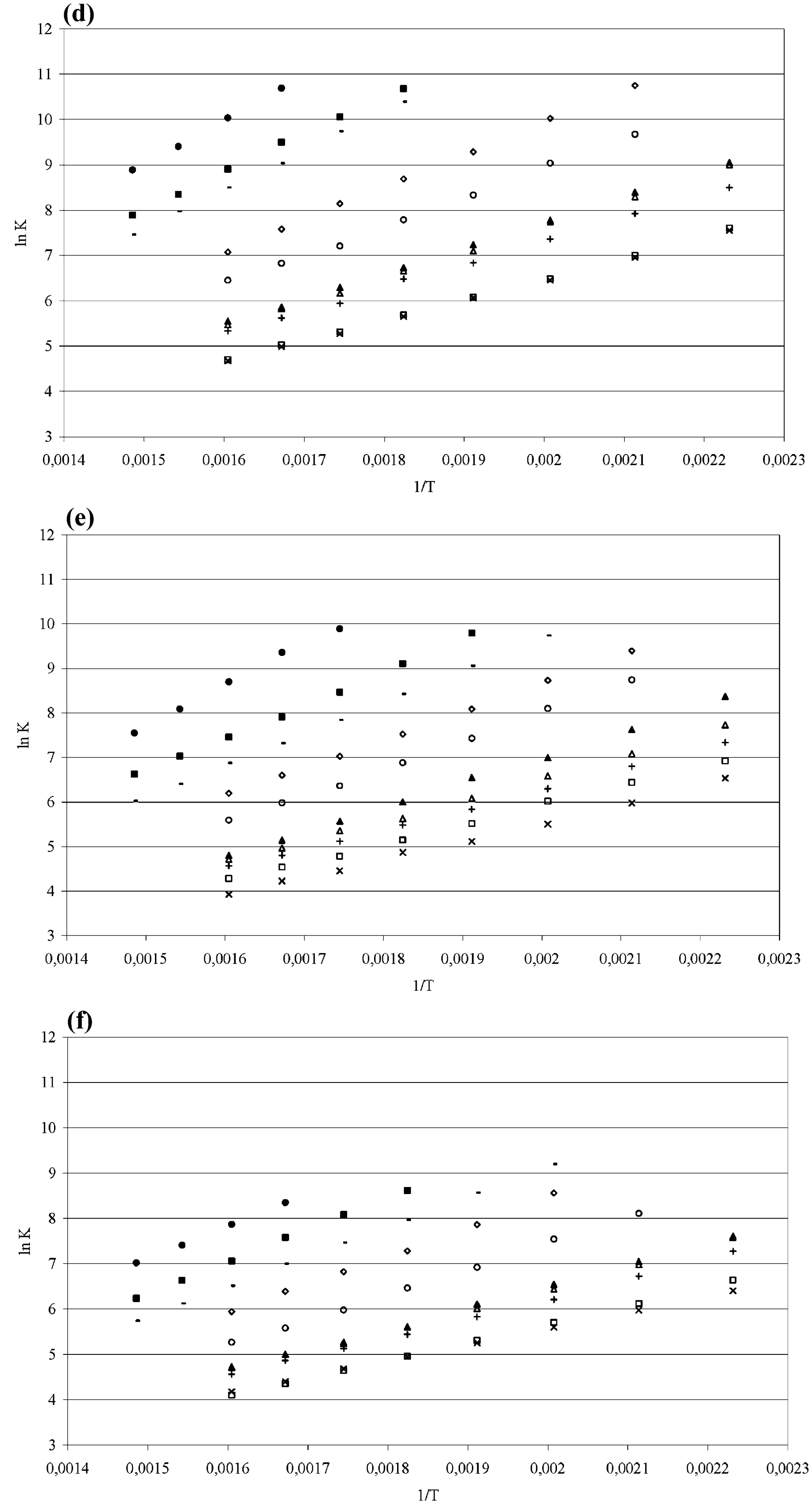
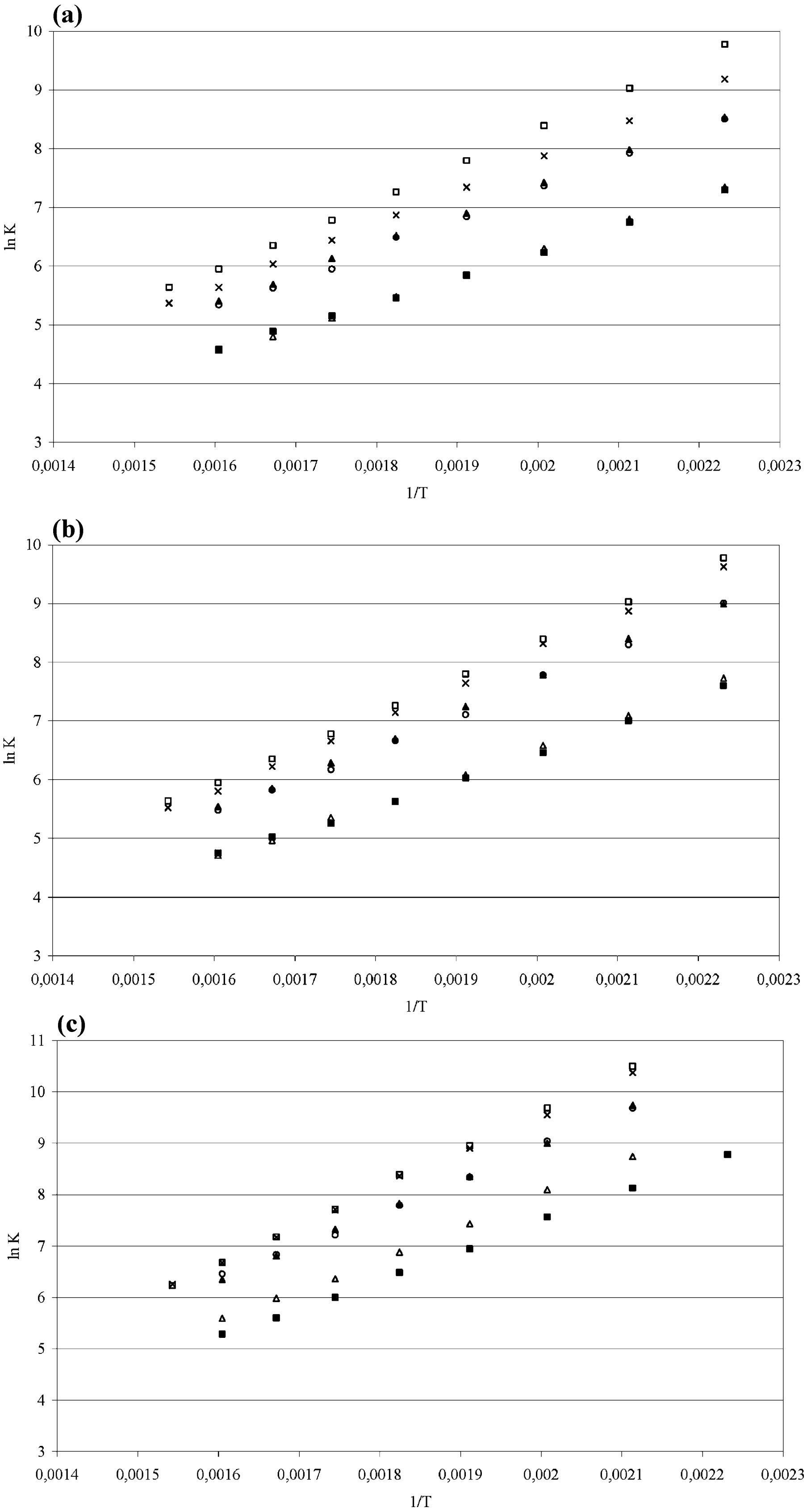


Figure 1. Plot of ln K vs 1/T for (a) LiLSX, (b) KLSX, (c) NaLSX, (d) NaX, (e) NaY 2.4, and (f) NaY 3.4: x, 2-methylbutane; □, *N*-pentane; Δ, 3-methylpentane; ▲, *N*-hexane; ○, *N*-heptane; ◇, 2,2,4-trimethylpentane; +, cyclohexane; -, chlorobenzene; ■, toluene; and ●, *meta*-xylene.

The adsorbents are also characterized by their dehydration factor f defined by

$$f = 1 - \frac{\text{dehydrated mass}}{\text{total mass}} \qquad (6)$$

To measure the hydrated mass, the sample is left in contact with air at room temperature over a period of around 12 h. The dehydration is then performed by raising the temperature to


(a)
ln K
1/T
10
9
8
7
6
5
4
3
0,0014
0,0015
0,0016
0,0017
0,0018
0,0019
0,002
0,0021
0,0022
0,0023
(b)
ln K
1/T
10
9
8
7
6
5
4
3
0,0014
0,0015
0,0016
0,0017
0,0018
0,0019
0,002
0,0021
0,0022
0,0023
(c)
ln K
1/T
11
10
9
8
7
6
5
4
3
0,0014
0,0015
0,0016
0,0017
0,0018
0,0019
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0,0021
0,0022
0,0023

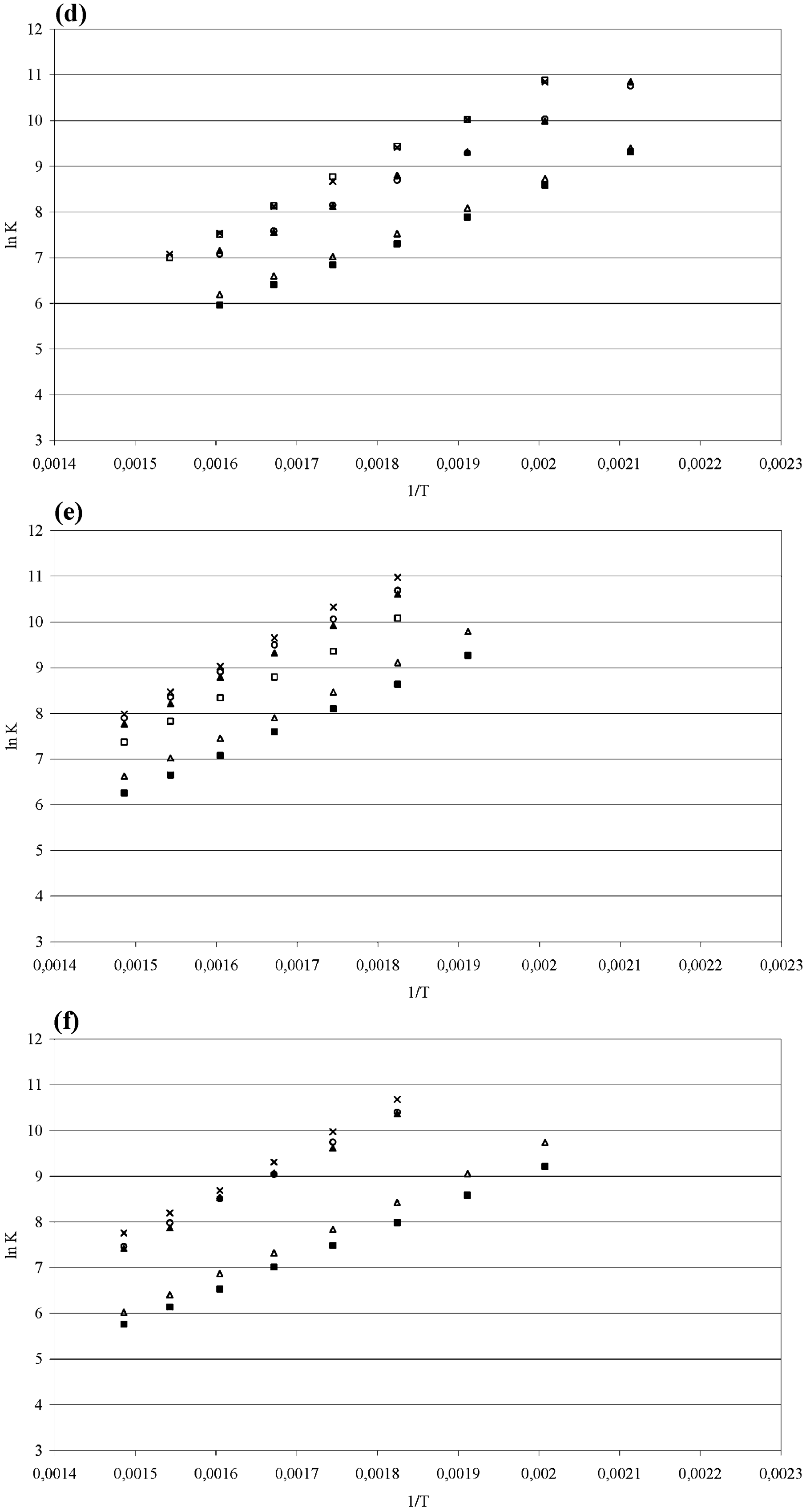

Figure 2. Plot of ln *K* vs 1/*T* for (a) cyclohexane, (b) 3-methylpentane, (c) *N*-heptane, (d) 2,2,4-trimethylpentane, (e) toluene, and (f) chlorobenzene: x, LiLSX; □, KLSX; ▲, NaLSX; ○, NaX; Δ, NaY *2*.4; ■, NaY 3.4.

673.15 K (1 K per minute) in a chromatograph oven under a helium flow.

All these characteristics are given in Tables 2 and 3.

Adsorbates. The studied probes are alkanes (2-methylbutane, *n*-pentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, *n*-hexane, *n*-heptane, 2,2,4-trimeth-

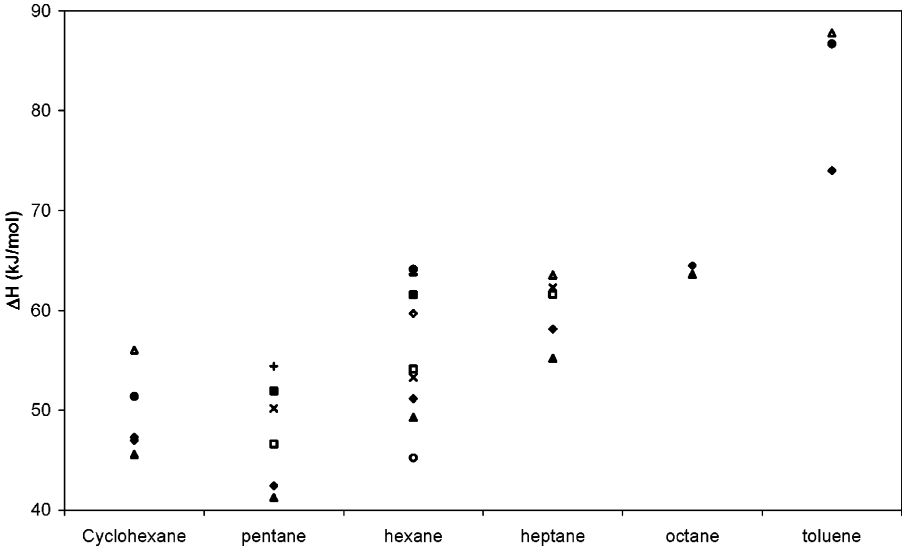

Figure 3. Comparison of some adsorption enthalpies for NaX and various hydrocarbons: ◆, this work; ◇, Inel et al., 2002; Δ, Ruthven; ●, Ruthven; ×, Askin and Inel, 2001; ■, Kiselev; +, Dubinin; ○, Eberly; □, Tarek et al., 1995; ▲, Diaz et al., 2004; -, Fiedler.

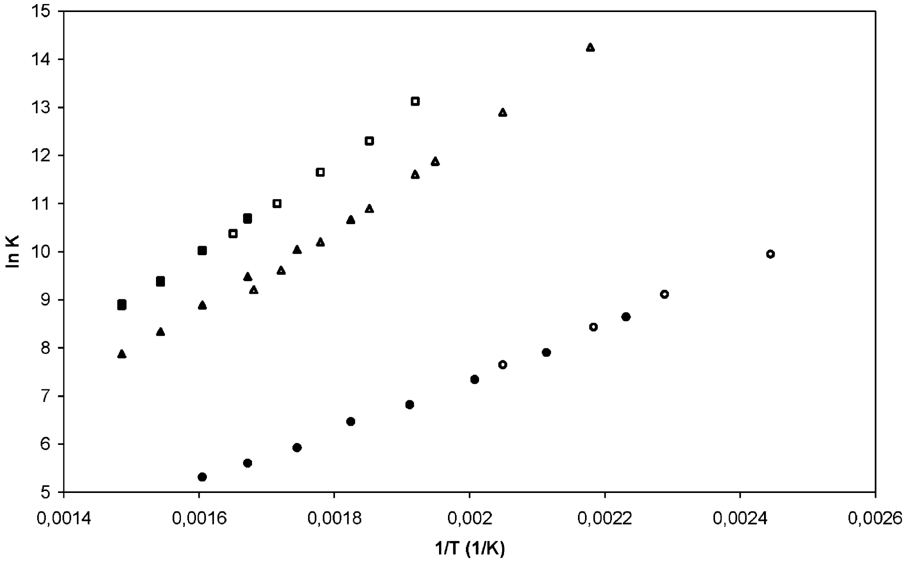

Figure 4. Comparison of Henry constants between ref 11 and our work (full symbol) on NaX: ○●, cyclohexane; Δ▲, toluene; □■, xylene.

Table 14. Pre-exponential Factor of the van't Hoff Equation for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	0.042418	0.025646	0.082864	0.071407	0.072204	0.216315
n-pentane	0.038904	0.027470	0.078898	0.069849	0.068694	0.091840
cyclohexane	0.039617	0.023572	0.067994	0.053514	0.070038	0.095889
2-methylpentane	0.019370	0.010362	0.032133	0.033180	0.046755	0.062958
3-methylpentane	0.022184	0.010940	0.030183	0.025185	0.045394	0.070370
2,3-dimethylbutane	0.019312	0.010642	0.030031	0.032224	0.051577	0.142137
n-hexane	0.021361	0.011050	0.034050	0.029694	0.013604	0.057325
n-heptane	0.007942	0.004970	0.014838	0.018976	0.011294	0.020658
2,2,4-trimethylpentane	0.004279	0.003060	0.010940	0.011351	0.018581	0.013200
chlorobenzene	0.005466		0.004455	0.004435	0.010005	0.016810
toluene	0.005083	0.013328	0.009045	0.011985	0.011639	0.013730
m-xylene	0.005239	0.155600	0.003000	0.003729	0.002387	0.026128
p-xylene	0.005410	0.020905	0.003175	0.004015	0.001837	0.017951

ylpentane, cyclohexane) and aromatic compounds (toluene, *meta*-xylene, *para*-xylene, and chlorobenzene).All compounds are HPLC grade with purity higher than 99 % (toluene purity is higher than 99.8 %, and the purity of 2,2,4-trimethylpentane and cyclohexane is higher than 99.5 %).

The carrier gas used is nitrogen, as no different behavior is observed by using helium or nitrogen.

Results

Adsorption Parameters. The experimental determinations of the Henry constants were achieved at temperatures ranging from (448.15 to 623.15) K for alkanes, from (523.15 to 673.15) K for toluene, from (498.15 to 673.15) K for chlorobenzene, and from (573.15 to 673.15) K for xylenes. Data points were taken at temperature intervals of 25 K.

Table 15. Adsorption Energy $-\Delta U$ (kJ·mol^{-1}) for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	41.76	44.91	37.39	37.82	33.91	29.55
n-pentane	42.22	44.17	37.77	38.07	35.80	33.54
cyclohexane	46.16	50.28	41.87	42.60	37.15	35.66
2-methylpentane	50.57	53.75	46.48	46.31	39.88	38.22
3-methylpentane	50.06	53.74	46.66	47.18	40.10	37.87
2,3-dimethylbutane	50.55	53.68	46.66	46.50	39.56	34.07
n-hexane	50.11	53.31	46.30	46.76	47.01	38.94
n-heptane	59.86	62.12	54.79	53.63	51.95	47.14
2,2,4-trimethylpentane	67.55	69.09	60.29	59.97	52.59	53.16
chlorobenzene	72.30		71.88	72.09	59.39	55.01
toluene	74.29	65.41	69.77	68.97	61.76	58.88
m-xylene	80.70	57.20	81.83	80.94	76.19	59.64
p-xylene	80.56	68.38	81.49	80.57	76.94	61.96

Table 16. Adsorption Enthalpy $-\Delta H$ (kJ·mol^{-1}) at 573 K for LiLSX, NaLSX, KLSX, NaX, and NaY

	LiLSX	KLSX	NaLSX	NaX	NaY 2.4	NaY 3.4
2-methylbutane	46.52	49.68	42.15	42.59	38.67	34.31
n-pentane	46.99	48.93	42.53	42.83	40.56	38.30
cyclohexane	50.93	55.05	46.63	47.36	41.91	40.42
2-methylpentane	55.33	58.52	51.24	51.08	44.64	42.98
3-methylpentane	54.82	58.50	51.43	51.94	44.86	42.64
2,3-dimethylbutane	55.32	58.44	51.43	51.27	44.32	38.83
n-hexane	54.87	58.08	51.07	51.53	51.77	43.71
n-heptane	64.63	66.88	59.55	58.39	56.72	51.91
2,2,4-trimethylpentane	72.31	73.85	65.05	64.74	57.35	57.93
chlorobenzene	77.06		76.64	76.85	64.15	59.78
toluene	79.06	70.18	74.53	73.73	66.53	63.65
m-xylene	85.47	61.97	86.60	85.70	80.96	64.40
p-xylene	85.32	73.14	86.26	85.34	81.70	66.73

The temperature dependence of the Henry constants for alkanes and aromatics on faujasites is presented in Tables 4 to 13 at temperatures from (448.15 to 673.15) K.

Figure 1a,b,c,d,e,f presents plots of the logarithm of the Henry constant vs inverse temperature for all adsorbates on a given zeolite.

Figure 2a,b,c,d,e,f presents plots of the logarithm of the Henry constant vs inverse temperature for a given adsorbate on all zeolites.

For all faujasite zeolites and all compounds (alkanes and aromatics), the plots of ln K vs $1/T$ for the temperature range studied have a linear trend. All plots are straight lines ($r^2 > 0.9995$).

We give the pre-exponential factor and the adsorption energy of the van't Hoff law in Tables 14 and 15. The adsorption enthalpy at 573.15 K is also given in Table 16.

For all compounds, the adsorptive behavior is almost the same for NaX and NaLSX. For the most adsorbed compounds (toluene, xylenes), the Henry constant is lower for NaLSX than for NaX.

For alkanes, when the number of carbon atoms of the adsorbate increases, the Henry constant on a given zeolite increases. A similar trend was already found for NaY 2.7.[3] Toluene is more adsorbed than 2,2,4-trimethylpentane and less adsorbed than the xylenes. For *meta*- and *para*-xylene, any interesting selectivity can be seen on zeolites used; that is, Henry's constants are almost the same on each sample.

The accessibility to the microporous network has been taken into account by adsorbing molecules with different molecular size and structure (linear, monobranched, and dibranched alkanes). The Henry constants and adsorption enthalpies, which are almost the same for *n*- and iso-alkanes on each zeolite LSX and X, fail to show any thermodynamic and kinetic selectivity. Whereas for Y zeolites, there is a small difference on K. Also, an interesting selectivity is found for the separation of *n*-/iso-alkanes. This selectivity at low coverage increases when the temperature decreases and reaches 1.9 at 448 K.

The selectivity factor is defined as the ratio of the Henry constants of two compounds under the same experimental conditions.

Discussion

Some previous work[6,7,11,12,14] for many hydrocarbons only on 13X (NaX) can be found in the literature. The majority of measurements were done using the pulse chromatography technique. The deviation of experimental adsorption heat is very significant (~30 %) and reaches 20 kJ·mol^{-1} as shown by Figure 3. More recently, some interesting results[6] were published on pentane, hexane, heptane, octane, and cyclohexane with adsorption enthalpies of, respectively, (41.25, 49.28, 55.19, 63.62, and 45.56) kJ·mol^{-1}. These results are close to the adsorption enthalpies presented here. The comparison between Henry's constants and heat of adsorption data[11] on NaX leads to a very good agreement of cyclohexane and xylenes as presented in Figure 4. The deviation on heat of adsorption is, respectively, (4 and 3) kJ·mol^{-1}. For toluene, the shape is slightly different and gives a deviation around 12 kJ·mol^{-1} for ΔU. Other previous works[17,21,22] on the comparison of the toluene Henry constant show a good agreement at high temperature between the two experimental techniques (chromatography and gravimetry), as in the range (230 to 350) °C, the maximum deviation on the Henry constant is 15 % and the average deviation is 7.5 %.

With the zeolites used in this study, it can be seen that when the Si/Al ratio decreases the Henry constant increases for a given compound as mentioned recently.[23] If the Si/Al ratio decreases, the number of compensating cations or adsorption sites increases. Then if the number of adsorption sites increases, the negative charge of oxygen atoms in the zeolitic framework increases;[24] therefore, interactions between the porous media and the adsorbate are more important, and Henry's constants must be higher. As the number of adsorption sites is higher, the adsorbate is more attracted by the zeolite so the adsorption heat at zero coverage is high: the smaller the compensating cation is, the higher the Henry constant and the heat of adsorption are (this is observed for all compounds except for xylenes where the adsorption heat is quite close for NaLSX and LiLSX but lower for KLSX).

There is a large difference of K between X and Y zeolites: when Si/Al goes from 2.4 to 1.2, the Henry constant is multiplied by around 2, whereas when Si/Al goes from 3.8 to 2.4, the Henry constant is multiplied by around 1.2. The main difference between the X-type faujasite and NaY is the occupancy of site III by Na compensating cations.[10,23] The increase of the site numbers and location explain the large difference of K observed between X and Y zeolites for the adsorption of hydrocarbons.

Conclusion

In this paper, we present adsorption data for nine alkanes (linear and branched) and four aromatic and chlorinated compounds on various faujasite zeolites in the low partial pressure domain (in the Henry region) under catalytic temperatures ranging from (448.15 to 673.15) K.

These measurements have been obtained using the well-known pulse chromatography. Some comments relating these results to the structural characteristics of the adsorbent are provided. More significant is that the Henry constant increases with rising Si/Al ratio and probe molecule carbon number.

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