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Determining Volatile Organic Compounds' Adsorption Isotherms on Dealuminated Y Zeolite and Correlation with Different Models

Taoufik El Brihi, Jean-Noël Jaubert,* and Danielle Barth

Laboratoire de Thermodynamique des Séparations, Institut National Polytechnique de Lorraine,
Ecole Nationale Supérieure des Industries Chimiques, 1 Rue Grandville, 54000 Nancy, France

Laurent Perrin

Laboratoire de Chimie Physique Macromoléculaire, INPL, ENSIC, CNRS UMR 7568, 1 Rue Grandville,
54000 Nancy, France

Adsorption isotherms of two volatile organic compounds, toluene and *m*-xylene, on dealuminated Y zeolite (DAY) were measured at (25, 35, 45, and 55) °C using a vacuum microbalance system. The experimental data obtained were correlated with different existing adsorption isotherm models such as the Langmuir model and the Freundlich model.

Introduction

From an environmental point of view, it is necessary to limit and control vapor emissions because they affect the change of climate, the growth and decay of plants, and the health of human beings and of all animals. Environmental protection regulations for volatile organic compounds' (VOCs') emission, introduced under the 1990 Clean Air Act amendments, have accelerated the development of VOCs' abatement systems. Add-on control techniques are broadly classified into two types: destruction (biofiltration, thermal oxidation, catalytic oxidation, reverse flow reactor) and recovery (adsorption, condensation, membrane separation).[1] Among these methods, zeolite adsorption is widely used. In this study, the considered zeolite, is a dealuminated Y zeolite, here abbreviated as DAY zeolite. This zeolite is a relatively new zeolite, and it exhibits the FAU (faujasite) structure. It has a 3-dimensional pore structure. The pore diameter is large (7.4 Å), since the aperture is defined by a 12 member oxygen ring and leads into a larger cavity[2] of diameter 12 Å.

A comparison of the properties of this material with those of the activated carbon, which is the common commercial adsorbent, was given by Otten et al.[3] The advantages of this and in general those of the dealuminated faujasites are essentially its incombustibility, its great stability, its hydrophobic character, and its regenerability at low temperature.[4,5] In comparison, the activated carbon shows some inconveniences:[3] it is a flammable material, it does not desorb efficiently high-boiling solvents, and it is a hygroscopic material requiring relative humidity control. Moreover, zeolite systems offer improved safety, simplicity of operation, and easy maintenance, explaining why the adsorption on hydrophobic zeolite is one effective solution for the removal of VOCs.[3,4] However, the application of zeolite for removal of VOCs has only recently gained attention.[6,7] There are relatively limited studies done on hydrophobic zeolites as adsorbents for VOCs. Sakuth et al.[8] have shown the influence of the surface polarity on the adsorbate phase composition containing a polar and a nonpolar component, toluene and 1-propanol, respectively. They have used a flow-type apparatus for vapor adsorption experiments. Ryu et al.[9] measured the adsorption equilibrium of toluene and gasoline vapors on DAY zeolite F-20 by a static volumetric method. Bathen et al.[10] measured isotherms for the system zeolite DAY/ethanol/air by using the desorptive method. In this work, the vapor adsorption properties of toluene and *m*-xylene were studied in Wessalith DAY zeolite F20. Adsorption isotherms were measured at four different temperatures using a vacuum microbalance system: (25, 35, 45, and 55) °C. The experimental data obtained were correlated with the following adsorption isotherms: Langmuir and Freundlich.

Table 1. Physical Properties of *m*-Xylene and Toluene

	m-xylene	toluene
molecular weight, MW/g·mol^{-1}	106.7	92.14
normal boiling point, T_{eb}/°C	139.1	110.6
vapor pressure, P^s/kPa	1.126	3.794
298 K	1.962	6.235
308 K	3.279	9.875
318 K	5.283	15.13
328 K		
liquid density at 20 °C, ρ_{liq}/g·cm^{-3}	0.836	0.867

Experimental Section

The VOCs selected in this study were toluene (mass fraction 0.99 purity) and *m*-xylene (mass fraction 0.98 purity). They were respectively purchased from Carlo Erba and Aldrich. The physical properties of these VOCs are listed in Table 1. DAY zeolites samples were supplied by Degussa-Hüls, which uses a proprietary process in which a special silicon tetrachloride treatment yields a Y zeolite with almost all of the aluminium sites occupied by silicon. The samples were in the form of solid extrudates (diameter = 2 mm). This zeolite allows the adsorption of VOCs from polluted air without exhausting the capacity by adsorbing water vapor. In comparison with activated carbon, this zeolite exhibits an extremely low water uptake (the standard water adsorption value according to Degussa is 5

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* To whom correspondence should be addressed. E-mail: jean-noel.jaubert@ensic.inpl-nancy.fr. Fax number: +33 3 83 17 51 52.

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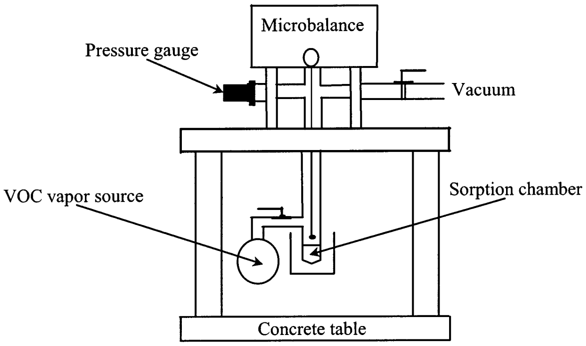

Figure 1. Schematic description of the electromagnetic suspension microbalance.

Table 2. Adsorbent Properties

property	value
loss on ignition/%	3.38
BET surface area/m^2·g^{-1}	615
micropore volume/cm^3·g^{-1}	0.250
macropore and mesopore volume/cm^3·g^{-1}	0.539
binder amount/mass %	17
bulk density/g·cm^{-3}	0.496
particle density/g·cm^{-3}	0.809
external void porosity (ϵ_I)	0.387
particle porosity (ϵ_P)	0.436
bed porosity (ϵ_B)	0.654

g/100 g at $P/P^s = 0.07$). DAY zeolites are nonflammable and stable at temperatures up to 1000 °C. Due to the high Si/Al ratio, these zeolites are unchanged by strong mineral acids and aggressive gases.[11]

The loss on ignition was measured by thermogravimetry under helium flow using a SeTaram Tag 24 apparatus. The low measured value (3.38%), obtained after water vapor equilibrium, is due to the hydrophobic character of this zeolite. The BET surface area, micropore volume, and binder amount of the DAY zeolite sample used were measured with a ϕ-Sorb from the GIRA Society using liquid nitrogen at $T = 77$ K. The apparent density, the macropore and mesopore volumes, the external void porosity, the particle porosity, the bed porosity, and the particle density were determined by porosimetry using a Micromeritics apparatus. Unfortunately, we were not able to determine the Si/Al ratio. The measured physical properties of the DAY zeolite are listed in Table 2.

A SARTORIUS 4201 electromagnetic suspension microbalance was installed for the measurement of the adsorbed quantities of vapors in zeolites. It has a ±0.01 mg resolution and a ±0.02 mg precision, for a measuring full scale of 100.00 mg. A schematic diagram of the apparatus is shown in Figure 1. The temperatures of the VOC vapor, of the sorption chamber, and of the magnet chamber were separately controlled.

In a typical experiment, about 15 mg of DAY zeolite was evacuated at 60 °C under 0.01 Pa during 2 days. Such a procedure was followed according to the previous work by Otten et al.,[3] who explained that the DAY zeolite could be completely regenerated in such conditions. Then the VOC vapor source was connected to the sorption chamber. The mass was digitized and monitored as a function of time by a computer. The mass was obtained by averaging five mass values acquisitioned at 0.1 s intervals around the time point (one point every 1 s). The background noise, averaged by means of a statistical function in the assistant software, was subtracted from the measured values. By this way, smooth, reproducible sorption curves were obtained. The sorption experiments were carried out below atmospheric pressure, and the sample mass was measured over a large range of vapor pressures. To avoid any condensation of VOC in the gas phase, the pressure of the VOC (P_{VOC}) was kept lower than the VOC saturated vapor pressure (P^s) at the sorption chamber temperature. Attention was paid to maintain $P_{VOC} < 0.8P^s$. The VOC saturated vapor pressures, listed in Table 1, were calculated using the following equation:[12]

$$P^s/\mathrm{Pa} = 10^{(A+(B/T)+C\cdot\log_{10}(T)+DT+ET^2)} \tag{1}$$

where A, B, C, D, and E are compound dependent parameters.

Results and Discussion

The adsorbed amounts for pure *m*-xylene and toluene at four different temperatures on DAY zeolite are summarized in Tables 3 and 4. In comparison with the results obtained by the volumetric method,[9] the values of the saturation limit are quite similar (more or less 5%). However, one observes higher differences in the adsorption capacities at low pressures (more or less, 15%). This can be due essentially to two factors. First factor: Ryu et al.[9] used a volumetric method in order to determine the adsorbed quantities whereas a gravimetric method was used in this study. These two techniques present difficulties in the measurement of the adsorption capacities at low pressures. However, in the volumetric method, the accuracy of the data depends on the precision with which the equilibrium pressure is measured. Besides, the existence of dead volume, the value of which is never known with high precision, is a source of error. That is why the gravimetric method remains the most accurate method for measuring gas−solid equilibrium data for pure gases. Second factor: the ratio Si/Al which influences the ad-

Table 3. Experimental Adsorption Isotherms of Toluene on DAY Zeolite Measured with a Microbalance

$t = 25$ °C		$t = 35$ °C		$t = 45$ °C		$t = 55$ °C	
P^a/Pa	q^b/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}
208.3	1.014 ± 0.001	216.4	0.850 ± 0.001	208.3	0.780 ± 0.001	224.9	0.790 ± 0.001
404.4	1.285 ± 0.001	404.4	1.065 ± 0.001	224.9	0.799 ± 0.001	281.6	0.859 ± 0.001
653.5	1.386 ± 0.001	563.8	1.158 ± 0.001	281.6	0.913 ± 0.001	653.5	1.083 ± 0.001
1312	1.449 ± 0.001	662.2	1.195 ± 0.001	404.4	1.027 ± 0.001	1312	1.219 ± 0.001
2615	1.516 ± 0.001	1198	1.307 ± 0.001	653.5	1.150 ± 0.001	2215	1.279 ± 0.001
2994	1.520 ± 0.001	2215	1.377 ± 0.001	1198	1.249 ± 0.001	2994	1.293 ± 0.001
		2994	1.387 ± 0.001	1312	1.258 ± 0.001		
				2215	1.325 ± 0.001		
				2615	1.339 ± 0.001		
				2994	1.344 ± 0.001		

[a] P is the pressure of toluene in the sorption chamber. [b] q is the equilibrium number of moles of toluene adsorbed per kilogram of DAY zeolite.

Table 4. Experimental Adsorption Isotherms of *m*-Xylene on DAY Zeolite Measured with a Microbalance

t = 25 °C		t = 35 °C		t = 45 °C		t = 55 °C	
P^a/Pa	q^b/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}
21.77	1.233 ± 0.001	23.86	1.250 ± 0.001	26.13	1.150 ± 0.001	26.13	1.096 ± 0.001
26.13	1.304 ± 0.001	37.21	1.330 ± 0.001	44.30	1.240 ± 0.001	48.23	1.173 ± 0.001
48.23	1.469 ± 0.001	48.23	1.363 ± 0.001	85.69	1.273 ± 0.001	147.0	1.254 ± 0.001
61.98	1.526 ± 0.001	79.11	1.393 ± 0.001	158.3	1.292 ± 0.001	211.8	1.269 ± 0.001
85.69	1.582 ± 0.001	160.7	1.445 ± 0.001	344.4	1.319 ± 0.001	356.2	1.282 ± 0.001
112.7	1.629 ± 0.001	344.4	1.450 ± 0.001			657.5	1.282 ± 0.001
147.0	1.654 ± 0.001	864.9	1.455 ± 0.001			864.9	1.292 ± 0.001
158.3	1.667 ± 0.001						
261.8	1.696 ± 0.001						
344.4	1.710 ± 0.001						
657.5	1.733 ± 0.001						

[a] P is the pressure of m-xylene in the sorption chamber. [b] q is the equilibrium number of moles of m-xylene adsorbed per kilogram of DAY zeolite.

Table 5. Langmuir Parameters for Pure VOC Adsorption on DAY Zeolite

t/°C	parameter	toluene	m-xylene
25	q_m/mol·kg^{-1}	1.583	1.747
	b/Pa^{-1}	0.00933	0.111
	Δq/%	1.58	0.38
35	q_m/mol·kg^{-1}	1.470	1.461
	b/Pa^{-1}	0.00646	0.299
	Δq/%	0.43	0.78
45	q_m/mol·kg^{-1}	1.425	1.332
	b/Pa^{-1}	0.00603	0.255
	Δq/%	1.01	0.58
55	q_m/mol·kg^{-1}	1.369	1.296
	b/Pa^{-1}	0.00599	0.206
	Δq/%	0.40	0.22
overall avg deviation/%		0.86	0.47

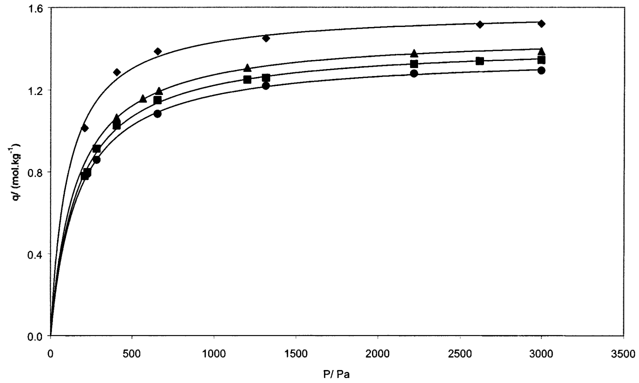

Figure 2. Correlation of the experimentally determined toluene adsorption isotherms with the Langmuir model (—) at four temperatures: ◆, T/K = 298.15; ▲, T/K = 308.15; ■, T/K = 318.15; ●, T/K = 328.15.

sorbed quantity[13] may vary between 1 and 20 for the Wessalith DAY zeolite F20.[9] This means that two samples of the same commercial zeolite may have different Si/Al ratios. Unfortunately, we were not able to measure such a ratio as well as Ryu et al.[9] It is thus highly probable that both zeolites were different. Moreover, it is well-known that the binder content and the crystallinity also affect the adsorbed quantities. Because none of these values are given by Ryu et al.,[9] it is impossible to know whether the same zeolite was used. For this reason, comparison of our data with those of Ryu et al.[9] is very difficult.

To correlate our experimental VOC adsorption data, the Langmuir and the Freundlich equations were used.

Langmuir Equation. The Langmuir model supposes that the molecules of gas and the adsorbed molecules are in dynamic equilibrium. One assumes that the adsorbed molecules do not interact and that the surface covers itself gradually with a monolayer.[14] If q is the adsorbed quantity (moles of VOC per kilogram of DAY zeolite) and P is the pressure of the adsorbate in the sorption chamber, the Langmuir isotherm can be written as

$$q = q_m \frac{bP}{1 + bP} \tag{2}$$

where q_m represents the quantity of gas required to cover one gram of adsorbent with a monomolecular layer. This quantity is reached only at infinite pressure. b represents the Langmuir constant. This parameter depends on the temperature: it decreases with increase of temperature, according to a relation of the type

$$b = A \exp\left(\frac{B}{T}\right) \tag{3}$$

where A and B are constants and T is the absolute temperature.

The Langmuir isotherm verifies Henry's law for the low pressures. Indeed, the limiting slope of this isotherm at low pressures is

$$\lim_{P\to 0} \frac{dq}{dP} = \lim_{P\to 0} \frac{q_m b}{(1 + bP)^2} = q_m b \tag{4}$$

To correlate our data, b and q_m were numerically determined at each temperature by minimizing the following objective function:

$$\mathrm{OF} = \sum_{i=1}^{n_{\exp}} |q_{\exp} - q_{\mathrm{calc}}|^2 \tag{5}$$

In eq 5, q_{calc} is the calculated adsorbed quantities at experimental pressure P. $q_{\exp}$ is the experimental adsorbed quantities at experimental pressure P. $n_{\exp}$ is the number of experimental points at a given temperature. The parameters obtained and the corresponding percent deviations (Δq/%) are summarized for each temperature and for both VOCs in Table 5. Such deviations were classically determined by

$$\Delta q/\% = \frac{100}{n_{\exp}} \sum_{i=1}^{n_{\exp}} \left| \frac{q_{\exp} - q_{\mathrm{calc}}}{q_{\exp}} \right| \tag{6}$$

The corresponding calculated adsorption isotherms are shown in Figures 2 and 3. The present investigation showed that the Langmuir equation gives a good fit for both

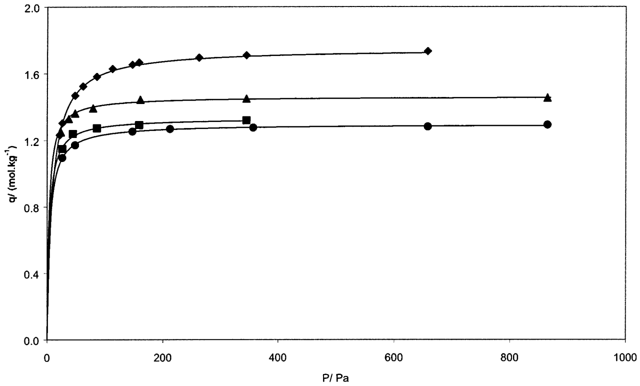

Figure 3. Correlation of the experimentally determined *m*-xylene adsorption isotherms with the Langmuir model (—) at four temperatures: ◆, T/K = 298.15; ▲, T/K = 308.15; ■, T/K = 318.15; ●, T/K = 328.15.

Table 6. Adsorption Data for the Adsorption of Pure *m*-Xylene and Toluene on DAY Zeolite at $P/P^s = 0.1$ Expressed in Moles of Adsorbate per Kilogram of Zeolite

	adsorption capacity at $P/P^s = 0.1$			
	m-xylene		toluene	
t/°C	$q_{0.1}$/mol·kg^{-1}	% q_m	$q_{0.1}$/mol·kg^{-1}	% q_m
25	1.618	92.61	1.234	76.25
35	1.436	98.29	1.177	78.36
45	1.316	98.79	1.219	85.53
55	1.284	99.07	1.233	90.74

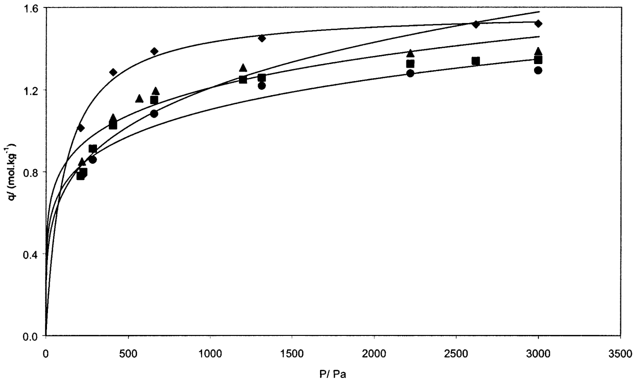

Figure 4. Correlation of the experimentally determined toluene adsorption isotherms with the Freundlich model (—) at four temperatures: ◆, T/K = 298.15; ▲, T/K = 308.15; ■, T/K = 318.15; ●, T/K = 328.15.

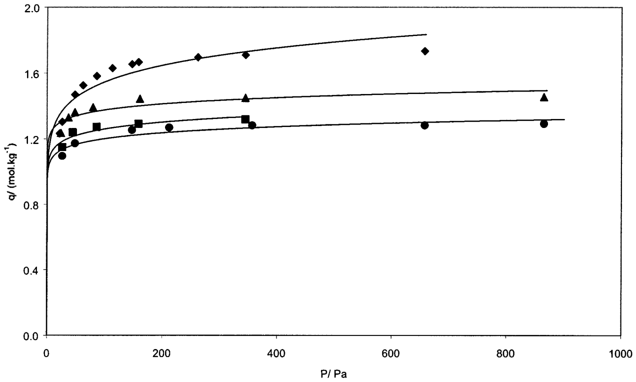

Figure 5. Correlation of the experimentally determined *m*-xylene adsorption isotherms with the Freundlich model (—) at four temperatures: ◆, T/K = 298.15; ▲, T/K = 308.15; ■, T/K = 318.15; ●, T/K = 328.15.

systems. Indeed, the overall average deviation calculated from eq 6 with n_{exp} being equal to the total number of data points and given in Table 5 is less than 1% for both VOCs. The mechanism of VOC adsorption is by volume filling of zeolite micropores by physical adsorption.[15] The VOC isotherms are of type I according to the IUPAC classification.[16] The toluene and the *m*-xylene belong to the same chemical family, so the toluene saturation amount adsorbed is close to that of the *m*-xylene. The slope of these isotherms, at low adsorptive pressures and at low temperature, is very steep. Indeed, the values of experimental adsorbed quantities at $P/P^s = 0.1$, listed in Table 6, for the both VOCs are close to those obtained at saturation. So the first molecules are adsorbed at low pressures and it was difficult to obtain data at very low pressure. That is why the values of the parameters b are not very precise. Nevertheless, the *m*-xylene parameter b is higher than that of toluene, which indicates that the affinity of DAY zeolite for *m*-xylene is stronger than that for toluene.

Freundlich Isotherm. Another relation that is often used to describe adsorption is the Freundlich isotherm.[17] It is an empirical relation. The Freundlich equation is represented as

$$q = KP^{1/n} \tag{7}$$

where K and n are empirical constants characteristic of the gas−adsorbent couple. This equation does not reduce to Henry's law at low pressure. Indeed, the Freundlich equation has an infinite slope at the origin:

$$\lim_{P\to 0} \frac{\mathrm{d}q}{\mathrm{d}P} = \lim_{P\to 0} \frac{KP^{1/n-1}}{n} = \infty \tag{8}$$

The two constants (K and n) were determined by minimizing the objective function defined in eq 5. The corresponding calculated adsorption isotherms are shown in Figures 4 and 5. From these figures, it is possible to assert that the Freundlich model is not suitable to the description of both VOCs' adsorption on DAY zeolite.

Conclusion

Adsorption isotherms of toluene and *m*-xylene on DAY zeolite were measured at four different temperatures ranging from 25 °C to 55 °C. DAY zeolite was used because it offers many practical advantages, such as, for example, total regeneration at low temperature.

The results were correlated with the Langmuir and the Freundlich models. The Langmuir model was found to be suitable to describe the adsorption of VOCs on DAY zeolite at all four temperatures. The Freundlich model was not satisfactory.

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