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Determination of the Henry Constant for Zeolite-VOC Systems Using Massic and Chromatographic Adsorption Data

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Abstract. Both the inverse gas chromatographic method and the dynamic gravimetric-calorimetric method were tested in order to determine the Henry constant for toluene on a Na-faujasite type zeolite. We used the pulse technique for the chromatographic method and a system generating low concentration of VOC in a helium flow for the gravimetric technique. The experimental determinations of the Henry constants for toluene were achieved in two different temperature ranges (from 363 to 548 K for gravimetry and from 548 to 673 K for chromatography). The results presented in this paper show the complementarity of two different techniques for the Henry constants determination. The Henry constants obtained with the two techniques at 548 K differ from 8%.

Keywords: adsorption, chromatography, gravimetry, VOC, zeolites, Henry constant

1. Introduction

The determination of adsorption isotherms in the low partial pressure range for zeolite—Volatile Organic Compound (VOC) systems is of prime importance for industrials and scientists. Adsorption on microporous solids is a well known technique for gas purification (VOC removal). Consequently, the measurement of experimental data in the low pressure range is the first step of any industrial process sizing. Moreover, these data are quite important to understand adsorption mechanisms of the first molecules in the zeolite cages. Generally, isotherms for this kind of systems are of type I. They have a strong initial slope and a plateau covering almost all the partial pressure domain. It is quite difficult to measure the first points of the isotherm because the initial slope is in the very low partial pressure zone. Theretofore, the most used technique for this kind of measurement is pulse chromatography. It allows easy and fast measurements but its use is often limited to high temperatures (down to 423 K). The dynamic gravimetry technique can be used in a larger temperature domain (from 673 K down to ambient temperature) if an efficient system generating low VOC partial pressure in helium is used.

In this work, we present adsorption data in the very low pressure region obtained with these two experimental techniques: the dynamic gravimetry and the inverse gas chromatography. We studied a Na-faujasite type zeolite NaY (with a Si/Al ratio of 2.43)—Toluene system. The experimental measurements of the Henry constants for toluene were achieved in two different temperature ranges (363 to 548 K for gravimetry and from 548 to 673 K for chromatography).

2. Experimental Techniques

2.1. Chromatographic Method

The chromatographic method has been used, described and explained in details in many previous works: (Ruthven, 1984; Ruthven and Kaul, 1993; Denayer and Baron, 1997; Denayer et al., 1998a and b; Askin and Inel, 2001 or Tümsek and Inel, 2003) so that, we will just give a short summary of the experimental procedure.

The column filled with the adsorbent is placed in the oven of a HP 5890 chromatograph equipped with a

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TCD detector. Before any measurement, the temperature was raised to 648 K with a rate of 1 K per minute and maintained at this temperature during a night under a flow of inert gas in order to regenerate the adsorbent. A mass flow controller (0–10 Nl/h) was used to regulate the flow of carrier gas (helium or nitrogen). After this regeneration step, the temperature is set to the experimental temperature. The used toluene is a HPLC grade (99.8%). Toluene is injected with a syringe in the heated injector, pass through the column where it is adsorbed and desorbed and goes to the Thermal Conductivity Detector.

The experimental run provides the toluene concentration profile in helium at the column outlet. The first moment (retention time) of this profile is related to the Henry constant by Eq. (1).

$$\mu = \frac{V_{\text{column}}}{Q_T}[\varepsilon + (1-\varepsilon)\rho_c.RTK'] + \frac{V_d}{Q_T} \tag{1}$$

with $\varepsilon = \varepsilon_i + \varepsilon_p(1-\varepsilon_i)$

where:

- μ is the retention time (s);
- V_{column} is the column volume (m^3);
- V_d is the dead volume (m^3);
- Q_T is the total volume flow ($m^3 \cdot s^{-1}$);
- T is the bed temperature (K);
- R is the perfect gas constant ($Pa \cdot m^3 \cdot K^{-1} \cdot mol^{-1}$);
- ε is the total porosity;
- ε_i is the bed porosity;
- ε_p is the pellet macro-porosity;
- ρ_c is the crystal density ($kg \cdot m^{-3}$)
- K' is the Henry constant ($mol \cdot kg^{-1} \cdot Pa^{-1}$) ·

K' is defined by: $K' = \frac{q}{P}$
with:

- q is the VOC adsorbed quantity ($mol \cdot kg^{-1}$);
- P is the VOC partial pressure (Pa).

The Henry constant K' may be expressed in a dimensionless form K. Thus, $K = K'\rho_c RT$ where ρ_c is the density of the zeolite crystal (calculated from an ideal crystal structure).

Equation (1) is only valid if the column is working in the Henry domain (initial linear part of the isotherm). This hypothesis is checked by performing several experimental runs with different injected volumes of toluene for which we calculate the retention times. When the retention time does not depend on the injected volume, the hypothesis is valid. Typically, the injected volume is between 0,05 and 0,3 μl.

2.2. *Gravimetric Method*

Before any measurement, the sample was heated up to 673 K with a rate of 5 K per minute under a dynamic vacuum of 10^{-4} kPa. The temperature of 673 K is then maintained during a 15 h period. The adsorbent is cooled down to the adsorption temperature under a helium flow. The helium flow is replaced by a helium-toluene flow during the adsorption process. Using a gas generation system with a permeation/diffusion tube gives a constant and known concentration of toluene in the helium carrier gas. The use of either permeation or diffusion tube depends on the concentration we need for the experimental process. The toluene/helium flow is about 2 Nl/h at the inlet of the balance. The concentration of toluene is controlled with a FID detector. The stability of the toluene concentration during the gravimetric experiment is more or less 2%. The balance allows the sample mass uptake determination. Knowing the toluene concentration in the helium/toluene flow, it is possible to determine the toluene partial pressure. Each experimental run provides a data point of the isotherm so that the initial part of the isotherm may be determined if adequate toluene partial pressure are generated. The complete description of both the experimental device and procedure are given elsewhere (Nokerman et al., 2002; Dutour et al., 2004).

For measurements, the zeolite sample was pelletized in a press by applying a pressure around 45 bar. For chromatographic studies, we used the 400 to 800 μm fraction to fill a 1/4" diameter stainless steel column (length between 1.5 and 5 cm). For gravimetric studies we used the 800 to 1000 μm fraction.

3. Results

These two complementary techniques were used to determine the Henry constant of toluene on a NaY zeolite with a Si/Al ratio of 2.43 at different temperatures.

The dynamic gravimetric technique gives data of adsorbed mass as a function of the partial pressure of adsorbate. The Henry constant is determined by minimizing the discrepancies between the experimental data and a theoretical linear isotherm. Results are provided at 363, 423 and 548 K. For the chromatographic method, we provide direct Henry constants obtained

Table 1. Experimental K values (determined by chromatography and gravimetry).

Temperature (K)	Chromatography	Gravimetry
363		57362722
423		688718
548	6434	6969
573	3627	
598	1948	
623	1113	
648	708	
673	470	

from the theoretical treatment of the chromatographic signal (Eq. (1)) for temperatures ranging from 548 to 673 K with a step of 25 K. The results are presented in Table 1.

The Henry constants outside the measuring temperature range are determined by extrapolating data with the van't Hoff law.

$$K = K_0 \exp\left(\frac{-\Delta U}{RT}\right) \quad \text{or} \quad K' = K_0' \exp\left(\frac{-\Delta H}{RT}\right) \tag{2}$$

in which ΔU is the adsorption energy (kJ/mol) and ΔH is the isosteric heat of adsorption (kJ/mol). The adsorption energy and the isosteric heat of adsorption are related by the following relation:

$$\Delta U = \Delta H + RT \tag{3}$$

where ΔU and ΔH are negative. ΔU is a constant (not depending on the temperature) whereas ΔH is temperature dependent. If we plot Ln K' as a function of 1/T, the slope provides an average value of the isosteric heat of adsorption. The real isosteric heat of adsorption may be calculated using Eq. (3) in which ΔU is the slope of the plot Ln K versus 1/T.

Chromatographic and gravimetric experimental data for the Henry constants of toluene on NaY 2.43 are plotted in Fig. 1.

The adsorption energy, the average isosteric heat of adsorption and the isosteric heat of adsorption at two temperatures are given in Table 2 for each technique.

The deviation on ΔU and ΔH are calculated with the following relation ($X = \Delta U$ or ΔH):

$$\text{Deviation} = 2 * \frac{X_{\text{chromatography}} - X_{\text{gravimetry}}}{X_{\text{chromatography}} + X_{\text{gravimetry}}} * 100 \tag{4}$$

Extrapolated values for the Henry constants outside the measuring ranges are also presented in Fig. 1 and in Table 3.

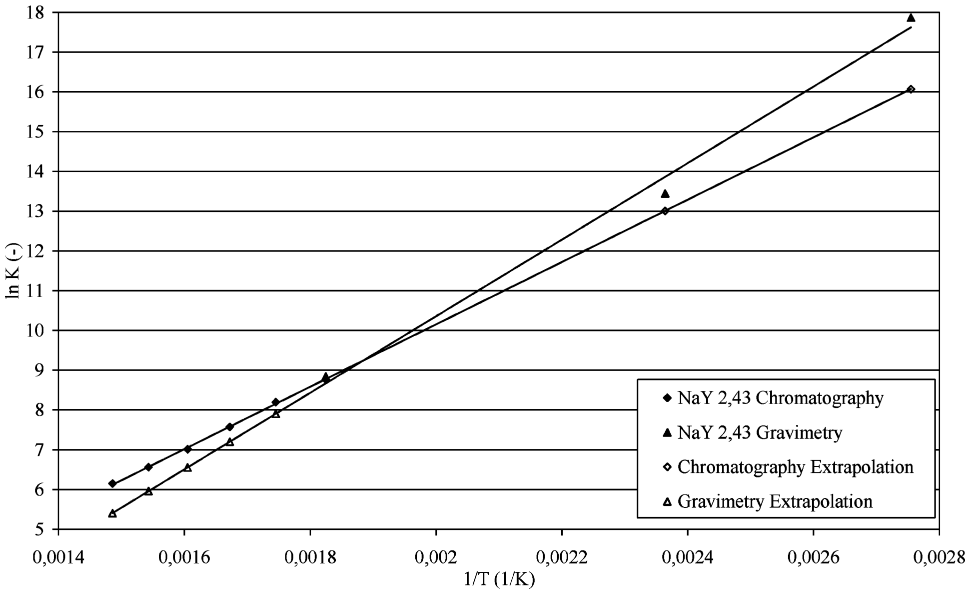

Figure 1. Ln K versus 1/T for toluene on zeolite NaY 2.43 (Chromatographic and Gravimetric data).

Table 2. ΔU (kJ/mol), Average ΔH (kJ/mol) and ΔH (kJ/mol) for toluene on zeolite NaY 2.43.

	Chromatography	Gravimetry	Deviation (%)
ΔU (kJ/mol)	−65,21	−80,18	−20.6
$\Delta H_{\text{average}}$ (kJ/mol)	−70,29	−83,89	−17.6
ΔH (kJ/mol) at 548 K	−69,77	−84,74	−19.4
ΔH (kJ/mol) at 673 K	−70,81	−85,78	−19.1

Table 3. Experimental and extrapolated K values for toluene on zeolite NaY 2.43 (values in italic are extrapolated data).

Temperature (K)	Chromatography	Gravimetry	Deviation (%)
363	*9 518 403*	57 362 722	83.4
423	*445 184*	688 718	35.4
548	6 434	6 969	8.0
573	3 627	*2 717*	25.1
598	1 948	*1 345*	31.0
623	1 113	*704*	36.7
648	708	*388*	45.3
673	470	*223*	52.5

Deviations are calculated using Eq. (5) except for 548 K (Eq. (4) with X = K).

$$\text{Deviation} = \frac{X_{\text{experimental}} - X_{\text{extrapolated}}}{X_{\text{experimental}}} * 100 \quad (5)$$

The results show that the two techniques give quite consistent results in the overlapping temperature range: the deviation is 8% at 548 K. However, comparing the extrapolated data obtained by one technique to the measured data obtained by the other technique show that important discrepancies may occur due to the uncertainties on the slope of the Ln K versus 1/T plot if few data are available as it is the case of the gravimetric method.

4. Conclusion

The results presented in this paper show the complementarity of two different techniques: inverse gas chromatography and gravimetry for measurement in the low partial pressure range. The first one is fast (it gives a direct Henry constant), quite simple but may operate only at high temperature; the other does not require any mathematical treatment and gives direct massic data; it may operate at low temperature. The chromatographic method fails to determine the Henry zone as the gravimetric method makes it possible. The two methods provide consistent results in their common temperature range. The extrapolation procedure must be handled with care and should be based on numerous and reliable data in a wide temperature range.

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References

Askin, A. and O. Inel, "Evaluation of the Heat of Adsorption of some N-Alkanes on Alumina and Zeolite by Inverse Gas Chromatography," *Separation Science and Technology*, **36**(3), 381–397 (2001).

Denayer, J.F. and G.V. Baron, "Adsorption of Normal and Branched Paraffins in Faujasite Zeolites NaY, HY, Pt/NaY and USY," *Adsorption*, **3**, 251–265 (1997).

Denayer, J.F., G.V. Baron, J.A. Martens, and P.A. Jacobs, "Chromatographic Study of Adsorption of N-Alkanes on Zeolites at High Temperature," *Journal of Physical Chemistry B*, **102**(17), 3077–3081 (1998a).

Denayer, J.F., W. Souverijns, P.A. Jacobs, J.A. Martens, and G.V. Baron, "High-Temperature Low-Pressure Adsorption of Branched C5-C8 Alkanes on Zeolite Beta, ZSM-5, ZSM-22, Zeolite Y and Mordenite," *Journal of Physical Chemistry B*, **102**(23), 4588–4597 (1998b).

Dutour, S., J. Nokerman, S. Limborg-Noetinger, and M. Frere, "Simultaneous Determination of Mass and Calorimetric Adsorption Data of Volatile Organic Compounds on Microporous Media in the Low Relative Pressure Range," *Measurement Science and Technology*, **15**, 185–194 (2004).

Nokerman, J., S. Dutour, M. Frere, S. Limborg-Noetinger, and S. Jullian, "Characterisation of Porous solids Using Low Pressure VOC Adsorption Data," in *Proceedings of the 6th International Symposium on the characterization of Porous Solids*, pp. 267–274, 2002.

Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, John Wiley and Sons, Canada, 1984.

Ruthven, D.M. and B.K. Kaul, "Adsorption of Aromatic Hydrocarbons in NaX Zeolite. 1. Equilibrium," *Ind. Eng. Chem. Res.*, **32**, 2047–2052 (1993).

Tümsek, F. and O. Inel, "Evaluation of the Thermodynamic Parameters for Adsorption of Some N-Alkanes on A type Zeolite Crystals by Inverse Gas Chromatography," *Chemical Engineering Journal*, **94**, 57–66 (2003).