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Measurement and Modeling of Single- and Multi-Component Adsorption Equilibria of VOC on High-Silica Zeolites

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From pure and binary gas adsorption equilibria measurements carried out using a volumetric method for three volatile organic compounds (methyl ethyl ketone, toluene (TOL), and 1,4-dioxane) on two high-silica zeolites, desaluminated faujasite Y (Fau Y) and ZSM-5 (Sil Z), co-adsorption was investigated and modeled. Apart from steric exclusion taking place with TOL-containing mixtures on Sil Z, micropore filling was similar to distillation since the component with the lower volatility adsorbed preferentially. At low coverage, chemisorption on specific sites happened in favor of polar or major compound, whereas at saturation the adsorbent was selective for the minor compound. Second, a quantitative prediction of binary equilibria was performed using the ideal adsorbed solution theory (IAST), examining the influence of pure component adsorption fitting model. The efficiency of correlations when extending AST to real mixture behavior was satisfactory in most cases. For engineering purposes, Fau Y is to be considered as a high-adsorption capacity adsorbent, whose selectivity can be described qualitatively by the distillation analogy and predicted quantitatively with the IAST in case of quasi-ideal mixtures.

Introduction

It has been realized worldwide that atmospheric anthropogenic pollution is a great issue in today's environmental and sustainable development politics (1). Volatile organic compounds (VOC), which are commonly found as solvents in industrial processes and domestic use, are considered as major air contaminants for inducing directly health troubles and for being precursors of tropospheric ozone (2).

One of the main techniques available in effluent treatment is adsorption on a porous material, and until now, activated carbon is generally acknowledged to be a very efficient material (2, 3). However, in the past decade, interests arose to develop new adsorbents toward operating conditions for which activated carbon was inappropriate because of its inflammability and adsorption capacity dependence on effluent relative humidity (4). Zeolites are alumina-silica

molecular sieves that present very interesting adsorption properties. Originally found as a natural fossil (5), zeolites were then synthesized and used in the petroleum and chemical industries. Modifying their silica-to-aluminum ratio (Si/Al) led to hydrophobic properties, and zeolites were therefore examined toward VOC adsorption (6) in comparison with other adsorbents (7). High-silica zeolites (HSZ) offer notably a thermal and chemical stability, a high steric selectivity, and a complete regeneration at low temperatures (8). Apart from specific adsorption sites—being generally framework aluminum in partially desaluminated hydrophobic zeolites—inducing some polar affinity (9), selective co-adsorption on HSZ was reported to depend on adsorbent crystalline framework, component volatility, initial molar fraction of the gas phase, and adsorbent loading (10, 11). Yet understanding organic compound properties impact on adsorption and crystalline framework influence on selectivity remain insufficient for predictive thermodynamic and molecular modeling calculations (12) together with adsorption and separation processes development.

This study first aims at comparing adsorption properties of two commercial HSZ (desaluminated faujasite Y (13) and ZSM-5 (14)) toward three daily used industrial solvents chosen as model VOC: methyl ethyl ketone (MEK), toluene (TOL), and 1,4-dioxane (DIO) via pure and binary gas adsorption equilibria measurements. Second, a thermodynamic approach is investigated to predict adsorption behavior of binary systems, using the ideal adsorbed solution theory (IAST) established by Myers and Prausnitz (15). Since IAST-based calculations require a precise description of pure component adsorption data, especially in the low-coverage range (16), the influence of single-component isotherms modeling on predictions quality is discussed. Further studies of Myers and co-workers (17, 18) showed that solid heterogeneity was a major source of poor agreement between IAS calculated and experimental equilibria, especially in case of activated carbon and high-aluminum content zeolites. After desaluminumation, hydrophobic zeolites are regarded as highly homogeneous adsorbents that, therefore, may have a relatively small influence on selectivity (19). Extension of AST to real behavior of adsorbed phase through activity coefficients use (20) is investigated.

Experimental Section

Adsorbents. Two commercial high-silica zeolites were used in this work, desaluminated faujasite Y and ZSM-5. Zeolites were made of microcrystals fixed together as cylindrical pellets with a clay binder, creating a macroporous structure. The supplier kept undisclosed the chemical nature of binder together with details of desaluminumation technique, that leads to hydrophobic properties via high Si/Al ratio. The main characteristics of adsorbents are summarized in Table 1.

Adsorbates. MEK (99.5%), TOL (99+%), and DIO (99+%) were obtained from Aldrich Chemical Co. and used without further purification. They were chosen as model compounds having very different chemical structure and consecutive physical properties to enable a discussion about the influence of volatility and polarity, together with molecular sieve effect on competitive adsorption. The main properties of the three adsorbates are given in Table 2.

Isotherms. Batch adsorption isotherms were performed at a regulated fixed temperature (25 ± 1 °C) using a common volumetric method (21): a determined mass of adsorbent (ranging from 0.3 to 1 g) was introduced into a glass reactor (1.1 L) at atmospheric pressure, polluted by a liquid VOC injection through a septum (typically 50 μ L) followed by

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TABLE 1. Main Characteristics of Zeolites

type (symbol)	faujasite (Fau Y)	ZSM-5 (Sil Z)
crystalline framework	α -cages	interconnected channels
pore internal diameter (Å)	13	(5.7 × 5.1) and 5.4
clay binder content (wt %)	25	20
SiO ₂ /Al ₂ O ₃ (mol mol ⁻¹)	360	1880
BET surface area (m ² g ⁻¹)	650	300
active porous volume (cm ³ g ⁻¹)	0.24	0.18

TABLE 2. Main Properties of Adsorbates

property	methyl ethyl ketone	toluene	1,4-dioxane
symbol	MEK	TOL	DIO
formula	C ₄ H ₈ O	C ₇ H ₈	C ₄ H ₈ O ₂
molar volume 25 °C (cm ³ mol ⁻¹)	90.1	107.5	85.8
kinetic diameter (Å)	5.2	5.8	5.3
vapor pressure at 25 °C (kPa)	12.60	3.79	4.95
dipolar moment (D)	2.78	0.375	0

evaporation, leading to an initial concentration of about 0.5 mmol L⁻¹. Stirring times required to reach equilibrium were respectively 2 h for Sil Z and 1 h for Fau Y. Once equilibrium was attained, a gas sample was taken and analyzed by gas chromatography (HP 5890 II). Using the conventional assumption that the clay binder—with a low specific surface area as compared to the zeolites—does not take part in the adsorption mechanism (5), adsorbed quantities were normalized for pure zeolite material.

In case of binary mixtures, adsorption procedure was kept unchanged except that co-adsorption was performed using three different initial compositions—being equimolar ($Z_1 = Z_2 = 0.5$) and rich in components 1 and 2 (respectively, $Z_1 = 0.85$ and $Z_1 = 0.15$). The selectivity of adsorbent ($\eta_{1/2}$) was either directly represented in an X - Y isobaric equilibrium diagram or determined by calculation using eq 1 where X_i and Y_i are respectively the adsorbed and gas-phase molar fractions of the i th component and are plotted versus total pressure:

$$\eta_{1/2} = \frac{X_1 Y_2}{X_2 Y_1} \quad (1)$$

Reproducibility and repeatability of experimental data were checked by three different manipulators. Experimental errors were equal to 3% for equilibrium concentration and ranging from 3 up to 7% for adsorption capacity with increasing pressure.

Theoretical Models

Single-Component Isotherms Correlation. The experimental adsorption isotherms were fitted using Freundlich, Langmuir, Toth (which was intensively used to describe adsorption isotherms on zeolites (22)), and Dubinin–Astakhov equations. The models express the adsorbed quantity, Q (mol kg⁻¹), as a function of gas-phase pressure, p (Pa), as follows:

Freundlich Equation.

$$Q = K_f p^{1/n} \quad (2)$$

Langmuir Equation.

$$Q = \frac{Q_m K_l p}{1 + K_l p} \quad (3)$$

Toth Equation.

$$Q = \frac{Q_m K_t p}{[1 + (K_t p)^t]^{1/t}} \quad (4)$$

Dubinin–Astakhov Equation. Dubinin's approach is based on the earlier potential theory of Polanyi and on the concept of micropore filling. The Dubinin–Astakhov (D-A) approach is an extension of Dubinin–Radushkevich equation and represents the isotherm in terms of fractional filling ($\theta = W/W_0$) of the micropore volume with W_0 being the maximum adsorption capacity.

In eq 5, A_p is the Polanyi adsorption potential defined by eq 6, and m is the D-A equation adjustment parameter, ranging classically from 1.5 to 3 for activated carbon and from 2 to 4 or 5 in the case of zeolites (23):

$$\theta = \exp\left[-\left(\frac{A_p}{E}\right)^m\right] \quad (5)$$

$$A_p = RT \ln\left[\frac{P_s}{p}\right] \quad (6)$$

Optimization of the models parameters was carried out using the Simplex algorithm, by minimizing the objective function, $F(X)$, where X is the set of adjustable parameters and n is the number of experimental points:

$$F(X) = \sum_k^n [Q^{\text{exp}}(p_k) - Q^{\text{calc}}(p_k)]^2 \quad (7)$$

Binary Mixtures Modeling with IAST and RAST. Considering the adsorbed phase as a liquid, the IAST is based on the fundamental hypothesis that the multi-component adsorbate phase has the same spreading pressure (π) as that of the ideal single solution of the i th component, the spreading pressure being the difference between the interfacial tensions of the naked solid and that of the surface covered with adsorbate. Algorithm of adsorption capacities determination requires an accurate description of the pure component isotherms, but integration of the chosen model in the Gibbs equation may be more or less direct, depending notably on its number of adjustable parameters. This is clearly highlighted by the spreading pressure expressions obtained either with Langmuir (eq 8) or Toth (eq 9) models in which $\{0 \leq \theta < 1\}$ and $\{0 < t < 1\}$. The improvement of predictions accuracy when changing from 2 to 3 parameters is examined in balance of the very different CPU calculation times induced, which are decisive in dynamic breakthrough curve modeling:

$$\frac{\pi A}{RT} = Q_m \ln(1 + K_l C) \quad (8)$$

$$\frac{\pi A}{RT} = Q_m \left[\theta - \frac{\theta}{t} \ln(1 - \theta^t) - \sum_j \frac{\theta^{jt} + 1}{jt(jt + 1)} \right] \quad (9)$$

When thermodynamic consistency was satisfied (24), the AST was extended to real AST. Considering deviation from ideality, identified by nonsymmetrical X - Y curves in experimental isobaric equilibrium diagrams, Costa et al. (20) introduced liquid-phase activity coefficients (γ_i) when establishing chemical potential equality between phases at equilibrium. This extension enables the AST to describe azeotrope-like crossovers. Basic equations of the two models are summarized below using the Wilson model for activity coefficients with two adjustable parameters Λ_{ij} ($i \neq j$). The calculation procedure in both cases was described in the original publications as well as in a previous article for IAST (25).

IAS Model.

$$pY_i = p_i^0(\pi)X_i \quad (10)$$

RAS Model.

$$pY_i = p_i^0(\pi)X_i\gamma_i \quad (11)$$

Wilson Model.

$$\ln \gamma_i = 1 - \ln\left(\sum_j X_j \Lambda_{ij}\right) - \sum_k \frac{X_k \Lambda_{ki}}{\sum_j X_j \Lambda_{kj}} \quad (12)$$

Results and Discussion

Pure Component Isotherms. Adsorption isotherms for the three compounds were determined in the low relative partial pressure range $\{p/p_s \leq 0.1\}$ to reach total micropore filling but without further investigation of multilayer adsorption on external surface or capillary condensation in mesopores of crystallites observed classically when the isotherm describes the whole pressure range, up to $\{p/p_s = 1\}$. For all compounds, the isotherm curves obtained on Sil Z and Fau Y are respectively of type I and V of IUPAC classification (1985). Single-component equilibrium data are given in Table S1 (see Supporting Information). Using the assumption that the adsorbed phase is in the liquid state, micropore fillings are calculated, highlighting the steric exclusion of TOL on silicalite (52% for TOL versus 87% for MEK and DIO). This maximum adsorption capacity of 4 molecules per unit cell was commonly observed on pentasil zeolites by other researchers, the adsorption sites being 1 molecule per channels intersection (26). It was also reported that, as the partial pressure increases, a second “step” occurred in the adsorption isotherms of aromatics, such as benzene and *p*-xylene (27) but also of chlorinated compounds (28), leading to total pore filling. This was interpreted as a phase transition of ad molecules toward more ordered and denser packing state or in some cases as a change in the framework symmetry of the adsorbent. In this study, investigations of higher partial pressure equilibrium of TOL on Sil Z (up to $\{p/p_s = 0.35\}$) do not reveal any significant increase in adsorbed quantity. This difference of behavior may be due to the fact that the pentasil zeolite used here is a highly desaluminated ZSM-5 whereas the works previously mentioned either used directly synthesized silicalite, the aluminum-free pure silica ZSM-5, or ZSM-5 with a lower Si/Al ratio. The desalumination step leads indeed to a small decrease in pores dimension that is to be significant in these critical adsorption systems. When investigating DIO adsorption/desorption on silicalite, Rochester and Strachan (29) observed a large hysteresis loop (from 0.8 down to 0.1 in $\{p/p_s\}$) emphasizing the very close dimension of DIO molecules and zeolite pore size.

As expected, no molecular sieve effect takes place in the large pore faujasite. The difference of pore filling is much smaller (being 72, 73, and 82%, respectively, for TOL, DIO, and MEK) and could be attributed to the molecules flexibility toward maximum space occupation. These results are consistent with studies carried out on very similar systems (30, 31).

Experimental Selectivities of HSZ toward Binary Mixtures. Partially desaluminated hydrophobic zeolites still exhibit specific adsorption sites, from framework aluminum, that are to induce selective adsorption for polar compounds (32), whereas HSZ can be regarded as homogeneous adsorbents. In this work, both HSZ selectivity is examined toward each binary mixture. Extensive data are given in Table S2 (see Supporting Information). MEK-TOL and DIO-TOL

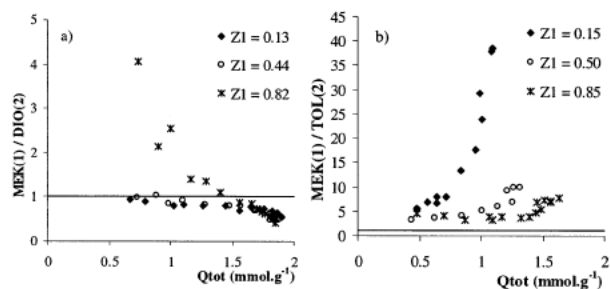


FIGURE 1. Selectivity of Sil Z toward MEK-DIO (a) and MEK-TOL (b) mixtures.

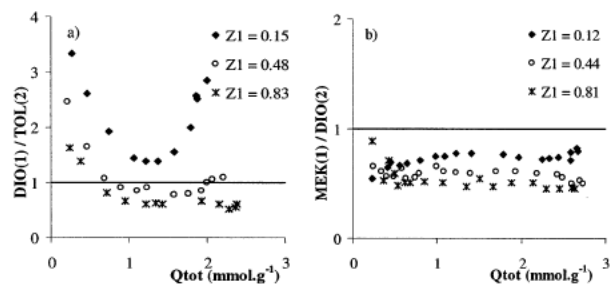


FIGURE 2. Selectivity of Fau Y toward DIO-TOL (a) and MEK-DIO (b) mixtures.

mixtures (from now on called TOL-containing mixtures) have qualitative similar co-adsorption behavior on both adsorbents.

Binary adsorption of MEK-TOL mixture on Sil Z presented in Figure 1b confirms the steric exclusion of TOL that leads to a global high selectivity for MEK ($\eta_{\text{MEK-TOL}} \gg 1$). With increasing pressure and loading, this tendency strengthens, TOL being displaced by the other compound at channels intersections, showing a maximum in its individual adsorption isotherms. This result is surprising since generally, on homogeneous hydrophobic adsorbents, the compound with the lower volatility adsorbed preferentially, as demonstrated in Figures 1a (at high loading) and 2b for MEK-DIO mixture and by Brosillon et al. (32) with an acetone/heptane mixture on partially desaluminated ZSM-5 where heptane displaced acetone, the more volatile compound. Therefore, as mentioned by Garrot et al. (10), this distillation analogy commonly observed on desaluminated faujasite has to be moderated in case of pentasil zeolite.

Moreover, considering the different desalumination techniques, various amounts of extra framework aluminum (EFAL) and silanol group (SiOH) can be formed and may induce some change in selectivity at low loading (30, 33). As well, the clay binder can exhibit some specific adsorption sites from its framework hydroxyl groups, however small its specific surface area may be (34). This co-influence of chemisorption, reported previously for an aqueous system (25), was noticed on Fau Y at low loading $\{Q_{\text{tot}} < 0.5 \text{ mmol g}^{-1}\}$, leading to a selective adsorption of the major compound in MEK-DIO binary system and of the other component in TOL-containing mixture, as shown in Figure 2a for DIO-TOL mixture. Rochester and Strachan (29) clearly presented the different specific adsorption interactions of DIO with hydroxyl groups.

Finally, at high loading, another parameter competitively controls selectivity in addition to volatility. Indeed, both HSZ are selective for the minor compound leading to different behaviors between the three initial molar fractions of the gas phase illustrated in Figures 1 and 2.

Binary Equilibria Modeling Using Adsorbed Solution Theory. *Pure Component Isotherm Modeling.* Values of regression parameters of pure gas isotherms fitting as well

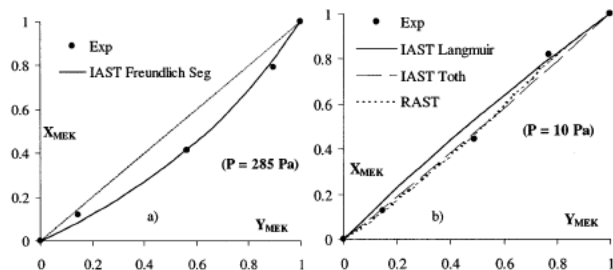


FIGURE 3. Isobaric selective X - Y diagrams: MEK-DIO mixtures on Fau Y (a) and Sil Z (b).

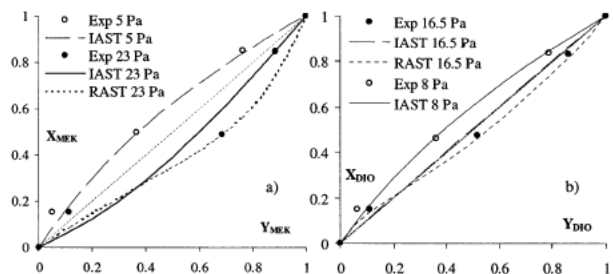


FIGURE 4. Isobaric selective X - Y diagram on Fau Y toward TOL-containing mixtures.

as Simplex objective function minimum (σ^2) are given in Table S3 (see Supporting Information). For Sil Z isotherms, Langmuir equation correlation is very satisfactory with only two adjustment parameters, but the best results are obtained with the Toth equation, for which the deviation of the model is well within the experimental uncertainty, improving notably the description of Henry's law region. For this reason, both models are compared in AST calculations. When using D-A model, the adsorbent-dependent parameter m is found to be different for the three compounds leading to more complex integration into IAST calculation (35). On the opposite, none of the models is to describe the type V curves obtained on Fau Y. These isotherms are then divided into three pressure ranges—where Freundlich equation can be applied separately as proposed by Tien (36)—and are perfectly fitted, enabling IAS consecutive calculations.

AST-Based Predictions/Correlations. As a preliminary remark, good or very good predictions are obtained at low loading, as shown in Figures 3 and 4, where the idealization is quite satisfactory and the active species have similar adsorption properties, as pointed out by Myers and Prausnitz (15). This statement has to be moderated for the selective adsorption of Sil Z toward MEK in the $\{Z_1 = 0.85\}$ —MEK-DIO mixture exhibited at intermediate loading, which is assumed to come from specific chemisorption, MEK being the major compound. Then, as expected, the steric exclusion of TOL on Sil Z cannot be predicted by the IAST, but interestingly a negative deviation of selectivity is observed between IAS and experimental data. This may suggest that TOL adsorbs preferentially in the common adsorption sites, being the channels intersections, contrary to the assumption made from the decrease of TOL adsorbed amount with increasing pressure in its individual isotherm in binary mixtures.

More surprisingly, in case of MEK-DIO quasi-ideal liquid mixture on Sil Z, the IAST is ineffective in predicting the selective adsorption of DIO at high loading, and changing from Langmuir to Toth model does not improve the calculations. In fact, this theory was used quite successfully by other researchers when looking at binary adsorption on high-silica ZSM-5 (19, 23). According to single-component isotherms, MEK has the highest adsorption energy and is expected to adsorb preferentially, as predicted by IAST.

Nevertheless, the strong interactions between DIO and Sil Z, due to the critical dimension and shape of DIO molecules as compared to Sil Z channels (29), are suspected to induce limitations in the counter-diffusion of MEK and DIO. Indeed at intermediate loading, where adsorbate-adsorbate interactions are smaller, IAST predictions are in qualitative agreement with experimental data, as shown in Figure 3b. The difference between the two single-component isotherms-fitting models is still small but significant, since the integration for spreading pressure is sensitive to the low surface area portion of pure gas isotherm. Yet, co-adsorption exhibits an azeotropic behavior which cannot be predicted by the IAST but could be well correlated by means of activity coefficients in RAST.

On the large pore desaluminated faujasite Y, the co-adsorption of the quasi-ideal MEK-DIO mixture can be well predicted in the whole pressure range, as shown in Figure 3a at high loading. However, in case of TOL-containing mixtures, non-idealities are not modeled by the IAST as presented by Figure 4 at intermediate loading. Negative deviations from Raoult's law are observed for experimental activity coefficients. The correlations using Wilson model developed for vapor-liquid equilibrium (VLE) lead to fairly good results, except that some overadsorption phenomenon explained by a synergetic effect due to adsorbate-adsorbate interactions cannot be correctly described by the AST with a VLE model since the RAST does not take into account the dependence of activity coefficients (24) on spreading pressure. Therefore, it is clear from the results presented in Figure 4 that, when looking at ideal liquid mixtures, the AST is fully efficient for binary adsorption predictions, but real behavior emphasizes the differences between adsorbed and liquid phases, as shown by limitations in spreading pressure modeling.

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Supporting Information Available

Three tables detailing pure gas and binary mixtures equilibrium data at 298 K and regression parameters for pure gas isotherms modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Nomenclature

A	surface area of adsorbent (m^2)
A_p	Polanyi adsorption potentiel (mol J^{-1})
E	characteristic adsorption energy (J mol^{-1})
K_f	Freundlich model adsorption capacity coefficient ($\text{mol Pa}^{-1/n} \text{kg}^{-1}$)
K_l	Langmuir model equilibrium coefficient (Pa^{-1})
K_t	Toth model equilibrium coefficient (Pa^{-1})
m	Dubinin-Astakhov model adjustment parameter
n	Freundlich model adsorption energy distribution coefficient
p	gas-phase total pressure induced by VOC concentration (Pa)
p_s	saturation vapor pressure (Pa)
$p_i^0(\pi)$	equilibrium pressure for pure component i , at spreading pressure π (Pa)

Q	amount adsorbed (mol kg ⁻¹)
Q_m	maximum adsorption capacity defined in Langmuir and Toth model (mol kg ⁻¹)
Q_{tot}	experimental total amount adsorbed in mixture systems (mol kg ⁻¹)
R	ideal gas constant (8.3145 J mol ⁻¹ K ⁻¹)
t	Toth model adjustable parameter
T	temperature (K)
W	micropore volume (cm ³)
W_0	maximum micropore adsorption capacity (cm ³)
X_i	adsorbed phase molar fraction of i th component at equilibrium
Y_i	gas-phase molar fraction of i th component at equilibrium
Z_i	initial molar fraction of i th component
Greek Letters	
γ_i	activity coefficient of i th component in the adsorbed phase
$\eta_{1/2}$	selectivity of adsorbent toward component 1 vs component 2 at equilibrium
Λ_{ij}	binary parameters of Wilson model for activity coefficients ($i \neq j$)
θ	fractional filling of micropore volume
π	spreading pressure (J m ⁻²)
σ^2	Simplex objective function minimum

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