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Modeling of Adsorption Isotherm of a Binary Mixture with Real Adsorbed Solution Theory and Nonrandom Two-Liquid Model

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Gas-phase adsorption equilibria of diluted mixtures of methyl-ethyl-ketone and isopropylanol on activated carbon were investigated. Experimental isotherms were determined by a constant volume method. Single-component adsorption isotherms were fitted by the frequently used Toth model with good accuracy. Then adsorption isotherms were determined for different binary mixtures (with different initial ratio of the two components). Binary mixtures adsorption isotherms were calculated using the adsorbed solution theory. Ideal adsorbed solution theory (IAST) could not represent experimental data, but it was observed that increasing amount of MEK led to higher nonideality of the mixture. Then UNIversal QUAsi Chemical (UNIQUAC) and nonrandom two-liquids (NRTL) models were considered to describe activity coefficients of the adsorbed phase. The fitted parameters of UNIQUAC model depend on the ratio of the two components, whereas the NRTL model is able to fit all experiments with the same parameters, whatever the initial ratio may be. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 3109–3119, 2010

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Introduction

Since porous materials offer high selectivity and high capacity for volatile compounds, even at low-partial pressures, adsorption is a widely used process for the separation of gas mixtures, and especially recovery of VOC from polluted gaseous effluents. This latter application is of great interest since, even at low concentrations, VOC exhibit harmful effects to human health[1] and environment.[2]

Like the design of any other unit operation, the design of industrial adsorption equipment requires reliable equilibrium data which are, for multicomponent mixtures, the adsorbed amount of each component and the composition of the gaseous phase in equilibrium with the adsorbed phase at given temperature and pressure. In order to avoid fastidious and time-consuming experimental determination of too much data, models which can predict multicomponent data from single-component adsorption equilibria have been developed for a long time. Thus, only single-component isotherms for each component of the mixture have to be determined experimentally at the same temperature and on the same adsorbent.

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In 1965, Myers and Prausnitz proposed a technique for estimating the adsorption equilibria of a gaseous mixture from the known adsorption isotherms of the pure components.[3] This model, called the adsorbed solution theory (AST), is based on the analogy between vapor-liquid and gas-adsorbed phase equilibrium. Assuming ideal behavior of the adsorbed phase, Myers and Prausnitz showed that the ideal adsorbed solution theory (IAST) could provide good agreement with experimental data for methane-ethane and ethylene-carbon dioxide on activated carbon and for carbon monoxide-oxygen and propane-propylene on silica gel. Quinones et al.[4] also used with good accuracy the extension of the IAST to liquid-solid systems. However, from a theoretical point of view Myers and Prausnitz developed the adsorbed solution theory incorporating activity coefficients in the adsorbed phase to account for the deviations from ideality. When activity coefficients are calculated the method is known as real adsorbed solution theory (RAST). Thus, Steffan and Akgerman[5] showed that the real adsorbed solution theory could fit different binary liquid mixture isotherms very well by introducing and determining experimental activity coefficients, whereas the IAST could not fit these isotherms.

However, in order to make the RAST a reliable method, activity coefficients should not be empirically fitted to each set of data, but should instead be calculated from theoretically based models, under which our understanding of chemical-chemical interactions among sorbates leads to consistent set of values that should be consistent for any given sorbent, temperature, and pressure condition.

Myers and Prausnitz[3] pointed out that activity coefficients of the adsorbed phase should be functions of temperature, composition and spreading pressure, whereas in a liquid phase, activity coefficients depend on temperature and composition. Hence, estimation of activity coefficients of the adsorbed phase using correlations for liquid-vapor equilibrium is not thermodynamically consistent, since it does not take the spreading pressure into account. Hence, Talu and Zwiebel[6,7] proposed the spreading pressure dependant (SPD) model. In this model, activity coefficients are calculated using equations that are adapted from UNIQUAC (UNIversal QUAsi Chemical[8]) formulation, which estimates the activity coefficients in a liquid phase. Energies, which constitute the adjustable parameters of UNIQUAC formulation, are decomposed with single-component lateral and cross-lateral interaction potentials. The first ones are estimated with the help of isosteric heat of adsorption at the same spreading pressure as the mixture, and the others are estimated using a mixture rule including binary interaction parameters, which must be regressed from gaseous phase and adsorbed phase equilibrium data of binary mixtures over a range of composition. However, it must be noted that determination of isosteric heats of adsorption requires additional experiments since for this determination single-component isotherms have to be known for more than one temperature (at least three). This model has been recently used by Garcia-Galdo et al.[9] with a liquid-solid system and provided good results.

Nevertheless, several authors tried to calculate these coefficients with the help of correlations usually used for liquid-vapor equilibria even if they do not take the spreading pressure into account. The most frequently encountered correlations are Wilson and UNIQUAC equations.[10,8] Indeed, these two models show an important advantage: for multicomponent systems, only binary parameters are required. Thus, Costa et al.[11] only with binary systems data, predicted with good accuracy ternary adsorption equilibrium for hydrocarbon mixtures onto activated carbon, calculating activity coefficients by means of Wilson and UNIQUAC equations. They obtained much better agreement with experimental values using RAST than using IAST. More recently, Krishna[12] also used the RAST combined with Wilson equations. Earlier, Calleja et al.[13] compared the RAST-SPD model to the IAST and to the RAST combined with Wilson equations: experimental adsorption data of binary, ternary and quaternary mixtures of ethylene, propane, propylene and carbon dioxide on 13X zeolite have been fitted to these three models. They concluded that the best model was the RAST-Wilson model even with the limitation of using a vapor-liquid equilibrium equation for calculating the activity coefficients in the adsorbed phase. However, in all these articles, studied mixtures were not diluted in air. In fact there are very few studies in literature regarding the modeling of adsorption isotherms of diluted mixtures.[14] Monneyron et al.[15] studied binary diluted mixtures (among 1,4 dioxane, methyl ethyl ketone and toluene). They showed that RAST combined with Wilson equations led to better results than IAST, but failed in some cases. More recently Kim et al.[16] and Lillo-Rodenas et al.[14] predicted with good accuracy diluted mixture adsorption isotherms using IAST. It must be noted that Kim et al.[16] dealt with very low-adsorbate loadings of methyl ethyl ketone, methyl isobutyl ketone and toluene (<500 mg/m^3), and that Lillo-Rodenas et al.[14] dealt with a benzene-toluene mixture at low concentration. Very low-adsorbate loadings, in the first case, and the fact that benzene-toluene mixture is known to have an ideal behavior while in liquid phase, in the second case, could explain why IAST predicts accurately adsorption isotherms.

We have then decided to investigate RAST model combined with models where, for multicomponent mixture, only binary parameters are needed, so that the prediction of gas-phase adsorption isotherms of multicomponent mixtures requires only binary experimental data (in order to identify the binary parameters) in addition of experimental single component isotherms. We have previously compared RAST-SPD to RAST-UNIQUAC,[17] and, like Calleja et al.[13] who, earlier, obtained better results with RAST-Wilson than with RAST-SPD, we observed that RAST-UNIQUAC gave better results to reproduce experimental binary adsorption equilibrium. Moreover, it can be thought that if the adsorbate-adsorbate interactions were greater than the adsorptive potential, perhaps the RAST combined with a liquid-vapor model for calculating activity coefficients could fit the experimental data of adsorbed phase and gaseous phase equilibria sufficiently well, avoiding additional experiments since the SPD model needs the determination of single-component isotherms for more than one temperature (at least three). So we have implemented the real adsorbed solution theory calculating activity coefficients by the means of two classical liquid-vapor equilibrium models: the nonrandom two-liquid formulation (NRTL) (Renon and Prausnitz[18]), and the UNIversal QUAsi Chemical formulation (UNIQUAC) (Abrams and Prausnitz[8]). Indeed, there exist a large number of models for

the representation of the molar excess Gibbs energy as a function of concentration at constant temperature, which are used to correlate liquid-vapor equilibrium data. Out of these, three models — Wilson, NRTL and UNIQUAC — show an important advantage: for multicomponent systems, only binary parameters are required. This is due to the concept of local composition, which has been used in the derivation of these models. The concept is based on the hypothesis of Wilson that the local concentration around a molecule will be different from the bulk concentration when there is a difference between the interaction energy of the central molecule with the molecules of its own kind and that with the molecules of the other kind. This difference introduces nonrandomness at the molecular level. In the Wilson and NRTL equations, local volume fractions and local molar fractions, respectively, are used, while UNIQUAC uses the local area fractions as the primary concentration variable, so that it is applicable to solutions containing small or large molecules. It should be noted, that UNIQUAC, which has been derived using statistical mechanics, presents a stronger theoretical base than the two other formulations and often shows a slight superiority to represent experimental data of liquid-vapor equilibrium of binary and ternary systems[19] or experimental data of liquid-liquid equilibria.[20] As it has already been mentioned, Wilson and UNIQUAC equations have been often used to describe activity coefficients in adsorbed phase,[11,12,13,15] while NRTL equation has been seldom reported in this context.[5] Wilson and UNIQUAC formulations use two adjustable parameters, while NRTL formulation uses three adjustable parameters per binary pair, which is often considered as a disadvantage since it complicates the model. However, perhaps the presence of three adjustable parameters could give a better fit of experimental data of adsorption of binary mixtures. We then decided to implement the real adsorbed solution theory (RAST), combined with NRTL, and then with UNIQUAC, in order to compare the ability of these two formulations to reproduce gaseous phase and adsorbed phase equilibrium data of binary mixtures over a range of composition. It is expected that the presence of the three adjustable parameters of NRTL formulation could give a better fit of experimental data. UNIQUAC has been preferred to Wilson formulation as the model with two adjustable parameters compared to NRTL, because of its stronger theoretical base. The experimental data are obtained with a simple constant volume method described in the following.

Methods and Materials

Adsorbates

The two organic volatile compounds studied were methyl ethyl ketone (MEK) and isopropyl alcohol (IA). These compounds were chosen because they are daily used industrial solvents, and because they represent two chemical families with different properties (see Table 1). MEK has been often studied with a nonpolar compound like toluene or benzene, on different adsorbents: Kim et al.[16] studied it with toluene on activated carbon (AC), Huang et al.[21] studied it with benzene on activated carbon fibers (ACF), and Monneyron et al.[15] studied it with toluene on two high-silica zeolites (HSZ). AC and ACF exhibited higher selectivity for the nonpolar component, while HSZ presented a higher selectivity for MEK probably due, on this type of adsorbent, to the steric exclusion of toluene. Just like MEK, isopropanol has often been selected as model compounds (Kim et al.[22] and Fournel et al.[23]). It can be seen in Table 1 that isopropanol is a polar compound too. So it can be interesting to verify if there is competition between isopropanol and MEK.

Table 1. Main Properties of Selected Adsorbates

	Isopropyl Alcohol	Methyl Ethyl Ketone
Symbol	IA	MEK
Formula	C_3H_8O	C_4H_8O
Density	0.785	0.805
Molecular Weight (g/mol)	60.1	72.11
Vapour Pressure at 20°C (kPa)	4.39	9.49
Kinetic Diameter (Å)	4.5	5.2
Dipolar Moment (D)	1.7	2.8

They were used as single solutes and as binary mixtures. Concentrations varied from 150 to 7,000 mg/m^3.

Adsorbent

The employed activated carbon was provided by Carbio12. It is made from coconut shell. The characterization of its porous texture was carried out using the micromeritics accelerated surface area and porosimetry system (ASAP 2010) apparatus, which uses the principle of physical adsorption to obtain adsorption and desorption isotherms and information about the surface area and porosity of a solid material. It performs surface area analyses and pore size and pore-volume distributions, using nitrogen as the standard gas. The BET surface area calculated by ASAP 2010 software is 1074 m^2/g, which is in accordance with value supplied by Carbio 12 (1,000 to 1,100 m^2/g). The Horvath-Kawazoe differential pore-volume plot exhibits a pore-size peak about 5.7 angstrom. At last, the pH value supplied by Carbio 12 is 10/11.

Equilibrium data measurements

Experimental setup is shown on Figure 1. All experiments were performed at atmospheric pressure. The gaseous mixture was generated by introducing a liquid mixture of one or two VOC, in a heated air stream using a syringe pump (Harvard apparatus PHD-2000). This mixture of VOC was vaporized in the air stream that was circulated by a piston pump in a closed loop made up from PTFE tubing and a 20 L balloon flask where the adsorption could take place. This balloon flask was locked in a drying oven (Fisher Bioblock Scientific Venticell) to obtain the required temperature. Humidity was measured, and was always about 50%. The gaseous-phase composition was continuously measured with a parallel gas chromatograph analyzer (Varian micro-GC CP-4900). When VOC concentration was homogeneous in the gaseous phase, adsorbent (activated carbons) was introduced in the balloon flask. Then adsorption started: VOC concentration in the gaseous phase decreased and when it no longer varied, the thermodynamic equilibrium was reached. Then a simple

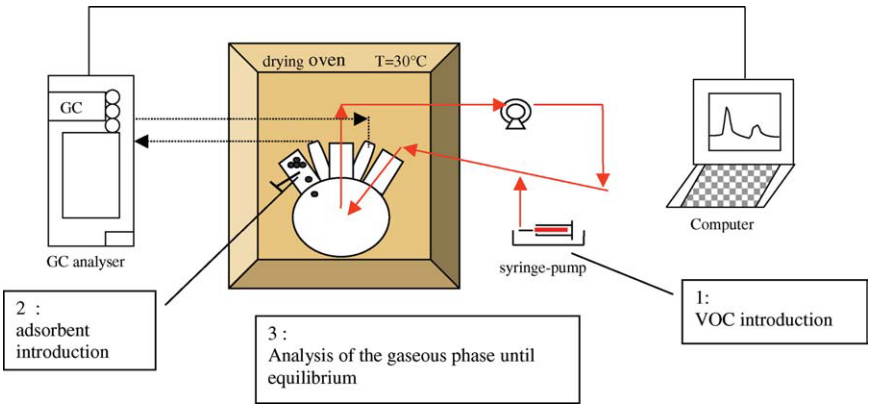

Figure 1. Experimental setup.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mass balance allows the calculation of the adsorbed amount of each component at equilibrium (n_i)

$$n_i = \frac{(C_{i,0} - C_{i,e})V}{m} \quad (1)$$

The mass of adsorbent (m) in all experiments was approximately 40 mg or 80 mg, and the circuit volume (V) was roughly 22.38 L. $C_{i,0}$ is the initial gaseous-phase concentration, $C_{i,e}$ is the experimental gaseous-phase concentration at equilibrium.

It should be noted that since the chromatograph was equipped with a thermal conductivity detector (TCD), which did not destroy the gas sample, this one was injected back into the balloon. Hence, the mass balance was not affected by the gas sampling. And, as far as the apparatus calibration is concerned, we first accomplished a setup calibration *in situ*: the initial concentration was calculated knowing the injected VOC quantity and estimating the total volume of the experimental loop. The two calibration curves, concentration of MEK vs. peak area, and concentration of isopropanol vs. peak area, appeared to be linear with a coefficient of determination equal to 0.9946 and 0.9966, respectively. In order to confirm that the measured concentration was equal to what was calculated (that would not be the case with dead volume in the balloon flask), this calibration setup was also verified using an external gas generator (Calibrage PUL-200). The calibration curves obtained with the external gas generator were identical to the first ones, proving that there was no dead volume in the batch reactor. Moreover, it justifies *a posteriori* the use of room air: the range of VOC concentration (150 to 7,000 mg/m^3) does not justify the use of bottle air or air coming from air zero generator, contrary to studies dealing with indoor air treatment for example.[24]

The relative error on the concentration measurement was 8%, and reproducibility were checked several times by duplicating attempts for the same experimental point: it was about 4%.

Theoretical Models

Single-solute adsorption isotherms

Adsorption isotherm represents the experimental adsorbed amount as a function of partial pressure at a given temperature. The oldest and still commonly used isotherm formula is the so-called Langmuir equation which expresses the equilibrium between adsorption and desorption at given temperature for a monolayer, with the assumption of noninteracting particles on a homogeneous surface (Rouquerol[24]). The langmuir isotherm considered as an empirical law has been useful to described monolayer adsorption, but since Langmuir hypothesis was not always fulfilled, some other empirical formulas such as Langmuir-Freundlich or Toth equations, which are generalized forms of Langmuir equations, have been introduced (Rouquerol[24] and Brouers[25]). According to Brouers,[25] the quite universal successful use of these empirical laws can be explained by the fact that heterogeneity of the surface- and pore-size distribution on the one hand, and the influence of lateral molecular interactions on the other hand could counterbalance each other. In this work, the experimental single-solute adsorption isotherms were fitted using Langmuir, Langmuir-Freundlich and Toth equations. Toth equation provided the best results. This equation was previously used for gas adsorption studies by Monneyron et al.[15] on high-silica zeolites, and by Lillo-Rodenas et al.[14] on activated carbon. For this equation (Eq. 2), expresses the adsorbed amount of component i at equilibrium, n_i (mol.g^{-1}) as a function of the partial pressure of the single solute i in the gaseous phase p_i (Pa)

$$n_i = \frac{n_{mi} K_i p_i}{\left(1 + (K_i p_i)^{t_i}\right)^{1/t_i}} \quad (2)$$

Where n_{mi} is the maximum adsorbed quantity (for high values of p_i), and K_i and t_i are the adjustable parameters of Toth model. Ki can be regarded as a thermodynamic equilibrium constant for the adsorption process. According to Terzyk,[26] the parameter t_i is said to characterize the system heterogeneity. For $t_i = 1$, the isotherm is reduced to the Langmuir isotherm. The more this parameter is lower than unity, the more heterogeneous is the system. On the other hand, if this parameter is greater than the unity, the lateral interactions between the adsorbed molecules are greater than the adsorptive potential.

Binary mixture adsorption isotherms

Spreading Pressure. When adsorption occurs, the amount of adsorbed molecules depends on the surface area of the

adsorbent. This results in an additional degree of freedom for equilibrium between the adsorbed phase and the gaseous phase, compared to liquid-vapor equilibrium. This additional degree of freedom is marked by π, the spreading pressure, which is the intensive variable associated with the extensive variable A, the area of the adsorbent. This spreading pressure may be pictured as the difference between the solid-surface tension without adsorbed molecules and this tension with molecules adsorbed on the solid surface. For single-component adsorption, the spreading pressure can be calculated with the use of a single-component equilibrium isotherm model $n_i(p_i)$ (Toth in the studied case). The following equation is often referred to as the Gibbs adsorption equation

$$\frac{\pi A}{RT} = \int_0^{P_i^0} n_i(p_i)\, d(\ln p_i) \tag{3}$$

where A is the specific area of adsorbent (m^2/g), R is the perfect gas constant, P_i^0 is the partial pressure of component i (single adsorbate) at equilibrium at T and π, and n_i is the number of moles of component i (single adsorbate) in the adsorbed phase per unit mass of adsorbent and depends on p_i by Eq. 2.

Adsorbed Solution Theory. In order to calculate multicomponent adsorption equilibria, we apply the adsorbed solution theory (AST), which was first described by Myers and Prausnitz.[3] It is based on the equilibrium criterion that for each component the chemical potential in the adsorbed phase is equal to the chemical potential in the gaseous phase. If the gas is assumed to be ideal, this leads to

$$Py_i = \gamma_i(T, \pi, \bar{x}) x_i P_i^0(T, \pi) \tag{4}$$

Where P is the total pressure, y_i and x_i are the molar fraction in the gaseous and adsorbed phase, and γ_i is the activity coefficient in the adsorbed phase depending on temperature, spreading pressure and adsorbed-phase composition, and representing the ratio between fugacity of component i in the adsorbed mixture (depending on temperature, spreading pressure and adsorbed phase composition), and fugacity of component i in the reference state (single solute adsorbed at the same temperature and spreading pressure as the mixture), depending on temperature and spreading pressure. $\bar{x}$ is a vector which contains the molar fraction in the adsorbed phase of all the components of the mixture.

This expression can be regarded as a modified form of the equilibrium law for vapor-liquid systems. The vapor pressure at the equilibrium temperature $P_i^{sat}(T)$ is replaced by $P_i^0(T,\pi)$, which is the equilibrium partial pressure of the single-solute i adsorbed at the same spreading pressure and temperature as the mixture, and is given by a Gibbs adsorption equation (Eq. 3).

Then the AST model can be summarized as follows (nc is the number of components):

Data

$$P, T, (y_i \; i = 1, n_c), A$$

Variables

$$(x_i, P_i^0(T, \pi),\ \gamma_i(T, \pi, \bar{x}), i = 1, n_c), \pi$$

Set of equations

$$Py_i = \gamma_i(T, \pi, \bar{x}) x_i P_i^0(T, \pi) \qquad i = 1, n_c \tag{4}$$

$$\ln(\gamma_i) = \text{function}(T, \pi, \bar{x}) \qquad i = 1, n_c \tag{5}$$

$$\frac{\pi A}{RT} = \int_0^{P_i^0} n_i(p_i)\, d(\ln p_i) \qquad i = 1, n_c \tag{6}$$

$$\sum_{i=1}^{n_c} x_i = 1 \tag{7}$$

We have to solve a problem constituted with a set of $(3n_c + 1)$ variables, and a set of $(3n_c + 1)$ equations. Once the problem has been solved, the adsorbed amount of each component may be calculated as follows

$$n_i = x_i n_t \tag{8}$$

With the total adsorbed amount calculated with the following expression

$$\frac{1}{n_t} = \sum_{i=1}^{n_c} x_i \frac{1}{n_i^0} + \frac{RT}{A} \sum_{i=1}^{n_c} x_i \left(\frac{\partial \ln \gamma_i}{\partial \pi} \right)_{x_i, T} \tag{9}$$

n_i^0 is the amount of component i adsorbed at the reference state (single-solute adsorbed at the same temperature and spreading pressure as the mixture), and is given by Eq. 2 applied to P_i^0.

This equation can be obtained from the definition of molar area of mixing (Myers and Prausnitz[3])

$$a^m = a - \sum_{i=1}^{n_c} x_i a_i{}^0 = \frac{A}{n_t} - \sum_{i=1}^{n_c} x_i \frac{A}{n_i^0} = RT \sum_{i=1}^{n_c} x_i \left(\frac{\partial \ln \gamma_i}{\partial \pi} \right)_{x_i, T} \tag{10}$$

As mentioned previously, the adsorbed solution theory has been solved several times assuming the ideality of the adsorbed phase: in this case the activity coefficients are equal to unity. When ideality cannot be assumed, activity coefficients have to be calculated.

In this work, as it has been already discussed, activity coefficients are evaluated using two classical liquid-vapor equilibrium models, nonrandom two liquids (NRTL) (Renon and Prausnitz[18]), and UNIversal QUAsi Chemical (UNIQUAC) (Abrams and Prausnitz[8]) for which only binary parameters are required for multicomponent systems.

Then, Eq. 5 is replaced by UNIQUAC or NRTL model as described later, where γ_i is not a function of π. Since γ_i is not a function of π, and Eq. 9 is replaced by the following equation

$$\frac{1}{n_t} = \sum_{i=1}^{n_c} \frac{x_i}{n_i^0} \tag{11}$$

The second term on the righthand side of Eq. 9 would be taken into account if use was made of the SPD model to estimate activity coefficients.

Activity Coefficient Models. Activity coefficients estimated using UNIQUAC model are expressed as follows

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{12}$$

Combinatorial part

$$\ln \gamma_i^C = \ln \frac{\varphi_i}{x_i} + \frac{z}{2} s_i \ln \frac{\vartheta_i}{\varphi_i} + \ell_i - \frac{\varphi_i}{x_i} \sum_j x_j \ell_j \tag{13}$$

Residual part

$$\ln \gamma_i^R = s_i \left[1 - \ln \left(\sum_{j=1}^{nc} \vartheta_j \tau_{ji} \right) - \sum_{j=1}^{nc} \frac{\vartheta_j \tau_{ij}}{\sum_{k=1}^{nc} \vartheta_k \tau_{kj}} \right] \tag{14}$$

With

$$\varphi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{15}$$

$$\vartheta_i = \frac{s_i x_i}{\sum_j s_j x_j} \tag{16}$$

$$\ell_i = \frac{z}{2}(r_i - s_i) - (r_i - 1) \tag{17}$$

and

$$\tau_{ji} = \exp\left(-\left(\frac{u_{ji} - u_{ii}}{RT}\right)\right), \qquad \tau_{jj} = \tau_{ii} = 0 \tag{18}$$

Where s_i and r_i are, respectively, area and volume parameters of component i, z is a coordination number that is generally taken equal to 10, u_{ij} represents energy of interaction between components i and j, and $(u_{ij} = u_{ji})$ $(u_{ji} - u_{ii})$ $(i \neq j)$ are the adjustable parameters of UNIQUAC model. So the number of adjustable parameters is equal to $n_c(n_c-1)$. Hence, there are two adjustable parameters for a binary mixture.

Activity coefficients estimated using NRTL model are expressed as follows

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \left(\frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}} \right) \right) \tag{19}$$

With

$$\tau_{ji} = \frac{(g_{ji} - g_{ii})}{RT}, \qquad \tau_{jj} = \tau_{ii} = 0 \tag{20}$$

and

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}), \qquad G_{jj} = G_{ii} = 1 \tag{21}$$

g_{ji} represents energy of interaction between components i and j, $(g_{ij} = g_{ji})$

α_{ij} nonrandomness parameter, and $\alpha_{ij} = \alpha_{ji}$

$(g_{ji} - g_{ii})$ $(i \neq j)$, and α_{ij} $(i \neq j)$ are the adjustable parameters of NRTL model. So the number of adjustable parameters is equal to $3(n_c(n_c - 1))/2$. Hence, there are three parameters for a binary mixture.

Solution Methods

Single-solute adsorption isotherms

For each component, the three adjustable parameters n_{mi}, K_i and t_i, of Toth equation, are calculated by minimizing the following criterion (least-squares method) using Gauss-Newton algorithm

$$LS1 = \sqrt{\frac{1}{n_{exp}} \sum_{j=1}^{n_{exp}} \frac{(n_{i,j,exp} - n_{i,j,calc})^2}{(n_{i,j,exp})^2}} \tag{22}$$

where n_{exp} is the number of obtained experimental equilibria.

Solution of IAST

Since all the activity coefficients are taken equal to one in the ideal adsorbed solution theory, the problem includes $(2n_c + 1)$ equations (n_c Eq. 4, n_c Eq. 6 and Eq. 7), and $(2n_c + 1)$ variables $((x_i, P_i^0(T, \pi), i = 1,n_c), \pi)$. It has been solved by the Newton-Raphson method. The integral term in each Equation (6) has been estimated using a Runge Kutta Merson algorithm, $n_i(p_i)$ being calculated by Toth model using the parameters n_{mi}, K_i and t_i identified with the help of single-solute adsorption isotherms.

The most commonly known problem of Newton-Raphson method lies in initialization step. We have chosen the following initialization: $(x_i)_{init} = y_i/\Sigma y_k$, $(P_i^0)_{init} = y_i P/(x_i)_{init}$, and π close to 0.001 $N.m^{-1}$.

Once the problem has been numerically solved, the adsorbed amount of each component and the total adsorbed amount are determined using Eqs. 8 and 11.

Solution of RAST

The problem includes $(3n_c + 1)$ equations (n_c Eqs. 4, n_c (5), n_c (6) and (7)), and $(3n_c + 1)$ variables $((x_i, P_i^0(T,\pi), \gamma_i(T,\pi,\bar{x}), i = 1,n_c), \pi)$. Equation 5 expressed by Eqs. 12 to 18 if UNIQUAC model is chosen, or by Eqs. 19 to 21 if NRTL model is chosen. Then with given values of adjustable parameters of UNIQUAC or NRTL, the RAST is solved in the same way as IAST. The solution of IAST is used as initialization of RAST.

Once the problem has been numerically solved, the adsorbed amount of each component, and the total adsorbed amount are determined using Eqs. 8 and 11.

Identification of binary interaction parameters

Parameters of UNIQUAC or NRTL model have to be determined. Indeed, for a binary mixture, values of these parameters can be found in literature for vapor-liquid equilibrium, but these values are not expected to provide good results since in this case we deal with vapor-adsorbed-phase

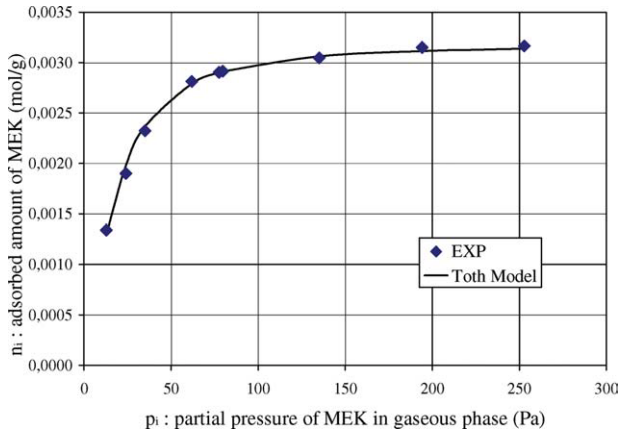

Figure 2. Comparison of Toth's model with experimental data for MEK at 30°C, 1 atm.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

equilibrium. So the adjustable parameters of UNIQUAC or NRTL were identified by minimizing the following criterion (least-squares method) using Gauss-Newton algorithm

$$LS2 = \sqrt{\frac{1}{n_{exp}}\frac{1}{nc}\sum_{i=1}^{nc}\sum_{j=1}^{n_{exp}}\frac{\left(n_{i,j,exp}-n_{i,j,calc}\right)^2}{\left(n_{i,j,exp}\right)^2}} \qquad (23)$$

where n_{exp} is the number of obtained experimental equilibrium.

Hence, the solution of the Gauss-Newton algorithm provided the parameters which provided "best fits" to the experimental data.

All along this identification problem solution, numerous RAST problems had to be solved in order to estimate adsorbed amounts, as well as derivatives of the RAST model with respect to UNIQUAC or NRTL parameters (these derivatives being estimated using numerical perturbations). For a given experimental point, the first RAST problem was initialized using IAST solution and the following RAST problems were initialized using the previous solution.

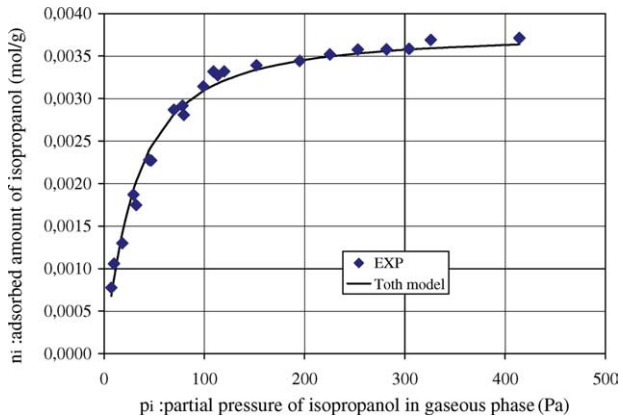

Figure 3. Comparison of Toth's model with experimental data for isopropyl alcohol at 30°C, 1 atm.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 2. Parameters of Single-Component Isotherms Model (Toth's Model)

Component i	MEK	IA
n_{mi} (mmol.g^{-1})	3.18	3.77
K_i (Pa^{-1})	3.65 10^{-2}	2.70 10^{-2}
t_i	1.71	1.27
Least Square Criterion (LS1 Eq. (22))	0.0209	0.0660

Results and Analyses

Single-solute adsorption isotherms

Figures 2 and 3 show experimental data obtained for MEK and IA, respectively. Experimental data are well fitted with Toth model as shown on these figures. The fitted parameters for the two components are listed in Table 2.

MEK and IA exhibit maximum adsorption amount relatively close (3.18 and 3.77 mmol.g^{-1}, i.e., 229 and 226 mg.g^{-1}). It must be noted that for the two components the parameter t is greater than the unity. According to Terzyk[27], when this parameter is greater than unity, the lateral interactions between the adsorbed molecules are greater than the adsorptive potential. Then, it can be thought that since the adsorbate-adsorbate interactions are greater than the adsorptive potential, the RAST combined with a liquid-vapor model for calculating activity coefficients will fit the experimental data of adsorbed phase gaseous phase equilibrium sufficiently well.

Binary diluted mixture adsorption isotherms

As mentioned earlier by Lipatov et al.[27] and Lipatov et al.[28] the adsorbent mass and the initial ratio between the two components before the adsorption takes place have an influence on the composition of the final equilibrium. In order to investigate influence of adsorbent mass and influence of initial composition of the gaseous phase, six binary diluted mixtures have been studied (these influences are discussed elsewhere[17]). Mass of adsorbent and initial ratio between partial pressure of MEK and partial pressure of IA for each binary diluted mixture are listed in Table 3.

For each binary diluted mixture, three, four or five equilibrium points were experimentally determined changing the initial total VOC concentration (but the initial ratio was kept constant). Table 4 summarizes these data.

Isobaric selective X-Y diagrams can be drawn with these data, X_i is the adsorbed-phase molar fraction of component i at equilibrium (in fact x_i, that is given by Eq. 9), and Y_i is

Table 3. Characteristics of the Six Studied Binary Diluted Mixtures

Mixture	Initial ratio between partial pressures $(p_{MEK}/p_{Iso})_0$	Adorbent mass m (g)
1	0.17	80
2	0.68	80
3	3.47	80
4	0.18	40
5	0.71	40
6	3.26	40

Table 4. Equilibrium Data of the Six Studied Binary Diluted Mixtures

Mixture	Initial total VOC pressure $(p_{MEK}+p_{IA})_0$ Pa	Total VOC pressure at equilibrium $p_{MEK}+p_{IA}$ Pa	Partial pressure at equilibrium p_{MEK} Pa	Partial pressure at equilibrium p_{IA} Pa	Number of adsorbed moles n_{MEK} mmol/g	Number of adsorbed moles n_{IA} mmol/g
1	58.66	39,64	3.98	35.66	0.489	1.597
	103.74	78,28	8.83	69.45	0.664	2.135
	147.82	118,97	14.12	104.85	0.709	2.420
	174.10	145,21	18.66	126.55	0.712	2.479
2	29.62	16,69	4.81	11.88	0.818	0.592
	52.04	34,45	11.23	23.22	1.118	0.822
	82.81	59,45	20.65	38.80	1.453	1.109
	109.63	86,05	30.83	55.22	1.421	1.137
	135.96	108,65	38.76	69.89	1.651	1.342
3	30.30	16,65	11.43	5.22	1.313	0.173
	63.80	44,01	31.80	12.21	1.915	0.245
	97.63	74,15	54.88	19.27	2.249	0.310
	135.45	111,6	84.72	26.88	2.297	0.328
	162.58	138,74	105.92	32.82	2.278	0.342
4	61.37	52,91	7.75	45.16	0.447	1.393
	116.43	104,6	15.05	89.55	0.581	2.018
	173.61	159,32	22.41	136.91	0.751	2.369
	231.91	216,7	31.49	185.21	0.772	2.580
5	29.42	23,52	8.57	14.95	0.810	0.468
	63.25	53,59	20.57	33.02	1.242	0.856
	116.21	103,89	41.63	62.26	1.448	1.207
	161.04	148,35	60.48	87.87	1.487	1.295
6	51.17	43,6	32.13	11.47	1.516	0.117
	87.78	77,03	57.74	19.29	2.115	0.292
	149.14	137,88	104.57	33.31	2.113	0.348

the molar fraction of component *i* among the total COV in the polluted air at equilibrium and is defined by

$$Y_i = \left(\frac{y_i}{y_{MEK} + y_{Iso}}\right)_{equilibrium} = \left(\frac{p_i}{p_{MEK} + p_{Iso}}\right)_{equilibrium} \quad i = MEK, \quad Iso \quad (24)$$

It clearly appears on Figure 4 that activated carbon exhibits a higher selectivity for MEK although it is the more volatile component. This fact cannot be explained by steric exclusion, since MEK kinetic diameter (5.2 Å) is higher than IA kinetic diameter(4.5 Å). It must be due to the surface functional groups of the employed activated carbon: the chemical structure of MEK could explain that it has much stronger electrochemical interactions with the activated carbon surface than the isopropanol. Since the pH of the surface of the activated carbon is about 10, it could include nucleophilic groups (which are by definition Lewis bases). The carbonyl group of MEK, which is electrophilic, could then bond these nucleophilic groups.

We have then tried to simulate the 25 experiments:

- Using IAST model, each experiment can be simulated independently from the others.
- We have also tried to simulate each experiment independently from the others using UNIQUAC-RAST model: binary interaction parameters of the UNIQUAC model are taken to be equal to those of the liquid-vapor equilibrium.
- At last for each mixture, values of the binary interaction parameters have been fitted with the least-squares method as described in section identification of binary interaction parameters.

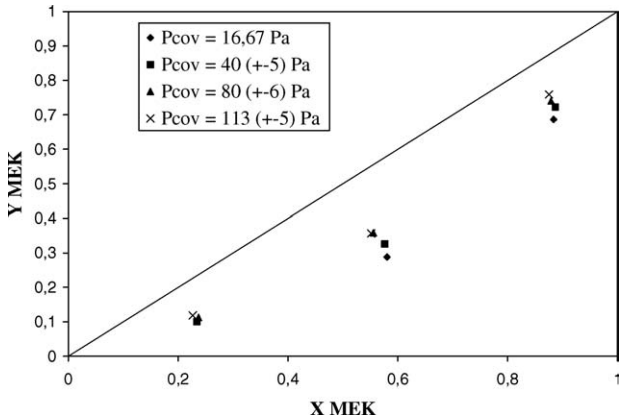

Figure 4. Isobaric selective diagrams: diluted MEK-Isopropyl alcohol mixtures on activated carbon (data are those of experiments of mixtures 1, 2 and 3).

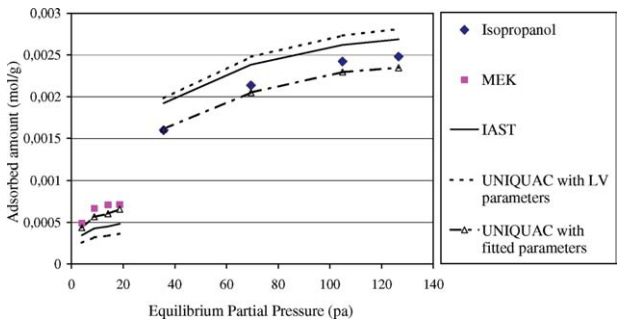

Figure 5. Results for mixture 1 (m_{ads} = 80 mg and initial molar ratio = 0.17).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

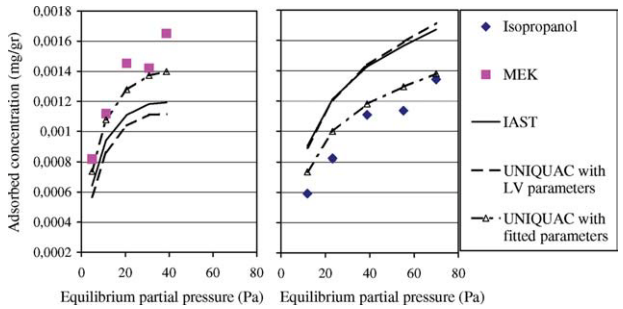

Figure 6. Results for mixture 2 (m_{ads} = 80 mg and initial molar ratio = 0.68).

Results for experiments of mixtures 1, 2 and 3 can be seen on Figures 5, 6 and 7. Results for experiments of mixtures 4, 5 and 6 are not presented here, for sake of clarity of presentation, but lead to the same conclusions.

It must be noted that IAST gives better results for mixtures where the isopropyl alcohol is in great excess (mixtures 1 and 4), but calculated values are not in agreement with experimental data using IAST model. And, as expected, the same conclusion holds using UNIQUAC-RAST model with liquid-vapor equilibrium parameters. UNIQUAC-RAST model fits the experimental data with good accuracy when binary interaction parameters are identified for each mixture. These results confirm that nonideality of the mixture must been taken into account and that activity coefficients describing this nonideality are different from the liquid-vapor equilibrium ones. However, it must be noted that values of the fitted UNIQUAC parameters are different from one mixture to another. This is not satisfactory. Indeed, if the model and its parameters have physiochemical meaning for the system, parameters should not depend on composition. So in order to establish the ability of UNIQUAC model to represent all the data with constant parameters, we have fitted the binary interaction parameters of UNIQUAC model with experimental data of mixtures 1, 2 and 3 simultaneously. Then we have also fitted these parameters with experimental data of mixtures 4, 5 and 6 simultaneously.

Results are shown in Figures 8 and 9 for mixtures 1, 2 and 3, and in Figures 10 and 11 for mixtures 4, 5 and 6. Calculated values are in agreement with experimental data only for mixture 3, and for isopropyl alcohol for mixture 6. It should be noted that experimental data for MEK in mixture 6 seems to be dubious: the first and the third experimental points seems to be underestimated. Nevertheless the common characteristic of mixtures 3 and 6 is that MEK, which is the preferentially adsorbed compound (see Figure 4), is in excess. For the four other mixtures, IA is the component in excess and the model overestimates its adsorbed amount and underestimates MEK adsorbed amount.

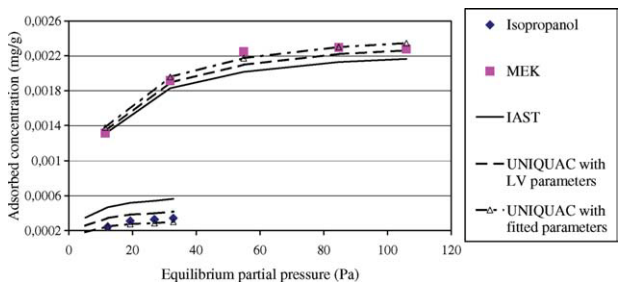

Figure 7. Results for mixture 3 (m_{ads} = 80 mg and initial molar ratio = 3.47).

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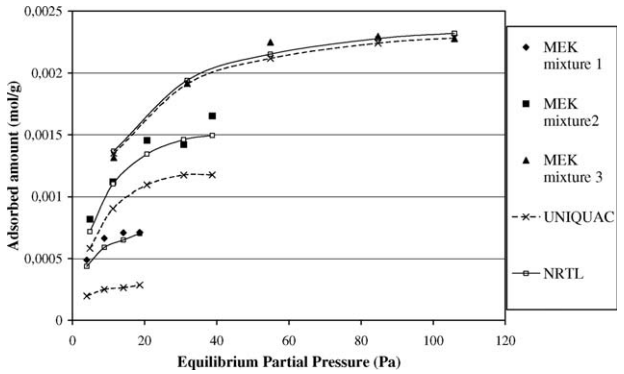

Figure 8. Results for MEK for mixture 1, 2 and 3 (m_{ads} = 80 mg and initial molar ratio MEK/IA is 0.17 for mixture 1, 0.68 for mixture 2, and 3.47 for mixture 3).

The parameters of UNIQUAC (resp. NRTL) model are fitted with all the experiments of these three mixtures.

So UNIQUAC model can not represent three mixtures simultaneously for each mass of adsorbent. This means that this model does not represent all the physical interactions occurring during the binary mixture adsorption since the spreading pressure is not taking into account. So we have implemented RAST with NRTL model. As it was already mentioned, UNIQUAC has a stronger theoretical base than NRTL for the calculation of activity coefficients in a liquid phase. However, since we try to use them for the calculation of activity coefficients in a adsorbed phase, it is expected that, since the adsorbate-adsorbate interactions are greater than the adsorptive potential (as suggested by the value of the parameter t in Toth's model), a liquid-vapor model for the calculation of activity coefficients could fit the experimental data sufficiently well and that the NRTL model could give a better fit of experimental data than UNIQUAC model.

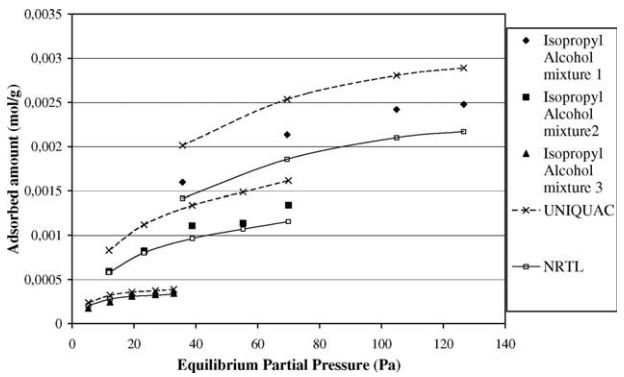

Figure 9. Results for IA for mixtures 1, 2 and 3 (m_{ads} = 80 mg, and initial molar ratio MEK/IA is 0.17 for mixture 1, 0.68 for mixture 2, and 3.47 for mixture 3).

The parameters of UNIQUAC (resp. NRTL) model are fitted with all the experiments of these three mixtures.

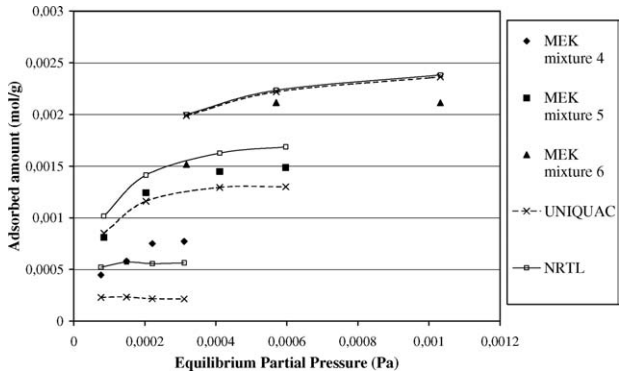

Figure 10. Results for MEK for mixtures 4, 5 and 6 (m_{ads} = 40 mg, and initial molar ratio MEK/IA is 0.18 for mixture 4, 0.71 for mixture 5, and 3.26 for mixture 6).

The parameters of UNIQUAC (resp. NRTL) model are fitted with all the experiments of these three mixtures.

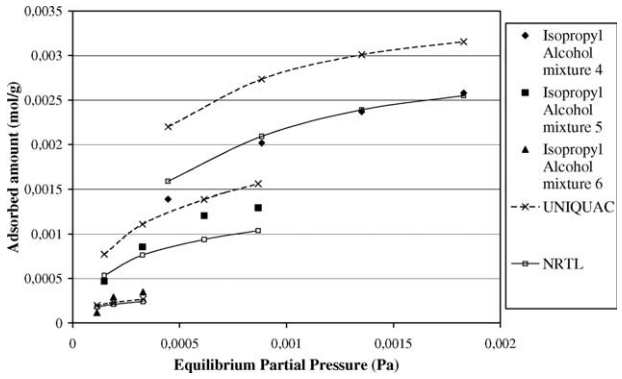

Figure 11. Results for Isopropyl alcohol for mixtures 4, 5 and 6 (m_{ads} = 40 mg, and initial molar ratio MEK/IA is 0.18 for mixture 4, 0.71 for mixture 5, and 3.26 for mixture 6).

The parameters of UNIQUAC (resp. NRTL) model are fitted with all the experiments of these three mixtures.

Identification of parameters was performed in the same way (mixtures 1, 2 and 3 simultaneously and then mixtures 4, 5 and 6 simultaneously). Results are also shown in Figures 8 and 9 for mixtures 1, 2 and 3, and on Figures 10 and 11 for mixtures 4, 5 and 6. The two models predict nearly the same adsorbed amounts for mixtures 3 and 6 where MEK is in excess. Results accuracy is slightly better for mixture 5, and quite better for mixtures 2. The major difference lies in mixtures 1 and 4 (where isopropyl alcohol is in great excess), which are clearly better predicted by NRTL model.

At last we identified UNIQUAC and NRTL parameters with the six mixtures simultaneously. Unsurprisingly UNIQUAC failed to represent each mixture with good accuracy. NRTL represents each mixture with good accuracy: only the predicted values for mixture 1 are slightly worse.

The criterion calculated by Eq. 23 was reported in Table 5 for IAST, UNIQUAC-RAST and NRTL-RAST models. Moreover, we have calculated least-square criteria for each mixture when parameters are identified using three mixtures simultaneously (values in italic in Table 5). For the mixtures 4, 5 and 6, for example, a fit that is about 10% ''worse'' in terms of the objective function (i.e., the least-square criterion LS2 — Eq. 23) is associated with a variation between +59% and −30% for τ_{12}, between +3.5% and −5% for τ_{21} and between +2.8% and −4% for α_{12} for NRTL model, while it is associated with a variation between +98% and −100% for τ_{12}, and between +25% and −41% for τ_{21} for UNIQUAC model. Hence, the RAST-NRTL model is very sensitive to τ_{21} and α_{12}, while the RAST-UNIQUAC model is less sensitive to binary parameters.

It appears that the criterion is well ameliorated using NRTL instead of UNIQUAC. The great difference between criteria for RAST-NRTL model with three mixtures (1, 2, 3 or 4, 5, 6) can be explained by dubious experimental data for MEK in mixture 6. It can be noted that mixtures 1 and 4 for which the isopropyl alcohol is in great excess exhibit the best criteria for IAST model. In fact the increasing amount of MEK in the binary mixture leads to higher nonideality. The experimental data of the mixtures with little amount of MEK are fitted with good accuracy with RAST-NRTL model, whereas the RAST-UNIQUAC model fails to represent them.

Conclusions

Experimental and theoretical studies were conducted in order to evaluate the performance of different models to estimate the adsorption of a diluted mixture of two VOCs. Single-solute adsorption isotherms were determined and represented by Toth's model with good accuracy. The experimental results of binary mixtures adsorption demonstrated that the adsorption affinity of methyl ethyl ketone was higher than that of isopropyl alcohol, leading to higher selectivity whatever the initial ratio of these two components might be. Use of IAST was not satisfactory to estimate adsorption isotherms, but enabled to show that the increasing amount of MEK in the binary mixture led to higher nonideality. Moreover, the use of RAST combined with UNIQUAC model confirmed that nonideality of the mixture had to be taken into account, and that activity coefficients describing this nonideality were different from the liquid-vapor equilibrium ones. However, UNIQUAC failed to represent several mixtures simultaneously (the same two components but with different ratio), whereas NRTL model gave good results even with the limitation of using a vapor-liquid equilibrium

Table 5. Least-Square Criteria Obtained with the Three Different Models

	Least Square Criterion LS2 (Eq. (23))		
	IAST	RAST-UNIQUAC	RAST-NRTL
mixtures 1, 2, 3	0.55 *(0.29-0.42-0.81)*	0.31 *(0.45-0.28-0.17)*	0.09 *(0.11-0.08-0.07)*
mixtures 4, 5, 6	0.93 *(0.26-0.53-1.65)*	0.40 *(0.52-0.27-0.34)*	0.21 *(0.15-0.17-0.31)*
mixtures 1, 2, 3, 4,5 and 6	0.75	0.37	0.20

equation for calculating the activity coefficients in the adsorbed phase.

Notation

A = specific area, $m^2.g^{-1}$
$C_{i,0}$ = concentration of component i in the balloon before adsorption, $mol.m^{-3}$
$C_{i,e}$ = concentration of component i in the balloon at equilibrium ($mol.m^{-3}$)
G_{ij} = parameter of UNIQUAC model, Eq. 21
g_{ij} = energy of interaction between i and j in NRTL model
$(g_{ji} - g_{ii})$ = adjustable parameter of NRTL model
ℓ_i = parameter of UNIQUAC model for component i, Eq. 17
K_i = constant of Toth's model for component i, Pa^{-1}
m = mass of adsorbent, g
n_c = number of components
n_{exp} = number of experimental equilibria
n_i = number of adsorbed moles of component i per g of adsorbent, $mol.g^{-1}$
n_{mi} = maximum number of adsorbed moles of component i per g of adsorbent in Toth's model, $mol.g^{-1}$
P = pressure, Pa
p_i = partial pressure of component i in the gaseous phase, Pa
P_i^0 = equilibrium partial pressure of single solute i at T and π, Pa
R = perfect gas constant, 8.314 $J.mol^{-1}.K^{-1}$
r_i = volume parameter of component i
s_i = area parameter of component i
T = temperature, K
t_i = parameter of Toth's model for component i
u_{ij} = energy of interaction between i and j in UNIQUAC model
$(u_{ji} - u_{ii})$ = adjustable parameter of UNIQUAC model
$\bar{x}$ = vector of composition, $x_1,\ldots x_{nc}$
x_i = molar fraction of component i in the adsorbed phase
y_i = molar fraction of component i in the gaseous phase

Greek letters

α_{ij} = adjustable parameter of NRTL model
γ_i = activity coefficient of component i in the adsorbed phase
ϕ_i = parameter of UNIQUAC model for component i, Eq. 15
π = spreading pressure, $N.m^{-1}$
τ_{ij} = parameter of UNIQUAC (Eq. 18) or NRTL (Eq. 20) model
ϑ_i = parameter of UNIQUAC model for component i, Eq. 16

Subscripts

calc = calculated value used in Eqs. 22 and 23
exp = experimental value used in Eqs. 22 and 23
i = component i
j = component j or j^{th} experiment used in Eqs. 22 and 23
k = component k

Literature Cited

1. Foster KL, Fuerman RG, Economy J, Larson SM, Rood MJ. Adsorption characteristics of trace volatile organic compounds in gas streams onto activated carbon fibers. *Chem Mater*. 1992;4(5): 1068–1073.
2. Le Cloirec P. *Les Composés Organiques Volatiles (COV) Dans L'environnement*. Paris, France: Lavoisier Tec & Doc; 1998.
3. Myers AL, Prausnitz JM. Thermodynamics of mixed-gas adsorption. *AIChE J*. 1965;11(1):121–127.
4. Quinones I, Cavazzini A, Guiochon G. Adsorption equilibria and overloaded band profiles of basic drugs in a reversed-phase system. *J Chromatogr A*. 2000;877:1–1.1.
5. Steffan DG, Akgerman A. Thermodynamic Modeling of binary and ternary adsorption on silica gel. *AIChE J*. 2001;47(5):234–1246.
6. Talu O, Zwiebel I. Multicomponent adsorption equilibria of non ideal mixtures. *AIChE J*. 1986;32(8):1263–1276.
7. Talu O, Zwiebel I. Spreading pressure dependant equation for adsorbate phase activity coefficients. *Reactive Polym*. 1987;5(1):81–91.
8. Abrams DS, Prausnitz JM. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J*. 1975;21:116–128.
9. Garcia-Galdo JE, Cobas-Rodriguez J, Jauregui-Haza UJ, Guiochon G. Improved model of multicomponent adsorption in reversed-phase liquid chromatography. *J Chromatogr A*. 2004;1024:9–14.
10. Wilson GM. Vapor -liquid equilibrium XI: a new expression for the excess free energy of mixing. *J Am Chem Soc*. 1964;86:127–130.
11. Costa E, Sotelo JL, Calleja G, Marron C. Adsorption of binary and ternary hydrocarbon gas mixtures on activated carbon: experimental determination and theoretical prediction of the ternary equilibrium data. *AIChE J*. 1981;27(1):5–12.
12. Krishna R. Diffusion of binary mixtures across zeolite membranes : entropy effects on permeation selectivity. *Int Comm Heat Mass Transfer*. 2001;28(3):337–346.
13. Calleja G, Jimenez A, Pau J, Dominguez L, Perez P. Multicomponent adsorption equilibrium of ethylene, propane, propylene and CO_2 on 13X zeolite. *Gas Sep Purif*. 1994;8(4):247–256.
14. Lillo-Rodenas MA, Fletcher AJ, Thomas KM, Carzola-Amoros D, Linares-Solano A. Competitive adsorption of a benzene-toluene mixture on activated carbons at low concentration. *Carbon*. 2006;44(8):1455–1463.
15. Monneyron P, Manero MH, Foussard JN. Measurement and modelling of single and multi-component adsorption equilibria of VOC on high-silica zeolites. *Environ Sci Technol*. 2003;37(11):2410–2414.
16. Kim D, Cai Z, Sorial GA. Determination of gas phase adsorption isotherms - a simple constant volume method. *Chemosphere*. 2006; 66(8):1758–1764.
17. Fernandes N. *Contribution à L'étude de L'adsorption sur Charbon Actif d'un Mélange Gazeux de Composés Organiques Volatils (C.O.V.)*. Université de Pau et des Pays de l'Adour: Pau, France; 2005. PhD Thesis.
18. Renon H, Prausnitz JM. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J*. 1968;14:135–144.
19. Monfort JP, Rojas RMDL. A study of simplified molecular models in phase equilibrium prediction. *Fluid Phase Equilibria*. 1978;2:181–198.
20. Sorensen JM, Magnussen T, Rasmussen P, Fredenslund A. Liquid-liquid equilibrium data: their retrieval, correlation and prediction: correlation. *Fluid Phase Equilibria*. 1979;3:47–82
21. Huang ZH, Kang F, Zeng YP, Yang JB, Liang KM. Adsorption of trace polar methy-ethyl-ketone and nonpolar benzene vapors on viscose rayon-based activated carbon fibers. *Carbon*. 200240:1363–1367.
22. Kim KJ, Kang CS, You YJ, Chung MC, Woo MW, Jeong WJ, Park NC, Ahn HG. Adsorption-desorption characteristics of VOCs over impregnated activated carbons. *Catal Today*. 2006;111:223–228.
23. Fournel L, Mocho P, Fanlo JL, Le Cloirec P. External capillary condensation and adsorption of VOCs onto activated carbon fiber cloth and felt. *Environ Technol*. 2005;26(11):1277–1288.
24. Ondarts M, Hort C, Platel V, Sochard S. Evaluation of indoor air treatment by two pilot-scale biofilters packed with compost and compost-based material. *WIT Trans Ecology Environ*. 2008;116:499–508.
25. Rouquerol F, Rouquerol J, Sing K. *Adsorption by Powders and Porous solids*. New-York: Academic Press; 1999.
26. Brouers F, Sotolongo O, Marquez F, Pirard JP. Microporous and heterogeneous surface adsorption isotherms arising from Levy distributions. *Physica A*. 2005;349:271–282.
27. Terzyk AP, Chatlas J, Gauden PA, Rychlicki G, Kowalczyk P. Developing the solution analogue of the Toth adsorption isotherm equation. *J Colloid Interface Sci*. 2003;266:473–476.
28. Lipatov Y, Todosijchuk T, Chornaya V. Influence of component ratio on adsorption of polymer mixtures under phase separation of solutions. *J Colloid Interface Sci*. 1999;215:290–295.
29. Lipatov Y, Todosijchuk T, Chornaya V, a Menzheres G. Dependence of the adsorption of polymer mixtures from solution on the amount of an adsorbent. *J Colloid Interface Sci*. 2002;246:29–33.

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