Thermodynamic Modeling of Binary and Ternary Adsorption on Silica Gel

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Qualitative and quantitative characterization and prediction of multicomponent adsorption equilibria are essential for design of environmental remediation processes such as soil vapor extraction, bioventing, and thermal desorption. Single component, binary- and ternary-mixture isotherms on silica gel were measured by the frontal analysis chromatography technique. Binary organic mixtures were composed of environmentally relevant VOCs, hexane/benzene (nonpolar/nonpolar), and hexane/trichloroethylene (nonpolar/slightly-polar). Water binaries were water with hexane, benzene, or trichloethylene. Organic mixtures exhibited enhanced adsorption, where the adsorbed amount for each component was increased due to the second component. Water/hexane and water/benzene mixtures showed noncompetitive adsorption, where water adsorbed onto polar sites and n-hexane or benzene adsorbed onto nonpolar sites. Competition for polar adsorption sites was observed for the trichloroethylene adsorption in water. Adsorption data of n-hexane/benzene/water showed that n-hexane and water were independently adsorbing onto different adsorption sites. Furthermore, n-hexane and benzene with water showed the same adsorption behavior as without water. For the mixture of n-hexane/trichloroethylene/water, only the amount of water adsorbed was reduced compared to the pure species adsorption of water. The adsorption equilibria of n-hexane and trichloroethylene were not influenced in comparison to their pure species isotherms. Mixture isotherms were modeled with IAST, MSAM, and RAST. The nonideal adsorbed phase was characterized using activity coefficients.

Introduction

The prediction of contaminant adsorption isotherms is probably the most important information necessary for design of a remediation process for removal of volatile organic contaminants (VOCs) from soil, such as soil vapor extraction, bioventing, and thermal desorption (Thibaud et al., 1992). Normally, the conditions under which the adsorption equilibrium is established are ambient temperature and atmospheric pressure for *in-situ* remediation processes such as soil vapor extraction and bioventing.

Soil is a heterogeneous solid with a very complex matrix consisting of clays, silica, organic matter, and so on, all of which, individually, may be polar or nonpolar adsorbents. In addition, the subsurface soil contains water as moisture. Therefore, investigating the multicomponent adsorption equilibrium including water as an additional component is essential for the design of remediation processes. Although there are many studies on coadsorption of VOCs and water on soil, and organics and water on carbon, there are very few studies on coadsorption of organics and water on polar adsorbents. Recently, we reported on binary adsorption/desorption on/from soil which had more or less nonpolar adsorbent characteristics and observed that uptake of individual species always decreased when coadsorbed with another species (Guo et al., 1998). The objective of this work was to study the influence of polarity on adsorption equilibria and the prediction of binary VOC mixture isotherms with thermodynamic models on a well-defined polar adsorbent such as silica gel. Another objective was to characterize the nonideality of the adsorbed phase in terms of the adsorbed-phase activity coefficients. A final objective was to study VOC adsorption in presence of water and model the thermodynamics of the system.

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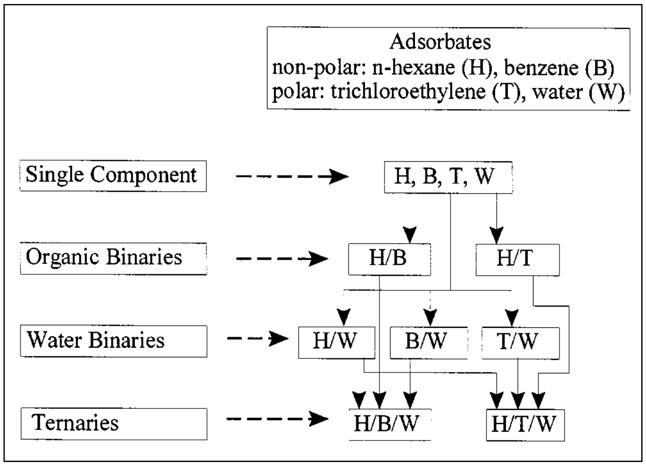

Figure 1. Combination of binary and ternary mixtures studied.

A dynamic response technique, frontal analysis chromatography, was used to measure adsorption breakthrough curves from which the equilibrium data can be calculated (Thibaud et al., 1993). The mixtures were chosen based on their polarity (defined in terms of the dipole moments) of the species. The binary and ternary mixtures studied are shown in Figure 1. The adsorption isotherm of one component was obtained at constant concentration of the other component(s).

We have used the ideal adsorbed solution theory (IAST), the multispace adsorption model (MSAM), and the real adsorbed solution theory (RAST) for prediction and modeling of the binary adsorption isotherms. It is important to note that this study uses a polar adsorbent with both nonpolar and polar adsorbates and their binary and ternary mixtures, and the adsorption measurements are at temperatures below the normal boiling point of the adsorbates, which is representative of subsurface interactions.

Experimental Method

Materials

The silica gel used in this study was "Davisil" grade 645 from Aldrich Chemicals Co. (Deerfield, IL), which is a low-density silica gel with an average pore diameter of 150.6 Å and a specific surface area of 381.6 m^2/g. Silica gel contains up to 5 wt. % water, which is mainly present in form of chemically bound hydroxyl groups. The presence of hydroxyl groups imparts a degree of polarity to the surface. All chemicals were supplied by Aldrich Chemicals Co. (Deerfield, IL) and had a purity of 99% or higher. The gases used to operate the experimental setup, air, hydrogen, helium, and nitrogen were all purchased from Bob Smith Corp. (Bryan, TX). All chemicals and gases were used as received.

Apparatus and procedure

Multicomponent adsorption equilibria were determined by frontal analysis chromatography. In this technique, the response of an initially clean adsorbent bed (that is, free of adsorbate) to a step change in the adsorbate concentration(s) at the inlet of the bed was determined at the outlet of the bed to obtain the components' breakthroughs. The experimental setup is shown in Figure 2. It can be divided into three sections: the flow equilibration section, the adsorption section, and the data acquisition section.

The purpose of the flow equilibration section was to produce a dilute gas mixture of desired composition and maintain a steady gas flow. Helium or nitrogen was used as the carrier gas. The carrier gas was fed as two separate streams, with the flow rate of each adjusted by mass-flow controllers. One stream is passed through a water saturator, which is kept in a water bath at 20°C, to avoid condensation in the following tubing. The tubing throughout the apparatus was held at 24 ± 1°C. This stream was saturated by water and the relative humidity was adjusted by mixing it with the second carrier gas stream. Thus, it is possible to adjust the relative humidity between 0 and $\sim 85\%$. The desired organic concentrations were adjusted by injecting the organic compounds into the humidified carrier gas stream via two separate syringe pumps. The injection of the organic compounds improved the precision of the measurements by lowering the VOC concentration fluctuations and broadened the data range. For pure compounds as well as for mixtures, data could be collected nearly up to saturation limits of the VOCs in the carrier gas.

The sorption section consisted of an adsorbent packed column equipped with a bypass line. The adsorbent column was bypassed during adjustment of the flow rates to avoid contamination of the adsorbent bed before the adsorption process started. To start the adsorption process, the gas mixture stream was switched from the bypass to the adsorbent bed. The switch initiated a positive step of the contaminant concentrations at the inlet of the adsorbent column. The effluent of the column was then continuously analyzed by online gas chromatography. The adsorption process was assumed completed when the effluent concentrations were stable and constant and equal to the inlet concentration for each species. The adsorbent bed at that time would be saturated by the organic contaminants.

The stream of mixed gases introduced to the adsorption column was a binary (single component adsorption), ternary (binary component adsorption), or quaternary (three component adsorption) system consisting of a carrier gas and the adsorbing organic compounds and water. Helium or nitrogen, the carrier gas, was at room temperature and it was considered to be nonadsorbing or negligibly adsorbing. An advantage of such a system was that the flow rate during the adsorption process was constant, because only the dilute components adsorb and therefore the gas-phase mass reduction due to adsorption is negligible.

The effluent gas stream was analyzed online by using a sampling valve (Valco) and a HP 5986A gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) in series. As a reference to the TCD, a humidity transmitter (HT) (Valiasa) was used to determine the water concentration. Since organic compounds would cause an offset for the humidity transmitter signal, the HT was only employed to determine the humidity in the carrier gas without organic contaminants. Therefore, first the humidity was adjusted, then the humidity transmitter was bypassed and the organic compounds were injected. The humidity detector was used to calibrate the TCD for water

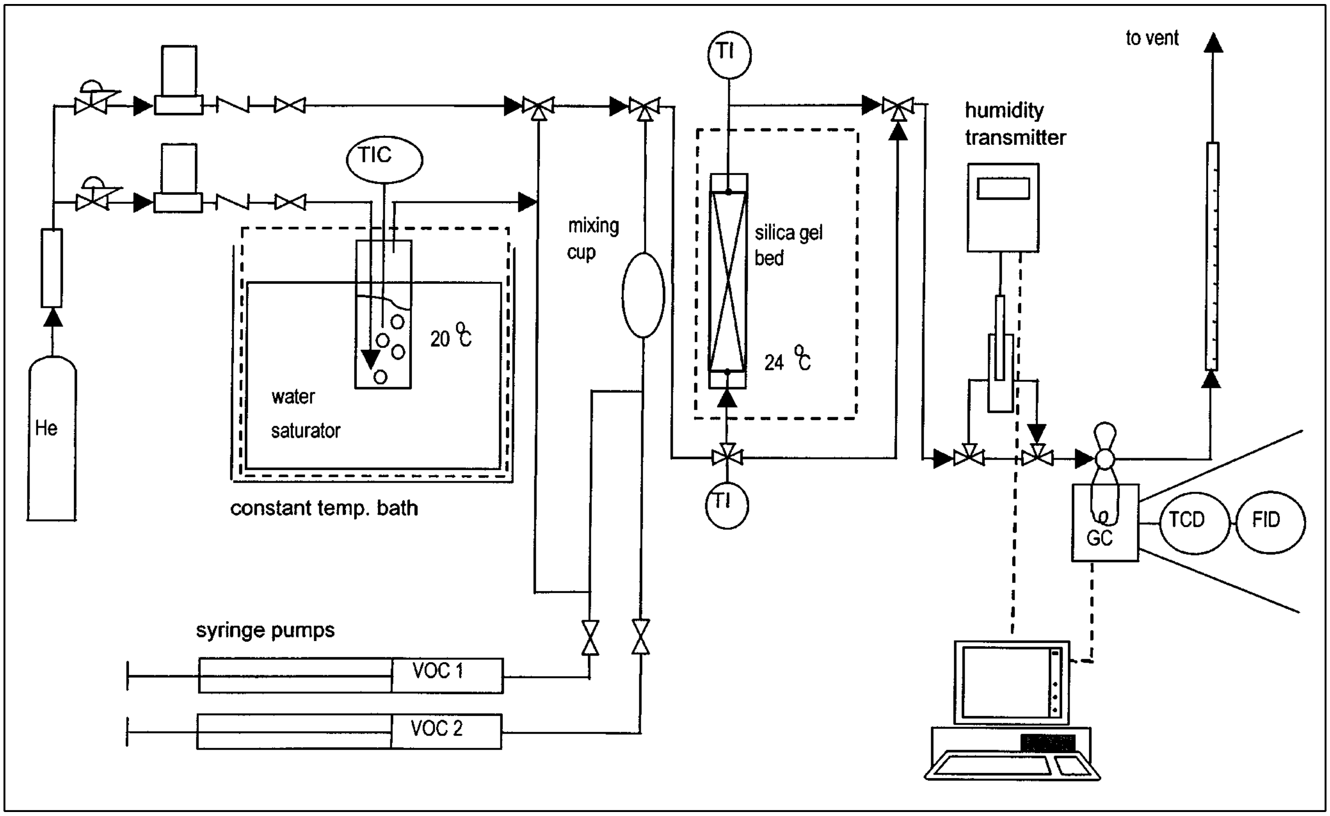

Figure 2. Experimental setup.

analysis. It was experimentally verified by the TCD that the humidity of the carrier gas remained constant throughout the experiments. A Porapaq P column was used for isothermal separation of the components. The flow rate of the gas mixture in the adsorption apparatus was determined with a soap bubble meter. The exhaust stream of the soap bubble meter was connected with the venting system of the laboratory.

Results and Prediction of Equilibrium Data

Single component adsorption

All single component isotherms showed BET-type II behavior. The single component adsorption isotherms were modeled by both the three-parameter and the four-parameter Brunauer-Deming-Deming-Teller (BDDT) equations (Brunauer et al., 1938, 1940). The four-parameter BDDT equation is less known, but is more appropriate to evaluate whether there is capillary condensation (Kast, 1988). This equation gives a smooth transition from multilayer adsorption to capillary condensation. The data indicated that the specific, monolayer adsorption capacity increased with increasing polarity of the VOC adsorbate molecules. The specific monolayer adsorption capacity of water did not fall exactly onto the same trend (Steffan, 1999). *Nonpolar* molecules showed mainly van der Waals (vdW) interactions or only weak coulomb forces with the silica gel surface. The coulomb forces were due to induced dipoles. But *polar* molecules interacted stronger with the *polar* surface due to dipole interactions and exhibit therefore stronger coulomb forces. However, the VOCs investigated were relative large molecules where vdW interactions were still dominant. Israelachvili (1984) measured the contributions of permanent dipole, induced dipole, and vdW interactions to the molecular interaction for some molecule pairs with strong dipole moments in vacuum at 293 K. He observed that even for molecules with strong dipole moments, like HCl or NH_3, vdW forces dominated the pair interactions. Water was the only molecule where dipole interactions made the dominant contribution to the pair interaction. Therefore, one would expect that water is the only molecule where dipole interactions dominate the surface forces as well.

Binary adsorption of VOCs

For the binary VOC mixtures, the adsorption isotherm of one component was measured over the whole range of relative vapor pressures while the concentration of the second component was fixed. Different concentrations of the second component were considered. Mixture isotherms compared to the pure species isotherms are shown in Figures 3 and 4. In these (and subsequent) figures, "1" is the component whose concentration was varied and "2" is the component whose concentration was held constant. Gas-phase concentrations were expressed as partial pressure normalized with the vapor pressure; hence, in Figure 3, for example, $P_1/P_{1,o}$ is partial pressure of hexane in the gas phase divided by its vapor pressure. Vapor pressures at 24°C are given in Table 1.

Enhanced adsorption of one component in the presence of the other component was observed for both mixtures. For the

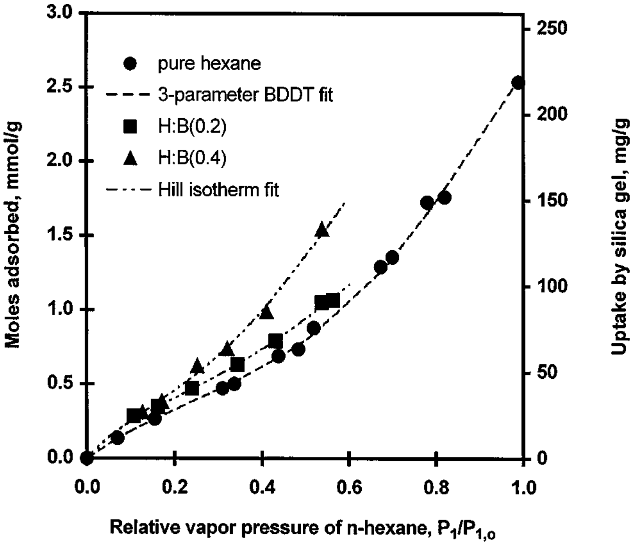

Figure 3. Adsorption isotherms of *n*-hexane in the presence of benzene on dry silica gel at 297 K and at relative vapor pressures of benzene, $P_2/P_{2,o} = 0.2$ and 0.4.

Dry nitrogen was used as carrier gas.

nonpolar/nonpolar *n*-hexane and benzene mixture, the *n*-hexane uptake was increased when coadsorbed with benzene compared to the pure component adsorption. Nye et al. (1994) observed a similar adsorption behavior for the coadsorption of *m*-xylene with *n*-dodecane on air- and oven-dried soil. They explained this adsorption behavior with the formation of multilayers at higher relative vapor pressures, which more than compensated for any competition for adsorption sites.

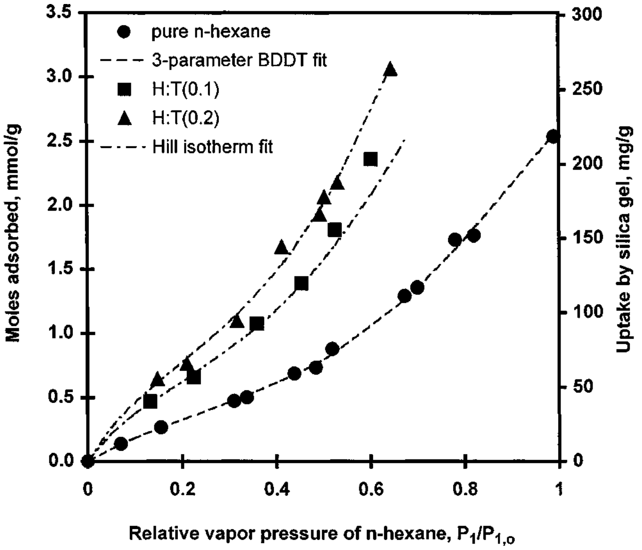

Figure 4. Adsorption isotherm of *n*-hexane in the presence of TCE on dry silica gel at 297 K and at relative vapor pressures of TCE $P_2/P_{2,o} = 0.1$ and 0.2.

Dry nitrogen was used as carrier gas.

Table 1. Vapor Pressures of Compounds

Compounds	Vapor Press., $P_{i,o}$ (mm Hg) at 24°C
n-Hexane	144.0
Benzene	90.7
Trichloroethylene	71.7
Water	22.4

We hypothesize that competition for adsorption sites and interactions between the adsorbates in the adsorbed phase take place together, the former decreases the adsorbed amount of each species whereas the latter increases that. In this case, adsorbed phase attractive interactions were stronger, increasing formation of multilayers. The *nonpolar/polar* adsorbate mixture *n*-hexane and trichloroethylene behaved in a similar manner. Compared to the *n*-hexane/benzene mixture, the increase in the adsorbed amount due to coadsorption of the second component was significantly higher. This indicated that interactions of the components in the adsorbed phase were even stronger for this system. Probably due to the polarity of trichloroethylene, the adsorbate-adsorbate interactions were strengthened by the induction of dipole moments into *n*-hexane. *n*-Hexane was the molecule with the highest polarizability (Table 2). It could also be that strong vdW interactions between *n*-hexane, trichloroethylene and the induced dipole moments made the polar sites of silica gel more accessibile for *n*-hexane.

Binary Adsorption of VOC/Water Mixtures

Figure 5 shows *n*-hexane/water mixture isotherms at fixed partial pressures of water of 0.6 kPa, 1.5 kPa, and 2.1 kPa corresponding to the gas-phase relative humidities of 20% (0.2), 50% (0.5), and 70% (0.7). The mixture isotherms are compared to the pure species isotherm of *n*-hexane. It was observed that the number of moles of *n*-hexane adsorbed was not affected by the presence of water, since pure species and mixture isotherms of *n*-hexane were identical within experimental precision for all three water concentrations. In Figure 6, the mixture isotherms of benzene in the presence of water are given. Again, the mixture isotherms at three different fixed relative humidities of 20%, 50% and 70% were compared to the pure component adsorption isotherm of benzene. Like hexane/water, benzene/water mixture isotherms were identical to the pure species benzene isotherm at all three relative humidities.

Figure 7 shows the isotherm data of the trichloroethylene at the three relative humidities of 20%, 50% and 70%. Due

Table 2. Polarizability of VOCs and Water (Huyskens et al., 1991)

Adsorbates	$\alpha \times 10^{-24}$ cm^3
n-Hexane	11.90
Benzene	10.40
Trichloroethylene	9.58*
Water	1.35*

*These values were estimated with the group contribution method given by Huyskens et al. (1991).

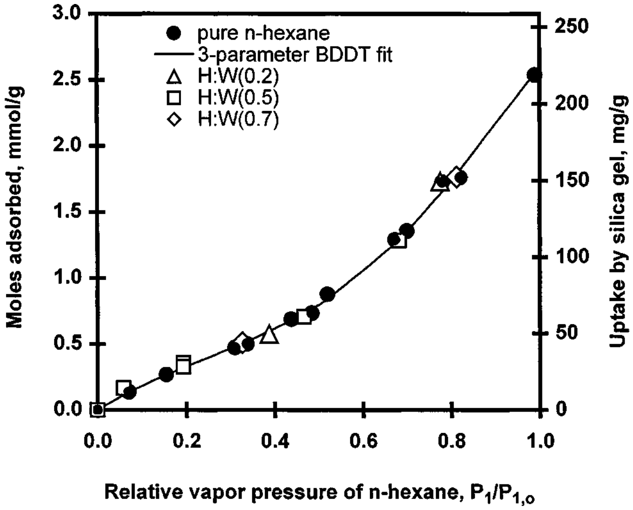

Figure 5. Adsorption isotherm of *n*-hexane (*H*) in the presence of water (*W*) on silica gel at 297 K.

Helium was used as the carrier gas. The numbers given in the brackets are relative vapor pressures $P_2/P_{2,o}$ of water.

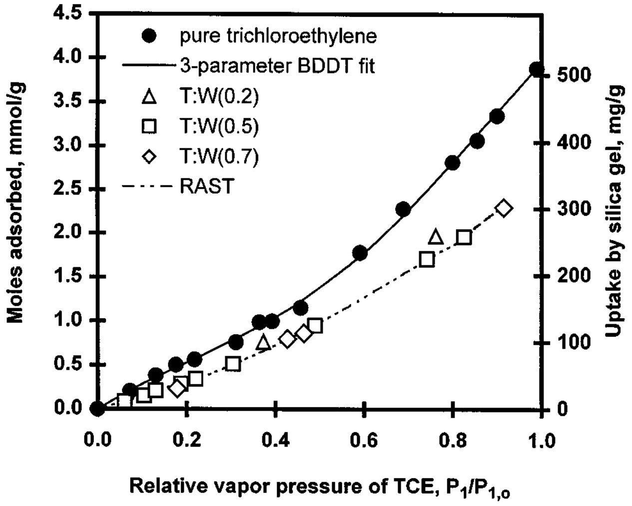

Figure 7. Adsorption isotherm of T or TCE in the presence of water (*W*) on silica gel at 297 K.

Helium was used as carrier gas. The numbers given in the brackets are relative vapor pressures $P_2/P_{2,o}$ of water.

to the competitive adsorption behavior in the presence of water, the amount of trichloroethylene adsorbed was decreased. However, the effect of the relative humidity on the amount of trichloroethylene adsorbed was very low. A small trend could be concluded for the mixture isotherm at a relative humidity of 20%. Here, the decrease of the amount of trichloroethylene adsorbed is slightly less than that for 50% and 70% relative humidity, where both isotherms are identical. The dependency of the trichloroethylene isotherm on the relative humidity was only significant at low water concentrations. At higher relative humidities, multilayer adsorption and capillary condensation of water may be masking the competitive adsorption behavior. We hypothesize that multilayer adsorption or capillary condensation compensated the reduction of the trichloroethylene amount adsorbed due to competition with water. In the higher range of relative vapor pressures, both compounds (trichloroethylene and water) adsorbed in multiple layers and the competition for adsorption sites became less significant. This conclusion is also in agreement with the experimental observation reported by Adamson (1996). He observed that the adsorbent made its influence directly felt only up to the second adsorption layer when multilayer adsorption occurred.

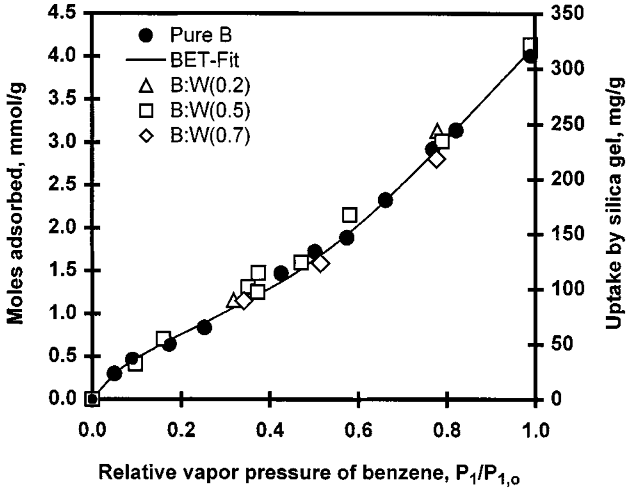

Figure 6. Adsorption isotherm of benzene (*B*) in the presence of water (*W*) on silica gel at 297 K.

Helium was used as carrier gas. The numbers given in the brackets are relative vapor pressures $P_2/P_{2,o}$ of water.

Thermodynamic Modeling of Binary Adsorption Isotherms

We have used the ideal adsorbed solution theory (IAST), the multispace adsorption model (MSAM), and the real adsorbed solution theory (RAST) for prediction and modeling of the binary mixture isotherms from pure component isotherms. All of these theories were developed for gas mixture adsorption, above the normal boiling point of their components (for many gases above critical temperatures) on rather inert, noninteracting adsorbents, and for monolayer adsorption. The systems studied here are quite different in that the adsorbent is polar, the adsorbates of different polarities are adsorbing at temperatures below their boiling point, and their mixtures are expected to adsorb in multilayers and be nonideal. Furthermore, water is immiscible with the organics in liquid state.

The MSAM was developed by Gusev et al. (1996). It describes separately the adsorption in "spaces" close to, and far from, the adsorbent surface. In space I, close to the adsorbent surface, the adsorbate molecules interact strongly with the adsorbent. The molecules in space II are further away from the surface, and they interact with the molecules in space I and are assumed not to interact directly with the surface. The inputs to the calculation are the pure-species adsorption isotherms and a single parameter *R*, characteristic of the adsorbent that can be obtained from very limited mixture data.

The model equations and the use of this theory are thoroughly discussed by Steffan and Akgerman (1998), and Jensen et al. (1997).

The IAST was developed by Myers and Prausnitz (1965), and is a special case of the RAST, with activity coefficients equal to unity. The IAST is a predictive method to calculate mixture equilibrium data from pure component isotherm data. As input function for the pure species isotherms, the three-parameter BDDT equation was used. The RAST is an extension of the IAST to systems with nonideal adsorption behavior. Costa et al. (1981) were the first to extend IAST to RAST by fitting Gibbs excess models like the Wilson and UNIQUAC equations, which are developed to describe the nonidealities in the liquid phase of vapor liquid equilibria, to adsorbed phase activity coefficients. However, in activity coefficient models developed for vapor liquid equilibria, only the composition dependency of the activity coefficients is taken into account. It was later shown by Talu (Talu, 1984; Talu and Zwiebel, 1986, 1987) that a simple analogous application of Gibbs excess models from vapor liquid equilibria (VLE) to vapor adsorption equilibria (VAE) was not entirely possible. Talu showed that the adsorbed phase activity coefficients should also depend on the spreading pressure and developed a spreading pressure dependent (SPD) model based on the UNIQUAC equation. This model requires single component adsorption data at different temperatures to determine the isosteric heat of adsorption. In our study, however, these data were not measured. Sakuth (1993) criticized the choice of the virial equation as a single component isotherm and the mathematical complexity of this model, which led into numerical instabilities. Sakuth (1993) extended the real adsorbed solution theory (RAST) to a predictive theory (PRAST) by using the Henry's constants from pure component isotherms to predict the activity coefficients at the infinite dilution limits, which in turn are used to determine the binary interaction parameters in Gibbs excess models. He used the UNIQUAC equation for the modeling of adsorbed phase activity coefficients.

In RAST (or IAST) the mixture isotherms are calculated from pure component isotherms. In addition to the single component isotherm, the gas composition y_i and the pressure P of the gas-phase mixture has to be known. It is assumed that the spreading pressure for each component in the mixture is equal to the mixture spreading pressure giving

$$\left.\frac{A\pi}{RT}\right|_{\text{mixture}} = \int_0^{P_i^o(\pi)} \frac{n_i}{P_i}\, dP = \int_0^{P_j^o(\pi)} \frac{n_j}{P_j}\, dP_j \qquad (1)$$

where $P_i^o(\pi)$ and $P_j^o(\pi)$ are the equilibrium gas pressures for the components i and j at the same spreading pressure and temperature as the adsorbed mixture and n_i and n_j are the pure component isotherm functionalities. The equilibrium relationship is

$$y_i P = \gamma(x_i, \pi)\, x_i P_i^o(\pi) \qquad (2)$$

the activity coefficients are unity in IAST. Equation 1 yields a relation for $P_i^o(\pi)$ in terms of $P_j^o(\pi)$, which combined with Eq. 2 for $c/2$ binary pairs in a mixture of c components, gives a system of c equations with c unknowns. This system of algebraic equations can be solved numerically for the composition of the adsorbed phase x_i. To be thermodynamically consistent, the sum of mole fractions in each phase has to be equal to unity

$$\sum_{i=1}^{c} y_i = 1 \qquad \text{and} \qquad \sum_{i=1}^{c} x_i = 1 \qquad (3)$$

The total number of moles adsorbed for a nonideal adsorbed phase is then given as

$$\frac{1}{n_t} = \sum_{i=1}^{c} \frac{x_i}{n_i^o} + \sum_{i=1}^{c} x_i \left[\frac{\partial \ln \gamma_i}{\partial \left(\frac{\pi A}{RT} \right)} \right]_{T, x_i} \qquad (4)$$

where $n_i^o = n_i^o[P_i^o(\pi)]$ is the number of moles adsorbed for the pure species i at the same temperature and spreading pressure as the mixture, which can be calculated from the pure component isotherm. In the case of an ideal adsorbed phase, the second term on the right, the partial derivative of the activity coefficients with respect to the spreading pressure, is zero.

In using the RAST, activity coefficients for the components had to be calculated from the experimental data. Before activity coefficients could be calculated using Eq. 2, the spreading pressure of the mixture had to be calculated. It was crucial for this calculation to consider the carrier gas as a third component of the mixture and treat the system as a ternary mixture. However, it was assumed that the carrier gas was not adsorbing on silica gel [negligible adsorption, $K \cong 10^{-8}$ mmol/(g$_{\text{silica}}$·bar)], and, therefore, the adsorbed phase is considered as a binary mixture. The carrier gas was, however, the gas-phase component with the highest partial pressure.

Sakuth (1993) investigated mixtures of components adsorbing from a gas phase consisting of active adsorbing species and an inert carrier gas as well. He kept the sum of the partial pressures of the adsorbing species in the gas mixture constant by varying the composition of the adsorbing species. By doing so, he was able to neglect the partial pressure of the carrier gas in the mixture, since it was always kept constant. In this study, we did not conduct the experiments in the same manner, since the mixture adsorption equilibria had to be investigated over the whole range of adsorption regions into the multilayer region and, therefore, over the whole range of relative vapor pressures close to saturation.

The spreading pressures were calculated by integrating the Gibbs adsorption isotherm using the chemical potential of the gas phase, and were therefore defined by the gas-phase composition and pressure

$$\frac{a}{RT} d\pi = d \ln P + \sum_{i=1}^{c} x_i d \ln y_i \qquad (\text{constant } T) \qquad (5)$$

A consistency test was performed applying the differential form of the Gibbs-Duhem Eq. 6

$$\sum_{i=1}^{c} x_i \left.\frac{\partial \ln \gamma_i}{\partial x_1}\right|_{T,\pi,x_{i\neq 1}} = \left[\frac{1}{n_t} - \sum_{i=1}^{c} \frac{x_i}{n_i^o}\right] \left.\frac{\partial\left(\frac{\pi A}{RT}\right)}{\partial x_1}\right|_{T,\pi,x_{i\neq 1}} \qquad (6)$$

Eubank (1999) argued that the differential form of the Gibbs-Duhem equation is usually a better test for thermodynamic consistency than the integral test, which was suggested by Talu (1984). The differential consistency test shows the actual consistency of each data point, whereas the integral test shows the average consistency of all data points together, where negative and positive deviations may cancel out each other (Steffan, 1999).

Myers (1993) suggested obtaining activity coefficients directly from the Gibbs-Duhem equation. To smooth some of the scatter in the data, we calculated the activity coefficients directly from Eq. 6. The RAST calculation was performed using directly the experimental activity coefficients obtained from the data analysis. The composition of the adsorbed phase was determined by Eq. 1. The total number of moles for the adsorbed phase was calculated with Eq. 4, where the partial derivative was evaluated numerically from Eq. 7 (Sakuth, 1993).

$$\frac{\partial \ln \gamma_i}{\partial\left(\frac{\pi A}{RT}\right)} = \lim_{\Delta x_k \to 0} \frac{\ln \gamma_i(x_k,\pi_k) - \ln \gamma_i(x_{k-1},\pi_{k-1})}{\pi_k - \pi_{k-1}},$$

$$\Delta x_k = x_k(\pi_k) - x_{k-1}(\pi_{k-1}) \qquad (7)$$

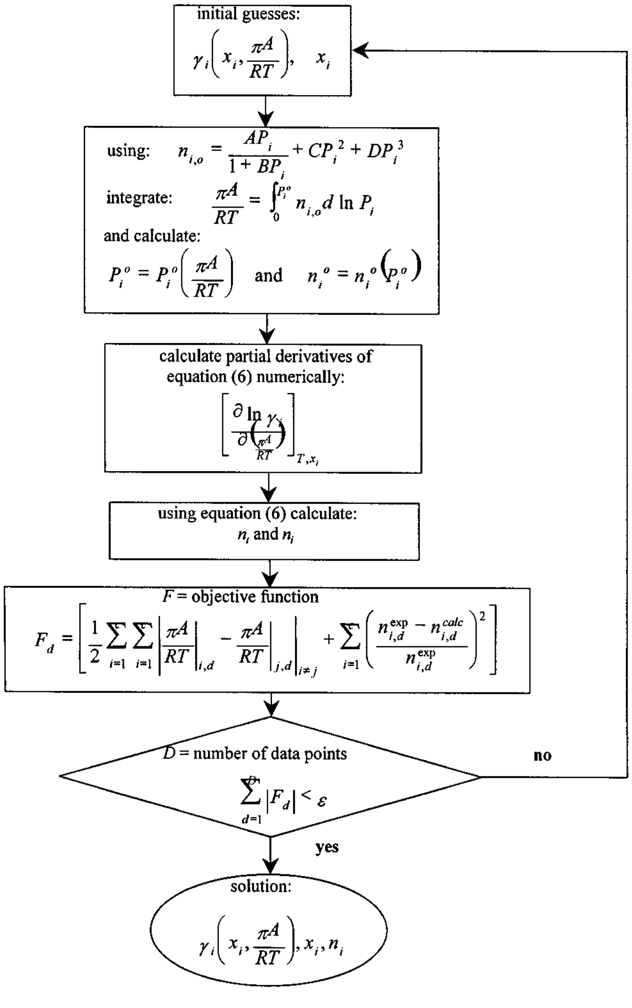

Figure 8. Procedure for iterative calculation to fit mixture isotherms with the RAST.

The iterative calculation procedure for fitting mixture isotherms with the RAST is shown in Figure 8. The experimental activity coefficients were used as initial guesses and corrected accordingly during the calculation.

The prediction of the *n*-hexane (1)/benzene (2) mixture isotherm at a fixed relative vapor pressure $P_2/P_{2,o} = 0.2$ of benzene with the IAST, MSAM, and RAST are shown in Figure 9. The MSAM and IAST both result in fair predictions at low hexane partial pressures and MSAM predictions are better than the IAST predictions. However, one has to consider that the MSAM has an additional parameter R, which was fitted to mixture adsorption data. At all fixed benzene partial pressures, MSAM with $R = 0.9$ gave the best fit. IAST and MSAM calculations on a carrier gas free basis (binary hexane/benzene) and with carrier gas (ternary carrier gas/hexane/benzene) gave identical results. At higher *n*-hexane concentrations, the prediction error increased, due to insufficient fits of the pure species isotherms in the range of capillary condensation. Sakuth (1993) criticized in general the application of the adsorbed solution theory in the range of multilayer adsorption to capillary condensation. He argued that the assumption of the same adsorbent surface area freely accessible for all adsorbate species is not satisfied in the range of capillary condensation. However, if one improves the pure species isotherm fits in the range of capillary condensation, the predictions of the mixture isotherms would improve sig-

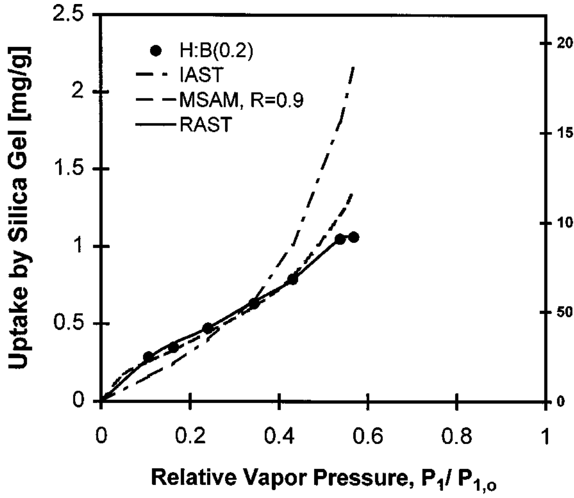

Figure 9. Predictions of the *n*-hexane adsorption isotherm in the presence of benzene (nonpolar/nonpolar mixture), $P_2/P_{2,o}$ constant at 0.2.

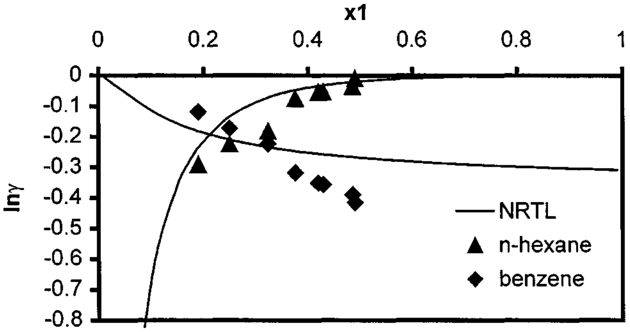

Figure 10. Activity coefficients of *n*-hexane(1) and benzene(2) for the mixture at a fixed relative vapor pressure of benzene of $P_2/P_{2,o} = 0.2$.

nificantly, which lets one conclude that the application of the adsorbed solution theory is justified also in the range of multilayer adsorption. Valenzuela and Myers (1989) also mentioned that predictions by means of the IAST, and, therefore, also the MSAM, are accurate when the amount adsorbed is less than half of the saturation capacity of the adsorbent. They argued further that at higher coverage, negative deviations from the equilibrium equation of adsorption have been observed for some systems. These deviations are caused primarily by energetic heterogeneity and by adsorbed-phase nonidealities.

RAST calculations were performed to investigate deviations from the equilibrium equation of adsorption. The experimental activity coefficients for *n*-hexane/benzene system are shown in Figure 10. The parameters obtained for the NRTL model were $\tau_{12} = -0.317$, $\tau_{21} = 0.481$, and $\alpha_{12} = 8.439$. The thermodynamic consistency of most of the data was within 80% (Steffan, 1999). The adsorbed-phase activity coefficients were below unity, unlike the activity coefficients for a liquid phase *n*-hexane/benzene mixture. Myers (1983) postulated that activity coefficients on *heterogeneous* surfaces have to be below unity due to interactions of the adsorbates with the heterogeneous surface. However, his explanation entirely neglects the adsorbate-adsorbate interactions, taking only the heterogeneity effect of the surface on the adsorbed phase into account. For multilayer adsorption, the importance of the heterogeneity effect of the surface decreases with the increasing number of layers. In this case, molecular interactions cannot be neglected any more. Adsorbed phases can have either negative or positive deviations from Raoult's analog law or equilibrium relation for multilayer adsorption like liquid mixtures. Myers explanation is also not capable to explain the enhanced adsorption of *n*-hexane observed experimentally for the *n*-hexane/benzene mixture considering no molecular interactions.

Figure 11 shows the *n*-hexane/trichloroethylene mixture isotherms at fixed trichloroethylene partial pressures $P_2/P_{2,o}$ of 0.1 and 0.2. The IAST underpredicted both isotherms due to the nonideal behavior of the adsorbed phase. The predictions of the MSAM are closer to the experimental data than the predictions of the IAST. Although the MSAM takes molecular interactions into account to some degree using quadratic mixing rules in the second space, the predictions are still off. The adsorbate mixture in this case was a mixture of *nonpolar* (hexane) and *polar* (tricholoroethylene) molecules. Considering the approximate *polarizabilities* in Table 2, *n*-hexane was the molecule with the highest polarizability. It was therefore more than likely that the polar trichloroethylene molecules induced temporary or permanent dipole moments into *n*-hexane. The adsorbent silica gel has hydroxyl groups on its surface, which impart a degree of polarity to the surface, and is therefore a *polar* adsorbent, but it has at least two different types of adsorption sites, *nonpolar* and *polar*. Since trichloroethylene induced dipoles into *n*-hexane, it was likely that the polar adsorption sites on silica gel became accessible for *n*-hexane in the presence of trichloroethylene. We hypothesized, therefore, that the adsorption of *n*-hexane in the presence of trichloroethylene was enhanced due to the strengthening of the molecular interactions in the adsorbed phase and the accessibility of *polar* adsorption sites on silica gel due to *polarized* *n*-hexane molecules.

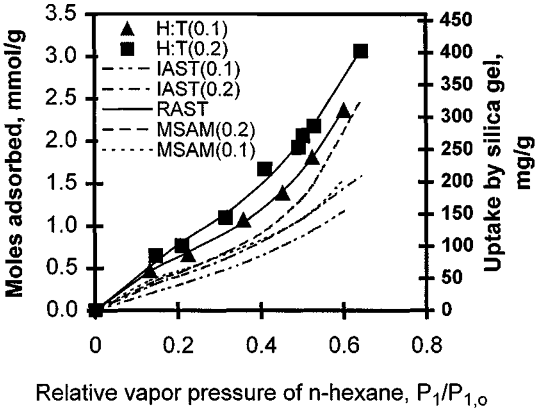

Figure 11. Predicted *n*-hexane adsorption isotherms in presence of trichloroethylene (*nonpolar/polar* mixture), at fixed trichloroethylene relative partial pressures of $P_2/P_{2,o} = 0.1$ and 0.2.

The calculation procedure described above for the RAST was used to obtain the activity coefficients. The experimental activity coefficients obtained in this way with Eq. 6 for the *n*-hexane/trichloroethylene mixture at a fixed relative vapor pressure 0.2 of trichloroethylene are shown in Figure 12. The adsorbed-phase activity coefficients were less than unity for this binary mixture as well. The best fit for the experimental adsorbed-phase activity coefficients could be obtained with equal accuracy by the Van Laar equations or the NRTL activity coefficient model. Both models were developed to correlate activity coefficients for fluid phases; hence, the accuracy of the adsorbed-phase activity coefficients was not very good. The parameters obtained with the Van Laar model for the *n*-hexane/trichloroethylene mixture at a fixed relative vapor pressure $P_2/P_{2,o} = 0.2$ of trichloroethylene were $A = -1.17$ and $B = -7.38$. For the same mixture, the parameters obtained for the NRTL model were $\tau_{12} = 9.44$, $\tau_{21} = -1.17$, and $\alpha_{12} = 1.62$. The mixture isotherms calculated using these excess Gibbs free energy models, but taking into account the spreading pressure dependency of the activity coefficients numerically, did not fit the experimental data very accurately.

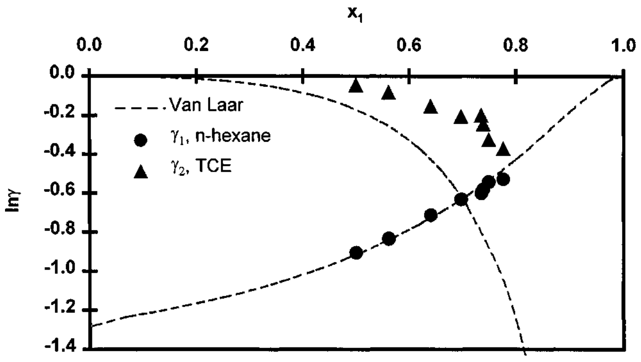

Figure 12. **Activity coefficients of *n*-hexane (1) and trichloroethylene (2) for the mixture at a fixed relative vapor pressure of trichloroethylene of $P_2/P_{2,o} = 0.2$.**

Myers' (1986) Gibbs excess model in combination with most of the common Gibbs excess models for the fluid phase, like Margules, Van Laar, NRTL, UNIQUAC, and so on, was used to tackle this task as well. The results were not satisfactory. The prediction error was higher than ±20%; therefore, no activity coefficient models were used for the RAST calculation. The RAST calculation was performed using directly the experimental activity coefficients obtained from the data analysis. The fits for the mixture isotherms obtained with the RAST are shown in Figure 11. It is significant that this type of adsorption behavior could be explained with the RAST, which was not shown in the literature previously. Sakuth (1993) even doubted that a model based on the adsorbed solution theory could describe the adsorption equilibria in the multilayer adsorption region. He avoided this region in his study by setting the total adsorptive pressure significantly below the vapor pressure of the compound with the lowest vapor pressure. The only theoretical studies known to simulate systems in the multilayer adsorption region are studies based on statistical mechanics simulations, like studies published by Kruk et al. (1995) and Gordon and Glandt (1997).

Figures 5 and 6 show the mixture isotherms of hexane/water and benzene/water at different relative humidities. In both cases it was observed that the amount of organic adsorbed was not affected by the presence of water, indicating no competitive adsorption or adsorption enhancement. This adsorption behavior is called *noninfluenced* adsorption of apparently independently adsorbing species. Water is a polar molecule with a strong dipole moment. Even though *n*-hexane has the highest polarizability and water has the highest dipole moment of all adsorbates investigated, no dipole induction of *n*-hexane took place. That leads to the conclusion that there were no interactions in the adsorbed phase. This is reasonable considering that *n*-hexane and water are practically immiscible in the liquid state and no direct molecular interactions occur there. One can further hypothesize that the molecules of each species were adsorbed on different adsorption sites. This could be confirmed when total number of moles of the mixture adsorbed was analyzed. Figure 13 shows the total number of moles adsorbed at all three relative water vapor pressures of 0.2, 0.5 and 0.7 for hexane/water. The data were compared to the predictions made with the *two-site adsorption model.* The two-site adsorption model is a very simple mixture adsorption model that can be used for the case in which components of a mixture adsorb on different sites and the amounts adsorbed are not affected by the presence of the other components. The amounts adsorbed for each species were calculated from the pure component isotherms and added together. The predictions of the two-site adsorption model matched the data well for 20% and 50% relative humidity. However, at 70% relative humidity, the model overpredicted the experimental data. Comparing these results to the experimental results presented in Figure 13, it is clear that the adsorption of water becomes limited at higher relative humidities. It was therefore very likely that the presence of *n*-hexane limited the capillary condensation of water due to a *spreading effect* at the *n*-hexane/water interface. The surface tension of water would be reduced due to the *spreading effect* at the *n*-hexane/water interface. This could have caused a significant reduction of the capillary condensation of water. Similarly, the *two-site adsorption model* matched the benzene/water data at 20% and 50% RH. At 70% RH, the two-site model overpredicted the total number of benzene and water adsorbed (Figure 14). Again, we hypothesize that the *spreading effect* at the benzene/water interface reduced the surface tension of water and therefore its ability to condense.

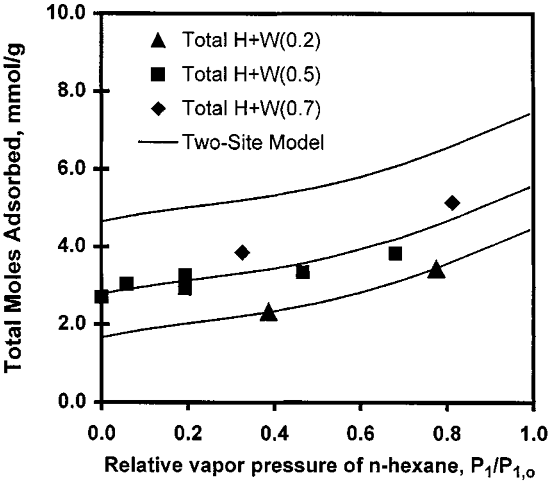

Figure 13. **Total number of moles adsorbed of *n*-hexane (H) and water (W) on silica gel at 297 K.**

Helium was used as carrier gas. The numbers given in the brackets are relative vapor pressures $P_2/P_{2,o}$ of water.

The trichloroethylene/water mixture isotherms could not be modeled with the two-site adsorption model. The suitable model was the RAST. The activity coefficients obtained in the adsorbed phase for the trichloroethylene/water mixture at 50% relative humidity of the second component water are shown in Figure 15. Surprisingly, the activity coefficients were greater than unity, which was very unusual for the adsorbed phase. Most activity coefficients reported in the literature are less than unity. Myers (1983) even postulated that the activity coefficients for the adsorbed phase have to be less than unity. This mixture contained a polar chlorinated hydrocarbon and water, and the adsorption equilibrium was established on a polar adsorbent, which was capable of making hydrogen bonds

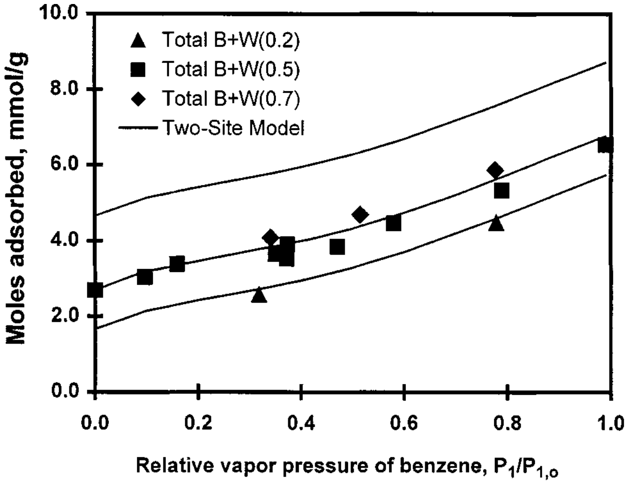

Figure 14. Total number of moles adsorbed of benzene (B) and water (W) on silica gel at 297 K.

Helium was used as carrier gas. The numbers given in the brackets are relative vapor pressures $P_2/P_{2,o}$ of water.

with water. Also, the adsorption equilibrium was established at 297 K, which was a temperature below the normal boiling points of all adsorbates. Myers (1983) argued that the surface perturbs the interactions of the adsorbed molecules to such an extent that there is no correlation between the excess free energies of the adsorbed solutions and bulk liquid solutions. If this were the case, one would expect some mixtures to show positive deviations from the equilibrium law of adsorption and others to show negative deviations. In his argument, he concluded further that since all of the excess free energies are negative, as all of the results presented in the literature so far, and uncorrelated with bulk liquid properties, it would be possible that the phenomenon could not be explained by nonideal adsorbate interactions, but due to the heterogeneity of the surface. We argue that trichloroethylene and water were competing for the same type of adsorption sites (hydrophilic adsorption sites) and not adsorbing independently on two different types of sites. If this were the case, this adsorption behavior and therefore the course of the activity coefficients could be explained by nonideal adsorbate interactions only. The heterogeneity of the adsorbent surface plays a secondary role. According to the arguments made by Myers (1983), it would be possible in this case that activity coefficients in the adsorbed phase showed positive deviations from the equilibrium equation of adsorption.

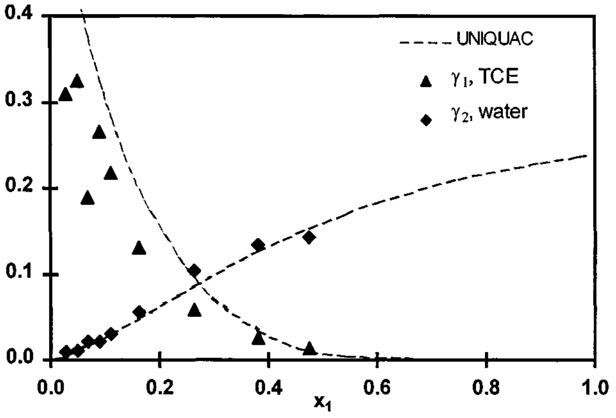

Figure 15. Activity coefficients of TCE(1) and water(2) for the mixture at a fixed relative humidity of $P_2/P_{2,o} = 0.5$.

However, Talu and Myers (1988) and Sakuth (1993) also mentioned that the phenomenon of negative deviations from the equilibrium equation of adsorption is only characteristic for adsorption in micropores. The adsorption mechanism in meso- and macropores is different. In meso- and macropores it is more likely that multilayer adsorption and association effects on adsorption sites occur. Also, intermolecular association effects at higher relative vapor pressures become more dominant. Myers et al. (1982) observed positive deviations from the adsorption equilibrium equation for the adsorption of benzene/cyclohexane vapor mixtures on nonporous graphite. Other authors reported positive deviations as well (Sakuth, 1993; Hoppe and Worch, 1982; Miller et al., 1987; Trubnikov and Tolmachev, 1982; Worch, 1982).

The experimental activity coefficients for the trichloroethylene/water mixture at a fixed relative humidity of 50% could be fitted best with the UNIQUAC model. In fitting the UNIQUAC model to the adsorbed-phase activity coefficients, the following values for the binary interaction parameters $\Delta u_{12} = 0.64$ and $\Delta u_{21} = 0.81$ were obtained. The calculated trichloroethylene/water mixture isotherm for 50% relative humidity fitted the experimental isotherm data within an accuracy of better than ±20% (Figure 7). However, better accuracy could be obtained by fitting the activity coefficients directly to experimental isotherm data, as described above. The trichloroethylene mixture isotherms at fixed relative humidities of 50% and 70% were modeled with the same RAST fit. In this humidity range, the trichloroethylene/water mixture isotherm was independent of the relative humidity. The mixture isotherm at 20% relative humidity was modeled with a separate RAST fit. In the range of lower relative humidities the adsorption equilibrium of trichloroethylene was dependent on the concentration of water.

To complete the data analysis, the total number of moles for the mixtures at all three relative humidities was calculated and compared to RAST fits (Figure 16). The RAST did fit the total number of moles adsorbed sufficiently well indicating that nonideal molecular interactions dominated over surface heterogeneity in the adsorbed phase.

Ternary Mixture Adsorption of VOC Mixtures in Presence of Water

The main purpose of investigating the adsorption behavior of ternary mixtures was to determine if the coadsorption of water vapor would alter the binary VOC equilibria and, if so, how it would alter these equilibria. The first ternary mixture was *n*-hexane, benzene, and water together with the carrier gas helium. Figure 17 compares the ternary *n*-hexane/benzene/water isotherm with the binary *n*-hexane/benzene and pure component *n*-hexane isotherms. The ternary mixture isotherm of *n*-hexane is identical to the one for the binary mixture of *n*-hexane and benzene. Both mixture isotherms show enhancement of adsorption compared to the pure com-

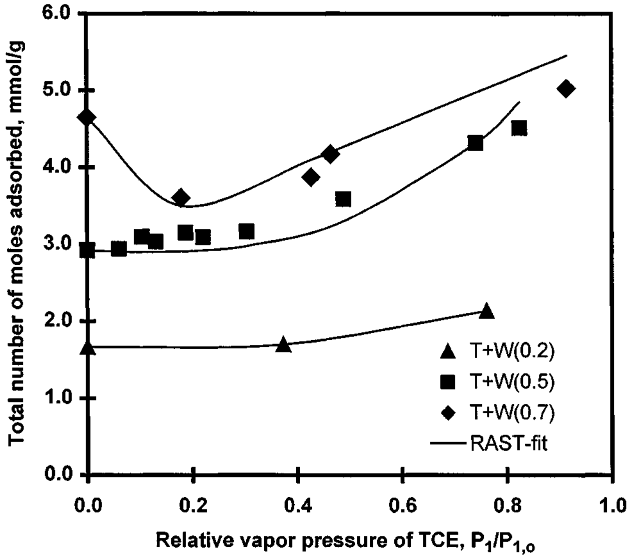

Figure 16. Total number of moles of trichloroethylene and water adsorbed on silica gel at 297 K.

Helium was used as carrier gas. The numbers given in the brackets are relative vapor pressures $P_2/P_{2,o}$ of water.

ponent isotherm. The ternary and binary mixture isotherms can be predicted with the multispace adsorption model (MSAM) (Gusev et al., 1996; Steffan and Akgerman, 1998). In Figure 18 the number of moles of benzene adsorbed in the binary hexane/benzene mixture and the ternary mixture are compared. The figure also has the predicted benzene adsorption from the pure species BDDT fit. The BDDT-values matched the data of benzene adsorbed in the ternary mixture indicating that the number of moles of benzene adsorbed was neither reduced nor enhanced due to coadsorption with *n*-hexane and water. Here, a difference in the adsorption behavior was between benzene adsorbing in the binary mixture *n*-hexane/benzene and the ternary mixture *n*-hexane/benzene/water. In coadsorption of benzene and *n*-hexane, there also was enhancement in the amount of benzene adsorbed (Steffan, 1999). This enhancement could not be observed for benzene adsorbing simultaneously with *n*-hexane and water. Figure 18 also shows that the adsorption of water vapor in the ternary mixture was slightly reduced at higher relative vapor pressures compared to the BDDT-value calculated from pure component adsorption. Based on these observations, we hypothesize that *n*-hexane and water were adsorbing onto two different types of sites in the ternary mixture as well.

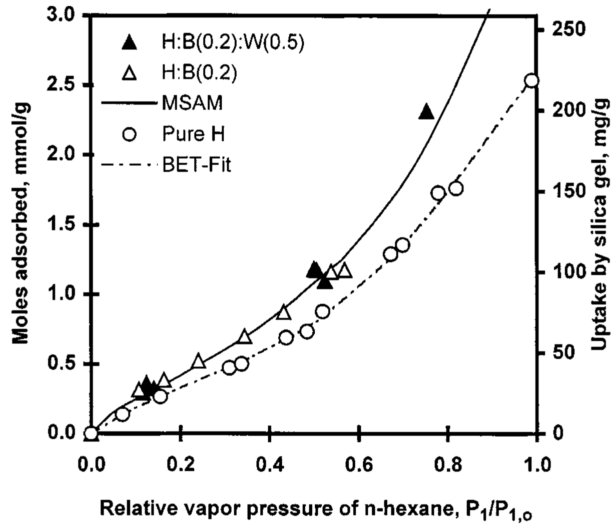

Figure 17. Ternary adsorption isotherm of *n*-hexane in the presence of benzene and water on silica gel at 297 K.

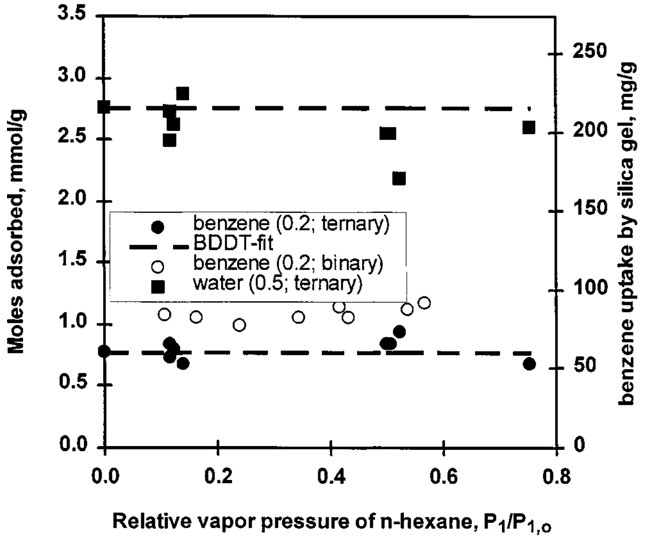

Figure 18. Number of moles of benzene and water adsorbed in the ternary *n*-hexane/benzene/water mixture and benzene adsorbed in binary *n*-hexane/benzene mixture over the relative vapor pressure of *n*-hexane and predictions with the BDDT equation.

The second ternary mixture is the mixture of *n*-hexane and trichloroethylene in the presence of water. Figure 19 shows that the moles of *n*-hexane adsorbed in the ternary mixture is equal to the amount adsorbed as a pure component. The ternary *n*-hexane mixture isotherm was identical with the BDDT-fit of the pure species *n*-hexane isotherm. The adsorption of *n*-hexane was *noninfluenced* in the presence of trichloroethylene and water. Secondly, we compared the moles of trichloroethylene and water adsorbed in the ternary mixture with the value given from the pure species BDDT-fit for each component. The pure species BDDT fitted value matched the experimental equilibrium data of trichloroethylene in the ternary mixture quite well (Figure 20), although a slight decreasing trend can also be concluded. The experimental data of water adsorbed in the ternary mixture were lower than the pure component BDDT-fit value. The amount of water adsorbed was reduced also at low relative vapor pressures of *n*-hexane in the presence of *n*-hexane and trichloroethylene. Since *n*-hexane and water were adsorbing independently onto different types of adsorption sites, water molecules were either displaced by trichloroethylene or the multilayer adsorption capacity of water was reduced due to

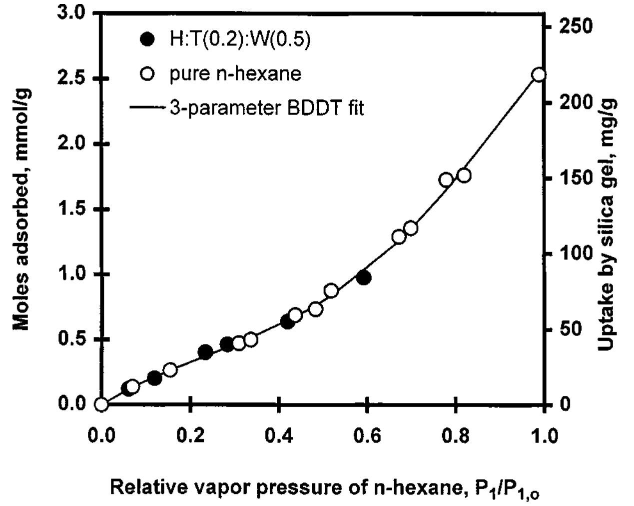

Figure 19. Ternary adsorption isotherm of *n*-hexane in the presence of trichloroethylene and water on silica gel at 297 K.

the *spreading effect* at the *n*-hexane water interface. It was also possible that trichloroethylene which is partially miscible with water altered the surface tension of water and changed therefore the multilayer adsorption properties of water.

In summary in the ternary mixture *n*-hexane/trichloroethylene/water, as well as in the binary mixture of *n*-hexane/water, *n*-hexane and water were adsorbing indepenently onto two different types of adsorption sites. However, the enhanced adsorption of *n*-hexane and trichloroethylene in the presence of each other could not be observed for the ternary mixture. Molecular interactions in the adsorbed phase, as observed for the binary mixture pairs of *n*-hexane/trichloroethylene and trichloroethylene/water, balanced or compensated each other in case of the ternary mixture. If all three species had adsorbed completely, independently they would have been adsorbed onto three different types of sites. This could not be the case since we had shown that the components of the binary mixtures of *n*-hexane/trichloroethylene and trichloroethylene/water were adsorbing more or less onto the two types of adsorption sites of silica gel. Their distribution over these sites was determined by their interactions in the adsorbed phase. So except for *n*-hexane and water, which were adsorbing onto different sites, trichloroethylene was adsorption partially distributed over both types of sites and interacting with either species *n*-hexane or water in the adsorbed phase.

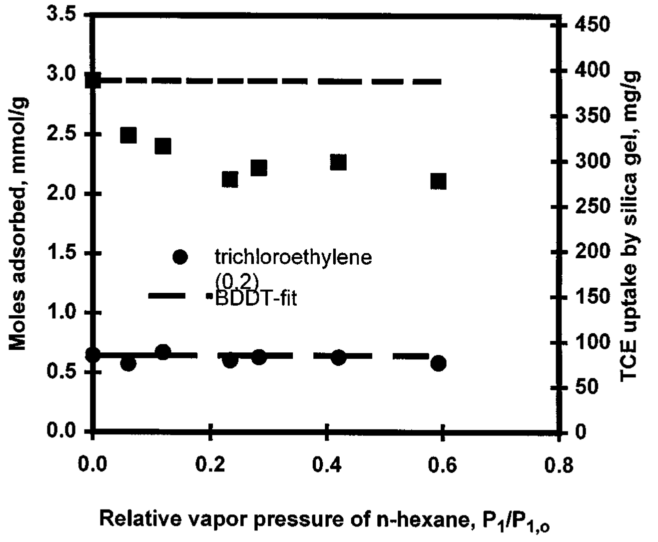

Figure 20. Number of moles of trichloroethylene and water adsorbed in the ternary *n*-hexane/trichloroethylene/water mixture.

Predictions with the BDDT equation for the pure component trichloroethylene and water isotherms.

Conclusions

This study shows that on a polar adsorbent, such as silica gel, the uptake of individual species increases in presence of a coadsorbate for organic mixtures. When two species are coadsorbed, the adsorbate-adsorbate interactions are strengthened due to the adsorbent-adsorbate interactions and altered by effects due to the heterogeneity of the adsorbent surface. The effect is more pronounced when polar adsorbates are used. Two models were used to predict the binary adsorption isotherms. The MSAM prediction is sufficiently good for nonpolar adsorbate binaries at low concentrations, which display a weak nonideal adsorption behavior. The RAST was used to analyze the adsorbed-phase properties of these mixtures and to model the mixture isotherms. The RAST could fit mixture isotherms displaying multilayer adsorption very well. The activity coefficients for both mixtures were less than unity.

Adsorption isotherms of binary mixtures of *n*-hexane/water, benzene/water and trichloroethylene/water were determined. Also, the mixture isotherms of the first two systems showed that the equilibrium was not altered compared to the pure component adsorption equilibrium. This type of adsorption behavior is called noninfluenced adsorption. This type of adsorption equilibria can be predicted with the two-site adsorption model, using the pure component adsorption isotherms. The total number of moles adsorbed for both mixtures could be predicted by summation of the uptake over the two adsorption-sites. At higher relative vapor pressure of water, where multilayer adsorption merged into capillary condensation, the total number of moles adsorbed was overpredicted. This phenomenon is explained with the spreading effect at the interface between the organic phase and the water phase. Trichloroethylene and water were adsorbing onto the same type of adsorption sites and competing for it. The mixture isotherms showed a reduction in the amount of trichloroethylene adsorbed compared to the pure species isotherm. This type of adsorption behavior could be modeled with the RAST. For this mixture, the experimental activity coefficients were above unity.

Adsorption equilibria of two ternary mixtures were also investigated. The first one was *n*-hexane/benzene/water. The ternary mixture isotherm of *n*-hexane was identical to the binary mixture isotherm for the *n*-hexane/benzene mixture. It was concluded that *n*-hexane and water were adsorbing onto different adsorption sites. Benzene and water were slightly competing for adsorption sites. The second ternary mixture was *n*-hexane/trichloroethylene/water. The adsorption of *n*-hexane was not influenced by the presence of the other two components. Trichloroethylene was adsorbing on both types of adsorption sites and interacting with either species *n*-hexane or water in the adsorbed phase.

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