Binary Adsorption Equilibrium of Organics and Water on Activated Carbon

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Adsorption isotherms of hexafluoropropylene (HFP), methanol and ethanol were measured under dry and humid conditions using Norit R1 carbon. The presence of water lowered the HFP capacity over the whole pressure range as compared to the single component isotherm, while increasing the methanol and ethanol capacity. The Dubinin-Radushkevich equation was applicable for methanol, and ethanol, and the Dubinin-Astakhov equation gave a satisfactory description for water. The ideal adsorbed solution (IAS) theory satisfactorily described the binary, miscible systems of methanol and ethanol with water. Because water and HFP are not miscible, the IAS theory cannot be used. This binary system was described well by the independent co-adsorption of the two components, that is, HFP vapor is adsorbed in the micropore volume left free by water.

Introduction

In practical vapor adsorption processes, ranging from industrial adsorption columns to gas mask canisters, water vapor is often present in the feed. It has been shown that water has mostly a negative influence on the performance of the adsorption process (Adams et al., 1988; Farris et al., 1994; Branton et al., 1995; Lavanchy and Stoeckli, 1997). Especially in air purification processes, water is often present in a much higher concentration than the components that have to be adsorbed. The influence of water vapor on the adsorption process should therefore be looked at more closely. The exact adsorption mechanism of water is not fully understood, but it is generally agreed that two factors play an important role: the surface chemistry and the porosity. Although, in general, activated carbon is hydrophobic in nature, water vapor does adsorb on activated carbon, in particular at high relative humidities. Furthermore, carbons can be made hydrophilic by oxidation, which may already result in a considerable amount of adsorbed water at low relative pressures. Carbon-oxygen surface groups can be formed by reaction with oxidizing gases (oxygen, ozone, nitrous oxide, nitric oxide, carbon dioxide, and so on) and with oxidizing solutions (nitric acid, hydrogen peroxide, and so on) (Marsh et al., 1997). Thus, water vapor competes with organic compounds to become adsorbed on activated carbon. This article focuses on the modeling of the simultaneous adsorption of water and organic compounds. Equilibrium sorption of the organic vapors hexafluoropropylene (HFP), methanol, and ethanol was investigated, under dry as well as under humid conditions on Norit R1 carbon. The ideal adsorbed solution theory (IAS) was used to predict the binary equilibrium results.

Theory

Single component equilibrium

A widely-known model for single component adsorption has been developed by Dubinin from ideas originally put forward by Polanyi. This theory for the volume filling of micropores, known as the potential theory, is based on the idea that attractive forces originate from the adsorbent surface. These forces build a force field (potential field) which only extends

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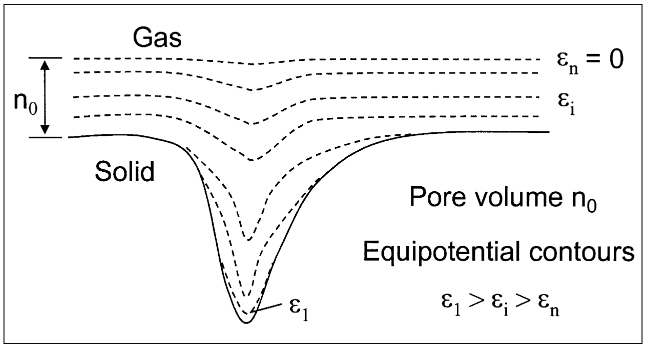

Figure 1. Equipotential contours ϵ_i above the adsorbent surface according to Polanyi theory.

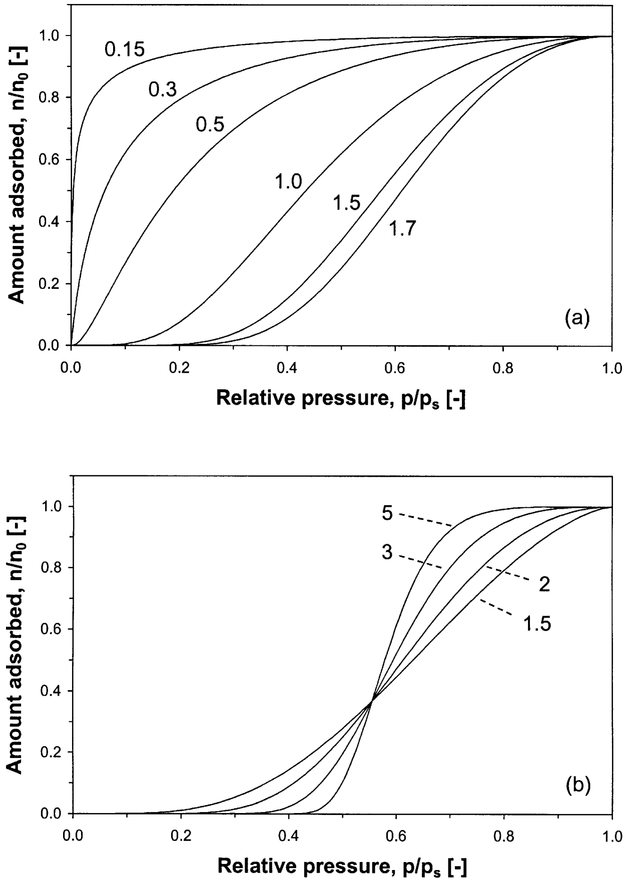

Figure 2. Dubinin-Astakhov adsorption isotherm as function of parameters *B* and *m*, (Eq. 2).

(a) Varying B, $m = 2$; (b) $B = 1.7$, varying m.

over short distances. This surface force field can be represented by equipotential contours above the surface (see Figure 1). The space between each set of equipotential surfaces corresponds to a definite adsorbed volume. The adsorbed pore volume, W, is a function of the potential field ϵ. This relation is called the characteristic curve and is temperature-independent.

The most commonly used relation based on the potential theory is the Dubinin-Radushkevich adsorption isotherm

$$\theta = \exp\left(-B^2\left[\ln\left(\frac{p_s}{p}\right)\right]^2\right) \quad \text{with} \quad B = \frac{RT}{\beta E_0}, \qquad (1)$$

where β is the affinity coefficient of the adsorptive, and E_o (J/mol) is the characteristic energy of the adsorbent. An advantage of the Dubinin-Radushkevich equation is that it can be easily extended to different temperatures, once the adsorption parameters have been determined for one temperature. The temperature is restricted, though, to a value below the critical temperature of the adsorptive. Above the critical temperature, the concept of saturated vapor pressure does not exist. The standard relations to evaluate the saturated vapor pressure cannot be extrapolated above the critical temperature. Nevertheless, different methods have been reported to estimate the vapor pressure above the critical temperature (Amankwah and Schwarz, 1995). Dubinin and Astakhov generalized the Dubinin-Radushkevich equation on the basis of further experiments, in particular with zeolites, to the so-called Dubinin-Astakhov adsorption isotherm (Stoeckli, 1998)

$$\theta = \exp\left(-B^m\left[\ln\left(\frac{p_s}{p}\right)\right]^m\right) \quad \text{with} \quad B = \frac{RT}{\beta E_0}, \qquad (2)$$

where m is introduced as an extra fit parameter that is considered to be a measure of the heterogeneity of the porous material. Depending on the solid and on the type of micropores, the exponent m varies typically from 1.5 to 5. For typical industrial activated carbons, the exponent m is 2, which corresponds to the classical Dubinin-Radushkevich equation. An advantageous feature of the Dubinin-Astakhov equation is that it is capable of describing the adsorption isotherm of water (Lodewyckx, 1998; Stoeckli, 1998; Lavanchy and Stoeckli, 1999). For the adsorption of water on activated carbon, values of parameter m, between 2 and 7 have been reported. Adsorption isotherm equations like the Dubinin-Radushkevich or the Langmuir equation are not capable of describing the adsorption isotherm of water. Figure 2 shows the Dubinin-Astakhov adsorption isotherm as a function of the parameters B and m. An increase of parameter B, that is, a decrease of the characteristic energy, shifts the isotherm from "favorable" to "unfavorable." The slope of the isotherm at the inflection point depends on parameter m. An increase of parameter m results in a steeper adsorption isotherm.

Multicomponent equilibrium

The IAS theory has been developed by Myers and Prausnitz (1965). This theory is based on solution thermodynamics, and the basic thermodynamic equations for this theory are the same as those for vapor-liquid equilibria. It can be used to calculate adsorption equilibria for mixtures on the basis of experimental data for the pure-component adsorption equilibria at the same temperature. The validity of the thermodynamic equations for the adsorbed phase rests upon three assumptions (Myers and Prausnitz, 1965).

- Thermodynamically inert adsorbent, that is, negligible change in the internal energy during adsorption at constant temperature.

- Temperature-invariant area of the adsorbent, which is the same for all adsorbates.
- The Gibbs definition of adsorption applies.

Using the equilibrium criterion, which states that the chemical potential for each component in the adsorbed phase is equal to that in the gas phase and the concept of activity coefficients, yields the equation of equilibrium for mixed-gas adsorption

$$Py_i = P_i^0 \gamma_i x_i \quad \{i = 1,2,\ldots,N\}, \tag{3}$$

where P (Pa) is the total pressure, y_i is the mol fraction of component i in the gas phase, x_i is the mol fraction of component i in the adsorbed phase, γ_i is the activity coefficient of component i in the adsorbed phase, and N is the number of components present in the mixture. The variable P_i^0 is the equilibrium gas-phase pressure corresponding to the adsorption of pure component i at the same spreading pressure π and the same temperature as for the adsorbed mixture. If one assumes that the adsorbed mixture is ideal (ideal solution), the activity coefficients are equal to unity and Eq. 3 reduces to a kind of Raoult's law. The Gibbs adsorption isotherm approach yields the spreading pressure π. The integrals of the individual isotherms for the spreading pressure $\psi_i^0(P_i^0)$ are given by

$$\psi_i^0\left(P_i^0\right) = \frac{\pi A}{RT} = \int_0^{P_i^0} \frac{n_i(p)}{p} dp \tag{4}$$

Since the mixing process is carried out at a constant spreading pressure π, the integrals for the spreading pressure must be equal for every component

$$\psi_1^0\left(P_1^0\right) = \psi_2^0\left(P_2^0\right) = \psi_N^0\left(P_N^0\right) \tag{5}$$

where $n_i(p)$ is the adsorption isotherm of component i, and A (m^2/kg) is the specific area of the adsorbent.

After the Eqs. 3 to 5 are solved simultaneously with the additional condition

$$\sum_{i=1}^{N} x_i = 1, \tag{6}$$

the total amount adsorbed n_t is calculated from

$$\frac{1}{n_t} = \sum_{i=1}^{N} \frac{x_i}{n_i^0}, \tag{7}$$

where n_i^0 is the amount of pure component i adsorbed at the spreading pressure π and the temperature of the adsorbed mixture, that is, at P_i^0. The amount adsorbed of component i is then given by

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

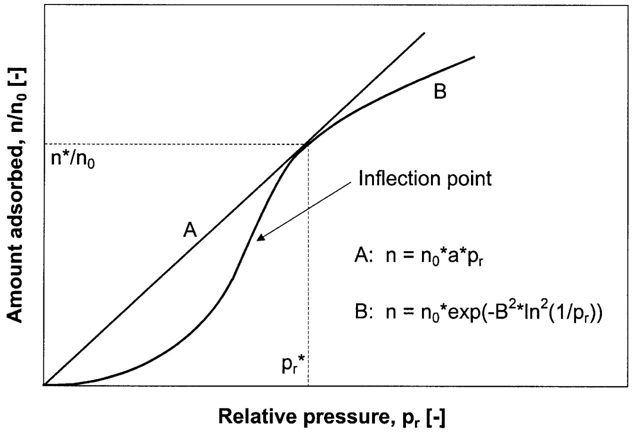

Figure 3. Modified Dubinin-Radushkevich equation ensuring thermodynamic correctness.

Different adsorption isotherm expressions for single components can be used to predict adsorption from mixtures using the IAS theory, which is thermodynamically consistent and exact at the limit of zero pressure (Valenzuela and Myers, 1989). The Dubinin-Radushkevich adsorption isotherm model gave very good results in the description of single component equilibrium adsorption (Linders et al., 1997; Linders, 1999). Furthermore, it has been shown in a series of articles (Lavanchy et al., 1996; Lavanchy and Stoeckli, 1997; Stoeckli et al., 1997) that the introduction of the Dubinin-Radushkevich equation in the IAS theory leads to a satisfactory description of the binary adsorption of organic vapors. Therefore, it was decided to incorporate the Dubinin-Radushkevich equation for organic components and the Dubinin-Astakhov equation for water into the IAS theory.

The Dubinin-Radushkevich equation does not reduce to Henry's Law in the low-pressure limit (see Figure 3). Hobson and Armstrong (1963) were the first to bring attention to this problem (Sundaram and Yang, 1998). An inflection point is observed at a low relative pressure. A tangent can be drawn from the origin, resulting in a point of contact with the Dubinin-Radushkevich curve at a relative pressure p_r^*, which is usually very small ($\mathrm{pr}_r^* < 10^{-10}$). To ensure thermodynamic correctness, the Dubinin-Radushkevich equation was modified by dividing the isotherm in two parts (see Figure 3). The lower part of the isotherm is given by the linear relationship

$$\theta = \frac{q}{q_{\text{sat}}} = \frac{n}{n_0} = a\frac{p}{p_s} = a p_r \quad p_r \le p_r^*, \tag{9}$$

and, for relative pressures $p_r > p_r^*$, the Dubinin-Radushkevich equation is applied as given by Eq. 1. It can be shown that the Henry constant a and the pressure at the point of contact p_r^* are given by

$$a = \exp\left(\frac{1}{4B^2}\right) \text{ and } p_r^* = \exp\left(-\frac{1}{2B^2}\right) \text{ with } B = \frac{RT}{\beta E_0}. \tag{10}$$

The experimental water isotherm exhibits an S-shaped curve, as will be shown later. With the appropriate parameter values, the Dubinin-Astakhov equation also exhibits an S-shape and describes the water isotherm fairly well. Therefore, the

Dubinin-Astakhov equation was not divided in two parts, although this implies that it is thermodynamically inconsistent.

The single component adsorption isotherm equations, in this case Dubinin-Radushkevich for organics and Dubinin-Astakhov for water, complete the set of IAS equations to describe the equilibrium composition of binary or multicomponent mixtures. The integrals of the individual isotherms for the spreading pressure in Eq. 4, $\psi_i^0(P_i^0)$, can now be calculated. It appears that the Dubinin-Radushkevich equation provides an analytical expression for the integral

$$\psi_i^0(P_i^0) = n_0 \exp\left(-\frac{1}{4B^2}\right) + n_0 \frac{\sqrt{\pi}}{2B}\left[\operatorname{erf}\left(\frac{1}{2B}\right) - \operatorname{erf}\left(B \ln\left(\frac{p_s}{P_i^0}\right)\right)\right] \quad (11)$$

where "erf" is the error function. The Dubinin-Astakhov equation did not provide an analytical solution for the integral at first sight. Lavanchy and Stoeckli (1997), however, state that an analytical solution exists for the function $\psi_i^0(P_i^0)$ using the Dubinin-Astakhov equation. They derived an analytical solution based on the incomplete Gamma function. Because their solution is rather complicated to implement, the integral was numerically determined.

The approach discussed so far, combining the IAS theory with the Dubinin-Radushkevich, and the Dubinin-Astakhov equations for the prediction of multicomponent equilibrium, may only be applied to vapor mixtures that are miscible in the adsorbed phase. Therefore, only the systems water/methanol and water/ethanol will be described with the IAS theory. In the liquid state water is often not miscible with organic components such as hexafluoropropylene (HFP). Under these circumstances, the IAS approach is no longer valid. Therefore, the system water/HFP will be described as a first approximation by the independent co-adsorption of the two components. HFP vapor is adsorbed in the micropore volume left free by water. Lavanchy and Stoeckli (1999) show that, for moderate degrees of micropore filling, the approach of independent coadsorption gives satisfactory results for vapors of immiscible liquids, such as water and an organic compound.

Head Space Analysis Method

Adsorption isotherms were measured using the head space analysis method (Schoene et al., 1984; Linders et al., 1997). Briefly, the method utilizes the following procedure (see Figure 4). A known amount of carbon is put into a vial of known volume, which is sealed gas-tight with a rubber cap. Subsequently, the adsorptive is injected into the vial. The exact amount injected is determined by weighing. After equilibration in a thermostated bath, typically lasting hours for organic compounds and several days for water vapor, the gas-phase concentration of the adsorptive is analyzed by gas chromatography. The amount adsorbed on the activated carbon is calculated from the mass balance. An adsorption isotherm is constructed by injecting various amounts of adsorptive. In case an adsorption isotherm is determined for a liquid, such as water, a glass tube is placed inside the vial (see Figure 4). The liquid is injected in this tube in order to prevent direct contact between the liquid and the carbon.

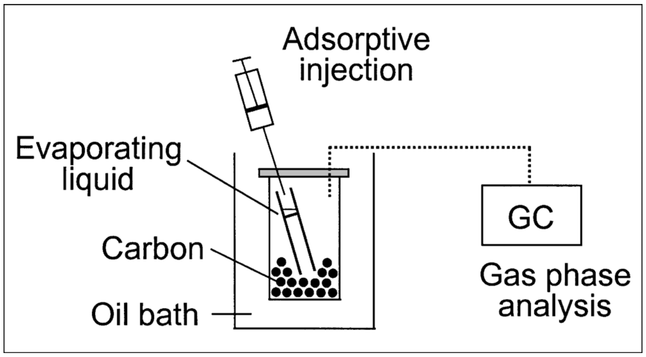

Figure 4. Head space analysis method.

The equilibrium adsorption isotherms of HFP, methanol, ethanol, and water were measured on Norit R1 carbon. Before experimental use, the carbon was conditioned in a vacuum oven at a temperature of 393 K. The experimental data were collected over a large pressure range, covering four to five orders of pressure decades. In addition, the adsorption isotherms of HFP, methanol, and ethanol were measured under humid conditions. The Norit R1 carbon was conditioned at a relative humidity of about 60%, which was followed by the adsorption of the component concerned. The conditioning resulted in an amount of pre-adsorbed water approximately 0.25 mL/g in the case when ethanol and methanol were the second adsorptive, and it resulted in approximately 0.28 mL/g in the case when HFP was the second adsorptive. All the isotherms were measured at a temperature of 303 K.

Results and Discussion

The results of the single component adsorption isotherms are shown in Figure 5 together with the adsorption isotherms in the presence of water. The binary data are also tabulated (see Table 1 for HFP; methanol and ethanol data can be found in Table 3). The experimental data are described with the Dubinin-Radushkevich model. It is seen that in the presence of water the amount of HFP adsorbed is lower over the whole pressure range, as compared to the single component isotherm. A different result is observed for methanol and ethanol. In the presence of water ethanol adsorbs better in the low-pressure regime compared to the single component adsorption isotherm. This is more distinct for methanol where even a doubling of the amount adsorbed is seen in the low-pressure regime. The increased adsorption of both methanol and ethanol in the presence of water may be attributed to water that is acting as additional adsorption sites. Methanol and ethanol dissolve very well in water, which apparently results in an extra adsorption capacity at low partial pressures, as compared to the situation that no water is present on the carbon. At higher pressures, ethanol and methanol eventually adsorb less compared to the single component adsorption isotherm. In Table 2 the results of the adsorption isotherm parameters are listed. The capacity for HFP has been decreased by almost a factor of two, whereas, for ethanol and methanol, the capacity decrease is smaller. Furthermore,

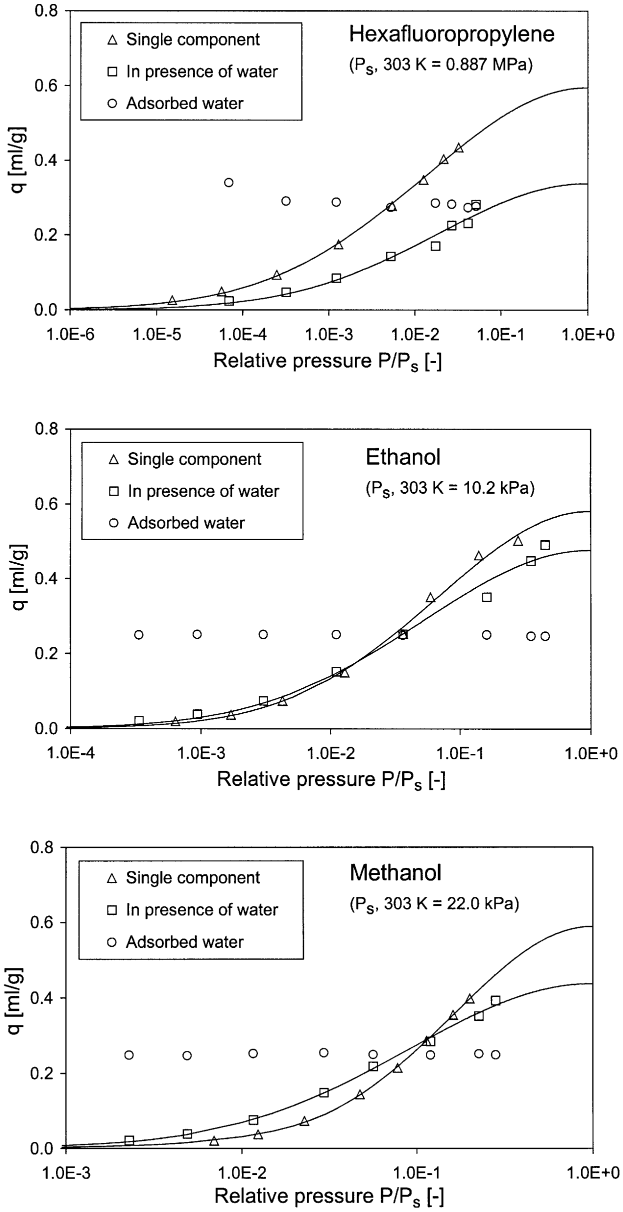

Figure 5. Adsorption isotherms of HFP, ethanol and methanol on Norit R1 at 303 K.

Results are shown of the single component adsorption isotherms (△) and the adsorption isotherms in the presence of water vapor (□). The amount of adsorbed water (○) is plotted against the relative pressure of the considered component, that is, HFP, ethanol or methanol. Liquid densities at 303 K: $\rho_{HFP} = 1.278$ g/mL, $\rho_{\text{ethanol}} = 0.780$ g/mL, $\rho_{\text{methanol}} = 0.798$ g/ml, $\rho_{\text{water}} = 0.996$ g/mL.

Table 1. Vapor Phase Pressure and Adsorbed Composition for the Binary System HFP/Water on Norit R1 at a Temperature of 303 K.

Relative Pressure		Amount Adsorbed (mL/g)*	
HFP [10^{-3}]	Water	HFP	Water
0.069	0.502	0.0233	0.340
0.32	0.457	0.0469	0.290
1.23	0.501	0.0845	0.287
5.29	0.689	0.1423	0.273
17.5	0.699	0.1704	0.285
27.1	0.697	0.2248	0.282
41.8	0.698	0.2311	0.273
51.7	0.699	0.2815	0.276

*Liquid densities at 303 K: $\rho_{\text{HFP}} = 1.278$ g/ml, $\rho_{\text{water}} = 0.996$ g/mL.

parameter *B* changes when the adsorption isotherm is determined in the presence of adsorbed water. It appears that a lower value of parameter *B* represents a higher amount adsorbed at lower pressures, which has been observed for ethanol and methanol. A higher value represents less adsorption at lower pressures, as has been observed for HFP. An explanation for this is that water acts as additional adsorption sites for ethanol and methanol, which can be seen as an extra attractive force. This results in an increase of the characteristic energy, and thus a decrease of parameter *B*. In the case of HFP adsorbed water acts as a repulsive force, which decreases the characteristic energy, resulting in an increase of parameter *B*.

The adsorption isotherm of water is shown in Figure 6. The curve exhibits an S-shape, which is typical for a water adsorption isotherm on carbon. The carbon hardly adsorbs any water below 30% relative humidity. Above a relative humidity of about 45%, a strong increase is observed in the water adsorption. At present, the description of the water adsorption isotherm is still not completely satisfactory (Patrick, 1995). Dubinin and Serpinsky (1981) have proposed a model that can be used successfully in the range of relative pressures between approximately 0.35 and 0.80. This model incorporates the number of primary adsorption centers and the ratio between the rate constants of adsorption and desorption. Here, the Dubinin-Astakhov model is used to describe the water adsorption isotherm. It was demonstrated by several authors (Lodewyckx, 1998; Stoeckli, 1998; Lavanchy and Stoeckli, 1999) that the water adsorption isotherm can be described well with the Dubinin-Astakhov model. Furthermore, this equation was easily incorporated into the IAS the-

Table 2. Dubinin-Radushkevich Adsorption Isotherm Parameters of HFP, Ethanol and Methanol on Norit R1 at a Temperature of 303 K*

Component	Parameter	Pure Component	In Presence of Water
HFP	$q^{\dagger}_{\text{sat}}$ (mL/g)	0.595	0.338
	B	0.1656	0.1796
	σ^{2**} [10^{-6} (mL/g)^2]	30.2	304.8
Ethanol	$q^{\dagger}_{\text{sat}}$ (mL/g)	0.581	0.476
	B	0.2635	0.2405
	σ^{2**} [10^{-6} (mL/g)^2]	224.8	486.4
Methanol	$q^{\dagger}_{\text{sat}}$ (mL/g)	0.589	0.437
	B	0.3915	0.2965
	σ^{2**} [10^{-6} (mL/g)^2]	5.0	65.5

*Parameters are given for the pure components and in the presence of adsorbed water. Amount of pre-adsorbed water was approximately 0.25 mL/g† in case of ethanol and methanol, and 0.28 mL/g† in case of HFP.
**Variance σ^2 = sum of squared residuals/d.f.; d.f. = degrees of freedom = number of experimental data points minus number of parameters of the isotherm equation.
†Liquid densities at 303 K: $\rho_{\text{HFP}} = 1.278$ g/mL, $\rho_{\text{ethanol}} = 0.780$ g/mL, $\rho_{\text{methanol}} = 0.798$ g/mL; $\rho_{\text{water}} = 0.996$ g/mL.

Table 3. Experimental and Calculated Adsorption for the Binary Systems Methanol/Water and Ethanol/Water on Norit R1 at a Temperature of 303 K*

Relative Pressure		Methanol		Water Calc.
Methanol [10^{-3}]	Water	Exp.	Calc.	
2.3	0.583	0.0207	0.0325	0.2204
4.9	0.588	0.0379	0.0554	0.2251
11.7	0.589	0.0752	0.0965	0.2228
29.6	0.604	0.1478	0.1610	0.2242
56.6	0.610	0.2176	0.2185	0.2092

Relative Pressure		Ethanol		Water Calc
Ethanol [10^{-3}]	Water	Exp.	Calc.	
0.34	0.580	0.0210	0.0306	0.2047
0.94	0.605	0.0384	0.0573	0.2291
3.0	0.605	0.0740	0.1082	0.2083
11.1	0.649	0.1519	0.1828	0.2139
36.3	0.719	0.2519	0.2603	0.2049

*Amount of adsorbed water was 0.248 mL/g for the methanol and 0.250 mL/g for the ethanol series, corresponding to a relative humidity of about 60%. Calculations were performed using the IAS theory. Liquid densities at 303 K: $\rho_{\text{methanol}} = 0.798$ g/mL, $\rho_{\text{water}} = 0.996$ g/mL, $\rho_{\text{ethanol}} = 0.780$ g/mL.

ory, so that binary calculations could be performed. Indeed, as shown in Figure 6, the Dubinin-Astakhov model describes the experimental data well.

Prediction of binary equilibrium

Instead of describing the adsorption isotherms of hexafluoropropylene (HFP), methanol, and ethanol in the presence of water with a new set of Dubinin-Radushkevich parameters, a much more satisfactory method is to predict the equilibrium composition of the binary mixture from the single component adsorption isotherm parameters. The systems water/methanol and water/ethanol are miscible in the adsorbed phase and, therefore, these systems can be described by the IAS theory with the Dubinin-Radushkevich equation for methanol and ethanol and the Dubinin-Astakhov equation for water. The isotherm parameters for the pure components were used as given in Table 2 for ethanol and methanol and in Figure 6 for water. The calculated binary predictions are given in Table 3 and compared in Figure 7. The amount of adsorbed water was approximately the same for all samples, namely 0.248 ± 0.002 mL/g for the methanol series and 0.250 ± 0.002 mL/g for the ethanol series. The single component adsorption isotherms are also given in Figure 7, that is, the Dubinin-Radushkevich fits.

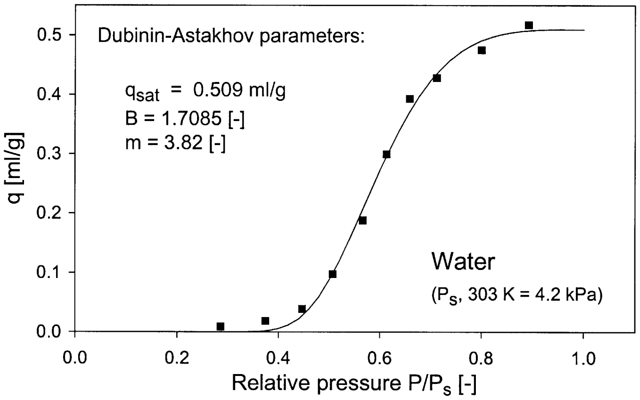

Figure 6. Adsorption isotherm of water on Norit R1 at 303 K.

The experimental data (■) are fitted with the Dubinin-Astakhov model (solid line).

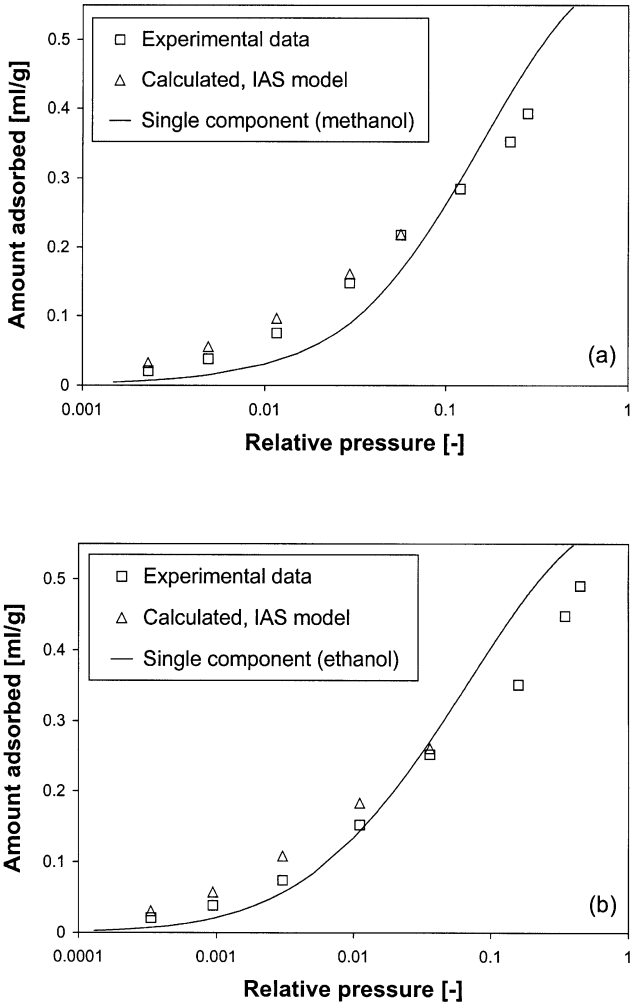

Figure 7. Experimental (□) vs. calculated (△) adsorption of the binary systems (a) methanol/water and (b) ethanol/water on Norit R1 at a temperature of 303 K.

The amount of adsorbed water was 0.248 mL/g for the methanol series and 0.250 mL/g for the ethanol series, corresponding to a relative humidity of about 60%. The calculations were performed using the IAS theory. The solid line represents the single component adsorption isotherm (Dubinin-Radushkevich).

The calculations did not converge for the data points at relative pressures higher than 0.1 and, therefore, no calculated results are given for these data points. Both Table 3 and Figure 7 show that the calculated amounts adsorbed for the binary systems agree fairly well with the experimental determined values, although the methanol data agree somewhat better than the ethanol data. Generally, the calculated amounts of adsorbed water are lower than the experimental values, whereas the calculated amounts of adsorbed methanol

Table 4. Activity Coefficients γ_i for Binary Systems Methanol/Water and Ethanol/Water as Function of the Composition Calculated with the Wilson Equation

Composition, mol Fraction		Activity coefficients γ_i			
MeOH or EtOH	Water	Methanol	Water	Ethanol	Water
0.05	0.95	1.72	1.0	4.55	1.01
0.1	0.9	1.60	1.01	3.49	1.03
0.3	0.7	1.29	1.06	1.82	1.20
0.5	0.5	1.12	1.16	1.31	1.49

and ethanol are higher than the experimental values. The single component adsorption isotherms are also given in Figure 7. The IAS model correctly predicts the increased adsorption in the presence of water that is observed for both methanol and ethanol at low relative pressures.

By using the IAS theory, it is not assumed that the bulk binary liquid systems are ideal, only that the adsorbed phase behaves as an ideal mixture. Of course, the adsorbed binary system may not be ideal in reality. Therefore, activity coefficients were calculated using the Wilson equation (see Table 4) (Gmehling et al., 1981). Activity coefficients give at least an idea whether or not the system is indeed ideal. It appears that the binary system methanol/water is not far from ideal. The activity coefficients for methanol and water are, at most, 1.8 and 1.1, respectively. The system ethanol and water is further away from ideality. The activity coefficients for ethanol and water are, at most, 4.6 and 1.2, respectively. This confirms the observation that the methanol data agree better than the ethanol data. As it is not believed that the adsorbed phase behaves ideally in the case where the liquid phase is not ideal (for equal compositions), this implies that incorporating activity coefficients might even improve the description of the binary system. This will be addressed in future work.

In contrast to the binary systems involving methanol and ethanol, the IAS theory cannot be used for the description of the binary system water/HFP. Because water and HFP are not miscible, the IAS approach is no longer valid. As a first approximation, the system water/HFP will be described by the independent co-adsorption of the two components. HFP vapor is adsorbed in the micropore volume left free by water. The HFP isotherm in the presence of water is described as follows. The amount of adsorbed water, 0.285 mL/g, was subtracted from the single component HFP capacity, 0.595 mL/g, resulting in a "binary" HFP capacity of 0.31 mL/g. Furthermore, the single component HFP parameter $B = 0.1656$ was used. This combination of the "binary" capacity and the B parameter from the single component isotherm described the HFP isotherm almost as well as when these parameters were fitted (these fitted results are given in Table 2). In the former case the variance is $391\cdot10^{-6}$ (mL/g)2, whereas in the latter case the variance is $305\cdot10^{-6}$ $(\mathrm{mL/g})^2$ (see Table 2). Thus, it is concluded that, for the conditions present in the binary experiments described here, the HFP isotherm in the presence of water can be described with the independent co-adsorption model in which the capacity of HFP is determined by the amount of adsorbed water.

Conclusion

In the presence of water the amount of adsorbed HFP on Norit R1 carbon is lower over the whole pressure range, as compared to the single component isotherm. On the contrary, methanol and ethanol adsorb better in the presence of water in the low-pressure regime compared to the single component adsorption isotherm. The increased adsorption may be attributed to water that is acting as additional adsorption sites. Both methanol and ethanol dissolve very well in water, which apparently results in an extra adsorption capacity at low partial pressures, as compared to the situation when no water is present on the carbon.

Methanol and ethanol are miscible with water and, therefore, the IAS theory was applicable to describe these binary systems. The Dubinin-Radushkevich isotherm was applicable for methanol and ethanol, and the Dubinin-Astakhov isotherm gave a satisfactory description for water. As a first estimate, the results are satisfying. Based on these isotherms, the IAS model correctly predicted the increased adsorption in the presence of water. The calculated amounts of adsorbed water were lower than the experimental values, whereas, for methanol and ethanol, higher values were calculated than the experimental ones. The IAS theory cannot be used for the system water/HFP, because water and HFP are not miscible. This binary system could be well described by the independent co-adsorption of the two components, that is, HFP vapor is adsorbed in the micropore volume left free by water.

Notation

a = Henry constant
A = surface area of adsorbent per unit mass, $\mathrm{m^2/kg}$
B = parameter in Dubinin-Radushkevich equation
E_o = characteristic energy of adsorbent, J/mol
m = fit parameter in Dubinin-Astakhov equation
n = amount adsorbed, mol/g, mL/g
n_0 = amount adsorbed at saturation, mol/g, mL/g
p = partial pressure, Pa
p_r = relative pressure
p_s = saturated vapor pressure, Pa
P = total pressure, Pa
P_i^0 = equilibrium gas phase pressure of pure component i at the mixture spreading pressure and temperature, Pa
q = amount adsorbed, mol/g, mL/g
q_{sat} = amount adsorbed at saturation, mol/g, mL/g
R = gas constant, J/mol/K
T = temperature, K
x = adsorbed phase mol fraction
y = gas phase mol fraction
β = affinity coefficient of the adsorptive
γ = activity coefficient in the adsorbed phase
ϵ = equipotential contour, J/mol
θ = surface occupancy
π = spreading pressure, N/m
ρ = liquid density, $\mathrm{kg/m^3}$
ψ_i^0 = integral of individual isotherm for the spreading pressure, mol/kg

Subscripts

i = ith component in mixture

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