

Gas Phase Adsorption of Volatile Organic Compounds and Water Vapor on Activated Carbon Cloth

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This research examined the use of activated carbon cloths (ACC) to remove low concentrations of acetaldehyde, acetone, benzene, and methyl ethyl ketone from air. This work has applications in producing filtration systems for indoor air environments, industrial gas streams, and spray paint booths. Adsorption isotherms were measured for volatile organic compound adsorbate concentrations in the 10–1000 ppmv range and for water vapor from 0 to 95% relative humidity. The Dubinin–Radushkevich model was used to predict equilibrium adsorption capacities in the 100 ppbv to 10 000 ppmv concentration range. The adsorption of acetone–benzene mixtures on ACC was experimentally measured and then modeled using ideal adsorbed solution theory.

Introduction

Granular activated carbon (GAC) and powdered activated carbon (PAC) have long been used to effectively treat drinking water, waste water, industrial gas streams, and indoor air environments. Undesired contaminants are removed by adsorption onto activated carbon. This research examined the use of activated carbon cloths (ACC) to remove low concentrations of volatile organic compounds (VOCs) from air. This work has applications in producing filtration systems for indoor air environments, industrial gas streams, spray paint booths, and other applications where removal of gas phase contaminants is important. ACC typically exhibit higher adsorption capacities and faster adsorption kinetics than GAC.¹ Because ACC is present in the form of a cloth, it can be regenerated in-situ by applying an electrical current to the ACC and using its natural resistance to provide heat, which then regenerates the ACC. ACC can also be chemically tailored to allow preferential adsorption of certain compounds.^{2,3} The pore size distribution of a typical ACC lies over a narrow range in the micropore region (pore width < 2 nm), and these micropores exist on the fiber surface, permitting rapid adsorption of gases.^{1,4}

The ACC samples used in this study (ACC-5092) were obtained from American Kynol, Inc. (New York, NY). The starting material for the manufacture of ACC is cross-linked phenol–aldehyde fibers (novoloid fibers). These fibers are infusible and insoluble and have very high resistance to chemical attack.¹ Novoloid fibers are carbonized and activated in a one-step process to produce ACC. As the fibers are activated for longer times, the surface area of the ACC, the pore volume,

and the mean pore size all increase.^{1,4} This makes it possible to tailor the level of activation of the fibers for the optimal adsorption of a particular compound. ACC are produced by gradually heating the novoloid fibers to 900 °C in an atmosphere of steam and/or carbon dioxide. This may be either a batch or continuous process. Specific surface areas as high as 2500 m²/g may be obtained, but due to increased costs and diminishing yields, ACC with specific surface areas of 1500 or 2000 m²/g are usually the practical limit for most purposes.¹

Experimental Procedure

The experimental apparatus used to measure adsorption isotherms for VOC concentrations in the ppmv range consisted of a gas generation system and a gravimetric balance (Cahn Model C-2000). The gravimetric balance is used to detect the mass of an ACC sample that is exposed to a gas stream containing a known concentration of a select organic compound in a carrier gas of hydrocarbon-free air (Matheson Gas Products, Inc.). The gravimetric balance is able to sense changes in mass of as small as 1 µg. The compressed hydrocarbon-free air has a certified maximum hydrocarbon concentration of <0.1 ppmv and a water vapor concentration of <3 ppmv. The oxygen content is between 19.5 and 23.5% by volume. Additionally, the hydrocarbon-free air is passed through a gas purifier and drier (Drierite Model L68GP), which uses silica gel to remove water vapor to a terminal dryness of 0.005 mg/L or a dew point temperature of –37.7 °C. A 5 Å molecular sieve is also part of the purifier to remove dilute concentrations of hydrocarbons. The adsorption isotherms were measured at room temperature (25 ± 1 °C) and a total pressure of 1 atm.

Manufacturer certified compressed gas cylinders (Matheson Gas) were used to generate gas streams containing the organic adsorbates in hydrocarbon free air. The water vapor gas stream was generated by passing a hydrocarbon-free air stream through two Erlenmeyer flasks in series containing water and gas dispersion tubes. The dew point of the gas stream was measured using a dew point hygrometer (General Eastern), which was then converted to relative humidity using the temperature of the system. Mass flow controllers (Tylan General Model FC-280) regulated the amount of VOC or water vapor and dilution air entering the system. Once the gas stream was generated, it was then passed through the gravi-

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metric balance containing the ACC sample. The ACC sample adsorbed VOCs or water vapor and thus gained mass until equilibrium was achieved. Adsorption equilibrium was assumed to occur when the change in mass of the sample with respect to time approached zero (no noticeable change in mass over approximately a 4 h period). The gain in sample mass was recorded, and the mass ratio of adsorbed material to ACC was determined. For contaminant concentrations in the 10–50 ppmv range, the time required to reach equilibrium was typically between 2 and 6 days for ACF masses of 10–30 mg and total gas flows of 100 cm³/min. The experimental system also provides for thermal regeneration of the ACC prior to the adsorption measurement to desorb any volatile materials that may have adsorbed onto the ACC sample during its manufacture, storage, and handling. Heating tape was wrapped around the hangdown tube of the gravimetric balance and was heated to about 140 °C during regeneration of the ACC.

Several multicomponent adsorption experiments were performed using mixtures of acetone and benzene. The experimental system for the multicomponent adsorption experiments consisted of a Cahn gravimetric balance to measure the total mass adsorbed, a multiported hangdown tube on the gravimetric balance for gas sampling, and a gas chromatograph/mass spectrometer (GC/MS) (Hewlett-Packard GC Model 5890 Series II, MSD Model 5971). The upstream and downstream concentrations of acetone and benzene were measured by taking samples of the gas stream with a gastight syringe (250 μL) and analyzing them with the GC/MS. The difference between the upstream and downstream organic concentrations was the amount adsorbed on the ACC sample. Calibrations of the GC/MS were performed at the beginning and at the end of each experiment.

Equilibrium Adsorption Modeling

The Dubinin–Radushkevich (DR) equation was used to describe the physical adsorption of the organic compounds examined in this study.⁵ The DR equation can be represented by

$$W = W_0 \exp -(A/\beta E_0)^2$$

where W (mg/g) is the adsorption capacity, W_0 (mg/g) is the total volume of the micropores accessible to the given adsorbate, A (kJ/mol) is the differential molar work and is equal to $RT \ln(P/P_0)$, β is the affinity coefficient, and E_0 (kJ/mol) is the characteristic adsorption energy.

Water vapor adsorption onto activated carbon was described using an extension to the equations developed by Dubinin and Serpinski.⁶ The Dubinin–Serpinski equation only described water vapor adsorption in the relative pressure range of 0.05–0.5. Modifications developed by Barton, Evans, and MacDonald can describe the entire water vapor adsorption isotherm.⁷ The equation relates partial pressure of water vapor to a four-parameter nonlinear equation represented by

$$P/P_0 \approx h = \frac{a}{ca_0 + ca[1 - \exp(-k^2(a - a_c)^2)]}$$

where P/P_0 is the relative pressure of water vapor, a (mmol/g) is the amount of water adsorbed at the corresponding P/P_0 , and a_0 (mmol/g), c , k (g/mmol), and a_c (mmol/g) are fitting parameters.

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Table 1. BET and DR Surface Areas and Total Pore Volumes for ACC Using N₂ at 77 K

ACC sample	BET surface area (m ² /g)	DR surface area (m ² /g)	total pore vol (cm ³ /g)
ACC-15	730	1040	0.379
ACC-20	1330	1870	0.694
ACC-25	1860	2510	1.023

Table 2. DR Parameters for VOC Adsorbates and ACC

	ACC-15	ACC-20	ACC-25
acetaldehyde			
W ₀ (mg/g)	219.4	361.6	63.6
V ₀ ^a (cm ³ /g)	0.274	0.462	0.0812
E ₀ (kJ/mol)	14.5	11.9	16.3
acetone			
W ₀ (mg/g)	432.9	453.1	332.9
V ₀ ^a (cm ³ /g)	0.548	0.574	0.421
E ₀ (kJ/mol)	15.4	13.6	13.1
benzene			
W ₀ (mg/g)	394.7	613.2	486.6
V ₀ ^a (cm ³ /g)	0.450	0.699	0.555
E ₀ (kJ/mol)	23.9	17.8	17.2
MEK			
W ₀ (mg/g)	389.3	700.8	719.2
V ₀ ^a (cm ³ /g)	0.483	0.870	0.893
E ₀ (kJ/mol)	21.4	14.8	13.0

^a Calculated from W_0 and the adsorbate liquid density.

Ideal adsorbed solution theory (IAST) was used to model the adsorption of acetone–benzene mixtures. The theory behind IAST and a detailed description of calculation procedures are presented elsewhere.^{4,8,9}

Results and Discussion

Adsorption properties for three Kynol-based ACC were examined in this study. Nitrogen BET surface areas measured at 77 K for the materials ranged from 730 m²/g for the least activated ACC to 1860 m²/g for the most activated ACC (Table 1). The same starting material and activation procedure, as reported by the manufacturer, American Kynol, were used for all ACC samples, but the activation time was varied to produce ACC with different surface areas and pore volumes.¹

Adsorption isotherms were measured for VOC adsorbate concentrations in the 10–1000 ppmv range and for water vapor from 0 to 95% relative humidity. The DR equation was used to extend adsorption capacity characterization for the VOC adsorbates into the 100 ppbv to 10 000 ppmv range using the experimental data obtained in the 10–1000 ppmv concentration range (Table 2). This was done to make the data useful for a wide variety of applications, such as indoor air filtration (ppbv levels of contaminants), filtration of VOCs from spray paint booths (100s of ppmv), and organic solvent recovery (about 1000–10 000 ppmv). According to previous research,^{10,11} extrapolating adsorption isotherm data from higher adsorbate concentrations to lower adsorbate concentrations produces little deviation from experimental measurements and those predicted by the DR equation, but extrapolating to higher concentrations produces more deviation. The deviation

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(11) Dubinin, M. M. In *Chemistry and Physics of Carbon*; Walker, P. L., Ed.; Dekker: New York, 1966; p 51.

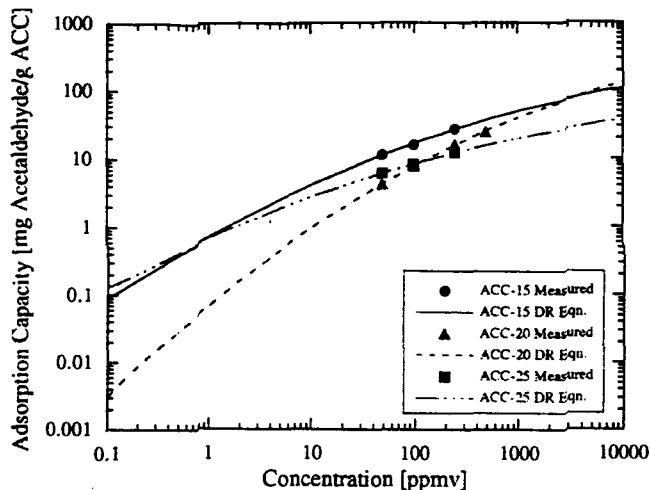


Figure 1. Experimental and DR modeled adsorption isotherms for acetaldehyde and ACC.

between the experimental results and the extrapolated results should result in an acceptable error for most applications over the concentration ranges examined in this research.

Since water vapor is ubiquitous in most environments, the adsorption of water vapor was also examined on ACC. Competitive adsorption with acetone and benzene (a polar and nonpolar adsorbate, respectively) was also examined, because most gaseous filtration systems must adsorb multicomponent VOC mixtures. Competitive adsorption between water vapor and VOCs is discussed elsewhere.^{4,12}

The adsorption capacities for acetaldehyde (Figure 1) were only measured up to 250 or 500 ppmv, depending on the ACC sample, because acetaldehyde converts to acetic acid in the presence of oxygen when the concentration is high enough.^{13,14} In the case of acetaldehyde, ACC-15 had the greatest adsorption capacity. ACC-25 had a higher adsorption capacity than ACC-20 until about 100 ppmv, and then ACC-20 started to exhibit the highest adsorption capacity. The adsorption capacities for acetaldehyde and ACC were far less than the adsorption capacities for any of the other VOC adsorbates, mainly due to the low boiling point and high vapor pressure (1000 Torr) of acetaldehyde at 25 °C.

In the case of acetone (Figure 2), there was a trend of lower specific surface area having the higher adsorption capacity; that is, ACC-15 adsorbed more acetone at a given concentration than ACC-20, which adsorbed more than ACC-25 for concentrations between 10 and 1000 ppmv.

It can be seen from the experimental results that more benzene was adsorbed on the three ACC samples over the concentration range examined than was adsorbed for either acetone, acetaldehyde, or methyl ethyl ketone (MEK). ACC-15 had a higher adsorption capacity for benzene (Figure 3) than ACC-20 at low concentrations (<100–200 ppmv), but at higher concentrations ACC-20 exhibited higher adsorption capacity than ACC-15. ACC-25 had a lower adsorption capacity than ACC-20 for benzene in the 10–~1000 ppmv range.

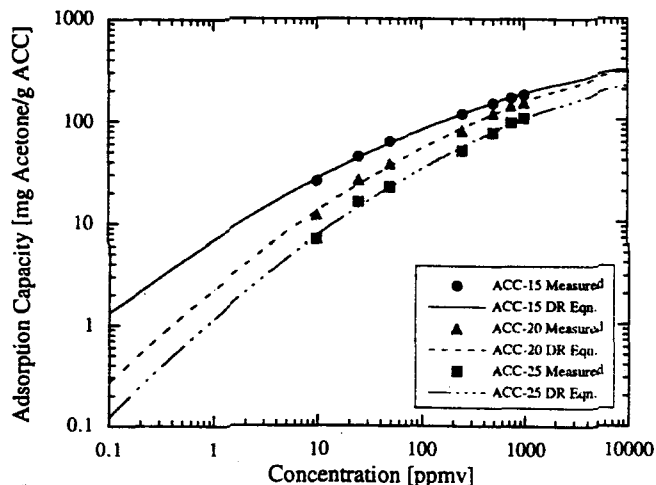


Figure 2. Experimental and DR modeled adsorption isotherms for acetone and ACC.

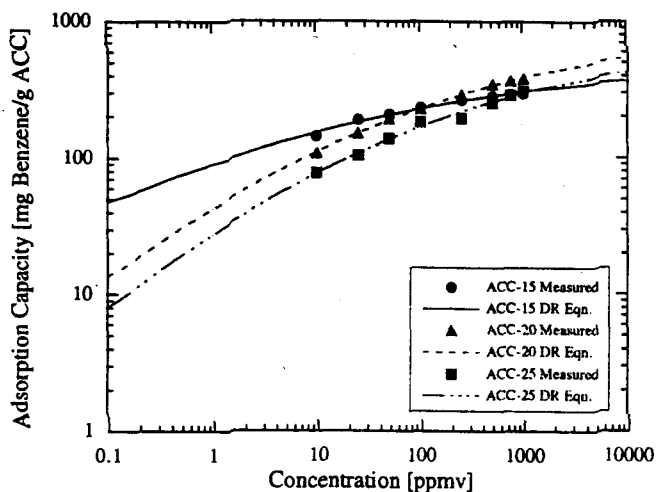


Figure 3. Experimental and DR modeled adsorption isotherms for benzene and ACC.

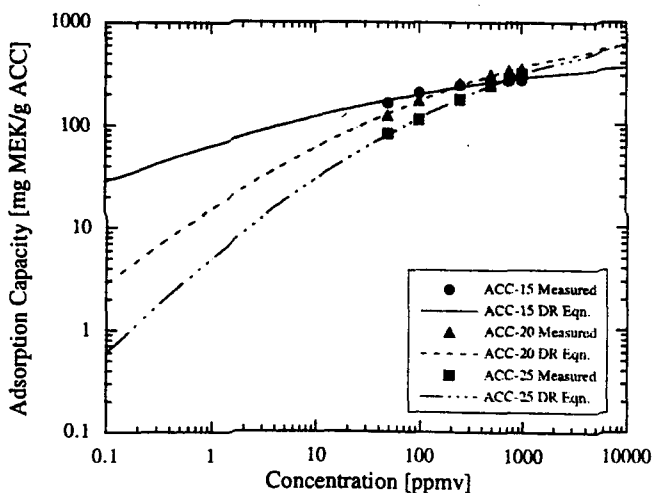


Figure 4. Experimental and DR modeled adsorption isotherms for MEK and ACC.

The adsorption capacities for MEK on ACC (Figure 4) were nearly as great as those observed for benzene over the 10–1000 ppmv concentration range. ACC-15 had the highest adsorption capacity (235 mg/g) for MEK up to about 200 ppmv until it was exceeded by ACC-20. Likewise, the adsorption capacity of MEK on ACC-25 (260 mg/g) exceeded that of ACC-15 at around 650 ppmv.

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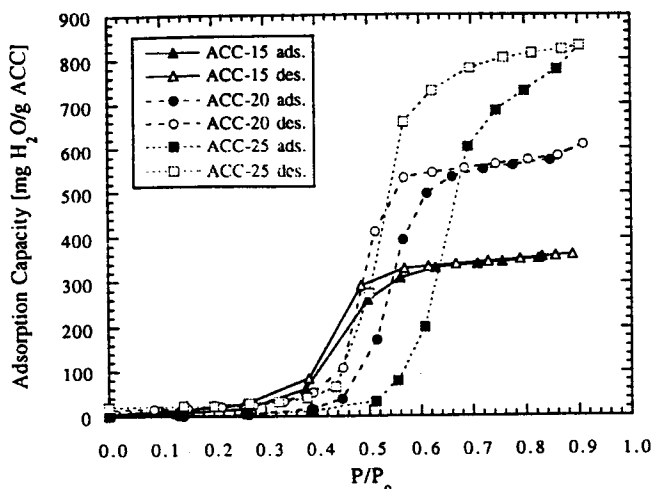


Figure 5. Adsorption isotherms for water vapor and ACC.

As expected, all of the VOC adsorbates exhibited a type I isotherm by Brunauer's classification. It can be stated for all of the adsorbates that as the concentration in the gas stream increases, ACC-25 will eventually have a greater adsorption capacity than ACC-20 and that ACC-20 will have a greater adsorption capacity than ACC-15, due to the differences in micropore volume of the ACC samples.

Adsorption and desorption isotherms for water vapor at relative humidities between 0 and ~95% and ACC-15, ACC-20, and ACC-25 are presented in Figure 5. Significant water vapor adsorption did not occur until ~30% relative humidity for ACC-15, ~45% relative humidity for ACC-20, and ~50% relative humidity for ACC-25. These results indicate that water vapor adsorption may interfere with hydrocarbon adsorption at relative humidity values $> \sim 30\%$.

It can be seen in Figure 5 from the differences in the measurements for water vapor adsorption and desorption that water vapor adsorption onto ACC exhibits hysteresis. The spread or width of the hysteresis loop increased, as did the total amount adsorbed at saturation, with increased surface area. The most widely accepted explanation for the observed hysteresis is that in the desorption process small pores constrict the openings to larger pores such that adsorbed water in the larger pores is not desorbed until the relative pressure corresponds to that of the smaller pore size.¹⁵ The DS-4 equation was used to fit the water vapor adsorption data for the three ACC. Best-fit parameters for the DS-4 equation were determined using a nonlinear parameter estimation algorithm present in the software package *HiQ* (National Instruments Corp.). The results of fitting the DS-4 equation to the water vapor adsorption isotherm data for the three ACC are presented in Table 3 and Figure 6.

The results of the IAST calculations along with experimental data for acetone-benzene mixtures are presented in Figure 7. The experimental data represent a total gas phase organic concentration of 1000 ppmv (0.76 mmHg). Experimental gas phase mole fractions (y_i) of acetone and benzene examined were 0, 0.25, 0.50, 0.75, and 1.00. IAST did well predicting the total amount of organic adsorbed, but it overpredicted benzene adsorption and underpredicted acetone adsorption.

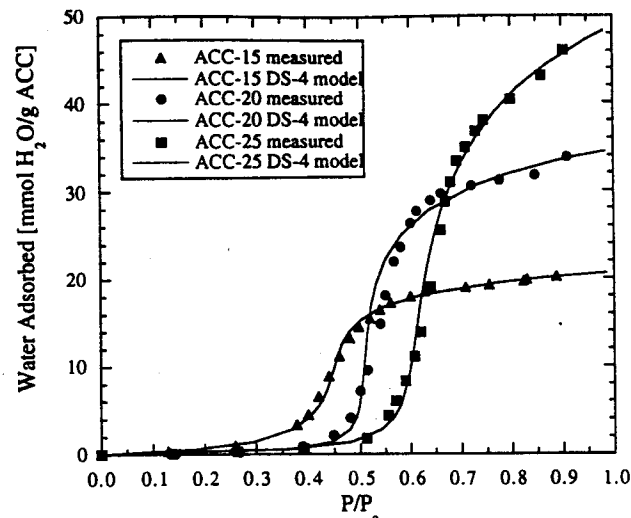


Figure 6. Measured and DS-4 modeled adsorption isotherms for water vapor and ACC.

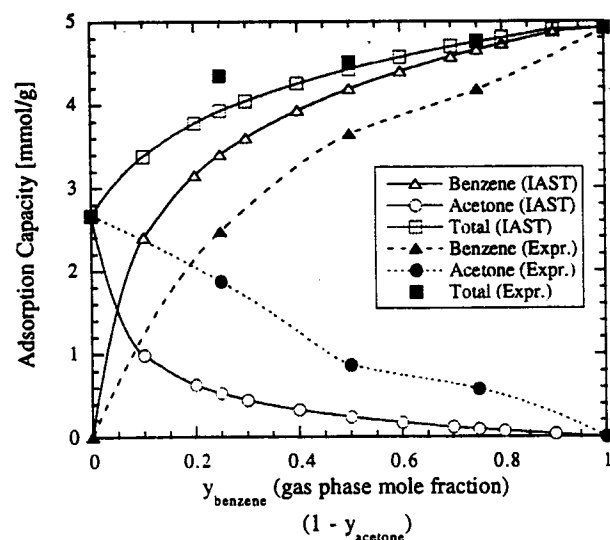


Figure 7. Measured and IAST modeled adsorption of acetone and benzene on ACC-20 at 1000 ppmv (0.76 mmHg) total concentration.

Table 3. DS-4 Parameters for Water Vapor Adsorption on ACC

ACC sample	a_c	a_0	c	h
ACC-15	25.6	0.935	2.03	0.154
ACC-20	47.9	0.228	1.93	0.0639
ACC-25	81.9	0.390	1.62	0.0292

Adsorbed phase activity coefficients (γ_i) were calculated and are presented in Table 4. For the acetone-benzene mixture at a total pressure of 0.76 mmHg, benzene exhibited activity coefficients > 1 , while acetone exhibited activity coefficients < 1 . The values of the activities coefficients show that the acetone-benzene mixture is highly nonideal. For the 0.25 benzene-0.75 acetone gas phase mole fraction mixture, IAST overestimated the adsorbed phase mole fraction (x_i) of benzene by 52% and underestimated the acetone adsorbed phase mole fraction by 222%; for a 0.75 benzene-0.25 acetone mixture, IAST overestimated the benzene adsorbed phase mole fraction by 12% and underestimated the acetone adsorbed phase mole fraction by 513% (Table 4).

As can be seen in Table 4, differences in the IAST predicted values and the experimental data are due to

Table 4. Calculated Activity Coefficients for Acetone-Benzene Mixtures at a Total Pressure of 0.76 mmHg

adsorbate	y_{acetone}	y_{benzene}	calcd	measd	γ_i	% deviation from ideality
			x_i	x_i		
benzene	1.0	0.00	0.00	0.00		
	0.75	0.25	0.866	0.569	1.52	52
	0.50	0.50	0.946	0.808	1.17	17
	0.25	0.75	0.980	0.879	1.12	12
	0.00	1.00	1.00	1.00	1.00	0
acetone	0.00	1.00	0.00	0.00		
	0.25	0.75	0.0197	0.121	0.163	513
	0.50	0.50	0.0540	0.192	0.280	257
	0.75	0.25	0.134	0.431	0.310	222
	1.00	0.00	1.00	1.00	1.00	0

nonidealities of the adsorbed phase mixture and must be compensated for by introducing activity coefficients into adsorbed solution theory (AST) and using a relationship, such as the Wilson equation, to calculate the activity coefficients of the mixture components.¹⁶ Currently, there are no methods for predicting adsorbed phase activity coefficients without experimental mixture data. To obtain the parameters needed in an activity coefficient relation, an extensive and accurate data set

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is needed (15 or more data points at a range of adsorbate partial pressures and gas phase mole fractions), because the relationships typically involve three or more parameters for each component in a set of nonlinear equations. Due to the limited data set available for acetone and benzene, it was not possible to make modifications to AST utilizing activity coefficients in an attempt to better its predictions.

Summary and Conclusions

Adsorption isotherms were measured for acetaldehyde, acetone, benzene, MEK, water vapor, and three ACC samples. For the 10–1000 ppmv concentration range examined, benzene exhibited the highest adsorption capacity on ACC, followed by MEK, acetone, and acetaldehyde. Water vapor adsorption was not significant on ACC until relative humidities rose above ~50% ($P/P_0 > 0.5$), when capillary condensation of $H_2O(g)$ occurred within ACC pores. IAST did well predicting the total amount adsorbed of a 1000 ppmv acetone-benzene mixture but overpredicted the individual amount of benzene adsorbed and underpredicted the amount of acetone adsorbed. The errors between the IAST modeled results and the experimental data are due to adsorbed phase nonidealities.

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