

An Emerging Class of Volatile Organic Compound Sorbents: Friedel–Crafts Modified Polystyrenes. 2. Performance Comparison with Commercially-Available Sorbents and Isotherm Analysis[†]

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The performance of Friedel–Crafts modified polystyrene (FCMPS) as a volatile organic compound (VOC) sorbent is compared with commercially available polymers and activated carbon. Detailed analyses of the equilibrium isotherms are presented, including vapor phase isotherm temperature dependence and isosteric heats of sorption. Although significant absorption contributions are observed for the polymeric sorbents of this study, the data are mathematically well represented by Polanyi potential analysis. FCMPS can be synthesized with desirable performance qualities such as ultimate VOC sorption capacity of ~2 mL/g, competitively high capacity in dilute streams versus activated carbon, insensitivity to humidity in vapor phase applications, and comparative ease of regeneration.

Introduction

In part 1 of this paper, the synthesis and characterization of FCMPS polymers were reported, including their performance as VOC sorbents in aqueous and vapor phase applications. In part 2, the class of FCMPS is compared with commercially available VOC sorbents, including other polymers and activated carbon.

Polymeric sorbents are of interest for both aqueous and vapor phase applications. Typically, investigators collect some combination of sorbent characterization, aqueous, and vapor phase equilibrium isotherm data (Browne and Cohen, 1990; Cornel and Sontheimer, 1986; De Sonier, 1990; Gregg and Sing, 1982; Gusler et al., 1993; Noll et al., 1992; Simpson et al., 1993; Weber and van Vliet, 1981). In several of the above studies, the characterization results (e.g., nitrogen sorption at 77 K) are compared with sorption in the aqueous or vapor phase. Such comparisons typically amount to discussion of isotherms and their relationship to the pore volume and BET surface area. Rarely do any of the published studies compare aqueous and vapor phase studies with characterization results. In addition, very few aqueous and vapor phase equilibrium sorption isotherms are presented up to the limit of unit activity (i.e., to the aqueous phase solubility or saturation vapor pressure). Most isotherm analyses presented are based on adsorption, which is of questionable theoretical validity since polymeric sorbents also have significant absorption contributions (see part 1, and references therein). The goal of such comparisons is usually to develop a rapid screening technique for promising sorbent candidates or a predictive tool for sorption capacity estimation.

The objectives of the studies presented in part 2 of this paper were to (1) compare the performance of FCMPS with commercially available alternative VOC

sorbents and (2) assess the utility and limitations of sorption equilibrium isotherm analyses by comparison of aqueous, vapor, and low-temperature nitrogen isotherm results.

Survey of Available Equilibrium Isotherm Data.

In a previous publication (Simpson et al., 1993), aqueous phase sorption of various priority pollutants by polymeric sorbents (XAD resins) was compared with an activated carbon. Several other studies have presented comparisons of related sorbent/sorbate systems (Browne and Cohen, 1990; Cornel and Sontheimer, 1986; De Sonier, 1990; Gregg and Sing, 1982; Gusler et al., 1993; Weber and van Vliet, 1981). However, none of the above studies have included FCMPS since they have only recently been made commercially available. Dow Chemical Co. (1993) presented a partial isotherm for XUS 43493 (a FCMPS) for aqueous phase sorption of phenol.

For vapor systems, a variety of activated carbons have been well studied (Grant and Manes, 1966; Gregg and Sing, 1982; Manes and Hofer, 1969; Noll et al., 1989; Wood, 1992), however, comparisons with polymeric sorbents are available in limited cases (Noll et al., 1992). Sarlis (1992) presented an extensive vapor phase study of the commercially available macroporous resin XAD4. Using a gravimetric "differential reactor" technique, vapor phase isotherms were generated at various temperatures for benzene, toluene, *p*-xylene, carbon tetrachloride, trichloroethylene, and tetrachloroethylene by XAD4 and a beaded activated carbon. Isosteric heats of sorption were calculated from the isotherm temperature dependencies. For FCMPS, few vapor phase VOC sorption equilibrium data are available in the literature. Vapor sorption of normal and fluorinated alkanes, methanol, acetone, and water by custom-synthesized FCMPS has been published (Belyakova et al., 1986). Also, incomplete sorption isotherms of toluene, *p*-xylene, methanol, and others are available from Dow Chemical Co. (1993) for commercially available FCMPS beads XUS 43493.

Isotherm Analysis. Often, parameters for the Freundlich isotherm (Noll et al., 1992), the Langmuir isotherm (Alben et al., 1988), and the Polanyi potential theory (Gusler et al., 1993; Manes and Hofer, 1969; Sontheimer et al., 1988; Weber and van Vliet, 1981) are calculated to characterize the adsorbate/adsorbent systems. The above isotherm parameters provide informa-

[†] This is the second in a two-part series on Friedel–Crafts modified polystyrene (FCMPS) and various commercially available VOC sorbents (polymeric and activated carbon). Part 1 described the synthesis and characterization of FCMPS, including their performance in aqueous and vapor phase applications (Simpson, E. J.; Koros, W. J.; Schechter, R. S. *Ind. Eng. Chem. Res.* **1995**, *35*, 1195).

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tion about adsorbate/adsorbent interactions and maximum solute capacity of the adsorbent. Aqueous and vapor phase Langmuir and Freundlich parameters were calculated for the activated carbon used in the present study and are presented elsewhere (Simpson et al., 1993, Simpson, 1995). Since these isotherms cannot accommodate polymeric sorbents over the wide activity ranges used in the present study, only Polanyi potential theory analysis is presented here in detail.

The Polanyi potential theory assumes there is a fixed available volume near the adsorption surface. The adsorption potential, ϵ , is defined as the free energy or work required to remove the solute from a potential surface to the bulk solution and, assuming Henry's law applies, may be calculated for the aqueous phase by:

$$\epsilon = RT \ln(C_{L,\text{sat}}/C_L) \quad (1)$$

where ϵ is the adsorption potential, R is the universal gas constant, T is temperature, C_L is the aqueous phase concentration, and $C_{L,\text{sat}}$ is the aqueous phase solubility. In the vapor phase, for an ideal gas one may substitute C_L with P_V and $C_{L,\text{sat}}$ with $P_{V,\text{sat}}$, where P_V and $P_{V,\text{sat}}$ are the equilibrium partial pressure and saturation vapor pressure of the sorbate, respectively. As suggested by Manes and Hofer (1969), Crittenden et al. (1987), and Sontheimer et al. (1988), the characteristic curve for a given adsorbent can be obtained by:

$$\ln q_v = \ln q_{v,0} + b(\epsilon/V_m)^\alpha \quad (2)$$

where q_v and $q_{v,0}$ are the volumetric sorption level (cm^3 of solute sorbed/g of sorbent) and "limiting sorption volume", respectively; V_m is the molar volume; and b and α are empirical constants.

The potential theory was originally developed by Polanyi (1932) for gas phase adsorption and has been studied more extensively for the gas phase case. Several researchers have reported modifications to Polanyi's approach, namely, Manes (Grant and Manes, 1966; Manes and Hofer, 1969) and Dubinin (1979, 1975). To obtain a sorbent's characteristic curve and accommodate sorbates of widely varying molecular properties, three normalizing parameters have commonly been incorporated: molecular parachor (Duisterwinkel, 1993), molar polarization (Wood, 1992), and liquid molar volume (Grant and Manes, 1966; Noll et al., 1989). There appears to be some dispute as to which of the above parameters best normalizes results. In the present study, molar volume was chosen as the normalizing parameter as shown in eq 2.

The detailed studies of Manes and co-workers (Grant and Manes, 1966; Manes and Hofer, 1969; Manes, 1984) investigated the use of Polanyi potential theory for both aqueous and vapor phase adsorption of a variety of compounds by activated carbons. While none of these studies showed direct comparisons between aqueous and vapor phase results, both Manes (1984) and Polanyi (1932) did examine the effect of competing sorbates on the adsorption potential. For water-immiscible sorbates, Manes suggested the vapor phase characteristic curve measured at 100% relative humidity is equivalent to the aqueous phase curve. At 100% relative humidity, the "net" adsorption potential of the sorbate is equal to its normal adsorption potential minus the adsorption potential of an equal volume of water:

$$\epsilon'/V_m = \epsilon/V_m = \epsilon_w/V_w \quad (3)$$

where ϵ' and ϵ are the net and normal adsorption potentials of the organic sorbate, respectively; ϵ_w is the adsorption potential of water vapor at an *equal adsorbed volume*; and V_m and V_w are the molar volumes of the organic and water, respectively. The correction amounts to subtraction of the water vapor characteristic curve from the normal characteristic curve of the organic and is analogous to the displacement of adsorbed water by the organic. Manes suggested this correction should be most important at low adsorbed volumes and diminish as the adsorptive capacity of water is approached. Grant et al. (1984) used a form of eq 3 to predict adsorption of toluene, heptane, and methylene chloride onto activated carbon at various relative humidities.

Pierce (1992) compared aqueous and vapor phase sorption of benzene by XAD4 and a beaded activated carbon. Since benzene was the only sorbate compared, the y -axis was left unchanged (i.e., mass uptake) while the x -axis was "normalized" by equating the vapor and aqueous phase concentration units as follows:

$$C_v = C_L \left(\frac{1 \times 10^{-6} \text{ L of Bz.}}{1 \text{ L of air}} \right) \left(\frac{1 \text{ L of Bz.}}{1 \text{ mg of Bz.}} \right) \times \left(\frac{1 \text{ mol of Bz.}}{22.4(298/273) \text{ L of Bz.}} \right) \left(\frac{78 \text{ 000 mg of Bz.}}{1 \text{ mol of Bz.}} \right) \quad (4)$$

where C_v is the vapor phase benzene concentration in ppmv. This "normalization" does not take into consideration the aqueous phase solubility or the saturation vapor pressure of benzene. Since this approach ignores such thermodynamic considerations, it is not surprising that poor agreement was found between aqueous and vapor phase data.

Heat of Sorption. To obtain an understanding of the energetics of sorption, one of the various heats of sorption can be calculated. The heat of sorption can be measured directly by calorimetry (Ross and Oliver, 1964; Young, 1962) or calculated if one knows the equilibrium isotherm temperature dependence. Perhaps the most commonly reported value is the isosteric heat of sorption:

$$\Delta H_{\text{iso}} = -R \left(\frac{\partial \ln P}{\partial (1/T)} \right)_q \quad (5)$$

where ΔH_{iso} is the vapor phase isosteric heat of sorption. The isosteric heat of sorption is calculated from the slope of a plot of $\ln P$ versus $1/T$ (T is an absolute temperature here) for a constant loading q (called an isostere). Of particular interest is the dependence of ΔH_{iso} upon q . For adsorbents with a homogeneous surface, ΔH_{iso} is a constant value for all loadings. More commonly, ΔH_{iso} varies with q , and the degree of surface heterogeneity can be qualitatively described by this relationship.

Experimental Section

Materials. The same materials listed in part 1 of this paper were used for the aqueous and vapor phase studies presented here. In addition, macroreticular resin beads were obtained from Rohm and Haas, Inc. (XAD2, XAD4, XAD16; Philadelphia, PA); activated carbon from Calgon Corp. (ACF400, Filtrasorb 400; Pittsburgh, PA); and FCMPS beads from Dow Chemical Co. (XUS43493, XU43502, "bridged copolymers"; Midland, MI).

Aqueous and Vapor Phase Equilibrium Isotherm Measurement. Procedures for the equilibrium isotherm measurement were described in detail in part 1 of this paper and in a previous publication (Simpson

Table 1. Properties of Sorbates Used in the Aqueous and Vapor Phase Studies^a

sorbate	$C_{L,sat}$ (mg/L)	V_m (30 °C) (cm ³ /mol)	Antoine constants or $P_{V,sat}$ [4] (@ T , °C)			density [5] (g/cm ³); [T , (°C)]
			A	B	C	
benzene	1710 1769 [1] 1696 [2]	90	6.0179	1203.7	219.9	$0.899-1.04 \times 10^{-3}T$
CCl ₄	850 883 [3]	97		114 mmHg (25 °C)		1.583 (25 °C)
chlorobenzene	510 491 [1]	102.7	6.0796	1419	216	$1.131-1.17 \times 10^{-3}T$
CHCl ₃	8000 7925 [1]	81.6		242.4 mmHg (30 °C)		$1.515-2.01 \times 10^{-3}T$
ethanol	miscible	60.6		72.3 mmHg (30 °C)		0.76 (30 °C)
hexane	8	132.6		181 mmHg (30 °C)		0.65 (30 °C)
naphthalene	32	131.4 (85 °C)	6.1638	1760	205.2	0.975 (85 °C)
toluene	572 580 [2]	106.8	6.0844	1347.6	219.79	$0.886-8.9 \times 10^{-4}T$
TCE	1185	91		72.9 mmHg (25 °C)		1.456 (25 °C)
water		18.1		31.8 mmHg (30 °C)		0.996 (30 °C)
<i>p</i> -xylene	207 179 [1]	125.1	6.1138	1452.2	215.16	$0.877-9.29 \times 10^{-4}T$

^a The values with a number in brackets [] afterward are literature values from the following references: [1] Mackay and Shiu, 1981; [2] Keeley et al., 1988; [3] Montgomery and Welkom, 1990; [4] Boublik et al., 1984 (all vapor pressure data); [5] Gallant, 1968 (all densities). Unless otherwise noted, data are provided at 25 °C for aqueous phase (deionized water) sorbates and 30 °C for vapor phase sorbates. Antoine constants use the equation $\log P_{V,sat} = A - B/(X + T)$, where $P_{V,sat}$ and T are in units of KPa and °C, respectively.

Table 2. Properties of Sorbents Used in the Aqueous and Vapor Phase Studies^a

trade name	ACF400	XUS 43493	XU 43502	FCMPS-CMEE-0.5%	XAD2	XAD4	XAD16
manufacturer	Calgon	Dow	Dow	Custom	Rohm & Haas	Rohm & Haas	Rohm & Haas
BET surface area (m ² /g)	1089 (3) 1075 [2]	1109 (5) 1100 [4]	878 (2) 1080 [4]	918 (4)	364 350 [3]	761 (2) 870 [2] 760 [3]	765 806 [2]
pore volume (cm ³ /g)							
measured (N ₂ @ 77 K)	0.62 0.62 [1]	0.95 1.16 [4]	0.82 0.94 [4]	0.69 (3)	0.63 0.76 [1]	1.2 1.14 [2]	1.22 1.4 [2]
calculated (dry density)		0.85	0.51	0.32 (4)	0.51	0.95 (3)	1.19 (3)
swell ratio (V_{sol}/V_{dry})							
toluene	1	1.15	1.08	2.7 (2)	1.15	1.32	1.32
chlorobenzene		1.18	1.15	3.1	1.17	1.49	1.33
ethanol	1	1.13		2.8	1.13	1.29	1.32
lot no.		930409-A1	930908-MDP	FC 10a	6-9512	7-1473	6-3117

^a Values with a number in parentheses () afterward are the average of multiple measurements, while values with a number in brackets [] afterward are manufacturer or literature values from following references: [1] Browne and Cohen, 1990; [2] Gusler et al., 1993; [3] Weber and van Vliet, 1981; [4] Dow Chemical Co., 1993.

et al., 1993). Isotherms were measured either in the aqueous phase by HSGC or in a stirred cell with on-line UV detection and in the vapor phase using a quartz spring sorption cell. In the aqueous phase studies, the highly hydrophobic polymeric sorbents were prewetted and rinsed. Properties of the sorbates used in the aqueous and vapor phase studies are shown in Table 1.

Sorbent Characterization. All of the sorbents used in the study were characterized for pore volume and BET surface area using a Micromeritics Accusorb 2100E physical adsorption analyzer. Swell ratios in organic solvents were measured for all of the polymeric sorbents. Properties of the sorbents used in the study are summarized in Table 2.

Results and Discussion

Aqueous and Vapor Phase Sorption Equilibrium. Selected aqueous phase sorption equilibrium isotherms were measured at 25 °C for benzene, carbon tetrachloride, chlorobenzene, chloroform, toluene, trichloroethylene, and *p*-xylene by ACF400, XAD resins, Dow XUS 43493, and custom-synthesized FCMPS. The custom-synthesized FCMPS samples used a starting poly(styrene/divinylbenzene) (PSDVB) with 0.5% DVB and were cross-linked to a theoretical 100% level with chloromethyl methyl ether (CMME) or chloromethyl ethyl ether (CMEE) as described in part 1 of this paper.

Samples cross-linked with CMME and CMEE have nearly identical properties; thus, isotherm results can be considered essentially interchangeable.

Selected vapor phase sorption equilibrium isotherms were measured at temperatures ranging from 30 to 90 °C for benzene, chlorobenzene, ethanol, hexane, naphthalene, *p*-xylene, toluene, and water by ACF400, XAD4, Dow XUS 43493 and XU 43502, and custom-synthesized FCMPS.

Figures 1 and 2 show comparative results for aqueous and vapor phase toluene sorption. Figure 1 shows that at low aqueous phase concentrations FCMPS-CMEE-0.5% and XUS 43493 have similar sorption capacities compared to ACF400; however, at higher concentrations both polymers have capacities well above that of ACF400, particularly FCMPS-CMEE-0.5%. XAD4 has the lowest capacity at low toluene concentrations, but its capacity at high concentrations is comparable to that of FCMPS-CMEE-0.5%.

The vapor phase results are presented as a "normalized volumetric isotherm," with volumetric uptake (q_v , in cm³/g) versus a normalized concentration ($P_{V,T}/P_{V,sat}$). In comparison to the aqueous phase results, the ACF400 vapor phase toluene isotherm shown in Figure 2 is somewhat sharper in its transition from an initially high slope to a nearly constant adsorption level. Thus, for low vapor activities ($P_V/P_{V,sat}$), ACF400 has a slightly higher sorption capacity when compared with FCMPS-

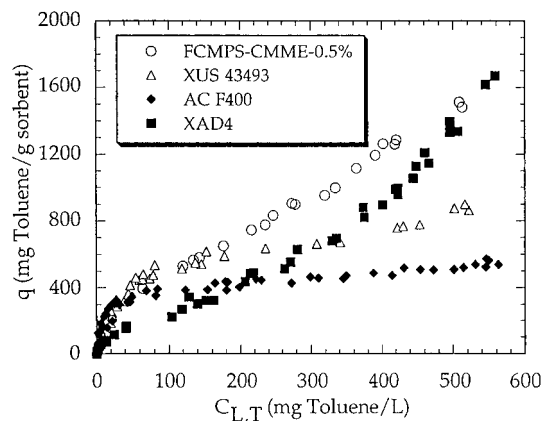


Figure 1. Aqueous phase toluene sorption isotherm results for FCMPs-CMME-0.5%, Dow XUS 43493, ACF400, and XAD4 at 25 °C.

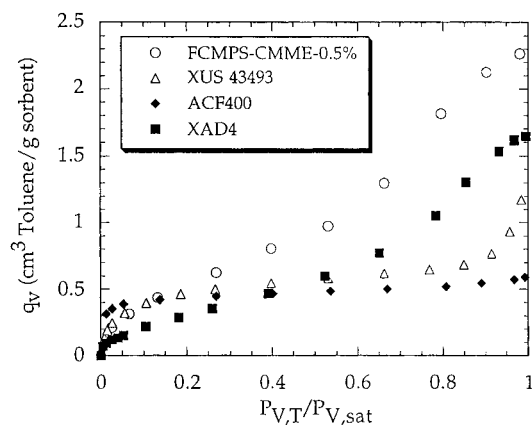


Figure 2. Vapor phase toluene sorption isotherm results for FCMPs-CMME-0.5%, Dow XUS 43493, ACF400, and XAD4 at 30 °C.

CMME-0.5% and XUS 43493. At higher vapor activities, the comparative capacities of the sorbents are the same as in the aqueous phase case.

For other sorbates, the same isotherm shapes were observed for both the aqueous and vapor phases for each of the sorbents in the present study, with the notable exceptions of ethanol and water. For the sake of brevity, the individual isotherms are presented elsewhere (Simpson, 1995); instead, additional results are deferred to the isotherm analysis section.

In a previous publication (Simpson et al., 1993), it was shown that the normalized volumetric isotherms represent a convenient form to compare results for different sorbates by a given sorbent. In general, this is true when viewed in comparison with isotherms of mass uptake versus concentration; however, sorbate selection in the present study tested the limitations of the normalized volumetric isotherms. Figures 3 and 4 show the vapor phase normalized volumetric isotherms of various sorbates for ACF400 and XUS 43493. Sorbates with high molar volumes (e.g., hexane, 132.6 cm³/mol) are the highest on the normalized volumetric plots, while sorbates with low molar volumes (e.g., ethanol, 60.6 cm³/mol) are the lowest.

In the case of water, all of the sorbents show far lower sorption capacities versus the organic solutes in the study. The polymeric sorbents are all highly hydrophobic and do not wet in the aqueous phase, so one would expect they would have lower sorption capacity for water vapor when compared with organics. Thus, it is not surprising that FCMPs-CMME-0.5% and XAD4 exhibit very little capacity (0–0.08 cm³/g) for water vapor

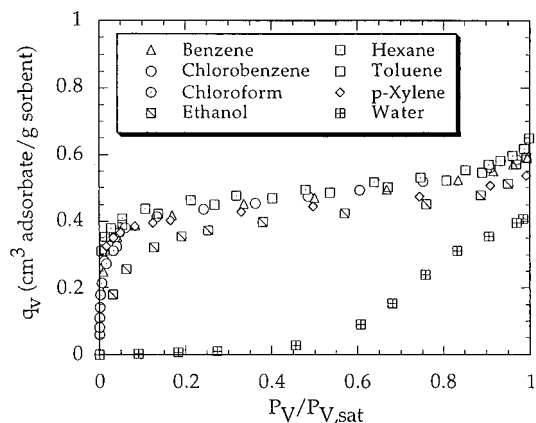


Figure 3. Vapor phase normalized volumetric sorption isotherms for ACF400 at 30 °C.

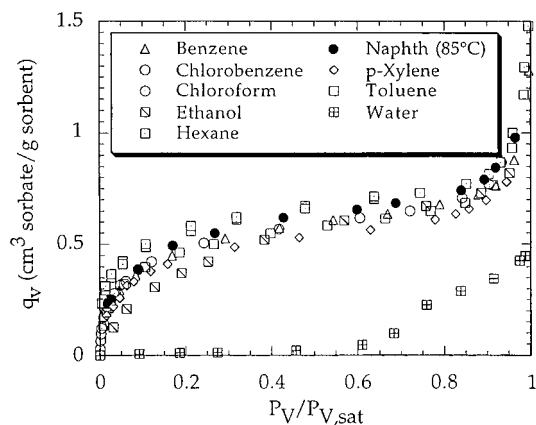


Figure 4. Vapor phase normalized volumetric sorption isotherms for XUS 43493 at 30 °C.

at all activities. It is perhaps difficult to explain why the custom-synthesized FCMPs do not sorb water vapor, while Dow XUS 43493 shows a significant capacity for water vapor at high activities (~0.45 cm³/g). Apparently, the different synthesis conditions for the XUS 43493 versus the custom-synthesized FCMPs create a polymer with a significantly higher affinity for water. Since it is well-known that high humidities adversely affect the vapor sorption capacity of activated carbons (Grant et al., 1984), it is not surprising that ACF400 shows significant capacity for water vapor at high activities (~0.4 cm³/g).

The isotherm for naphthalene was measured at 85 °C to operate above the melting point and at a temperature where the vapor pressure is measurable. Since naphthalene has a melting point of 80.3 °C, operating above this temperature also allows knowledge of the liquid density and thus prevents complication of data analysis and interpretation. It is generally accepted that the bulk liquid density should be used in calculating the molar volume of the adsorbed phase (Grant and Manes, 1966). However, it is also widely recognized that for solids the adsorbed phase volume is considerably less predictable (Shen and Wang, 1992). From a practical standpoint, the high melting point of naphthalene presented an experimental challenge versus the other organics in the study. Thus, only one isotherm was measured for XUS 43493.

Polanyi Potential Theory Characteristic Curves.

As shown in part 1 of this paper (with supporting references), absorption contributes to the total sorption for the polymer sorbents used in the present study. Nevertheless, previous researchers have used Polanyi potential theory to analyze polymeric sorbent results

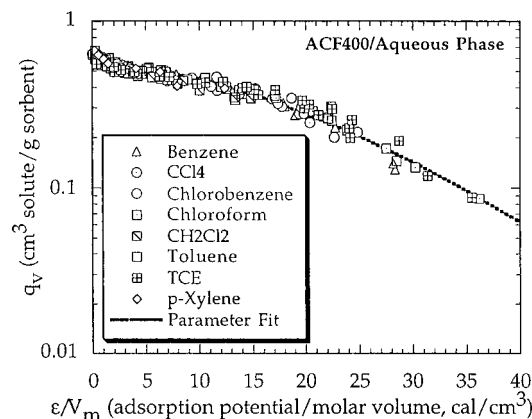


Figure 5. Polanyi adsorption potential plot for ACF400 for aqueous phase at 25 °C, with parameter fit from for all data points ($R^2 = 0.96$).

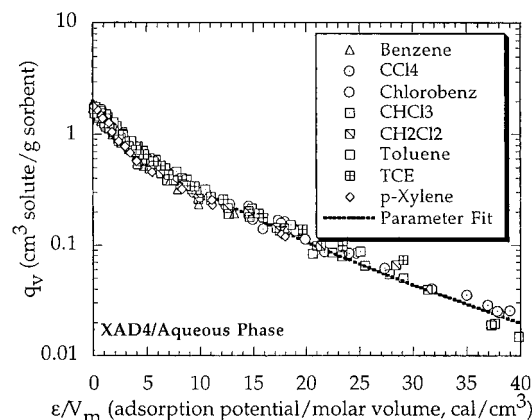


Figure 6. Polanyi potential plot for XAD4 for aqueous phase at 25 °C, with parameter fit for all data points ($R^2 = 0.988$).

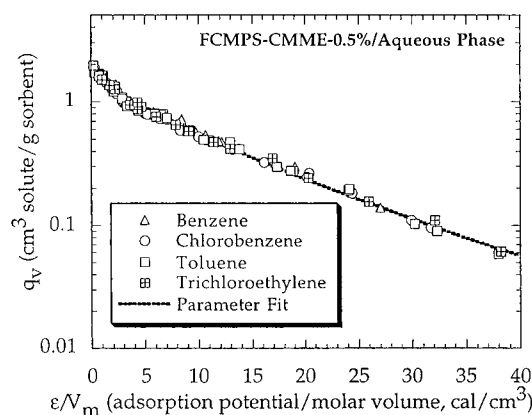


Figure 7. Polanyi potential plot for FCMPs-CMEE-0.5% for aqueous phase at 25 °C, with parameter fit for all data points ($R^2 = 0.992$).

(Weber and van Vliet, 1981; Gusler et al., 1993). While it is recognized that the theoretical development of the Polanyi combined adsorption/pore filling model is not strictly met by the polymer sorbents, the results for selected polymers in the present study were analyzed with this technique. As shown in Figures 5–8, for each sorbent in the present study, data for the various solutes correlate very well on a Polanyi potential plot. Polanyi plots were obtained for each sorbent in both the aqueous and vapor phases, and the regressed parameters are summarized in Tables 3 and 4. From the tables, one can see the regression results were excellent, with R^2 values ranging from 0.94 to 0.993. The “limiting sorption capacity” values, $q_{v,0}$, for XAD4 (~ 2 cm³/g) and FCMPs-CMEE (~ 1.8 cm³/g) far exceed that of ACF400

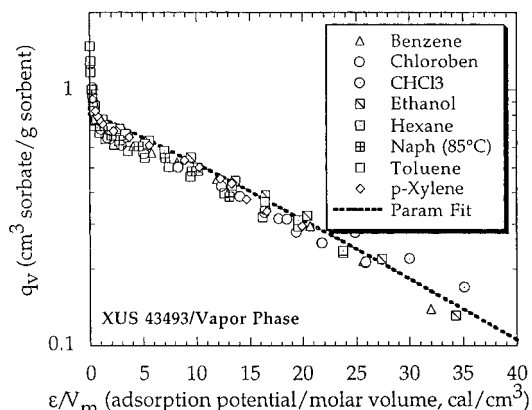


Figure 8. Vapor phase Polanyi potential characteristic curve for XUS 43493, with parameter fit for all data points shown ($R^2 = 0.97$).

Table 3. Polanyi Potential Theory Parameters for Aqueous Phase Sorption^a

sorbent	aqueous phase Polanyi potential param			
	$q_{v,0}$ (cm ³ /g)	b	α	R^2
ACF400				
all solutes	0.56	-0.005	1.65	0.96 ($n = 66$)
toluene	0.60 [1]	-0.01	1	0.947
chlorobenzene	0.46 [1]	-0.01	1	0.947
carbon tetrachloride	0.42 [2]		2	
XAD4				
all solutes	1.99	-0.404	0.661	0.988 ($n = 225$)
toluene	0.81 [1]	-0.025	1	0.976
chlorobenzene	0.67 [1]	-0.018	1	0.992
carbon tetrachloride	0.41 [2]		2	
XUS 43493	0.80	-0.0052	1.79	0.981 ($n = 103$)
FCMPs-CMEE-0.5%	1.85	-0.21	0.762	0.992 ($n = 109$)

^a The values with a number in brackets [] afterward are literature values from the following references: [1] Gusler et al., 1993; [2] Weber and van Vliet, 1981. Values for b for carbon tetrachloride are not listed due to the modified form of the Polanyi analysis used for these data.

Table 4. Polanyi Potential Theory Parameters for Vapor Phase Sorption

sorbent	vapor phase Polanyi potential param			
	$q_{v,0}$ (cm ³ /g)	b	α	R^2
ACF400	0.541	-0.0057	1.433	0.985 ($n = 82$)
XAD4	1.82	-0.464	0.643	0.996 ($n = 79$)
FCMPs-CMEE	1.81	-0.276	0.7	0.993 ($n = 61$)
FCMPs-CMME	1.99	-0.299	0.703	0.993 ($n = 83$)
XUS 43493	0.804	-0.034	1.1	0.943 ($n = 113$)

(~ 0.55 cm³/g). The exponent parameter, α , is different for each sorbent in the study. A value of ~ 1.6 was regressed for ACF400, while XAD4 and FCMPs-CMEE have α values below 1.

Weber and van Vliet (1981) used a two-coefficient Dubinin isotherm (a “modified” Polanyi potential plot) to analyze aqueous phase data for various solutes onto XAD4 and ACF400. Their isotherms for carbon tetrachloride showed good agreement with the present study and were measured to reasonably high solute concentrations ($C_L \sim 0.5 C_{L,sat}$). As shown in Table 3, their data analysis technique dramatically underestimates the limiting sorption volume of both ACF400 and XAD4 for carbon tetrachloride (the only solute common to both studies). Their analysis suggests $q_{v,0}$ values of 0.419 cm³/g (vs 0.56 cm³/g in this study) for ACF400 and 0.41 cm³/g (vs ~ 1.99 cm³/g) for XAD4.

Gusler et al. (1993) used the Polanyi potential theory to obtain characteristic curves for toluene, chlorobenzene, phenol, and benzoic acid sorption by ACF400 and XAD4. Apparently, they arbitrarily set the exponent value, α , to unity. Since their isotherms were not

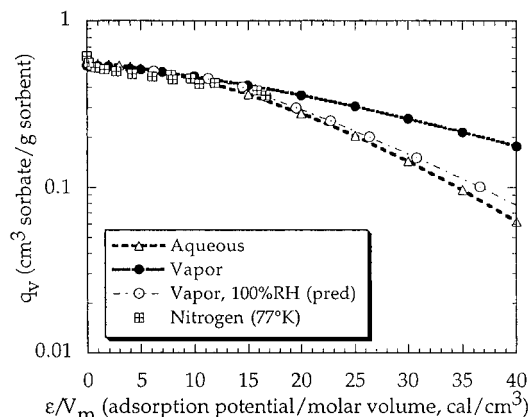


Figure 9. Comparative Polanyi potential characteristic curves for aqueous and vapor phases, including data for nitrogen adsorption at 77 K and vapor phase 100% RH prediction for ACF400.

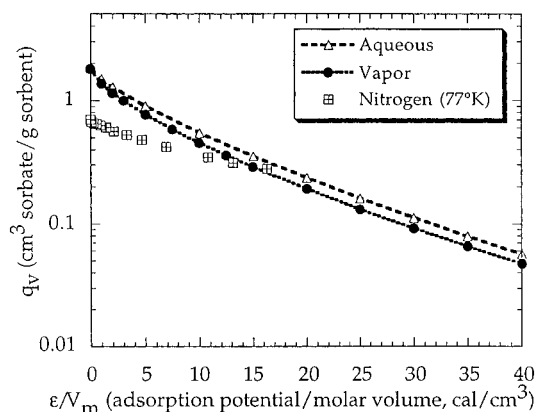


Figure 10. Comparative Polanyi potential characteristic curves for aqueous and vapor phases, including data for nitrogen sorption at 77 K for FCMPs-CMEE-0.5%.

measured to $C_{L,sat}$, their analysis suggested the $q_{v,0}$ values of XAD4 were significantly lower than the analysis of the present study as shown in Table 3. Their values for ACF400 are in slightly better agreement with those of the present study.

The results of Weber and van Vliet (1981) and Gusler et al. (1993) both suggest $q_{v,0}$ varies with respect to the solute. In agreement with the prediction of the Polanyi potential theory, the actual isotherm data of the present study suggest that $q_{v,0}$ is *invariant* with respect to the solute. However, the shape of the isotherms for ACF400 and XUS 43493 created considerable difficulty for the regression analysis. For both sorbents, the isotherms have sharp upturns at low values of ϵ/V_m (as $C_L \rightarrow C_{L,sat}$ or $P_v \rightarrow P_{v,sat}$). The resulting values of $q_{v,0}$ from regression analysis of data for the individual solutes varied substantially more than the experimental data. The above discrepancies demonstrate the benefit of measuring the sorption isotherms up to the aqueous solubility (or saturation vapor pressure). If one only measures the isotherms at low activities, a gross underestimation of $q_{v,0}$ results.

Comparison of Aqueous and Vapor Phase Studies with Characterization Results. In the preceding discussion (see also part 1 of this paper), examples have been cited of differences between nitrogen (77 K), aqueous phase, and vapor phase sorption results. Figures 9–11 illustrate these differences in the form of Polanyi potential plots for ACF400, FCMPs-CMEE-0.5%, and XUS 43493. The characteristic curves shown for each sorbent are from the regression of data for *all* sorbates studied in each individual phase.

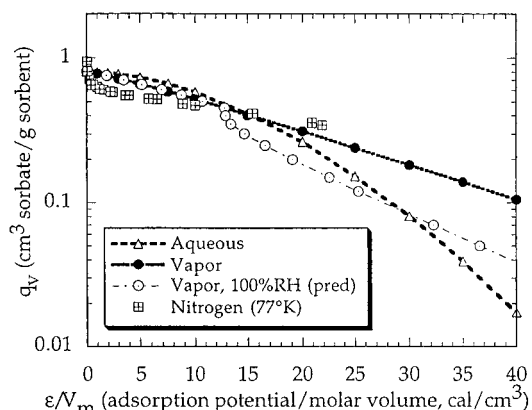


Figure 11. Comparative Polanyi potential characteristic curves for aqueous and vapor phases, including data for nitrogen sorption at 77 K and vapor phase 100% RH prediction for Dow XUS 43493.

As shown in Figure 9, when the data for ACF400 are compared on a Polanyi potential plot, nitrogen adsorption capacity at 77 K agrees very well with aqueous and vapor phase capacities. The capacities of ACF400 in the aqueous and vapor phases are essentially equal at high activities (low ϵ/V_m values). The difference between aqueous and vapor phase sorption at low activities (high ϵ/V_m values) is more easily seen on a Polanyi potential plot than on the normalized volumetric isotherms. The predicted vapor phase isotherm at 100% relative humidity (RH) using water vapor adsorption data for ACF400 and eq 5.2 is also shown in Figure 9. The 100% RH prediction demonstrates the difference between the aqueous and vapor phase results with remarkable accuracy. The example of ACF400 shows the Polanyi potential theory can treat the case of competitive adsorption between water and water-immiscible sorbates.

In Figure 10, the comparative Polanyi plot for FCMPs-CMEE-0.5% demonstrates a somewhat different trend. Aqueous phase sorption is slightly higher than that in the vapor phase at all values of $\epsilon/V_m > 2$. The enhanced aqueous phase sorption may be attributable to the wetting procedure. As mentioned previously in part 1, even after all of the organic wetting solvent is removed, the polymers remain in a "preswollen" state. Perhaps this procedure opens the polymer structure, allowing enhanced levels of aqueous phase VOC sorption versus the vapor phase. The nitrogen sorption levels at 77 K are markedly lower than aqueous and vapor phase sorption levels at low values of ϵ/V_m . Since FCMPs-CMEE-0.5% does not sorb significant quantities of water vapor, its vapor phase sorption capacities are unaffected by 100% RH. Each of the custom-synthesized FCMPs and XAD resins in the present study followed the same behavior as the FCMPs-CMEE-0.5%.

The comparative Polanyi plots for XUS 43493 shown in Figure 11 represent more complicated behavior. Nitrogen sorption at 77 K agrees poorly with both aqueous and vapor phase sorption, although the shape of the plot resembles the vapor phase more closely. The aqueous phase characteristic curve is slightly higher than that of the vapor phase at high activities and significantly lower at low activities. Recall from Figure 4 that XUS 43493 sorbs significant amounts of water vapor. However, the prediction of vapor phase sorption at 100% RH by Polanyi analysis does not explain the difference between aqueous and vapor phase sorption with the same precision as in the case of ACF400.

The unusual behavior of XUS 43493 shown in Figure 11 might be explained as follows. As demonstrated by

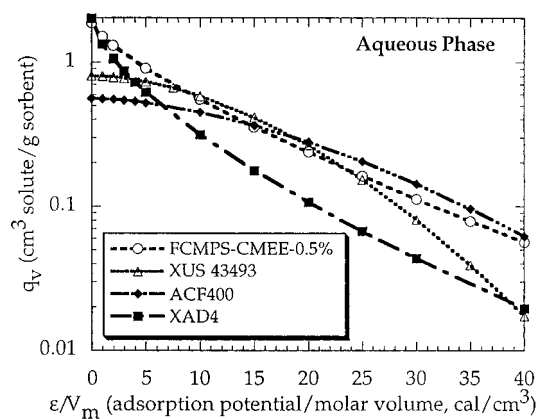


Figure 12. Polanyi potential characteristic curves for the aqueous phase for FCMPs-CMEE-0.5%, XUS 43493, ACF400, and XAD4.

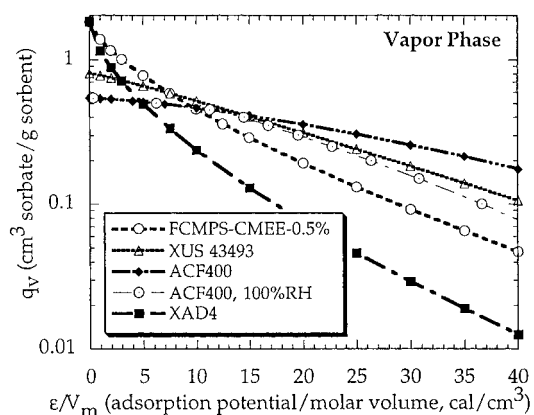


Figure 13. Polanyi potential characteristic curves for the vapor phase for FCMPs-CMEE-0.5%, XUS 43493, ACF400 (including 100% RH prediction), and XAD4.

the figure for FCMPs-CMEE-0.5% (and other polymers not shown here), one might expect *aqueous* phase sorption to be higher for polymeric sorbents; this behavior is observed for XUS 43493 at high activities. As shown for ACF400 in Figure 9, for sorbents with significant capacities for water vapor one would expect *vapor* phase sorption to be higher at low activities; XUS 43493 also displays this type of behavior. The fact that the 100% RH does not clearly explain the differences at low activities is perhaps due to overlapping effects in the aqueous phase of (1) competitive organic/water sorption (decreases aqueous phase sorption at low activities) and (2) enhanced sorption due to the wetting procedure (increases aqueous phase sorption).

Figures 12 and 13 show comparisons of Polanyi potential plots for ACF400, XAD4, FCMPs-CMEE-0.5%, and XUS 43493 for the aqueous and vapor phases, respectively. These plots are from regression of the data for all sorbates in the present study. Thus, these plots best represent the expected comparative capacities of the sorbents in each individual phase. In the aqueous phase, ACF400 and FCMPs-CMEE-0.5% have comparable capacities in very dilute solutions (high values of ϵ/V_m), while FCMPs-CMEE-0.5% surpasses ACF400 at higher activities. In the vapor phase, ACF400 has the highest capacity in very dilute vapor streams, while XUS 43493 matches ACF400 in capacity at intermediate activities. FCMPs-CMEE-0.5% has the highest capacity of the sorbents at higher activities (ϵ/V_m of <9). The predicted vapor phase curve at 100% RH for ACF400 is also shown in Figure 13, demonstrating FCMPs-CMEE-0.5% has a more competitive sorption capacity in high-humidity, dilute streams. As in the case of ACF400, XUS 43493 would also be expected to show a

Table 5. Aqueous and Vapor Phase Toluene Sorption Capacities for ACF400, FCMPs-CMEE-0.5%, XUS 43493, and XAD4 Calculated from Polanyi Potential Parameters

toluene			sorption capacity, q (mg/g)			
ϵ/V_m	$C_{L,CL,sat}$	$C_{L,T}$ (mg/L)	ACF400	FCMPs-CMEE	XUS 43493	XAD4
39.6	0.0008	0.46	56	50	16	17
16.6	0.05	28.6	288	267	311	129
12.8	0.1	57.2	346	369	420	195
8.9	0.2	114.4	402	523	532	308
5.1	0.4	228.8	450	772	628	526
2.8	0.6	343.2	470	1001	668	769
1.2	0.8	457.6	480	1244	686	1079
0.6	0.9	514.8	483	1386	690	1295

ϵ/V_m	$P_V/P_{V,sat}$	$C_{V,T}$ (ppmv)	ACF400	FCMPs-CMEE	XUS 43493	XAD4
40	0.0008	38.4	151	40	96	10.8
16.8	0.05	2 400	336	212	324	91
12.9	0.1	4 800	372	297	392	141
9	0.2	9 600	407	429	471	231
5.1	0.4	19 200	438	652	562	414
2.9	0.6	28 800	453	873	620	627
1.3	0.8	38 400	461	1126	661	915
0.6	0.9	43 200	463	1285	678	1123

significant decrease in sorption capacity in the vapor phase at 100% RH at low activities.

Table 5 compares aqueous and vapor phase sorption capacities (q , in mg of sorbate/g of sorbent) of the sorbents for toluene as calculated from the Polanyi potential parameters at various values of ϵ/V_m . Perhaps more useful are the equivalent aqueous and vapor phase concentrations included in the tables. From the concentrations in the table, one can see that the Polanyi plots emphasize the dilute concentration range. The range of ϵ/V_m values > 15 encompasses aqueous and vapor phase toluene concentrations *less than* 40 mg/L and 3300 ppmv (parts per million by volume), respectively (alternatively, activities < 0.06). While this range is very important for many applications, a majority of the experimental data in the present study were obtained at higher concentrations. At these higher concentrations, one also sees the equilibrium sorption capacities of the polymeric sorbents are remarkably high. For FCMPs-CMEE-0.5%, the ultimate capacity amounts to 140% by weight for toluene (alternatively, the value is $\sim 250\%$ for carbon tetrachloride).

Limiting Sorption Volume Comparisons. Evidence of Absorption. The total capacity, or limiting sorption volume, was measured in the aqueous and vapor phases and during liquid nitrogen characterization studies. The limiting sorption volumes were also obtained from regression analysis of the Polanyi potential plots. Table 6 summarizes limiting sorption volumes obtained by each of the above techniques for ACF400, FCMPs-CMEE-0.5%, XUS 43493, and XAD4. The values of $q_{v,0}$ in Table 6 are presented as average values of *individual sorbates* as opposed to values obtained from regression of data for all sorbates (i.e., as presented in Tables 3 and 4).

The data show ACF400 has a limiting adsorption volume ($q_{v,0}$) in the aqueous and vapor phases in close agreement with the pore volume measured by nitrogen adsorption at 77 K. The experimental values are fairly reproducible ($< 8\%$ standard deviation from the mean), while the Polanyi potential analysis provides a good prediction.

When compared with ACF400, each of the polymeric sorbents follows a distinctly different pattern. The pore volumes measured by nitrogen sorption at 77 K all exceed the values estimated by dry (or bulk) density

Table 6. Comparison of "Limiting Sorption Volumes" in Various Environments for ACF400, FCMPs-CMEE-0.5%, XUS 43493, and XAD4^a

max capacities (all values in cm ³ /g)	ACF400	FCMPs-CMEE	XUS 43493	XAD4
pore volume				
measured (N ₂ , 77 K)	0.62	0.69	0.95	1.2
calculated (density)		0.32	0.85	0.95
aqueous phase				
experimental	0.62 (7.8)	1.98	1.04	1.75 (3.8)
Polanyi	0.61 (20.8)	1.77 (9.9)	0.81 (5.1)	2.19 (13)
vapor phase				
experimental	0.58 (4.9)	1.86 (7.1)	1.23 (16.7)	1.66 (1.6)
Polanyi	0.56 (6.6)	2.03 (9.0)	0.97 (17)	1.8 (9.5)
swell ratio (toluene)		2.7	1.15	1.32

^a Values in parentheses represent the percent standard deviation from the mean. Experimental values were used only when the capacity was available at $C_L/C_{L,sat}$ or $P_V/P_{V,sat} > 0.98$. The swell ratios in toluene are dimensionless.

analysis by a rather large margin. Perhaps the largest uncertainty in the estimated pore volumes is in knowledge of the actual polymer phase density (on a nonporous basis). While a value of 1.1 g/cm³ was used for the polymers, a sensitivity analysis showed a value of ~1.7 g/cm³ would be required to explain the large discrepancies in measured (nitrogen, 77 K) and estimated pore volumes. It seems highly unlikely that the polymer phase densities could reach such high values. Thus, absorption effects would appear to be present in the nitrogen sorption isotherms for the polymeric sorbents. The reported pore volumes and surface areas for the polymeric sorbents must therefore be considered "apparent".

Even more pronounced are the differences between the nitrogen pore volumes and the aqueous and vapor phase limiting sorption volumes. For FCMPs-CMEE-0.5%, the limiting sorption volume in the vapor phase is 2.85-fold the nitrogen pore volume. These differences are also reflected in Figure 10, where the sorption levels of nitrogen at 77 K were well below the aqueous and vapor phase VOC capacities. The discrepancy between VOC sorption capacities and nitrogen pore volumes is greatest for the polymeric sorbents with the highest swell ratios in toluene. This is additional clear evidence of absorption contributions to total sorption capacity.

For the polymeric sorbents, the values of $q_{v,0}$ obtained by Polanyi potential analysis generally show larger standard deviations when compared with experimental values. The shapes of the sorption isotherms at high activities created considerable difficulty for the regression analysis. The shape of the XUS 43493 caused the Polanyi analysis to underestimate $q_{v,0}$, while the custom-synthesized FCMPs and XAD4 $q_{v,0}$ values were typically overestimated. None of the experimental values shown in the table were extrapolated. All values were from measurements at activities > 0.98 . Thus, while the regression analysis in general shows a good fit to the data, the true values of $q_{v,0}$ are best represented by experimental measurement.

Vapor Phase Sorption Isotherm Dependence. In the preceding discussion, isotherms at various temperatures were presented in some of the comparisons. The acceptability of doing so is demonstrated in Figures 14 and 16. Figure 14 shows normalized vapor sorption isotherms for toluene by ACF400 at 30, 50, 60, and 90 °C. Toluene sorption by ACF400 does not depend on temperature when the results are normalized volumetrically. For comparison, Figure 15 demonstrates the marked temperature dependence when the same data are presented in the traditional manner with sorption on a mass basis versus pressure.

Figure 16 shows normalized vapor sorption isotherms for toluene by XUS 43493 at temperatures of 30 and 70

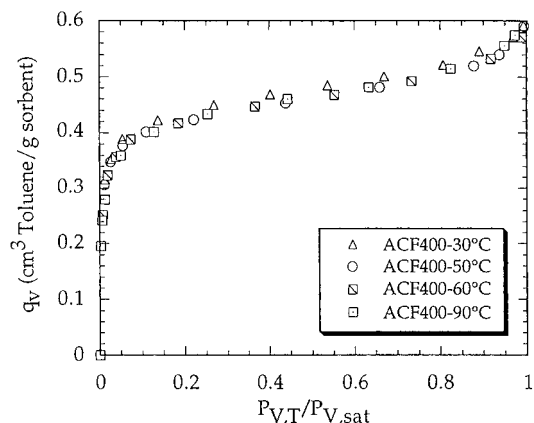


Figure 14. Vapor phase toluene normalized volumetric sorption isotherm results for ACF400 at 30–90 °C.

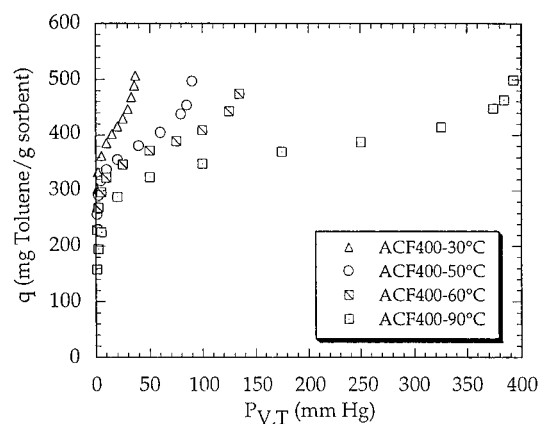


Figure 15. Vapor phase toluene sorption isotherm results for ACF400 at 30–90 °C.

°C and for XU 43502 at 30 °C. The figure shows toluene sorption by XUS 43493 does not depend on temperature when the results are presented in this manner. The figure also shows XUS 43493 and XU 43502 have nearly identical equilibrium capacities as stated in Dow's marketing literature (Dow Chemical Co., 1993). The only difference in capacity is observed at high vapor activities ($P_V/P_{V,sat} > 0.9$), where XUS 43493 shows a higher total capacity versus XU 43502. Figure 16 also shows isotherm data from Dow's marketing literature for XUS 43493, demonstrating reasonable agreement.

Normalized volumetric sorption isotherms were shown to be independent of temperature for several other sorbent/solute combinations. Thus, it was concluded that all sorbents used in the present study obeyed such a pattern. The lack of temperature dependence shown in Figure 14 is also observed when the data are presented on Polanyi potential plots.

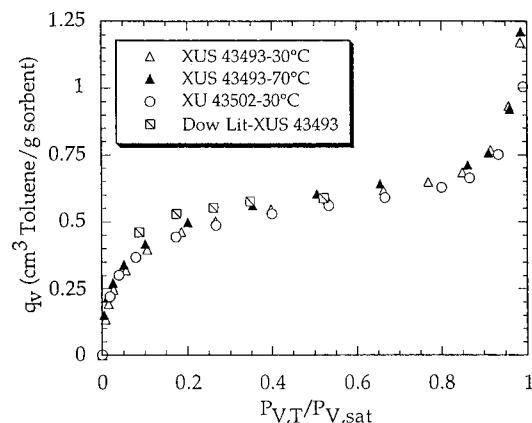


Figure 16. Vapor phase toluene sorption isotherm results for XUS 43493 at 30 and 70 °C, with comparison to XU 43502 and data from manufacturer's literature (Dow Chemical Co., 1993).

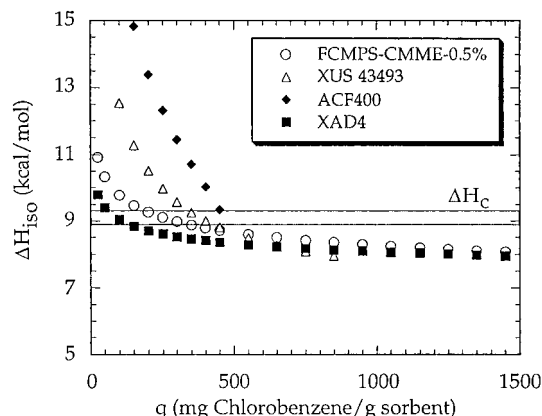


Figure 17. Vapor phase ΔH_{iso} for chlorobenzene sorption by ACF400, XAD4, XUS 43493, and FCMPS-CMME-0.5% predicted from Polanyi parameters.

Vapor Phase Heats of Sorption. The vapor phase isotherm temperature dependence allows calculation of isosteric heats of sorption. Also, since the Polanyi potential characteristic curves were found to be temperature independent, ΔH_{iso} values could be predicted (Dubinin, 1975). These predictions were made by first choosing a value of q . Then, q_v and $P_{V,sat}$ values were calculated for three temperatures (30, 50, and 70 °C) using the density versus temperature relationship and Antoine equation constants. Lastly, the equilibrium pressures (P) were calculated using the Polanyi parameters obtained from regression analysis. Good agreement was observed between ΔH_{iso} values calculated from experimental data and predicted from Polanyi potential parameters.

The relationship between ΔH_{iso} and q followed a similar pattern for each sorbent/sorbate combination. ΔH_{iso} was highest at low q values and decreased to a nearly constant value at high q values. Since ΔH_{iso} varies with respect to q , the sorption sites for all sorbents in the present study can be considered heterogeneous in nature. Figure 17 shows comparative plots of ΔH_{iso} versus q for ACF400, XUS 43493, FCMPS-CMME-0.5%, and XAD4 for vapor phase chlorobenzene sorption. Interestingly, ACF400 shows a markedly higher ΔH_{iso} at all q values. Adsorption is particularly strong at low coverages for ACF400 when compared with the polymeric sorbents. It is difficult to explain why the ΔH_{iso} values for XUS 43493 are higher than those for FCMPS-CMME-0.5% at low q values. Presumably, this is another difference attributable to the alternate synthesis route used for the commercial XUS

43493 versus the custom-synthesized polymers of the present study.

For vapor phase adsorption, the isosteric heat of adsorption typically exceeds or is equal to the heat of condensation and the "net" heat of sorption is given by:

$$\Delta H_{iso,net} = \Delta H_{iso} - \Delta H_c \quad (6)$$

where $\Delta H_{iso,net}$ and ΔH_c are the net isosteric heat of sorption and heat of condensation, respectively. $\Delta H_{iso,net}$ describes the heat effect of the interaction of the sorbate with the surface and should be exothermic.

For chlorobenzene, the values of ΔH_{iso} for each of the polymers in the present study extend below the range of the heat of condensation for higher values of q . This phenomenon would appear to be due to superimposed absorption heat effects. When absorption is significant, the net heat of sorption will also contain the energy required to form a "hole" in the polymer matrix for the absorbed penetrant molecule (Gou, 1989). Since this term generally involves energy input to the system (a negative term with the present sign convention), its magnitude could cause the net isosteric heat of sorption to be less than zero in some cases (i.e., a net endothermic process). As shown in Figure 17, this appears to be the case for the polymers used in the present study. This observation further supports the hypothesis that absorption contributes to the total sorption in the polymeric sorbents.

Practical Considerations. The above figures and tables are very useful tools for choosing the most effective sorbent for VOC removal applications. However, the calculated equilibrium capacity values in Table 5 do not include certain practical considerations: (1) vapor phase capacity losses due to humidity, (2) regeneration and capacity losses on reuse, and (3) incomplete capacity utilization due to sorption kinetics.

The capacities of ACF400 and XUS 43493 will clearly be affected by high-humidity vapor streams, while XAD resins and FCMPS synthesized by the techniques of the present study will be unaffected.

In industrial applications, the need for off-site reactivation of activated carbon is costly and inconvenient. On the other hand, activated carbon is initially much cheaper on a weight basis; thus, on-site, efficient regeneration must necessarily be a key economic lever for polymeric sorbents. The relative ease of regeneration of polymeric sorbents when compared with activated carbon can be surmised from Figure 17. Initial coverage on the ACF400 is remarkably strong ($\Delta H_{iso,net} > 6$ kcal/mol for low q), presenting a difficult challenge for complete sorbate removal. Conversely, the strength of sorption for polymers is comparatively much smaller, suggesting near complete desorption should be attainable.

Comparative ease of regeneration for FCMPS samples was further demonstrated with nitrogen gas in short, packed columns at adiabatic conditions (80 °C, equal time and flow). Samples of ACF400 and FCMPS-CMME-0.5% beads were preequilibrated with an aqueous solution of chlorobenzene (~450 mg/L) and dewatered. The results dramatically favor regeneration of the FCMPS polymer. For ACF400, the initial loading was 60% by weight, with a loading after regeneration of 23% by weight (61% removal). For FCMPS-CMME-0.5%, the initial loading of chlorobenzene was ~3.5-fold higher than that of ACF400 at 220%, with almost complete regeneration (3% by weight final loading, or 98+% removal). These results show that, at comparative conditions, FCMPS is significantly easier to regen-

erate than ACF400. The present study was clearly not exhaustive for regeneration conditions. As such, the authors do not mean to imply the above results represent the degrees of regeneration attainable in *absolute* levels.

Capacity on reuse was examined comparatively for ACF400, XUS 43493, XAD4, and FCMPs-CMME-0.5% in the quartz spring vapor sorption cell. After measurement of the sorption isotherm, full vacuum was applied until desorption was complete (1–24 h). The cycle was repeated up to four times. Each of the polymer sorbents in the present study shows the same capacity on repeated sorption/desorption cycles. ACF400 could not be completely desorbed for any of the sorbates in the present study at 30 °C by full vacuum alone. After applying full vacuum for up to 48 h, typically 10–25% of the original capacity of the ACF400 remained adsorbed. Such capacity losses are consistent with observed losses in practical applications (Kline et al., 1994). For ACF400, presumably higher temperatures would be required to facilitate more complete sorbate removal.

Qualitative observations of the vapor phase sorption kinetics indicated that ACF400, XAD4, XUS 43493, and FCMPs-CMME-0.5% all equilibrated at similar rates. The time required to reach equilibrium varied from 0.05 to 0.5 h for these materials, depending on the temperature, activity, and sorbate. The notable exceptions include the Dow FCMPs bead product, XU 43502, and some of the custom-synthesized FCMPs. The XU 43502 has nearly equal equilibrium capacity when compared with XUS 43493 but differs in the average bead size (~1.5 mm versus ~0.7 mm for XUS 43493). The time required to reach equilibrium for XU 43502 was in some cases several hours, particularly at low vapor activities. The XU 43502 beads are being marketed as low-pressure drop sorbents for packed columns, but potential users may confront significant kinetic issues based on the findings of the present study.

Certain synthesis conditions rendered low-porosity FCMPs samples which have very slow kinetic responses. As % DVB in the starting polymer is increased, porosity decreases and the kinetics of VOC sorption become much slower. The same effect is observed for samples synthesized at lower total cross-linking levels.

A limited attempt at *quantitative* kinetic studies of FCMPs-CMME-0.5% was complicated somewhat by the polydispersity of the spherical beads. The kinetics appear to be non-Fickian, so the calculated effective diffusion coefficients do not have strict physical meaning. However, the order of magnitude ($D_{\text{eff}} \sim 10^{-4}$ – 10^{-5} cm²/s) and the associated diffusional half-times ($t_{1/2} = 25$ – 140 s) suggest that kinetics should not markedly limit the utility of FCMPs.

Conclusions

The present study represents a thorough comparison of aqueous and vapor phase equilibrium data with liquid nitrogen characterization results. The custom-synthesized FCMPs were found to be particularly effective as VOC sorbents when compared with commercially available polymeric sorbents and activated carbon. The FCMPs have competitive VOC sorption capacities in dilute aqueous and vapor streams, are insensitive to humidity, and possess remarkably high ultimate sorption capacities (~2 mL/g). Data analysis demonstrated several interesting findings.

For the systems of the present study, the differences between nitrogen sorption at 77 K and aqueous and vapor phase VOC sorption are nicely illustrated by Polanyi potential plots. For ACF400, close agreement is observed between nitrogen adsorption at 77 K, and aqueous and vapor phase VOC sorption. The curve predicted by Polanyi analysis for vapor phase sorption at 100% relative humidity is in close agreement with the aqueous phase curve. For XUS 43493, the comparative plot represented more complicated behavior. At low activities, it is suggested that overlapping effects of competitive organic/water sorption and enhanced sorption due to the wetting procedure confound the comparison. For XAD4 and FCMPs-CMEE-0.5%, aqueous phase sorption is slightly higher than vapor phase sorption at all activities. This effect is likely attributable to the preswelling caused by the wetting procedure in aqueous phase studies.

While it is acknowledged that the Polanyi potential analysis lacks theoretical validity for the polymeric sorbents due to overlapping absorption contributions, excellent parameter fits were obtained. Nevertheless, the isotherm shapes of all sorbents made it difficult for the regression analysis to correctly predict $q_{v,0}$, the limiting sorption volume, with the same precision obtained through experimental measurement. The value of $q_{v,0}$ was found to be invariant with respect to the sorbate for a given sorbent in a given phase.

ACF400 showed the highest ΔH_{iso} for all values of q , implying complete regeneration is more difficult versus polymeric sorbents. For the polymeric sorbents, the curves of ΔH_{iso} versus q fell below the range of ΔH_c at high q values. This observation suggests the heat required to form a hole in the polymer matrix is appreciable, further supporting the conclusion that absorption contributes to total sorption in the polymeric sorbents.

Qualitative regeneration and kinetic studies demonstrated the FCMPs polymers should prove to be feasible in practical applications. It is recommended that these issues, as well as other practical considerations, be studied in further detail to facilitate wider acceptance of polymeric sorbents in industrial applications.

Acknowledgment

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Nomenclature

b = empirical constant
 C_L = equilibrium aqueous phase concentration, mg/L
 $C_{L,\text{sat}}$ = aqueous phase solubility, mg/L
 C_V = vapor phase concentration, ppmv
 P_V = equilibrium partial pressure, atm
 $P_{V,\text{sat}}$ = saturation vapor pressure, atm
 q = equilibrium sorption level, mg/g
 q_v = equilibrium volumetric sorption level, cm³/g
 $q_{v,0}$ = "limiting sorption volume", cm³/g
 R = universal gas constant, cal/mol K
 T = temperature, K

V_m = molar volume, cm³/mol
 V_w = molar volume of water, cm³/mol

Greek Symbols

ΔH_{iso} = vapor phase isosteric heat of sorption, kcal/mol
 $\Delta H_{iso,net}$ = "net" isosteric heat of sorption, kcal/mol
 ΔH_c = heat of condensation, kcal/mol
 ϵ = Polanyi adsorption potential, cal/mol
 ϵ' = "net" Polanyi potential of the organic sorbate, cal/mol
 ϵ_w = Polanyi adsorption potential of water vapor, cal/mol
 α = empirical constant, exponent for Polanyi characteristic curve

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