

Sorption of Organics from Aqueous Solution onto Polymeric Resins

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The uptake of phenol, toluene, chlorobenzene, and benzoic acid by several polymeric resins and activated carbon was investigated experimentally. Presentation of the sorption data in terms of the number of sorbed monolayers and fractional pore volume filled indicated that, for the polymeric resins, solute uptake cannot be viewed as only a surface adsorption phenomenon. It is suggested that the aqueous phase uptake of phenol, toluene, chlorobenzene, and benzoic acid by the polymeric resins is attributable, in part, to solute absorption. The present study also suggests that solute uptake is affected by the swelling of some of the polymeric resins in water.

Introduction

Increasing concern for public health and environmental quality has led to the establishment of limits on the acceptable environmental levels of specific pollutants. Consequently there has been a growing interest in developing and implementing various methods of removing specific organics from water. Although there are a number of methods for removing organics from aqueous systems such as aeration, biological degradation, oxidation, and adsorption, adsorption is often the preferred separation process since it can be used for removing a variety of organics from aqueous systems (McGuire et al., 1978; Suffet et al., 1988). Traditionally, activated carbon has been used as the choice adsorbent for water and wastewater treatment. Activated carbon is referred to as a "wide-spectrum" adsorbent because it can remove a wide variety of organics (Suffet, 1980). A great deal of literature already exists on equilibrium adsorption onto activated carbon, and a number of excellent sources for activated carbon adsorption data are available that contain individual isotherm parameters (Dobbs and Cohen, 1980; McGuire and Suffet, 1980; Speth and Miltner, 1990) and empirical correlations for a wide variety of organics, using parameters such as polarizability, total molecular surface area (TSA), and molecular connectivity (Nirmalakhandan and Speece, 1990; Belfort, 1984).

In recent years polymeric resins have been increasingly viewed as an alternative to activated carbon for the removal of specific organics from contaminated water. Early investigations demonstrated that, on a mass basis, polymers have a lower sorption capacity for most organics than activated carbon (Suffet et al., 1978; Weber and van Vliet, 1980). However, polymeric resins have been shown to selectively remove lower molecular weight organics (Suffet, 1980). The wide variations in functionality, surface area, and porosity available for polymeric resins present the possibility of customizing resins for the selective removal of specific organic solutes (Kunin, 1977; Cornel and Sontheimer, 1986). Also, regeneration of polymeric resins can easily be accomplished with a solvent (Grant and King 1990), while a high temperature and/or steam is needed for the regeneration of activated carbon (Cairo et al., 1982).

The majority of the studies on the use of polymeric resins in water treatment have relied on the same theories and models which have been used to quantify activated

carbon adsorption data (Itaya, 1984; Weber and van Vliet, 1981a,b; Dinopoulou, 1985; Paleos, 1969). It is important to note that the removal of organics by activated carbon is regarded as a surface phenomenon (McGuire and Suffet, 1978; Weber and van Vliet, 1980), and thus adsorption capacity scales with the surface area available for adsorption. In contrast, a number of studies with polymeric resins have suggested that solute uptake by polymeric resins is a more complex phenomenon. For example, the study of Neely (1980) revealed that the adsorption capacities of Rohm & Haas carbonaceous resins XE-340, XE-347, and XE-348 and the polymeric Rohm & Haas resins XE-225A, XAD-1, XAD-2, and XAD-4 for chloroform did not scale with the available surface areas of the resins. In a later study, Cornel and Sontheimer (1986) also found that the uptake capacities of polystyrene-divinylbenzene resins for trichloroethylene did not correlate with the resins' surface areas. More recently Garcia and King (1989) demonstrated that total uptake (determined by weight difference after centrifugation) of aqueous acetic acid solutions by cross-linked resins of poly-(methylpyridine) increased with increasing acetic acid concentration, and the increase was attributed to the ability of the polymeric resin to swell. In all of the above three cases, part of the uptake was attributed to swelling, or absorption into the polymer matrix. It is also worth noting that some polymeric resins are not completely wet by water (Rixey and King, 1988; Rixey, 1987). Thus, for nonwetting resins, volatile organic solutes can adsorb from the gas phase (trapped within the resin pores) upon volatilization, or adsorb onto the resin surface directly from the water phase (Rixey and King, 1988; Rixey, 1987). Rixey and King (1988) have suggested that, for mixtures, simultaneous uptake from the gas and liquid phases can allow for improved selectivity when there is a significant difference in the vapor pressure of the solutes.

Solute removal by activated carbon is usually quantified via theoretical or empirical isotherms. For example, theoretical models such as the Langmuir model (Langmuir, 1918), the Brunauer-Emmett-Teller multilayer isotherm (1938), Everett's phase exchange model (1964, 1984), the vacancy solution model of Suwanayuen and Danner (1980), and the heterogeneous surface isotherm (Jaroniec et al., 1981) postulate the existence of a two-dimensional adsorbed phase. Another theoretical view is that adsorption consists of pore-volume filling (Polanyi, 1932; Dubinin, 1967). However, if absorption or swelling of the polymer matrix occurs, neither theoretical view is an accurate representation of solute uptake by polymeric resins.

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Table I. Physical Properties of Solutes

solute	molecular weight	density, g/cm ³ (temp, °C)	aqueous solubility, mg/L (temp, °C)
phenol	94.11 ^a	1.0576 (41) ^b	87 000 (25) ^c
toluene	92.15 ^a	0.8699 (20) ^a	550 (25) ^f
benzoic acid	122.13 ^a	1.0749 (130) ^a	3100 (22) ^d
chlorobenzene	112.56 ^a	1.1056 (20) ^a	476 (25) ^e

^a Weast (1985). ^b Thurman (1982). ^c Howard (1989). ^d Williams (1978). ^e Horvath (1985). ^f Hefter (1989).

It is well accepted that, with activated carbon, solute uptake rarely exceeds a monolayer. In contrast, several studies have suggested that the removal of organics by polymeric resins involves mechanisms different from simple surface adsorption. For example, Neely (1980) noted a correlation between swelling in pure chloroform and the aqueous phase sorption capacity for chloroform for the Rohm & Haas resins XAD-1, XAD-2, and XAD-4. In a later study Cornel and Sontheimer (1986) investigated the sorption of organics by a series of custom-made polystyrene-divinylbenzene resins. Cornel and Sontheimer suggested that solute uptake was due to three mechanisms: (1) adsorption on the surface of permanent pores; (2) uptake in latent pores where the volume of latent pores is defined as the difference between the volume uptake of a precipitator and the volume of water uptake; and (3) uptake in the gel regions defined as the volume uptake by solvating organics where Cornel and Sontheimer defined a solvent as an organic which has a solubility parameter close that of polystyrene and will dissolve polystyrene chains, and a precipitator is an organic which will not dissolve the polystyrene chains although it will dissolve the styrene monomer. More recently, Garcia and King (1989) investigated the uptake of acetic acid by a series of basic resins which they classified as gel resins or macroreticular resins. Garcia and King concluded that the poly(vinylpyridine) resins they investigated, most of which were gel resins, swell significantly, but for the macroreticular resins, such as XAD-12, uptake is primarily due to pore filling.

In the present study, we extended previous studies on the sorption of organics by polymeric resins, by providing new solute equilibrium sorption data, to demonstrate that solute uptake by commercially available macroreticular resins can involve both absorption and adsorption. Solute uptake results are presented for the aqueous sorption of four substituted benzene compounds of widely varying aqueous solubility—phenol, toluene, benzoic acid, and chlorobenzene—on both polar and nonpolar polymeric resins covering a wide range of specific surface area and pore volume, and activated carbon. The physical properties of the four compounds are summarized in Table I. The presented data cover a solute concentration range of 70–80% of the saturation concentration for the solutes studied which is a significantly higher concentration range than commonly reported for solute adsorption studies.

Experimental Section

The aqueous-phase sorption of phenol, toluene, chlorobenzene, and benzoic acid onto several polymeric resins—Reillex-425, XAD-8, XAD-4, XAD-16, and XAD-12—was obtained using the “bottle-point” method for which each bottle yields one datum of amount adsorbed, q (mmol/g), in equilibrium with a bulk concentration, C_{eq} (mmol/L). The method involves adding a known quantity of resin and a known volume of solution to glass vials and agitating them for a sufficient time period to establish adsorption equilibrium. Concentrations were measured

Table II. Properties of Polymeric Resins and Activated Carbon: Adsorbent Properties/Results of Nitrogen BET Analysis

adsorbent	total area, m ² /g		pore volume, cm ³ /g	average pore radius, Å
	this study	manufacturer		
F-400	1075	1050–1200 ^b	0.652	14.7
XAD-8	126	140 ^a	0.633	98.0
XAD-16	806	860 ^b	1.404	41.0
XAD-4	773	760 ^a	0.974	23.2
	870 ^f		1.184 ^f	
Reillex-425	89	90	0.67	156
	46 ^e		0.46 ^e	
XAD-12	21	22 ^d	0.28	240

^a Weber and Van Vliet (1981). ^b McGuire and Suffet (1978). ^c Reillex Report 2 (1987). ^d Garcia and King (1989). ^e Results for batch used for the chlorobenzene experiments. ^f Results for batch used for the phenol experiments.

in a UV spectrophotometer, and the amount sorbed was calculated from a mass balance on the solute in the aqueous phase.

Materials. Phenol and chlorobenzene were obtained from Fisher Scientific (Fair Lawn, NJ), toluene was obtained from J.T. Baker Co. (Phillipsburg, NJ), and benzoic acid was obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI). All three compounds were ACS reagent grade, and were used without further purification. *Optima* grade *n*-hexane, used to extract toluene from water for the initial ultraviolet calibration, was obtained from Fisher. Methanol, acetonitrile, and acetone, used in resin preparation and cleaning, were ACS reagent grade, and were also obtained from Fisher.

Different commercial resins were used in the adsorption studies. Reillex-425, which is a poly(vinylpyridine) matrix cross-linked with divinylbenzene, was obtained from Reilley Industries, Inc. (Indianapolis, IN). A cross-linked polyacrylate resin (XAD-8) and a resin made of a nitro-polystyrene matrix cross-linked with divinylbenzene (XAD-12) were obtained from Rohm & Haas, Inc. A polymeric resin composed of polystyrene-divinylbenzene (XAD-4) and one composed of only divinylbenzene (XAD-16) were also obtained from Rohm & Haas. Finally, activated carbon (F-400) was obtained from Calgon Corp. (Pittsburgh, PA).

Resin Characterization. Surface area and pore size analyses were done via nitrogen adsorption in an Autosorb-1 sorption system (Quantachrome, Corp., Syosset, NY), and the results are presented in Table II. The samples used for analysis were taken from the same sorbent batch used in the sorption experiments without further modification. The total nitrogen BET (Brunauer-Emmett-Teller) surface area was calculated from measurements of the volume of adsorbed nitrogen as a function of relative pressure, p/p_{sat} (Gregg and Sing, 1981; Lowell and Shields, 1984). The total pore volume and average pore radius were determined from the same nitrogen isotherm (Lowell and Shields, 1984). For the activated carbon, which is a microporous resin with the majority of the surface area in pores 20 Å in radius and smaller, the total BET surface area was determined from the nitrogen adsorption data obtained from the relative pressure range $0.0 < p/p_{sat} < 0.15$ (Lowell and Shields, 1984). For the polymeric resins, the BET surface area was determined from the relative pressure range for mesoporous materials ($20 \text{ Å} < r_p < 500 \text{ Å}$) (Lowell and Shields, 1984).

The swelling ratio, $R = V_{solvent}/V_{dry}$, is defined as the ratio of the volume of the resin immersed in a solvent to

Table III. Swelling Ratios of Polymeric Resins

solvent	swelling ratio, $R = V_{\text{solvent}}/V_{\text{dry}}$				
	XAD-12	Reillex-425	XAD-4	XAD-8	XAD-16
water	1.17	1.16	1.02	1.14	1.02
acetone	1.25	1.24	1.17	1.21	
benzoic acid-acetone (18.57 mol %)	1.46	1.40	1.30	1.31	
phenol (88 wt %)	1.64	1.52	1.18	1.20	1.22
toluene	1.00	1.17	1.17	1.22	1.21
chlorobenzene	1.20	1.17	1.27		1.40

its volume in the dry state, determined at room temperature (22°C). In this study the swelling ratio, R , was determined by measuring the height of a packed bed of the resin in the dry state and when an excess of solvent was added. Swelling ratios obtained in this work are presented in Table III. The above method was found to be satisfactory as verified by using optical microscopy to determine the change in the resin's diameter upon swelling. For example, for Reillex-425, the volume change was determined via optical microscopy to be 14.8%, compared to a volume change of 16.5% obtained by measuring the change in the height of the resin bed in a graduated cylinder. The above results are in agreement with the degree of swelling of 12-16% reported by the manufacturer for Reillex-425 (Reilley Industries, Inc., 1987).

Resin Preparation. The resin, Reillex-425, was refluxed in methanol for 4 h, and then refluxed in acetonitrile for 4 h after air-drying. Subsequently, the Reillex-425 resin was thoroughly washed with distilled water. The Reillex-425 resin was allowed to air dry, and then placed in a 105-110 °C oven for 2-4 h prior to storage in a desiccator. Sorption experiments using Reillex-425 which had been dried at 110 °C and Reillex-425 which had not been dried and was stored wet demonstrated no effect of the resin pretreatment on sorption capacity.

Resin XAD-12 was cleaned by rinsing with acetone (10 L/L of dry resin), and then thoroughly rinsed with distilled water as suggested by the manufacturer. XAD-12 resin was stored wet in 0.05 M NaOH to prevent biological degradation (Garcia and King, 1989). The XAD-4 and XAD-16 resins were both refluxed in methanol for 10 h, and then rinsed with distilled water. After air-drying, XAD-4 was dried in a vacuum oven at 105 °C, and XAD-16 was dried in an oven at 80 °C, and then stored in a desiccator. Analogous to the case for Reillex-425, sorption experiments comparing dried and never dried (stored wet) XAD-4 and XAD-16 resins demonstrated no difference in sorption capacity.

Activated carbon F-400 was ground and sieved, and the 40/50 U.S. Sieve fraction (300-425- μ m equivalent diameter) was used for the sorption experiments. The activated carbon was washed with 0.2 M HCl according to the manufacturer's recommended procedure (Calgon Corp., 1986) and rinsed thoroughly with distilled water. The pH of the effluent was measured to ensure that all of the acid was removed from the carbon. The carbon was then dried in a vacuum oven at 105 °C 12 h before it was cooled and stored in a desiccator.

The cross-linked polymethacrylate resin, XAD-8, was prepared according to the procedure of Ram and Morris (1982) and Thurman *et al.* (1978) to ensure removal of contaminants and byproducts from the manufacturing process. A 50-g batch of XAD-8 was washed sequentially in a Soxhlet extraction column with three solvents, 24 h each: methanol, acetonitrile, and diethyl ether. The resin was then allowed to dry at ambient temperature in the fume hood for 1 day followed by vacuum drying for 1 day

at 80 °C. Analysis of blanks using XAD-8 indicated that this procedure was adequate for removal of any possible contaminants from the resin. The clean, dry resin was stored in an air-tight jar out of direct sunlight.

Prior to use in the sorption experiments Reillex-425, XAD-4, and XAD-16 resins were wet with acetone or methanol (200 mL/g) and thoroughly rinsed with distilled water (2.5 or more L/g of resin) until the ultraviolet spectrum of the rinse water showed no absorbance in the ultraviolet spectrophotometer greater than 0.001 absorbance unit for the wavelength range 190-500 nm. For XAD-12 the resin was thoroughly rinsed with distilled water to remove the NaOH solution, and the pH of the effluent was checked to ensure that all of the aqueous NaOH had been removed.

Sorption Experiments. The sorption experiments consisted of placing a carefully measured quantity of resin in a known volume of aqueous solution of the solute in a 14- or 18-mL vial sealed with Teflon-lined screw caps. Saturated aqueous solutions or appropriate dilutions of the saturated stock solution were added to the vial, and the volume was recorded. For each sorption experiment a blank, consisting of the resin and water, and a control, consisting of the stock solution, were also prepared. The vials were rotated on a 3-ft-long rack that provided end-over-end agitation at a rate of 15 rpm. The sorption experiments were carried out for 7 days at room temperature (22 °C). Each set of sorption experiments was conducted over a period of 7 days which was determined to be sufficient to reach sorption equilibrium (Gusler, 1993).

To determine the amount of water retained by the resins, the procedure of Rixey (1987) and Grant (1988) was used. A sample of the wet resin from the same batch used for the sorption experiments was weighed, placed in a beaker, allowed to air dry for at least 4 h, and then oven-dried and reweighed repeatedly until the sample reached a constant weight. The water loss was used to calculate the mass fraction of water in the prewetted sample. The percent mass of water retained by the polymeric resins ranged from about 50% to 70%.

Analysis. Aqueous phenol samples, benzoic acid samples, chlorobenzene samples, and toluene samples were analyzed directly by ultraviolet spectroscopy using a Hewlett-Packard 8452a diode array spectrophotometer. The values obtained for the extinction coefficients are 376.2 (L/cm)/mg at 261 nm and 477.9 (L/cm)/mg at 267 nm for toluene, 167.7 (L/cm)/mg at 270 nm for benzoic acid, 914.8 (L/cm)/mg at 257 nm, 770.3 (L/cm)/mg at 263 nm and 1124.2 (L/cm)/mg at 270 nm for chlorobenzene, and 71.13 (L/cm)/mg at 268 nm for phenol.

The sorption capacity, Q (mmol/g), was determined from a solute mass balance on the sorption vials given the initial bulk solution concentration and the final bulk solution concentration when equilibrium was reached:

$$Q = \frac{(C_0 - C_{\text{eq}})V}{m} \quad (1)$$

in which C_0 is the initial concentration (mmol/L) before being contacted with the resin, C_{eq} is the final equilibrium concentration (mmol/L), V is the volume of solution (L), m is the mass of the resin (g), and Q is the amount sorbed (mmol/g).

Solute uptake was also expressed in terms of the number of equivalent surface monolayers (θ) and as the fraction of the pore volume filled (F_p). The above two measures of solute uptake were defined as

$$\theta = \frac{0.001Q}{MW} N_A \frac{\sigma}{A_s} \quad (2)$$

where N_A is Avogadro's number, σ is the surface area of an adsorbed molecule, MW is the molecular weight, Q is the amount sorbed (mg/g), and A_s is the specific surface area of the sorbent determined from BET analysis. The surface area occupied by an adsorbed molecule, σ , was estimated from the following correlation given by McClellan and Harnsberger (1967):

$$\sigma = 1.091([MW/(\rho N_A)]^{2/3}) \quad \text{cm}^2/\text{molecule} \quad (3)$$

where ρ is the density of the adsorbate, (g/cm³) and the liquid density at the melting point was used for phenol and benzoic acid. The densities used are given in Table I. The values of σ obtained from eq 3 were 34.3 Å² for toluene, 30.5 Å² for phenol, 33.3 Å² for chlorobenzene, and 35.8 Å² for benzoic acid. Grant (1988) and Farrier *et al.* (1979) reported values of 45 and 28 Å² for the molecular area of phenol, respectively, while Farrier *et al.* (1979) reported using a molecular area of 45 Å² for benzoic acid. Therefore, the present estimates of the area occupied by the molecule are at the low end of the range referenced in the literature, and therefore will result in a conservative estimate of the number of equivalent monolayers of solute uptake.

The fraction of the pore volume filled, F_p , was determined for each system using the following formula:

$$F_p = \frac{[C_0 V - C_{eq}(V - MV_p)] \times 10^{-6}}{V_p \rho} \quad (4)$$

where F_p represents the fraction of the pore that is filled at equilibrium, V is the volume (mL) of solution added to the sorption vial, V_p is the specific pore volume of the sorbent (cm³/g or mL/g), C_0 and C_{eq} are the initial and equilibrium concentrations (mg/L), respectively, M is the mass of the resin (g), and ρ is the density of the solute (g/cm³). For benzoic acid and phenol which are solids at room temperature, the liquid density at the melting point was used. Finally, the specific pore volume of the sorbent was determined from the nitrogen adsorption experiment.

Results and Discussion

Sorption isotherms were obtained for the uptake of toluene, benzoic acid, chlorobenzene, and phenol by the polymeric Reillex-425, XAD-4, XAD-12, and XAD-16 resins and activated carbon (F-400), in addition to phenol sorption by the polymeric XAD-8 resin. The sorption isotherms are plotted in terms of the number of equivalent monolayers and the equivalent fraction of occupied pore volume instead of the traditional amount sorbed expressed in milligrams per gram or millimoles per gram. The above presentation of the data was selected in order to clearly demonstrate the deviation of solute uptake by polymeric resins from the normally accepted mechanism of surface adsorption. It is worth noting that most adsorption theories for liquid phase adsorption are based on a solute uptake limit of one monolayer or one pore volume. Therefore, the applicability of adsorption theories can be determined by plotting the data in terms of fractional pore volume occupied by the solute, and number of equivalent monolayers. The presentation of the sorption isotherms in terms of equivalent monolayers can also be more revealing when multiple adsorbed layers are present. Furthermore, previous work by Browne and Cohen (1990) demonstrated that when the sorption capacity is expressed

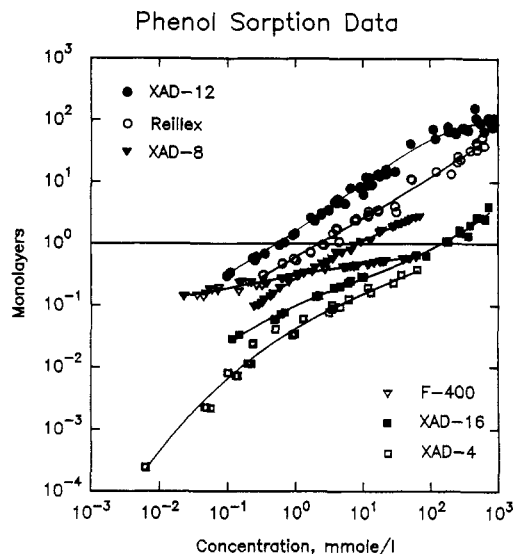


Figure 1. Phenol sorption data for XAD-4, XAD-8, XAD-12, XAD-16, Reillex-425, and F-400 expressed in terms of the number of monolayers.

on a surface area basis, one can more easily assess solute-sorbent affinity.

Phenol Sorption. Results for phenol sorption onto activated carbon and the polymeric resins in terms of monolayers is shown in Figure 1. For the hydrophilic resins, XAD-8, XAD-12, and Reillex-425, phenol uptake far exceeded a monolayer reaching 50 monolayers for Reillex-425 at a concentration of 615 mmol/L, and 75 monolayers for XAD-12 at a concentration of 850 mmol/L. In contrast, for the hydrophobic resin XAD-4 and for activated carbon F-400, phenol uptake did not exceed a monolayer. The N=O group of XAD-12, the pyridine group of Reillex-425, and the ester linkages of XAD-8 provide sites for hydrogen-bonding which explains the higher affinity of phenol for these resins relative to XAD-4 or F-400. The hydrogen-bonding capability of XAD-7, which is structurally similar to XAD-8, has been thoroughly discussed by Payne and Ninomiya (1990) and Maity *et al.* (1991), who investigated the uptake of polar compounds such as phenols and indoles onto XAD-4 and XAD-7. The ability of poly(vinylpyridine) resin (Reillex-425) to hydrogen bond was also noted by Chanda *et al.* (1985a), who investigated the uptake of phenols and carboxylic acids by poly(vinylpyridine), and in an earlier study by Kawabata and Ohira (1979), who investigated the uptake of phenol by poly(vinylpyridine) resins. It is also worth noting that Garcia and King (1989), who investigated the uptake of acetic acid by a series of basic polymeric resins including XAD-12 and some poly(vinylpyridine) gel resins, modeled the uptake as an acid-base exchange reaction. Finally, XAD-16, which is composed of divinylbenzene, is primarily hydrophobic, but XAD-16 sorption data lies between the hydrophobic resins and the hydrophilic resins. The above trend is consistent with the observation that, in a solution of 88 wt % phenol, XAD-16 swelled by 22% while XAD-4 swelled by 18% (Table III).

Toluene Sorption. Toluene sorption capacity, in terms of monolayers, was highest for the two polar resins, XAD-12 and Reillex-425, exceeding a monolayer coverage at concentrations above about 1 mmol/L, and reaching a surface coverage of three monolayers for Reillex-425 and seven monolayers for XAD-12 at about 4 mmol/L as shown in Figure 2. In contrast, the sorption capacity of activated carbon, F-400, for toluene was less than a monolayer. Toluene sorption capacity for the hydrophobic resins,

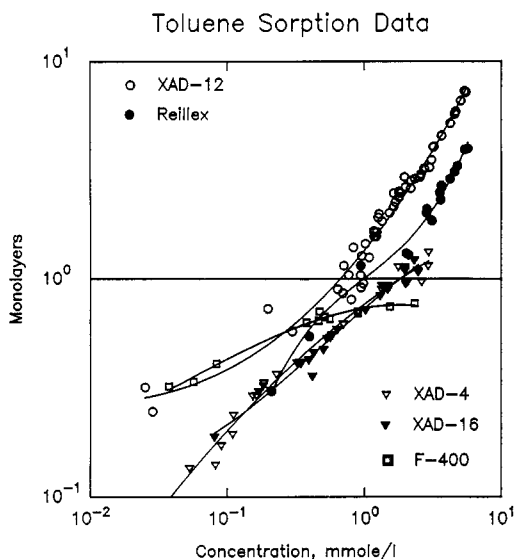


Figure 2. Toluene sorption data for XAD-4, XAD-12, XAD-16, Reillex-425, and F-400 expressed in terms of the number of monolayers.

XAD-4 and XAD-16, was significantly less than for the polar resins, XAD-12 and Reillex-425 and reached a monolayer coverage at concentrations of 2 mmol/L for both resins. The higher affinity of toluene for the polar resins is surprising, but it can be rationalized on the basis of ability of the resins to swell in water. As shown in Table III, Reillex-425 swelled by 17% in toluene relative to 17% and 21% swelling of the hydrophobic XAD-4 and XAD-16 resins, respectively. Thus, it is reasonable to conclude that the affinity of toluene for Reillex-425 is approximately equal to the affinity for the XAD-4 and XAD-16 resins. The striking difference, however, is that Reillex-425 exhibited about 16% swelling in water relative to almost no swelling (< 2%) for the XAD-4 and XAD-16 resins, respectively. Thus, it is postulated that the swelling of Reillex-425 by water expands the resin's pore structure, thereby making more of the resin's pores accessible to toluene. Although the polar resin XAD-12 did not swell in toluene, it did swell in water by about 17%. Thus, it is also plausible that the high toluene sorption capacity of XAD-12 is due to an increase in the accessible pore volume due to the resin swelling in water. The above assertion is supported by the study of Chanda *et al.* (1985) who attributed the higher uptake of phenol by poly(vinylpyridine) relative to polybenzimidazole to the greater ability of the poly(vinylpyridine) resin to swell in water.

Benzoic Acid Sorption. Benzoic acid sorption also showed the same qualitative trends that were observed for toluene and phenol, as illustrated in Figure 3. The highest solute uptake, in terms of monolayers, occurred for XAD-12 and Reillex-425, which reached 30 and 6 monolayers, respectively, at a concentration level of 8 and 13 mmol/L, respectively. The hydrophobic sorbents, XAD-4 and XAD-16, and activated carbon F-400, sorbed less than the equivalent of a monolayer for much of the concentration range, with sorption capacity approaching or slightly exceeding a monolayer above a concentration of about 25 mmol/L. For the polar resins, XAD-12 and Reillex-425, the high affinity of benzoic acid for these resins is likely to be due to a hydrogen-bonding mechanism, similar to the case for phenol. Both Reillex-425 and XAD-12 contain basic functional groups, the pyridine for Reillex-425 and the N=O for XAD-12, and therefore an acid-

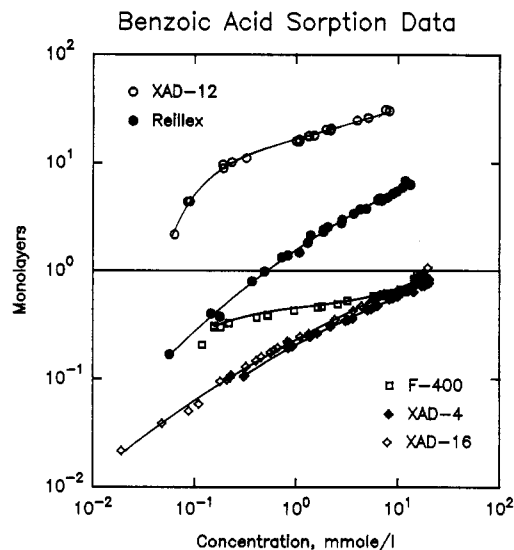


Figure 3. Benzoic acid sorption data for XAD-4, XAD-12, XAD-16, Reillex-425, and F-400 expressed in terms of the number of monolayers.

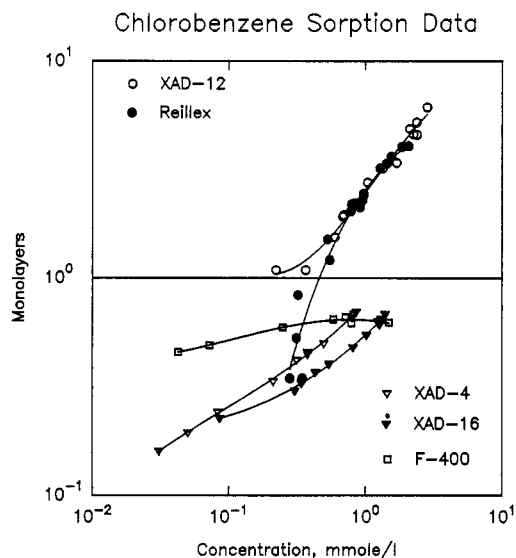


Figure 4. Chlorobenzene sorption data for XAD-4, XAD-12, XAD-16, Reillex-425, and F-400 expressed in terms of the number of monolayers.

base interaction may be responsible for the high uptake of benzoic acid by these two resins.

Chlorobenzene Sorption. Chlorobenzene sorption capacity, in terms of monolayers, followed the same general trend observed for toluene with the two polar resins, XAD-12 and Reillex-425, with solute uptake reaching about seven monolayers. In contrast, chlorobenzene uptake by XAD-4, XAD-16, and F-400 did not exceed a monolayer as shown in Figure 4. As was the case for toluene, the swelling of the hydrophobic resins XAD-4 and XAD-16, in chlorobenzene was higher than for the hydrophilic resins (Table III). The unexpected affinity of chlorobenzene for the hydrophilic XAD-12 and Reillex-425 resins is believed to be linked to the swelling of these resins in water which could possibly increase the pore volume which is accessible to the solute.

Adsorption and/or Absorption? Overall the sorption results suggest a fundamental difference in uptake mechanisms for the polymeric resins and activated carbon. Although activated carbon has a very strong adsorption bond, as indicated by the difficulty in regenerating

activated carbon (Grant and King, 1990) and its higher heat of adsorption for many organic solutes (Costa *et al.*, 1988) relative to polymeric resins (Paleos, 1969; Gustafson *et al.*, 1968; Itaya *et al.*, 1984), solute uptake only barely exceeded a monolayer. In contrast, the hydrophilic polymeric resins, XAD-12 and Reillex-425, demonstrated uptakes far exceeding a monolayer, and for the case of phenol the sorption capacity reached 75 and 50 monolayers, respectively. It is unrealistic to assume that the formation of multiple layers on the surface can reach 50 or more layers, because it is unlikely for solute-surface interactions to extend to a range beyond a few monolayers. The London or dispersion interaction potential which decreases as separation distance to the sixth power (Hiemenz, 1986) and even an ion-ion interaction potential which decreases as separation distance to the first power could not be expected to account for the uptake of 50 or more monolayers. The assumption that only surface interactions account for solute uptake is especially unlikely when the sorbing species can penetrate the cross-linked resin. In addition, if solute uptake is assumed to be entirely due to adsorption, then if multilayers are present, one should expect to see multiple plateaus in the sorption isotherm. However, for the sorption isotherms obtained in this study there are no plateaus, nor is there a "limiting adsorption" which is often assumed in adsorption theories (Jossens *et al.*, 1978; Toth, 1981; Suwanayuen and Danner, 1980). The lack of any plateaus and the large number of monolayers which would have to exist if only adsorption occurs suggest that solute uptake by polymeric resins is not due entirely to surface adsorption. Furthermore, if solute uptake was due to adsorption, then solute uptake should scale with surface area as noted by Browne and Cohen (1990) in their study of TCE and CHCl_3 adsorption. A similar conclusion was reached in the earlier study of Cornel and Sontheimer (1986) who noted that the adsorption of *p*-nitrophenol onto five different cross-linked high surface area ($>100 \text{ m}^2/\text{g}$) polystyrene-divinylbenzene resins correlated with the surface area. In contrast, it is emphasized that in the present work solute uptake did not correlate with surface area. The lack of correlation between the amount of solute adsorbed and surface area was also reported in earlier studies by Neely (1980) for the uptake of chloroform onto XAD-2, XAD-4, and XE-340, and by Cornel and Sontheimer (1986) for the uptake of trichloroethylene by polystyrene-divinylbenzene resins. In both of the above cases, the authors attributed the failure of solute uptake to correlate with surface area to absorption into the polymer matrix. Although the hydrogen-bonding ability of the resins such as Reillex-425 and XAD-12 has been noted (Kawabata and Ohira, 1979; Maity *et al.*, 1991; Garcia and King, 1989; Chanda *et al.*, 1985a), the swelling of these resins by both the solute and water is also important to consider since the swelling of the resin increases the number of hydrogen-bonding sites which are accessible to the solute. This assertion is supported by the study of Chanda *et al.* (1985) who attributed higher uptake of phenols and carboxylic acids by poly(vinylpyridine) resin relative to poly(benzimidazole) resin, which is a stronger Lewis base than the poly(vinylpyridine) resin, to the greater ability of poly(vinylpyridine) to swell.

An alternative model to surface adsorption is offered by theories that postulate that sorption occurs by condensation into the pores. The Polanyi theory is one such popular theory that assumes that the solute "condenses" into the pore volume (Polanyi, 1932). Thus, by expressing the mass sorbed by the resins as equivalent pore volumes, one can determine the likelihood of sorption occurring via

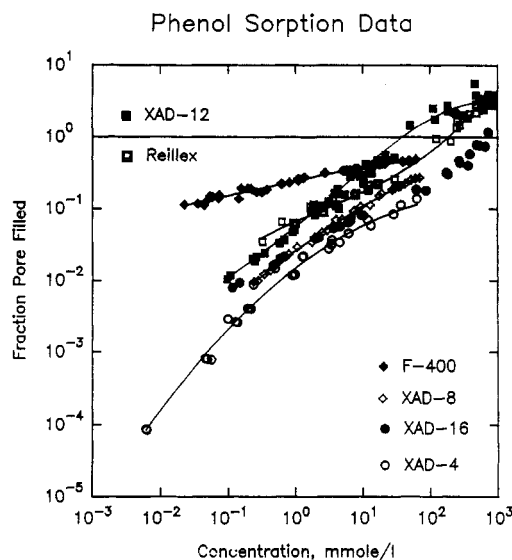


Figure 5. Phenol sorption data for XAD-4, XAD-8, XAD-12, XAD-16, Reillex-425, and F-400 expressed in terms of the fraction of the pore volume filled.

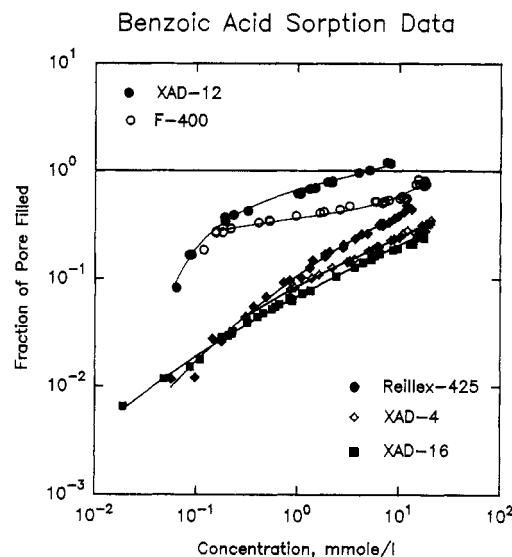


Figure 6. Benzoic acid sorption data for XAD-4, XAD-12, XAD-16, Reillex-425, and F-400 expressed in terms of the fraction of the pore volume filled.

pore filling. Sorption in excess of the total pore volume would suggest penetration into the resin matrix. As depicted in Figures 5 and 6, the sorption capacity of XAD-12 for both phenol and benzoic acid exceeded one pore volume, with the sorption capacity reaching approximately 2.0 and 1.2 pore volumes, respectively, at concentrations of 850 and 8 mmol/L, respectively. Also, phenol uptake by Reillex-425 exceeded the pore volume, reaching approximately 2.5 at a concentration of 625 mmol/L as seen in Figure 5. The significant solute uptake in excess of the pore volume of the resins is most likely to be due to absorption into the polymer matrix. It is interesting to note that the highest solute uptakes for phenol and benzoic acid, expressed as the number of monolayers or pore volumes, were obtained for Reillex-425 and XAD-12 which had surface areas of 90 and 21 m^2/g , respectively. In contrast, solute uptake for phenol and benzoic acid barely exceeded a monolayer (with the exception of the phenol/XAD-16 system) for the high surface area resins, XAD-4 and XAD-16, with surface areas of 770 and 806 m^2/g , respectively. These results are consistent with the study of Cornel and Sontheimer (1986) who also suggested, on

the basis of *p*-nitrophenol uptake by polystyrene-divinylbenzene resins, that resin swelling due to solute uptake is more apparent with the low surface area polymeric resins. Finally, it is noted that for toluene and chlorobenzene, the fraction of pore volume filled did not exceed unity for any of the resins studied. This result is consistent with the fact that toluene and chlorobenzene should have a higher affinity for the nonpolar resins, XAD-4 and XAD-16, which have high specific surface areas, relative to the polar resins, XAD-12 and Reillex-425, which are low surface area resins.

A quantitative analysis of pore filling as a plausible solute uptake mechanism is offered by the analysis of the sorption data in terms of the Polanyi isotherm. Polanyi (1932) suggested that a "characteristic curve", for a given adsorbent, could be obtained for the adsorption of similar compounds onto the adsorbent by plotting the natural log of the adsorbed volume of solute against its "adsorption potential" given as $\epsilon = RT \ln(C_s/C)$, where C_s is the solute solubility concentration (Hofer and Manes, 1969), C is the solute equilibrium concentration, R is the gas constant, and T is the temperature. The characteristic curve can be obtained by fitting the data to the equation (Manes and Hofer, 1969; Hacskeylo and Le Van, 1985)

$$\ln W = \ln W_0 - B(\epsilon/V)^n \quad (5)$$

in which W_0 is the limiting adsorption volume, W is the volume of adsorbed solute, B is the affinity coefficient (Manes and Hofer, 1969), ϵ is the adsorption potential given by $RT \ln(C_s/C)$, V is the molar volume of the solute, and n is an empirical constant, usually taken to be unity for the Polanyi theory. The Polanyi theory has been extensively discussed in the literature in relation to its applicability to liquid-phase adsorption of organic solutes onto activated carbon (e.g., Wang *et al.*, 1981; Manes and Hofer, 1969; Manes, 1980, and references therein) and to a limited extent for polymeric resins (Itaya *et al.*, 1984; Hasanain and Hines, 1981).

In the present analysis the Polanyi curve fits were obtained for the sorption of toluene, phenol, chlorobenzene, and benzoic acid, onto the five adsorbents Reillex-425, XAD-4, XAD-12, XAD-16, and F-400 and for the phenol/XAD-8 system. The parameters B , and W_0 and the correlation coefficient are shown in Table IV. The limiting adsorption volume, W_0 , for F-400 was found to be nearly equal to the BET pore volume (obtained from nitrogen adsorption) for toluene, and lower by 7.6% and 10.6% for benzoic acid and phenol, respectively, with the exception of chlorobenzene for which a W_0 value 47% lower than the BET pore volume was obtained. The above results are in general agreement with the findings of Manes and Woheleber (1971). For the polymeric resins, the limiting adsorption volume varies significantly with the solute, and for the case of phenol and benzoic acid W_0 was also found to exceed the pore volume, indicating the Polanyi isotherm (eq 5) does not adequately describe the sorption mechanism. In particular, the variation of W_0 with the solute, as argued by Tedaldi and Rogers (1991), is suggestive of solute absorption.

Although the high solute uptake of phenol and benzoic acid by Reillex-425 and XAD-12 is attributed to absorption into the polymeric matrix in the present study, the fractional solute uptake due to absorption relative to adsorption has not been quantified. Cornel and Sontheimer (1986) proposed an approach whereby the difference in the volume expansion of a bed packed with the polymeric resin relative to the total volume of solute uptake (measured in a sorption experiment) is equal to the amount

Table IV. Polanyi Isotherm Parameters

sorbent	Polanyi parameters ^a	toluene	benzoic acid	chlorobenzene	phenol	N ₂ ^d
F-400	W_0	0.600	0.489	0.463	0.572	0.652
	B	0.010	0.010	0.005	0.007	
	r	0.973	0.972	0.973	0.989	
XAD-4	W_0	0.808	0.363	0.673	0.840	0.974
						1.18 ^c
	B	0.025	0.021	0.018	0.028	
XAD-12	r	0.988	0.997	0.996	0.987	
	W_0	0.081	0.497	0.078	1.38	0.284
	B	0.044	0.015	0.030	0.023	
XAD-16	r	0.964	0.998	0.987	0.988	
	W_0	0.777	0.475	0.643	1.16	1.40
	B	0.023	0.024	0.018	0.019	
Reillex	r	0.990	0.995	0.981	0.995	
	W_0	0.190	0.455	0.202	2.28	0.680
						0.464 ^b
XAD-8	B	0.035	0.026	0.037	0.023	
	r	0.999	0.995	0.985	0.997	
	W_0				1.08	0.633
	B				0.022	
	r				0.997	

^a W_0 , cm³/g; B , J/cm³, r , correlation coefficient. ^b This value corresponds to the resin batch used for the chlorobenzene sorption experiments. ^c This value corresponds to the resin batch used for the phenol sorption experiments. ^d Values obtained from nitrogen adsorption measurements using Autosorb-1.

Table V. Solubility Parameters of Polymers and Solvents

solvent or polymeric resin	solubility parameter, (cal/cm ³) ^{1/2}
water	23.4 ^a
benzoic acid	11.74 ^b
chlorobenzene	9.6 ^b
phenol	12.1 ^c
toluene	8.9 ^a
XAD-12	11.5 ^d
Reillex-425	10.7 ^d
XAD-4	9.1 ^d
XAD-16	9.1 ^d
XAD-8	9.45 ^d

^a Grulke (1989). ^b Beerbower *et al.* (1984). ^c Barton (1983). ^d Hildebrand solubility parameter of polymers calculated according to the group contribution method of Barton (1983).

of absorbed solute. The above method, however, is highly approximate since it does not account for internal swelling of the resin which is not expected to be reflected in a change in the volume of the resin (i.e., the resin's diameter may remain unchanged by internal swelling of the porous resin). It has been suggested that NMR spectroscopy may allow one to distinguish between a liquid phase in the pores and an absorbed phase in the polymeric matrix (Allen, 1992), and future research in such a direction may ultimately lead to improved understanding of the coupling of adsorption and absorption.

Swelling Measurements. As further support for the assertion that solute absorption accounts for at least part of the uptake of organics by polymeric resins, swelling of the polymeric resins in the pure solvents and aqueous concentrated solute solutions was measured. The solubility parameters for the solvents and polymers are presented in Table V, and the swelling ratios, defined as the ratio of the resin's volume in the solvent to the dry resin's volume, are presented in Table III. The polar resins, XAD-8, Reillex-425, and XAD-12, swelled in water by 14%, 16%, and 17%, respectively, while the nonpolar resins, XAD-4 and XAD-16, revealed negligible swelling. It is also noted that the three polar resins, XAD-8, Reillex-425, and XAD-12, also swelled to a greater degree than the nonpolar resins, XAD-4 and XAD-16, in concentrated aqueous solutions of phenol and benzoic acid. For example, the percent of swelling in the phenol solution

obtained for Reillex-425 and XAD-12, 52% and 64%, respectively, was significantly higher than the degree of swelling obtained for XAD-4 and XAD-16, 18% and 22%, respectively. These results indicate that the ability of the resin to swell, possibly due to structural and chemical differences, is higher for XAD-12 and Reillex-425 than for XAD-4 and XAD-16.

It is important to note that hydrogen-bonding is possible for some polar organics with the XAD-8 (Payne and Maity, 1990; Maity *et al.*, 1991), Reillex-425 (Chanda *et al.*, 1985a), and XAD-12 (Garcia and King, 1989) resins and that the swelling of these resins can be affected by hydrogen-bonding. Swelling equilibrium is obtained when the change in the free energy of elastic deformation, $\Delta G_{\text{elastic}}$, is balanced by the free energy of mixing, ΔG_{mixing} , or (Flory, 1953)

$$0 = \Delta G_{\text{elastic}} + \Delta G_{\text{mixing}} \quad (6)$$

Since the enthalpy change due to elastic deformation is generally small (Flory, 1953), one can write eq 6 as

$$\Delta S_{\text{elastic}} = \Delta G_{\text{mixing}}/T \quad (7)$$

where $\Delta S_{\text{elastic}}$, the change in the entropy of elastic deformation upon swelling, is negative (due to the fewer number of configurations available to the network chains as they are stretched). Hydrogen-bonding of the solute with the polymeric resins would result in a favorable free energy state (i.e., lower free energy), a proportional decrease in the elastic entropy of deformation, and consequently a greater degree of swelling.

Finally, the results of the present study suggest that those resins that showed the highest degrees of swelling in water or concentrated aqueous solute solutions also revealed higher sorption capacities expressed as the fraction of the pore volume filled. The swelling measurements reinforce the assertion that the ability of the solute or solvent to swell the matrix of the polymeric resins is important in determining the resin's sorption capacity for a particular organic.

Conclusion

The ability of some polymeric resins to swell or absorb organics makes them fundamentally different from activated carbon. One is cautioned that existing theories of solute uptake by polymeric "adsorption" resins fail to account for the possibility that solute absorption can occur in addition to adsorption. Also, the use of adsorption models that utilize "maximum adsorption" as one of the model parameters (e.g., Langmuir, 1918; Polanyi, 1932; Tóth, 1981; Jossens *et al.*, 1978; Suwanayuen and Danner, 1980) will produce erroneous estimates of the "true" sorption maximum for polymeric resins in which solute adsorption can take place. Previous studies on solute sorption by polymeric resins (Neely, 1980; Cornel and Sontheimer, 1986; Garcia and King, 1989) and the data presented in this work suggest that the ability of polymeric resins to swell, either due to the solvent or due to the solute, should be considered along with information on the surface area and pore volume of the resins when considering solute sorption by polymeric resins. The results of the current study clearly suggest that more experimental and theoretical investigations will be needed to further elucidate and quantify absorption as one of the mechanisms for the uptake of organics from aqueous solutions by polymeric resins.

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Literature Cited

- Allen, D. T. (Department of Chemical Engineering, University of California, Los Angeles, Los Angeles CA, 90024). Personal communication, April 23, 1992.
- Barton, A. F., Ed. *Handbook of Solubility Parameters and Other Cohesion Parameters*; Chemical Rubber Co. Press: Boca Raton, FL, 1983.
- Belfort, G.; Altshuler, G. L.; Thallam, K. K.; Feerick, C. P.; Woodfield, K. L. Selective Adsorption of Organic Homologues onto Activated Carbon from Dilute Aqueous Solutions. Solvophobic Interaction Approach - V The Effect of Simple Structural Modifications with Aromatics. In *Fundamentals of Adsorption*; Myers, A. L., Belfort, G., Eds.; Engineering Foundation: 345 E. 47th St, New York, NY, 1984; pp 77-94.
- Browne, T. E.; Cohen, Y. Aqueous-Phase Adsorption of Trichloroethene and Chloroform onto Polymeric Resins and Activated Carbon. *Ind. Eng. Chem. Res.* 1990, 29, 1338-1345.
- Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of Gases in Multicomponent Layers. *J. Am. Chem. Soc.* 1938, 60, 309-319.
- Cairo, P. R.; Coyle, J. T.; Davis, J. T.; Neukrug, H. M.; Suffet, I. H.; Wickland, A. Evaluating Regenerated Activated Carbon Through Laboratory and Pilot-Column Studies. *J. Am. Water Works Assoc.* 1982, 74 (2), 94-102.
- Chanda, M.; O'Driscoll, K. F.; Rempel, G. L. Sorption of Phenolics onto Cross-Linked Poly(4-vinylpyridine). *React. Polym.* 1983, 1, 39-48.
- Chanda, M.; O'Driscoll, K. F.; Rempel, G. L. Sorption of Phenolics and Carboxylic Acids on Polybenzimidazole. *React. Polym.* 1985, 4, 39-48.
- Coasta, E.; Calleja, G.; Marijuan, L. Comparative Adsorption of Phenol, P-Nitrophenol and P-Hydroxybenzoic Acid on Activated Carbon. *Adsorp. Sci. and Technol.* 1988, 5 (3), 213-228.
- Cornel, P.; Sontheimer, H. Sorption of Dissolved Organics from Aqueous Solution by Polystyrene Resins - I. Resin Characterization and Sorption Equilibrium. *Chem. Eng. Sci.* 1986, 41 (7), 1791-1800.
- Dinopoulou, G. Sorptive Behavior of a Multicomponent Solution of Phenolics with Synthetic Resin. M.S. Thesis, Illinois Institute of Technology, 1985.
- Dobbs, R. A.; Cohen, J. M. *Carbon Adsorption Isotherms for Toxic Organics*; EPA-600/8-80-023; Municipal Environmental Research Laboratory, Office of Research and Development, Environmental Protection Agency, U.S. Government Printing Office: Washington, DC, April 1980.
- Dubinin, M. M. Adsorption in Micropores. *J. Colloid Interface Sci.* 1967, 23, 487-499.
- Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- Garcia, A. A.; King, C. J. The Use of Basic Polymer Sorbents for the Recovery of Acetic Acid from Dilute Aqueous Solution. *Ind. Eng. Chem. Res.* 1989, 28, 204-212.
- Grant, T. M. *Irreversible Adsorption of Phenolic Compounds by Activated Carbons*. Ph.D. Thesis, Department of Chemical Engineering, University of California, Berkeley, 1988.
- Grant, T. M.; King, C. J. Mechanism of Irreversible Adsorption of Phenolic Compounds by Activated Carbons. *Ind. Eng. Chem. Res.* 1990, 29, 264-271.
- Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area, and Porosity*, 2nd ed.; Academic Press: London, 1982.
- Grulke, E. A. Solubility Parameter Values. In *Polymer Handbook*, 3rd ed.; Brandup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989; p 519.
- Gusler, G. M. Removal of Organics from Aqueous Solutions using Polymeric Resins. Ph. D. Thesis, University of California, Los Angeles, in preparation.
- Gustafson, R. L.; Albright, R. L.; Heisler, J.; Lirio, J. A.; Reid, O. T., Jr. Adsorption of Organic Species by High Surface Area Styrene-Divinylbenzene Copolymers. *Ind. Eng. Chem. Process Des. and Dev.* 1968, 7 (2), 107-115.
- Hacsakaylo, J. J.; Le Van, M. D. Correlation of Adsorption Equilibrium Data Using a Modified Antoine Equation: A New Approach for Pore-Filling Models. *Langmuir*. 1985, 1, 97-100.
- Hasanain, M. A.; Hines, A. L. Application of the Adsorption Potential Theory to Adsorption of Carboxylic Acids from Aqueous Solutions onto a Macroreticular Resin. *Ind. Eng. Chem. Process Des. Dev.* 1981, 20 (4), 621-25.
- Hefter, G. T. Toluene. In *Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C₅ and C₇*; Kertes, A. S., Ed.; IUPAC

- Solubility Data Series; Pergamon Press: Oxford, New York, 1989; Vol. 37, pp 369-341.
- Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*, 2nd ed.; Marcel Dekker, Inc.: New York, 1986.
- Hofer, L. J. E.; Manes, M. Adsorption on Activated Carbon from Solvents of Different Refractive Index. *Chem. Eng. Prog. Symp. Ser.* 1969, 65 (96), 84-88.
- Horvath, A. L. Chlorobenzene. In *Halogenated Benzenes, Toluenes, and Phenols with Water*; Kertes, A. S., Ed.; IUPAC Solubility Data Series; Pergamon Press: Oxford, New York, 1985; Vol. 20, pp 153-182.
- Howard, P. H. *Handbook on Environmental Fate and Exposure Data for Organic Chemicals*; Lewis Publishers, Inc.: Chelsea, MI, 1989.
- Itaya, A.; Kato, N.; Yamamoto, J.; Okamoto, K. Liquid Phase Adsorption Equilibrium of Phenol and its Derivatives on Macroporous Adsorbents. *J. Chem. Eng. Jpn.* 1984, 17 (4), 389-395.
- Jaroniec, M.; Patrykiewicz, A.; Borowko, M. Statistical Thermodynamics of Monolayer Adsorption from Gas and Liquid Mixtures on Homogeneous and Heterogeneous Solid Surfaces. *Prog. Surf. Membr. Sci.* 1981, 14, 1-68.
- Jossens, L.; Prausnitz, J. M.; Fritz, W.; Schlünder, E. U.; Myers, A. L. Thermodynamics of Multi-solute Adsorption from Dilute Aqueous Solutions. *Chem. Eng. Sci.* 1978, 33, 1097-1106.
- Kawabata, N.; Ohira, K. Removal and Recovery of Organic Pollutants from Aquatic Environment. 1. Vinylpyridine - Divinylbenzene Copolymer as a Polymeric Adsorbent for Removal and Recovery of Phenol from Aqueous Solution. *Environ. Sci. Tech.* 1979, 13 (1), 1396-1402.
- Kunin, R. Polymer Adsorbents for Treatment of Waste Effluents. *Polym. Eng. Sci.* 1977, 17 (1), 58-62.
- Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Silica, and Mica. *J. Am. Chem. Soc.* 1918, 40, 1361-1403.
- Lowell, S.; Shields, J. E. *Powder Surface Area and Porosity*, 2nd ed.; Chapman and Hall: New York, 1984.
- Maity, N.; Payne, G. F.; Chipchovsky, J. L. Adsorptive Separations Based on the Differences in Solute-Sorbent Hydrogen Bonding Strengths. *Ind. Eng. Chem. Res.* 1991, 30, 2456-2463.
- Manes, M. The Polanyi Adsorption Potential Theory and its Applications to Adsorption from Water Solution onto Activated Carbon. In *Activated Carbon Adsorption of Organics from the Aqueous Phase*; Suffet, I. H., McGuire, M. J., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; Vol. 1, Chapter 2, pp 43-63.
- Manes, M.; Hofer, L. J. E. Application of the Polanyi Adsorption Potential Theory to Adsorption from Solution on Activated Carbon. *J. Phys. Chem.* 1969, 73 (3), 584-590.
- McClellan, A. L.; Harnsberger, H. F. Cross-Sectional Areas of Molecules Adsorbed on Solid Surfaces. *J. Colloid Interface Sci.* 1967, 23, 577-599.
- McGuire, M. J.; Suffet, I. H. Adsorption of Organics from Domestic Water Supplies. *J. Am. Water Works Assoc.* 1978, 70, 621.
- McGuire, M. J.; Suffet, I. H. The Calculated Net Adsorption Energy Concept. In *Activated Carbon Adsorption of Organics from the Aqueous Phase*; Suffet, I. H., McGuire, M. J., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; Vol. 1.
- McGuire, M. J.; Suffet, I. H.; Radziul, J. V. Assessment of Unit Processes for the Removal of Trace Organic Compounds from Drinking Water. *J. Am. Water Works Assoc.* 1978, 70 (10), 565-572.
- Neely, J. W. A Model for the Removal of Trihalomethanes from Water by Ambersorb XE-340. In *Activated Carbon Adsorption of Organics from the Aqueous Phase*; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; Vol. 2, Chapter 17, pp 417-424.
- Nirmalakhandan, N.; Speece, R. E. Prediction of Aqueous Solubility of Organic Chemicals Based on Molecular Structure - II. Applications to PNAs, PCBs, PCDDs, etc. *Environ. Sci. Technol.* 1989, 23 (6), 708-713.
- Paleos, J. Adsorption from Aqueous and Nonaqueous Solutions on Hydrophobic and Hydrophilic High Surface - Area Copolymers. *J. Colloid and Interface Sci.* 1969, 31 (1), 7-18.
- Payne, G. F.; Ninomiya, Y. Selective Adsorption of Solutes Based on Hydrogen Bonding. *Sep. Sci. Technol.* 1990, 25, (11,12), 1117-1129.
- Polanyi, M. Section III - Theories of the Adsorption of Gases. A General Survey and Some Additional Remarks. *Trans. Faraday Soc.* 1932, 28, 316-333.
- Ram, N. M.; Morris, J. C. Selective Passage of Hydrophilic Nitrogenous Organic Materials through Macroporous Resins. *Environ. Sci. Technol.* 1982, 16, 170-174.
- Reillex Report No. 2.; Reilley Industries, Inc.: 1510 Market Square Center, 151 N. Delaware St., Indianapolis, IN 46204, 1987.
- Rixey, W. G. Non-Wet Adsorbents for the Selective Recovery of Polar Organic Solutes from Dilute Aqueous Solution. Ph.D. Thesis, Department of Chemical Engineering, University of California, Berkeley, 1987.
- Rixey, W. G.; King, C. J. Non-Wetting Adsorbents for the Recovery of Solutes from Dilute Aqueous Solutions. In *Fundamentals of Adsorption*; Liapis, A. I., Ed.; Engineering Foundation: New York, 1987.
- Sips, R. On the Structure of a Catalyst Surface. *J. Chem. Phys.* 1948, 16 (5), 490-495.
- Speth, T. F. Predicting Equilibria for Single Solute and Multicomponent Aqueous-Phase Adsorption onto Activated Carbon. M.S. Thesis, Michigan Technological University, 1986.
- Speth, T. F.; Miltner, R. J. Technical Note: Adsorption Capacity of GAC for Synthetic Organics. *J. Am. Water Works Assoc.* 1990, February, 72 -75.
- Suffet, I. H. An Evaluation of Activated Carbon for Drinking Water Treatment: A National Academy of Science Report. *J. Am. Water Works Assoc.* 1980, 72 (1), 41-50.
- Suffet, I. H.; Brenner, L.; Coyle, J. T.; Cairo, P. R. Evaluation of the Capability of Granular Activated Carbon and XAD-2 Resin to Remove Trace Organics from Treated Drinking Water. *Environ. Sci. Technol.* 1978, 12 (12), 1315-1322.
- Suffet, I. H.; Baker, R. J.; Yohe, T. L. Pretreatment of Drinking Water to Control Organic Contaminants and Taste and Odor. In *Pretreatment in Chemical Water and Wastewater Treatment*; Hahn, H. H., Klute, R., Eds.; Springer-Verlag: Berlin, Heidelberg, 1988.
- Suwanayuen, S.; Danner, R. P. A Gas Adsorption Isotherm Equation Based on Vacancy Solution Theory. *Am. Inst. Chem. Eng. J.* 1980, 26 (1), 69-74.
- Tedaldi, D. J.; Rogers, J. Polanyi Theory: Application to Sorption of Volatile Organic Compounds onto Soil under Varying Humidity Conditions. ASCE 1991 National Conference on Environmental Engineering.
- Thurman, C. Phenol. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Grayson, M., Exec. Ed.; Eckroth, D., Assoc. Ed.; John Wiley & Sons: New York, Chichester, Brisbane, Toronto, and Singapore, 1982; Vol. 17, pp 373-384.
- Thurman, E. M.; Malcolm, R. L.; Aiken, G. R. Prediction of Capacity Factors for Aqueous Organic Solutes Adsorbed on a Porous Acrylic Resin. *Anal. Chem.* 1950, 50, 775-778.
- Tóth, J. A Uniform Interpretation of Gas/Solid Adsorption. *J. Colloid and Interface Sci.* 1981, 79 (1), 85-95.
- Van Vleet, B. M.; Weber, W. J., Jr. Comparative Performance of Synthetic Adsorbents and Activated Carbon for Specific Compound Removal from Wastewaters. *J. Water Pollut. Control Fed.* 1976, 48, 120.
- Wang, S. W.; Hines, A. L.; Pedram, E. Extension of the Adsorption Potential Theory to Multi-Solute Adsorption of Aliphatic Acids from Dilute Aqueous Solution. *Ind. Eng. Fundam.* 1981, 20 (4), 350-355.
- Weast, R. C., Ed. in chief; Astle, M. J.; Beyer, W. H., Assoc. Eds. *CRC Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Raton, FL, 1985.
- Weber, W. J., Jr.; van Vleet, B. M. Fundamental Concepts for Applications of Activated Carbon in Water and Wastewater Treatment. In *Activated Carbon Adsorption of Organics in Water and Wastewater Treatment*; Suffet, I. H., McGuire, M. J., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; Vol. I, Chapter 1, pp 15-41.
- Weber, W. J., Jr.; van Vleet, B. M. Synthetic Adsorbents and Activated Carbons for Water Treatment: Statistical Analyses and Interpretations. *J. Am. Water Works Assoc.* 1981a, 73 (8), 426-431.
- Weber, W. J., Jr.; van Vleet, B. M. Synthetic Adsorbents and Activated Carbons for Water Treatment: Overview and Experimental Comparisons. *J. Am. Water Works Assoc.* 1981b, 73 (8), 420-426.
- Williams, A. E. Benzoic Acid. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Grayson, M., Exec. Ed.; Eckroth, D., Assoc. Ed.; John Wiley & Sons: New York, Chichester, Brisbane, Toronto, and Singapore, 1978; Vol. 3, pp 778-792.

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