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Use of Adsorbents for Recovery of Acetic Acid from Aqueous Solutions Part I—Factors Governing Capacity

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USE OF ADSORBENTS FOR RECOVERY OF ACETIC ACID
FROM AQUEOUS SOLUTIONS
PART I - FACTORS GOVERNING CAPACITY

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ABSTRACT

Measurements have been made of the preferential uptake of acetic acid from aqueous solutions onto activated carbons and polymeric sorbents. Interpretation of the data shows that adsorption properties are determined by surface area and chemical effects.

For styrene-divinylbenzene macroreticular resins, adsorption densities are nearly identical to those at the liquid-vapor interface, indicating that adsorption behavior is dominated by aqueous-phase non-idealities. The capacities of basic polymeric sorbents can be interpreted in terms of the degree of saturation of basic groups, and in terms of relative basicities, which were gauged through Gutmann Donor Numbers, the solvatochromic basicity parameters of Kamlet, et al., Hammett Parameters, and values of pK_a determined by titration. Low solvatochromic acidity

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parameter or Acceptor Number is also important for capacity, so as to reduce competitive sorption of water.

The adsorption properties of activated carbons with different surface densities of heteroatoms can be rationalized through a simple model based upon the existence of a uniform, selective adsorption layer. Differences in the degree of surface heterogeneity are probably also important. The effect of the pH of the aqueous phase upon capacity can be interpreted through a two-solute competitive adsorption model, involving ionized and un-ionized species.

INTRODUCTION

Many organic chemicals, notably carboxylic acids, alcohols, glycols, and related substances, can be made from biomass by fermentation. Complicating the recovery of these products are the facts that they are usually produced in dilute and complex aqueous solutions, and that the biological system is often sensitive to heat and/or contamination.

Adsorption, or more generally sorption (including bulk uptake) by solids is an attractive method for recovery of these substances, since many adsorbents are non-contaminating, and since no heating is involved in the primary adsorption step. This presentation covers those properties of adsorbents which are important for recovery of organic chemicals from aqueous solution. The prototype solute considered is acetic acid. For brevity, the term "adsorption" is used generally, including some cases where substantial bulk uptake may occur.

Since the relative volatility of water to acetic acid is

nearly unity at low acid concentration and since water is more volatile than acetic acid, alternatives to conventional distillation are desirable even in non-biological systems. Present and past commercial processing methods include azeotropic distillation, solvent extraction with simple solvents, and extractive distillation^{1, 2, 3}. Solvent extraction with chemically complexing extractants has also been explored and developed recently^{4,5,6,7}. Adsorption presents another alternative, with the feature that process economics can be comparable to those for solvent extraction, in addition to the advantage of not contaminating the aqueous solution.

There are at least three important characteristics to be considered for recovery of acetic acid from aqueous solutions by adsorption:

- (1) the uptake capacity of the adsorbent for acetic acid,
- (2) the selectivity for uptake of acetic acid as opposed to water and other solutes, and
- (3) regeneration of the adsorbent, a step which may also exhibit selectivity.

Part I of this work is concerned with factors affecting capacity, Part II examines factors influencing selectivity, and Part III reports measurements of regenerability by solvent leaching.

EXPERIMENTAL

Materials

Sources and measured chemical compositions of the adsorbents used are given in Tables I and II. Polymeric adsorbents are tallied in Table I, while activated carbons are described in Table II. Listed in both Table I and Table II are

TABLE I.
Sources and Properties of Polymer and
Pyrolyzed-Polymer Sorbents.

Nitrogen surface areas are measured, except where noted]

Adsorbent Designation	Source	Type of Adsorbent	10^{-3} x Nitrogen Surface Area Area (m^2/kg)
XAD-2	Rohm & Haas Corp.	Styrene-Divinylbenzene Copolymer	340
XAD-4	Rohm & Haas Corp.	Styrene-Divinylbenzene Copolymer	760
XAD-7	Rohm & Haas Corp.	Acrylic ester-Divinyl- benzene Copolymer	450**
XAD-12	Rohm & Haas Corp.	Poly (N oxide)	23
XE-309	Rohm & Haas Corp.	Poly(4-Vinylpyridine)	33**
XE-340	Rohm & Haas Corp.	Pyrolyzed Sulfonated Styrene-Divinylbenzene Copolymer	390
XE-348	Rohm & Haas Corp.	Pyrolyzed Sulfonated Styrene-Divinylbenzene Copolymer	630
XE-378	Rohm & Haas Corp.	Poly(2-Vinylpyridine)	6**
R-PVP	Reilly Tar & Chemical Co.	Poly(4-Vinylpyridine)	<10
WGR	Dow Chemical Company	Epoxy Polymer with Tertiary Amine Groups	<5
MWA-1	Dow Chemical Company	Styrene-Divinylbenzene Copolymer with Tertiary- Amine Groups	23
DVB	Polysciences, Inc.	Poly(divinylbenzene)Resin	920
A-340	Diamond Shamrock, Inc.	(Duolite) Polyethylene- diamine, cross-linked with epichlorohydrin (a gel-type resin)	low
PBI	Celenese Chemical Co.	Polybenzimidazole (powder form)	--

* - Nitrogen surface areas are measured, except where noted.
** - Manufacturer's stated value.

TABLE II.
Sources and Properties of Activated Carbons

Carbon	Source	Elemental Analysis (wt. %)							$10^{-3} \times$ Nitrogen Surface Area* m ² /kg
		C	H	N	S	O	Ash	Total	
Witcarb 950	Witco	95.14	0.55	0.06	2.73	0.90	0.5	99.9	1050
Columbia	Witco	91.89	0.88	0.14	2.72	2.12	2.8	100.6	1300
G-BAC	Union Carbide	94.86	0.91	0.04	0.11	1.1	0.1	97.1	1280
GX-031	Amoco	79.91	0.45	0.10	0.11	0.76	19.0	100.3	2350
Row 0.8S	Norit	77.22	0.82	0.62	0.14	10.28	4.6	93.7	650
Filtrisorb									
100	Calgon	87.06	0.81	0.70	0.74	2.16	6.5	98.0	850
200	"	88.80	0.85	0.49	0.68	1.03	5.7	97.6	814
300	"	87.48	0.54	0.48	0.74	0.65	6.6	96.5	930
400	"	89.54	0.48	0.39	0.63	0.52	5.3	96.9	830
100 OX		72.0	0.47	0.93	--	9.7	--	83.1	500
XE-340**	Rohm	87.97	3.7	0.17	3.67	2.11	0.1	97.7	390
XE-348**	& Haas	93.32	0.67	0.13	3.71	0.68	0.1	98.6	630

* - Measured nitrogen surface areas are from Munson (1985).

** - Pyrolyzed sulfonated styrene/divinylbenzene resin.

two pyrolyzed sulfonated styrene-divinylbenzene adsorbents, Ambersorbs XE-340 and XE-348 (Rohm & Haas Corp.). The preparation of these materials is described by Neeley⁸.

Most adsorbents were pretreated before use to remove impurities.

The Rohm and Haas Amberlite XAD-2, -4, and -7 resins were washed repeatedly with methanol, acetone, and deionized water, then dried.

The Dowex WGR and MWA-1 and Celanese PBI resins were washed with water, methanol, 0.05 N HCl, and 0.05 N NaOH, and were then further purified by Soxhlet extraction with methanol for at least 24 hours. The final resins were then dried in a vacuum oven for at least two days at 82°C.

The Reilly PVP resin, Rohm and Haas Amberlites XE-309, XE-378, and XAD-12, Diamond Shamrock Duolite A-340, synthesized PEI, and Witco Witcarb 950, were washed with 0.10 N HCl, 0.1 N NaOH, methanol, and water, and were then dried in a vacuum oven at 18 to 36 kPa absolute pressure and 70°C for two days.

Bio-Rad AG-2X8 was purified by Soxhlet extraction with methanol, converted to the hydroxide form by equilibration with 1N NaOH, washed with water, and dried in the vacuum oven at 18 to 36 kPa and 70°C for four days.

Union Carbide G-BAC, Amoco GX-031, Westvaco Nuchar CX-0655, and Norit Row 0.8S carbons were washed with water and dried in a vacuum oven at 18 to 36 kPa absolute pressure and 90°C.

Witco Columbia carbon and Rohm and Haas Ambersorbs XE-340, and XE-348 were used as received. All water used in these experiments was distilled water further purified with a Milli-Q system (Millipore Corp.).

The glacial acetic acid used was Mallinckrodt Co., Analytical Grade with minimum 99.7% assay. All other chemicals were of Analytical Grade.

Batch Equilibrations

One gram of each adsorbent was equilibrated with 10 grams

of aqueous acetic acid solution of known concentration in a screw-cap glass vial having a total volume of 20 mL. Unless otherwise specified, the initial pH was the natural pH of acetic acid in solution. For experimentation at high pH, the pH was adjusted either by addition of sodium hydroxide or by controlling the relative proportions of potassium acetate and acetic acid in solution. The filled vials were equilibrated for at least two days in a shaker bath thermostatted at 30°C. The approach to equilibrium was followed in several cases, and an approach to within 5% of the total change upon achievement of equilibrium was found to occur within a few hours. Several multiples of this time were allowed during equilibrium measurements. More details are given by Munson⁹.

Points for composite adsorption isotherms were calculated as $(M_S \Delta x_A)/m$, where

M_S = weight of the feed solution

x_{Af} = weight fraction of acetic acid in aqueous solution after equilibration

x_{Ao} = weight fraction of acetic acid in aqueous solution before equilibration

$\Delta x_A = x_{Ao} - x_{Af}$

m = weight of dry adsorbent

The composite isotherm is equivalent to the surface excess^{10,11}.

Analytical Methods

The concentration of acetic acid in solution was measured by direct injection into a Varian Model 3700 gas chromatograph (GC) using a 36-cm Porapak Q column (Waters Associates) with a flame-ionization detector. The GC was operated at a constant oven temperature of either 150° or 170°C. For samples where the pH had been raised through addition of either NaOH or potassium

acetate, the pH was adjusted to a value of below 2.3 before analysis, by addition of concentrated H_2SO_4 .

The nitrogen surface areas of the adsorbents (Tables I and II) were determined from a BET plot obtained using a Model 201 BET Analyzer (Porous Materials Inc., Ithaca NY), and were based upon a molecular adsorption area of 16.2 sq. Ångströms for nitrogen. Multi-point BET N_2 surface areas were obtained for some samples from Pacific Sorption Service, Chico CA and from Porous Materials Inc., Ithaca NY.

For Ambersorb XE-348 the xenon BET surface area was also measured through a BET plot and was found to be 626 m^2/g , based upon a molecular adsorption area of 23.2 sq. Ångströms for xenon. This is in close agreement with the value of 634 m^2/g for nitrogen (Table I). Through use of a BET plot for adsorption of CO_2 by Amberlite XAD-2, the surface area was found to be 170 and 240 m^2/g , based upon reference pressures equal to the fugacities of solid CO_2 at 195 K and of hypothetical liquid CO_2 at 195 K, respectively. These values are substantially lower than the value of 340 m^2/g found with nitrogen adsorption (Table I), and may reflect a lower packing density of adsorbed CO_2 .

Carbon, hydrogen, and nitrogen contents (Table II) were analyzed by a Perkin-Elmer Model 240 Elemental Analyzer (Perkin-Elmer, Norwalk, Connecticut). The samples were burned with an excess amount of oxygen to generate CO_2 from carbon, H_2O from hydrogen, and N_2 from nitrogen. The concentrations of these compounds were determined with a thermal conductivity detector. The sulfur content was determined by the Grote Combustion method, where the sample was burned in oxygen, followed by absorption with a 3% H_2O_2 solution, followed by addition of BaCl_2 to precipitate BaSO_4 . The ash content was determined from the weight of the residue after the sulfur analysis.

The oxygen content was measured by using the Elemental Analyzer in modified form. The samples were pyrolyzed in helium at 970°C. All the oxygen in the sample should become carbon monoxide under these conditions. The pyrolysis gases were passed through a suspension of NaOH on asbestos to remove the acids. Carbon monoxide was then oxidized to carbon dioxide by passing the gas through mixed CuO and Cu at 670°C. The total amount of carbon dioxide was measured, and the amount of oxygen in the sample was thereby calculated. This oxygen measurement would not reveal oxygen combined in stable oxides in the ash, but should include oxygen in residual water. Samples were thoroughly dried before submission for analysis. All elemental analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley.

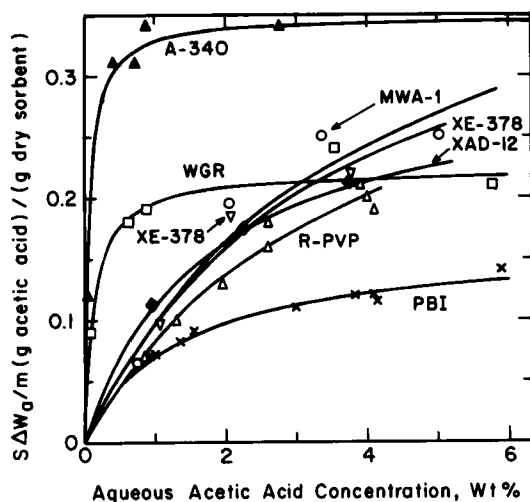


FIGURE 1
Composite sorption isotherms for functionalized polymeric sorbents.

RESULTS AND DISCUSSION

Figure 1 shows composite isotherms for adsorption of acetic acid, measured for various functionalized polymeric adsorbents. Figure 2 shows composite isotherms measured for various non-functionalized polymeric adsorbents, and for the pyrolyzed polymeric adsorbents. Figure 3 shows composite isotherms measured for activated carbons.

The results shown in Figure 2 for Amberlite XAD-7 agree well with earlier data reported by Paleos¹² for the same system at similar concentrations.

The composite isotherms of all the adsorbents show increasing depletion of acetic acid in solution (higher Δx_A) with increasing x_{Af} in this range of relatively low acid

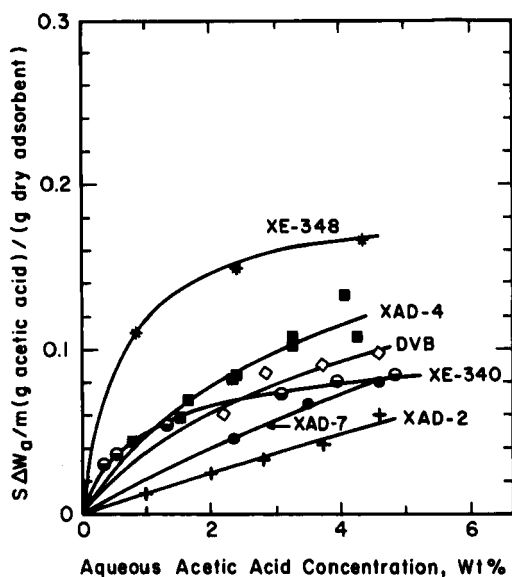


FIGURE 2
Composite adsorption isotherms for non-functionalized macroreticular and pyrolyzed polymeric sorbents.

concentrations. For high enough solute concentrations the depletion will be less and often negative¹¹.

Ambersorb XE-340 and Amberlites XAD-2 and XAD-4 are adsorbents which are not wetted by aqueous solutions of low enough solute concentration. The results shown in Figure 2 for these adsorbents were obtained under conditions where the adsorbents had initially been fully wetted by soaking in methanol, followed by displacement with water. Isotherm points have also been measured for these adsorbents under non-wetting conditions, and are reported elsewhere^{13,14}, where the differences between the isotherms for the adsorbents in the wetted and non-wetted states are interpreted. The capacities are lower in the non-wetted state than in the wetted state for XAD-2 and XAD-4, and are about the same for XE-340.

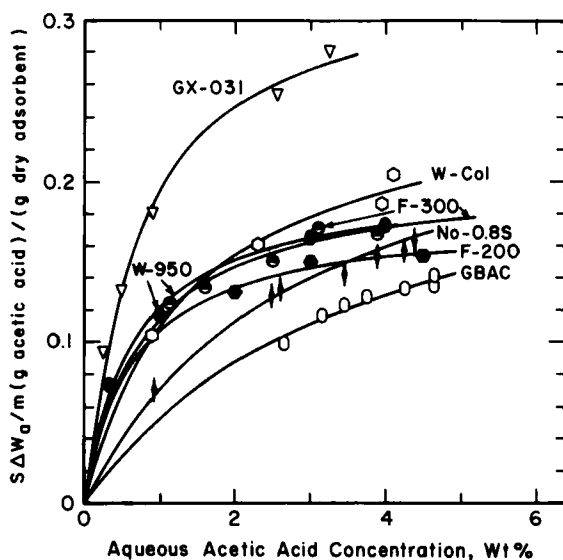


FIGURE 3
Composite adsorption isotherms for carbons.

Effect of Surface Area upon Capacity

Figure 4 shows the composite-isotherm adsorption capacities reduced by the measured nitrogen surface areas of the carbons, macroreticular resins, and pyrolyzed polymeric adsorbents. There is less spread among adsorbents in Figure 4 than in Figures 2 and 3, as would be expected for a surface-based phenomenon. Furthermore, the polymeric adsorbents exhibit capacities per unit surface area that are comparable to those of most of the carbons.

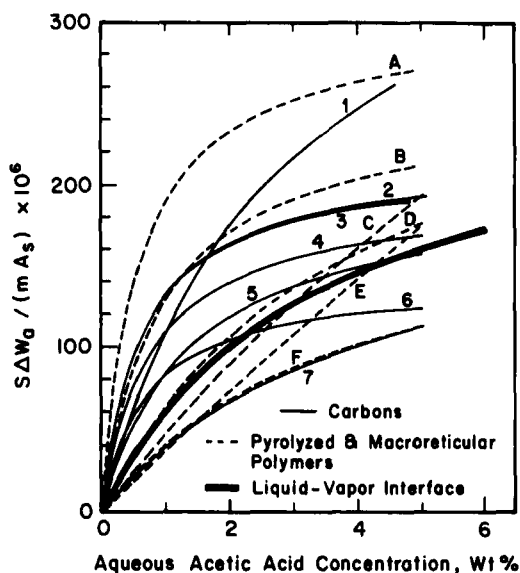


FIGURE 4

Normalized composite isotherms (acetic acid capacity/ N_2 surface area) for carbons, pyrolyzed polymers, and macroreticular polymer adsorbents. Key:

<u>Number</u>	<u>Carbon</u>	<u>Letter</u>	<u>Polymer</u>
1	No-0.8S	A	XE-348
2	F-200	B	XE-340
3	F-300	C	XAD-2
4	W-950	D	XAD-4
5	W-Co1	E	XAD-7
6	GX-031	F	DVB
7	GBAC		

Not shown in Figure 4 are results for those polymeric adsorbents for which nitrogen surface areas are less than 300 m^2/g . As has been shown by Albright¹⁵, as the specific surface area of a polymeric adsorbent decreases, the "working arena" for solute uptake shifts from surface adsorption to bulk infusion, or absorption. This shift occurs in the vicinity of surface areas of 500 m^2/g , or less if allowance is made for incomplete utilization of internal sites.

Measurements of breakthrough curves during fixed-bed operation¹⁶ have shown a significant retardation of equilibration rate for Dowex WGR during solute uptake, with the width of the breakthrough curve being substantially greater than that for Amberlite XAD-4, Reilly PVP, Witco Witcarb 950, and Union Carbide G-BAC. This phenomenon may be related to rate limitations resulting from the bulk-infusion mechanism in Dowex WGR.

Similarities between Liquid-Solid and Liquid-Vapor Interfaces

For Amberlites XAD-2 and -4, comparisons were made of adsorption densities from aqueous solution at the liquid-solid interface and at the liquid-vapor interface. The experimental data from Figure 2 for adsorption of acetic acid from aqueous solution by XAD-4 are replotted in terms of molar adsorption density in Figure 5. The (upper) solid curve for the wetted state in Figure 5 represents adsorption densities at the liquid-vapor interface calculated by application of the Gibbs adsorption isotherm¹⁷ to data for surface tensions of aqueous solutions of acetic acid¹⁸.

The very close agreement of the data points for the liquid-solid interface with the curve for the liquid-vapor interface shows that the adsorbed state is energetically very nearly the

same at the two types of interface. Similar results are obtained by comparing, on the one hand, the results reported by Gustafson, et al¹⁹ for adsorption of propionic and butyric acids from water onto XAD-2, and, on the other hand, adsorption densities at the liquid-vapor interface calculated by applying the Gibbs adsorption isotherm to surface-tension data for solutions of these two solutes in water¹⁸. (See Figure 6.)

Concomitant conclusions are that the adsorption behavior of these carboxylic acids from aqueous solution onto Amberlite XAD-2 and -4 are dominated by non-idealities in the aqueous phase (the "hydrophobic" effect), and that the interactions at the liquid-solid surface are non-specific. Additional evidence for the dominance of aqueous-phase non-idealities comes from the fact that adsorption data for quite different solutes can be collapsed onto what appears to be a single curve, when the composite-isotherm molar solute uptake is plotted against aqueous-phase

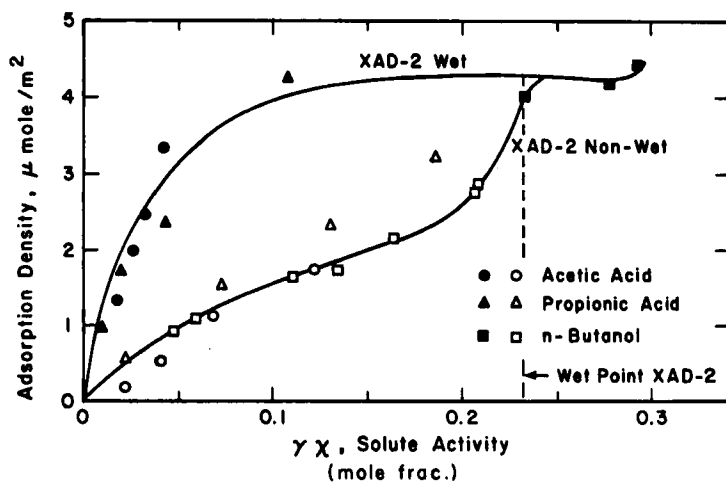


FIGURE 5
Surface excesses (composite-isotherm adsorption density) for Amberlite XAD-2 in the wetted and non-wet states.

solute activity, as shown in Figure 5^{13,14}, where data are shown for XAD-2 in both the wetted and non-wet states.

For reference, a curve is included in Figure 4 corresponding to the surface enrichment at a vapor-liquid interface.

In work reported elsewhere¹⁴, the adsorption densities of the Amberlite XAD resins at both solid-liquid and vapor-liquid interfaces have been further analyzed in terms of dispersion-force and polar contributions to surface energies.

Effect of Basic Functional Groups upon Capacities of Polymer Sorbents

Donor/Acceptor Classification. Interactions between solute and sorbent functional groups may be interpreted qualitatively in terms of Lewis acidity and basicity (electron donor-acceptor) mechanisms. The α and β "solvatochromic" parameters of

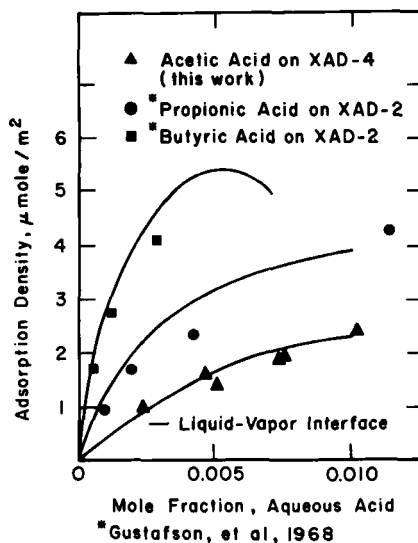


FIGURE 6
Fatty acid adsorption densities (surface excesses) on Rohm and Haas Amberlite XAD resins and at liquid/vapor interfaces.

Kamlet, et al.²⁰, are measures of these properties, as are the earlier Gutmann Acceptor Number (AN) and Donor Number (DN) scales^{21,22} and the the E and C parameters of Drago, et al.²³ A larger α or AN corresponds to greater ability of a molecule, or actually the functional group(s) on it, to accept electrons or serve as a Lewis acid in an association complex. A larger β or DN corresponds to a greater ability to donate electrons or serve as a Lewis base. A molecule may have substantial values of both α (or AN) and β (or DN) (e.g., water), low values of both (e.g., alkanes), or a high value of one and a low value of the other.

TABLE III.
Solvatochromic Parameters²⁰ and Donor and Acceptor
Numbers^{21,22} for Some Compounds.

COMPOUND	β	α	DN	AN
Hexane	"nil"	"nil"	--	0
Benzene	0.10	"nil"	0.1	8.2
Ethyl Acetate	0.45	"nil"	17.7	--
Diethyl Ether	0.47	"nil"	19.2	3.9
Formamide	--	0.66	24	39.8
Acetic Acid	--	1.09	24.5	52.9
Water	0.18	1.13	33*	54.8
Pyridine	0.64	"nil"	33.1	14.2
Ethanol	0.77	0.96	--	--
Ethylamine	--	--	55	--
Triethylamine	0.71	"nil"	61	--
Trimethyl Phosphine Oxide	1.02	"nil"	--	--

-- No value given.

* - The measured value of DN for water is 18. That value is indicative of the basicity of water in its unassociated state, i.e., in the gas phase or in a dilute solution of a non-associating solvent. The value of 33 is an estimate for pure liquid water from Gutmann²¹.

Values of α and β as reported by Kamlet, et al.²⁰ and AN and DN as reported by Gutmann²¹ and Jensen²² are shown in Table III for a number of molecules containing functional groups relevant to the experiments reported here. There it can be seen that acetic acid can function as both a Lewis acid and a Lewis base, which is reflected by the tendency of acetic acid to dimerize in vapor or organic liquid phases of low polarity. However in competition with water (W), acetic acid (A) is more of a Lewis acid ($AN_A/AN_W > DN_A/DN_W$). Thus it can be expected that, in competition with water, acetic acid will complex preferentially with adsorbed groups which impart high values of β or DN. This rationalizes, in part, the higher acetic acid capacities shown by the two tertiary-amine (MWA-1 and WGR) and two pyridine (R-PVP and XE-378) resins in Figure 1, although, as is shown in a later section, the density of functional groups within the sorbent should be taken into account as well. Amberlite XAD-12 is reported by Rohm and Haas to be a weak base, an N-oxide produced through oxidation of an amine resin. Thus it too presumably possesses a moderate-to-high values of β and DN, similar to those of a phosphine oxide.

Table IV reports isolated data obtained for equilibration of some other polymeric adsorbents with aqueous acetic acid solution. The sorbents are listed in order of decreasing capacity for acetic acid. Polyethyleneimine is a secondary amine with an exceptionally high density of amine groups, which accounts for its high capacity. The bottom three sorbents in Table IV contain groups having moderately high values of β or DN, but also having substantial values of α or AN. The capacities of these substances are low, a fact which is probably related to competitive water uptake due to their having Lewis acid, as well as Lewis base, properties.

Summarizing, functional groups with moderate-to-high β or DN, but low α or AN, are useful for promoting both capacity and selectivity for acetic acid.

Two other measures of basicity were also used to characterize polymeric sorbents²⁴:

1. Determination of the Hammett acidity parameter^{25,26}. This technique used adsorbed indicators, which change color according to whether they are in the neutral acid or conjugate-base forms.

The experimental technique involved slurring about 0.1 g of the polymer with 3 mL of isooctane. Three drops of indicator solution were added to the slurry. The indicator solution was prepared in water or water/ethanol. The

TABLE IV.

Capacity Data Obtained with Other Polymeric Adsorbents

Adsorbent	Source, or How Synthesized	W_A	$S/\Delta W_A /m$
PEI	Polyethyleneimine, 21% Crosslinked with epichlorohydrin	0.0199	0.509
AG-2X8	Quaternary Ammonium Resin in OH ⁻ Form, from Bio-Rad Laboratories	0.0245	0.17
		0.035	0.18
		0.037	0.18
Dowex MWC-1	Polyvinylmethacrylic Acid, from Dow Chemical Company	0.0293	0.030
PMMA	Polymethylmethacrylate (Reaction product of Dowex MWC-1, methanol, and sulfuric acid)	0.0294	0.012
Bio-Gel P-4	Cross-linked Polyacryl- amide, from Bio-Rad Laboratories	0.0297	0.010

 W_A in weight fraction

indicator solution was then acidified by dropwise addition of concentrated HCl, if it was not prepared in the acid form. After equilibration, the color of the adsorbed indicator and its intensity were noted. If the color corresponded to the base form, the Hammett parameter (H_0) for the polymer was taken to be greater than the pK_a for the indicator, and vice versa if the color was that for the acid form. The procedure was repeated until H_0 of the polymer was bracketed between two indicators, or an indicator was found which existed at an intermediate color. Table V lists the indicators used and the corresponding values of pK_a .

TABLE V.

Indicators Used in Measurements of Hammett Basicity Parameter

Indicator	-----Color-----		pK_a
	Acid	Base	
Thymol Blue (acid range)	Red	Yellow	1.65
Methyl Orange	Red	Yellow	3.45
Bromophenol Blue	Yellow	Blue	4.1
Bromochlorophenol Blue	Yellow	Blue	(4)
Methyl Red	Red	Yellow	5.0
Bromophenol Red	Yellow	Red	6.1
Bromocresol Purple	Yellow	Purple	6.46
Phenol Red	Yellow	Red	8.03
Thymol Blue (Alkaline Range)	Yellow	Blue	9.2
Phenolphthalein	None	Red	9.3
Nile Blue A	Blue	Purple	(9.5)
Clayton Yellow	Yellow	Red	(11)
Indigo Carmine	Blue	Yellow	(12.5)
2,4-Dinitroaniline	Yellow	Violet	(15)

2. Titration with 0.1 N HCl Solution. Following the development given by Helfferich²⁷, the pK_a for weak-base ion exchangers when titrated with HCl is given by

$$pK_a = pH - \log [Cl^-] + \log (([R] + [RH^+])/2) \quad (1)$$

where "pH" is the pH of the equilibrium aqueous phase at 50% neutralization of the resin. $[Cl^-]$ is the concentration of chloride ion, which may differ from $[H^+]$ if a salt is added in the titration. $([R] + [RH^+])$ is the total concentration of ionogenic groups.

TABLE VI.

Hammett Parameters and pK_a Values for Different Basic Resins

Resin	H _o	This Work	^{pK_a} Clifford and Weber ^{28,29}
<u>Quaternary Ammonium</u>			
Bio-Rad AG-2X8		>13	
<u>Secondary Amines</u>			
Duolite A-340	12-15	7	8.7
Polyethyleneimine	12-15		
<u>Tertiary Amines</u>			
Dowex MWA-1	8-9	8.8	7.6
Dowex WGR	9.3	7.8	7.9
<u>Poly (N Oxide)</u>			
Amberlite XAD-12	6.5-8	4.4	
<u>Polyvinylpyridines</u>			
Reilly PVP	6.4	4.9	
Amberlite XE-378	6.4		
<u>Polyacrylamide</u>	2.5-4		

Table VI lists Hammett basicity parameters and values of pK_a determined in the present work, along with values of pK_a reported by Clifford and Weber^{28,29}. The order of basicities determined by these methods agrees reasonably well with the conclusions of the above discussion of Solvatochromic Parameters and Donor and Acceptor Numbers.

Basic capacities of polymeric resins were determined from potentiometric titrations with HCl and from elemental analyses, assuming that each basic group contains one nitrogen atom. These calculated capacities were compared with the capacity corresponding to the upper plateau of the composite-isotherm curve for adsorption of acetic acid. These latter capacities were determined at low pH, where there should be no complications associated with ionization of acetic acid. Results are shown in Table VII, where it can be seen the adsorption capacities agree reasonably well with the results from the other two methods for Dowex MWA-1, Amberlite XAD-12, and Bio-Rad AG-2X8. For Dowex WGR and Duolite A-340, there may be more than one nitrogen atom per basic functional group. The lower capacity for Reilly PVP

TABLE VII.

Basic Capacities Calculated by Three Different Methods

Resin	-----Capacity (meq/g)-----		
	Analysis	Titration	Plateau
Duolite A-340	8.9	4	5.8
Dowex MWA-1	4.3	4	4.3
Dowex WGR	9.7	5.6	4.2
Amberlite XAD-12	3.9	3.5	3.7
Reilly PVP	(8)	9.6	3.5
Bio-Rad AG-2X8	3.1	2.5-3.2	3

determined by adsorption may be due to the weaker basicity of the pyridyl group, or to a lack of full access to internal basic sites -- e.g., steric hindrance.

Finally, it should be stressed that no single measure of basicity and/or acidity is sufficient for fully characterizing the sorption properties of polymeric resins. Steric factors can be important, and there are also specific favored pairings of types of acidity and basicity. A good example is afforded by data reported by Chanda, et al.^{30,31} for uptake of carboxylic acids and phenolics by poly(4-vinylpyridine) and polybenzimidazole. Poly(4-vinylpyridine) has greater capacities than polybenzimidazole for phenols, whereas polybenzimidazole has greater capacities than poly(4-vinylpyridine) for carboxylic acids. One apparent difference is between ionizing acidity or basicity, and hydrogen-bonding basicity or acidity. Amphiprotic hydrogen bonding may also be a factor for the carboxylic acids²⁰.

Factors Causing Differences among Capacities of Activated Carbons

Many activated carbons contain substantial quantities of oxygen (Table II). Available evidence indicates that the oxygen tends to be present in groups such as carboxylic, quinonic, and phenolic^{32,33}. A summary of the pertinent literature and of infrared spectroscopic characterization of surface functional groups on carbons is given elsewhere⁹.

Oxygenated surface groups may act as Lewis acids, Lewis bases, or both, depending upon the nature of the group. Usually oxygen has been associated with acidity; however the effects of particular groups upon adsorption from solution depend on the relative donor-acceptor capabilities of all species involved. The increased donor-acceptor character of oxygenated carbon surfaces is the reason that highly oxidized carbons tend to be

very hygroscopic, as observed by Mahajan, et al.³⁴, Youssef, et al.³⁵, and others. It is also in keeping with the observations of Cookson³² that adsorption of decane from aqueous solution was hindered by oxygenation of carbons under all conditions, and with other similar observations.

A very simplistic view of the effects of heteroatoms on adsorption by carbons can be obtained by analyzing the data with a model that postulates an adsorbed layer of uniform, solute-enriched composition, along with non-selective pore filling by bulk liquid. With the assumption that the adsorbed layer is composed of molecules of equal cross-section area (i.e., a constant number of moles of solute plus water adsorbed), the following equation may be derived³⁶:

$$\frac{x_1 x_2}{n_o \Delta x/m} = \frac{1}{n^s} \left[x_1 + \frac{1}{K - 1} \right]$$

where

$$K = \frac{x_1^s x_2}{x_2^s x_1} \quad (3)$$

Here x is the mole fraction in solution, x^s is the mole fraction in the adsorbate, 1 is acetic acid, 2 is water, $n_o \Delta x/m$ is the composite-isotherm adsorption expressed as moles acetic acid/g carbon, and n^s is the moles of adsorbed material in the selective layer/g of carbon. The parameters K and n^s can be determined from slopes and intercepts of straight lines placed through plots of the left-hand side of Equation 2 vs. x_1 for individual carbons, as shown elsewhere⁹.

A list of values for K and n^s derived in this way is presented in Table VIII. The normalized number of moles in the

selectively adsorbed layer (n^S /surface area) is shown in Figure 7, as a function of micromoles (oxygen + sulfur + nitrogen) per m^2 surface area of the carbon. This latter quantity is taken as a crude measure of the amount of surface functionality, making the assumption that most or all of the heteroatoms are present on the surface. This should be a good assumption for oxygen and for sulfur in the case of the pyrolyzed polymers. It is less appropriate when the heteroatom arises from the original source of the activated carbon, as for sulfur in the other cases and for

TABLE VIII.

Selective Layer Sizes (Moles) and Distribution Coefficients
Fitted to Data for Adsorption of Acetic Acid
from Aqueous Solution onto Carbons.

Adsorbent	O + S + N (mol/ m^2)	n^S (micromoles/ m^2)	K (dimensionless)
<u>Carbons</u>			
Amoco GX-031	0.25	2.0	797
Union Carbide GBAC	0.59	2.0	880
Calgon Filtrasorb 400	0.96	4.0	470
Calgon Filtrasorb 300	1.05	3.3	490
Witco Witcarb 950	1.39	3.1	500
Calgon Filtrasorb 200	1.48	3.6	670
Witco Columbia	1.75	3.0	290
Calgon Filtrasorb 100	2.45	4.1	330
Norit Row 0.8S	10.63	5.4	200
<u>Pyrolyzed Polymers</u>			
Ambersorb XE-348	2.66	4.9	470
Ambersorb XE-340	6.63	5.4	200

nitrogen. If allowance is made for heteroatoms not all being on the surfaces, the points for the two Witco carbons, and to a lesser extent the points for the Calgon Filtrasorb carbons may move to the left on Figures 7 and 8. Figure 8 shows K versus the same measure of functionality.

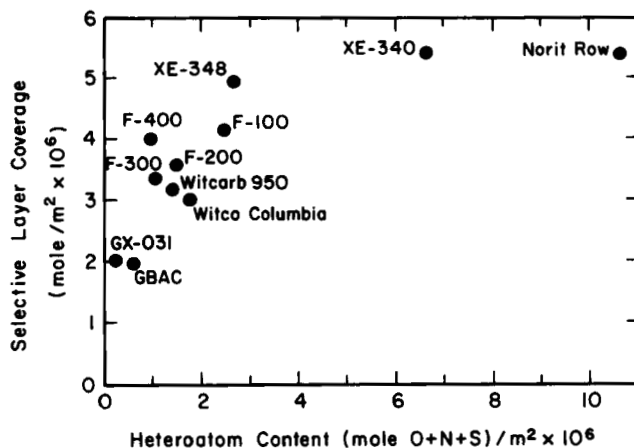


FIGURE 7

Selective layer coverage from Everett model, vs. surface density of heteroatoms.

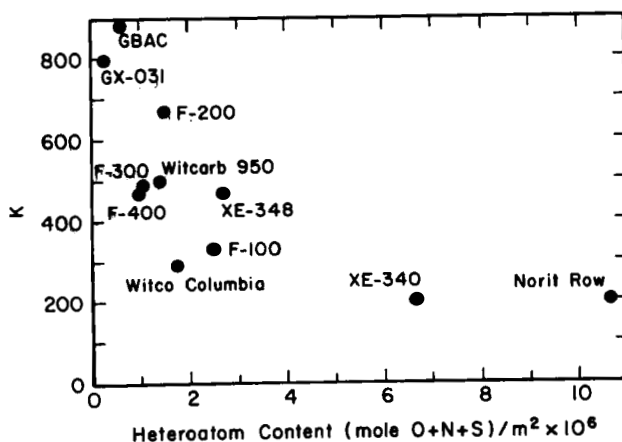


FIGURE 8

Surface selectivity from Everett model, vs. surface density of heteroatoms.

Other, similar models have been considered, such as one exchanging 4 moles of water per mole of acetic acid in the selective layer, i.e., assuming a constant volume of the selective layer. The quality of fit and the trend of the parameters are about the same as for Equation 2. Parameter fits were also made⁹ to a simple Langmuir equation and to the equations of Frumkin, Temkin, Toth, and Kiselev, as reported by Adamson¹⁷, and to the equation of Jossens, et al.³⁷, again with none of them appearing to be much superior to Equation 2.

Notice that the values of K in Table VIII are rather high, indicating very selective adsorption. Also, Figures 7 and 8 indicate an increase in the number of moles in the selective layer per unit surface area and a decrease in K as the surface density of heteroatoms increases. Since the functional groups on the carbon surfaces should be acidic for the most part, this result is in line with the conclusions from the studies of polymeric adsorbents, which show that increasing acidity (higher α or Acceptor Number) decreases selectivity for acetic acid, with respect to water.

On the molecular level, an explanation for the increase in size of the selective layer with increasing heteroatom density could be a transition from an adsorption geometry where the molecule lies flat on the surface for less polar surfaces to one where acetic acid adsorbs perpendicular to the surface with its acidic functional group associated with polar surface groups.

A plausible explanation for the trends in n^S and K in Figures 7 and 8 is surface heterogeneity. The parameters of Table VIII are fit to Equation 2 on the assumption that K is independent of surface coverage and adsorbate composition. Surface heterogeneity would be likely to cause K to be variable.

If K decreases with increasing coverage of the surface by solute, the resultant composite isotherm will exhibit a higher degree of curvature than if K is constant. Under the assumption of constant K , higher degrees of curvature lead to higher values of K when parameters are fitted to Equation 2. In the fitting process, higher K leads to lower n^S . Thus the trends of n^S and K shown in Figures 7 and 8 may result, at least in part, from greater surface density of heteroatoms giving a more homogeneous surface. Differences in surface heterogeneity may also affect the apparent nitrogen surface area in different ways; this would also affect the interpretation.

Effect of pH

The product broth of a fermentation process will usually be much more complex than the simple acetic acid - water system considered thus far. A fermentation broth is frequently buffered to a specific pH that optimizes the production rate. For a dissociating solute such as acetic acid, the pH can be expected to have a pronounced effect on the adsorption characteristics. In fact, for overall process optimization, the effect of pH on the separation scheme should be considered together with the effect of pH on the fermentation.

The effect of pH on adsorption has previously been the object of a number of investigations³⁸⁻⁴⁰. The general trend is that the adsorption of a weakly ionizable acid decreases with increasing pH. Getzen & Ward³⁸ used a simple competitive Langmuir isotherm for the ionized and unionized solutes and obtained a satisfactory fit of their data. Müller, et al.⁴⁰ developed a model which includes not only the effect of solute ionization, but also effects of surface charge, ionic strength, and surface heterogeneity. In the present work acetic acid

concentrations were high enough so that surface charge should have had only a minor effect.

The data points in Figure 9 show the measured surface excess of total acetic acid (un-ionized acetic acid plus acetate ion) on Witco Witcarb 950 as a function of pH of the aqueous solution for a constant feed concentration of 6.5% w/w total acetic acid. Similar data were also obtained for Union Carbide G-BAC⁹.

For interpretation of the data shown in Figure 9, composite isotherms were measured for adsorption of acetic acid from aqueous solution onto Witcarb 950 down to very low aqueous solute concentrations at pH = 2.3, and for adsorption of acetate ion at pH = 11. These results are shown in Figure 10. The solid curves are best fits obtained using single-solute Langmuir equations.

The solid curves shown in Figure 9 are calculated from the results in Figure 10 by means of the competitive two-solute Langmuir equation:

$$q_{1+2} = \frac{Q_1 K_1 C_1 + Q_2 K_2 C_2}{1 + K_1 C_1 + K_2 C_2} \quad (4)$$

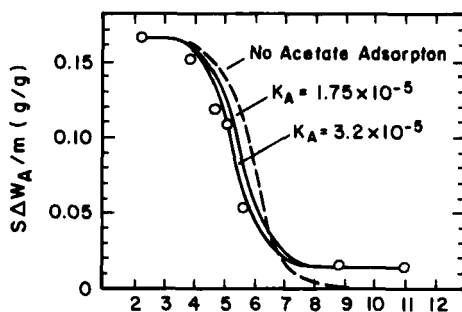


FIGURE 9
Effect of pH on the adsorption of total acetic acid onto Witcarb 950.

where 1 and 2 are undissociated acetic acid and acetate ion, respectively. The constants K and Q are pure-component Langmuir-isotherm constants determined from the low-pH and high-pH data of Figure 10. The broken line in Figure 9 is the prediction without allowance for competitive adsorption of acetate ion.

The pH of these aqueous solutions was adjusted by means of addition of NaOH. Therefore the ionic strength is not constant but varies with pH from approximately 0 to 1 M in NaCl. The pK_a of acetic acid varies from 4.76 to 4.5 over this range, the effect of which on the prediction is seen in Figure 9.

It can be seen that the competitive two-solute model fits the data well. Note also that the persistence of relatively high capacities in the pH range 5.0 to 5.5 results from the non-linearity of the isotherm for un-ionized acetic acid.

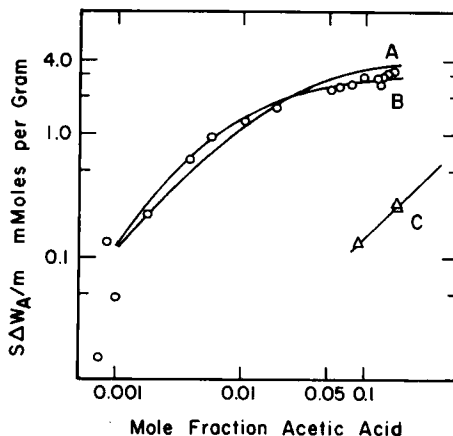


FIGURE 10

Composite isotherm for adsorption of acetic acid onto Witcarb 950, at 30°C. Curve A - best Langmuir equation fit through all data (pH 2.3). Curve B - best fit through data for mole fraction 0.005 and above (pH 2.3). Curve C - data for sodium acetate (pH 11).

The fit of data by the simple two-solute Langmuir equation is imperfect, but is probably as good as the data warrant. A model allowing for surface heterogeneity, such as that of Müller, et al.⁴⁰, may indeed fit the data better but will contain an additional adjustable parameter.

Figure 11 reports composite-isotherm capacities for total acetic acid measured for four polymeric resins -- Dowex MWA-1, Dowex WGR, Duolite A-340, Bio-Rad AG-2X8 (OH⁻ form), and Reilly PVP. The data for Dowex MWA-1 and Bio-Rad AG-2X8 were obtained by adjusting relative proportions of acetic acid and acetate ion to hold a total acetic acid concentration of 0.8 to 0.85 M. For the other resins, the pH was raised by addition of NaOH. For Dowex WGR the pH was also lowered by addition of H₂SO₄.

In each case in Figure 11 there is a drop-off of capacity in

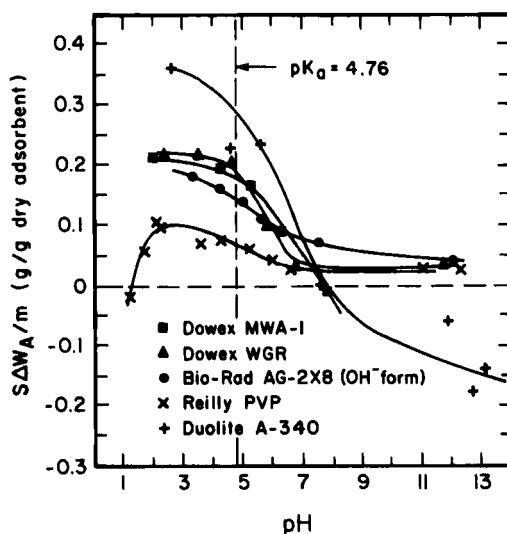


FIGURE 11
Composite sorption of total acetic acid vs. pH for various functionalized polymeric sorbents.

the range of pH 5 to 6, as would be predicted by the two-solute model, using pK_a for acetic acid in the range 4.5 to 4.76. Bio-Rad AG-2X8 exhibits adsorption of un-ionized acetic acid at low pH and ion exchange of OH^- for acetate at high pH, thereby giving two plateaux. Reilly PVP and Dowex WGR retain substantial capacities at high pH, also attributable to uptake of acetate ion. On the other hand, Dowex MWA-1 and Duolite A-340 selectively imbibe water at high pH, giving negative "uptakes" of acetate ion.

For Reilly PVP, there is also a drop-off below pH = 2, which is attributable to exchange of acetate for sulfate, which was added to lower the pH.

Chanda, et al^{30,31} report similar trends for the effect of pH on uptake capacities of phenolics and carboxylic acids from highly dilute aqueous solutions by Reilly PVP and Celanese polybenzimidazole.

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