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USE OF ADSORBENTS FOR RECOVERY OF ACETIC ACID FROM AQUEOUS SOLUTIONS PART II - FACTORS GOVERNING SELECTIVITY

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ABSTRACT

Measurements have been made of uptake of acetic acid and water from low-pH aqueous solution onto polymeric adsorbents and activated carbons. In additon to composite isotherms, isotherms were obtained for acetic acid and water individually by use of gas-chromatographic and Karl Fisher techniques for analyses of both bulk solution and the material taken up by the adsorbent. While capacities for acetic acid are determined by the surface area and the chemical nature of the adsorbent, selectivity is governed by the pore volume and the wetting and swelling tendencies of the sorbent, with the latter being particularly important for polymers. Activated carbons and pyrolyzed polymers give better selectivity than do common polymeric adsorbents.

Measurements of pore volume by immersion in various liquids were compared with pore volumes computed from nitrogen adsorption-desorption measurements and from mercury-intrusion

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porosimetry. The nitrogen adsorption-desorption results were interpreted to obtain micropore and mesopore volumes. The results from the different methods agree well, if allowance is made for lack of full wetting and for swelling tendencies. Higher selectivity for acetic acid over water is obtained for adsorbents having a large percentage of the pore volume as micropores.

Measurements of competitive adsorption of acetic acid and methyl ethyl ketone from aqueous solution onto different carbons and pyrolyzed polymers showed that a higher surface density of active hydrogen sites, as measured by reaction with $LiAlH_4$, leads to an improved selectivity for the carboxylic acid.

INTRODUCTION

In many adsorption processes, such as wastewater treatment, capacity is the primary or sole consideration in the selection of an adsorbent. However, for a separation scheme in which product is to be recovered, another important consideration is the selectivity with which the solute is removed. The selectivity for uptake of solute, as opposed to solvent, determines how concentrated the solute will be in the product recovered from the adsorbent, although additional selectivity can sometimes be achieved during regeneration as well. Selectivity among different solutes can also be important. Both forms of selectivity are considered here, with primary attention given to selectivity for solute over solvent.

Previously published adsorption isotherms for acetic acid[1,2,3, etc.] have nearly always been composite isotherms, as defined in Part I. However, the individual uptakes of solute and water cannot be determined by simply measuring the changes of

acetic acid concentration in the supernatant solution during equilibration.

The composite isotherm may be related to actual uptakes of the different components by the adsorbent as follows[4]:

$$(M_S \, \triangle x_A)/m = Y_A \, x_{Wf} - Y_W \, x_{Af} \qquad (1)$$

where

M_S = weight of the feed solution

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

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

x_{Ao} = weight fraction of water in initial aqueous solution

m = weight of dry adsorbent

Y_A = weight of acetic acid taken up per weight of dry adsorbent

x_{Wf} = weight fraction of water in aqueous solution after equilibration

Y_W = weight of water taken up per weight of dry adsorbent

Obtaining the individual uptakes of acetic acid and water, Y_A and Y_W, requires assumptions or definitions as to the boundaries of the adsorbed material. Some possible assumptions are discussed by Kipling[4]. The two most common definitions of the boundaries of the adsorbate are that of a monolayer and that of complete pore filling. The former considers only the surface layer, while the latter includes liquid that fills the pores, as well. Once an assumption is made defining the adsorbate, individual isotherms and a selectivity may be calculated. However, the selectivity calculated on this basis may not be the

same as that obtained in an operating adsorption device, because a different amount of adsorbate (or entrained material) may remain with the adsorbent.

To minimize this discrepancy, the operational definition of "adsorbate" for the present work is all fluid retained in any fashion by the adsorbent, after phase separation. This definition is identical to the pore-filling model for the special case in which the adsorbent does not swell, and interstitial fluid is removed completely. It should be stressed that the pore-filling definition includes both selectively and non-selectively imbibed liquid.

EXPERIMENTAL

Batch Equilibrations

The procedure was that described in Part I, except that after equilibration centrifugation was carried out in a 15-mL fritted glass funnel placed in a plastic centrifuge tube. The centrifuge itself was a Sorval Superspeed analytical centrifuge, Model RC-2, operated at 2000 rpm for 10 minutes. The machine was refrigerated and kept at 3 to 10°C to minimize evaporation loss. Most of the adhering bulk and interstitial liquid that can be removed from the adsorbents by centrifugation is removed under these conditions[5].

Fixed-Bed Measurements

Fixed-bed experiments were carried out in a Bio-Rad 1.5x25-cm jacketed glass column which was slurry-packed with hydrated aqueous adsorbent to a height of 15 cm, giving a packing volume of 26.5 mL. To keep the bed from fluidizing and to minimize the column dead volume, 0.5-cm glass beads were packed on top of the adsorbent bed to a height of 5 to 10 cm.

All lines and the column were filled initially with the feed aqueous solution of acetic acid. This solution was then pumped through the column by a Microflow Pulsafeeder Metering Pump (Interpace Corp., Lapp Insulator Division), and cooling water at 33°C was circulated in the column jacket. The solution flow rate was 1.0 mL/min, with the metering valve adjusted to provide a back pressure of 3 kPa, so as to minimize effects of pulsations from the pump. Five-mL samples were collected from the outlet hose in a graduated cylinder and were stored in sealed glass bottles.

Acetic acid concentrations were analyzed within 15 min, and analyses of adsorbents were made within three days. After an adsorption run, compressed laboratory air was used to blow the interstitial water out of the column, with the air flow being continued until 10 seconds after no liquid was seen leaving the column outlet. Mass balances showed that this procedure gave no significant amount of evaporation.

The desorption procedure was the same as the adsorption procedure except that solvent, instead of the acetic acid solution, was fed. Fractions were collected until concentrations of acetic acid and water were lower than 0.005 g/mL.

Analytical Methods

As for the results reported in Part I, 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 170C.

Adsorbates were recovered quantitatively from the adsorbents by back-extraction into HPLC-grade methanol (Burdick and Jackson,

Inc.), using about 10 mL of methanol to extract 1 g of adsorbent, agitated over a period of 6 hours. Analysis of these extracts for water was made by Karl Fischer colorimetric titration using a standard Karl Fischer reagent (J. T. Baker Chemical Co.). An alternative measurement of acetic acid and water was made by drying the adsorbent in an oven at 18 to 36 kPa absolute pressure and 75°C for two days, and then using this weight difference along with the depletion in acetic acid concentration observed for the raffinate phase in mass balances to calculate uptakes of acetic acid and water. These two methods gave the same results for the amounts of the individual components taken up by the adsorbent, within experimental error.

Measurement of Surface Active Hydrogen Content

Active hydrogen contents were determined by reaction with $LiAlH_4$. The reaction releases one mole of hydrogen gas from each mole of active hydrogen in surface acidic groups, such as carboxylic or hydroxyl. The method is similar to that used by Rivin[6] for carbon blacks.

A measured quantity of dry and pulverized adsorbent was placed in a 20-mL serum bottle with a magnetic stir bar. The bottle was capped with a rubber stopper, which was then pierced with a syringe needle to reduce the pressure to atmospheric. A known volume of a saturated solution of $LiAlH_4$ in diglyme [bis(2-methoxyethyl) ether] was then injected, and the bottle was stirred while the reaction proceeded for 5 min. Care was taken to prevent the reagent solution from contacting the stopper. The stopper was then pierced with a syringe needle attached to one leg of a manometer, which served to measure the volume of hydrogen released.

TABLE I.

Active Hydrogen Contents of Various Carbons, as Measured by Reaction with $LiAlH_4$.

Carbon	Active Hydrogen Content meq/g	microeq/m^2
Norit Row 0.8S	3.1 ± 0.1	4.8
Ambersorb XE-340	0.70 ± 0.01	1.79
Ambersorb XE-348	1.06 ± 0.03	1.69
Calgon Filtrasorb 100	0.86 ± 0.14	1.01
Filtrasorb 100 OX	1.37 ± 0.04	2.75
Witco Columbia	0.79 ± 0.03	0.61
Witcarb 950	0.48 ± 0.04	0.46
Amoco GX-031	1.11 ± 0.05	0.47

Active hydrogen contents measured for the various carbons are shown in Table I, expressed as milliequivalents/g and as microequivalents/m^2, and are arranged in decreasing order of active hydrogen content per unit nitrogen surface area. The active hydrogen contents of carbons determined in this way correlate relatively well with either total heteroatom (O+N+S) content or oxygen content, as given in Table II of Part I. The correlation with total heteroatom content is shown in Figure 1. The ratio of heteroatoms to active hydrogen is approximately 2:1, except for Ambersorb XE-340, where it is closer to 4:1. This may result from the preponderance of sulfonate groups in Ambersorb XE-340.

Characterization of Pore Volume and Pore-Size Distribution

Pore volumes and pore-size distributions were measured in several different ways, as follows:

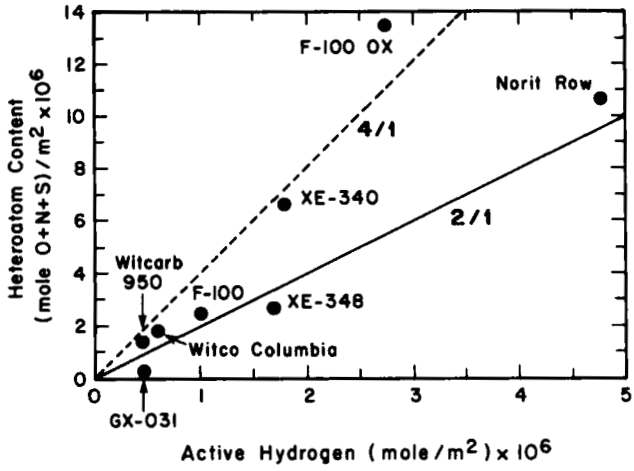

FIGURE 1
Relationship between measured total heteroatom (O+N+S) content and measured active hydrogen content, for various carbons and pyrolyzed polymers.

1. The weight increase was measured upon immersion in water (with and without methanol pretreatment), n-heptane, glacial acetic acid, and an aqueous solution containing 5% acetic acid (w/w). Excess liquid was removed by centrifugation before weighing.
2. An Aminco 60,000 psi (414 MPa) mercury-intrusion porosimeter was used to provide cumulative pore volume as a function of pore access radius down to 1.5 nm, assuming a contact angle of 140°.

3. Multi-point nitrogen adsorption and desorption isotherms were obtained using a Model 201 BET Analyzer (Porous Materials, Inc., Ithaca NY).

The procedure used for the nitrogen-sorption pore-volume analyses was, first, to degas the sample thoroughly at 200°C and 0.02 mm Hg absolute pressure for about one hour. The adsorption

leg of the isotherm was then measured by introducing known volumes of nitrogen and measuring the successively higher equilibrium pressures. As the relative pressure (ratio of pressure to vapor pressure of nitrogen) approaches unity, the procedure is reversed, removing known quantities of nitrogen from the chamber. In this way, adsorption and desorption isotherms were obtained in a single, continuous run.

The results of the nitrogen adsorption-desorption measurements were interpreted in three different ways:

1. application of the Kelvin equation, as described by Hiemenz[7],

2. the "MP" method for micropores, as described by Mikhail & Robbens[8], and

3. the "Model-less" method for mesopores, applied to the hysteresis loop, as described by Mikhail & Robbens[8] and Brunauer, et al.[9]

A non-porous reference material is required for the MP method, to generate the value of "C" in the BET equation. For this purpose electrode graphite[10] was chosen, yielding C = 3700 for the carbons. Values of micropore volume computed in this way for the carbons were generally within 10% of those computed using C = 110, the value reported by Mikhail and Robbens[8] for silica[11]. For styrene-divinylbenzene C should be close to 110.

The suggestion of Bruanauer, et al.[9] that a correction be applied to the mesopore volume to allow for an adsorbed film remaining in the pores was not followed, since the correction is small for hydraulic radii of 1.0 nm and above.

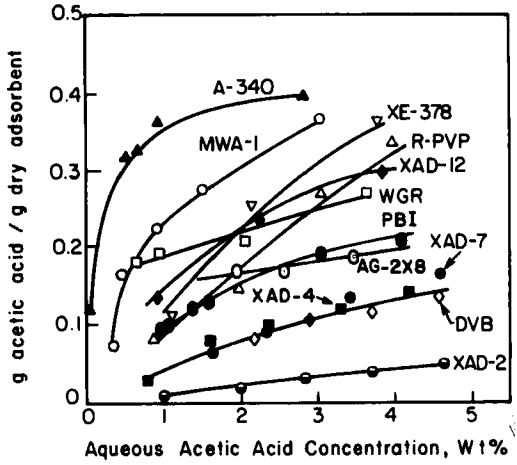

FIGURE 2
Individual sorption isotherms for acetic acid with polymeric sorbents.

RESULTS AND DISCUSSION --

SELECTIVITY FOR ACETIC ACID vs. WATER

Batch Equilibration Measurements

Figures 2 and 3 show measured individual uptakes of acetic acid for the various sorbents described in Part I. Figures 4 and 5 show measured uptakes of water, and Figures 6 and 7 show selectivities obtained between acetic acid and water. For clarity, these are reported as "inverse selectivities" -- the weight ratio of water to acetic acid taken up.

Individual uptake isotherms for acetic acid were close to the composite-isotherm uptakes reported in Part I. Only for sorbents with relatively high water uptakes was the difference substantial, and in those cases the individual uptake of acetic acid exceeded the composite uptake, as required by Equation 1.

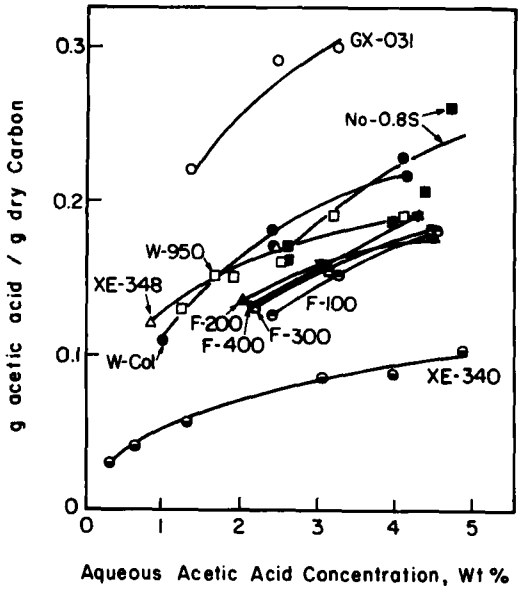

FIGURE 3
Individual adsorption isotherms for acetic acid with carbons and pyrolyzed polymers.

Comparison of Batch-Equilibration and Fixed-Bed Results

Figure 8 shows a typical result obtained from the fixed-bed measurements for adsorption with G-BAC carbon and solvent regeneration using methanol. Steps on Figure 8 correspond to collection and analysis of 5-mL portions of effluent. Similar results from other fixed-bed measurements are given by Frierman[5].

For batch-equilibration studies phase separation was accomplished by centrifugation, and in the fixed-bed studies it was accomplished by blowing air through the bed. Table II compares the individual uptakes of acetic acid and the ratios of acetic acid to water taken up, measured in the batch equilibrations shown in Figures 2-7 and in the fixed-bed experiments[5,12]. The agreement between the two different types

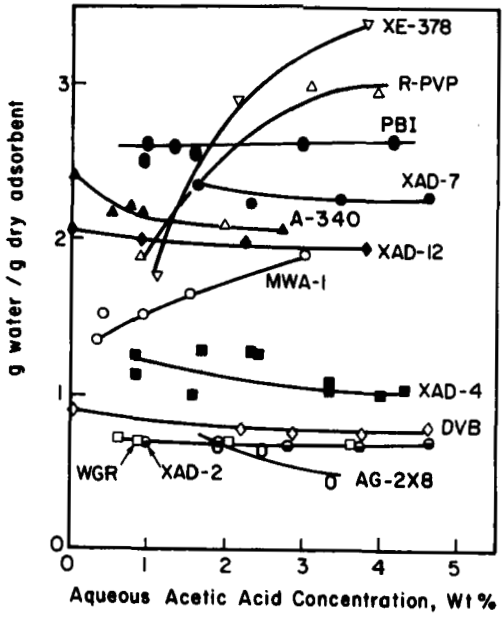

FIGURE 4
Individual sorption isotherms for water with polymeric sorbents.

TABLE II.

Comparison of Batch-Equilibration and Fixed Bed[5,6] Results for Adsorbents in Equilibrium with a 5% (w/w) Aqueous Acetic Acid Solution

[Entries are Batch Result/Fixed-Bed Result]

Adsorbent	g acetic acid/ g dry adsorbent	g acetic acid/ g water adsorbed
XAD-4	0.16/0.17	0.16/0.13
WGR	0.31/0.35	0.33/0.17
R-PVP	0.40/0.32	0.13/0.18
Witcarb 950	0.23/0.25	0.42/0.42
G-BAC	0.14/0.20	0.37/0.37
100% DVB	0.094/0.094	0.113/0.113

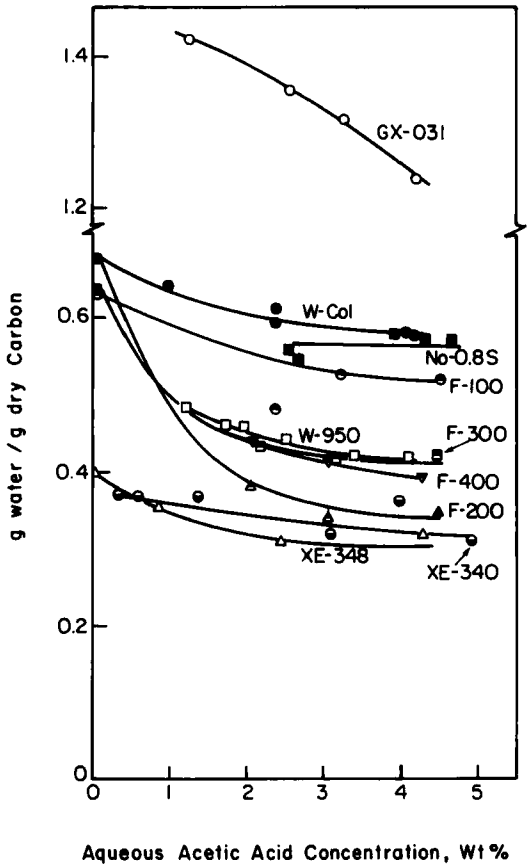

FIGURE 5
Individual adsorption isotherms for water with carbons and pyrolyzed polymers.

of experiments is generally good. Not reaching equilibrium in the fixed-bed runs would lead to lower total loadings of acetic acid and could lead to different ratios of acetic acid to water adsorbed. Less complete removal of the interstitial liquid by blowing the column with air, as opposed to centrifugation, would lead to higher acetic acid loadings and lower ratios of acetic acid to water taken up in the fixed-bed results. There are no

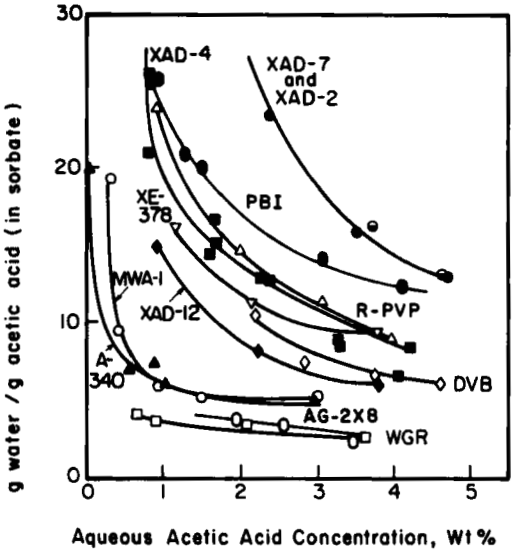

FIGURE 6
Inverse selectivity (proportion of water to acetic acid) in sorbate for polymeric sorbents.

such consistent patterns in the comparison of the data. The only case where the agreement between batch-equilibrium and fixed-bed results is poor is for water on Dowex WGR, where the mass of water adsorbed is much greater (50%) for the fixed-bed case. There data were taken when the procedure for blowing air through the column was being initially developed.

Generally speaking, the carbons (Figures 5 and 7) all have lower water capacities and better selectivities for acetic acid than do the resin adsorbents (Figures 4 and 6). Carbons have a more consolidatad structure than polymers, and polymers are subject to chain relaxation and swelling. Greater degrees of cross-linking may provide less uptake of bulk solution by the polymeric adsorbents, but this could also lead to lower transport rates.

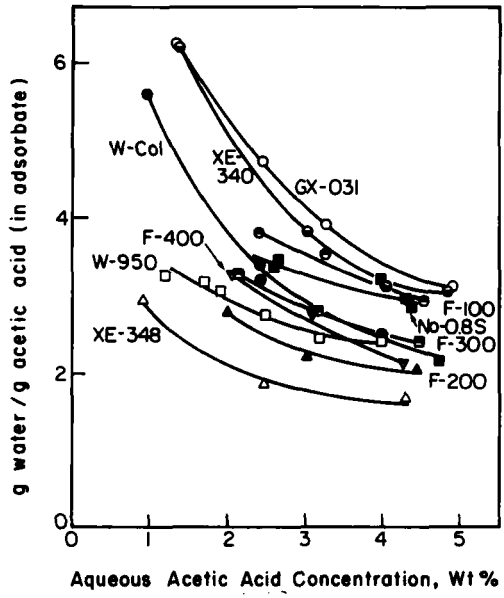

FIGURE 7
Inverse selectivity (proportion of water to acetic acid) in adsorbate for carbons and pyrolyzed polymers.

Swelling

In Figures 4 and 5 it should be noted that the water capacities of most adsorbents decrease as the concentration of acetic acid in the equilibrium solution increases. This is the behavior that would be expected for competitive adsorption between acetic acid and water for a limited number of surface sites, governed by the Law of Mass Action. For MWA-1, PVP and XE-378 the water uptake increases with increasing acetic acid concentration. This behavior must result from swelling of these adsorbents. In the absence of acetic acid the adsorbent has a low affinity for water. Adding acetic acid to the adsorbent then increases the water affinity because of the carbonyl group or other features of the adsorbed molecules or complex.

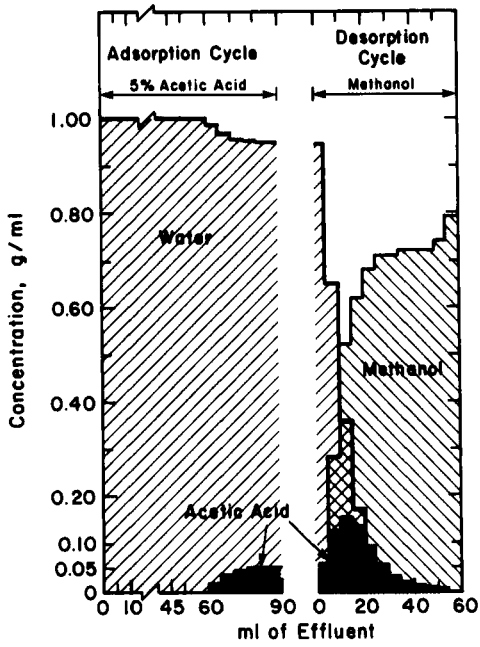

FIGURE 8
Compositions of incremental effluent samples from a fixed-bed run. Adsorption of acetic acid with Union Carbide G-BAC, followed by solvent regeneration with methanol.

The BET multi-point nitrogen sorption-desorption measurements for Ambersorbs XE-340 and XE-348, gave a desorption leg that did not return to the starting point of the adsorption leg. On the other hand, hysteresis loops for the carbons began above a relative pressure of about 0.4 and appeared to close at a relative pressure between 0.9 and 1.0. At a relative pressure of 0.1, the volume sorbed on the desorption leg was about 15 and 8 cm^3 (gas, at 0°C and 101.3 kPa) per gram sorbent higher than the volume sorbed on the adsorption leg, for XE-340 and XE-348, respectively. This phenomenon is probably attributable to swelling by nitrogen, which may also account for the fact these two materials show a much larger increase in nitrogen sorbed above a relative pressure of 0.8 than do the carbons.

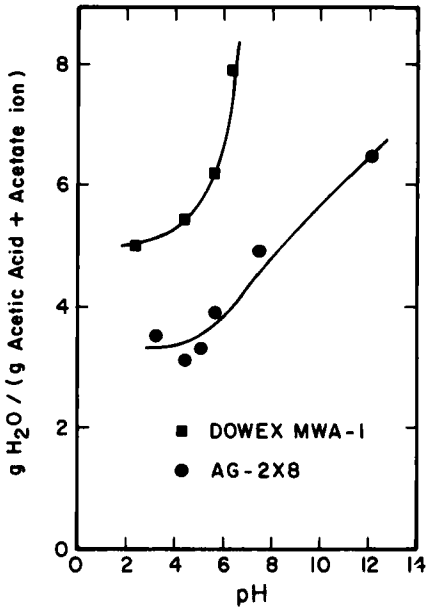

FIGURE 9
Inverse selectivity vs. pH for Dowex MWA-1 and Bio-Rad AG-2X8.

From the hydrogen contents reported in Part I and from the method of manufacture[13], it appears likely that the pyrolysis temperature for XE-340 is lower than that for XE-348. Therefore it is logical that XE-340 would swell more than does XE-348. The water uptakes and selectivities for these pyrolyzed polymers shown in Figures 5 and 7 therefore probably include contributions of both competitive surface adsorption and swelling by aqueous acetic acid solution.

Effect of pH

Figure 9 presents results of measurements of inverse selectivity, calculated from individual uptakes of acetic acid

and water, as a function of the pH of the equilibrium solution, for Dowex MWA-1 and Bio-Rad AG-2X8. As is evidenced by the composite isotherms presented in Figure 11 of Part I, the selectivity for acetic acid as opposed to water becomes much poorer as pH increases above pK_a for acetic acid. This reflects low uptake of acetate ion and some swelling resulting from the ionic content.

Relationship between Bulk-Solution Uptake and Pore Volume

In addition to the competition between acetic acid and water for specific surface sites and functional groups, the selectivity is also highly influenced by the pore-volume and/or swelling properties of the adsorbent. Solution in pores or in a gel structure which is not immediately adjacent to solid surface or polymer molecules should be taken up in a mostly non-selective fashion.

As was noted above, several different methods were used to characterize pore volume and pore-size distribution. Results for carbons and pyrolyzed polymers obtained by immersion in various liquids are shown in Table III. In each case, it is assumed that the liquid retains the density of the bulk liquid as it fills the pores, and that there is full removal of surface liquid through centrifugation. For Witco Columbia there is close agreement for different liquids. For Ambersorbs XE-340 and XE-348 the higher pore volumes with heptane and glacial acetic acid may correspond to some swelling in these liquids. For Amoco GX-031, there may be incomplete removal of methanol from the very fine pores of this high-surface-area carbon when methanol is displaced by water following pretreatment. For the Filtrasorb carbons and for Union Carbide G-BAC there may be incomplete wetting of fine pores by water and by aqueous (5% w/w) acetic acid.

TABLE III.

Pore Volumes Measured by Immersion in Liquids

	Pore Volume (mL/g dry adsorbent				
				Acetic Acid	
Adsorbent	Water*	Water**	n-Heptane	Glacial	Aqueous*
CARBONS:					
Witco Columbia	0.75	--	0.75	0.72	0.75
Witcarb 950	0.61	0.62	--	--	--
Union Carbide G-BAC	0.58	0.62	0.66	0.68	0.60
Amoco GX-031	1.65	1.49	1.60	1.55	--
Filtrasorb 300	0.61	--	0.67	--	0.60
Filtrasorb 400	0.62	--	0.68	0.70	0.60
Norit Row 0.8S	0.76	0.83	--	--	--
PYROLYZED POLYMERS:					
Ambersorb XE-340	--	0.41	0.53	0.52	0.42
Ambersorb XE-348	--	--	0.52	0.52	0.47

-- Not Measured

* - Without pretreatment

** - Pretreated by immersion in methanol, followed by replacement of methanol by water.

Table IV shows pore volumes measured by mercury porosimetry and by nitrogen adsorption-desorption using (1) the Kelvin equation (2) the MP method for micropores, and (3) the "model-less" method for mesopores. For these results, micropores were taken to have hydraulic radii below 1.0 nm, mesopores to have hydraulic radii between 1.0 and 8.0 nm, and macropores to have hydraulic radii greater than 8.0 nm. Also included for comparison are the n-heptane immersion values from Table III. Since both n-heptane and nitrogen are non-polar fluids, wetting and swelling properties should be similar.

TABLE IV.

Comparison of Pore Volumes for Activated Carbons and Pyrolyzed Polymers.

(Pore Volume in mL/g dry adsorbent)

Adsorbent: / Method:	Un. Car. G-BAC	Witco 950	Witco Col.	Amoco GX-031	Calgon F300	Calgon F400	Ambersorb XE-340	Ambersorb XE-348
n-Heptane Immersion	0.66	--	0.75	1.60	0.67	0.68	0.53	0.52
Kelvin Eq.	--	0.63	--	1.65*	--	--	0.72	--
Hg Intrusion	0.36	0.27	--	1.14	--	--	0.42	--
Micropore (MP Method)	0.54	--	0.55	1.09	0.53	0.48	0.20	0.33
Mesopore	0.12	--	0.04	0.03	--	0.06	0.12	0.11
Micropore + Mesopore	0.66	--	0.59	1.12	--	0.54	0.32	0.44
Micropore + Hg Intrusion	0.76	--	--	1.99	--	--	--	0.65
% Micropore**	82	--	73	68	79	71	38	63
% Micropore + Mesopore***	100	--	79	70	--	79	60	85

---

* - Reported by Marsh, et al.[14]
** - Micropore as % of n-heptane immersion.
*** - (Micropore + Mesopore) as % of n-heptane immersion.

Comparisons were made of pore-size distributions indicated by the porosimeter measurements and the BET analysis using the Kelvin equation, for Witcarb 950 and Ambersorb XE-348[12]. In the range of pore radii common to both methods (1.5 to 50 nm) the BET Kelvin method gives pore volumes ranging from 10 to 60% lower than the porosimeter.

Also included in Table IV are pore volumes obtained by adding the MP method micropore volumes to the "model-less" method

mesopore volumes ("Micropore + Mesopore"), and by adding the MP method micropore volumes to the incremental pore volume obtained by mercury porosimetry between 2.0 nm and 2500 nm pore radius ("Micropore + Hg Intrusion"). 2.0 nm was selected as the lower limit since the hydraulic radius is 1/2 the actual radius for cylindrical pores, and 1.0 nm was the upper-limit hydraulic radius taken for the MP micropore analysis. 2500 nm was taken as an upper limit so as to exclude any mercury intrusion volume attributable to interstitial spaces between particles.

From Table IV the following observations can be made:

1. Pore volumes determined by mercury intrusion are less than those determined by immersion in n-heptane or by the Kelvin equation, because the micropore volumes are substantial. Mercury intrusion does not measure most of the micropore volume.

2. The sums of the MP micropore volumes and the mercury-intrusion volumes for 2.0 < pore radius > 2500 nm exceed the heptane-immersion pore volumes by 15% to 25%. This can reflect a failing of the assumptions in any of the three methods, especially the 140^{o} contact angle assumed for mercury intrusion.

3. The micropore volumes are large fractions of the total pore volume for the carbons, but less so for the two pyrolyzed polymers. The mesopore volumes are larger fractions of the total for the pyrolyzed polymers, notably Ambersorb XE-340.

4. Adsorbents having a larger percent of the total pore volume present as micropores give better selectivities (less water uptake per acetic acid uptake). This can be seen by

comparing Table IV with Figure 7. This result is logical since material should be taken up more selectively in micropore volume than in mesopore or macropore volume. Another way of viewing this is to recognize that the ratio of selective adsorption surface to pore volume is greater for the micropores.

Given the above discussion, the agreement is good between pore volumes measured by immersion in aqueous and non-aqueous liquids, and by the various independent methods, as long as proper allowance is made for incomplete wetting and swelling. Thus it can be concluded that the selectivity for acetic acid (solute) over water (solvent) is primarily determined by the ratio of surface area to pore volume. Increased micropore volume as a fraction of total pore volume increases selectivity, swelling decreases selectivity, and lack of full wetting increases selectivity.

RESULTS AND DISCUSSION -- SELECTIVITY AMONG SOLUTES

A few experiments were made to determine the selectivities of adsorption of multiple organic solutes from aqueous solution. Figure 10 shows the results of measurements for simultaneous adsorption of acetic acid and methyl ethyl ketone (MEK) from aqueous solution onto various carbons and pyrolyzed polymers. The point marked "F100/OX" is for a sample of Calgon Filtrasorb 100 carbon which had been oxidized by heating it in concentrated nitric acid for three hours at 50°C, similar to the method described by Puri and Bansal[15]. The aqueous feed for these batch equilibrations was 2.5% w/w of each solute, and the pH was buffered at 2.0 by a mixture of tartaric and phosphoric acids and potassium biphthalate[12]. The buffering was used because the pH

would otherwise vary with the degree of adsorption of acetic acid. Experiments with an unbuffered feed showed that the presence of the buffer did not significantly affect the results.

The results are reported as Q_1c_2/Q_2c_1, where Q is the amount adsorbed, c is the concentration in the equilibrium solution, and 1 and 2 are acetic acid and MEK, respectively. Experiments at 1% w/w total feed solute content confirmed that this quantity changes very little with feed composition, as would be expected from a simple competitive Langmuir adsorption model.

In Figure 10 the adsorption selectivities are plotted against the surface density of active hydrogen, as determined by the $LiAlH_4$ method (Table I). For activated carbons, the selectivity for acetic acid over MEK increases with increasing surface acidity. Similar results were found[12] for competitive adsorption of acetic acid and acetone, where the selectivity factor actually changes from a value less than one (about 0.6) at low surface density of active hydrogen to a value greater than one (about 1.5) at high surface density of active hydrogen. These results can be rationalized by the concept that higher surface acidity encourages resonance hydrogen-bonded adsorption of the carboxylic group of acetic acid, with this effect outweighing any enhanced affinity of the oxidized surface for the carbonyl group of the ketone.

Also included in Figure 10 are predictions obtained from measurements[12] of independent adsorption isotherms of acetic acid and MEK, used together with the ideal adsorbed solution theory of Radke and Prausnitz[16] to predict the selectivity of adsorption. These predictions give good agreement for lower surface densities of active hydrogen, but indicate increasingly greater departures from ideality of the surface phase as surface acidity increases.

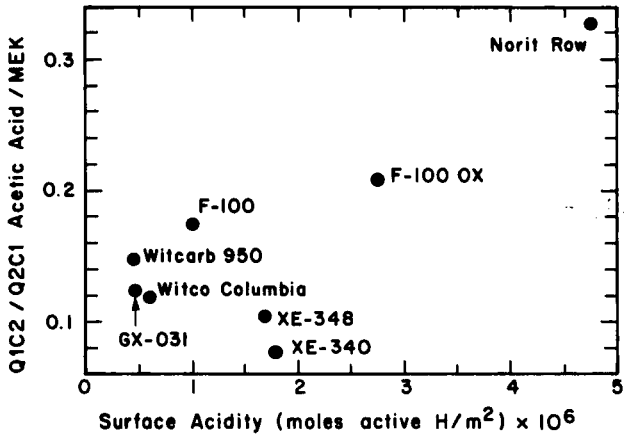

FIGURE 10
Measured separation factors for competitive adsorption of acetic acid and methyl ethyl ketone onto various carbons and pyrolyzed polymers.

Measurements of competitive sorption of acetic acid and MEK by Reilly PVP showed virtually complete selectivity for acetic acid, as might be expected from the fact that the pyridyl group is strongly basic, while the ketone is basic but not acidic and acetic acid is both acidic and basic.

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