Title

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Abstract

Measurements were made of preferential uptakes of acetic acid from aqueous solution onto basic polymer sorbents. Individual uptakes of water and acetic acid were measured as well. The sorption equilibria were interpreted through a chemical complexation model yielding sorption affinities and capacities for acetic acid. Basicity scales, such as pKa and Gutmann Donor Number (DN) based upon the monomeric functional group chemistry, were shown to explain the trends in sorption affinities. The use of different solvents to leach sorbed acetic acid from basic polymer sorbents was investigated as a means of regenerating the sorbents. It was found that regeneration can be improved by using solvents of high donicity. Aqueous ammonia proved to be effective for regenerating moderately strong base sorbents.

Table of Contents

Abstract

Chapter 2: Quantitative Determination of Basicity and Linear Free Energy Relations

Chapter 3: Sorption of Acetic Acid

Chapter 4: Recovery of Sorbed Acetic Acid

Appendices

List of Figures

Figure Page

List of Tables

Chapter 1: Introduction

Organic chemicals such as carboxylic acids, alcohols, and glycols can be produced by large-scale fermentation. Product recovery is difficult since these carbochemicals are produced in relatively dilute, complex solutions. Also of importance in selecting a separation scheme for product recovery is that biological systems are sensitive to contamination and heat.

Strategies for recovering these products have taken different routes depending on whether the solute has a higher or lower boiling point than water. Most carboxylic acids have higher boiling points than water. Acetic acid is less volatile than water, and the relative volatility of water to acetic acid is close to one at low acid concentrations[1]. Because of this, an alternative to conventional distillation is very desirable. Alternative separation methods which have been commercialized include azeotropic distillation[2] and solvent extraction combined with azeotropic distillation[3,4,5]. Product recovery schemes which are under development include membrane separation[6], solvent extraction with chemically complexing extractants[7,8,9,10], and adsorption[11,12].

Solid sorbents, which include adsorbents and absorbents, can selectively recover carbochemicals without contamination or heating recycle streams. High surface area adsorbents capitalize on the surface activities of these products -- effecting separation by excluding water via a hydrophobic surface. Absorbents, like weak base ion exchange resins, utilize basic chemical functional groups to complex preferentially with carboxylic acids such as acetic acid.

This work has focussed on the utility of solid phase chemical functional groups in recovering carboxylic acids from dilute aqueous solution. Specifically, the properties of weak base ion exchange resins that affect the sorption and recovery of carboxylic acids from aqueous solution were investigated. Basic polymer sorbents are classified as weak base ion exchange resins if the basic functional groups do not remain ionized at high pH.

However, so-called weak base ion exchangers such as amines are relatively strong bases, and they can readily sorb weak and strong acids from aqueous solution. In fact, at dilute concentrations, the selective removal (composite uptake) of weak acids versus water can be greater than that for activated carbons[11]. Also, unlike activated carbons, basic sorbents can selectively recover acids from complex mixtures such as fermentation broths which can contain alcohols, glycols, carboxylic acids, and other substances.

Weak base exchangers have been used previously to remove both weak and strong acids from aqueous solution[13,14,15,16,17]. However, systematic studies of resin basicity are not available, and studies of bulk solution uptake due to pore filling and swelling are scarce. Our focus has been to understand how exchanger properties such as functional group basicity and matrix chemistry affect sorption affinity, imbibition of liquid due to swelling, and regenerability. Acetic acid is used as a prototype carboxylic acid solute. The goal is to define the optimal basicity and structural chemistry of a basic polymer sorbent for the recovery of carboxylic acids from dilute aqueous solution.

A wide variety of nitrogen-based functional group sorbents has been investigated in this work. Most of the sorbents are commercially available, while a few are experimental. A tabulation of the basic polymer sorbents is provided in Table 1-1. Gel sorbents are microporous gels; solution uptake is accomplished primarily by swelling. Macroreticular sorbents are highly cross-linked and have pore sizes on the order of several hundred Ångströms; solution uptake is primarily by pore filling.

Table 1-1. Source and Classification of Basic Ion Exchangers

Sorbent Designation	Source	Sorbent Type (Macro, Gel, or Other)	Functional Group
Amberlite IR-4B	Rohm & Haas Corp.	Gel	Phenol-HCHO-Polyamine
Amberlite XAD-12	Rohm & Haas Corp.	Macro	N-oxide
Amberlite XE-309	Rohm & Haas Corp.	Macro	4-methyl-5-vinyl pyridine
Amberlite XE-378	Rohm & Haas Corp.	Gel	2-methyl-5-vinyl pyridine
Amberlite XE-379	Rohm & Haas Corp.	Macro	3-methyl-5-vinyl pyridine
Aurorez	Celanese Chemical Co.	Fixed Micropores*	Benzimidazole
AG-2X8	Bio-Rad Labs.	Gel	4° amine
Bio Gel P-4	Bio-Rad Labs.	Gel	Amide
Dowex MWA-1	Dow Chemical Co.	Macro	3° amine
Dowex WGR	Dow Chemical Co.	Gel	Epoxy-amine
Duolite A-340	Rohm & Haas Corp.	Gel	Epoxy-amine
Duolite ES-561	Rohm & Haas Corp.	Macro	Phenol-HCHO-Polyamine
P4VP	Reilly Tar & Chem. Co.	Gel	4-methyl-5-vinyl pyridine

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*Resin is microporous with average pore diameter of 80 Å. Swelling in water is 5%.

Chapter 1 References

1 Sanchez, P.A., M.S. Thesis, Dept. of Chemical Engineering, University of California, Berkeley (1983) p. 3 .

2 Othmer, D.F., Ind. Eng. Chem., 27, 250 (1935).

3 King, C.J., "Acetic Acid Extraction", in "Handbook of Solvent Extraction", Lo, T.C., Baird, M.H., Hanson, C., eds., John Wiley and Sons, p. 567 (1983).

4 Jones, E.L., Chem. & Ind., 38, 1590 (1967).

5 Hanson, C., Chem. Eng., 86, 83 (1979).

6 Busche, R.M., Biotechnology and Bioengineering Symp. No. 13, 597 (1983).

7 Helsel, R.W., Chem. Eng. Prog., 73, 55 (1977).

8 Wardell, J.M., King, C.J., J. Chem. Eng. Data, 4, 64 (1978).

9 Ricker, N.L., Pittman, E.F., King, C.J., Journal of Separation Process Technology, 1, 36 (1980).

10 Tamada, J., A., Ph.D. Dissertation, Dept. of Chemical Engineering, University of California, Berkeley (1988).

11 Kuo, Y., Munson, C.L., Rixey, W.G., Garcia, A.A.,Frierman, M., King, C.J., Separation and Purification Methods, 16, 31 (1987).

12 Chanda, M., O'Driscoll, K.F., Rempel, G.L., Reactive Polymers, 4, 39 (1985).

13 Adams and Holmes, J. Soc. Chem. Ind., 54, 1T (1935).

14 Myers, R.J, Eastes, J.W., Urquhart, D., Ind. Eng. Chem., 33, 1270 (1941).

15 Bishop, J.A., J. Phys. Chem., 50, 6 (1946).

16 Petersen, Sigfried, Ann. N.Y. Acad. Sci., 57, 144 (1953).

17 Sheperd, E.J., Kitchener, J.A., J. Chem. Soc. London, 86 (1957).

Chapter 2: Quantitative Determination of Basicity and Linear Free Energy Relations

An integral part of the characterization of basic ion exchange resins is the quantitative determination of base strength. Of primary importance is how the resin basicity relates to (1) the sorption affinity for carboxylic acids; (2) the selectivity for carboxylic acids over water; and (3) the reversibility of the resultant acid-base complex. The focus here will be on the nature of the monomeric functional group responsible for the resin basicity, with less regard for the polymer matrix. It is believed that for these three properties, the basicity of the monomeric unit plays an important role. The scales considered for resin characterization are derived from the following approaches: the familiar Bronsted-Lowry pKa scale [1,2], Gutmann Donor and Acceptor Numbers [3,4,5,6,7,8], the Drago E&C equation [9,10,11,12,13,14,15,16] and the solvatochromic comparison method [17,18,19,20,21,22,23,24,25].

2.1 Gutmann Donor-Acceptor Theory

Gutmann's scales are measures of Lewis acidity and basicity. Donor numbers (DN) are defined as the molar enthalpy of reaction of a highly diluted solution of a donor solvent (D) and antimony pentachloride in 1,2-dichloroethane:

$$D \;+\; SbCl_5 \;\rightarrow\; D-SbCl_5 \qquad -\Delta H_{SbCl_5} = DN \qquad\qquad \textit{Equation}\;\; 2-1$$

The major assumptions in the use and interpretation of donor numbers are: (1) only 1:1 adducts are formed; (2) DN is a measure of the equilibrium constant for the 1:1 adduct formation, as well as the energy of the D-$SbCl_5$ bond; and (3) the relative base strengths derived using $SbCl_5$ hold for other acceptor acids.

The third assumption has been questioned by several researchers. In fact, Gutmann cautions against the use of DN for predicting interactions between soft donor-acceptors, since $SbCl_5$ is classified as a hard acceptor[3]. The terminology of soft and hard acids and bases stems from a delineation put forward by Pearson[26] to help unify observations from earlier workers. Pearson believed it useful to separate acids and bases into two categories. Generally speaking, a hard acid is one that prefers to associate with a hard base, and pKa values can rationalize equilibrium and kinetic data for these species. Likewise, soft acids prefer soft bases, but in this case acid/base interactions of the soft Lewis type are more important. Since Gutmann based the DN scale on a hard acid, pKa values should correlate with DN for those solvents which exhibit ionizing acidity/basicity. This relationship is explored in a later section. A summary of DN values for 60 solvents is reproduced in Table A-1 of Appendix A.

Acceptor numbers are derived in a somewhat analogous fashion. Triethyl phosphine oxide (Et_3PO) is the reference donor. However, in this case the pure solvent (or acceptor) is used and the ^{31}P chemical shift induced by adduct formation is used to develop the scale. Arbitrarily, an AN value of 0 is assigned to hexane and 100 for $SbCl_5$. The other values are scaled accordingly using the ^{31}P chemical shifts. Interpretations and uses of AN follow the same basic assumptions stated for DN. Also in Appendix A is a table of AN values and ^{31}P NMR shifts.

2.2 Drago E&C Equation

Drago and coworkers[9-16], propose that the E&C equation:

$$-\Delta H = E_A E_B + C_A C_B \qquad \textit{Equation} \quad 2-2$$

can quantitatively predict the enthalpy of adduct formation (–ΔH) for a Lewis acid-base interaction. E_A and E_B are believed to reflect the electrostatic properties, while C_A and C_B reflect the covalent properties, of the acceptor and donor, respectively, which form a 1:1 adduct in the gas phase or in a weakly solvating solvent. The parameters were derived empirically from experimentally determined –ΔH values by fixing four sets of E&C parameters and using a least-squares regression analysis. In their compilations of data, the published E&C values have changed with the number and accuracy of their enthalpy data, as well as with their choice of compounds to include in the system. A table of their most recent values is reproduced in Table A-3 of Appendix A.

2.3 Solvatochromic Comparison Method

Kamlet, Abboud, Abraham, and Taft[17-25] have compiled a set of solvatochromic parameters π^*,α, and β which are utilized in developing linear free energy relations. The π^* parameter reflects solvent dipolarity/polarizability. It also appears that π^* can reflect solvent acidity. This will be discussed in the next section. β is a measure of the solvent's ability to donate an electron pair, and it is related to the Gutmann donor number as we will see in a later section. The α scale is an acidity parameter and provides a measure of the solvent's ability to donate a proton. One of the strengths of this method is that these properties were arrived at by averaging and comparing data obtained using different spectral techniques and systems, as well as data from a variety of other thermodynamic experiments. The researchers argue that other acid/base scales lump solvent interactions together while their system more realistically assesses the impact and importance of the different phenomena involved. A tabulation of π^*,α, and β is reproduced in Table A-4 of Appendix A.

2.4 Comparison and Correlation of Different Scales

Because of inherent similarities in the way that the above mentioned acid/base scales were developed, it is not surprising that there can be direct near-quantitative agreement between parameters from different systems. Moreover, as previously pointed out, the Gutmann DN parameters are based on measurement of a hard acceptor interacting with a donor. This would suggest that DN could correlate with pKa. Correlating and comparing parameters from different acid/base scales serves not only to provide a way of estimating missing or unavailable parameters in one system, but also emphasizes and strengthens the premise of quantitatively scaling solvent properties for use in predicting equilibrium or kinetic constants via linear solvation free energy relations (LFER). Limitations of a particular system are also brought out when these comparisons are made.

In Figures 2-1 and 2-2, Gutmann DN and AN for several solvents are compared with values of pKa in water at about 25 °C [27,28,29]. For the bases, as with the Bronsted pKa scale, the amines and ammonia are classified by the Gutmann scale as much stronger donors than pyridine. The pKa values for tetramethylurea and dimethylacetamide should be slightly higher than indicated on Figure 2-1 because pKa values for urea and acetamide are used instead, due to unavailability of the actual values. The small subset of data shown in these figures indicate that DN and AN generally correlate with pKa. Gutmann's scale may then take into account hard acid/base interactions.

Kamlet, Abboud and Taft[19,21] have pointed out relationships between Gutmann's DN and their β parameter, as well as between AN and α and π^*. Figure 2-3 shows that DN and β correlate quite well for all the available solvents except for 1,2-dimethoxyethane, pyridine, and most notably triethylamine. Pyridine is classified by Pearson as being a borderline base, while triethylamine is considered to be a hard base. These exceptions point out that the β scale emphasizes soft donicity while DN more heavily weights hard donicity.

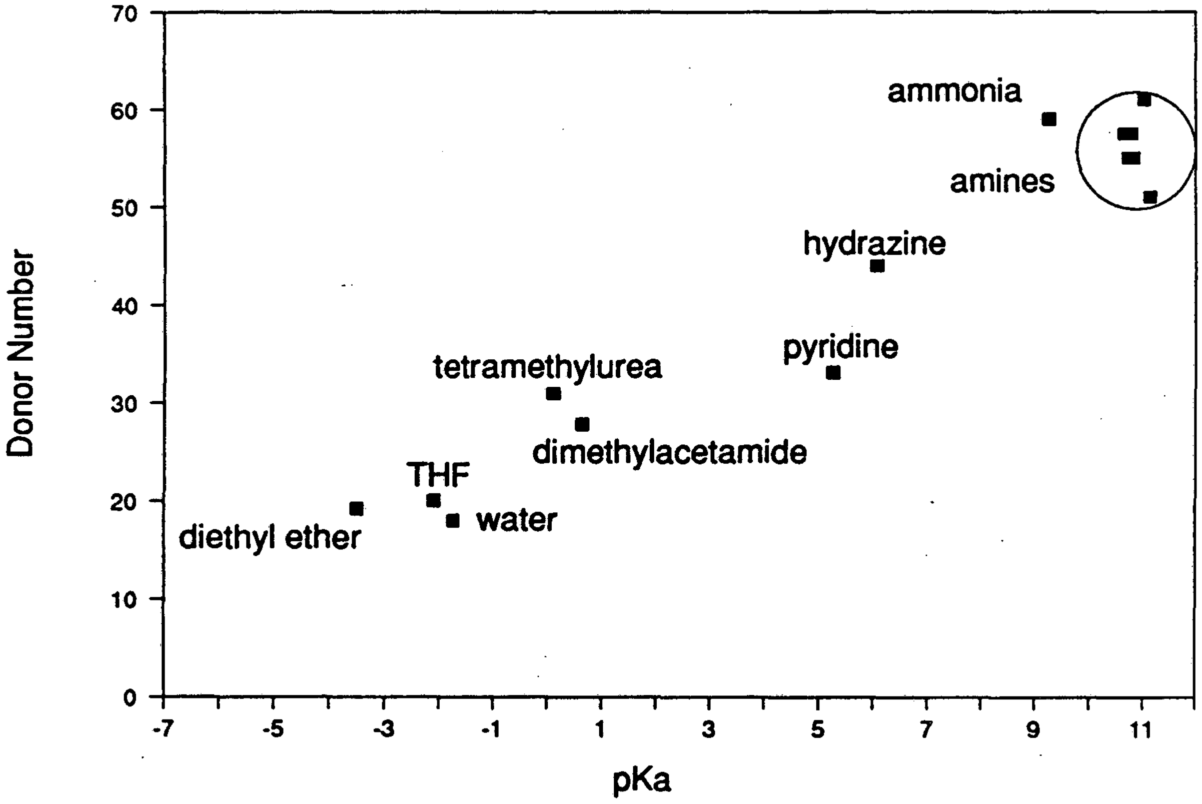


Figure 2-1. Comparison of DN With pKa for Various Solvents

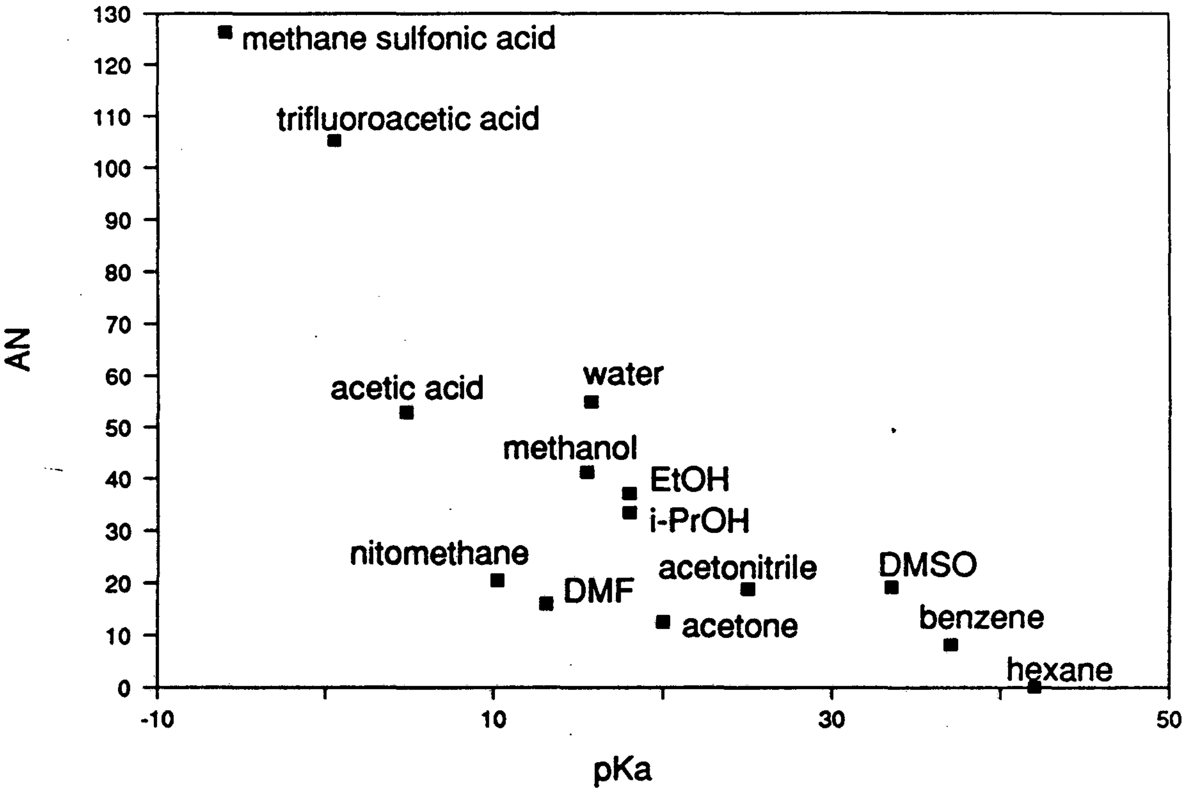


Figure 2-2. Comparison of AN With pKa for Various Solvents

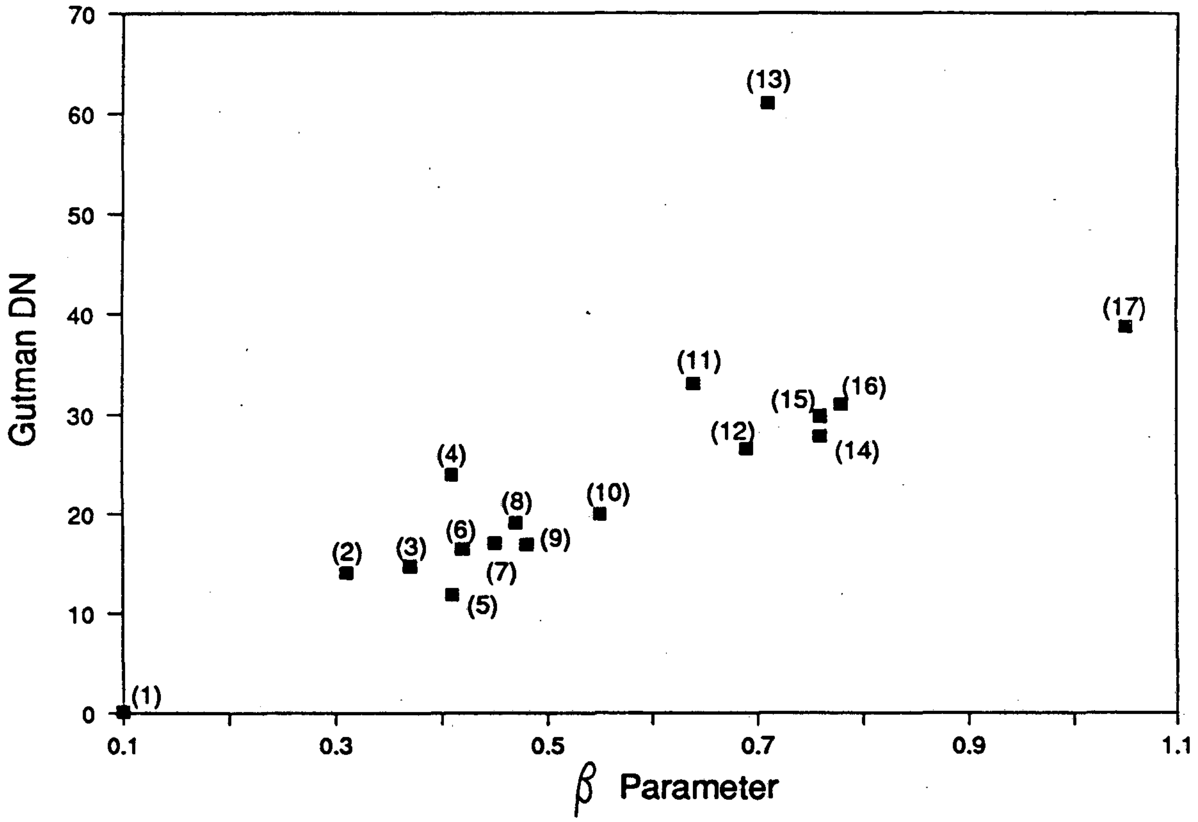


Figure 2-3. Comparison of DN With Solvatochromic β Parameter

Key to solvents Listed

(1) benzene
(2) acetonitrile
(3) p-dioxane
(4) dimethoxyethane
(5) benzonitrile
(6) methyl acetate
(7) ethyl acetate
(8) diethyl ether
(9) acetone
(10) tetrahydrofuran
(11) pyridine
(12) dimethyl formamide
(13) triethylamine
(14) dimethyl acetamide
(15) dimethyl sulfoxide
(16) tetramethylurea
(17) hexamethyl phosphoramide

From the comparisons shown in Figures 2-4 and 2-5 between the Drago E&C equation and β, we can see that for both hard ($SbCl_5$) and soft (I_2) reference acids, the same discrepancies between these two systems are present for borderline and hard bases. Figures 2-6 and 2-7 show that the C parameter plays the dominant role in the calculation of ΔH, since the scatter in the plot of C_B vs. β is similar to that in Figures 2-4 and 2-5. Recall that increasing values of C reflect increasing importance in soft or covalent character in the donor-acceptor interaction. Gutmann DN and the Drago E&C equation agree reasonably well as can be seen in Figure 2-8. Ammonia is the most notable outlying point, and the values for ethylamine also do not agree as well as the rest of the solvent values. Figures 2-9 and 2-10 show that the changes in the C parameter predominantly dictate changes in ΔH for these solvents, again because the scatter in Figure 2-9 is similar to that in Figure 2-8. Figure 2-10 also illustrates that E_B correlates with DN except for the amines and HMPA (hexamethylphosphoramide). Given that E_B reflects hard or electrostatic character, this correlation corroborates that the DN scale tends to emphasize hard interactions. To generalize the above observations several points can be made: (1) the DN scale emphasizes hard and borderline basicity; (2) the β scale emphasizes soft basicity; (3) the E&C equation emphasizes soft basicity and can deal with some amine solvents which exhibit borderline to borderline-hard basicity.

In sharp contrast to the discrepancies between β and DN, AN correlates well with α for HBD (hydrogen bond donor) solvents [19,21]. Figure 2-11 shows the relationship between α and AN for all the solvents for which data are available. The clump of points with $\alpha = 0$ are non-HBD solvents. When solvent polarity is taken into account using the π* parameter, both HBD and non-HBD solvents can be correlated resulting in the following equation:

$$AN = 1.3 + 14.34\pi^* + 34.78\alpha \qquad r^2 = 0.981 \qquad \textit{Equation} \quad 2-3$$

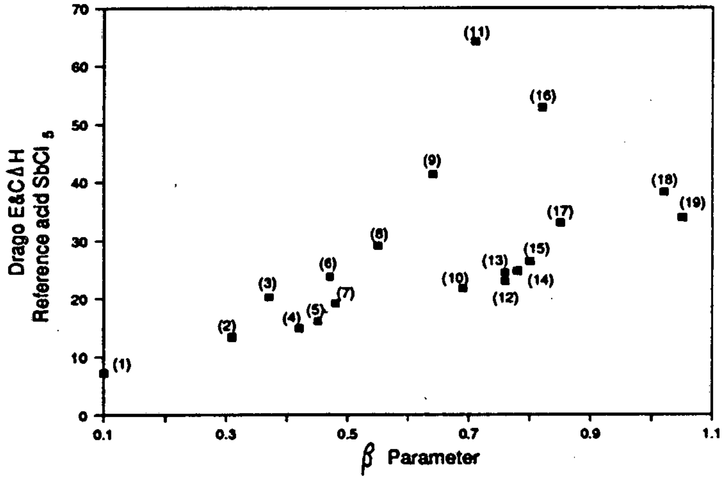


Figure 2-4. Comparison of Drago Enthalpy With Solvatochromic β Parameter. Reference Acid is $SbCl_5$.

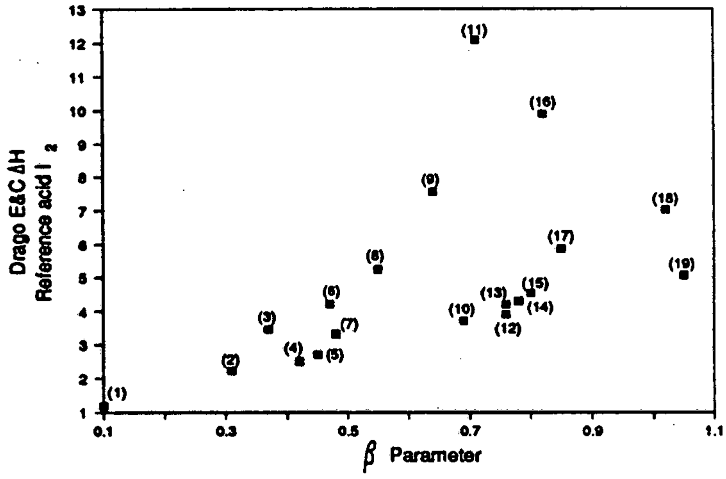


Figure 2-5. Drago Enthalpy Using I_2 as Reference Acid Vs. β Parameter

<u>Key to solvents Listed</u>

(1) benzene
(2) acetonitrile
(3) p-dioxane
(4) methyl acetate
(5) ethyl acetate
(6) diethyl ether
(7) acetone
(8) tetrahydrofuran
(9) pyridine
(10) dimethyl formamide
(11) triethylamine
(12) dimethyl acetamide
(13) dimethyl sulfoxide
(14) tetramethylurea
(15) tetramethylene sulfoxide
(16) 1-methylimidazole
(17) pyridine-N-oxide
(18) trimethylphosphine oxide
(19) hexamethyl phosphoramide

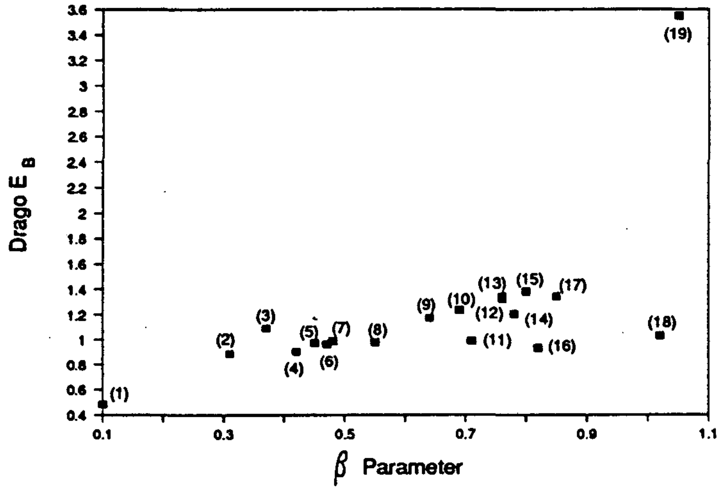


Figure 2-6. Drago E_B Vs. β Parameter

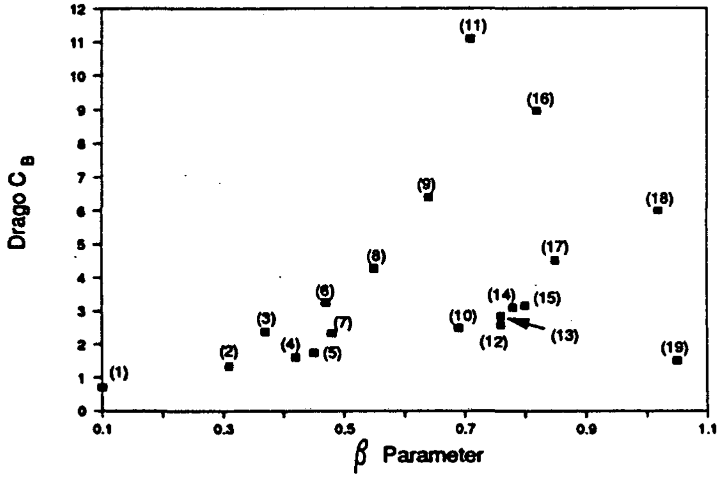


Figure 2-7. Drago C_B Vs. β Parameter

Key to solvents Listed

(1) benzene
(2) acetonitrile
(3) p-dioxane
(4) methyl acetate
(5) ethyl acetate
(6) diethyl ether
(7) acetone
(8) tetrahydrofuran
(9) pyridine
(10) dimethyl formamide
(11) triethylamine
(12) dimethyl acetamide
(13) dimethyl sulfoxide
(14) tetramethylurea
(15) tetramethylene sulfoxide
(16) 1-methylimidazole
(17) pyridine-N-oxide
(18) trimethylphosphine oxide
(19) hexamethyl phosphoramide

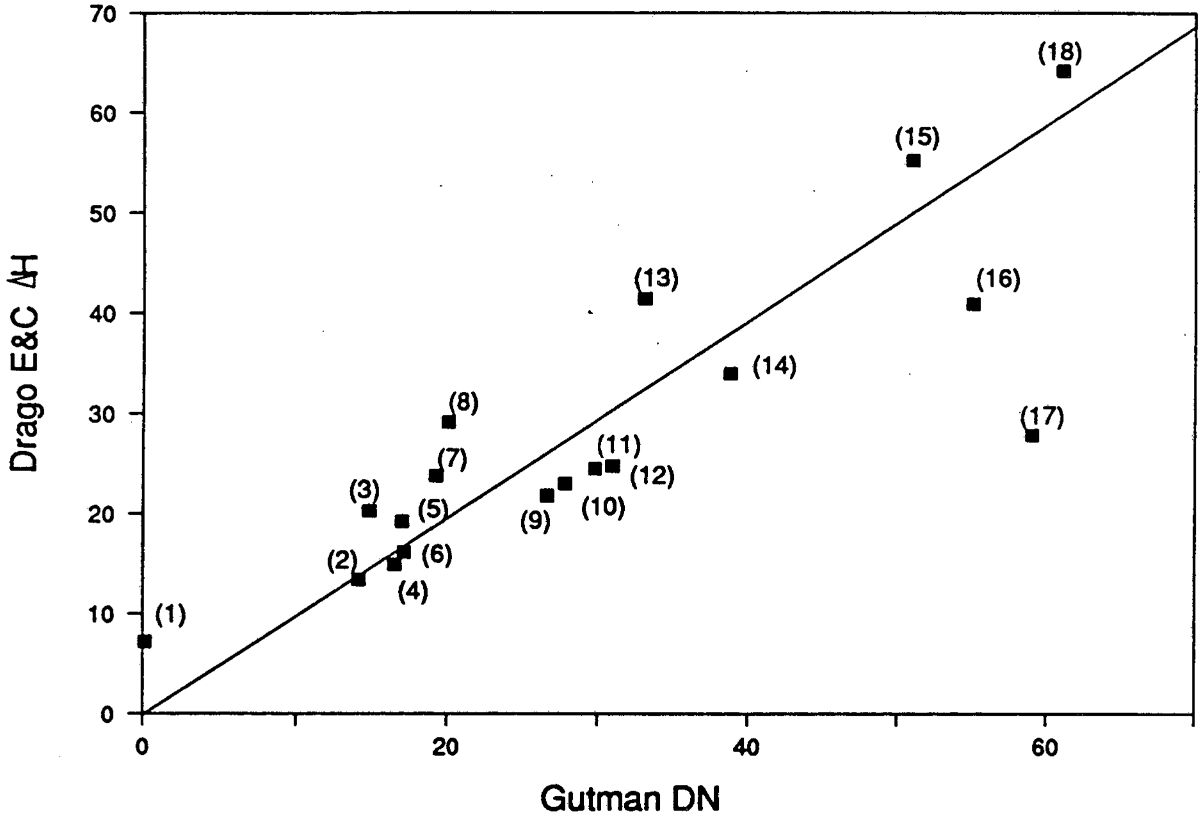


Figure 2-8. Comparison of Drago Enthalpy With DN

Key to solvents Listed

(1) benzene
(2) acetonitrile
(3) p-dioxane
(4) methyl acetate
(5) acetone
(6) ethyl acetate
(7) diethyl ether
(8) tetrahydrofuran
(9) dimethyl formamide
(10) dimethyl acetamide
(11) dimethyl sulfoxide
(12) tetramethylurea
(13) pyridine
(14) hexamethyl phosphoramide
(15) piperidine
(16) ethylamine
(17) ammonia
(18) triethylamine

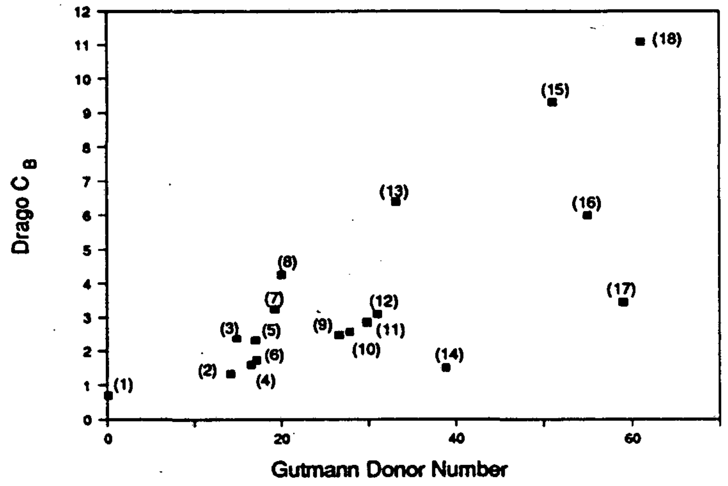


Figure 2-9. Comparison of Drago C_B With DN

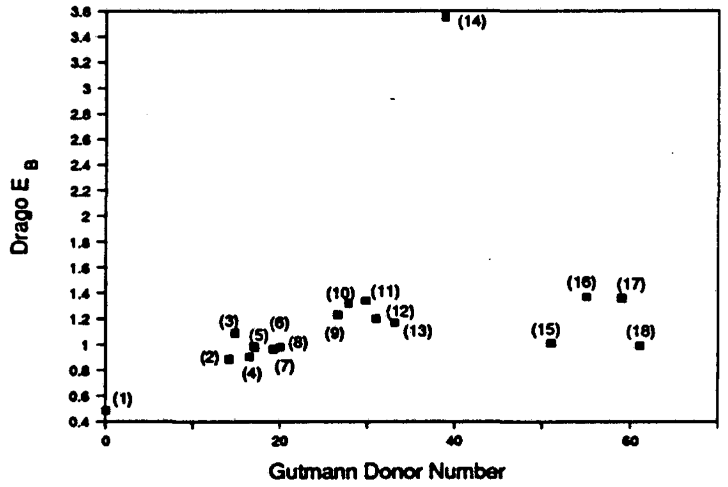


Figure 2-10. Comparison of Drago E_B With DN

Key to solvents Listed

(1) benzene
(2) acetonitrile
(3) p-dioxane
(4) methyl acetate
(5) acetone
(6) ethyl acetate
(7) diethyl ether
(8) tetrahydrofuran
(9) dimethyl formamide
(10) dimethyl acetamide
(11) dimethyl sulfoxide
(12) tetramethylurea
(13) pyridine
(14) hexamethyl phosphoramide
(15) piperidine
(16) ethylamine
(17) ammonia
(18) triethylamine

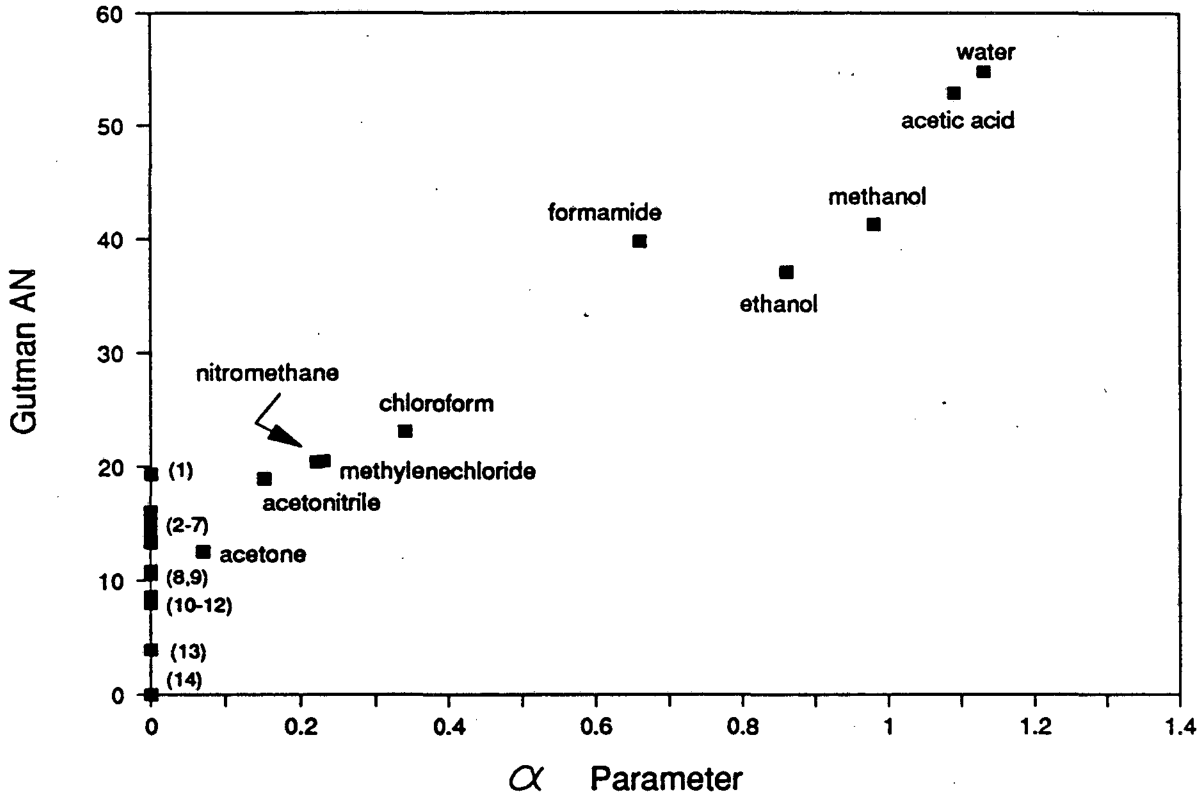


Figure 2-11. Comparison of AN With Solvatochromic α Parameter

<u>Key to solvents Listed</u>

(1) DMSO	(8) dioxane
(2) DMF	(9) hexamethyl phosphoramide
(3) benzonitrile	(10) carbon tetrachloride
(4) nitrobenzene	(11) benzene
(5) pyridine	(12) THF
(6) dimethyl acetamide	(13) diethyl ether
(7) n-methyl pyrrolidone	(14) hexane

Kamlet, Abboud and Taft[19,21] give an equation with slightly different coefficients because they omitted several non-HBD solvents -- hexamethylphosphoramide, benzene, carbon tetrachloride, pyridine, nitrobenzene, and benzonitrile -- and a borderline and a hard acid, nitromethane and acetic acid, from their analysis. Viewed from the solvatochromic method perspective, the AN scale is a lumped parameter combining polar/polarizability interactions with HBD effects. However, from the standpoint of the Gutmann AN scale, the π^* parameter can also be a measure of acidity. An example of this is nitrobenzene for which $\alpha=0$; yet it is commonly classified as an acid. The agreement between AN and the π^* and α parameters for even hard acids such as water and acetic acid is surprising. There are not many acid solvents for which the Drago E&C parameters, AN and solvatochromic compilations are available, hence useful comparisons between the E&C values and these other values cannot be made.

Chapter 2 References

1 Bronsted, J.N., Recl. Trav. Chim. Pays-Bas, 42, 718 (1923).

2 Lowry, T., Chem. Ind. (London), 42, 43, 1048 (1923).

3 Gutmann, V., "The Donor-Acceptor Approach To Molecular Interactions", Plenum, New York (1978).

4 Parker, A.J., Mayer, U., Schmid, R., Gutmann, V., J. Org. Chem., 43, 1843 (1978).

5 Gutmann, V., Electrochim. Acta, 21, 661 (1976).

6 Gutmann, V., Coord. Chem. Rev., 15, 207 (1975).

7 Gutmann, V., Struct. Bonding (Berlin), 15, 141 (1973).

8 Gutmann, V., Colloq. Int. Cent. Nat. Rech. Sci., No. 191, 347 (1970).

9 You, Xiaozeng, Drago, R.S., Miller, J.G., Huaxue Xuebao, 42, 660 (1984).

10 Drago, R.S., Parr, L.B., Chamberlain, C.S., J. Am. Chem. Soc., 99, 3203 (1977).

11 Marks, A.P., Drago, R.S., J. Am. Chem. Soc., 97, 3324 (1975).

12 Drago, R.S., Structure and Bonding (Berlin), 15, 73 (1973).

13 Drago, R.S., Vogel, G.C., Needham, T.E., J. Am. Chem. Soc., 93, 6014 (1971).

14 Drago, R.S. and Matwiyoff, N.A., "Acids and Bases", D.C. Heath and Co., Massachusetts, 1968, Chapter 3.

15 Drago, R.S., Chemistry in Britain, 3, 516 (1967).

16 Drago, R.S., Wayland, B.B., J. Am. Chem. Soc., 87, 3571 (1965).

17 Kamlet, M.J., Doherty, R.M., Abraham, M.H., Taft, R.W., Carbon, 23, 549 (1985).

18 Kamlet, M.J., Abrahams, M.H., Doherty, R.M., Taft, R.W., J. Am. Chem. Soc., 106, 464 (1984).

19 Kamlet, M.J., Abboud, J.L.M., and Taft, R.W., Prog. Phys. Org. Chem., 13, 485 (1983).

20 Kamlet, M.J., Abboud, J-L., M., Abraham, M.H., Taft, R.W., J. Org. Chem., 48, 2877 (1983).

21 Taft, R.W., Pienta, N.J., Kamlet, M.J., Arnett, E.M., J. Org. Chem., 46, 661 (1981).

22 Kamlet, M.J., Hall, T.N., Boykin, J., Taft, R.W., J. Org. Chem., 44, 2599 (1979).

23 Kamlet, M.J., Abboud, J-L., Taft, R.W., J. Am. Chem. Soc., 99, 6027 (1977).

24 Taft, R.W., Kamlet, M.J., J. Am. Chem. Soc., 98, 2886 (1976).

25 Kamlet, M.J., Taft, R.W., J. Am. Chem. Soc., 98, 377 (1976).

26 Pearson, R.G., J. Chem. Educ., 45, 581, 643 (1968).

27 Weast, R.C., ed., "CRC Handbook of Chemistry and Physics, 51st Edition", The Chemical Rubber Co., Ohio, pp. D-117,D-118 (1970).

28 Neckers, D.C. and Doyle, M.P., "Organic Chemistry", John Wiley and Sons, New York (1977).

29 Windholz, M., ed., "The Merck Index, 10th Edition", Merck & Co., Inc., New Jersey (1983).

Chapter 3: Sorption of Acetic Acid

3.1 Experimental Equipment and Procedures

3.1.1 Resin Preparation and Chemicals

All polymer sorbents were purified by Soxhlet extraction with methanol for at least 24 hours. The resins were then dried in a vacuum oven at 18 to 36 kPa and 45-50 °C for two to four days. After methanol Soxhlet extraction, the strong base quarternary amine sorbent, Bio-Rad AG-2X8, was converted to the hydroxide form by equilibration with 1N NaOH, followed by washing with water and drying in the vacuum oven.

The glacial acetic acid used was Mallinckrodt Co., Analytical Grade with minimum 99.7% assay. Karl Fischer grade methanol was used in the solvent leaching experiments. All other chemicals were of analytical grade. Water used in sorption, leaching and titration experiments was distilled and further purified with a Milli-Q system (Millipore Corp.).

3.1.2 Determination of Basicity and Capacity Using Elemental Analysis and Titration

Elemental analyses were conducted as previously described by Munson[1]: "Carbon, hydrogen, and nitrogen contents 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 from a thermal conductivity detector. Samples were thoroughly dried before submission for analysis. All elemental analyses were performed by the Microanalytical Laboratory, College of

Chemistry, University of California, Berkeley." Sulfur and oxygen contents were not determined for the basic polymer sorbents because they all have nitrogen functionality.

Titration of the polymer sorbents were conducted in the following manner. Milli-Q (Millipore Corp.) purified distilled water was boiled for 20 minutes and sealed from the atmosphere in order to eliminate absorbed CO_2. A known quantity of cleaned and dried sorbent (usually 1 gram) was slurried in 20 ml of water in a wide mouth beaker. A fritted glass sparger bubbled nitrogen through the solution to prevent CO_2 absorption during the course of the experiment. The pH of the solution was determined using a standard calomel electrode attached to a Corning Model 12 pH meter. Batch-wise addition of 0.1 N HCl was followed by observation of the approach to equilibrium using a Gould Recorder 110 chart recorder connected to the pH meter. Approximately 2 hours were required for equilibration during titrations. A blank was also run containing no adsorbent, in order to ensure accurate pH determination. Equilibration times between successive additions of acid were usually about three hours. Appendix B gives the results for the titrations of Dowex WGR, Dowex MWA-1, Reilly poly (4-methyl-5-vinyl-pyridine), Duolite A-340, Amberlite XAD-12, Aurorez, and Bio-Rad AG-2X8. Plots of acid added versus pH and acid sorbed versus pH are included in Appendix B.

3.1.3 Sorption of Acetic Acid From Aqueous Solution

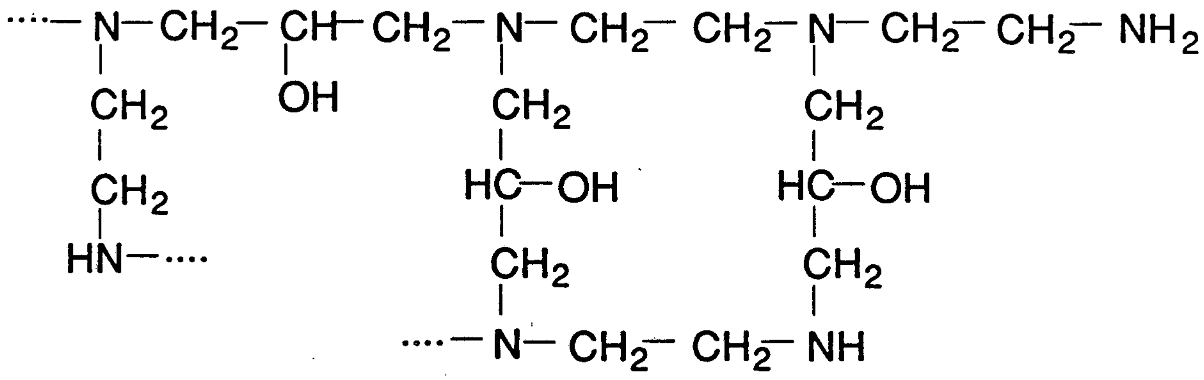
For the sorption experiments, about one gram of sorbent was equilibrated with 10 ml of acetic acid solution in a 20 ml scintillation vial. The pH was not altered nor were buffering agents used. Thus, the pH of acetic acid in solution dictated the initial pH. After equilibration, the basic polymer sorbent was found not to alter the pH substantially from the pH of the initial acetic acid solution. Equilibration was accomplished in a shaker bath (Precision Corporation) at 30 °C for about 48 hours. For all the sorbents investigated, supernatant concentrations showed no change after 20 hours.

Total solution uptakes were determined after equilibration by weighing before and after centrifugation in a 15 ml fritted glass funnel, of medium grade pore size, enclosed within a plastic centrifuge tube. The centrifuge used was an International Clinical Centrifuge, which was operated at 2000 rpm for 8 minutes. Nearly all of the interstitial and adhering bulk liquid is removed from the sorbents under these conditions[2]. The equilibrium concentration of acetic acid in solution was determined by colorimetric titration using 0.01 N NaOH and standard phenolpthalein indicator solution.

3.2 Resin Functional Group Chemistry and Physico-Chemical Properties

A variety of basic ion exchange resins were examined in this study for their abilities to recover acetic acid selectively from dilute aqueous solution. Tables 1-1, 3-1, and 3-2 summarize the resins used, giving physical and chemical properties along with a categorization of functional group chemistry. In Table 3-2, the column titled "Theoretical Capacity" is the resin capacity indicated by elemental analysis (nitrogen content), except for Aurorez where the value listed in this column is half the nitrogen content, since the imidazole structure contains one acidic and one basic nitrogen. The columns titled "Capacity for HCl" in Table 3-2 are titration results using HCl. This is not by any means an exhaustive compilation of the available basic ion exchange resins commercially available. However, most of the basic functional groups commercially available are represented.

The ion exchange resins used in this study all have nitrogen-based functionality. The general types of functionalities represented are phenol-formaldehyde-amine, N-oxide, pyridine, benzimidazole, tertiary amine, quarternary ammonium, amide, and epoxy-amine. Phenol-formaldehyde-amine and epoxy-amine resins are both condensation polymers. For these resins, the degree of crosslinking affects the basicity. They also have nitrogen atoms with different base strengths. A look at the chemistry of an epoxy-amine resin such as Dowex WGR or Duolite A-340 illustrates that at least three types of nitrogen (primary, secondary, and tertiary) are present, as is shown in Figure 3-1.



$pKa_{1^\circ} = 9.67$

$pKa_{2^\circ} = 9.15$

$pKa_{3^\circ} = 7.4$

Figure 3-1. Chemical Structure of Epoxy-Polyamine Resin

Table 3-1. Basic Ion Exchanger Properties[3,4,5,6]

Resin Name	Matrix	Functional Group	Porosity cc/cc	N_2 BET Area m^2/g
IR-4B	Alkyl	Phenol-HCHO-Polyamine	---	--
XAD-12	Styrene	N-oxide	0.45	22
XE-309	Pyridyl	4-methyl-5-vinyl pyridine	0.34	33
XE-378	Pyridyl	2-methyl-5-vinyl pyridine	0.01	6
XE-379	Pyridyl	3-methyl-5-vinyl pyridine	0.35	40
Aurorez	Benzimidazole	Benzimidazole	0.6-0.8	35
AG-2X8	Styrene	4° amine	---	--
BioGel P-4	Alkyl	Amide	low	--
MWA-1	Styrene	3° amine	---	23
WGR	Alkyl	Epoxy-amine	---	<5
A-340	Alkyl	Epoxy-amine	---	low
ES-561	Alkyl	Phenol-HCHO-Polyamine	---	--
P4VP	Pyridyl	4-methyl-5-vinyl pyridine	---	<10

--- Indicates a property that has not been measured.
(See Table 1-1 for manufacturer and resin type.)

Table 3-2. Physico-Chemical Properties of Basic Ion Exchangers[3,4,7,8,9,10]

Resin Name	Theoretical Capacity meq/g	Capacity for HCl meq/g	Capacity for HCl meq/ml	Apparent pKa•	Max. Temp., °C
IR-4B	10.27	10.23	2.5	5.3	100
XAD-12	3.9	3.5	1.4	4.4	---
XE-309	8.05	5.7	---	5.8	---
XE-378	8.6	5.8	---	3.4	---
XE-379	7.1	6.5	---	4.8	---
Aurorez	5.7	2.7-5	0.54	3.6-5.3	588
AG-2X8	3.1	2.5-3.2	---	>13	50-75
BioGel P-4	11.1	---	---	---	75
MWA-1	4.3	3.9	---	7.6/8.8	100
WGR	9.7	3.1	1.53	7.8/7.9	93
A-340	8.9	10.3	2.54	7/8.7	90
ES-561	6.36	4.5-5.2	1.22	---	---
P4VP	8.8	8.3/9.6	---	4.9	---

$$^{\bullet}\, pKa \;=\; pH \;-\; \log[Cl^{-}] \;+\; \log\frac{[X]}{2} \qquad (\alpha = 0.5)$$

where X is the total concentration of ionogenic groups and α is the degree of dissociation.[11]

The pKa values shown in Figure 3-1 were arrived at by utilizing a linear free energy relation (LFER) described by Perrin et al[12]. This LFER assigns $-\Delta pKa$ values to base weakening and base strengthening groups attached to α and β carbon atoms of an amine group. Starting with pKa values for 1°, 2°, and 3° amines of 10.77, 11.15, and 10.5 respectively, the contributions of base strengthening and/or weakening groups are summed up and subtracted from the starting value. A similar technique has been used to calculate pKa values for aliphatic acids [12]. For example, the nitrogen of greatest basicity for the epoxy-amine polymer is the primary amine. The pKa of this nitrogen group is calculated in the following manner:

$$pKa_{1^\circ} = 10.77 - \underset{\substack{\beta-\mathit{carbon}\\ \mathit{bonded}\\ \mathit{to}\ \ NR_2}}{1.1} = 9.67 \qquad \mathit{Equation}\ \ 3-1$$

For the secondary amine groups, the following calculation applies:

$$pKa_{2^\circ} = 11.15 - \underset{\substack{\beta-\mathit{carbon}\\ \mathit{bonded}\ \ \mathit{to}\\ OH}}{0.9} - 1.1 = 9.15 \qquad \mathit{Equation}\ \ 3-2$$

For alkylamines, the functional groups attached to the γ-carbon and beyond are relatively unimportant. Similar results are obtained using the Taft equation[13] :

$$pK = pK^{o} - \rho^{*}\Sigma(\sigma^{*}) \qquad \mathit{Equation}\ \ 3-3$$

where pK° is the ionization constant of the parent compound, ρ^{*} is a constant for the particular acid-base reaction, and σ^{*} is a constant that is a characteristic of a given substituent[12]. For example, the Taft equation for protonated primary amines is:

$$pK_{RNH_3^+} = 10.15 - 3.14(\sigma^*) \qquad \text{Equation } 3-4$$

Table A.1 of Perrin et al[12] contains σ^* for many substituents.

The pKa value for the weakest amine group in this structure (the 3° amine of pKa = 7.4) will be even lower when the 2° amine group protonates. An amminium ion bonded to a β-carbon results in ΔpKa of about 3.6 .

We would then expect that titration of a resin with polyamine functionality would yield at best a curve with several inflection points. Experimentally, mineral acid titration of a polyamine resin gives a curve with little or no inflection (see Appendix B), confirming the existence of a wide range of basicities.

Another feature of polyamine functionality is that measured sorption capacities for these resins can be lower than the theoretical values due to base-weakening effects of functional groups bonded to α and β carbons. Sorption capacities can also be a function of the acid strength of the sorbed solute. For weak acids, such as carboxylic acids, sorption capacities may be less than capacities measured using HCl.

The functional group chemistry of phenol-formaldehyde-amine type resins is also complex. Figure 3-2 illustrates the structure of a resin made from diethylenetriamine, phenol, and formaldehyde. This is presumed to be the structure of the resin Duolite ES-561.

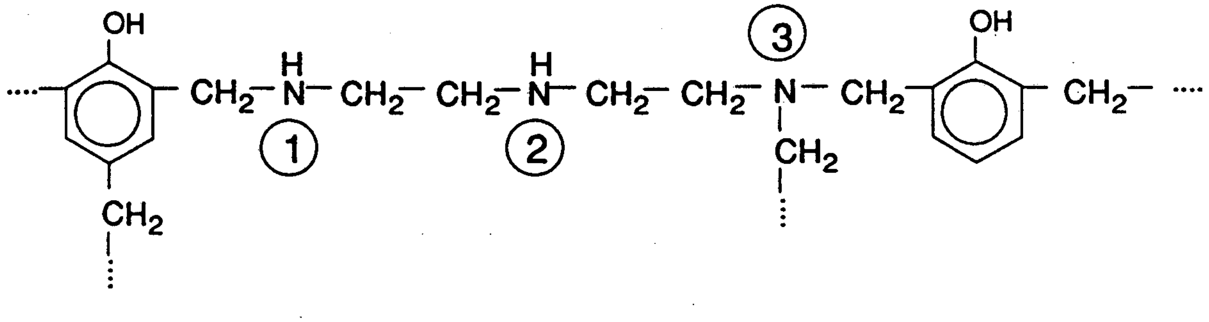


Figure 3-2. Chemical Structure of Phenol-Formaldehyde-Amine Resin

This polymer also contains at least three different types of basic nitrogens. The nitrogen labeled (2) in Figure 3-3 has a calculated pKa of about 9.4 by applying the *ΔpKa* method, and a pKa of about 9.3-9.6 when the Taft method is used. This nitrogen group has the highest basicity of the three labeled nitrogens because both the tertiary amine, labeled (3), and the 2° nitrogen, labeled (1), have a phenol group bonded to the α-carbons. Estimates for the pKa values of these nitrogens using the Taft equation are 7.1 and 6.1 for nitrogen (1) and (3) respectively. Titration of this resin with HCl also yields a curve with little or no inflection[8].

Amberlite IR-4B is made from triethylenetetramine, phenol, and formaldehyde. Its monomeric structure is similar to Duolite ES-561, but it contains another ethylamine link:

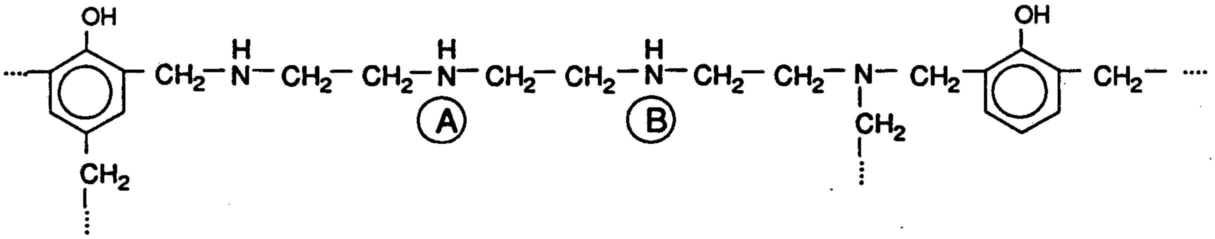


Figure 3-3. Chemical Structure of Amberlite IR-4B

In this structure, half the nitrogens have the highest pKa value; while the structure formed using diethylenetriamine has a third of its nitrogen with highest basicity. Thus upon protonation of the nitrogens with pKa = 9.1, for Duolite ES-561, the other nitrogen basicities drop by 2.7 (utilizing the *ΔpKa* method), giving extremely low pKa values. Following this line of reasoning, the working capacity for this resin when sorbing weak acids from solution would be a third of the stated manufacturer's values. On the other hand, Amberlite IR-4B might retain about one half of its capacity since, if nitrogen (A) or (B) protonates, the pKa of the unprotonated nitrogen group would be about 6.7 .

The preceding argument is speculative because it greatly depends on the acid strength of the solute being sorbed. However, in the next sections where acetic acid sorption data are discussed, the experimental data do indicate that the sorption capacities of these condensation polymers are lower than their theoretical capacities.

The monofunctional polymers have well characterized structures and basicities. Table 3-3 contains pKa values for the monomeric group using the ΔpKa method and the Taft equation.

Table 3-3. Monomer pKa for Monofunctional Polymer Sorbents

Sorbent	pKa method	Taft Equation	Tabulated Values
XAD-12	----	----	----
XE-309	6.1 (6.6)	5-6	----
XE-378	5.7 (6.1)	5-6	----
XE-379	5.8 (6.3)	5-6	----
Aurorez	----	5.0	5.23[*]
AG-2X8	----	----	----
BioGel P-4	----	----	-0.6[**]
MWA-1	9.1	8.7	----
P4VP	6.1 (6.6)	5-6	----

[*] Entry for 2-phenyl benzimidazole[14]
[**] Entry for acetamide[15]

All of the nitrogen groups in the sorbents listed in Table 3-1 are basic, except for those in Aurorez. Aurorez (polybenzimidazole) is a monofunctional sorbent, but the benzimidazole structure, shown in Figure 3-4, contains a basic and an acidic nitrogen. The tertiary nitrogen atom is basic, while the secondary nitrogen atom is acidic.

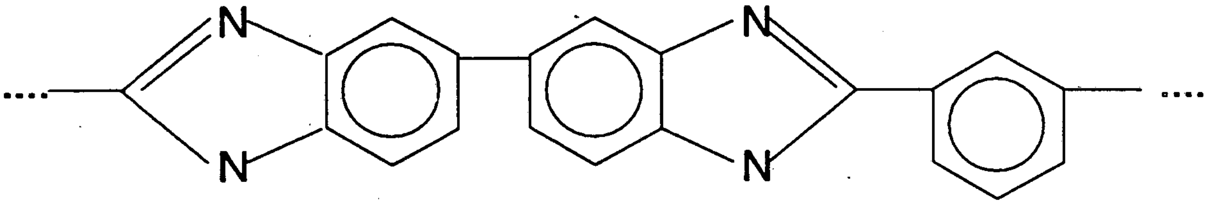


Figure 3-4. Monomer Chemical Structure of Aurorez

Its capacity measured through HCl titration, as stated by the manufacturer[4], is 4.5-5 meq/g. This value is slightly under half the total nitrogen content determined by elemental analysis, 11.4 meq/g (from Table 3-4).

The pyridine sorbents listed in Table 3-3 have two entries for their pKa values, estimated using the ΔpKa method. The first entry was determined by considering the monomeric pyridine structure along with the effect of the location of the methyl substitution. The entry in parentheses considers the vinyl group in the 5th position (which forms the polymeric structure) as a methyl group. It is not clear whether this is an accurate assessment since there are Taft equations for 2- or 4-styryl substituted pyridines which give lower pKa values than the unsubstituted pyridine equations. This is why a wide range is reported under the Taft equation column. Since it is unclear how to treat the 5-vinyl attachment, the pKa values which will be used in subsequent sections ignore the contribution of this substituent.

3.3 Individual and Composite Isotherms for Acetic Acid

Weak base ion exchange resins have been used to remove both weak and strong acids from aqueous solution [16]. Both molecular acid sorption and ion exchange have been investigated as mechanisms for the removal of carboxylic acids [17,18,19,20].

Most researchers report sorption data without specifying whether the measured uptakes are composite or individual values. Composite, or preferential, uptake (surface excess) is defined by the equation.

$$\frac{W_o \Delta C}{m} = \frac{W_o(C_{2i} - C_{2f})}{m} \qquad \textit{Equation} \quad 3-5$$

where W_o is the initial mass of liquid; m is the mass of sorbent used; and C_{2i} and C_{2f} are the initial and final solute concentration in units of weight fraction. The subscript 2 refers to the solute. Individual uptakes are defined as:

$$W_1^s = \frac{W_o(1 - C_{2i}) - W_f(1 - C_{2f})}{m} \qquad \textit{Equation} \quad 3-6$$

$$W_2^s = \frac{W_o C_{2i} - W_f C_{2f}}{m} \qquad \textit{Equation} \quad 3-7$$

where W_o and W_f are the initial and final masses of bulk liquid. The mass of liquid changes due to solution imbibition and sorption. The composite uptake can be viewed as a measure of the preference of the sorbent for the solute over the solvent, while the individual uptake results from a mass balance giving the total amounts of solute and solvent removed from solution. Using individual uptake values requires a distinction between sorbed solution and bulk liquid, whereas composite values are phenomenological. As described in Section 3.1.3, the amount of liquid which is sorbed is defined in this work as the mass of solution retained after centrifugation of the sorbent. Composite and individual uptakes can be nearly equal when the sorbent imbibes only small amounts of solvent[21].

Comparisons of individual and composite uptakes for acetic acid, at the natural pH of the solution with no added electrolytes, for all the sorbents studied are given in Figures 3-5 through 3-17 . The pH of the equilibrium solution was generally about 2.5 -- indicating that nearly all of the acetic acid is in molecular form. Data from various other sources are noted with references[4,21,22,23]. The general features of these comparisons are that (1) individual uptakes are higher than composite uptakes; (2) for all the sorbents except Bio Gel P-4, at low concentrations individual and composite uptakes are nearly equal; and (3) uptakes approach a limiting value for the stronger base sorbents. The individual isotherm should achieve an upper limiting value at high solute concentration if there is stoichiometric loading. As solute concentration increases, the composite isotherm should reach a maximum value, and at very high solute concentration it should eventually return towards zero. The composite isotherm is related to the individual uptakes of solute and solvent by the following expression[21]:

$$\frac{m_o \Delta C}{m} = W_2^s(1 - C_{2f}) - W_1^s C_{2f} \qquad \textit{Equation} \quad 3-8$$

This relationship explains why the individual uptakes of acetic acid must be lower than the composite values, and why, at low concentrations, composite and individual uptakes of acetic acid are nearly equal.

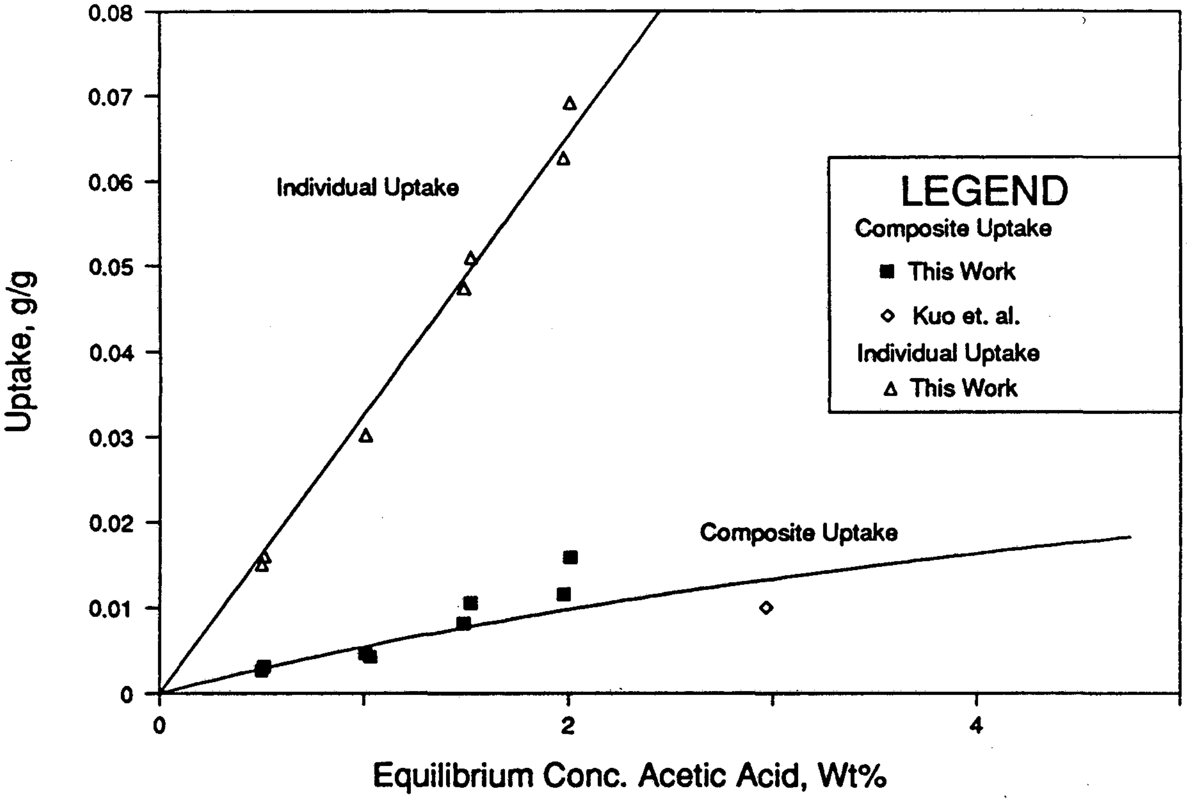


Figure 3-5. Sorption Isotherms For Bio-Rad Bio Gel P-4
(gram HOAc per gram dry resin)

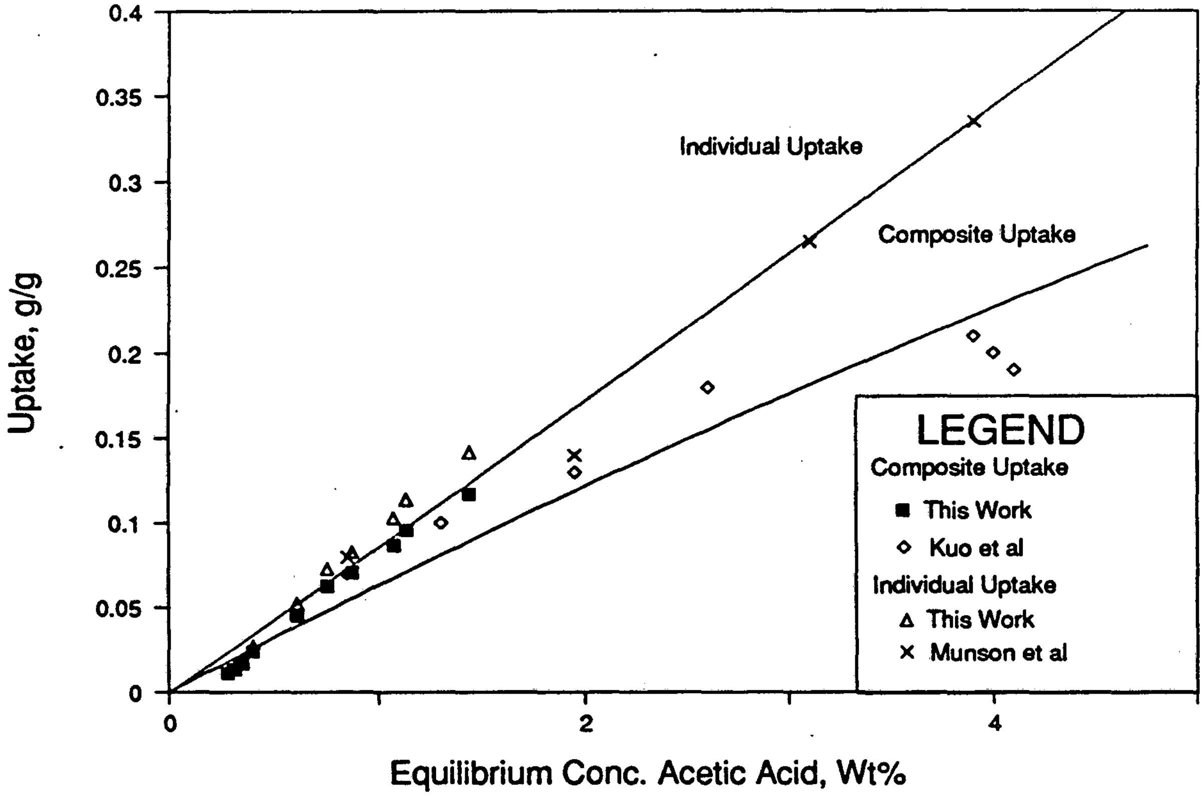


Figure 3-6. Sorption Isotherms For Reilly Tar & Chem Co.
Poly-4-methyl-5-vinyl-pyridine (gram HOAc per gram dry resin)

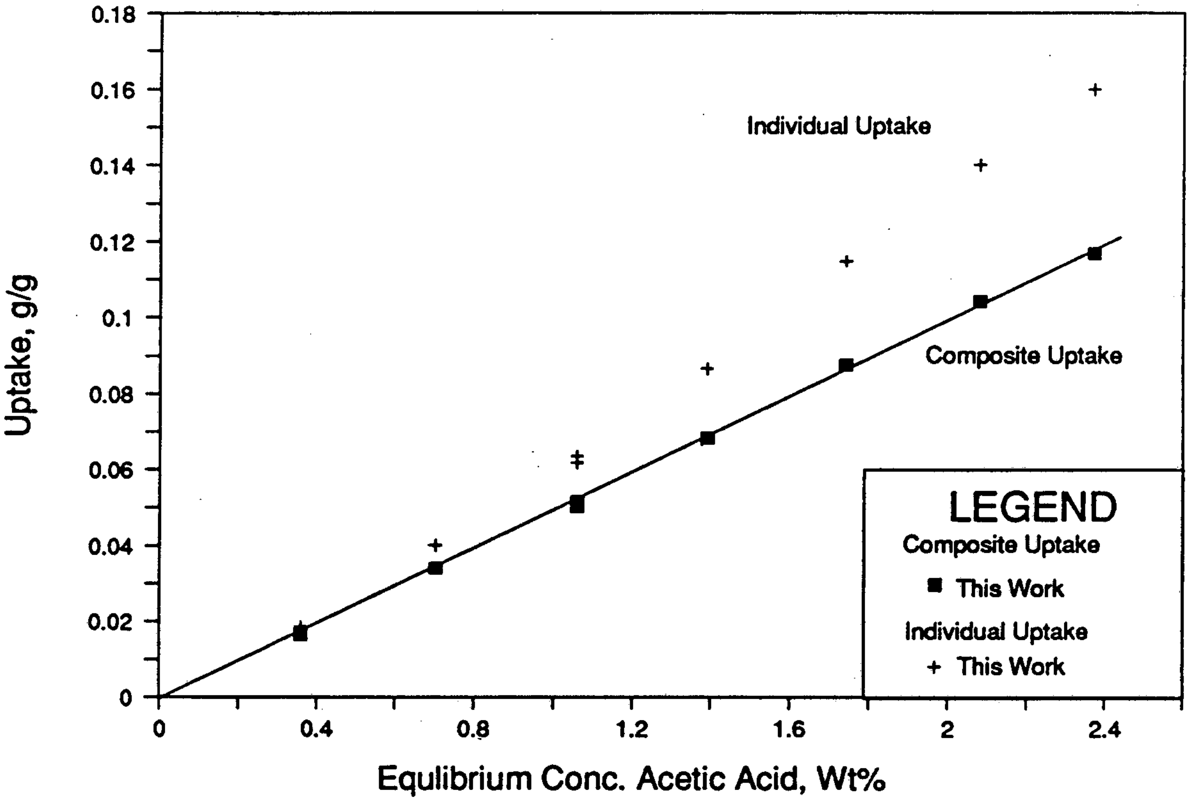


Figure 3-7. Sorption Isotherms For Rohm & Haas Amberlite XE-309
(gram HOAc per gram dry resin)

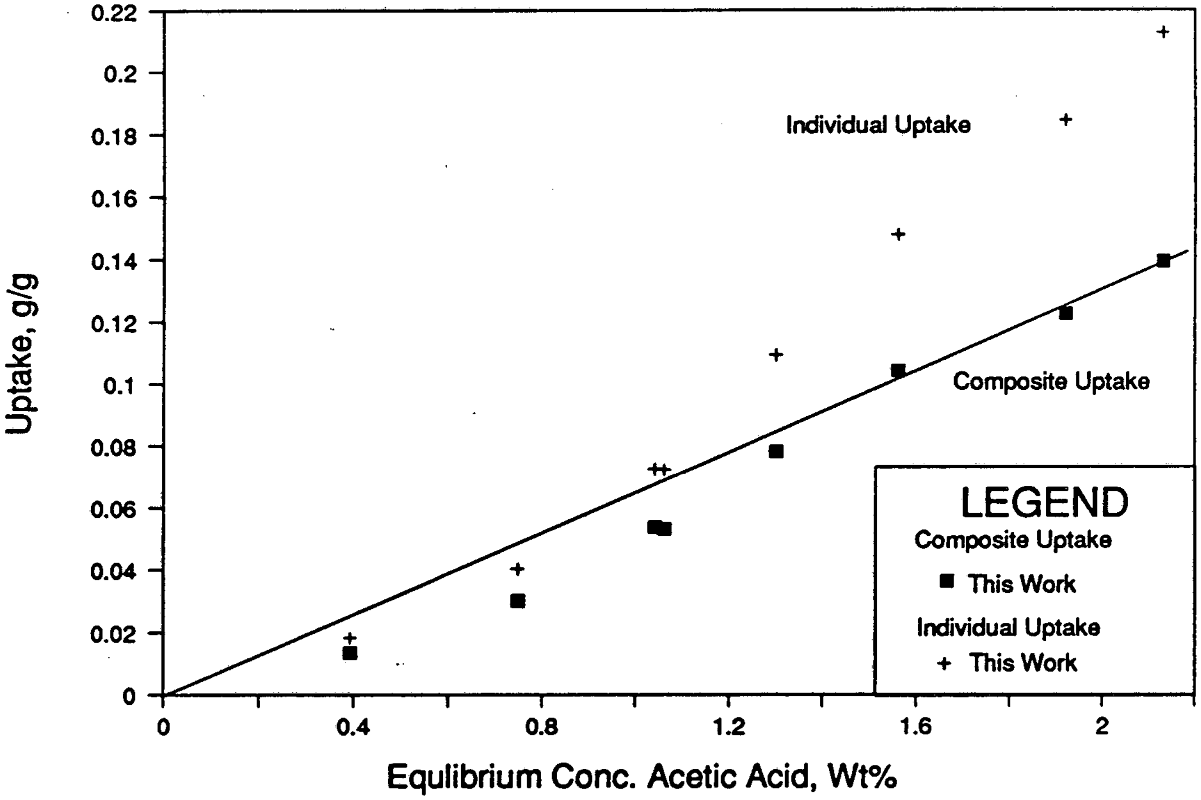


Figure 3-8. Sorption Isotherms For Rohm & Haas Amberlite XE-378
(gram HOAc per gram dry resin)

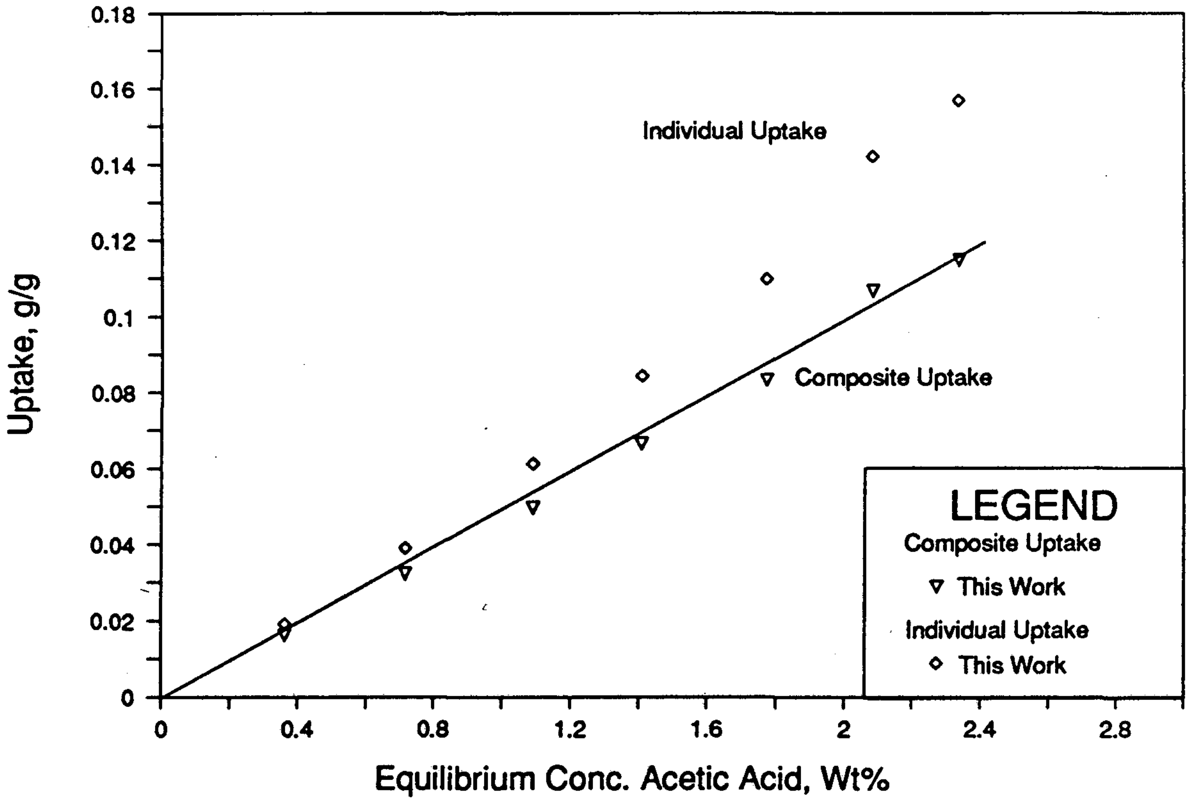


Figure 3-9. Sorption Isotherms For Rohm & Haas Amberlite XE-379
(gram HOAc per gram dry resin)

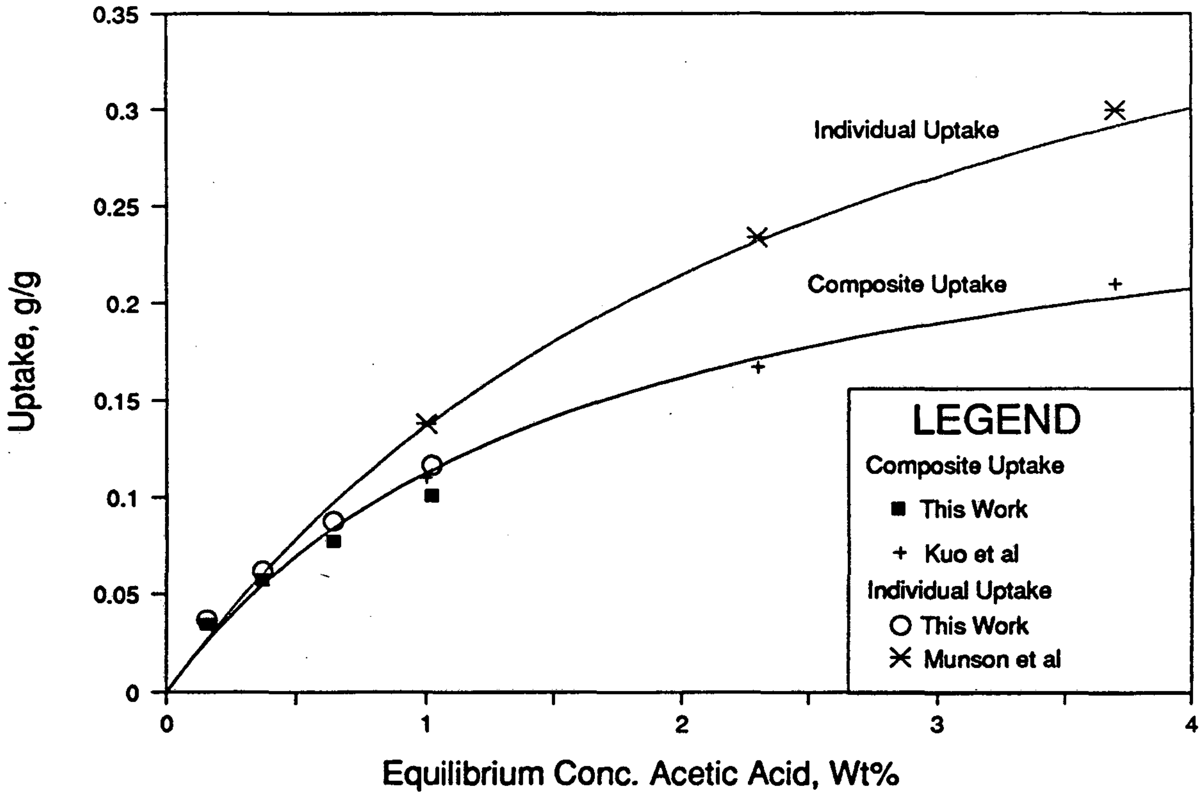


Figure 3-10. Sorption Isotherms For Rohm & Haas Amberlite XAD-12
(gram HOAc per gram dry resin)

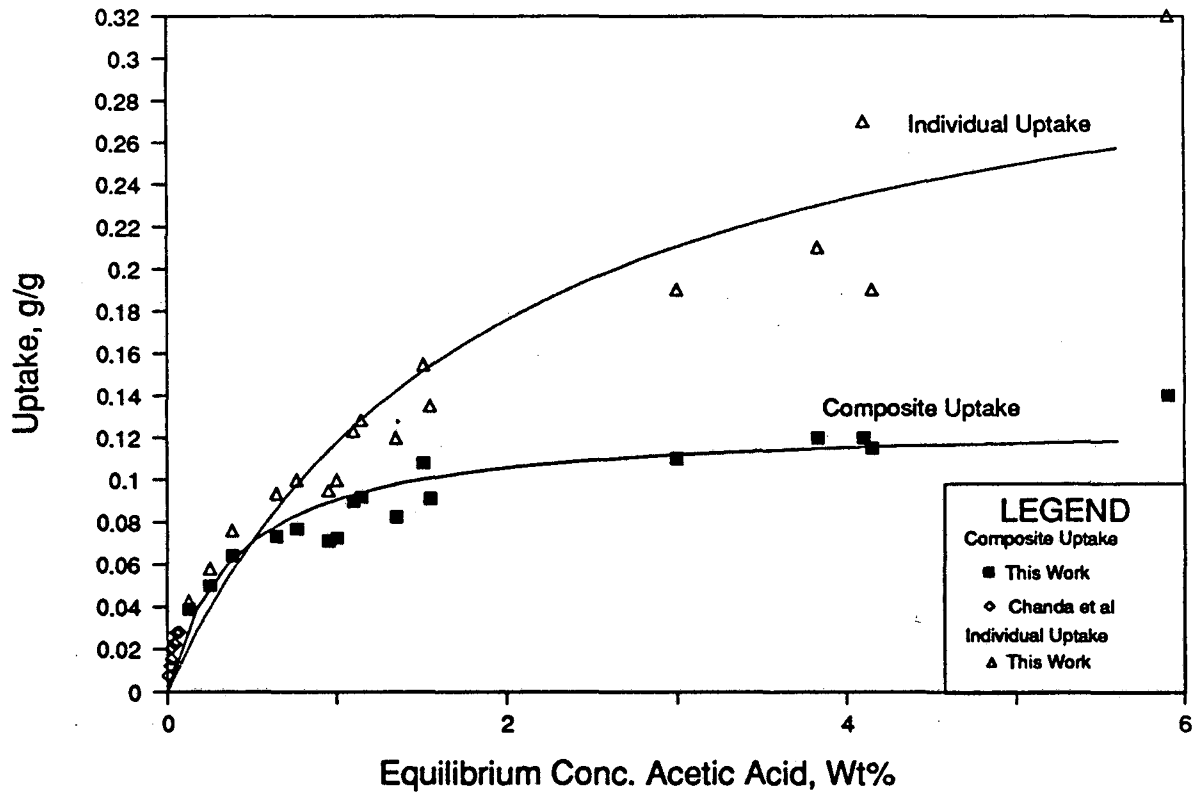


Figure 3-11. Sorption Isotherms For Celanese Aurorez
(gram HOAc per gram dry resin)

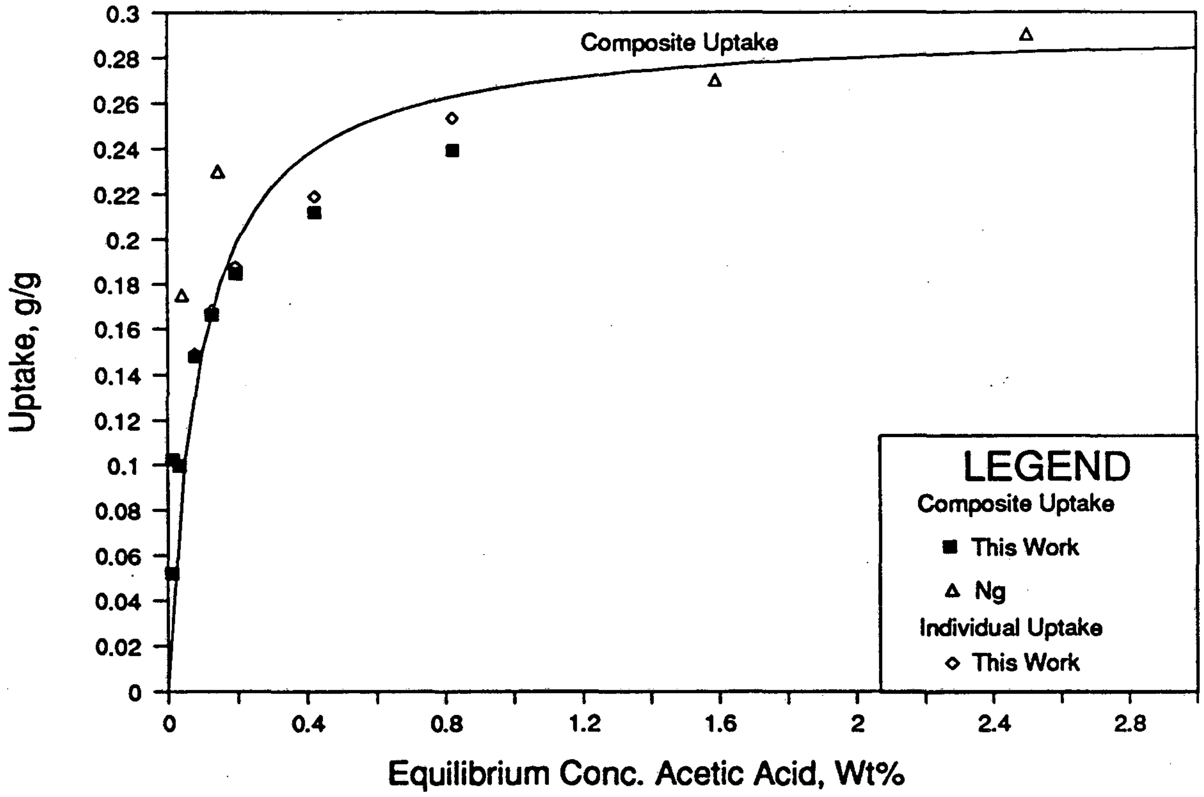


Figure 3-12. Sorption Isotherms For Dow Chem. Co. Dowex MWA-1
(gram HOAc per gram dry resin)

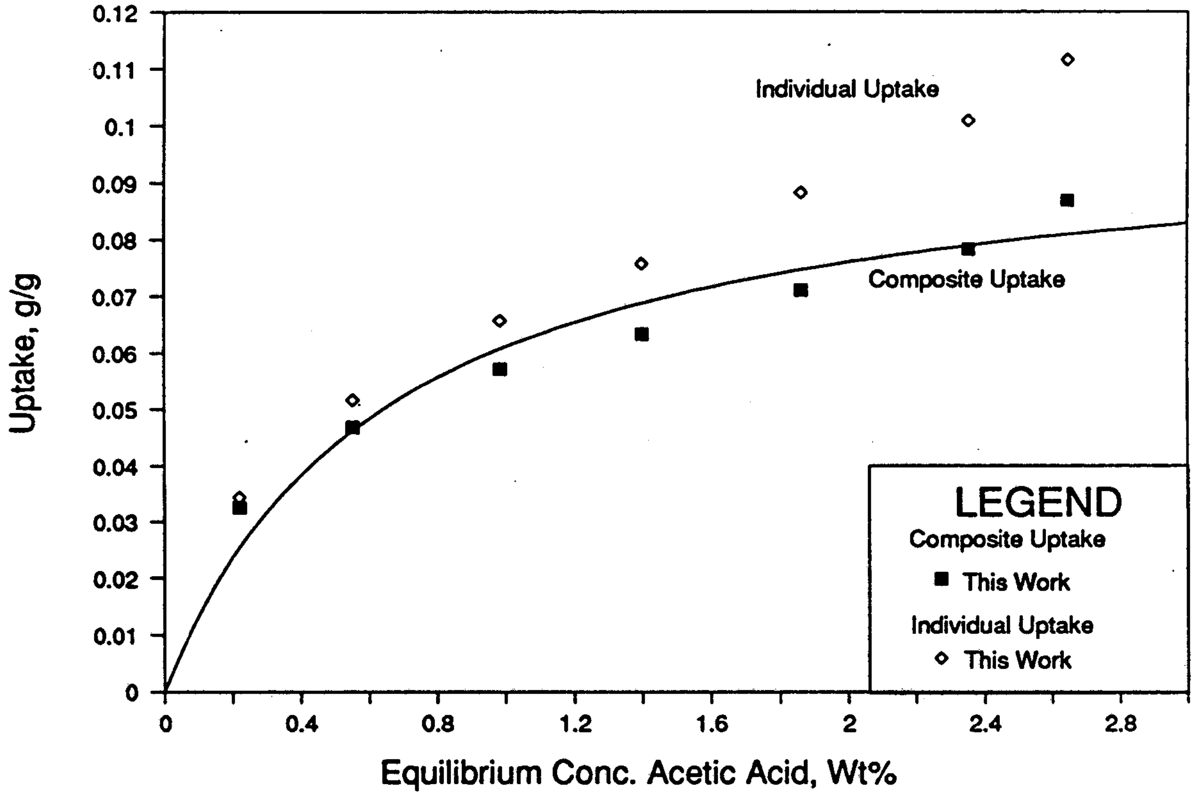


Figure 3-13. Sorption Isotherms For Rohm & Haas Duolite ES-561
(gram HOAc per gram dry resin)

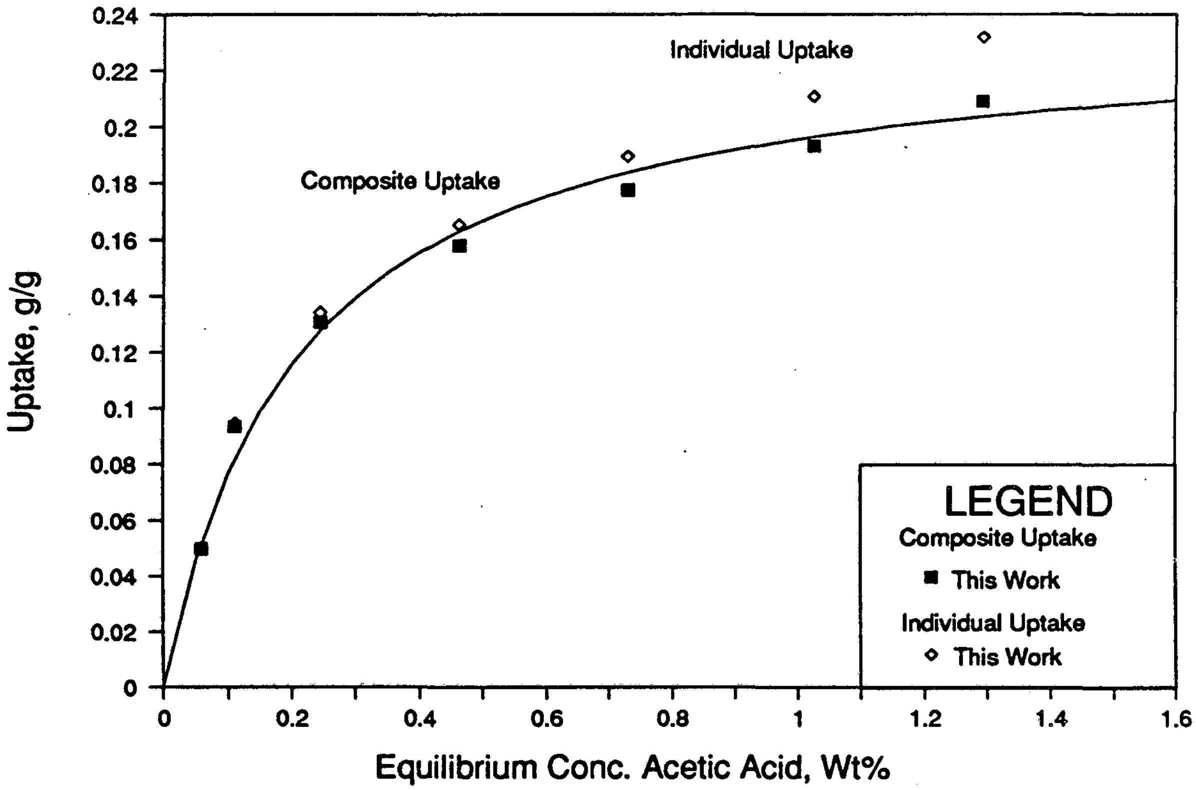


Figure 3-14. Sorption Isotherms For Rohm & Haas Amberlite IR-4B
(gram HOAc per gram dry resin)

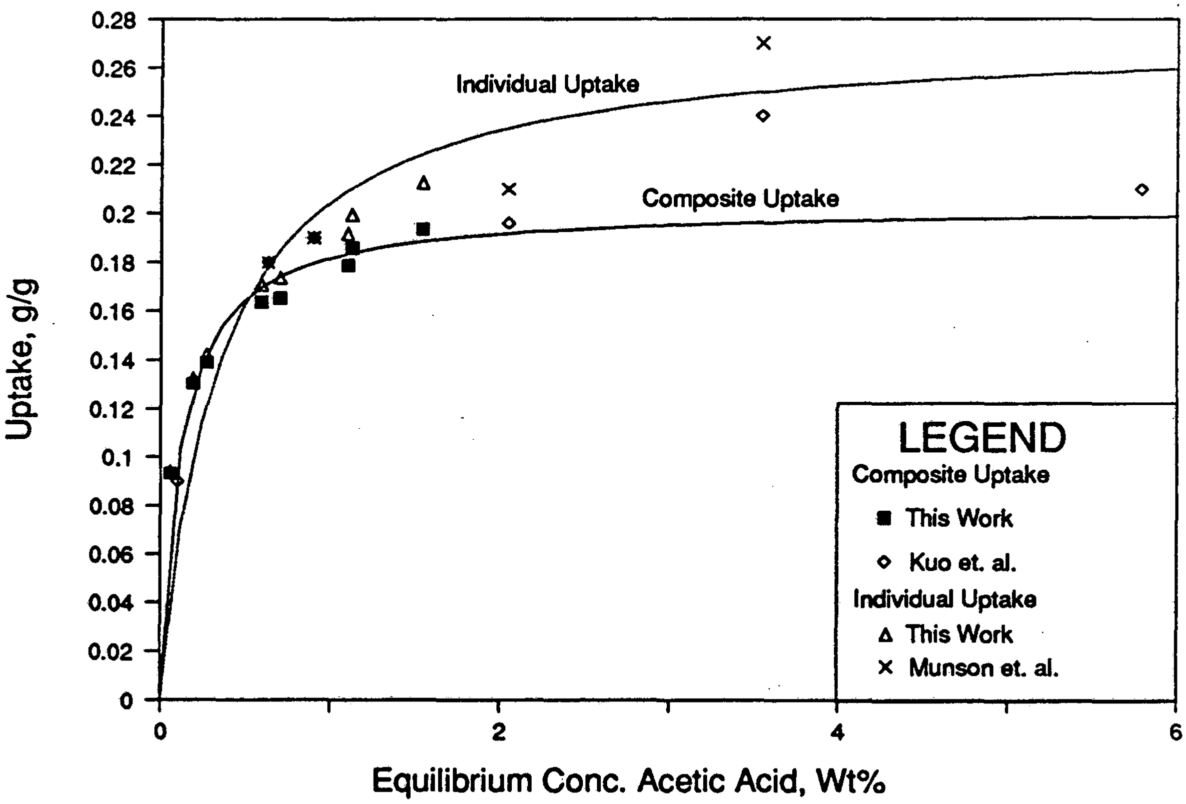


Figure 3-15. Sorption Isotherms For Dow Chem. Co. Dowex WGR
(gram HOAc per gram dry resin)

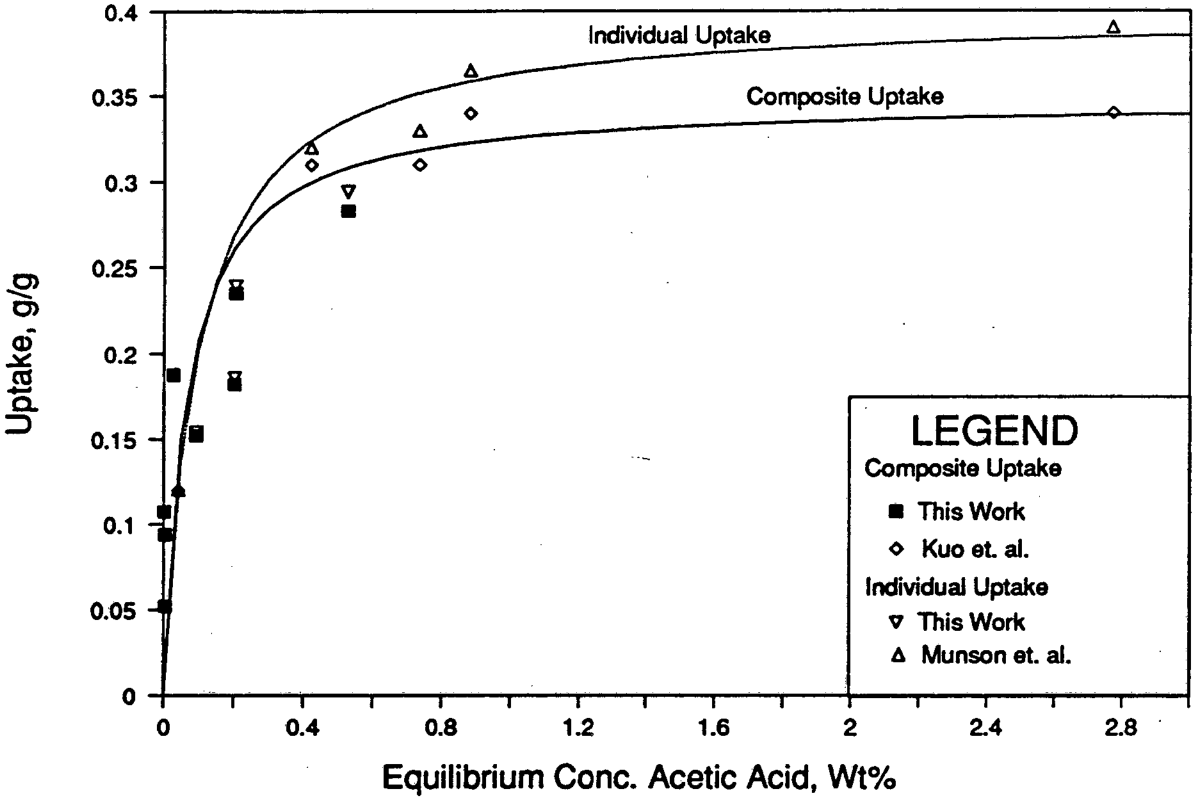


Figure 3-16. Sorption Isotherms For Rohm & Haas Duolite A-340
(gram HOAc per gram dry resin)

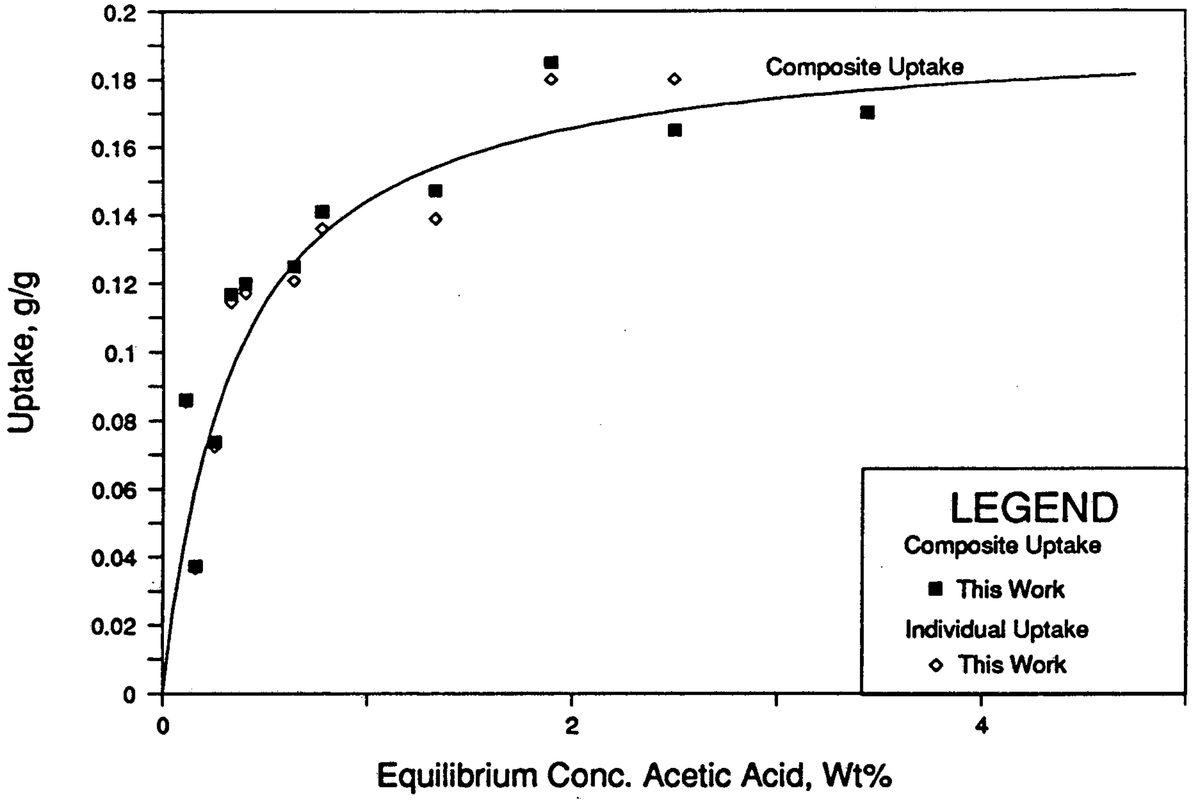


Figure 3-17. Sorption Isotherms For Bio-Rad AG-2X8
(gram HOAc per gram dry resin)

Another important observation is that the composite isotherms for the pyridine and amide sorbents (XE-309, XE-378, XE-379, P4VP, and BioGel P-4) shown in Figures 3-5 through 3-9 are essentially linear, whereas the other sorbents have curved or Langmuirian isotherms. This observation is important for the next section, where modeling of the sorption data is discussed. Linearity of the composite isotherm for the concentration range studied is a result of the high capacities exhibited by these sorbents and the relatively low basicities of their chemical functional groups.

3.4 The Ideal Exchange Model

A survey of the literature reveals that there is no general quantitative theory for the sorption of weak or non-electrolytes by functionalized polymer sorbents. Studies of the sorption of strong electrolytes leading to quantitative treatments of ion exchange have previously been the primary focus[16].

A simple, logical model that can rationalize acetic acid sorption data is a chemical complexation/exchange model. The proposed model is described by a pseudo-chemical reaction:

$$HOAc(l) \; + \; (H_2O)_n - B \;\; \rightarrow \;\; nH_2O(l) \; + \; HOAc - B \qquad Equation \quad 3-9$$

where (l) refers to the bulk liquid phase and B represents a basic functional group. The bond formation implied in this "reaction" should not be understood as a covalent bond; but rather it represents an association or complexation interaction. The concept of an acetic acid molecule competing with one or more water molecules allows for the use of the composite isotherm to determine the sorbent "phase" concentration of acetic acid, as long as the acetic acid is considerably enriched at the surface or sites. We can write an "equilibrium constant", or affinity constant, for this reaction:

$$K_1 = \frac{[HOAc - B]\,[H_2O(l)]^n}{[HOAc(l)]\,[(H_2O)_n - B]} \qquad Equation \quad 3-10$$

By assuming that (1) 1:1 complexes are formed (2) the solvent activity in dilute solution remains constant over the concentration range; (3) all the basic sites have equal basicity and accessibility; (4) the number of basic sites is a constant; and (5) the ratio of the remaining activity coefficients remains constant over the concentration range, the following expression results:

$$\frac{q}{q_m} = \frac{K C_{HOAc(l)}}{1 + K C_{HOAc(l)}} \qquad Equation \quad 3-11$$

where $K = \dfrac{K_1}{[H_2O(l)]^n}$

Equation 3-11 is of the same form as the familiar Langmuir equation. In fact, the assumptions used in deriving Equation 3-11 are essentially the same ones used to derive the Langmuir equation. The parameter q_m is the total capacity, q is the individual uptake, not counting acetic acid in the pore volume, and $C_{HOAc(l)}$ is the equilibrium concentration of acetic acid in the bulk liquid.

Equation 3-11 can also be put in a linear form:

$$\frac{C_{HOAc(l)}}{q} = \frac{C_{HOAc(l)}}{q_m} + \frac{1}{q_m K} \qquad Equation \quad 3-11a$$

Plotting $C_{HOAc(l)}/q$ versus $C_{HOAc(l)}$ yields q_m as the inverse of the slope and K as the inverse of the intercept divided by q_m.

A final assumption is made before applying this expression to the basic polymer sorption data. An acid solute is taken up by basic sorbents through chemical complexation and by non-selective uptake mechanisms such as pore filling or imbibition of solution upon swelling. Instead of using the individual uptake for the q parameter and subtracting solute held in pores, the composite uptake is used in this work. By using the composite value, non-selective uptake can largely be referenced out. The composite uptake is thus interpreted as a measure of the amount of acetic acid complexed with the basic functional groups in the sorbent. For high sorbent selectivities, the composite uptake approaches the actual surface or sorbent-site concentrations. For low sorbent selectivities, it would probably be more appropriate to add the bulk mole fraction to the surface mole fraction in order to obtain q.

Another way of arriving at the quantity of acetic acid complexed in the resin phase would be to utilize the dry-resin or swollen-resin pore volume and calculate the amount of non-selectively sorbed acetic acid assuming that the non-selectively sorbed solution is of the same concentration as the bulk phase. However, the volume of non-selectively sorbed solution is not easily determined, since an assumption is needed regarding the dividing line between selective and non-selective sorption. Moreover, it is difficult to determine the effective pore volume for sorbents that swell greatly. A final note on the difference between individual and composite uptake is that a distinction between the two values is important only for sorbents which have large pore volumes or high swelling affinities, and for high solute concentrations.

Obviously this model is simplistic. However, the principal driving force for the sorption of a simple carboxylic acid such as acetic acid should be the formation of 1:1

complex with the sorbent's basic functional group. The primary test of this model is whether the q_m and K parameters relate to the inherent properties of the sorbent. This question is explored in the next section.

3.4.1 Comparison of Model Parameters With Resin Capacity and Functional Group Basicity

Applying the ideal exchange model to the weak base polymer sorbents yields the fitted parameters q_m and K. The quarternary amine sorbent used in its hydroxide form, (Bio-Rad AG-2X8) was not included in the analysis because it is unclear whether the removal of acetic acid from solution is accomplished through sorption/complexation or ion exchange. It may also be that both phenomena are occurring for this resin. All the other sorbents used are weak base resins in their free base form. Values of q_m and K were determined from the slope and intercept of a plot in the form of Equation 3-11a .

In applying this model to the composite isotherm data shown in Figures 3-5 through 3-16 an adjustment was made for the amide and pyridine sorbents. Since available data spanned the linear region of the isotherm, the model was reduced to a one-parameter equation. The parameter q_m was set equal to the capacity determined by HCl titration or, when this information was not available, to the total N by elemental analysis (Table 3-4). It is believed that this approach yields a sorption affinity (K) which is more indicative of the tendency for 1:1 complex formation since these groups should be available for complexation with acetic acid as well as HCl. Justification of this reasoning is provided in the next section, where sorption affinity is related to the basicity of the monomeric functional group.

Table 3-4 compares the values of q_m so determined with several parameters which are inherent properties of the sorbent.

Table 3-4. Comparison of q_m with Other Measures of Capacity

Sorbent	Type	Total N By Elemental Analysis meq/g	Basic N By HCl Titration meq/g	Basic N By Monomer Chemistry meq/g*	Fitted Parameter qm meq/g
IR-4B	Poly	10.27	10.2	5.1	3.9
ES-561	Poly	6.36	4.8	2.1	1.7
A-340	Poly	8.9	10.3	4.7	5.8
WGR	Poly	9.7	3.1	4.9	3.8
MWA-1	Mono	4.3	---	4.3	4.9
XAD-12	Mono	3.9	---	3.9	4.8
Aurorez	Mono	11.4	2.7/4.5	5.7	2.2
P4VP	Mono	8.8	8.3	8.8	---
XE-309	Mono	---	5.7	5.7	---
XE-378	Mono	---	5.8	5.8	---
XE-379	Mono	---	6.5	6.5	---
BioGel P-4	Mono	---	---	11	---

*see Section 3.2

The first column identifies whether the sorbent is polyfunctional or monofunctional. The column titled "Basic N by Monomer Chemistry" is the amount of nitrogen in the sorbent structure with the highest basicity, determined using knowledge of the monomer chemistry and the elemental analysis, or, when elemental analysis was not available, the HCl titration results. As already noted, for a weak acid, such as acetic acid, the basicity of the functional group affects the driving force for the formation of an acid/base complex to a greater extent than for a strong acid such as HCl. Moreover, basic functional groups spaced apart by one or two methylene units can interact with each other, leading to base weakening of the groups. Also, sorption of an acetic acid molecule will affect the basicity of the close neighbor group greatly if the acid/base complex involves charge transfer, as in salt formation. This is analogous to monomer chemistry where there is a marked decrease in basicity of the neighboring amine group spaced one or two methylene groups away from a protonated amine.

In Table 3-4, the sorption data for the four polyfunctional sorbents give q_m values which are much lower than the capacities based on elemental analysis. The capacities based on the quantity of the most basic nitrogen functional groups more closely agree with the q_m values. Dowex WGR and Duolite ES-561 have functional groups which are not accessible to aqueous HCl since their titration capacities are lower than their total N by elemental analysis values. This is most notable for Dowex WGR, since only one third of its nitrogen is available.

Two out of the three monofunctional sorbents with q_m values listed show reasonable agreement between q_m and capacity estimates. For Aurorez two different capacities based on HCl titration results are reported, both of which are lower than the expected capacity by monomer chemistry. The titration capacity of 2.7 meq/g was measured in our laboratory, while the 4.5 meq/g value is the manufacturer's stated value[4]. Through personal communication with a company representative[24] it was found that drying of Aurorez with sorbed polar solvents such as water causes blockage of the pore openings in the sorbent particles. Drying after immersion in polar solvents therefore results in diminished capacity. All Aurorez samples used in this work were dried extensively, no doubt thereby causing the lower capacities determined by HCl titration and acetic acid sorption. Celanese Corp. recommends an alternative technique for drying Aurorez which involves displacement of the sorbed water by succeedingly less polar solvents, followed by vacuum oven drying[24]. This technique can actually increase sorbent surface area and thereby providing maximum capacity.

Table 3-5 reports sorption affinities derived by applying the ideal exchange model to determine q_m and K without restrictions, as well as sorption affinities, K_M, derived by reducing the ideal exchange model to a one-parameter model, fixing q_m to the value suggested by the monomer chemistry. Because of the loss in capacity by Aurorez upon drying, K_M for this sorbent is fixed to the capacity determined by HCl titration. In the subsequent analyses which investigate the relationship between sorption affinities and basicities, both sorption affinities are used.

The sorption affinity from the ideal exchange model was correlated with sorbent basicity via a linear free energy relation (LFER). This empirical approach has been used successfully to correlate pKa with equilibrium constants as well as rate constants[25]. The general form of a LFER is:

$$\ln k_i^{I} = a \ln k_i^{II} + b \qquad \textit{Equation} \quad 3-12$$

where k_i^{I} and k_i^{II} are equilibrium or rate constants for the ith species of the reaction series I and II respectively. In other words, if we know that a particular mechanism or complexation reaction in one reaction series is similar to that of another reaction series, then the free energies for each reaction set are linearly related. For sorption of acetic acid, we would expect that -log(K), where K is the sorption affinity, could be linearly related to the pKa, DN, or β value for the monomeric functional group in the polymer sorbent.

Table 3-5. List of Derived Sorption Affinities

Sorbent	Ideal Exchange Model Fitted K	Fixed q_m to Capacity By Monomer Chemistry K_M
IR-4B	29	11
ES-561	9.3	4.6
A-340	91	140
WGR	45	35
MWA-1	64	160
XAD-12	3.9	6.3
Aurorez	15	5.1*

*Based on $q_m = 2.7$ meq/g

Another method for determining the basicity of resins which has popular usage is the "apparent" pKa of the polymer obtained by titration of the resin with HCl[16]. Figure 3-18 compares the "apparent" pKa of the polymer versus the pKa of the most basic monomeric functional group in the sorbent. A parity line is drawn for reference. All the polymers have "apparent" pKa values lower than the pKa of their most basic monomeric functional group. There is also a wide scatter in the data, suggesting that some of the polymers have groups which appear to be much weaker than would be expected based on their monomer chemistry.

In Figure 3-19, -log(K) or pK is plotted versus the "apparent" pKa of the polymer. Also shown in this figure are lines of slope equal to -1. It might be expected that the "apparent" pKa would correlate with pK in an equation of the form: pK = -pKa + b ,

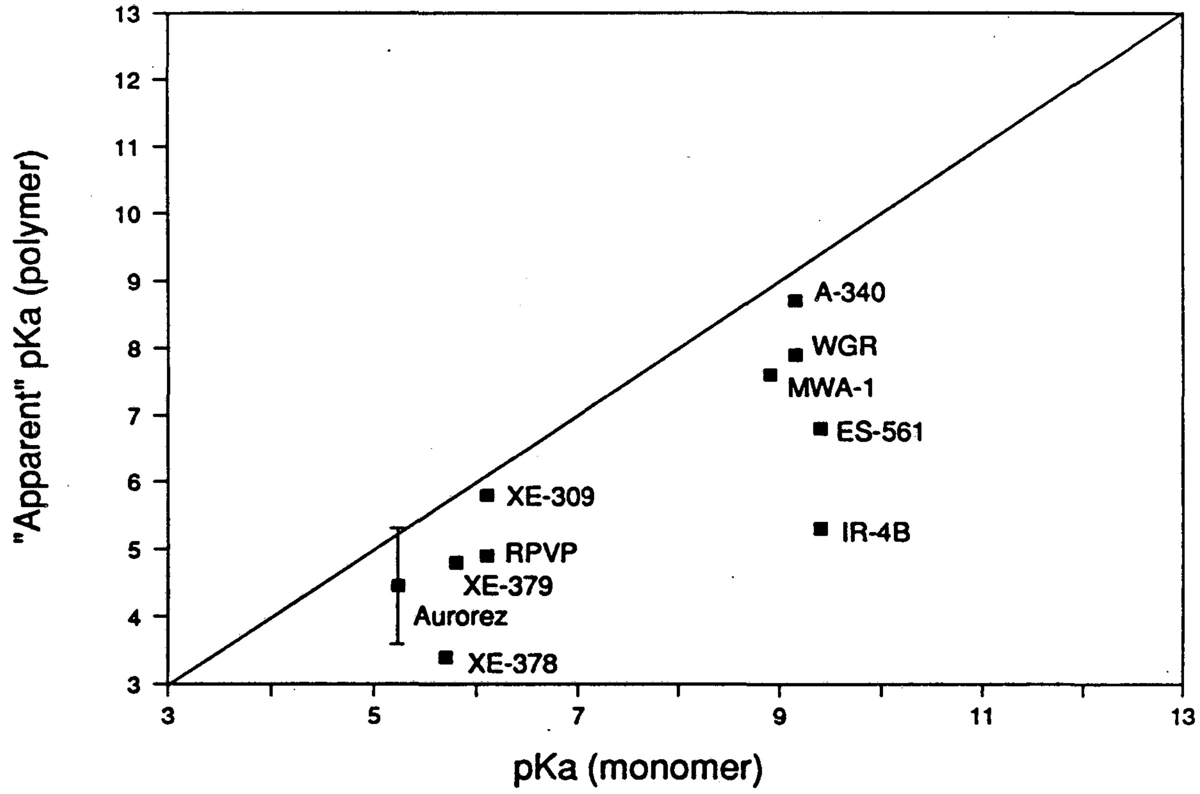


Figure 3-18. Comparison Between "Apparent" pKa and Monomeric Functional Group pKa

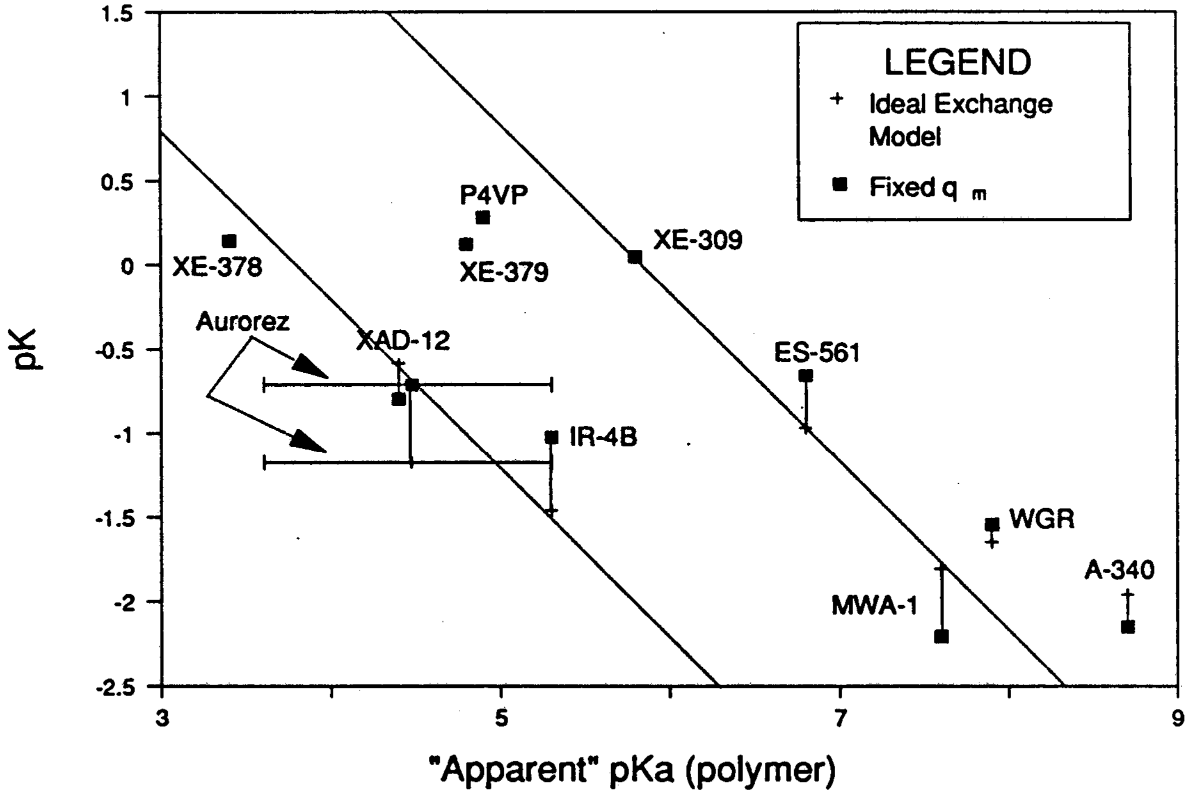


Figure 3-19. Correlation Between Sorption Affinity and "Apparent" pKa

where the intercepts account for differences between the acid dissociation constants for acetic acid and HCl, as well as differences in both aqueous and sorbent phase activity coefficients for these solutes. Some of the data correlate well, but there are four notable outliers -- XE-378, XAD-12, Aurorez, and Amberlite IR-4B. An "apparent" pKa value can be determined for XAD-12, although it is meaningless since the N-oxide group is not a hard base and does not protonate. Another complication is that the determination of a pKa for the polymer is made difficult by the need to interpret correctly the effects of Donnan equilibrium or electrical double layer formation in order to obtain the sorbent basicity. The "apparent" pKa determination does not address either of these effects.

Using the monomer basicity, Figures 3-20 and 3-21 show how pK correlates with pKa and DN. Figure 3-20 also contains a line of slope equal to -1 as a reference. For pKa (monomer) the pKa of the most basic functional group was used, while the donor numbers reflect available values for the different functionalities. Donor numbers for XAD-12 (poly N-oxide) and Aurorez (polybenzimidazole) were obtained from the Drago E&C equation, through the correlation between it and DN discussed in Section 2.4.

Of the two correlations, the correlation with DN is better. Another advantage to the DN scale is that XAD-12, a soft base, can be grouped with the other sorbents. The solvatochromic parameter, β, does not correlate well with pK (Figure 3-22). It would appear that the DN scale correlates with the sorption affinity for acetic acid since it is based on the enthalpy of adduct formation with a hard acceptor, $SbCL_5$. We could then speculate that DN correlates with pK because the nature of the donor complexes with the hard acceptors, $SbCl_5$ and acetic acid, are similar. Another interesting observation to make is that DN correlates to some extent with the monomeric functional group pKa (Figure 3-23), while β does not (Figure 3-24). Recall that Figure 2-1 shows a similar correlation between DN and pKa for various solvents.

Several researchers have investigated similar relationships between sorption affinity and acid/base strength. Addy and Andrews[26] studied the absorption of phenols from CCl_4

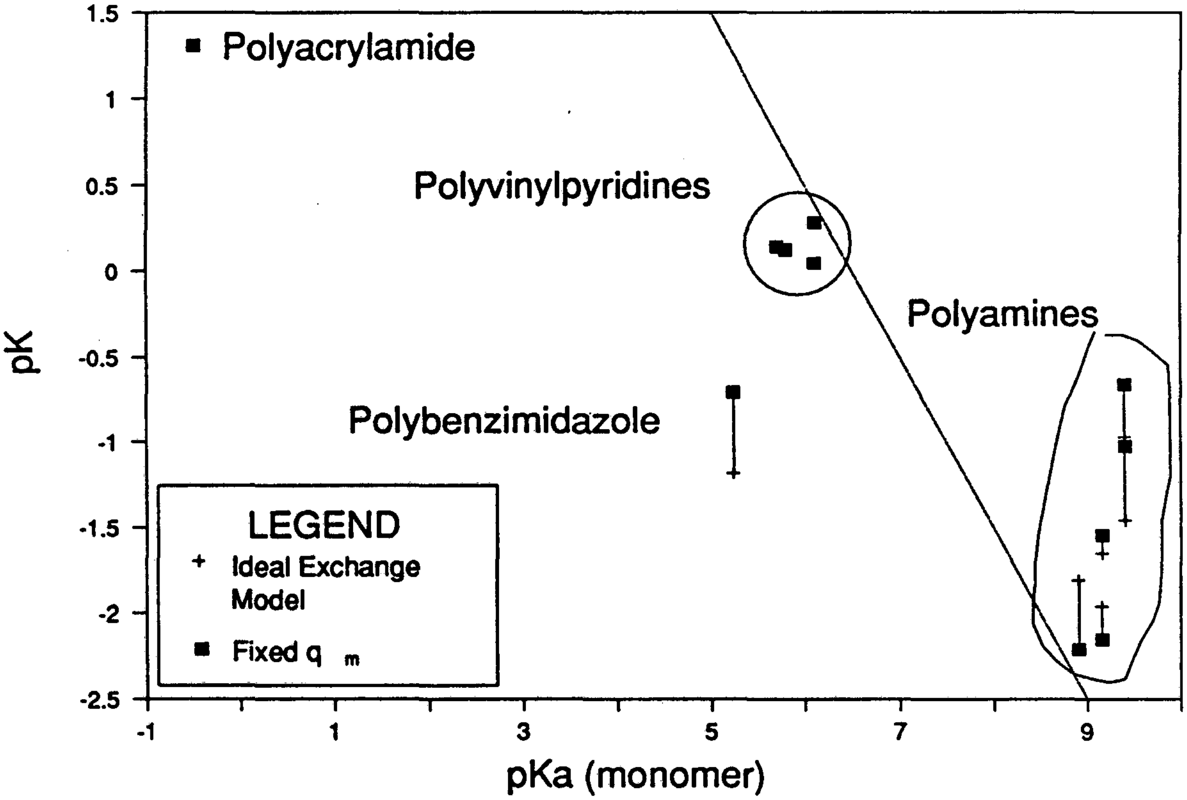


Figure 3-20. Correlation Between Sorption Affinity and Monomeric Functional Group pKa

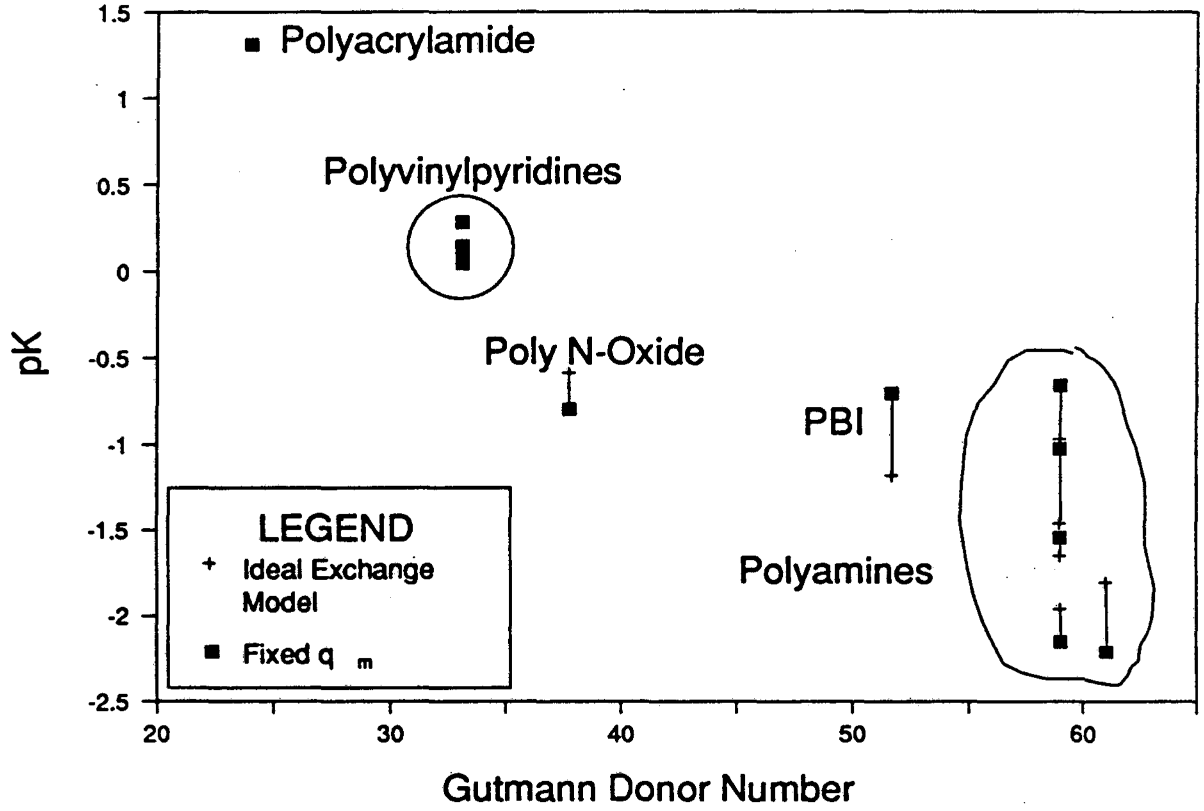


Figure 3-21. Correlation Between Sorption Affinity and Gutmann Donor Number

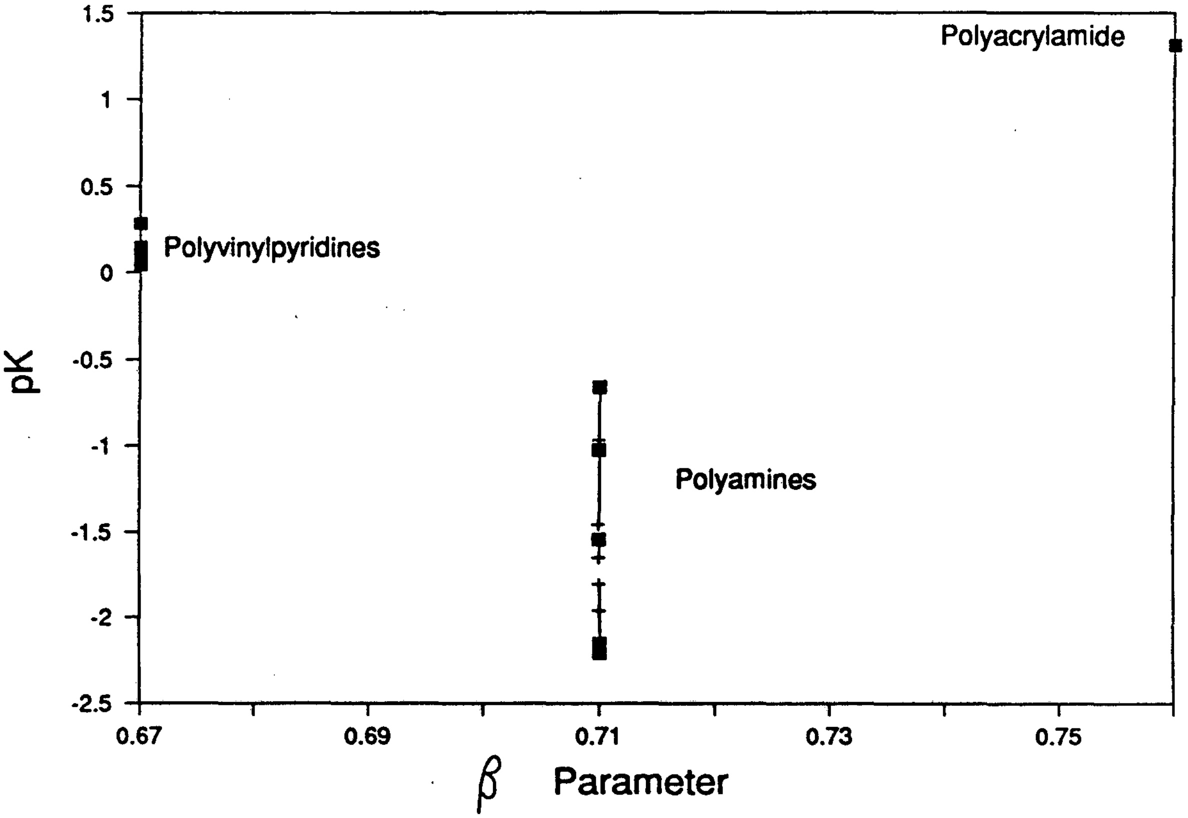


Figure 3-22. Correlation Between Sorption Affinity and Solvatochromic β Parameter

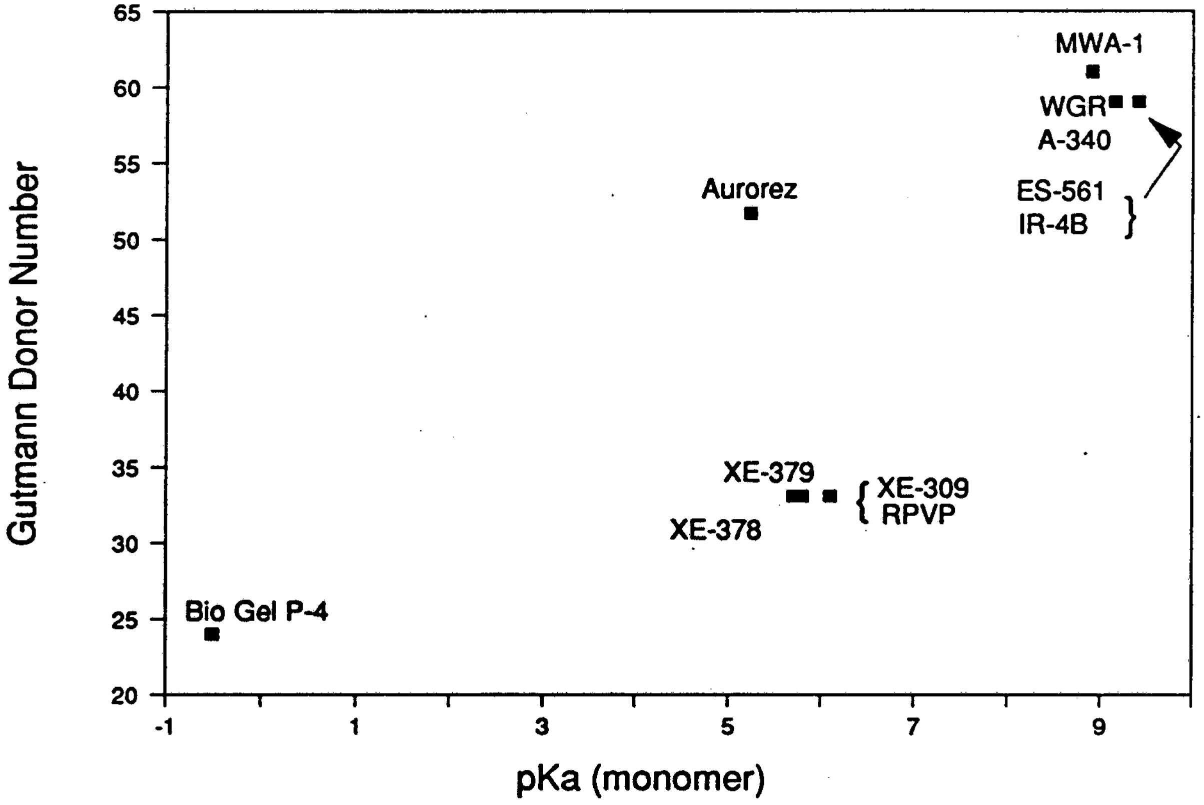


Figure 3-23. Correlation Between Monomeric Functional Group pKa and Gutmann Donor Number

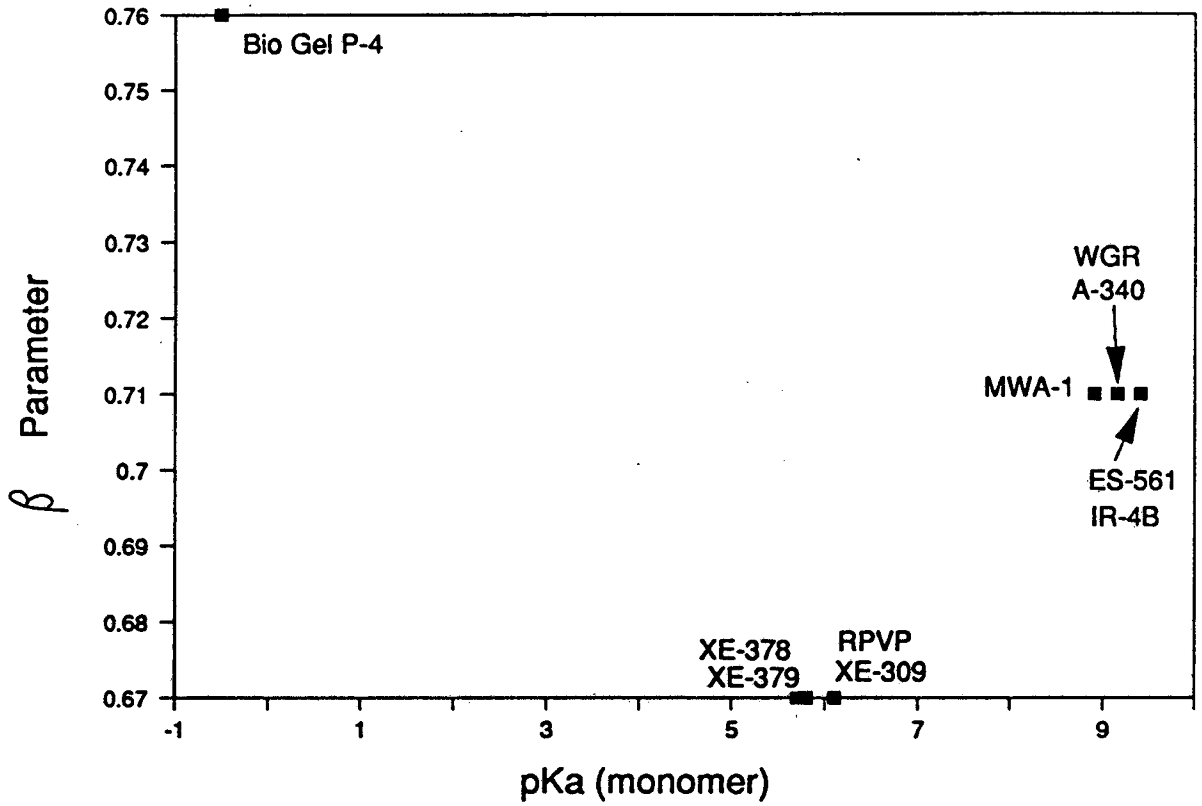


Figure 3-24. Correlation Between Monomeric Functional Group pKa and Solvatochromic β Parameter

and benzene solution by Nylon 6. They correlated the Hammett constant σ [27,28] for various substituted phenols with log(K), where K is an effective equilibrium constant for the absorption. By using the Hammett constant, in effect they correlated the pKa difference between phenols versus log(K). In both solvents, linear correlations between σ and log(K) with approximately equal slopes were observed. Saunders and Srivastava[29] also studied the effect of different solute basicities on the sorption affinity for a particular sorbent. They used a carboxylic acid ion exchange resin to sorb organic bases from water, ethanol, and ethanol-water solutions. They found that, after correcting for pK_B differences due to the presence of ethanol in the liquid phase, linear correlations existed between pK_B and two parameters determined from a distribution law which correlated the solute sorbate concentration with the equilibrium solute concentration in the bulk liquid phase. Both works, Addy et al and Saunders and Srivastava, ignored aqueous phase non-idealities. If liquid phase non-idealities are not markedly different among these solutes and/or if the acid-base interaction driving force is great, then this oversight is unimportant.

Chanda, O'Driscoll and Rempel [4] also investigated the sorption of different solutes using Aurorez and Reilly poly-4-methyl-5-vinylpyridine (designated either PVP, RPVP, P4VP, or RP4VP). From this study they concluded that for both sorbents the relative sorption affinities among phenols follow the trend of increasing affinity for increasing acidity. However, they reported that for sorption of carboxylic acids, hydrophobic interactions become important, and the trend of increasing sorption affinity for increasing acidity is not present.

It is better to generalize and state that both hydrophobicity and acidity are important for the sorption of polar organics from aqueous solution using basic sorbents. A way of illustrating this is to plot the sorption data of Chanda, O'Driscoll and Remple in the manner shown in Figures 3-25 and 3-26. In each figure the logarithm of the octanol/wa-

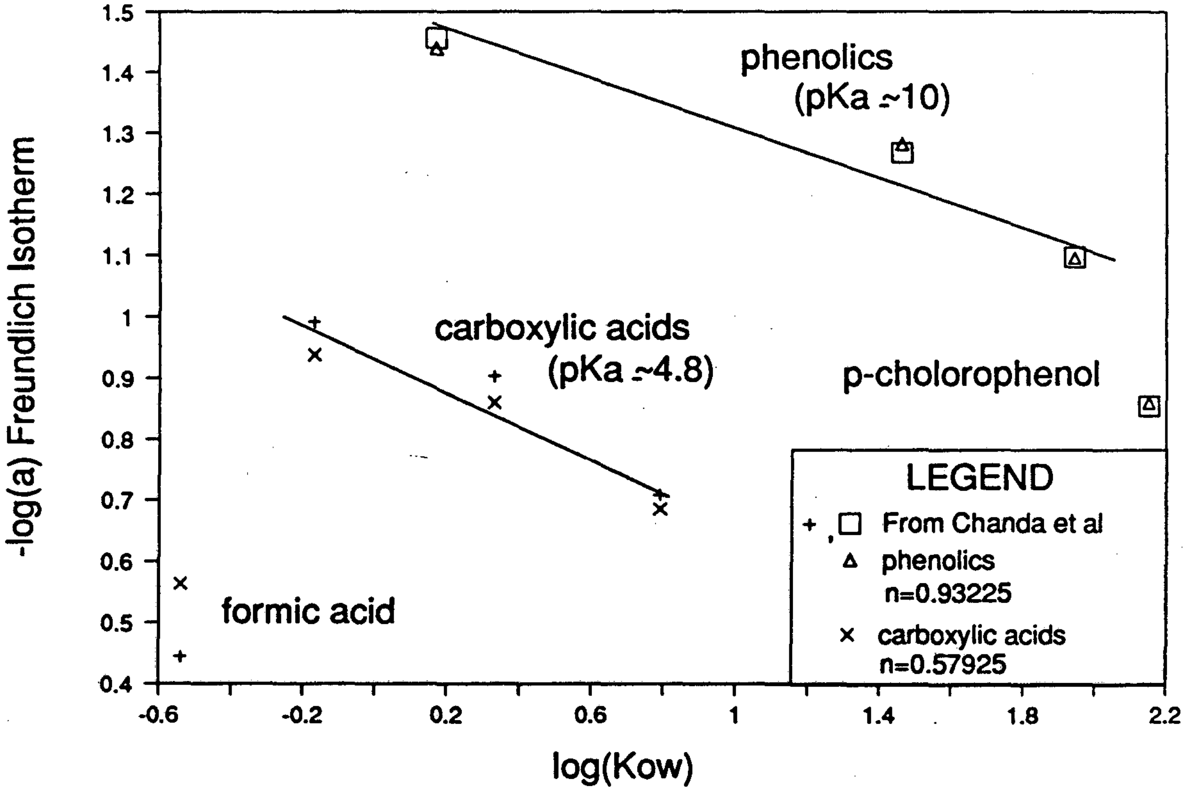


Figure 3-25. Effect of Solute Hydrophobicity On Sorption for Aurorez

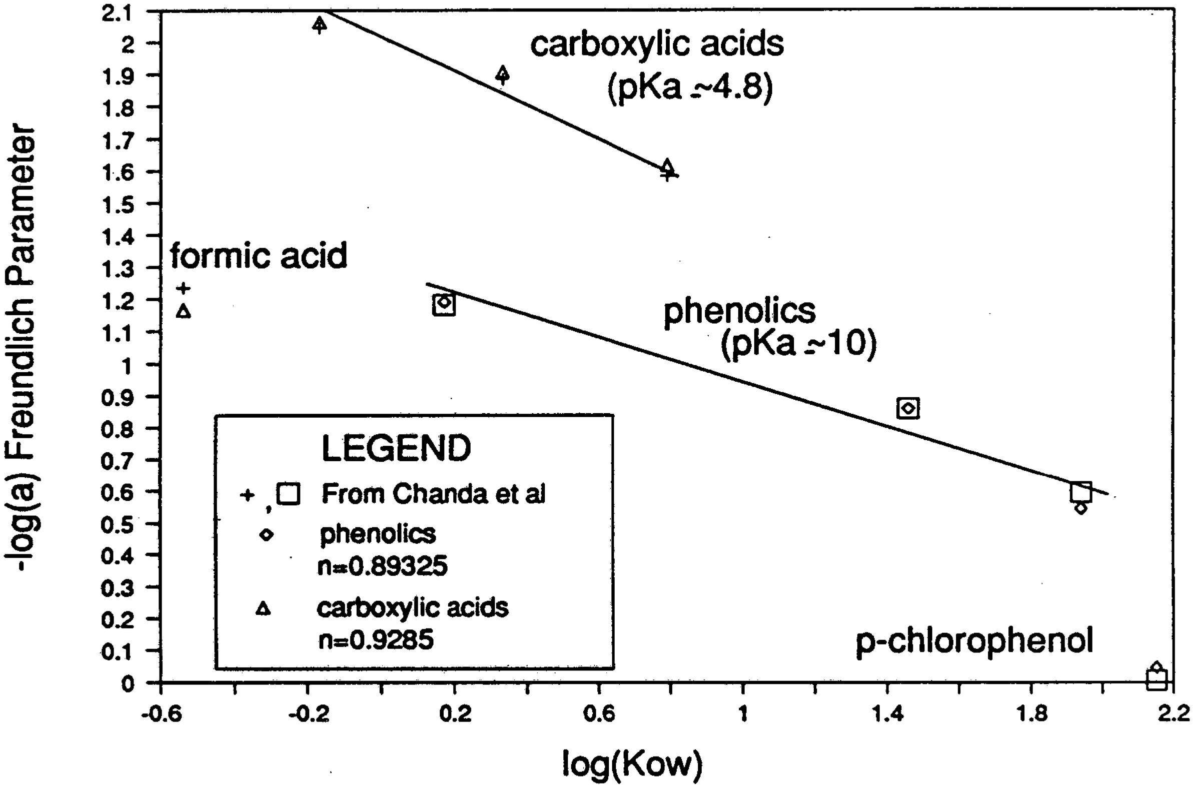


Figure 3-26. Effect of Solute Hydrophobicity On Sorption for Polyvinylpyridine

ter partition coefficient (K_{ow})[30] for each solute is plotted versus pa or -log(a), where a is the sorption affinity constant obtained by regressing the sorption data using a Freundlich isotherm.

$$x = aC^{n} \qquad \textit{Equation} \quad 3-13$$

$x = equilibrium \quad sorption \quad (mmol/g)$
$C = equilibrium \quad concentration \quad (mmol/g)$

Both figures show sorption affinity constants (a) given by Chanda, O'Driscoll and Rempel as well as sorption affinity constants calculated using their data and fixing the value of n in the Freundlich equation to an average n given in Table 3-6. An average n for each class of solute with P4VP and with Aurorez were determined, and then the a parameter which gave the best fit to the data was calculated. This was done in an effort to compare sorption affinities having the same units. Sorption affinities determined this way agree quite well with the affinities reported by Chanda, O'Driscoll and Rempel.

For both sorbents, the solutes of the same family which have roughly similar acidities follow a linear trend of increasing sorption affinity for increasing values of K_{ow}. In each family of solutes, Chanda et. al. used one solute (formic acid of pKa=3.75 and p-chlorophenol of pKa=9.4) which had a relatively greater acidity than the rest of the solutes in that family. Figures 3-25 and 3-26 show that for both sorbents, the data for formic acid and p-chlorophenol do not lie along the same line with the rest of the solutes in their respective families, and they exhibit higher sorption affinities.

This analysis suggests that the free energy of sorption is linearly related to the sum of the free energy of acid/base interaction and the free energy of transfer for a solute out of the aqueous phase to a nonpolar phase. In this case, K_{ow} was used as the measure of the free energy of solute transfer because values were available for all the solutes.

Octanol/water partition coefficients have been correlated with solubilities in water for phenols and they thus correlate weakly with infinite dilution activity coefficients for these relatively insoluble solutes.[31]

Table 3-6. Freundlich Parameters for Sorption by Aurorez and P4VP

		Chanda et al		Recalculated	
Sorbent	Sorbate	a	n	a	n
Aurorez	phenol	0.054	0.917	0.052	0.932
	p-cresol	0.080	0.935	0.080	0.932
	p-cholorophenol	0.140	0.927	0.138	0.932
	m-aminophenol	0.035	0.950	0.036	0.932
P4VP	phenol	0.138	0.894	0.138	0.893
	p-cresol	0.254	0.948	0.286	0.893
	p-cholorophenol	0.988	0.850	0.901	0.893
	m-aminophenol	0.066	0.881	0.064	0.893
Aurorez	formic acid	0.36	0.443	0.273	0.579
	acetic acid	0.102	0.64	0.115	0.579
	propionic acid	0.125	0.628	0.138	0.579
	n-butyric acid	0.196	0.606	0.207	0.579
P4VP	formic acid	0.058	1.003	0.068	0.929
	acetic acid	0.009	0.911	0.009	0.929
	propionic acid	0.013	0.905	0.012	0.929
	n-butyric acid	0.026	0.895	0.024	0.929

Another interesting observation concerning the data shown in Figures 3-25 and 3-26 is that Aurorez has a greater affinity for carboxylic acids than for phenols, while PVP has a greater affinity for phenols than for carboxylic acids. One possible explanation for this is that carboxylic acids are harder acids than phenols, and Aurorez (benzimidazole) is a harder base than PVP (pyridine).

A more direct method of incorporating hydrophobic effects and acid/base interactions would be to regress sorption data using aqueous phase activity instead of concentration.

Figures 3-27 and 3-28 show that, for the carboxylic acid solute data given by Chanda et al., regressing the sorption data for both sorbents using activities rather than concentrations narrows the differences in sorption affinity among n-butyric, acidic, and propionic acids.

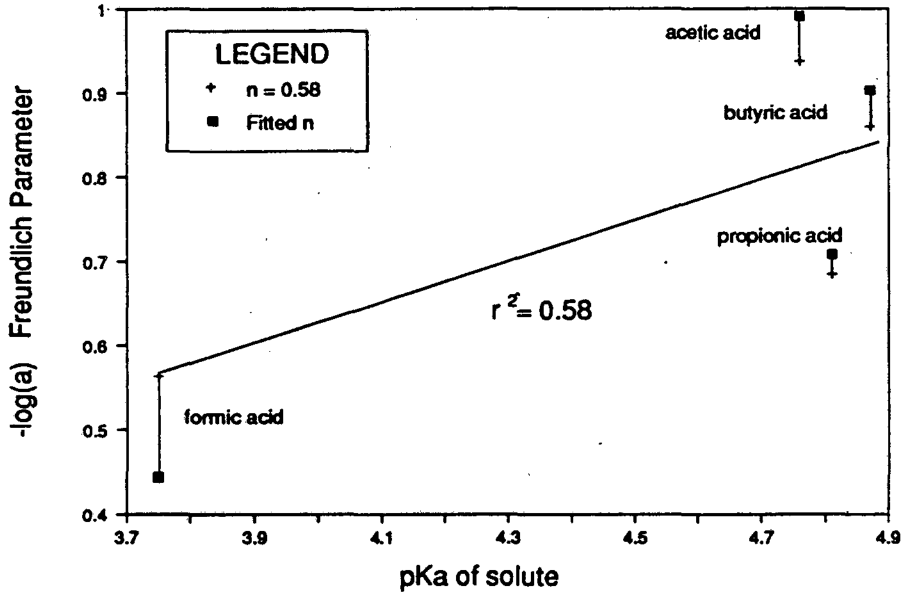
3.5 Sorbent Selectivity: Swelling and Pore Filling as Mechanisms for the Imbibition of Bulk Liquid

Polymer sorbents can imbibe bulk liquid by filling pores and/or by swelling. Fixed macroporosity can improve mass transfer, but the concentration of the solution in the pores should be close to the equilibrium bulk liquid concentration[21], with subsequent loss in selectivity. Relaxation of the polymeric structure leads to swelling, also hurting selectivity.

In the next two sections imbibition of bulk liquid by these two mechanisms is explored. Studying the imbibition properties of available commercial sorbents should provide insight towards the design of sorbents with more favorable solution uptake characteristics.

3.5.1 Effect of Increasing Acetic Acid Concentration on Swelling

Acetic acid and water have similar densities (1.05 g/cm^3 versus 1 g/cm^3 at 25 °C). Therefore, for sorbents of fixed pore structure which do not swell in solution, the use of centrifugation followed by gravimetric analysis to determine the mass of solution retained by the sorbent should yield solution uptakes which do not increase with increasing acetic acid concentration. Gel and weakly cross-linked sorbents which swell exhibit solution uptakes which increase with increasing acetic acid concentration. This is



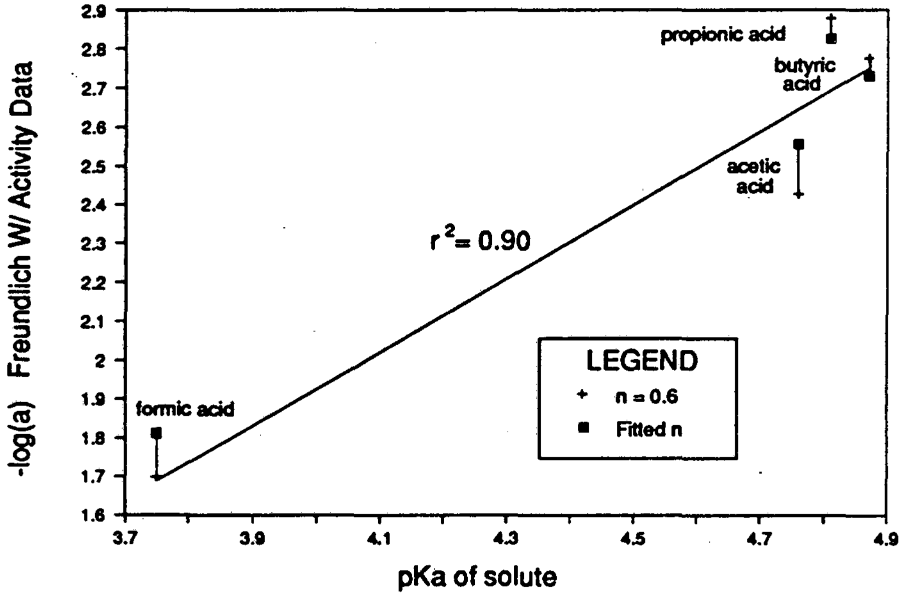
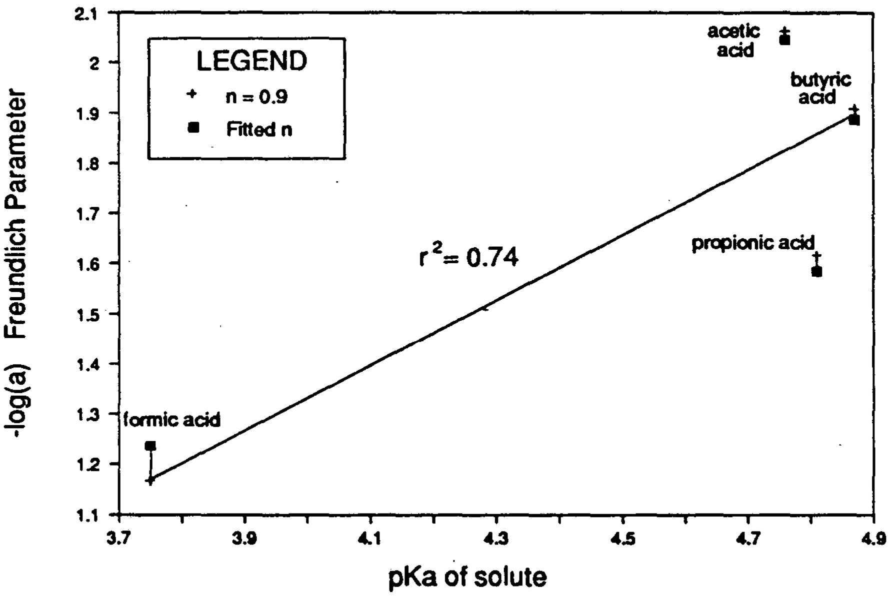


Figure 3-27. Effect of Solute Acidity On Sorption for Aurorez



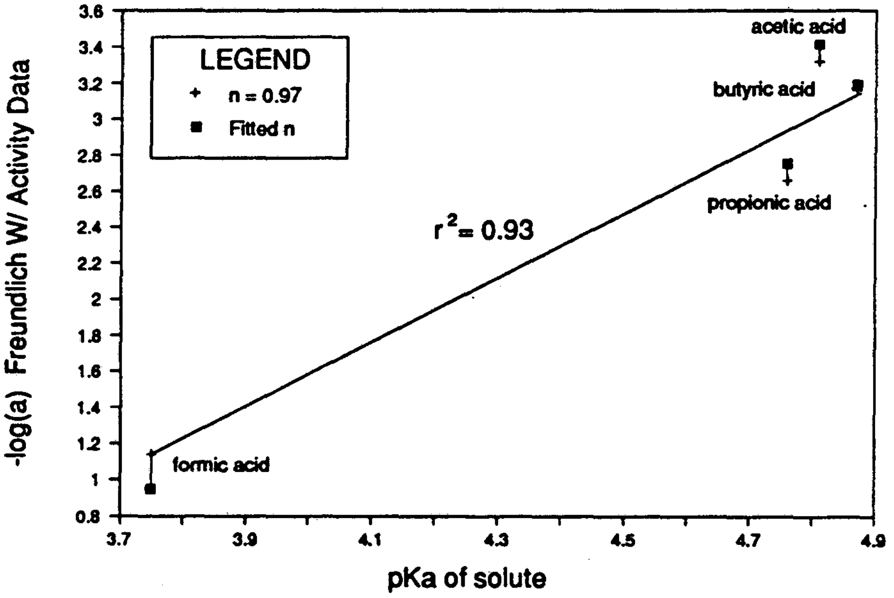


Figure 3-28. Effect of Solute Acidity On Sorption for Polyvinylpyridine

due to the relaxation of the polymer matrix to accommodate the acid/base complex as well as some associating or solvating water. Swelling may be necessary for the gel sorbents in order to provide accessibility of all the basic functional group sites without great transport rate limitations.

Figures 3-29 and 3-30 show how the total amount of solution sorbed increases with increasing equilibrium acetic acid concentration for all the sorbents studied. An informative way to display the solution uptake data for the various types of sorbents used is illustrated in Figures 3-31 and 3-32. For both graphs, the abscissa is the negative of the natural logarithm of the ratio of the water concentration in the sorbate phase to the bulk liquid water concentration. The amount of liquid sorbed is plotted versus this term because the logarithmic term may be proportional to an osmotic pressure π defined in the following equation[16] :

$$\pi = -\frac{1}{v_w} RT \ln\left(\frac{a_c^*}{a_c}\right) \qquad \textit{Equation} \quad 3-14$$

where a_c^* and a_c are the water activities in the sorbate and bulk liquid phases, and v_w is the partial molar volume of the solvent. Gregor[32] found that the osmotic pressure difference in ion exchangers is linearly related to the equivalent volume of the swollen exchanger. The equivalent volume (cm^3/equivalent) may be related to the amount of liquid sorbed if solution is taken up by imbibition due to swelling. Thus, if activity effects are neglected, or if the ratio of solvent activity coefficients in the sorbate and bulk liquid phases is constant, then the amount of liquid taken up by the sorbent may be linearly related to $-\ln(W_c^*/W_c)$.

Figure 3-31 contains data for all the weak base sorbents studied except for the Rohm and Haas polyvinylpyridine sorbents. Figure 3-32 compares solution uptakes for the

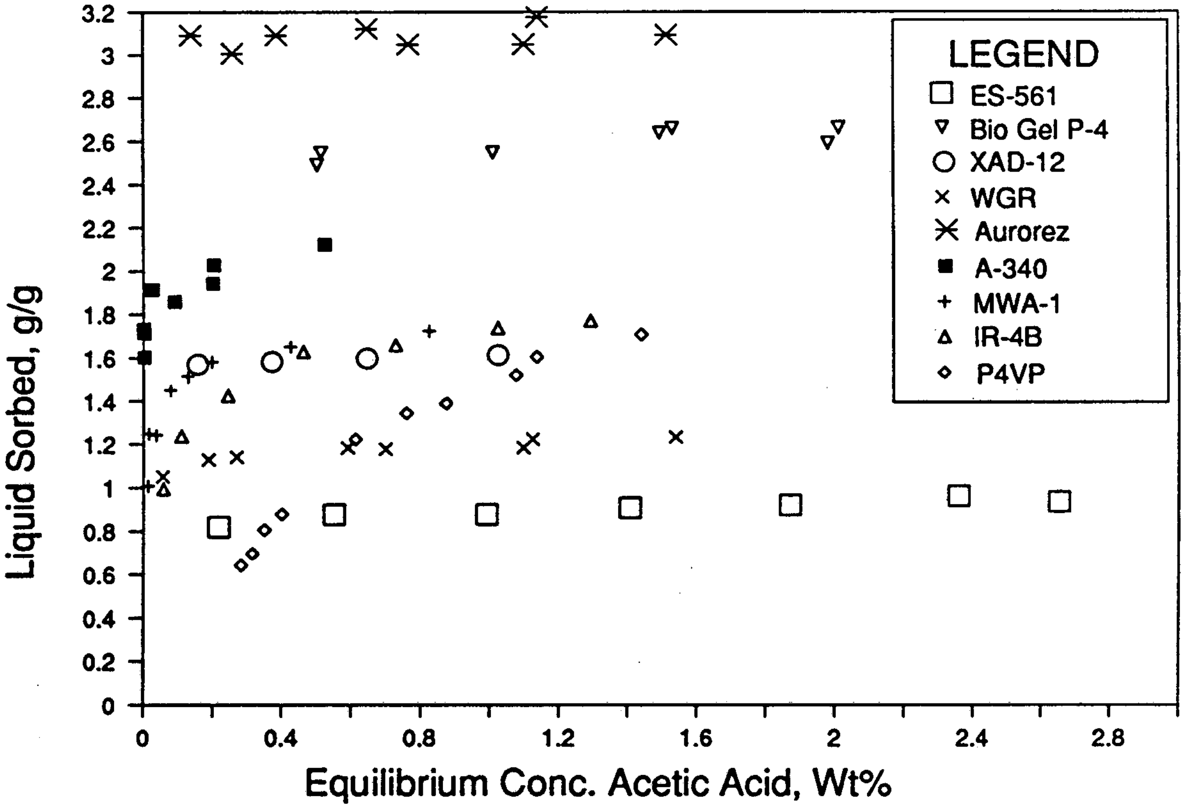


Figure 3-29. Effect of Acetic Acid Concentration on Imbibition of Solution for Selected Sorbents (gram solution per gram dry resin)

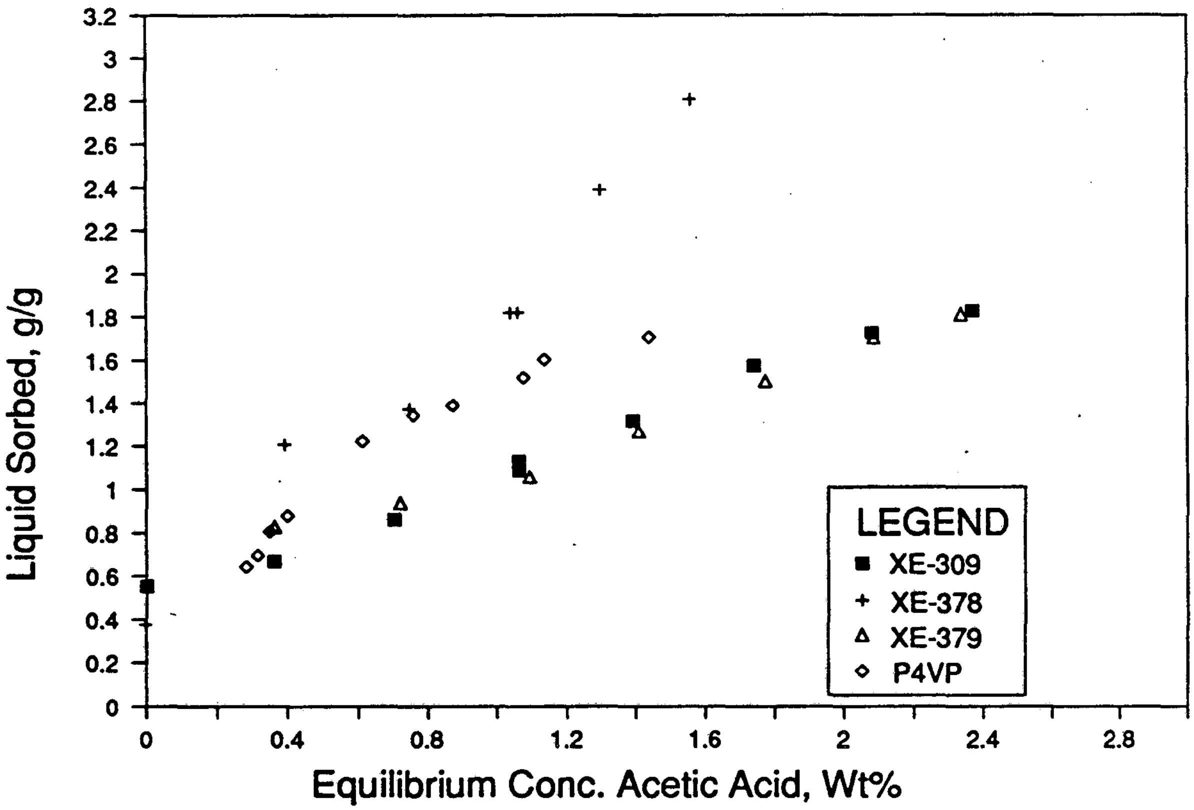


Figure 3-30. Effect of Acetic Acid Concentration on Imbibition of Solution
for Polyvinylpyridine Sorbents
(gram solution per gram dry resin)

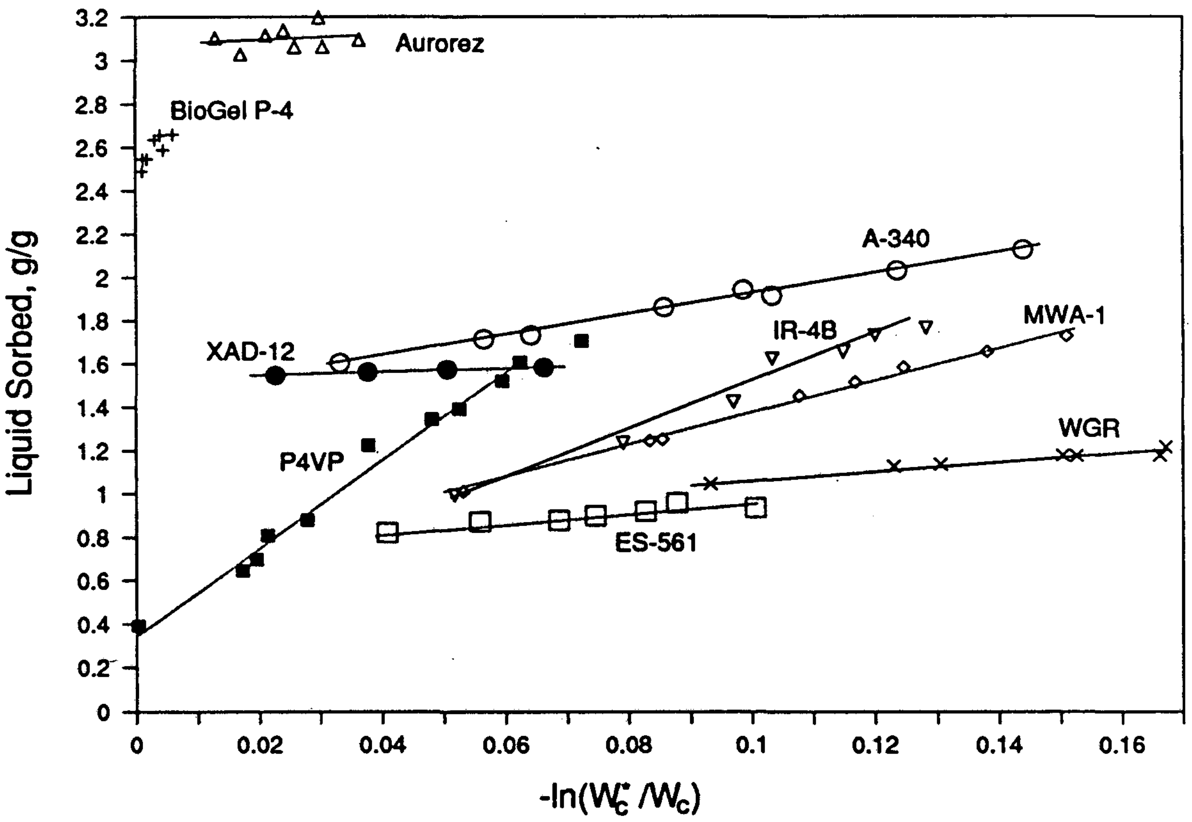


Figure 3-31. Imbibition of Solution Due To Pore Filling and Swelling for Selected Sorbents (gram solution per gram dry resin)

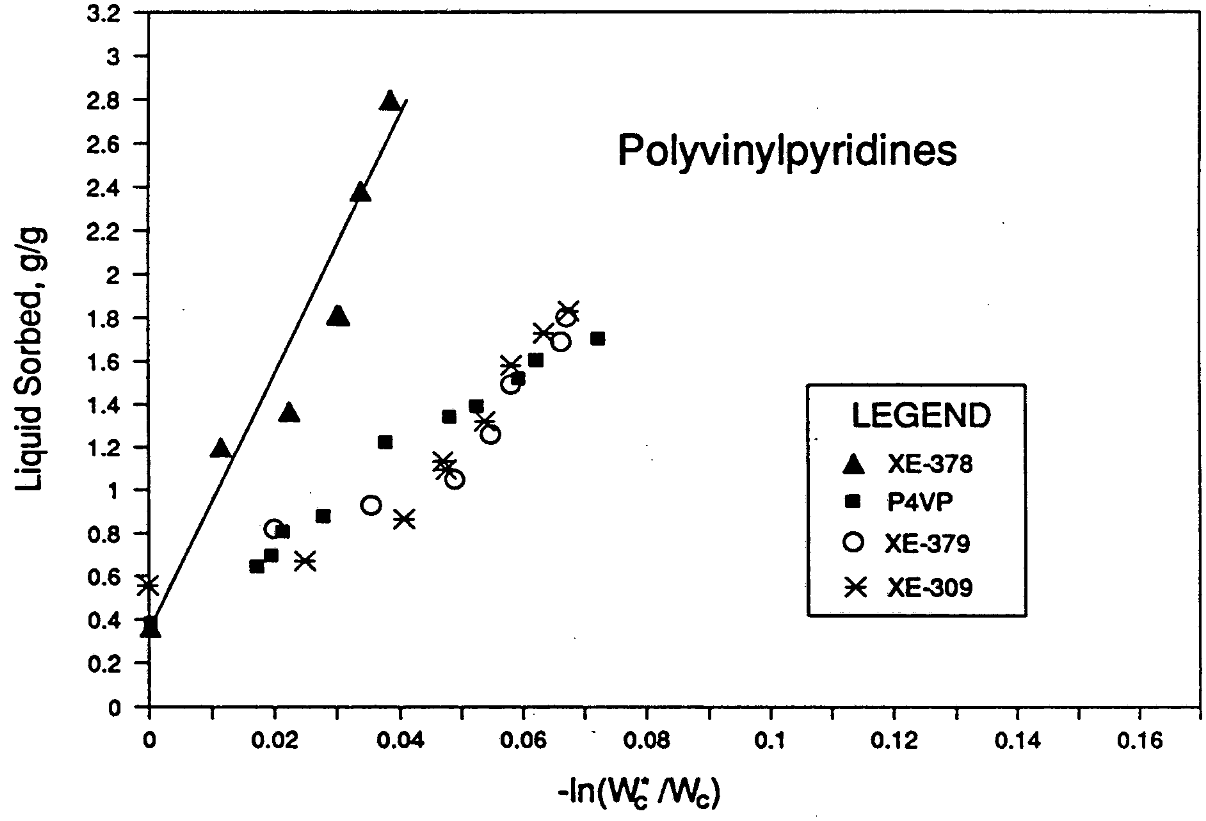


Figure 3-32. Imbibition of Solution Due To Pore Filling and Swelling for Polyvinylpyridine Sorbents (gram solution per gram dry resin)

polyvinylpyridine sorbents. As a point of reference, increasing values of the abscissa correspond to increasing equilibrium acetic acid concentration. In general, Figures 3-31 and 3-32 show that most of the sorbents have solution uptakes of 1-2 g/g . These data also point out that the polyvinylpyridine sorbents exhibit dramatic increases in solution uptakes due to swelling. Highly cross-linked condensation polymer sorbents such as Duolites A-340 and ES-561, Dowex WGR and Amberlite IR-4B exhibit much less swelling. Aurorez and Amberlite XAD-12 swell very little over the concentration range studied; their solution uptakes are primarily due to macropore filling.

3.5.2 Effect of Position of Methyl Substituent on Swelling Properties of Polyvinylpyridine Resins in Acetic Acid Solution

The Rohm and Haas polyvinylpyridine sorbents, XE-309, XE-378, and XE-379 have about the same nominal cross-linking percentage (7% divinylbenzene[3]). However, the 2-methyl pyridine sorbent, XE-378, swells markedly more than the 3 or 4-methyl substituted structures. One possible explanation for this effect is that the 2-methyl group causes greater expansion or relaxation of the polymer structure due to steric repulsion between neighboring acetic acid/pyridine nitrogen complexes and the methyl group. Steric effects have been shown to decrease the donor strength of 2-methyl-pyridine as compared to pyridine despite the increase in nitrogen donor strength created by a methyl substitution on the pyridine ring[33]. It is also possible that the nominal cross-linking may not reflect the true cross-linking percentage. Many researchers have shown that polymer swelling is greatly affected by the degree of cross-linking[34,35].

Another interesting feature of the polyvinylpyridine data is the curvature in the XE-309 and XE-379 data as compared to the data for Reilly P4VP and XE-378. Both XE-309 and XE-379 have substantial dry porosities (.34 and .35 cm^3/cm^3). The apparent curvature of the data may be due to pore filling at low values of the abscissa (low acetic acid concentration), followed by swelling at higher values. On the other hand, XE-378 and P4VP have lower dry porosity, and swelling is the dominant mechanism for solution uptake throughout the concentration range.

3.6 Summary and Conclusions

The sorption mechanism for a monobasic acid such as acetic acid was rationalized as a 1:1 complex formation with basic functional groups in the sorbent. Sorbents with functional groups which are not sufficiently spaced apart in the polymer matrix encounter base-weakening effects, leading to a lowering of their capacities for weak acids. Also, sorbents with functionalized cross-linking agents which are base weakening can have lower sorption affinities for weak acids.

Various methods for determining the basicity of sorbents and sorbent functional groups were examined for predicting sorption affinity. The Gutmann Donor Number was found to be a good barometer of sorption affinity. Determinations of "apparent" polymer pKa may also be useful, but they are subject to errors due to Donnan equilibrium and/or electrical double layer effects. The correct interpretation of titration results to determine "true" pKa values relies on modeling which requires hard to determine properties[16]. Monomer functional group basicity determinations such as pKa or DN are not dependent on knowledge of polymer matrix structure, and particular values for these scales can be easily found or calculated.

Selectivity for acetic acid over water can be compromised by both polymer swelling and macropore filling with bulk solution. Higher cross-linking for polyvinylpyridine sorbents (most are nominally 7% DVB) should improve their selectivities if they are kept macroreticular. Swelling is also undesirable from the standpoint of fixed-bed operations.

Very high porosity such as that found in the polybenzimidazole sorbent Aurorez is also undesirable. However, transport rate considerations will no doubt warrant some optimal degree of porosity.

Chapter 3 References

1 Munson, C.L., Ph.D. Dissertation, Dept. of Chemical Engineering, University of California, Berkeley (1985).

2 Frierman, M., M.S. Thesis, Dept. of Chemical Engineering, University of California, Berkeley (1983).

3 Naples, John, Rohm & Haas Co., Springfield, Pennsylvania, Personal Communication (1987).

4 Chanda, M., O'Driscoll, K.F., Rempel, G.L., Reactive Polymers, 4, 39 (1985).

5 Kuo, Y., Munson, C.L., Rixey, W.G., Garcia, A.A., Frierman, M., King, C.J., Separation and Purification Methods, 16, 31 (1987).

6 Kennedy, D.C., Ind. Eng. Chem. Prod. Res. Develop., 12, 56 (1973).

7 Petersen, Sigfried, Ann. N.Y. Acad. Sci., 57, 144 (1953).

8 Clifford, D., Weber, W.J., Jr., Report No. EPA-600/2-78-052, U.S. Environmental Protection Agency (1978).

9 "Dowex Ion Exchange Resins Engineer's Handbook", Dow Chemical Co., Midland, Michigan (1983).

10 "Chromatography, Electrophoresis, Immunochemistry, Molecular Biology, HPLC Price List L", Bio-Rad Labs., Richmond, California (1986).

11 Helfferich, F., "Ion Exchange", McGraw-Hill, New York, p. 85 (1962).

12 Perrin, D.D., Dempsey, B., Serjeant, E.P., "pKa Prediction of Organic Acids and Bases", Chapman and Hall, London (1981).

13 Taft, R.W., Lewis, I.C., J. Amer. Chem. Soc., 81, 5343 (1959).

14 Weast, R.C., ed., "CRC Handbook of Chemistry and Physics, 51st Edition", The Chemical Rubber Co., Ohio, pp. D-117,D-118 (1970).

15 Windholz, M., ed., "The Merck Index, 10th Edition", Merck & Co., Inc., New Jersey (1983).

16 Helfferich, F., "Ion Exchange", McGraw-Hill (1962).

17 Petersen, Sigfried, Ann. N.Y. Acad. Sci., 57, 144 (1953).

18 Myers, R.J., Eastes, J.W., Urquhart, D., Ind. Eng. Chem., 33(10), 1270 (1941).

19 Shepherd, E.J., Kitchener, J.A., J. Chem. Soc. London, 86 (1957).

20 Gustafson, R.L., Fillius, H.F., Kunin, R., Ind. Eng. Chem. Fundam., 9(2), 221 (1970).

21 Munson, C.L., Garcia, A.A., Kuo, Y., Frierman, M., King, C.J., Separation and Purification Methods, 16(1), 65 (1987).

22 Kuo, Y., Munson, C.L., Rixey, W.G., Garcia, A.A., Frierman, M., King, C.J., Separation and Purification Methods, 13, 31 (1987).

23 Ng, M., M.S. Thesis, Dept. of Chemical Engineering, University of California, Berkeley (1988).

24 Ramirez, J.E., Celanese Corp., Charlotte, NC 28232, Personal Communication (1987).

25 Jensen, W., "The Lewis Acid-Base Concepts, an Overview", Wiley, New York (1980).

26 Addy, J.K., Andrews, R.D., Macromolecules, 11(6), 1283 (1978).

27 Hammett, L.P., "Physical Organic Chemistry", Mc-Graw Hill Co., New York (1940).

28 Hammett, L.P., Chem. Rev., 17, 125 (1935).

29 Saunders, L., Srivista, R.S., J. Chem. Soc., 2111 (1952).

30 Klopman, G., Namboodiri, K., Schochet, M., J. of Comp. Chem., 6, 28 (1985).

31 Lyman, W.J., Reehl, W.F., Rosenblatt, D.H., "Handbook of Chemical Property Estimation Methods", McGraw Hill, New York, pp. 1-47 through 1-49 (1982).

32 Gregor, H.P., J. Am. Chem. Soc., 73, 642 (1951).

33 Drago, R.S. and Matwiyoff, N.A., "Acids and Bases", D.C. Heath and Co., Massachusetts, 1968, Chapter 3.

34 Errede, L.A., Macromolecules, 19, 654 (1986).

35 Naveh, J., Marcus, Y., Journal of Chromatography, 148, 495 (1978).

Chapter 4: Recovery of Sorbed Acetic Acid

4.1 Experimental Procedure

Solvent regeneration experimental procedures mirrored the sorption procedures explained in Section 3.1.3 . After centrifugation, the sorbent laden with acetic acid and water was placed in a clean 20 ml scintillation vial. Ten milliliters of solvent were added, and equilibration was conducted as described above. After equilibrium was reached (within 24 hours), the concentration of acetic acid in the bulk solvent phase was measured by direct injection of a 1 microliter sample into a Varian Model 3700 gas chromatograph equipped with a thermal conductivity detector and a 76 cm Poropak R column (Waters Associates) . The gas chromatograph was operated with temperature programming between 120 and 220 °C in the sequence (1) 1 minute at 120 °C; (2) 20 degrees per minute to 220 °C; (3) 2 minutes at 220 °C.

4.2 Solvent Leaching of Sorbed Acetic Acid

Solvent leaching may be more attractive as a means for recovering sorbed carboxylic acids from basic polymer sorbents than regeneration by volatilizing the solute[1] . Moreover, most sorbents are temperature sensitive, decomposing at temperatures above 100 °C. A notable exception to this temperature limit is Aurorez (see Table 3-2). It is also desirable that the sorbent be regenerated to a form where it can be reused. A regeneration scheme which would require consumption of chemicals is economically undesirable. A common, volatile solvent such as methanol is considered a suitable regeneration solvent. However, sorbents of high basicity are difficult to regenerate with methanol. It was found that solvent regeneration could be facilitated by using solvents of higher basicity.

4.2.1 Effect of Functional Group Basicity

Just as the analysis of the sorption data led to an ideal exchange model, solvent leaching data can be analyzed as a competition between the solvent and the basic functional group of the sorbent for acetic acid. In both cases, a 1:1 complex between acetic acid and a basic functional group is assumed. This competition can be expressed as the following reaction:

$$HOAc-B \quad + \quad nS(b) \quad \rightarrow \quad S_n-B \quad + \quad HOAc(b) \qquad \textit{Equation} \quad 4-1$$

where (b) represents the bulk liquid phase, S represents a solvent molecule, S_n-B is the solvent-functional group association, and the other terms are the same as in the ideal exchange model. For this reaction, an affinity constant can be defined

$$K_R^1 = \frac{[S_n-B][HOAc(b)]}{[HOAc-B][S(b)]^n} \qquad \textit{Equation} \quad 4-2$$

leading to the following expression:

$$\frac{q_R}{q_{mR}} = \frac{(1/K_R)C_{HOAc(b)}}{1+(1/K_R)C_{HOAc(b)}} \qquad \textit{Equation} \quad 4-3$$

where the subscript (R) distinguishes solvent leaching as opposed to sorption from aqueous solution. The form of Equation 4-3 is almost identical to the ideal exchange model because similar assumptions are made. The term q_R refers to the sorption (or retention) of acetic acid on the surface or on sites at a particular bulk solvent phase acetic acid concentration ($C_{HOAc(b)}$). However, as explained in Section 3.4, the composite uptake is used because the individual uptake reflects both complexed and non-selectively sorbed acetic acid. In the same vein, q_{mR} is considered to be the composite uptake capacity for retention of acetic acid, instead of the individual uptake capacity.

Obviously, there are several grossly simplifying assumptions in this model. The most important simplifications are the neglect of the effects of sorbed water and of the presence of water in the solvent phase. Also, reversibility of the acid/base complex is assumed. All the data are based on leaching sorbed acetic acid out from the sorbent. No experiments involving multicomponent sorption of acetic acid/water/solvent mixtures on fresh sorbent were performed. Multicomponent sorption and leaching results might be different.

The goal of modeling these data is to determine the efficacy of solvent leaching and the effects of both functional group and solvent basicity on sorbent regeneration. The parameter of interest is K_R. Capacities as determined by the q_{mR} parameter were found to be lower than q_m determined through the ideal exchange model and aqueous sorption data. This may be due to a competition between water and acetic acid for some of the basic sites.

Table 4-1 compares q_{mR} with q_m values from the ideal exchange model. All the q_{mR} values are lower than q_m except for ES-561, where the two quantities are equal. As with the sorption data, for the sorbents which have linear leaching isotherms, the value of q_{mR} is fixed to the total basic functional group concentration determined by HCl titration or, in the case of Bio Gel P-4, the theoretical capacity is used (see Table 3-2). All of these sorbents are monofunctional. The parameters q_{mR} and K_R were determined by linearizing Equation 4-3 as described in Section 3.4 . Appendix C contains leaching isotherms for all the sorbents investigated.

Of primary interest in this modeling effort is to quantify the affinity constant (K_R) for leaching acetic acid back into the bulk liquid phase. We would expect, in the same manner as with pK (sorption affinity), that pK_R is linearly related to a free energy term characterizing sorbent basicity. The most direct characterization of sorbent basicity and complexation affinity with acetic acid is the sorption affinity constant, K, itself. Figure 4-1 shows that pK correlates reasonably well with pK_R. As a point of clarification, increasing (more positive) values of pK_R indicate strong complexation with low degree of leaching while decreasing (more negative) values of pK indicate high affinity or strong complexation with the sorbent functional group. Also shown in Figure 4-1 is a line corresponding to $-pK_R = pK$. The data correlate with this equation, suggesting that the free energy of complexation is approximately equal in both solvents (methanol and water).

Table 4-1. Comparison Between q_{mR} and q_m

Polymer Sorbent	q_m, meq/g	q_{mR}, meq/g
IR-4B	3.9	2.3
ES-561	1.7	1.7
Duolite A-340	5.8	3.4
Dowex WGR	3.8	1.9
Dowex MWA-1	4.9	3.8
XAD-12	4.8	1.9
Aurorez	2.2	1.0

Using the same four measures of sorbent basicity that were used previously (Section 3.4.1), Figures 4-2 through 4-5 compare pK_R with the "apparent" polymer pKa, pKa of

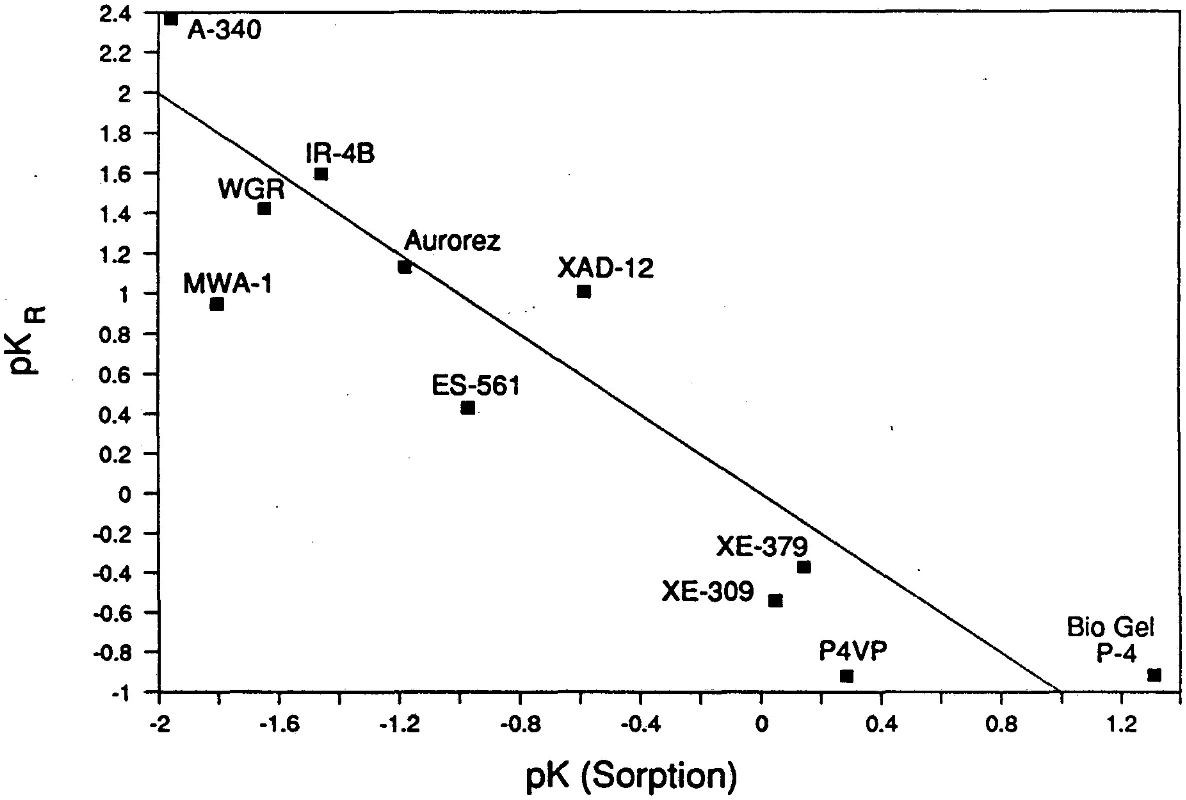


Figure 4-1. Correlation Between Sorption Affinity and Methanol Leaching Affinity

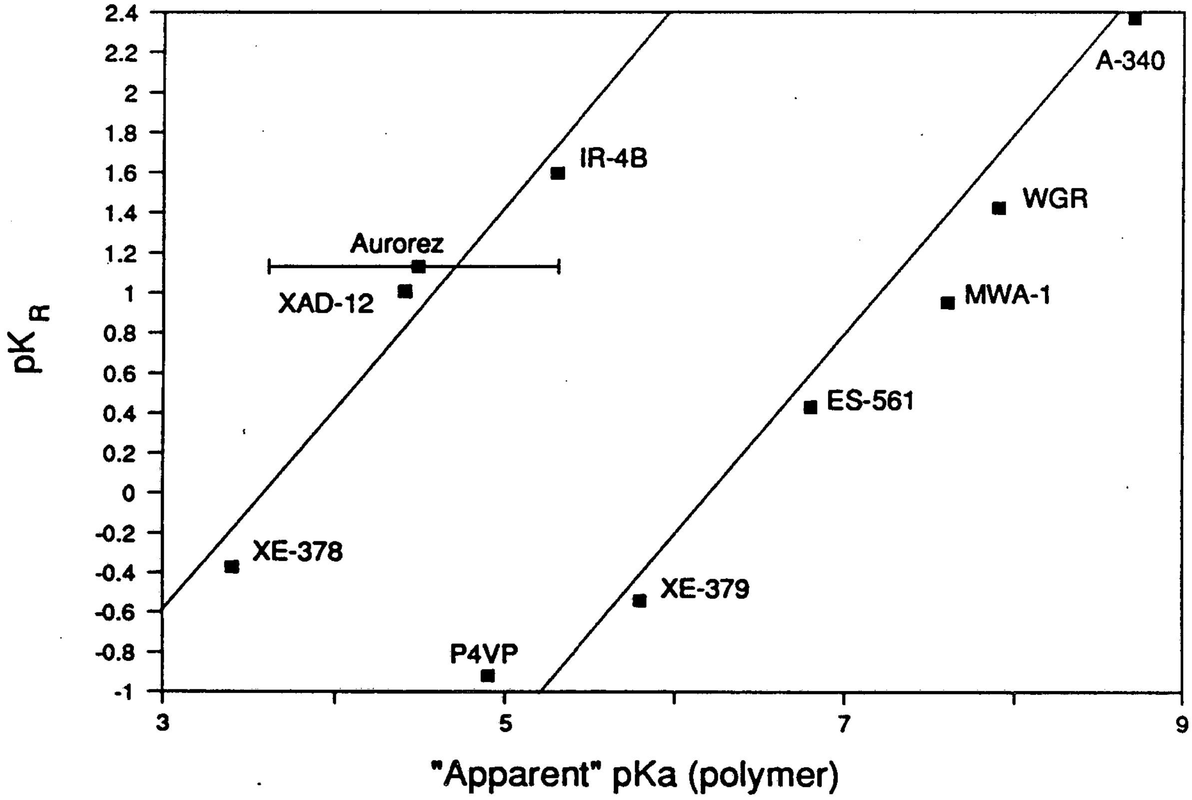


Figure 4-2. Correlation Between "Apparent" Polymer pKa and Methanol Leaching Affinity

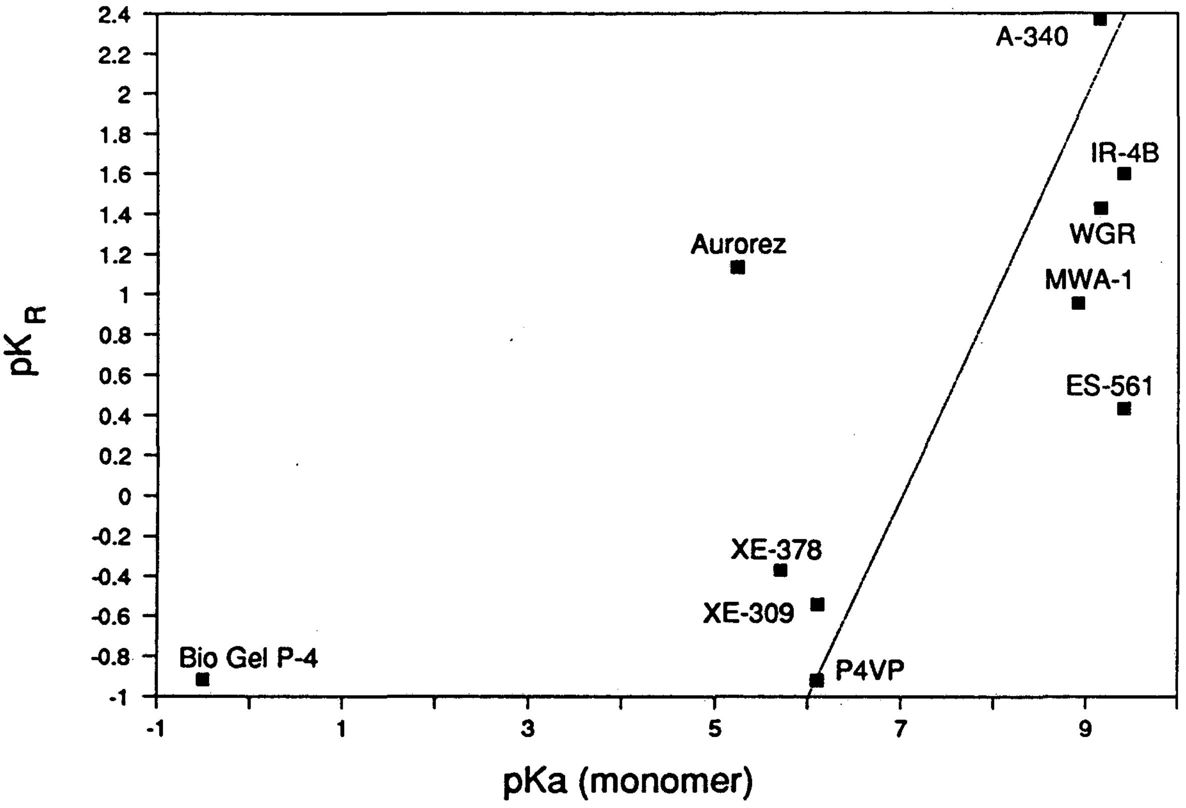


Figure 4-3. Correlation Between Monomeric Functional Group pKa and Methanol Leaching Affinity

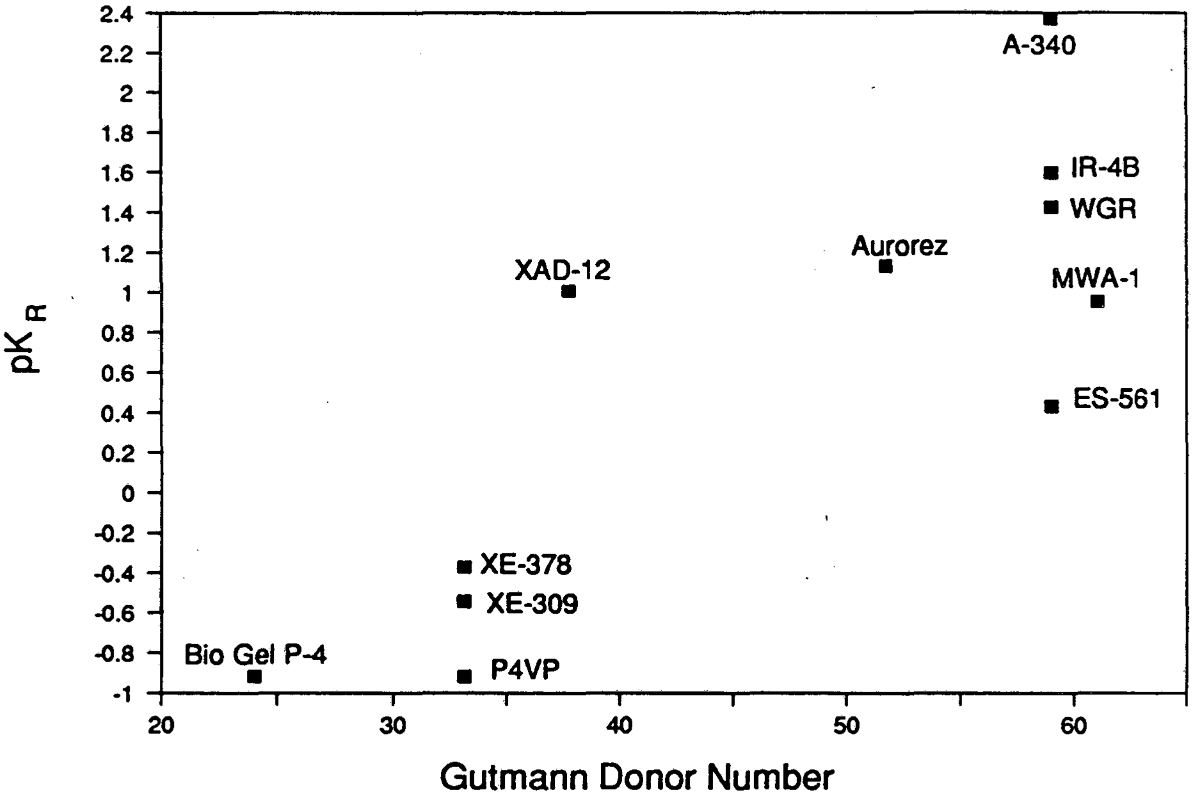


Figure 4-4. Correlation Between Gutmann Donor Number and Methanol Leaching Affinity

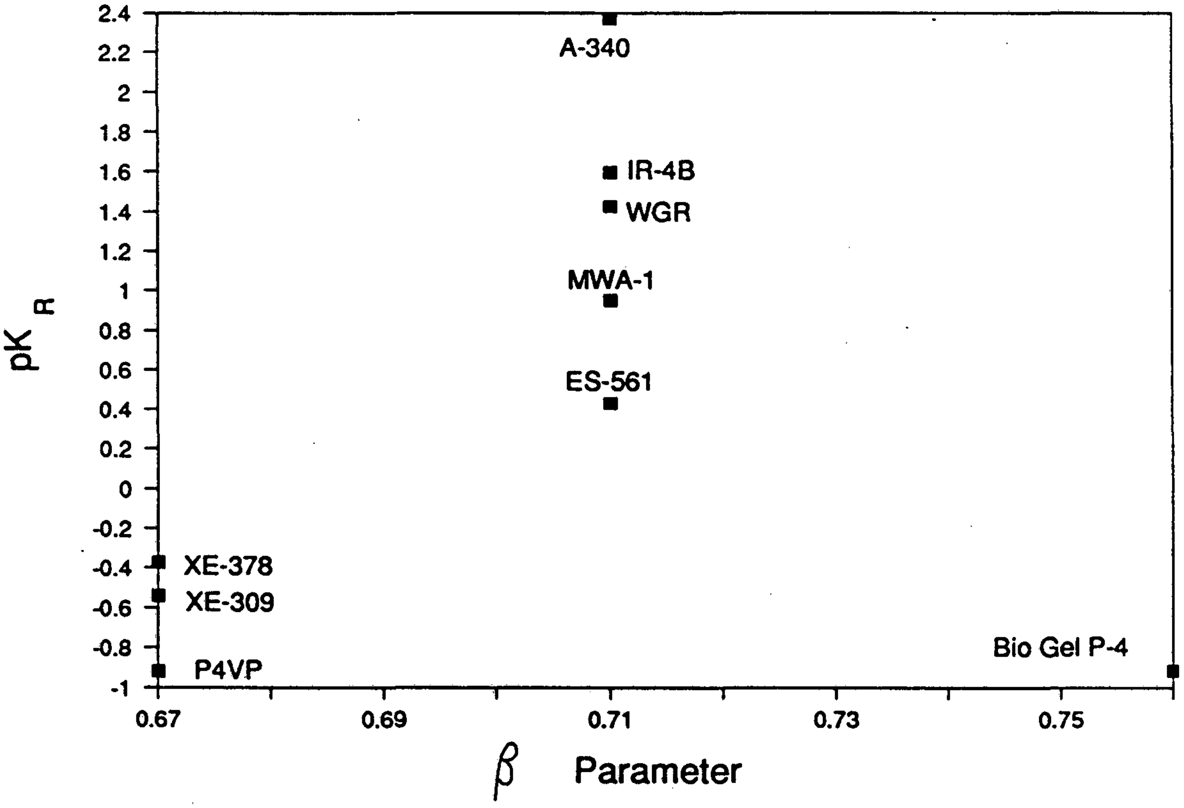


Figure 4-5. Correlation Between Solvatochromic β Parameter and Methanol Leaching Affinity

the most basic functional group on the sorbent, the Gutmann DN of the monomeric functional group, and the β parameter for the monomeric functional group. It is apparent from a comparison of Figures 4-1 and 3-19 that, except for XE-378, Aurorez, IR-4B and XAD-12, the "apparent" polymer pKa correlates strongly with both pK and pK_R. As in Figure 3-19, Figure 4-1 also contains two lines of slope = +1. There appears to be good agreement between these lines and the data for the two sets of sorbents. As discussed in Section 3.4.1, pK_R might be linearly related to the "apparent" pKa in an equation of the form: $pK_R = pKa + c$, where c accounts for differences in activity coefficients for acetic acid and HCl in both the bulk solvent and sorbent phases, and differences in the acid dissociation constants (pKa) for these solutes. However, it is important to stress that XAD-12 is not an ionizing base; it exhibits soft basicity only. The use of HCl titration to characterize sorbent basicity for this sorbent is solely phenomenological. For select groups of polymer sorbents, the "apparent" pKa determination may be useful, but it is difficult to predetermine which sorbents will be amenable to this basicity classification scheme.

Monomer basicities do not correlate with pK_R as well as with pK, as is shown by comparing Figures 4-2 and 4-3 with Figures 3-20 and 3-21. Figure 4-2 also contains a line of slope = +1 as a reference. This suggests that the effects of polymer properties on basicity may be more important in solvent leaching than in sorption from aqueous solution. The swelling characteristics of the sorbents in methanol may play an important role in solvent leaching behavior, as may the presence of water.

An important quantity for assessing the utility of methanol as a leaching solvent is the percentage recovery of acetic acid in these batch leaching experiments. Table 4-2 gives the highest percentage recovery of acetic acid using 0.5 or 1 g of dry sorbent and 10 ml of methanol. The percent recovery varies with equilibrium acetic acid concentration in the leachate as well as with the ratio of solvent to loaded sorbent. For a given solvent-to-sorbent ratio, the highest percentage recovery usually occurs at higher amounts of sorbed acid because there is a higher percentage of unselectively imbibed, uncomplexed acid.

Essentially complete regeneration for the pyridine sorbents is possible using methanol. It is clear from these data that methanol is not a suitable solvent for leaching acetic acid from the sorbents of stronger basicities such as, for example, Dowex WGR. In the next section, solvents with higher basicities than that of methanol are used to determine the viability of solvent leaching for stronger base sorbents.

Table 4-2. Recovery of Acetic Acid By Batch Leaching With Methanol

Polymer Sorbent	Percent Recovery (1g/10 mls)	Percent Recovery (0.5g/10 mls)
IR-4B	32	--
ES-561	67	--
Duolite A-340	9	27
Dowex WGR	--	54
Dowex MWA-1	32	51
XAD-12	44	--
Aurorez	53	68
P4VP	108	105
XE-309	100	--
XE-378	99	--
BioGel P-4	70	80

4.2.2 Solvents With Different Basicities

Solvents with different degrees of basicity were used to leach acetic acid from Dowex WGR. Appendix C gives the leaching isotherms for Dowex WGR using various solvents. After the leaching isotherms were modeled, as discussed in the previous section, leaching affinity constants K_R were determined. Figure 4-6 compares $-\log(1/K_R)$ or $-pK_R$ values with the hydrogen bond acceptor (HBA) basicity of the solvent determined through the solvatochromic β scale. The β scale is more useful than the DN scale in this analysis because values for a wide variety of solvents are available. Also, soft basicity is probably more important for these solvents. Note that for this graph higher values indicate higher affinity for the solvent phase and better leaching properties. The solvent labeled DMI is 1,3-dimethyl-2-imidazolidinone (Figure 4-7):

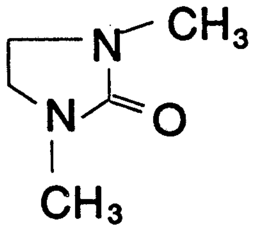


Figure 4-7. Chemical Structure of 1,3-Dimethyl-2-imidazolidinone

Chloroform was extremely ineffective as a regeneration solvent -- providing very low concentrations of acid in the bulk solvent phase. The chloroform datum point is shown as an arrow at zero instead of a discrete point because the amount of acetic acid in the chloroform phase could not be measured. Water is both an acid and a base; its basicity allows for the leaching of acetic acid back into the bulk aqueous phase. The water point may be higher because of the additional opportunity for acting as an acid in interacting with the C=O group of acetic acid. Also note that there is some hysteresis in the aqueous

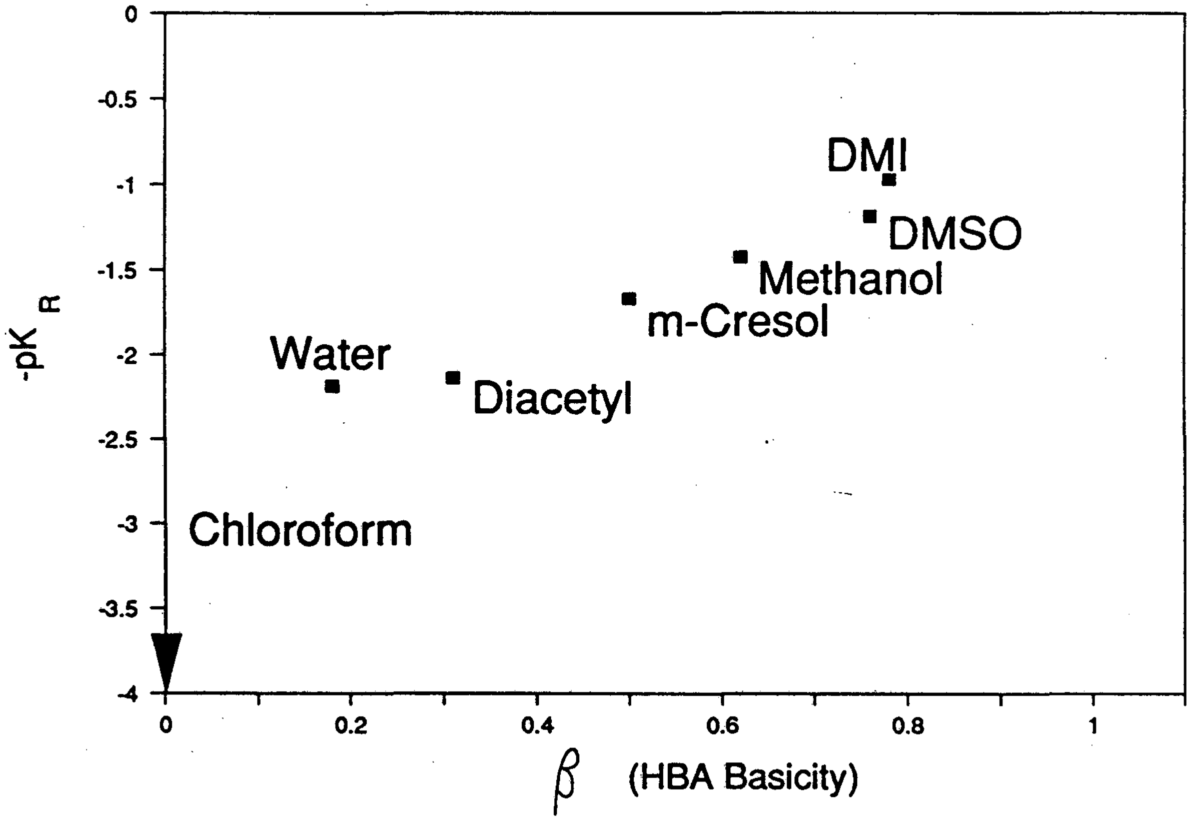


Figure 4-6. Correlation Between Solvent Solvatochromic β Parameter and Leaching Affinity

sorption/desorption isotherms since $-pK_R$ is more negative than pK (-2.2 versus -1.7). Table 4-3 gives the percentage recovery of acetic acid using these various solvents in the ratio of 10 ml of solvent to 1 gram of dry sorbent.

From the tabulated recovery values shown in Table 4-3 we can see that these solvents are probably not viable candidates for use in solvent leaching. A stronger base solvent, such as an amine, may be necessary. A volatile amine, such as methyl or ethyl amine in an organic modifier or diluent, could prove to be a successful regeneration solution.

Table 4-3. Percent Recovery of Acetic Acid From Dowex WGR By Batch Leaching

Solvent	Percentage Recovered (1g/10mls)
Chloroform	0
Water	19
Diacetyl	14
m-Cresol	20
DMSO	39
DMI	41

4.3 Aqueous Ammonia Regeneration of Sorbed Acetic Acid

An alternative regeneration medium which might also avoid consumption of chemicals is concentrated aqueous ammonia. Ammonia is a volatile ionizing base. Sorbed acid could be leached with aqueous ammonia, and the resultant salt could then revert back to molecular ammonia and acid through distillation. Experiments were performed with 0.1 <u>M</u> and 5 <u>M</u> aqueous ammonia as regenerants for Dowex WGR.

In a search for an analytical method, it was found that aqueous solutions of ammonia and acetic acid at high pH can be passed through a gas chromatography column with accurate determination of the total amount of acetic acid in the solution. Calibration curves for aqueous acetic acid with and without ammonia were identical, and the acetic acid peaks had identical residence times. Apparently, ammonium acetate is thermally cracked producing acetic acid and ammonia, which separate on the chromatograph column. The ammonia peak is buried in the large water peak because a hydrophobic column (Porapak R) was used. Thus, this analytical method gives a simple way of determining the amount of acid leached out of the sorbent, while also demonstrating that the salt can be reverted back to the molecular species by a chromatographic distillation.

4.3.1 Chemical Modeling of Leaching With Aqueous Ammonia

Full recovery of the acetic acid sorbed on Dowex WGR was possible using ammonium hydroxide. Table 4-4 summarizes the batch results for leaching with 5 M ammonium hydroxide. The first column gives the molar concentration of acetic acid in the aqueous solution used for the batch sorption experiment. The fourth column is the bulk liquid phase concentration of NH_4OAc in equilibrium with the regenerated sorbent. Taking the ratio of the values in column 4 to those in column 1 gives the degree of concentration in the combined sorption/regeneration cycle. The sorption step concentrates acetic acid in the sorbed phase relative to the bulk aqueous phase, while the regeneration with aqueous ammonia dilutes the acetic acid again, but keeps it more concentrated than it was in the aqueous feed. The third column gives the ratio of ammonium hydroxide solution used to the amount of sorbent. Finally, the fifth column is the percentage of acetic acid recovered in the regeneration. This table illustrates that sorption/regeneration gives a more concentrated acid solution and that potentially all the acetic acid can be recovered.

Table 4-4. Ammonium Hydroxide 5 M Regeneration of Dowex WGR

Starting Aqueous Solution Acetic Acid Conc., M	Sorbent Loading, g/g	Ratio of Ammonia Soln. to Resin, g/g	NH_4OAc Bulk Liquid Conc., M	Percent of Sorbed Acetic Acid Recovered, %
0.348	0.15	1.90	0.851	81
0.348	0.15	2.87	0.653	88
0.262	0.14	2.05	0.758	85
0.262	0.12	2.80	0.570	91
0.175	0.094	1.86	0.588	87
0.175	0.095	2.87	0.425	89
0.087	0.050	1.86	0.316	89
0.087	0.050	2.83	0.240	94

The way in which ammonia leaches acetic acid from the sorbent can be described through the following reaction:

$$NH_3(l) \quad + \quad HOAc(s) \quad \rightarrow \quad NH_4OAc(l) \qquad \textit{Equation} \quad 4-4$$

$$K = \frac{[NH_4OAc(l)]}{[NH_3(l)]\,[HOAc(s)]} \qquad \textit{Equation} \quad 4-5$$

where (l) and (s) refer to the bulk liquid phase and the sorbate (sorbed liquid) respectively. This expression allows for the leaching of complexed acid as well as acid trapped in the pore liquid or in the liquid occupying the cavity left by the swollen polymer matrix. From the equilibrium expression, a plot of the numerator versus the denominator should yield a line passing through the origin.

Figure 4-8 is a plot of the numerator of Equation 4-5 versus the denominator for regeneration of Dowex WGR using 0.1 M and 5 M ammonium hydroxide solution. The ammonia concentration in the bulk liquid phase was assumed to be the same as the initial concentration used; i.e., the fraction depletion of ammonia is small. The acetic acid concentration, expressed in moles/liter, is the total concentration of acetic acid in the sorbate at equilibrium. All the leached acid is assumed to be in the form of ammonium acetate since the gas chromatography results do not differentiate between molecular acetic acid and the ammonium salt. The data suggest a linear relation between the ordinate and the abscissa, however the line does not pass through the origin as required by Equation 4-5. Of the assumptions made in determining the values in Figure 4-8, the assumption that all the acetic acid leached out is in the form of ammonium acetate may have caused an overprediction of the ammonium acetate in the bulk liquid phase. This would shift the best fit line through the data away from the origin. From the solvent leaching results in the previous section, we know that some molecular acetic acid can be leached out of the sorbate by water, solely by dilution. In order to utilize the regeneration strength of ammonium hydroxide solution fully, the use of high concentrations, such as the commercial solution grade of 15 M, would be most desirable. Higher concentrations could fully recover sorbed acetic acid from a fixed bed of sorbent, using small bed volumes and yielding high concentrations of acetic acid in the leachate.

4.4 Summary and Conclusions

Solvent leaching with common, volatile solvents such as methanol is useful for recovering acetic acid from the weaker base sorbents. Not surprisingly, affinities for

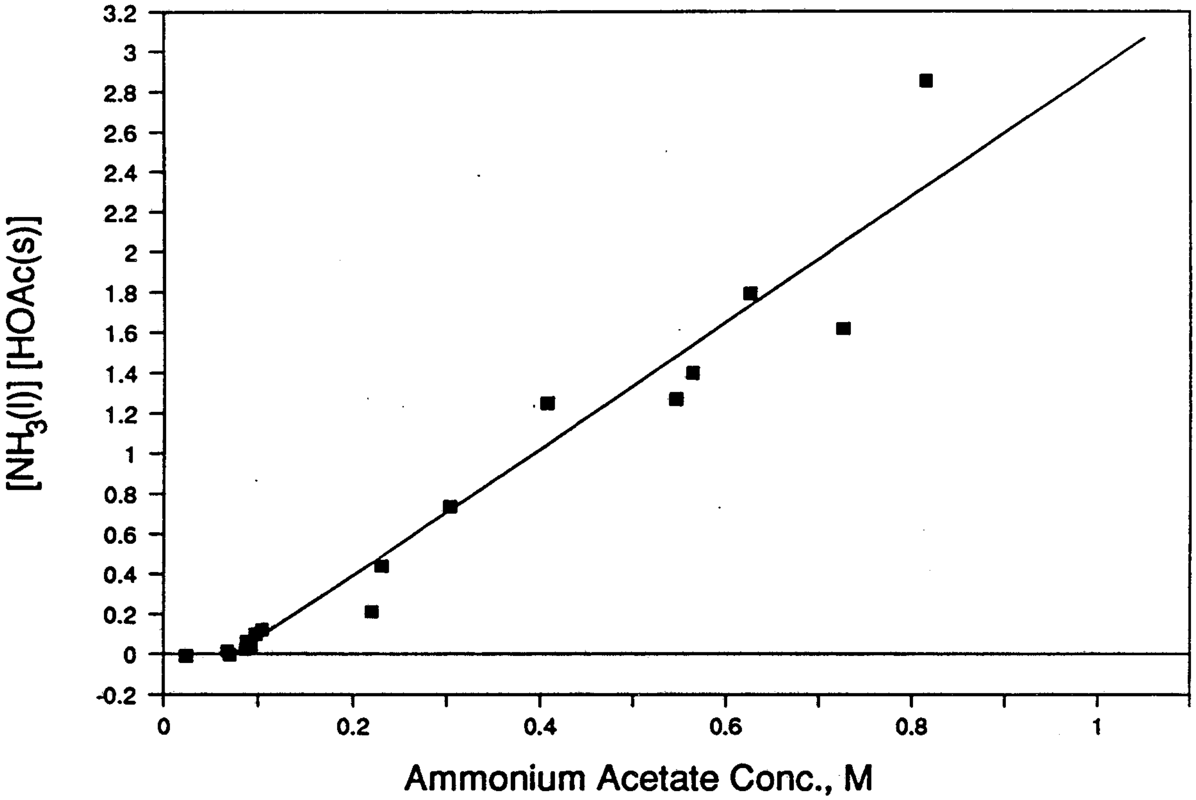


Figure 4-8. Regeneration of Dowex WGR Using Ammonium Hydroxide

solvent leaching with methanol were found to correlate inversely with sorption affinities. Using solvents of higher Lewis basicity can moderately improve the recovery of acetic acid from stronger base sorbents such as Dowex WGR. The use of harder bases such as methyl or ethyl amine in an organic diluent may be necessary to leach acetic acid from the more strongly basic sorbents.

Ammonium hydroxide can strip acetic acid sorbed on Dowex WGR yielding an aqueous ammonium acetate solution of higher concentration than the initial, pre-sorption aqueous acetic acid solution. It has been demonstrated that ammonia can subsequently be volatilized from solution, leaving molecular acetic acid. With ammonium hydroxide at high concentrations, it should be possible to recover sorbed acetic acid from weak base resins of high basicity using small numbers of bed volumes of leaching solution. This regeneration would also not incur chemical consumption costs and can be performed near room temperature -- an important consideration for most sorbents which have maximum operating temperatures between 75-100 °C.

Chapter 4 Reference

1 Frierman, M., Kuo, Y., Joshi, D., Garcia, A.A., King, C.J., Separation and Purification Methods, 16, 91 (1987).

Appendix A

Compilation of Gutmann Donor and Acceptor Numbers, Drago E&C Parameters, and Solvatochromic Parameters for Various Solvents

Table A-1. Donor Numbers of Various Compounds[1,2]

Solvent	DN, kcal/mol
1,2 Dichloroethane	
Benzene	0.1
Sulfuryl chloride	0.1
Thionyl chloride	0.4
Acetyl chloride	0.7
Tetrachloroethylene carbonate	0.8
Benzoyl fluoride	2.3
Benzoyl chloride	2.3
Nitromethane	2.7
Dichloroethylene carbonate	3.2
Nitrobenzene	4.4
Acetic anhydride	10.5
Phosphorous oxychloride	11.7
Benzonitrile	11.9
Selenium oxychloride	12.2
Phenylacetonitrile	14
Acetonitrile	14.1
Tetramethylenesulfone	14.8
Dioxane	14.8
Propanediol 1,2-carbonate	15.1
Benzyl cyanide	15.1
Ethylene sulphite	15.3
Iso-Butyronitrile	15.4
Benzophenone	16
Propionitrile	16.1
Ethylene carbonate	16.4
Phenylphosphonic difluoride	16.4
Methyl acetate	16.5
n-Butyronitrile	16.6
Acetone	17.0
Ethyl acetate	17.1
Water	18.0 (33.0)
Phenylphosphonic dichloride	18.5
Methanol	19
Diethyl ether	19.2
Ethanol	20
Tetrahydrofuran	20.0
Dimethoxyethane	20
Diphenylphosphonic chloride	22.4
Trimethyl phosphate	23.0
Tributyl phosphate	23.7
Formamide	24
Dimethylformamide	26.6
N-Methyl-e-caprolactam	27.1

Table A-1. Donor Numbers of Various Compounds (cont.)

Solvent	DN, kcal/mol
N-Methyl-2-pyrolidinone	27.3
N,N-Dimethyl acetamide	27.8
Dimethyl sulfoxide	29.8
N,N-Diethylformamide	30.9
Tetramethylurea	31
N,N-Diethylacetamide	32.2
Pyridine	33.1
Hexamethylphosphoramide	38.8
Hydrazine	44.0
Piperidine	51.0
Ethylenediamine	55.0
Ethylamine	55.5
Isopropylamine	57.5
tert-Butylamine	57.5
Ammonia	59.0
Triethylamine	61.0

Table A-2. Acceptor Numbers and Corresponding ^{31}P NMR shifts due to 1:1 adduct formation with Et_3PO for Various Compounds[1,2]

Solvent	^{31}P, ppm	AN
Hexane	0	0
Diethyl Ether	-1.64	3.9
Tetrahydrofuran	-3.39	8.0
Benzene	-3.49	8.2
Carbon tetrachloride	-3.64	8.6
Diglyme	-4.20	9.9
Glyme	-4.35	10.2
Hexamethyl phosphoramide	-4.50	10.6
Dioxane	-4.59	10.8
Acetone	-5.33	12.5
N-Methyl-2-pyrrolidinone	-5.65	13.3
Dimethyl acetamide	-5.80	13.6
Pyridine	-6.04	14.2
Nitrobenzene	-6.32	14.8
Benzonitrile	-6.61	15.5
Dimethyl formamide	-6.82	16.0
dichloroethane carbonate	-7.11	16.7
Propanediol 1,2-carbonate	-7.77	18.3
Methyl cyanide	-8.04	18.9
Dimethyl sulfoxide	-8.22	19.3
Dichloromethane	-8.67	20.4
Nitromethane	-8.74	20.5
Trichloromethane	-9.83	23.1
Isopropyl alcohol	-14.26	33.5
Ethyl alcohol	-15.80	37.1
Formamide	-16.95	39.8
Methyl alcohol	-17.60	41.3
Acetic Acid	-22.51	52.9
Water	-23.35	54.8
Trifluoro ethanoic acid	-44.83	105.3
Sulfonic acid	-53.77	126.3
Trifluoro sulfonic acid	-54.98	129.1
Antimony pentachloride	-42.58	100

Table A-3. E&C Parameters for Various Donors and Acceptors[3]

Acceptor	C_A	E_A
Iodine	1.00	1.00
Iodine monochloride	0.830	5.10
Iodine monobromide	1.56	2.41
Thiophenol	0.198	0.987
p-tert-Butylphenol	0.387	4.06
p-Methylphenol	0.404	4.18
Phenol	0.442	4.33
p-Fluorophenol	0.446	4.17
p-Chlorophenol	0.478	4.34
m-Fluorophenol	0.506	4.42
m-Trifluoromethylphenol	0.530	4.48
tert-Butyl alcohol	0.300	2.04
Trifluoroethanol	0.451	3.88
Hexafluoroisopropyl alcohol	0.623	5.93
Pyrrole	0.295	2.54
Isocyanic acid	0.258	3.22
Isothiocyanic acid	0.227	5.30
Perfluoro-t-butanol	0.731	7.34
Boron trifluoride (gas)	1.62	9.88
Boron trimethyl	1.70	6.14
Trimethylaluminium	1.43	16.9
Triethylaluminium	2.04	12.5
Trimethylgallium	0.881	13.3
Triethylgallium	0.593	12.6
Trimethylindium	0.654	15.3
Trimethyltin chloride	0.0296	5.76
Sulfur Dioxide	0.808	0.92
Bis(Hexafluoroacetylacetonate) Copper (II)	1.40	3.39
Antimony pentachloride	5.13	7.38
Chloroform	0.159	3.02
1-Hydroperfluoroheptane	0.226	2.45
Methylcobaloxime	1.53	9.14
Bis(Hexamethyl disilylamino zinc (II)	1.09	4.94

Donor	C_B	E_B
Pyridine	6.40	1.17
Ammonia	3.46	1.36
Methylamine	5.88	1.30
Dimethylamine	8.73	1.09
Trimethylamine	11.54	0.808

Table A-3. E&C Parameters for Various Donors and Acceptors (cont.)

Donor	C_B	E_B
Ethylamine	6.02	1.37
Diethylamine	8.83	0.866
Triethylamine	11.09	0.991
Acetonitrile	1.34	0.886
Chloroacetonitrile	0.530	0.940
Dimethylcyanamide	1.81	1.10
Dimethylformamide	2.48	1.23
Dimethylacetamide	2.58	1.32
Ethyl Acetate	1.74	0.975
Methyl Acetate	1.61	0.903
Acetone	2.33	0.987
Diethyl ether	3.25	0.963
Isopropyl ether	3.19	1.11
n-Butyl ether	3.30	1.06
p-Dioxane	2.38	1.09
Tetrahydrofuran	4.27	0.978
Tetrahydropyran	3.91	0.949
Dimethyl sulfoxide	2.85	1.34
Tetramethyl sulfoxide	3.16	1.38
Dimethyl sulfide	7.46	0.343
Diethyl sulfide	7.40	0.339
Trimethylene sulfide	6.84	0.352
Tetramethylene sulfide	7.90	0.341
Pentamethylene sulfide	7.40	0.375
Pyridine-N-oxide	4.52	1.34
4-Methylpyridine-N-oxide	4.99	1.36
4-Methoxypyridine-N-oxide	5.77	1.37
Tetramethylurea	3.10	1.20
Trimethylphosphine	6.55	0.838
Benzene	0.681	0.525
p-Xylene	1.78	0.416
Mesitylene	2.19	0.574
2,2,6,6-Tetramethyl-Pyridine N-Oxyl	6.21	0.915
1-Azabicyclo[2.2.1] Octane	13.2	0.704
7-Oxabicyclo[2.2.1] Heptane	3.76	1.08
Dimethyl selenide	8.33	0.217
1-Phospha-4-Ethyl-1,5,7-Trioxabicyclo[2.2.1] Octane	6.41	0.548
Hexamethyl phosphoramide	3.55	1.52
1-methylimidazole	8.96	0.934
Trimethylphosphite	5.99	1.03
4-Picoline	7.71	1.12
Piperidine	9.32	1.01
Trimethylphosphine oxide	5.99	1.03

Table A-4: Solvatochromic Parameters for Various Donors and Acceptors[4]

Solvent	π*	β	α
Aliphatic Hydrocarbons			
Cyclohexane	0	0	0
n-Hexane, n-Heptane	-0.08	0	0
Ethers and Orthoesters			
Anisole	0.73	0.22	0
Bis(2-methoxyethyl) ether	0.64	----	0
Dibenzyl ether	0.80	0.41	0
Diethyl ether	0.27	0.47	0
Diisopropyl ether	0.27	0.49	0
1,2-Dimethoxyethane	0.53	0.41	0
Di-n-butyl ether	0.24	0.46	0
Di-n-propyl ether	----	0.46	0
Dioxane	0.55	0.37	0
Diphenyl ether	0.66	0.13	0
Phenetole	----	0.20	0
Tetrahydrofuran	0.58	0.55	0
Tetrahydropyran	0.51	0.54	0
Trimethyl orthoacetate	0.35	----	0
Trimethyl orthoformate	0.58	----	0
Aldehydes and Ketones			
Acetone	0.72	0.48	0.07
Acetophenone	0.90	0.49	----
Acetylferrocene	----	0.58	----
Benzaldehyde	----	0.44	0
Benzophenone	----	0.46	0
Biacetyl	----	0.31	----
2-Butanone	0.67	0.48	0.05
Butyraldehyde	----	0.41	----
Cinnamaldehyde	----	0.53	0
Cyclohexanone	0.76	0.53	----
Cyclopentanone	0.76	0.52	----
Dicyclopropyl ketone	0.63	0.53	----
Dimethyl-τ-pyrone	----	0.82	----
Di-tert-butyl ketone	----	0.48	0
Flavone	----	0.66	----
3-Heptanone	0.59	----	----
Isobutyrophenone	----	0.42	----
Methyl cyclopopyl ketone	0.66	0.52	----
Methyl Isopropyl ketone	----	0.48	----
Methyl t-butyl ketone	----	0.45	----

Table A-4. Solvatochromic Parameters for Various Donors and Acceptors (cont.)

Solvent	π*	β	α
Aldehydes and Ketones			
p-(Dimethylamino) benzaldehyde	----	0.59	0
p-Chloroacetophenone	----	0.46	----
p-Chlorobenzaldehyde	----	0.42	0
p-Methoxyacetophenone	----	0.54	----
p-Methoxybenzaldehyde	----	0.49	0
p-Methylacetophenone	----	0.51	----
2-Napthaldehyde	----	0.43	0
p-Nitrobenzaldehyde	----	0.32	0
2-Pentanone	----	0.50	----
3-Pentanone	0.72	0.45	----
Phenylacetone	0.88	----	----
Propionaldehyde	----	0.40	----
Propiophenone	----	0.43	----
sym-dichloroacetone	----	0.34	----
1,1,1-Trichloroacetone	----	0.14	----
Esters			
Butyl acetate	0.46	----	0
Butyrolactone	0.87	0.49	0
Diethyl carbonate	----	0.38	0
Diethyl malonate	0.64	----	----
Dimethyl carbonate			
Ethyl acetate	0.55	0.45	0
Ethyl acetoacetate	0.61	----	----
Ethyl benzoate	0.74	0.41	0
Ethyl chloroacetate	0.70	0.35	0
Ethyl formate	0.61	----	0
Ethyl p-nitrobenzoate	----	0.40	0
Ethyl propionate	----	0.42	0
Ethyl trichloroacetate	0.61	----	0
Ethyl trifluoroacetate	----	0.19	0
Methyl acetate	0.60	0.42	0
Methyl benzoate	----	0.39	0
Methyl formate	0.61	----	0
Methyl trifluoroacetate	0.39	----	0
Phenyl benzoate	----	0.39	0
Propylene carbonate	0.81	----	0

Table A-4. Solvatochromic Parameters for Various Donors and Acceptors (cont.)

Solvent	π*	β	α
Amides and Ureas			
Dimethylacetamide	0.88	0.76	0
Dimethylformamide	0.88	0.69	0
Ethyl diethylcarbamate	----	0.65	0
Formamide	0.98	----	0.66
N-acetylpiperidine	----	0.73	0
N,N-Diethylacetamide	----	0.78	0
N,N-diethylpropionamide	----	0.75	0
N,N-Diethylbenzamide	----	0.70	0
N,N-Dimethylbenzamide	----	0.72	0
N,N-Dimethyl chloroacetamide	----	0.62	0
N,N-Dimethyl-p-nitrobenzamide	----	0.61	0
N,N-Dimethyltrifluoroacetamide	----	0.46	0
N,N-di-n-hexylacetamide	----	0.77	0
N,N-diphenylacetamide	----	0.64	0
N,N-diphenylpropionamide	----	0.61	0
N-Methylpyridine	----	0.78	0
N-Methylpyrrolidone	0.92	0.77	0
Tetraethylurea	----	0.71	0
Tetramethylurea	----	0.78	0
Amines			
Benzylamine	----	0.63	----
β,β,β-Trifluoroethylamine	----	0.37	----
Cyclopropylamine	----	0.60	----
1,4-Diazobicyclo[2.2.2]octane	----	0.73	0
Di-n-butylamine	----	0.70	----
n-Butylamine	----	0.72	----
N-methylimidazole	----	0.82	0
N,N-Dimethylaniline	0.90	----	0
N,N-Dimethylbenzylamine	0.49	0.57	0
N,N-Dimethyl-N-cyclohexylamine	----	0.71	0
N,N-Dimethyl-N-Propylamine	----	0.68	0
Propargylamine	----	0.57	----
Quinuclidine	----	0.80	0
Triallylamine	----	0.54	0
Triethylamine	0.14	0.71	0
Tri-n-butylamine	0.16	0.62	0
Tri-n-propylamine	----	0.56	0

Table A-4. Solvatochromic Parameters for Various Donors and Acceptors (cont.)

Solvent	π*	β	α
Sulfoxides			
Dibenzyl Sulfoxides	----	0.74	0
Diethyl sulfate	----	0.45	0
Diisopropyl sulfoxide	----	0.78	0
Dimethyl sulfoxide	1.00	0.76	0
Di-n-butyl sulfite	----	0.46	0
Di-n-butyl sulfoxide	----	0.83	0
Di-n-propyl sulfite	----	0.45	0
Diphenyl sulfoxide	----	0.70	0
Di-p-tolyl sulfoxide	----	0.72	0
Ethyl sulfate	0.69	----	0
Methyl Phenyl sulfoxide	----	0.71	0
Methyl p-nitrophenyl sulfoxide	----	0.60	0
Sulfolane	0.98	----	0
Tetramethylene sulfoxide	----	0.80	0
Phosphorous Compounds			
Diethoxy(chloromethyl) phosphine oxide	----	0.79	0
Diethoxy(dichloromethyl) phosphine oxide	----	0.74	0
Diethoxymethylphosphine oxide	----	0.84	0
Diethoxyphosphine oxide	----	0.76	0
Diethoxy(dimethylamino) phosphine oxide	----	0.88	0
Diethoxy(trichloromethyl) phosphine oxide	----	0.68	0
Diisopropoxyphosphine oxide	----	0.80	0
Dimethoxyethylphosphine oxide	----	0.81	0
Dimethoxyphosphine oxide	----	0.74	0
Hexamethylphosphoramide	0.87	1.05	0
Triethyl phosphate	0.72	0.77	0
Triethylphosphine oxide	----	1.05	0
Trimethyl phosphate	----	0.73	0
Trimethylphosphine oxide	----	1.02	0
Tri-n-butyl phosphate	0.65	----	0
Tri-n-propylphosphine oxide	----	1.04	0
Triphenyl phosphinate	----	0.62	0
Triphenylphosphine oxide	----	0.94	0

Table A-4. Solvatochromic Parameters for Various Donors and Acceptors (cont.)

Solvent	π*	β	α
Nitro Compounds and Nitriles			
Acetonitrile	0.85	0.31	0.15
Benzonitrile	0.90	0.41	0
β-Ethoxypropionitrile	----	0.48	0
Butyronitrile	0.71	----	----
Nitrobenzene	1.01	0.39	0
Nitromethane	0.85	----	0.23
p-(Dimethylamino)benzonitrile	----	0.53	0
p-Methoxybenzonitrile	----	0.46	0
Phenylacetonitrile	0.99	----	----
Propionitrile	0.71	0.37	----
Pyridines			
3-Bromopyridine	----	0.51	0
3,5-Dichloropyridine	----	0.42	0
4-Dimethylaminopyridine	----	0.87	0
2,4-Dimethylpyridine	----	0.74	0
2,6-Dimethylpyridine	----	0.76	0
4-Methoxypyridine	----	0.72	0
3-Methylpyridine	----	0.68	0
4-Methylpyridine	----	0.67	0
2-n-Butylpyridine	----	0.66	0
Pyridine	0.87	0.64	0
Pyridine N-oxide	----	0.85	0
Pyrimidine	----	0.48	0
Quinoline	----	0.64	0
2,4,6-Trimethylpyridine	----	0.78	0
Aromatics and Haloaromatics			
Benzene	0.59	0.10	0
Bromobenzene	0.79	0.06	0
Chlorobenzene	0.71	0.07	0
Cumene	0.41	----	0
Fluorobenzene	0.62	----	0
Iodobenzene	0.81	----	0
Mesitylene	0.41	----	0
m-Dichlorobenzene	0.67	----	0
m-Xylene	0.47	----	0
o-Dichlorobenzene	0.80	----	0
p-Xylene	0.43	----	0
Toluene	0.54	0.11	0

Table A-4. Solvatochromic Parameters for Various Donors and Acceptors (cont.)

Solvent	π*	β	α
Haloaliphatics			
Carbon tetrachloride	0.29	0	0
Chloroform	0.76	0	0.34
1,2-Dibromoethane	0.75	0	0
1,2-Dichloroethane	0.81	0	0
Methylene bromide	0.92	0	----
Methylene chloride	0.80	0	0.22
Methylene iodide	1.12	0	----
n-Butyl chloride	0.39	0	0
Pentachloroethane	0.62	0	----
1,1,2,2-Tetrachloroethane	0.95	0	----
Tetrachloroethylene	0.28	0	0
trans-1,2-dichloroethylene	0.44	0	0
1,1,1-Trichloroethane	0.49	0	0
1,1,2-Trichloroethane	0.83	0	----
Trichloroethylene	0.53	0	0
Perfluorinated Compounds			
Perfluorodimethyldecalin	-0.33	0	0
Perfluoro-n-heptane	-0.39	0	0
Perfluoro-n-hexane	-0.40	0	0
Perfluoro-n-octane	-0.41	0	0
Perfluorotri-n-butylamine	-0.36	----	0
Alcohols and Water			
Benzyl alcohol	0.98	0.50	0.43
1-Butanol	0.46	0.88	0.79
2-Chloroethanol	----	0.31	----
Ethanol	0.54	0.77	0.86
Ethylene glycol	0.85	0.52	0.92
2-Fluoroethanol	0.72	----	----
Hexafluoroisopropanol	0.65	----	----
Methanol	0.60	0.62	0.98
2-Methoxyethanol	0.71	----	----
2-Phenylethanol	0.88	0.61	----
1-Propanol	0.51	----	0.80
2-Propanol	0.46	0.95	0.78
tert-Butanol	0.41	1.01	0.62
Trifluoroethanol	0.73	----	1.35
Water	1.09	0.18	1.13

Table A-4. Solvatochromic Parameters for Various Donors and Acceptors (cont.)

Solvent	π*	β	α
Acids, Acid Halides, and Acid Anhydrides			
Acetic anhydride	0.76	----	0
Acetic acid	0.62	----	1.09
Benzoyl bromide	----	0.16	0
Benzoyl chloride	----	0.20	0
Benzoyl fluoride	----	0.16	0
Propionyl fluoride	----	0.20	0
Trifluoroacetic acid	0.50	----	----

References

1 Gutmann, V., "The Donor Acceptor Approach To Molecular Interactions", Plenum, New York (1978).

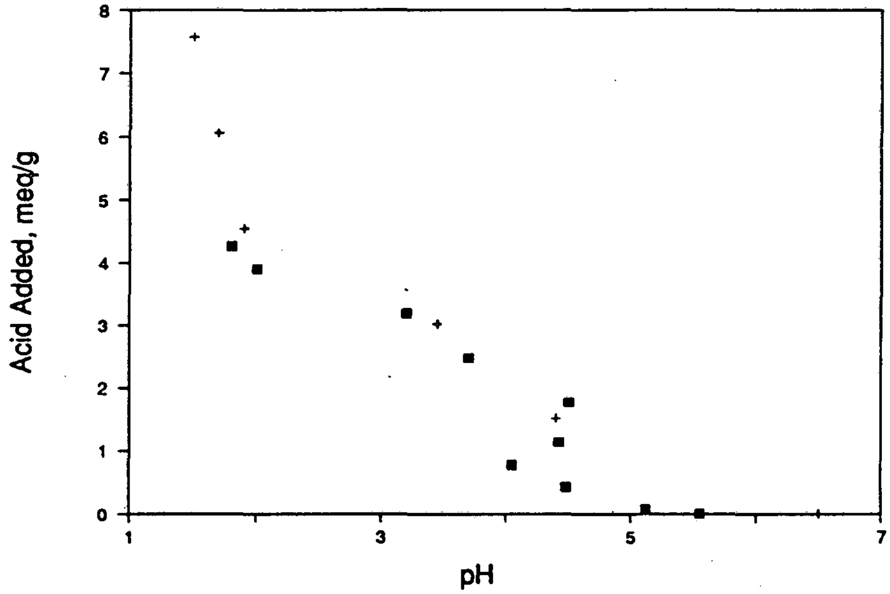
2 Jensen, W., "The Lewis Acid-Base Concepts, an Overview", Wiley, New York (1980).

3 Drago, R.S., Structure and Bonding (Berlin), 15, 73 (1973).

4 Kamlet, M.J., Abboud, J-L., M., Abraham, M.H., Taft, R.W., J. Org. Chem., 48, 2877 (1983).

Appendix B

HCl Titration of Dowex MWA-1, Dowex WGR, Reilly Tar & Chem. Co. Poly-4-methyl-5-vinyl-pyridine, Duolite A-340, Amberlite XAD-12, Aurorez, and Bio-Rad AG-2X8



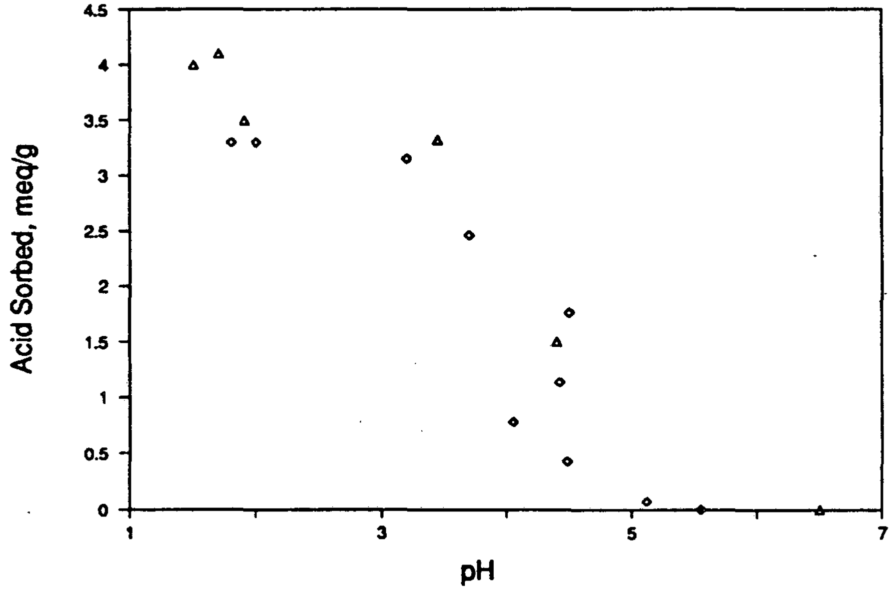


Figure B-1: HCl Titration of Dowex MWA-1 (Each symbol represents a titration with a different sample)

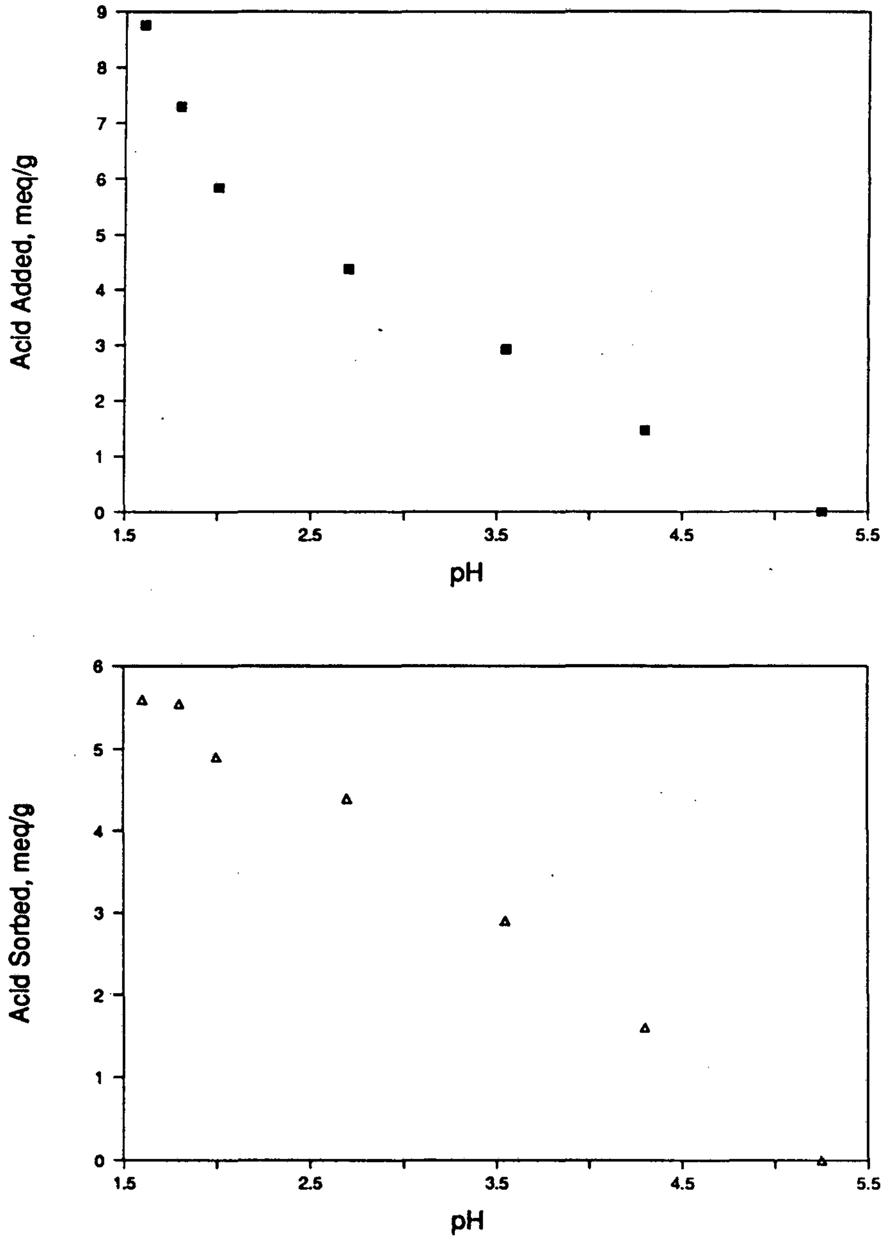


Figure B-2: HCl Titration of Dowex WGR

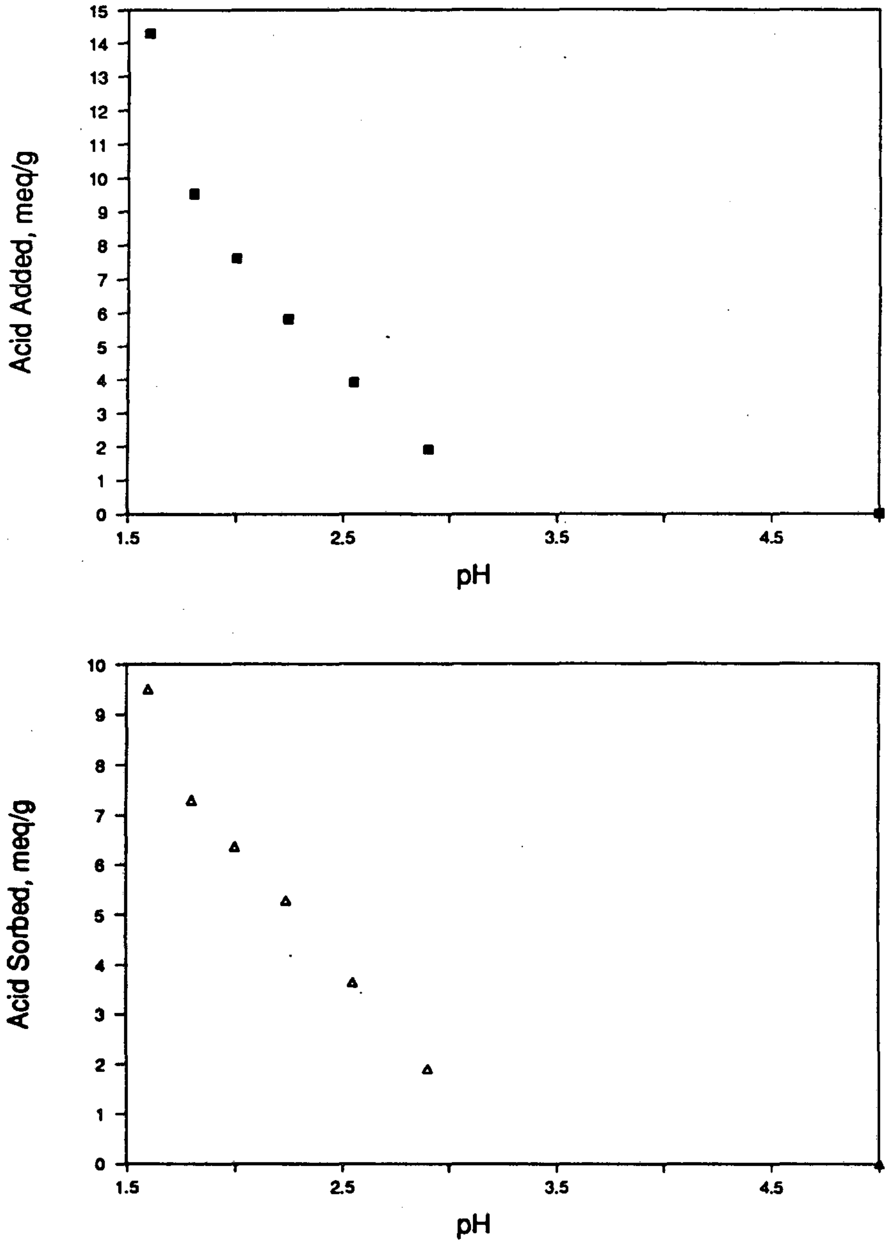
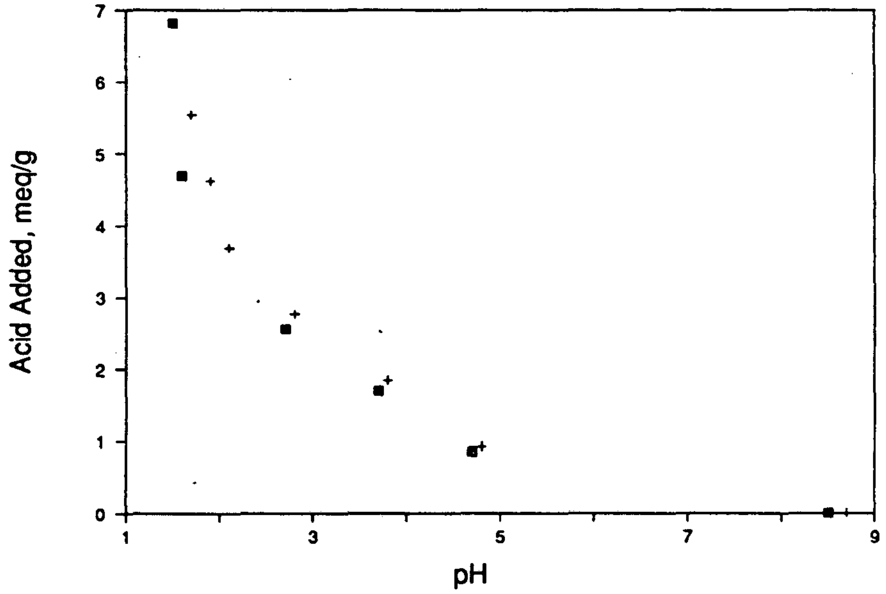


Figure B-3: HCl Titration of Reilly Tar & Chem. Co.
Poly-4-methyl-5-vinyl-pyridine



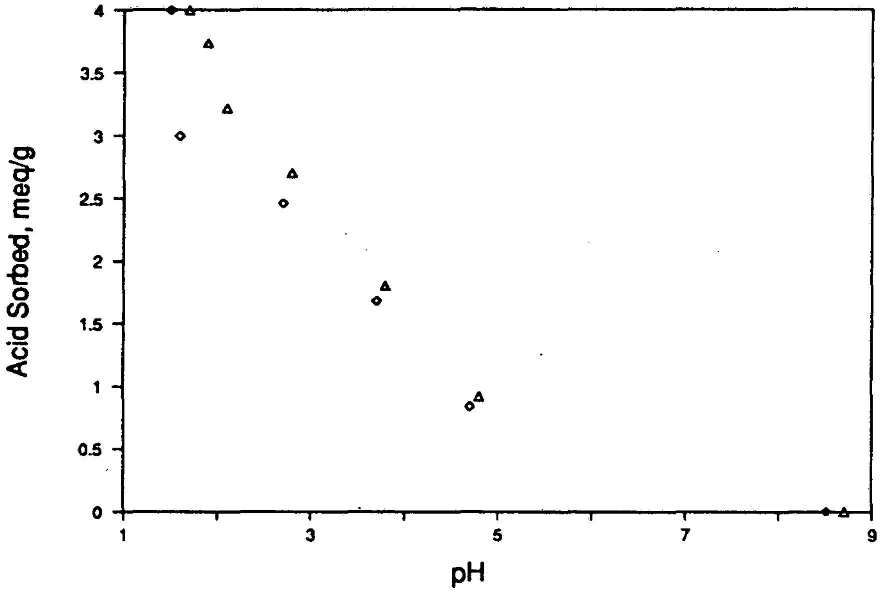


Figure B-4: HCl Titration of Duolite A-340 (Each symbol represents a titration with a different sample)

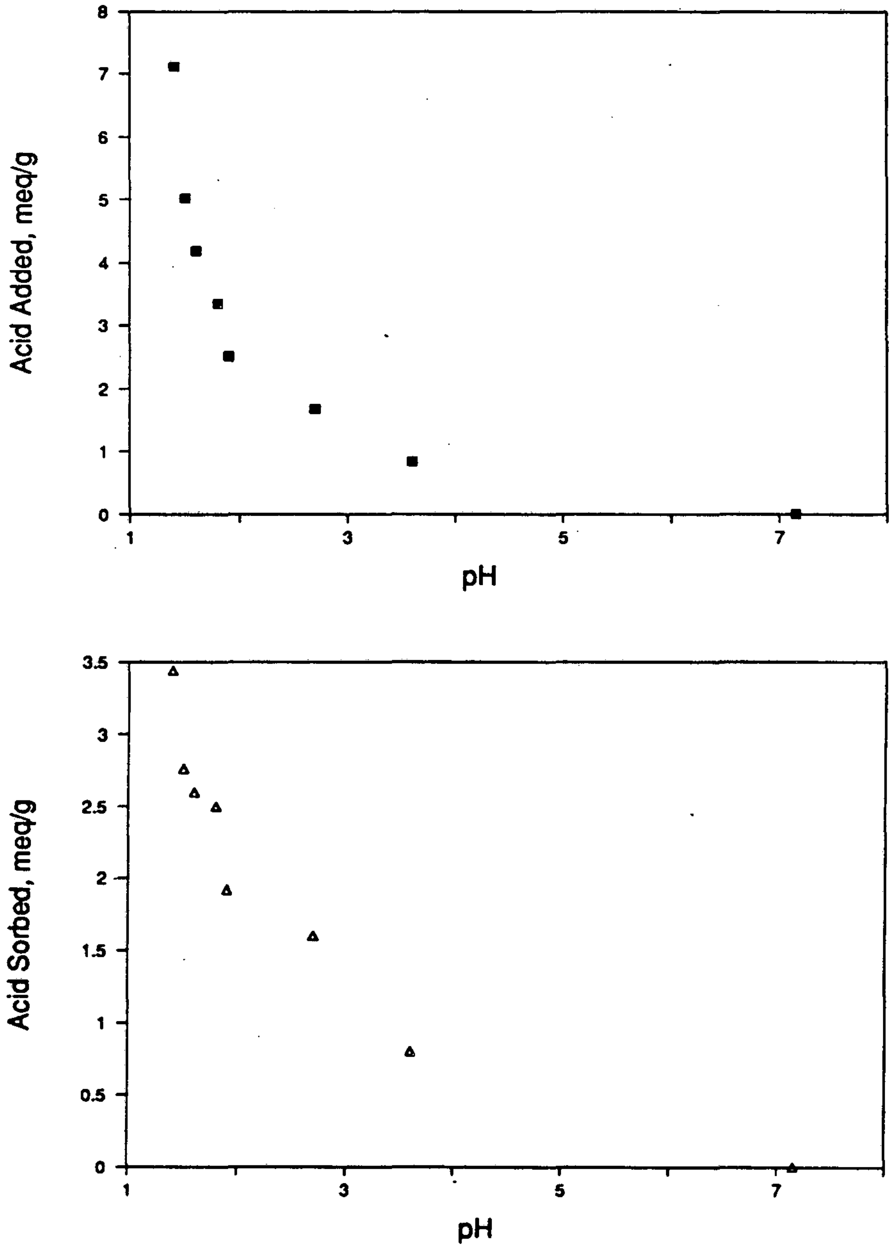


Figure B-5: HCl Titration of Amberlite XAD-12

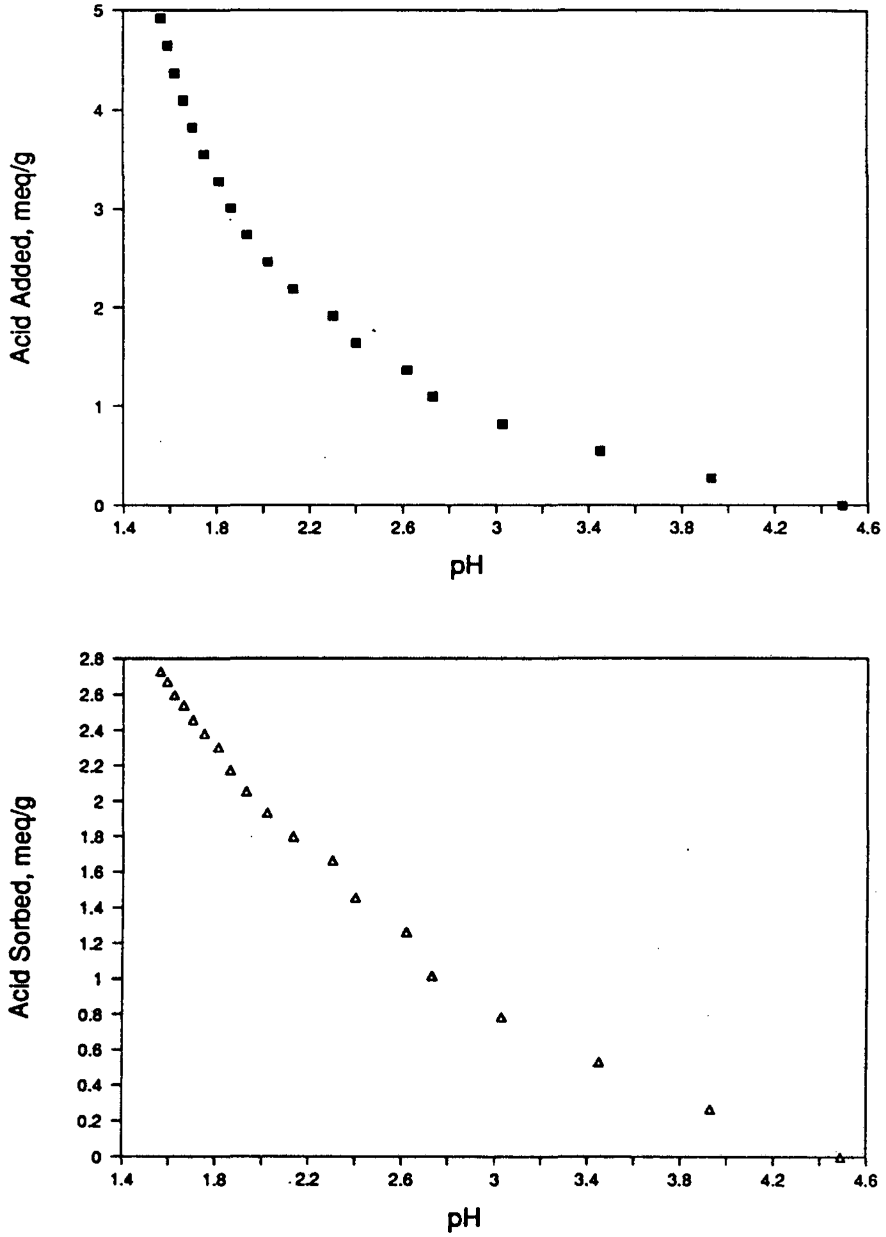


Figure B-6: HCl Titration of Auorez

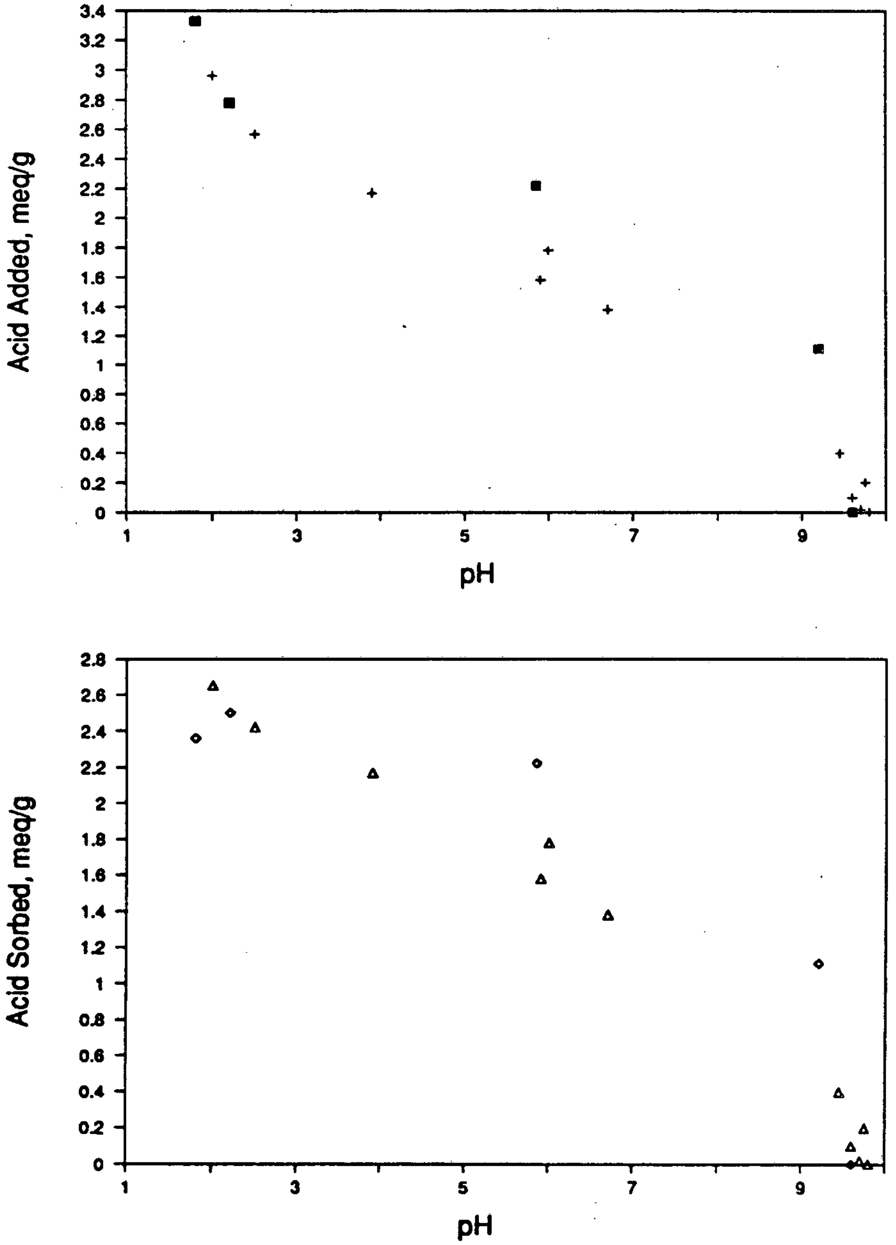


Figure B-7: HCl Titration of Bio-Rad AG-2X8 (Each symbol represents a titration with a different sample)

Appendix C

Solvent Leaching Composite Isotherms for Amberlite XE-378, Amberlite XE-309, Duolite ES-561, Amberlite IR-4B, Bio Gel P-4, Dowex MWA-1, Dowex WGR, Reilly Tar & Chem. Co. Poly-4-methyl-5-vinyl-pyridine, Duolite A-340, Amberlite XAD-12, Aurorez, and Bio-Rad AG-2X8

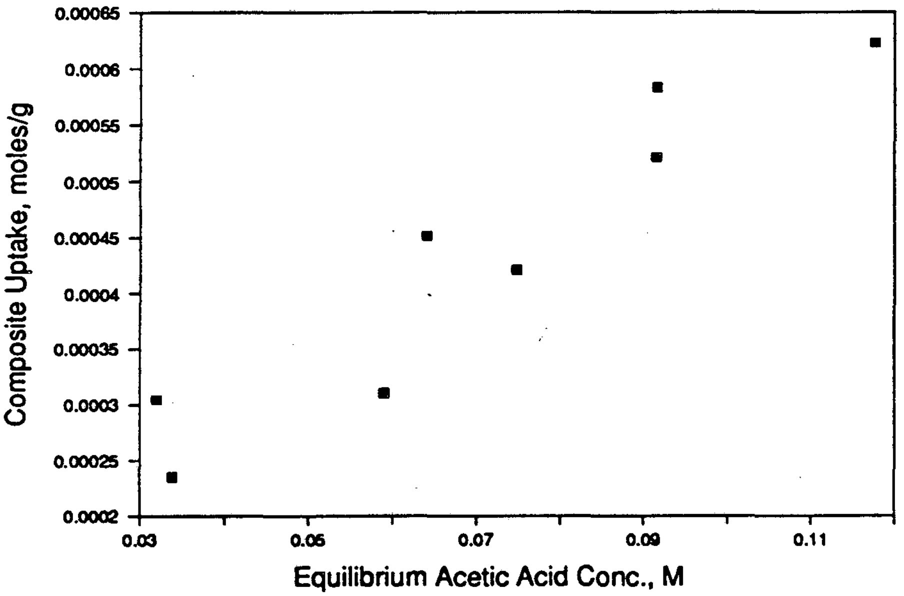


Figure C-1: Methanol Leaching Isotherm for Aurorez (moles acetic acid per gram dry sorbent)

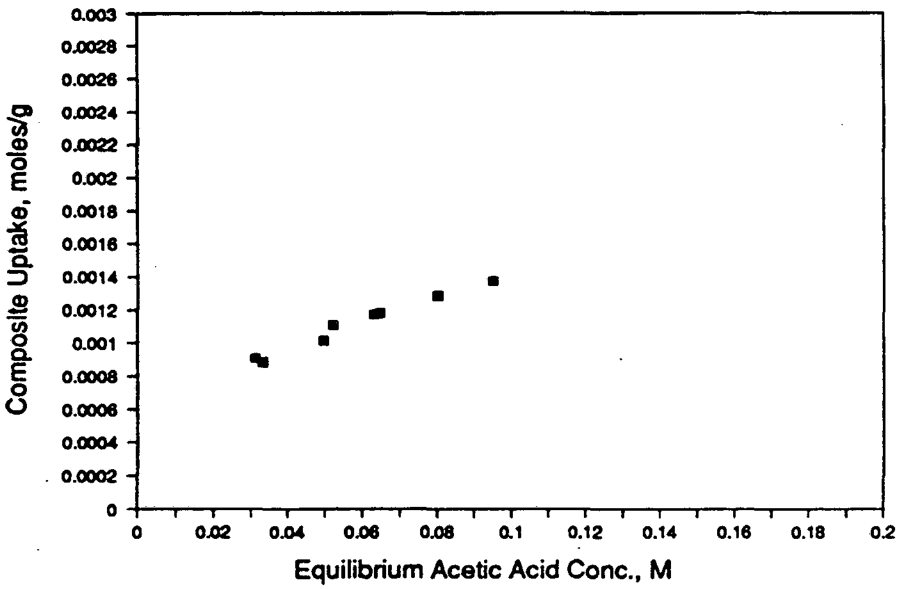


Figure C-2: Methanol Leaching Isotherm for Dowex WGR (moles acetic acid per gram dry sorbent)

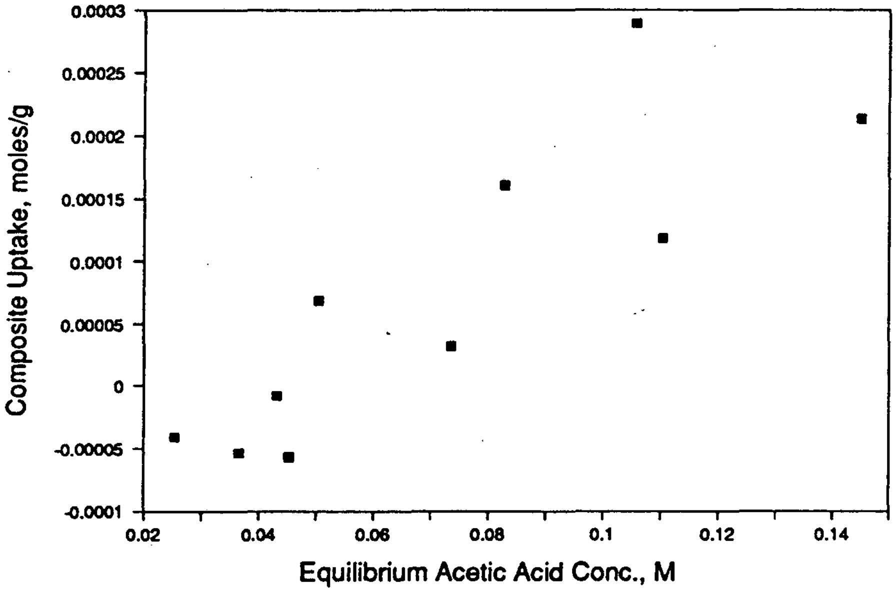


Figure C-3: Methanol Leaching Isotherm for P4VP (moles acetic acid per gram dry sorbent)

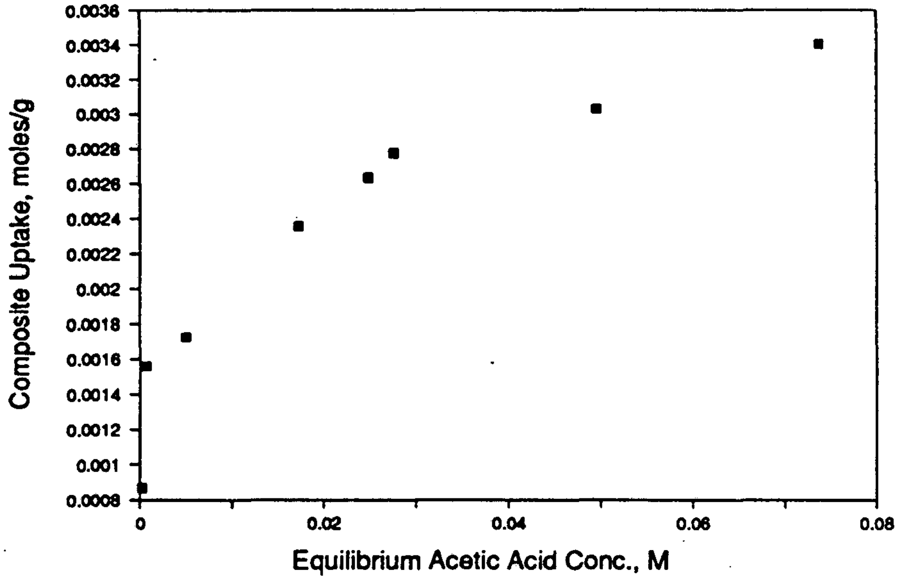


Figure C-4: Methanol Leaching Isotherm for Duolite A-340 (moles acetic acid per gram dry sorbent)

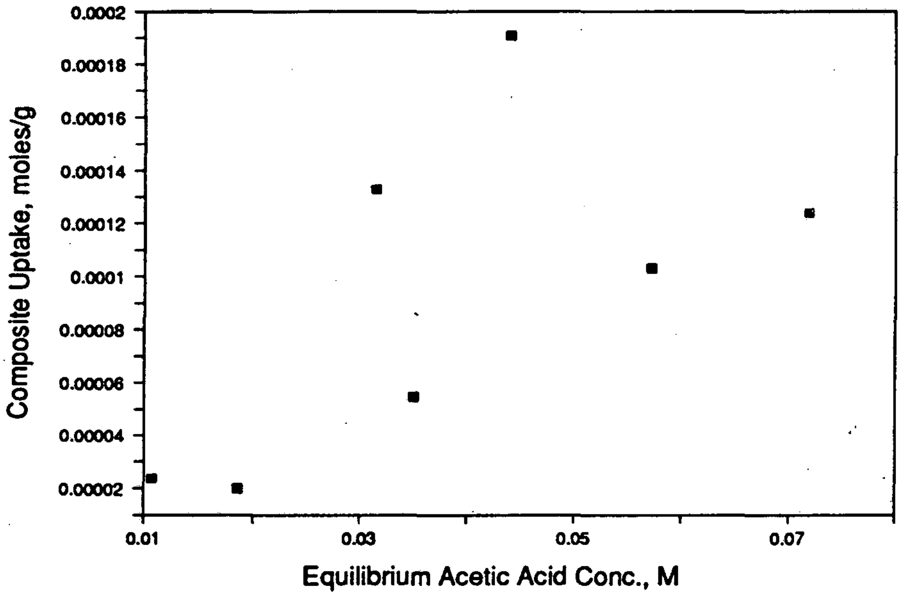


Figure C-5: Methanol Leaching Isotherm for Bio Gel P-4 (moles acetic acid per gram dry sorbent)

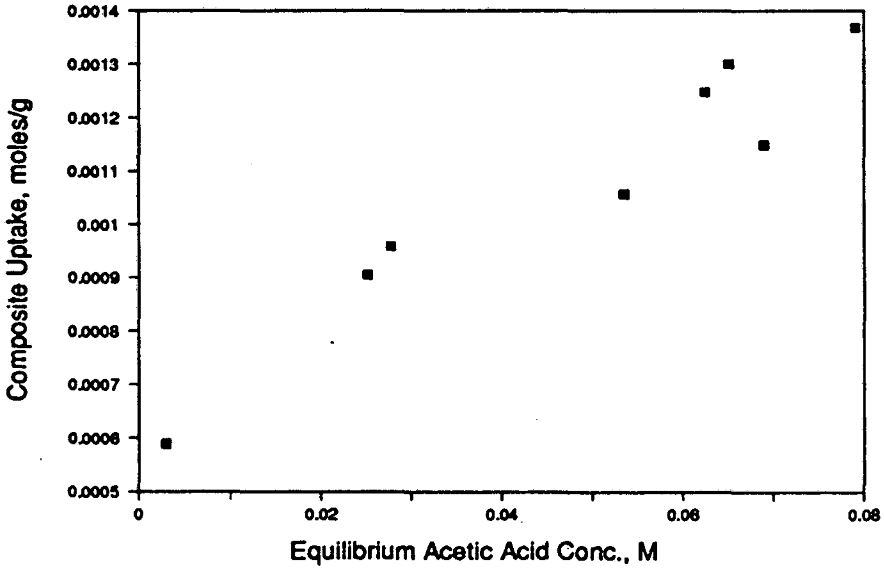


Figure C-6: Methanol Leaching Isotherm for Bio-Rad AG-2X8 (moles acetic acid per gram dry sorbent)

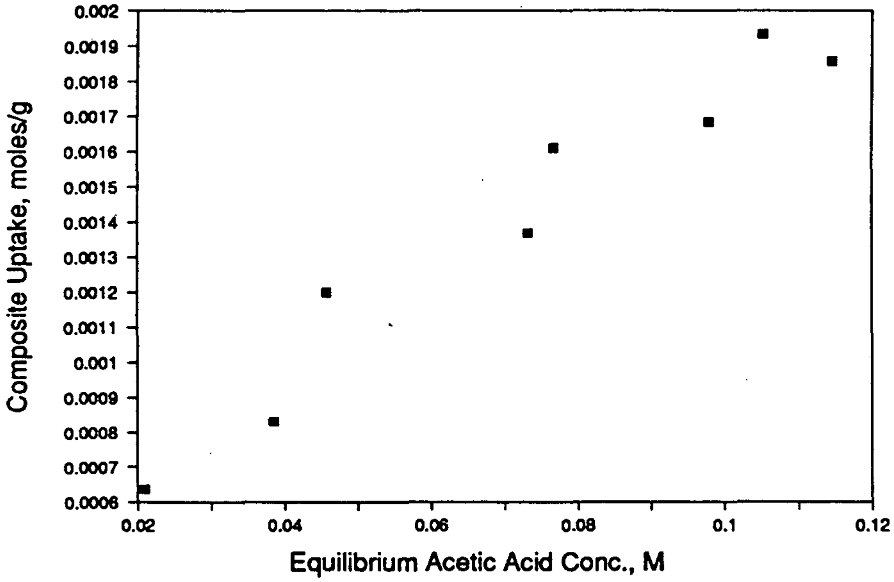


Figure C-7: Methanol Leaching Isotherm for Dowex MWA-1 (moles acetic acid per gram dry sorbent)

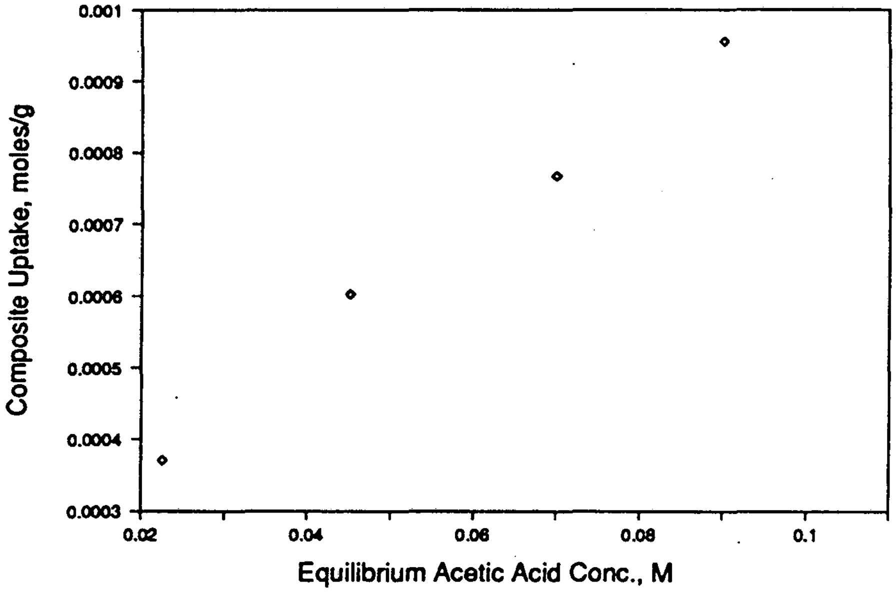


Figure C-8: Methanol Leaching Isotherm for XAD-12 (moles acetic acid per gram dry sorbent)

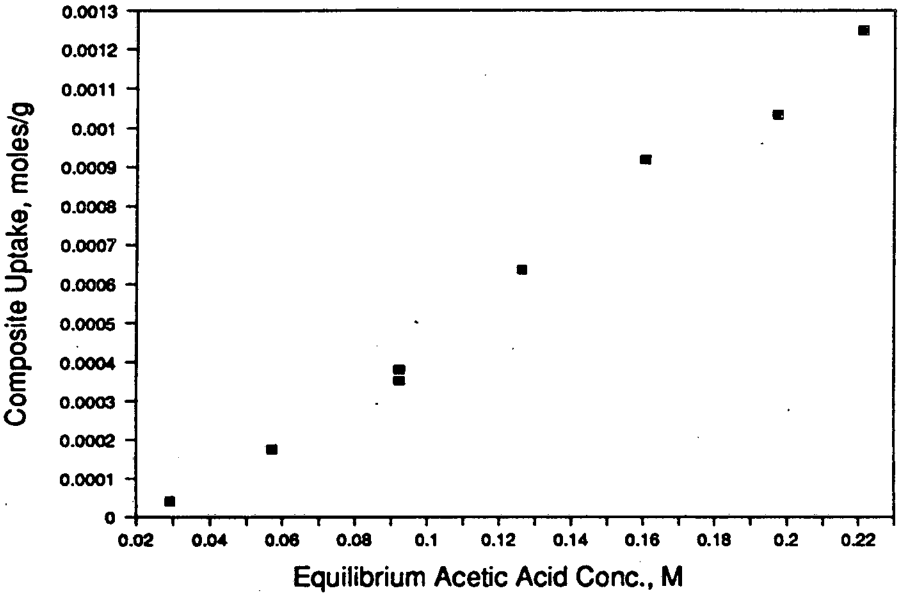


Figure C-9: Methanol Leaching Isotherm for XE-378 (moles acetic acid per gram dry sorbent)

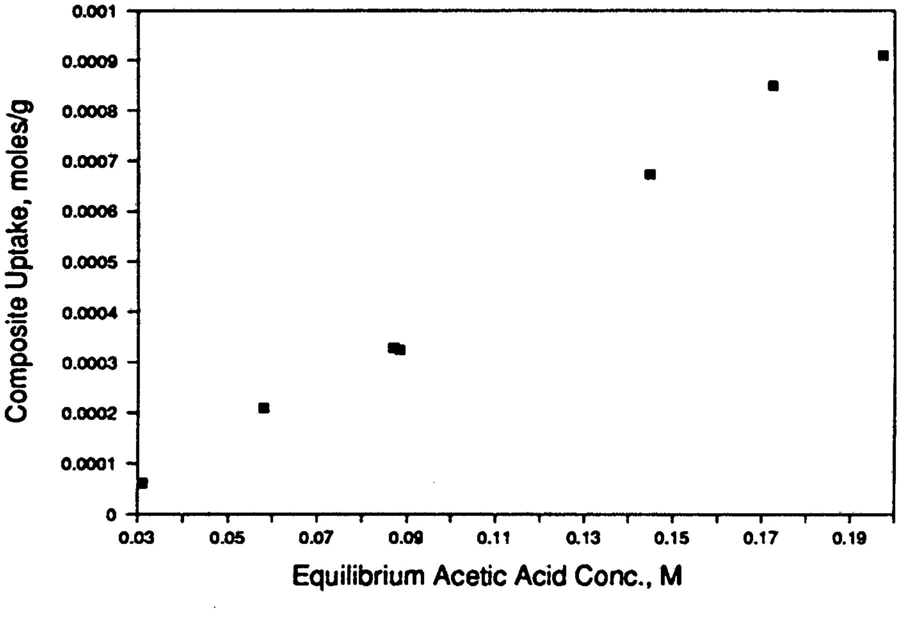


Figure C-10: Methanol Leaching Isotherm for XE-309 (moles acetic acid per gram dry sorbent)

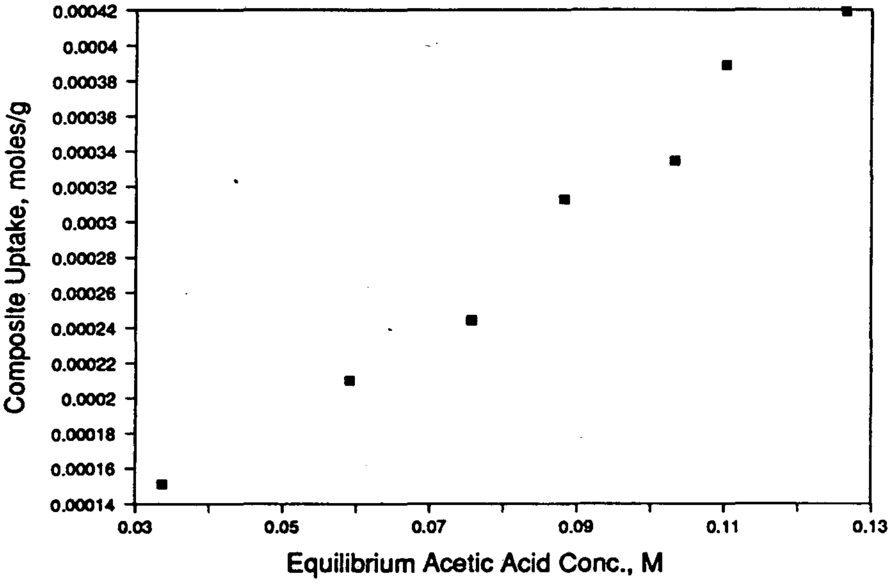


Figure C-11: Methanol Leaching Isotherm for Duolite ES-561 (moles acetic acid per gram dry sorbent)

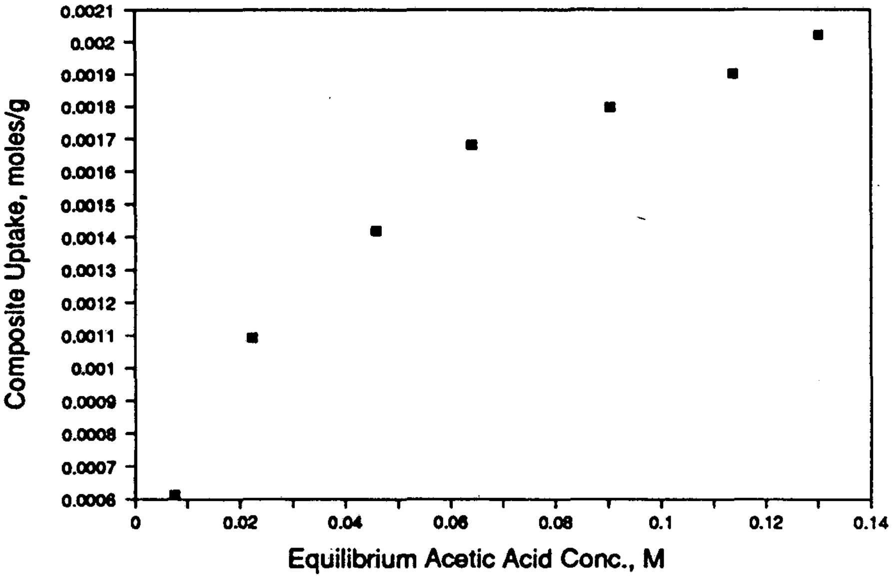


Figure C-12: Methanol Leaching Isotherm for IR-4B (moles acetic acid per gram dry sorbent)

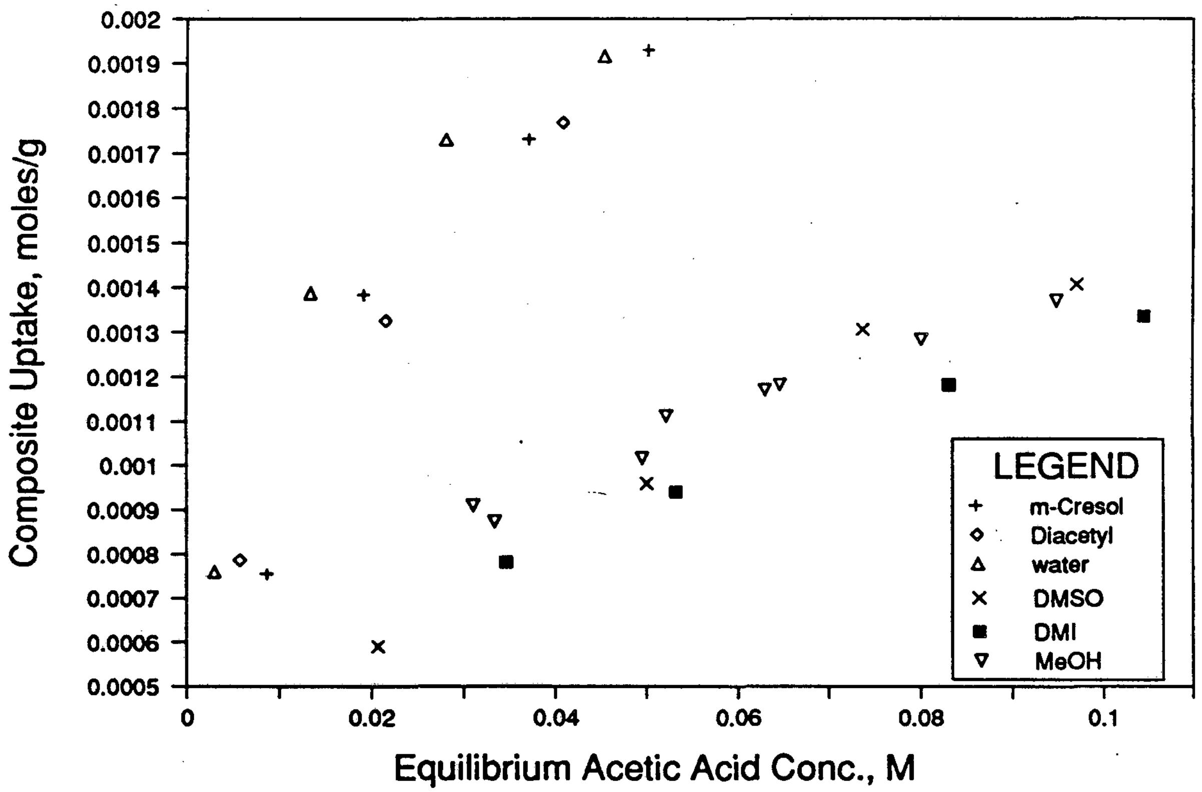


Figure C-13: Solvent Leaching Isotherms for Dowex WGR (moles acetic acid per gram dry sorbent)