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ADSORPTION STUDIES OF PHENOL AND
BENZOIC ACID ONTO AMBERLITE XAD-8 USING
RADIOLABELED SOLUTES FOR CONCENTRATION DETERMINATION

by

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science, Chemical and Petroleum-Refining Engineering.

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ABSTRACT

The sorptive characteristics of Rohm & Haas, Amberlite XAD-8 have been determined for phenol at 0., 25., and 70.°C, and for benzoic acid and a binary of phenol and benzoic acid at 25.°C. Amberlite XAD-8 has shown nearly a 4-times greater affinity for phenol than for that of benzoic acid. The adsorption of phenol is little affected by the presence of benzoic acid; whereas, the adsorption of benzoic acid may be enhanced by the presence of phenol.

The method of using radiolabeled solutes in determining concentration changes is desirable both for its ease in application and for its increased sensitivity over conventional methods.

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LIST OF NOMENCLATURE

A	Specific area of absorbant
C_i	Initial solute concentration, mg/ml
C_f	Final solute concentration, mg/ml
c_i	Curie, 3.7×10^{10} dps
cpm	Observed count rate, counts per minute
dpm	Actual count rate, counts per minute
cpm_i	Initial solution activity, cpm
cpm_f	Final solution activity, cpm
n	Uptake
n°	Equilibrium uptake
P	Total system pressure
P_0	Equilibrium pressure for pure component
q	Equilibrium uptake
r	Amount of resin used, g
R	Gas constant
T	Absolute temperature
V_s	Solution volumn
w	Weight of solute used, g
π	Spreading pressure
α	Separation factor

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INTRODUCTION

Estimates of current shale oil reserves, counting only shales with an oil content of 25 gallons of oil per ton of shale or more, amount to over 280 billion barrels of oil in Colorado alone. This represents over 10 times the amount of known domestic reserves of liquid petroleum. In order to limit our present dependence on foreign oil, the United States will need to exploit more reserves in the next 20 years than all the liquid energy the U.S. has consumed during the past century (Ely, 1967).

It is clear that a healthy oil shale industry would greatly alleviate some of our energy requirements; however, an oil shale industry would require special technology to take care of pollution and environmental concerns. It is estimated that a 1,000,000 BPD shale oil industry in Colorado (which is projected to be achieved in the next 10-15 years) would consume some 200,000-250,000 acre feet of water per year, if above ground retorting were to be used (Sparks, 1974).

The in situ retorting process, however, has gained wider acceptance in the past few years. When using the in situ

process, Colorado shales produce approximately equal amounts (by weight) of oil and water. This retort water has been shown to contain very high concentrations of organic carbon, including organic acids, Mg^{++} , Na^+ , K^+ , NH_4^+ , HCO_3^- , $SO_4^{=}$, Cl^- and other impurities. The actual amount of water produced and to what extent it is contaminated depends on the type and conditions of the retorting process and the nature of the oil shale. For example, analysis of the retort water from the Laramie Energy Research Center's 10-ton retort shows the following ranges of concentrations (mg/l) for the following impurities: Mg^{++} (3-350), K^+ (8-70), Na^+ (150-1300), NH_4^+ (6200-18,200), HCO_3^- (10,000-42,000), $SO_4^{=}$ (320-2,100), Cl^- (1,100-7,900), and Organic Carbon (2,830-10,660).

The characteristic "first acid" concentration in the same retort water is present at .56 to 1.21 weight percent. This "first acid" fraction represents the carboxylic acids such as benzoic acid and phenols (Jackson, et al, 1976).

Phenol and especially the chlorinated phenols are of special concern in that they are considered highly toxic and cannot be degraded by biological treatment systems. For these reasons much research is being done in the removal and recovery of the phenols by adsorption.

EPA limits on phenols and carboxylic acids concentration in treated waste water vary considerably according to the industry involved and its throughput. A typical value

would be a limit of 6 ppm on both phenols and on carboxylic acids (Burm, 1978).

The method found to be most feasible in cleaning the retort waters makes use of a combination of (1) chemical treatment with lime and heating to remove carbonates, most of the ammonia, and some organic materials; (2) adsorption on activated carbon-or-organic resins to remove the remaining organic material; and (3) cation and anion exchange to remove the rest of the ions to achieve the desired water purity (Hubbard, 1971).

Activated carbon is an efficient agent for removing organic solutes from water by adsorption; however, its characterization is limited by the fact that many organic species are not desorbed by the activated carbon. The surface of most activated carbons is heterogeneous in nature, adsorbing solutes both physically and also, because of the presence of oxygen-containing functional groups, chemically. Because of this "double" bonding effect, desorption of the organic material by one solvent medium is virtually impossible. Also, once all adsorption sites are filled, selective organic adsorption occurs and previously sorbed organic solutes are desorbed. Thus the recovered organic fraction may not represent the original sample composition (Leenheer and Huffman, 1976). Because of these considerations, adsorption on a

series of macroreticular resins is more easily utilized in water cleaning processes.

The reasons that adsorption is often more advantageous than other separation methods such as flash evaporation and freeze concentration are that adsorption is a low energy process not involving a phase transition (it occurs at low temperature and high vapor pressure so that few volatiles are lost) and adsorption is selective and can be used also for separation (Leenheer and Huffman, 1976).

Resins are generally quite specific as to polarity. For this reason a series of resins is needed to completely clean a process water stream. The three-dimensional styrene-divinylbenzene copolymers, which possess a macroreticular structure with a high surface area, generally adsorb by only one mechanism and are very stable under most operating conditions. They have been shown to have good hydraulic flow characteristics for column operation (Leenheer and Huffman, 1976).

It is the intent of this project to study an intermediate-polarity macroreticular adsorbant, Rohm and Haas Amberlite XAD-8, and to obtain the resins' adsorption characteristics for adsorbing phenol and benzoic acid from water both as single components and as a binary.

LITERATURE SURVEYAdsorption and Resins

Acidic surface oxides on activated carbon can influence the sorptive properties of the carbon including the equilibrium uptake and the rate of adsorption. Often these changes are irreversible because these surface groups may bind the solute chemically whereas adsorption is generally characterized as a physical process. The uptake of phenol on activated carbon is 91.65 mg/g-Resin at .0188 mg/ml concentration at 30.°C for 1 week equilibrium time (Coughlin, 1968).

In many of the isotherms characterizing organic solutes on resins, steps in the isotherm appear. These steps, according to Giles, et al (1960), may be attributed to a new surface which: (1) may be part of the exposed layer itself, implying true multilayer adsorption; (2) may be new area in which adsorption starts to penetrate, implying adsorption starting to take place onto less energetic active sites; or (3) may be part of the original surface, implying a reorientation of the adsorbed molecules to give more surface area of the resin. Sharma and Fort, Jr. (1974), found in their adsorption studies with activated carbon that the steps in their isotherms could best be explained by phenomenon (2) above. These isotherms

could not be fit to the BET isotherm which is based on true multilayer adsorption.

Snoeyink, Weber, and Mark, Jr. (1969), found that phenol adsorption onto activated carbon could not be characterized by the Langmuir equation except by dividing the phenol isotherm up into many sections. Larger sections, but not the entire isotherm, could be characterized by using the Freundlich equation. They also found that the pH of about 7.5 was optimum for the uptake of the organic solute (depending on the solute's pK), and that deviations on either side of this optimum resulted in decreased adsorptivity. The pK is $-\log K$, where K is the dissociation constant--the tendency of an acid to donate protons in solution. The pK is related to the pH of a solution through the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK} + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

Note that at equal concentration of proton acceptor and proton donor there is no more driving force for dissociation and $\text{pK} = \text{pH}$ (Lehninger, 1975).

During packaging of Amberlite resins, sodium chloride and sodium carbonate are added to the resins to control bacteria and mold growth during storage. These must be washed off with copious amounts of water. Since XAD-8 is commonly used to adsorb organics and organic acids, a wash containing a weak

base is used followed by an organic solvent wash, generally with methanol, to regenerate the resin for use.

Rohm and Haas (1975), found that flow rates of adsorbate in excess of 8 bed volumes per hour resulted in adsorbate leakage and lessened efficiency of the bed. They also found that the loading capacity will increase with higher molecular weight solutes, and the presence of electrolytes will increase adsorption for any given organic specie.

When desorbing phenol, washing the resin with caustic is used as the first regeneration step to ionize the phenol and form the more soluble sodium phenolate. The phenolates can then be eluted readily with organic solvents such as methanol or acetone. The use of more dilute caustic solution gives more favorable elution provided that a stoichiometric amount of caustic is present to react to form the phenolates.

Rohm and Haas (1975), found no lowering of phenol capacity of the Amberlite resins after 5 cycles of adsorbing and desorbing, and concluded that these resins are chemically and physically stable for lengthy periods. The advantage of using Amberlite resins over the higher surface area activated carbon is that the Amberlite resins have a greater capacity at elevated flow rates and the adsorption is generally physical by nature. Any solute highly soluble in an

organic solvent instead of water is a prime candidate for removal and recovery using Amberlite resins.

The intermediate-polarity Amberlite resins are efficient in recovering the non-ionic organic compounds. Amberlite XAD-7, and XAD-8 remove phenol with 86 percent retention efficiency and benzoic acid with 100 percent retention efficiency (Rohm and Haas, 1975).

The intermediate-polarity resins have an attraction for both the hydrophobic and hydrophilic end of a molecule. Thus, these resins work well in adsorbing hydrophobic materials from water and hydrophilic materials from organic solvents. This characteristic enhances the removal of phenol from waste waters containing other organic solutes.

Amberlite XAD-8 has less surface area than XAD-7 but has a larger average pore diameter (250 Å) and thus makes XAD-8 better in total capacity and flow rate for larger organic molecules such as substituted phenols and benzoic acid. Amberlite XAD-8 appears to be the most effective of the Amberlite resins in concentrating both high-molecular and low-molecular weight organic solutes because XAD-8 is easily purified, has a high capacity, and has a high efficiency of desorption (Malcolm, Thurman, and Aiken, 1977).

A survey of the literature revealed that Paleos (1969) measured the adsorption of phenol in Amberlite XAD-8 at 25°C. His data will be compared to this work in a later section.

Liquid Scintillation Counting

The method selected for analysis of the concentration changes was that of using radiolabeled solutes and scintillation counting. This method can offer a 10^3 - 10^6 increase in sensitivity over conventional spectroscopic or chromatographic quantitation techniques (Neame and Homewood, 1974).

Since the first simple scintillation counter was produced during WW II, many advances in radiation counting and in experimental methods using scintillation counting have been achieved. A fast scintillation decay time in the order of a few η seconds used in conjunction with a fast photomultiplier provides counting with time resolutions of less than 10^{-9} seconds (Shafroth, 1967).

Scintillation counters work by a source emitting radiation, this radiation then falls on a luminescent material that re-emits light. The light, in return, is picked up by a photosensitive cathode which gives off an electrical impulse that is counted and recorded. There are three major concerns in the design and operation of a scintillation counter: (1) the kinetic energy of radiation incident upon the luminescent material must be efficiently converted to excitation energy of the scintillator; (2) de-excitation should result in fluorescent radiation freely transmitted through the scintillator medium; and (3) the photosensitivity of the cathode should

be high so that maximum number of emissions are collected.

In choosing the window thickness, the spectral response curve of the photomultiplier cathode must be considered. The spectral response for a given cathode material is highest and thus most efficient for a given wavelength. The window slit and thickness is designed to allow the maximum of re-emitted light of this characteristic wavelength into the photomultiplier. The cathode material is dependent somewhat on the type of scintillator and thus the type of radiation involved.

Quenching, the de-activation of the re-emitted fluorescent radiation, can occur when the excitation energy is dissipated in the scintillator medium or when the mean free path to the cathode photomultiplier is too long for excitation to be maintained. Generally, distilled water and some organic solvents are good scintillator mediums that do not markedly reduce the re-emitted fluorescence. The quenching in any medium is found experimentally by comparison of the known disintegration rate and the observed count rate. The difference can be termed an "efficiency" and this efficiency is unique for that medium.

The effect of very small traces of impurities can be very deleterious to the quality of a scintillator material. Quenching due to these impurities can be of the internal, external or collisional, and inner filter or compound type.

Internal quenching is a blurring of the re-emitted fluorescent energy due to the rapid dissipation of excitation energy to vibrational energy within itself or to other molecules (impurities). External quenching is due to a loss of excitation energy due to an excess mean free path (the excitation state of most scintillator molecules is relatively short in duration). Filter quenching is due to the blocking of the fluorescent rays by particles within the scintillator medium (Birks, 1967).

EQUIPMENT AND PROCEDURE

Adsorption Studies

The resins as obtained from Rohm and Haas was contaminated and had to be purified prior to initiating an adsorption study. The resin was first slurried overnight in .1 N sodium hydroxide after which it was washed five times with reagent grade methanol. Slurrying with sodium hydroxide and the subsequent methanol washes removed the fines and desorbed contaminants from the resin. After the methanol wash, the resin was extracted for eight hours in a soxhlet extractor with diethylether. This was followed by an extraction with acetonitrile and then with methanol, each for twenty-four hours. The resin was stored in methanol until it was to be used. The final conditioning step prior to its use included: rinsing the resin with at least ten bed volumes of distilled water, drying the resin by aspirating and heating, and placing the resin in a vacuum desiccator until it was to be weighed for the adsorption studies.

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The radioactive phenol as obtained from Amersham laboratories was a small speck of irradiated solute sealed in a glass ampule. In order to quantitatively transfer all of the radioisotope to a volumetric flask the ampule was broken and both parts were rinsed at least 20 times with distilled water into a volumetric flask. The ampule parts were then filled with distilled water and allowed to sit for at least 24 hours to insure that all of the solute had been dissolved in the water and then that, too, was rinsed into the volumetric flask. The flask was then filled to the mark with distilled water, making a radiolabeled stock solution of the solute. The activity contained within the ampule is stated on the ampule and may be diluted to any given activity, e.g. a $250 \mu C_i$ ampule of phenol may be rinsed into a 250 ml volumetric flask giving a stock solution with an activity of $1 \mu C_i/ml$.

In choosing an equilibration time, a kinetic study was made by preparing 850 ml of 200 ppm phenol and benzoic acid and contacting these with 25 grams of resin. Periodically, a 1 ml aliquot of the solution was analyzed on a total carbon analyzer for carbon content. When no change in carbon content was observed in subsequent aliquots taken, adsorption equilibrium had been reached.

Later, a more accurate kinetic study was run by contacting 3.25 liters of radiolabeled phenol at 200 ppm with

125 grams of Amberlite XAD-8 at 25.°C. Periodically, a 1 ml aliquot of the solution was taken for radioassay. The aliquot was small enough so as not to disturb adsorption equilibrium. When the radioactivity (and thus, concentration) of subsequent aliquots ceased to change, the solution was at equilibrium with the resin.

In preparing the solutions for the batch adsorption runs, a quantity of phenol crystals was weighed to .00002 grams by difference on a piece of aluminum foil. The crystals were then transferred to a 100 ml, class A volumetric flask. The crystals were washed into the volumetric flask and then the foil itself was washed several times with distilled water to insure that all of the phenol had been transferred.

After the crystals had completely dissolved, 3 ml of radio-labeled isotope of the same material (phenol) with an activity of approximately $1 \mu \text{Ci/ml}$ was added to the volumetric using an Eppendorf pipet. This amount of radiolabeled solution insures enough activity for good counting statistics, yet has negligible solute mass and does not change the amount of phenol added to the flask. Finally, the volumetric was filled to the mark with distilled water.

After thorough mixing of the solutions made, a 5 ml sample of each was taken out with a clean, 5 ml glass vial and sealed in a scintillation vial for radioassay. From

these samples the activity corresponding to the initial activity was found.

The remaining 95 ml of solution was then added to glass bottles in which approximately 5 grams (weighed to .0001 g) of cleaned, dried resin had been added. These bottles were then placed in a Blue M, model BSM-3222A-1 refrigerated shaker bath for 144 hours. This time was established by the kinetic study. The agitator speed on the bath is variable from 50 to 200 cycles per minute with a shaking stroke of 0 to 1 15/16 inches. The temperature range is adjustable from 0° to +100°C. After the 144 hours of adsorption at the given temperature, a 10 ml sample of the solution was filtered through glass wool into a scintillation vial for radioassay. The radioassay of these samples gives the final activity of the solution and thus, by a linear relationship between activity and concentration, also gives the final concentration of the solution. In this way the final concentration, the uptake--or difference between final and initial concentration, and the amount of adsorbant are all known.

The used resin was filtered from the phenol solution with a Buchner funnel and then rinsed with two 25 ml aliquots of distilled water. The resin was then collected and stored in scintillation vials for desorption studies.

For safety in using the radioisotopes, the radioactive materials were kept under lock and key. All "hot" trays and syringes were appropriately marked and all waste stored in waste containers for later disposal. All personnel working in the laboratory wore disposable plastic gloves. A beta-counter was used periodically to monitor the radiation in the laboratory.

Liquid Scintillation Counting

The measurement of radioactivity using a liquid scintillation counter involves the accumulation of fluorescent light radiation given off by an excited scintillator molecule by a photomultiplier cathode. The photomultiplier cathodes converts the accumulated fluorescent radiation into electrical pulses. The pulses are processed by instrumental circuits (e.g., detection, time accumulation, amplification, and pulse analysis) and expressed in terms of time as a count rate, such as counts per minute (cpm). The count rate recorded by the liquid scintillation counter is always less than the actual disintegration rate ensuing from the radioactive decay process. This discrepancy is expressed in terms of counting efficiency. Efficiency losses result primarily from quenching. The relationship between disintegration rate (actual activity) and count rate (observed activity) is given by:

$$\text{dpm} = \text{cpm}/\text{efficiency}$$

In practice, the efficiency may be computed from the observed count rate (cpm) for a standard scintillation mixture containing a known amount of radioactivity in terms of disintegrations per minute (dpm). A knowledge of the counting efficiency allows the dpm or activity of similarly quenched samples to be determined from the count rate using the above equation. This method may be extended to variably quenched samples by use of a calibration curve relating the efficiencies for a series of variably quenched standards to another quench dependent parameter. The quench dependent parameter most commonly applied comes from instrumental monitoring of the pulse height spectral shift in the beta spectrum caused by quenching. The Beckman model LS-9000 liquid scintillation spectrometer employed in this study incorporates an advantageous modification to classical quench dependent spectral shift monitoring. The liquid scintillation counting instrument used will determine and store the third order polynomial regression coefficients of an efficiency calibration curve determined with a series of quenched standards and thereafter apply this data to compute the dpm from the measured cpm for any additional unknown sample.

Another useful concept in radioassay work is that of specific activity. It is often necessary to state the amount of radioactive material in terms similar to concentration, that is, per unit quantity of material, and this is called

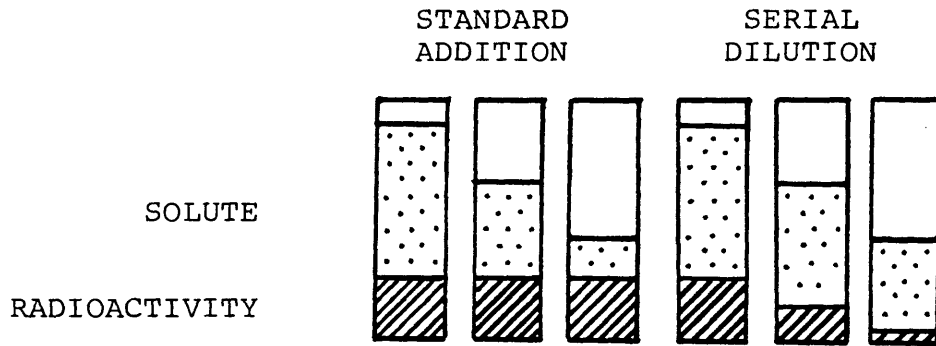
the specific activity. Most commonly, the units for specific activity are expressed in terms of the rate of disintegration either per unit quantity of labeled material, dpm/mg, or per unit volume of solution containing the labeled material, dpm/ml. The use of specific activity enables quantitation of the radio-nuclide content in a sample by measuring its radioactivity.

Adsorption isotherm studies entail the preparation of solutions with varying initial concentrations of solute and then measuring the subsequent changes in concentration. As the concentration diminishes, either in the original or final measurements, the accuracy of the analysis is also diminished. This is particularly apparent as the concentrations approach the detection limit of the analytical technique used. After evaluating alternate approaches for the addition of radio-activity into the solutions, an approach that enhances the sensitivity, and thus the accuracy of measurement, has been adopted.

Table 1 illustrates two methods of preparing a series of radioactive solutions with varying concentrations of solute and simulates counting results obtained from each for comparison. The two methods are termed "standard addition" and "serial dilution". The total area of each bar represents the assumed volume of 1000 ml for the simulated initial standards. The relative contributions and changes in solute

Table 1

Simulated Comparison of Standard Addition and Serial Dilution Radioassay Methods



	Initial Conditions (Volume = 1000 ml)					
CONCENTRATION ($\mu\text{g/ml}$)	10^3	10^2	10	10^3	10^2	10
AMOUNT SOLUTE (μg)	10^6	10^5	10^4	10^6	10^5	10^4
TOTAL DPM	10^7	10^7	10^7	10^7	10^6	10^5
SOLUTE SP. ACT. (DPM/g)	10^4	10^5	10^6	10^4	10^4	10^4
SOLUTION SP. ACT. (DPM/ml)	10^4	10^4	10^4	10^4	10^3	10^2
SENSITIVITY ($\mu\text{g/ml}$) ^a	.01	.001	.0001	.01	.01	.01
SENSITIVITY RATIO ^b	00001	00001	00001	00001	00001	.001
Following 95% Removal of Solute by Adsorption						
CONCENTRATION ($\mu\text{g/ml}$)	50	5	0.5	50	5	0.5
SOLUTE SP. ACT. (DPM/ μg)	10	10^2	10^3	10	10	10
SOLUTION SP. ACT. (DPM/ml)	500	500	500	500	50	5
SENSITIVITY ($\mu\text{g/ml}$) ^a	10	1	0.1	10	10	10
SENSITIVITY RATIO ^b	0.2	0.2	0.2	0.2	2	20

^aSENSITIVITY ($\mu\text{g/ml}$) = DETECTION LIMIT (DPM/ml) \div SOLUTE SP. ACT. (DPM/ μg). In this case, the DETECTION LIMIT is 100 DPM/ml.

^bSENSITIVITY RATIO = SENSITIVITY ($\mu\text{g/ml}$) \div CONCENTRATION ($\mu\text{g/ml}$)

and radioactivity among a series of three standards is illustrated by the shaded areas for each of the two methods.

In practice, one cannot distinguish radioactivity associated with the radiolabelled solute and the inactive solute once mixing has occurred and the shaded areas are shown only to aid in visualizing the differences between the two methods.

In the standard method three solutions are prepared (total volume 1000 ml) by quantitative addition of the necessary amounts of inactive solute (10^6 , 10^5 , and 10^4 μg) so that the final concentrations will be 10^3 , 10^2 , and 10 $\mu\text{g}/\text{ml}$, respectively. Equal amounts of radioactivity, 10^7 dpm (in the form of the corresponding radioactive solute), are then added and the solutions are diluted to the final volume. Note in this case as well as in the next, that it is assumed that the specific activity of the radiosolute used for labeling the standards is large enough to impart the indicated 10^7 dpm with negligible change in the final concentration of solute. In the serial dilution method the same initial solute concentrations of 10^3 , 10^2 , and 10 $\mu\text{g}/\text{ml}$ are achieved by serial dilution of the most concentrated stock which initially contains the same amount of radioactive solute.

The critical distinction between the two preparation methods is made apparent by comparison of the resultant

solute and solution specific activity values. In the standard addition method the solution specific activity remains constant at 10^4 dpm/ml due to the constancy of total amount of radioactivity added and the final volume. Note, however, that the solute specific activity increases as the concentration of solute decreases. In the serial dilution method the solute specific activity remains constant for the series (10^4 dpm/ μ g) and is governed only by the specific activity present in the initial most concentrated solution. In this case the solution specific activity decreases with decreasing concentration as a result of the recurrent dilution effect.

The inverse relationship between concentration and solute specific activity is an important consequence of the standard addition method and is contrasted by the non-dependency of the two parameters in the serial dilution method. The advantage of the standard addition method is revealed by inspection of the changes in sensitivity and sensitivity ratios for the initial standards and for the solutions after sorptive removal of the solute. The sensitivity of the radio-analytical technique is defined as the lowest concentration level for a given solution that can be reliably and accurately measured under the constraints of the adopted detection limit. In this simulation the detection limit is given the realistic value of 100 dpm/ml. This means that the sample may be

accurately analyzed for its radioactivity content to at least a 1 percent 2-sigma counting error if the sample contains at least 100 dpm/ml. The detection limit is a constraint established by the limitations of the equipment available and the counting time used. The sensitivity ratio is defined as the ratio between the sensitivity of a measurement to the measurement being attempted. The smaller the sensitivity ratio the larger the margin between the instrumental sensitivity and the actual concentration being determined and consequently the greater the accuracy of the measurement. As the sensitivity ratio increases and exceeds unity, the instrumental sensitivity approaches and exceeds the concentration measurement being attempted which diminishes the accuracy and reliability of the result.

Inspection of Table 1 will show that the standard addition method for introducing radioactivity results in ever-increasing sensitivity as the concentration decreases so that for a series of concentrations the sensitivity ratio remains constant. This is contrasted by the serial dilution method where the sensitivity remains constant as concentrations decrease so that the sensitivity ratio becomes proportionately larger (worse) as the concentration decreases. This latter case illustrates why the accuracy of concentration determination suffers as the concentration diminishes.

In summary, a radioanalytical approach will generally increase the sensitivity and accuracy of concentration type analyses. Furthermore, the addition of radioactivity by the standard addition method will afford an additional advantage in that the sensitivity of the radioanalytical method will be enhanced as the concentration to be analyzed becomes smaller. Thus, the overall statistical variance and accuracy of results will be the same over the entire concentration range. For these reasons, a radioanalytical approach using the standard addition procedure was used in the design of the adsorption isotherm studies.

Each aqueous sample was radioassayed in triplicate according to the following procedure. Aliquots (1 ml) of the aqueous sample were transferred with the aid of an Eppendorf pipet to glass scintillation vials and admixed with 12 ml of Dimilume-30 (Packard Inst. Co., Downers Grove, Ill.). Dimilume-30 is a complete scintillation cocktail for the counting of aqueous samples and affords a homogeneous, single phase mixture with the mixing proportions used. Samples were placed in the liquid scintillation counter (Beckman model LS-9000 Liquid Scintillation Spectrometer) and dark adapted for at least 30 min. prior to counting. Counting was performed in a wide open ^{14}C window and continued until a 2-sigma count rate error of 1 percent or less was

achieved. Random coincidence monitoring, an instrumental feature, was used to insure that the contribution of counting events not due to radioactivity disintegrations, e.g., chemiluminescence, was less than 0.1 percent. The counting efficiency was determined for each sample and used to compute the absolute activity as dpm values. Efficiency corrections were made by instrumental measurement of the Compton edge inflection point, a Beckman modification of the external standardization method, and interpolation of the counting efficiency from a microprocessor-stored efficiency calibration curve, previously obtained from a series of water quenched ^{14}C standards prepared in Dimilume. Final dpm values were automatically corrected for subtraction of a background count rate of 60 cpm (Farrier, 1977).

Each scintillation sample was counted twice according to the above procedure and the average dpm result computed. Each aqueous sample was split for triplicate radioassay, a total of six counts (each to a 1 percent or better, 2-sigma standard deviation counting error) contributed to the overall average dpm/ml computed for each sample. The coefficient of variation for the triplicate assays (computed from 50 results) was 0.77 ± 0.7 percent (Miller and Freund, 1965).

RESULTS AND DATA ANALYSIS

The kinetic studies run on the total carbon analyzer showed in all cases that equilibrium was reached after 44 hours for the benzoic acid system and after 104 hours for the phenol system. The kinetic study made by adsorbing a radiolabeled phenol solution onto the resin was used to determine an equilibration time. The results of this study, are tabulated in Table 2 and presented graphically in Figure 1. The flattening of the data between 40 and 65 hours of contact time suggests a decrease in adsorption for this period, and may represent the start of multilayer adsorption effects. To insure that ample contact time was provided for the adsorption runs, an equilibration time of 144 hours was chosen.

The adsorption of benzoic acid onto Amberlite XAD-8 at 25°C is presented in Table 3 and the isotherm for this system is shown in Figure 2 (see Appendix 1 for isotherm calculations). The spreading pressure for a pure component can be found by the method suggested by Kidnay and Myers (1966). First, $d \ln C/d \ln q$ versus q is plotted and then a graphical integration is performed on:

Table 2

Kinetic Study of Phenol at Adsorption onto Amberlite
XAD-8 at 25.°C

<u>Time hr.</u>	<u>Radioactivity dpm</u>
0	23370
.017	15914
.033	14361
.050	10750
.083	5410
.167	5509
.250	5120
.333	4590
.500	4299
.750	3840
1.0	3700
1.5	3470
2.0	3294
3	3197
8	2858
12	2714
17	2721
24	2661
32	2612
41	2557
48	2580
67	2493
73	2466
80	2373
88	2243
104	2092
118	2076
128	2058
139	2074

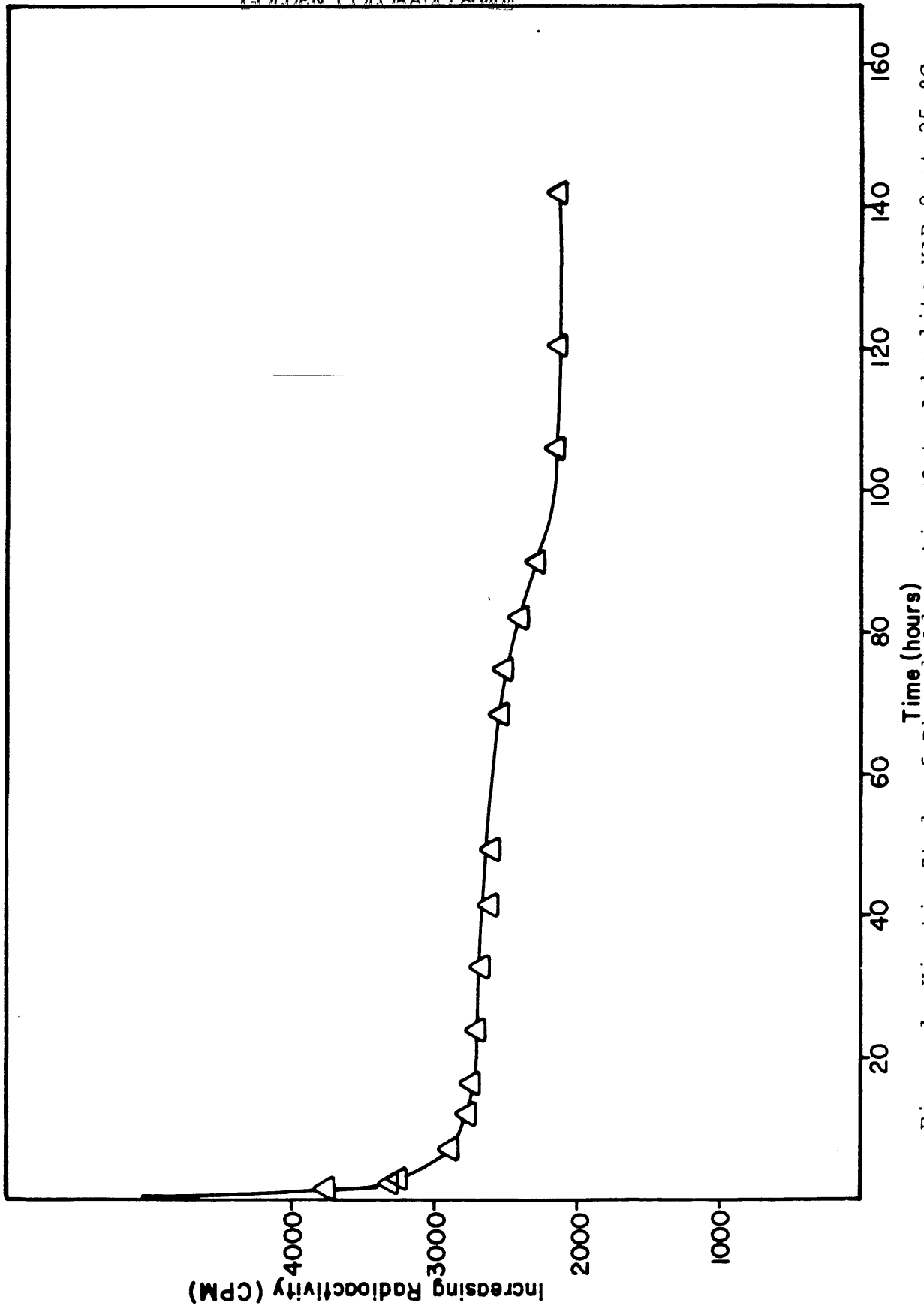


Figure 1. Kinetic Study of Phenol Adsorption onto Amberlite XAD-8 at 25.°C.

Table 3

Benzoic Acid Adsorption on Amberlite XAD-8 at 25°C

<u>final conc. mg/ml</u>	<u>uptake, mg/g-resin</u>
.4948	28.904
.3225	13.117
.2448	4.929
.1747	.486
.0599	.813
.0216	.896
.0275	.428
.0080	.227
.0052	.091
.0019	.097
.0009	.077
.0003	.032

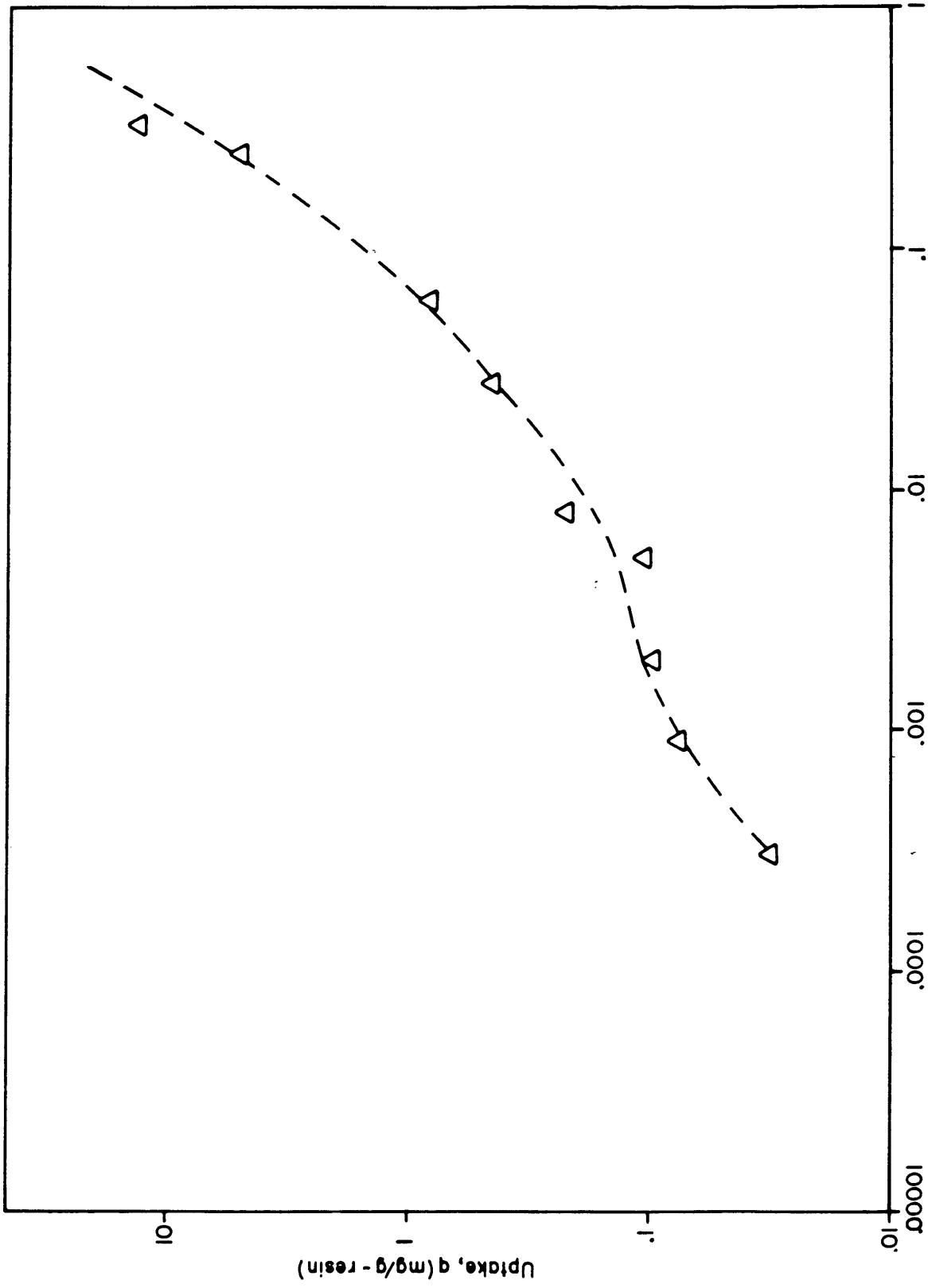


Figure 2. Equilibrium Uptake of Benzoic Acid on Amberlite XAD-8 at 25.°C.

$$\frac{\pi A}{RT} = \int_0^q \frac{d \ln C}{d \ln q} dq$$

to get the spreading pressure (see Appendix 2). The graphical integration and a plot of the resulting spreading pressure are presented in Figures 3 and 4.

The adsorption data of phenol onto Amberlite XAD-8 at 0., 25., and 70.°C is presented in Tables 4, 5, and 6 and the isotherms are shown in Figure 5. These isotherms have been shown to fit Radke's 3 parameter adsorption isotherm model with small (5 percent) error (see Appendix 3). The graphical integration and a plot of the resulting spreading pressure for pure phenol at 25.°C are presented in Figures 6 and 7.

The phenol data has been shown to be internally consistent by plotting $\ln C$ versus $1/T$ at constant uptakes for the three isotherms. The results of this graph are presented in Figure 8. From the slopes of the lines obtained, heats of adsorption can be calculated. The relatively constant heats of adsorption were calculated to be 11962 cal/g-mole which compares favorably with the heat of condensation of 11314 cal/g-mole for phenol.

The surface area of the Amberlite XAD-8 is reported by the manufacturer to be 140 m². A B.E.T. surface area analysis done on this resin by Coors Company of Golden, Colorado indicated a resin surface area of 149.3 m². By using the maximum

Figure 3. Plot of $\frac{d \ln C}{d \ln q}$ vs. q for Benzoic Acid at 25.°C.

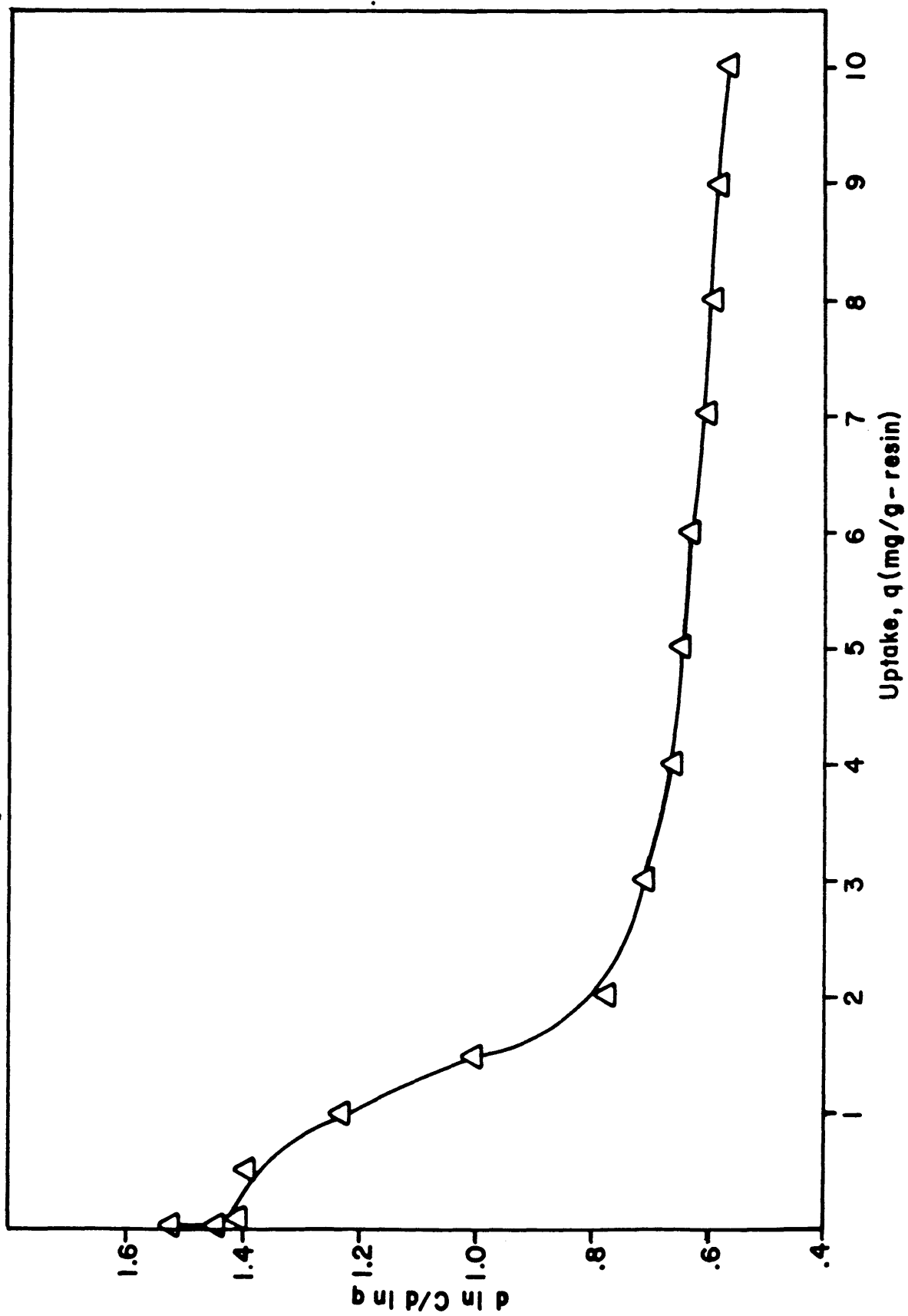


Figure 4. Spreading Pressure of Pure Benzoic Acid at 25.°C.

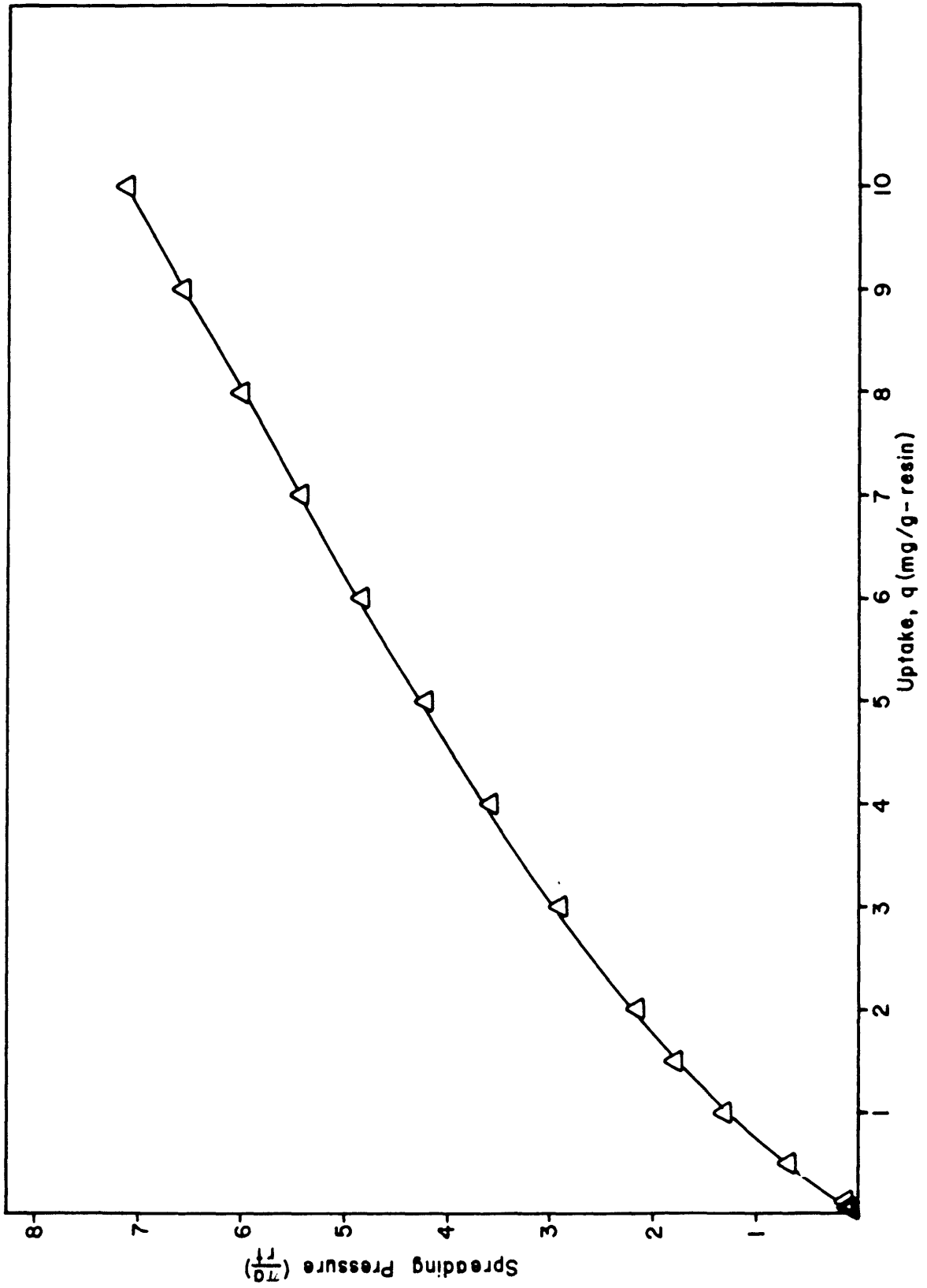


Table 4

Phenol Adsorption on Amberlite XAD-8 at 0°C

<u>Final conc. mg/ml</u>	<u>Uptake, mg/g-resin</u>
2.8583	135.736
.9366	77.080
.2490	34.404
.0888	18.988
.2070	9.015
.0078	3.732
.0033	1.692
.0021	.9193
.0007	.3704
.0004	.1842
.0002	.0914
.0001	.0362

Table 5

Phenol Adsorption on Amberlite XAD-8 at 25°C

<u>Final conc, mg/ml</u>	<u>Uptake, mg/g-resin</u>
3.6714	119.954
1.3259	70.124
.3248	31.678
.1088	16.920
.0306	9.156
.0163	3.835
.0063	1.899
.0036	.8986
.0016	.3572
.0014	.1673
.0011	.0760
.0006	.0266

Table 6

Phenol Adsorption on Amberlite XAD-8 at 70°C

<u>Final conc, mg/ml</u>	<u>Uptake, mg/g-resin</u>
4.903	96.8
1.797	60.8
.5325	27.86
.2460	14.4
.0736	8.11
.0390	3.17
.0158	1.53
.0093	.817
.0036	.328
.0018	.164
.0012	.077
.0010	.022

Figure 5. Equilibrium Uptake of Phenol on Amberlite XAD-8 at 0., 25., and 70.°C.

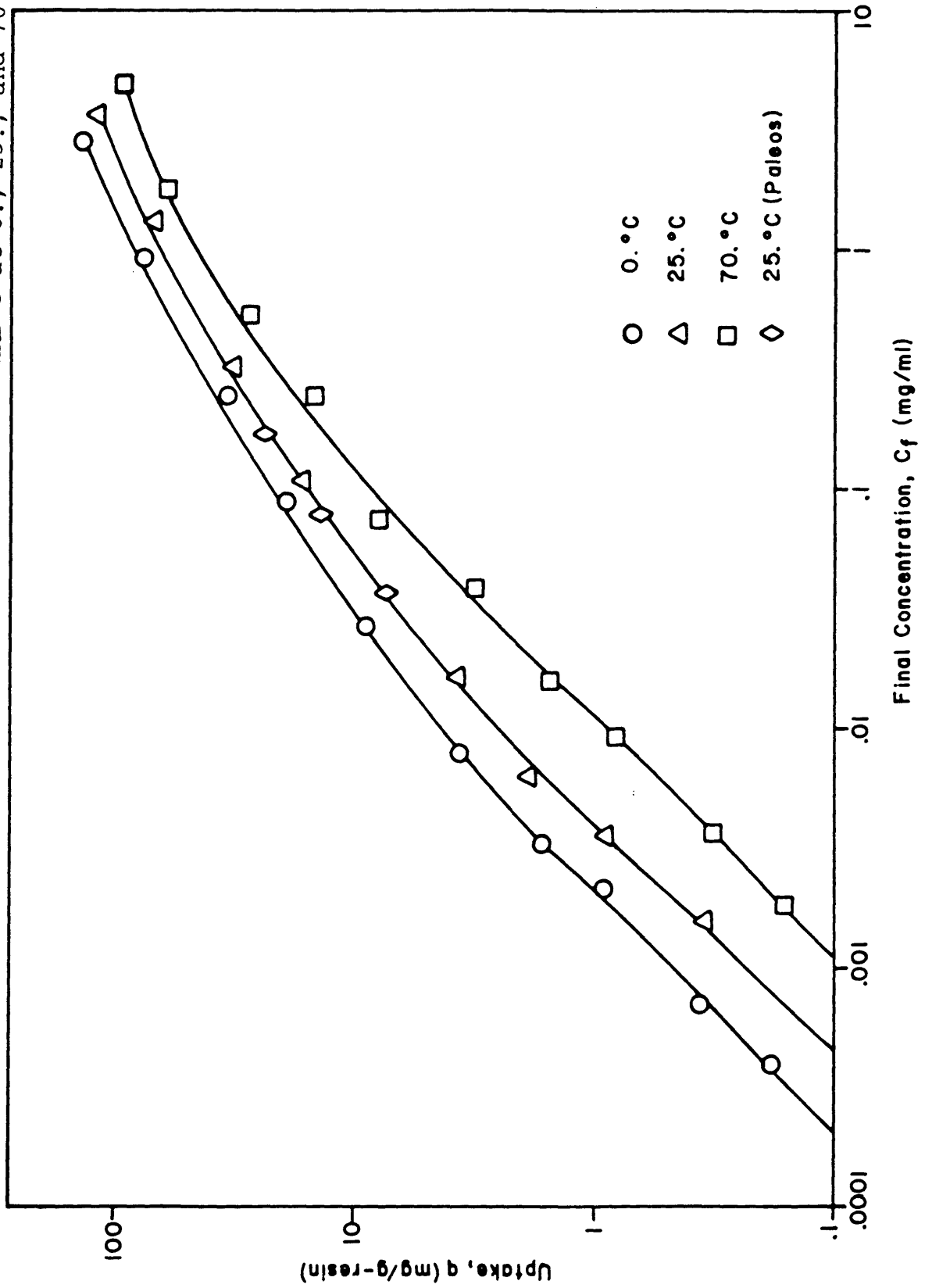


Figure 6. Plot of $\frac{d \ln C}{d \ln q}$ vs. q for Pure Phenol at 25.°C.

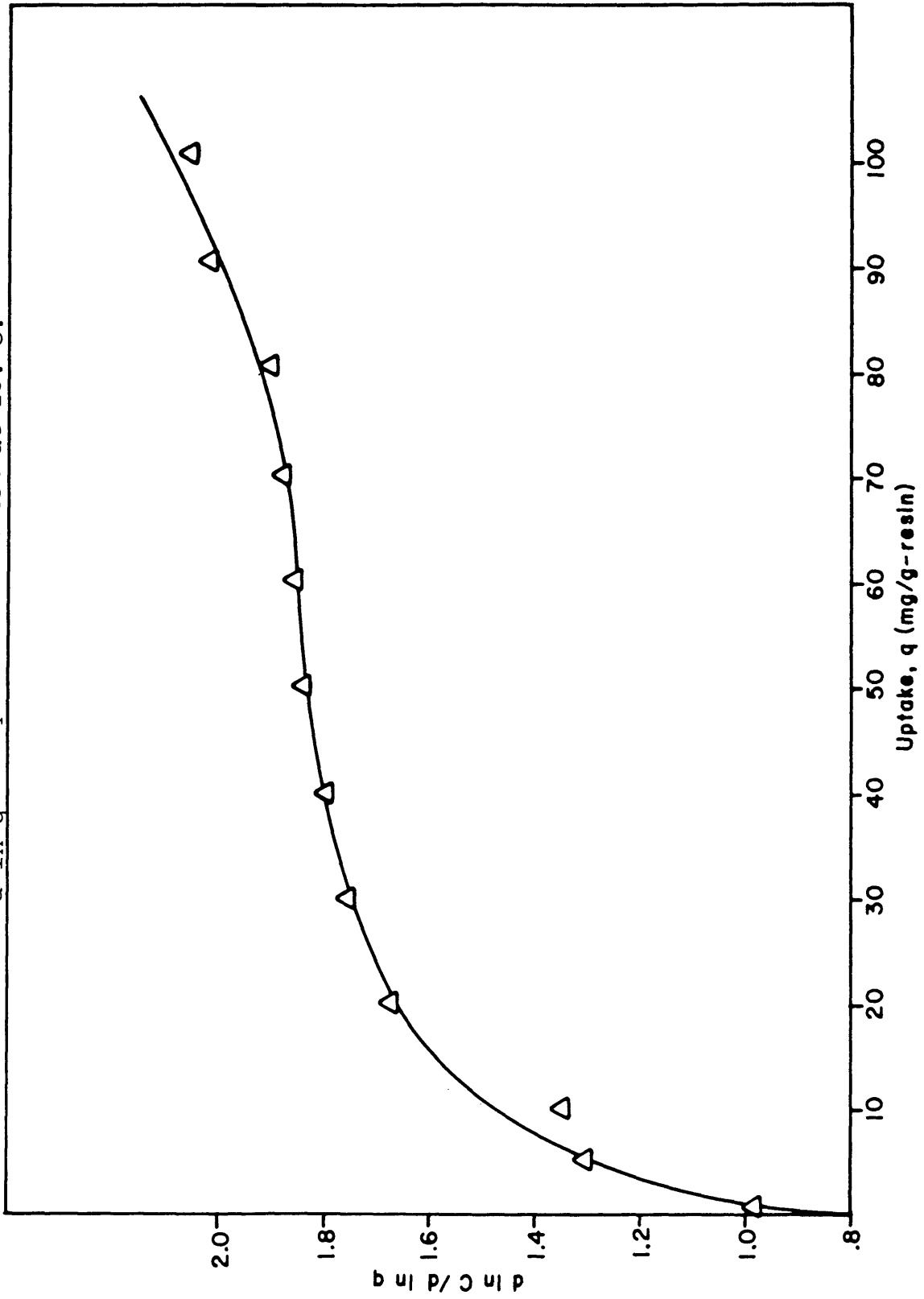


Figure 7. Spreading Pressure of Pure Phenol at 25. °C.

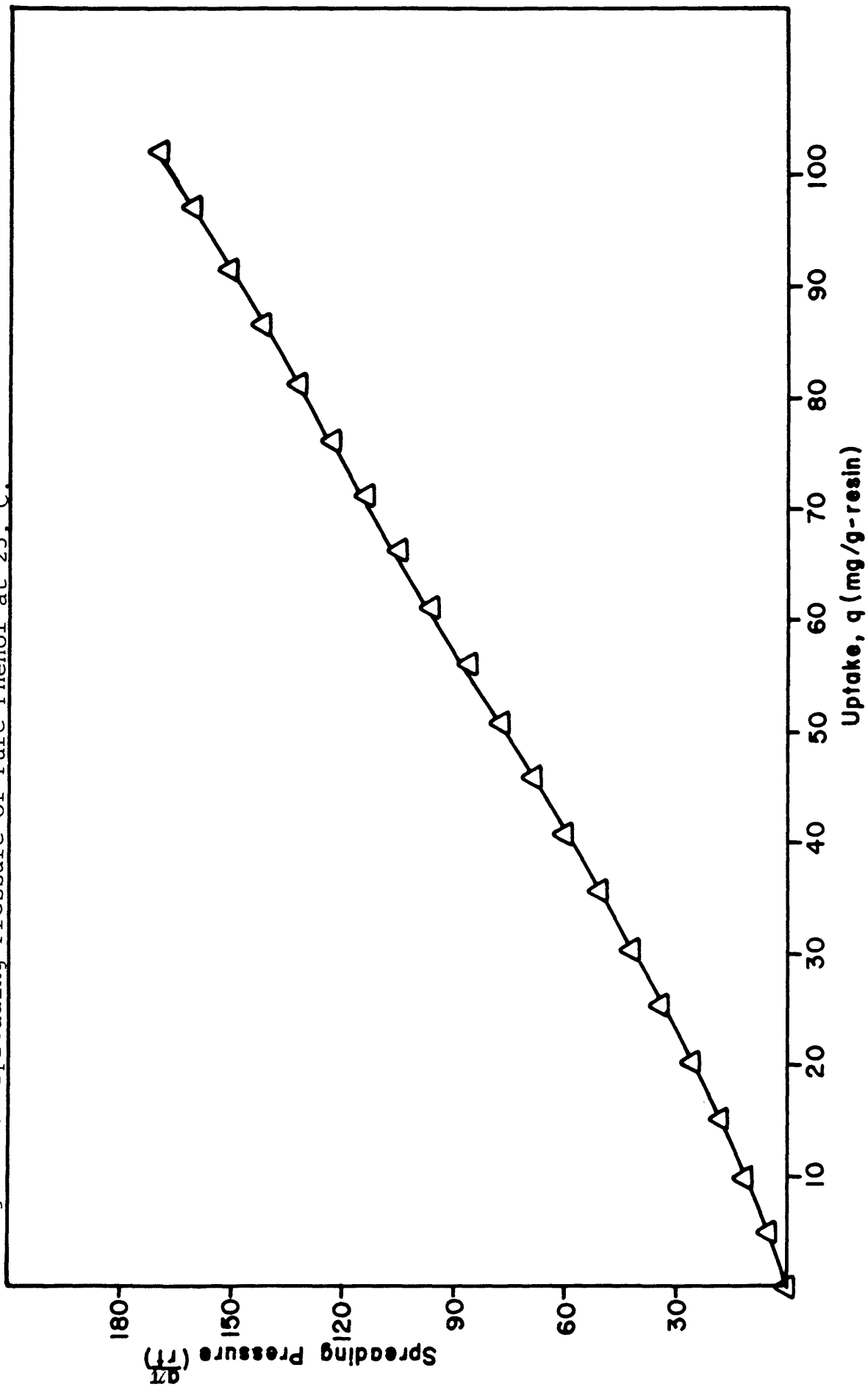
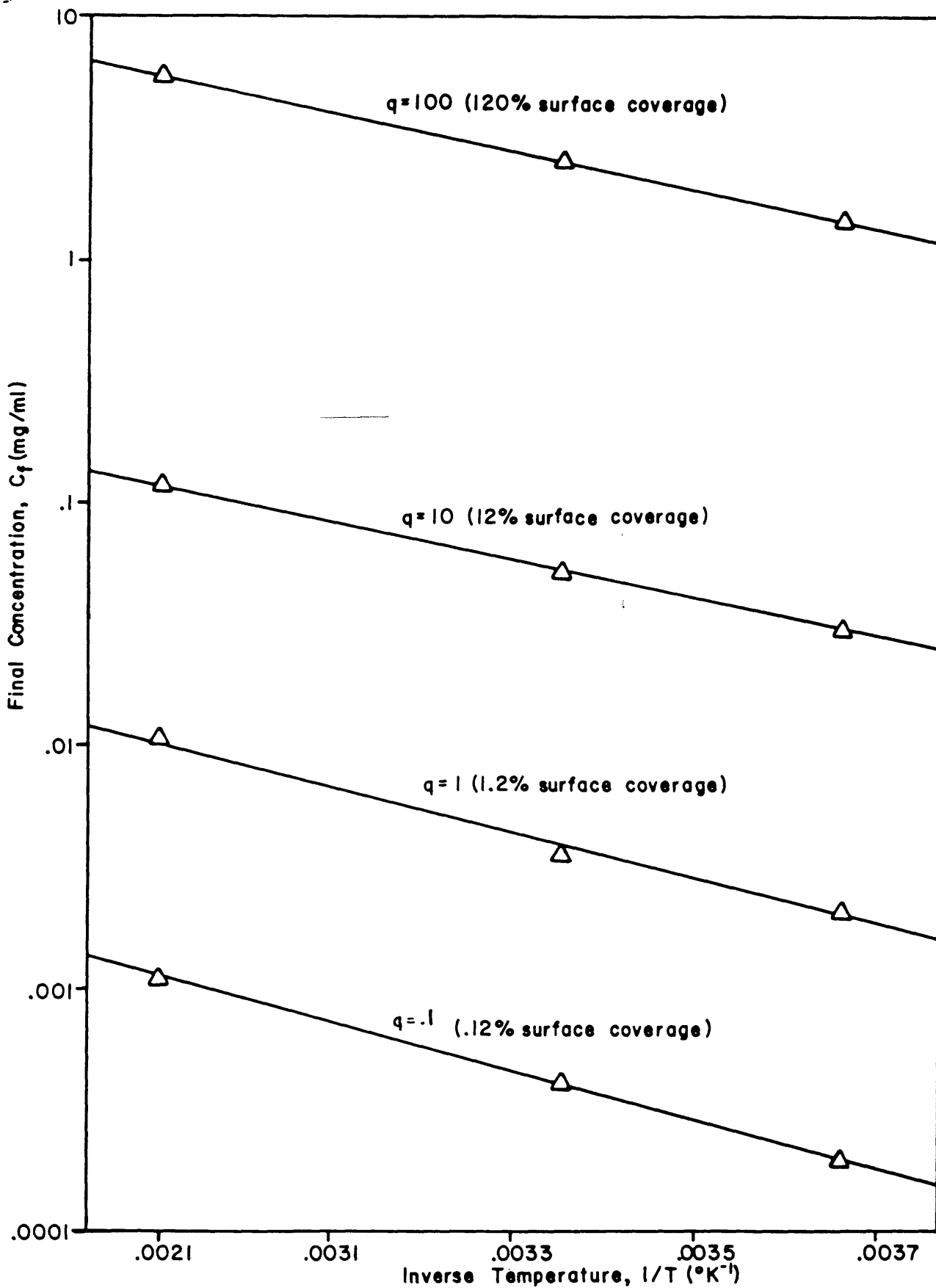


Figure 8. Heats of Adsorption of Phenol on Amberlite XAD-8.



uptake of phenol at 25°C it can be shown that there is 144 percent coverage of the resin surface. This coverage is based on a surface area per phenol molecule of 28 Å² (Singh, 1971). This same analysis was used to calculate the percent coverage of benzoic acid at 25°C and the highest coverage was found to be 43 percent, if a surface area per benzoic acid molecule of 45 Å² is assumed.

The phenol data at 25°C is compared graphically to the work of Paleos (1969) in Figure 5. This work compares extremely well with that of Paleos.

The adsorption of a binary mixture of varying concentrations of phenol and constant initial concentration of benzoic acid is tabulated in Table 7 and is compared graphically to the pure component adsorption isotherms in Figure 9. The adsorption of a binary mixture of varying concentrations of benzoic acid and constant initial concentration of phenol is tabulated in Table 8 and is compared graphically to the pure component adsorption isotherms in Figure 10. These figures suggest that the presence of benzoic acid has very little affect on the amount of phenol adsorbed except in the very dilute phenol concentration region, and that the adsorption of benzoic acid may be enhanced by the presence of phenol. The resin has a larger affinity for phenol than for benzoic acid as shown by a value for the separation factor (King, 1971) of $\alpha_{PB} = 3.75$ (see Appendix 4).

Table 7

Binary Adsorption of Phenol and Benzoic Acid on
Amberlite XAD-8 at 25.°C with Constant Initial
Benzoic Acid Concentration.

<u>Initial Phenol Conc. mg/l</u>	<u>Initial Benzoic Acid Conc. mg/l</u>	<u>Final Phenol Conc. mg/ml</u>	<u>Final Benzoic Acid Conc. mg/ml</u>	<u>Uptake of Phenol mg/g- resin</u>	<u>Uptake of Benzoic Acid mg/g- resin</u>
1007.9	1008.6	.08955	.29978	17.46567	13.48607
504.9	1003.6	.04443	.29812	8.74197	13.36986
201.4	1002.3	.01660	.29254	3.49371	13.51205
100.5	1001.9	.00965	.26610	1.73909	14.00883
68.1	1003.9	.00530	.23853	1.14943	14.48207
51.9	1002.3	.00546	.25405	.90498	14.17866
20.7	1001.3	.00246	.27289	.35605	13.83392
10.4	1005.9	.00145	.30296	.17395	13.34972
7.3	1004.3	.00100	.32708	.21256	12.84608
5.2	1002.5	.00064	.31903	.08850	12.77783
2.1	1003.6	.00030	.33605	.03414	12.63220
1.1	1003.4	.00016	.34368	.01793	12.52204

Figure 9. Binary Adsorption of Phenol and Benzoic Acid on Amberlite XAD-8 at 25.°C Initial Benzoic Acid Concentration Constant at 1000 ppm.

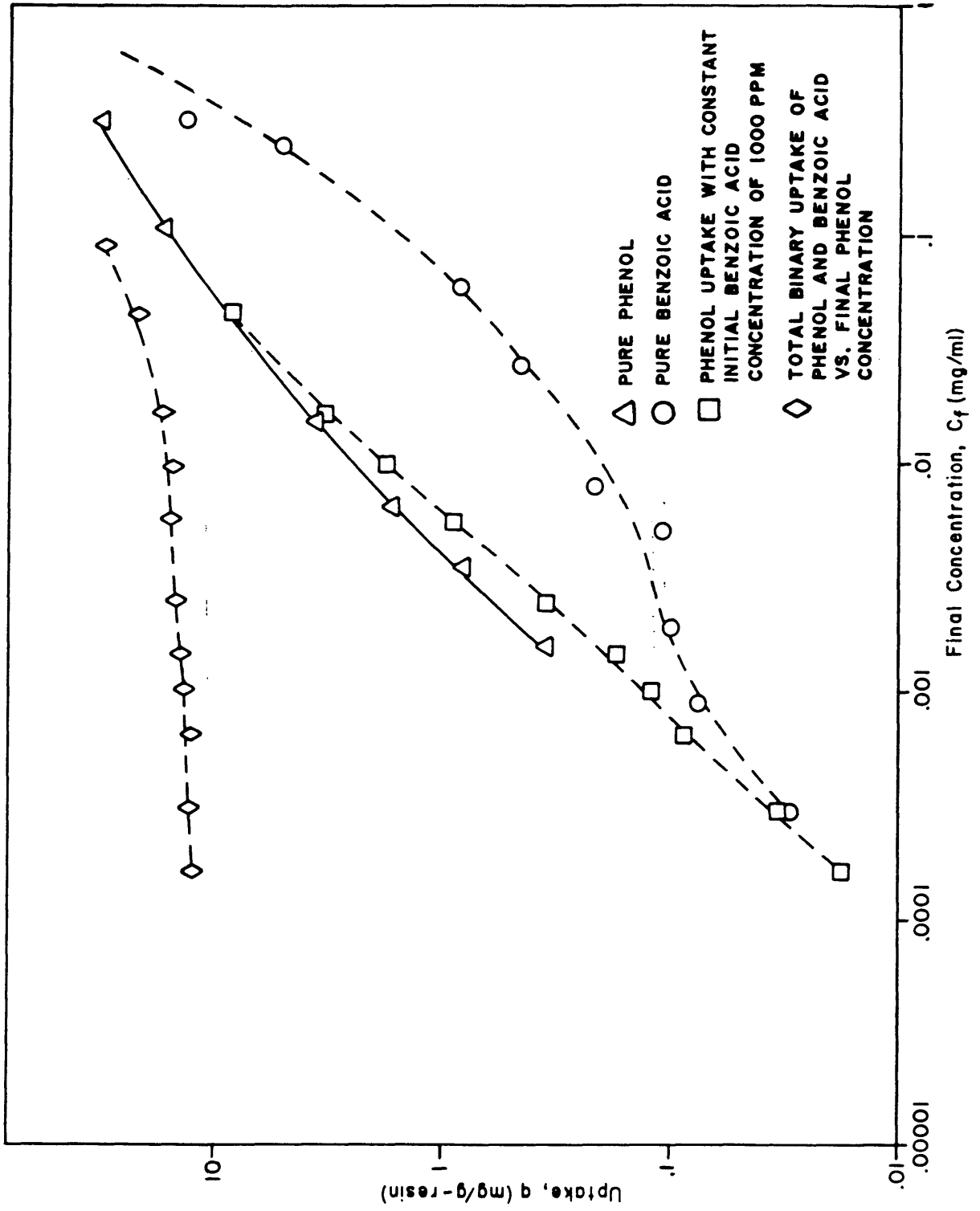
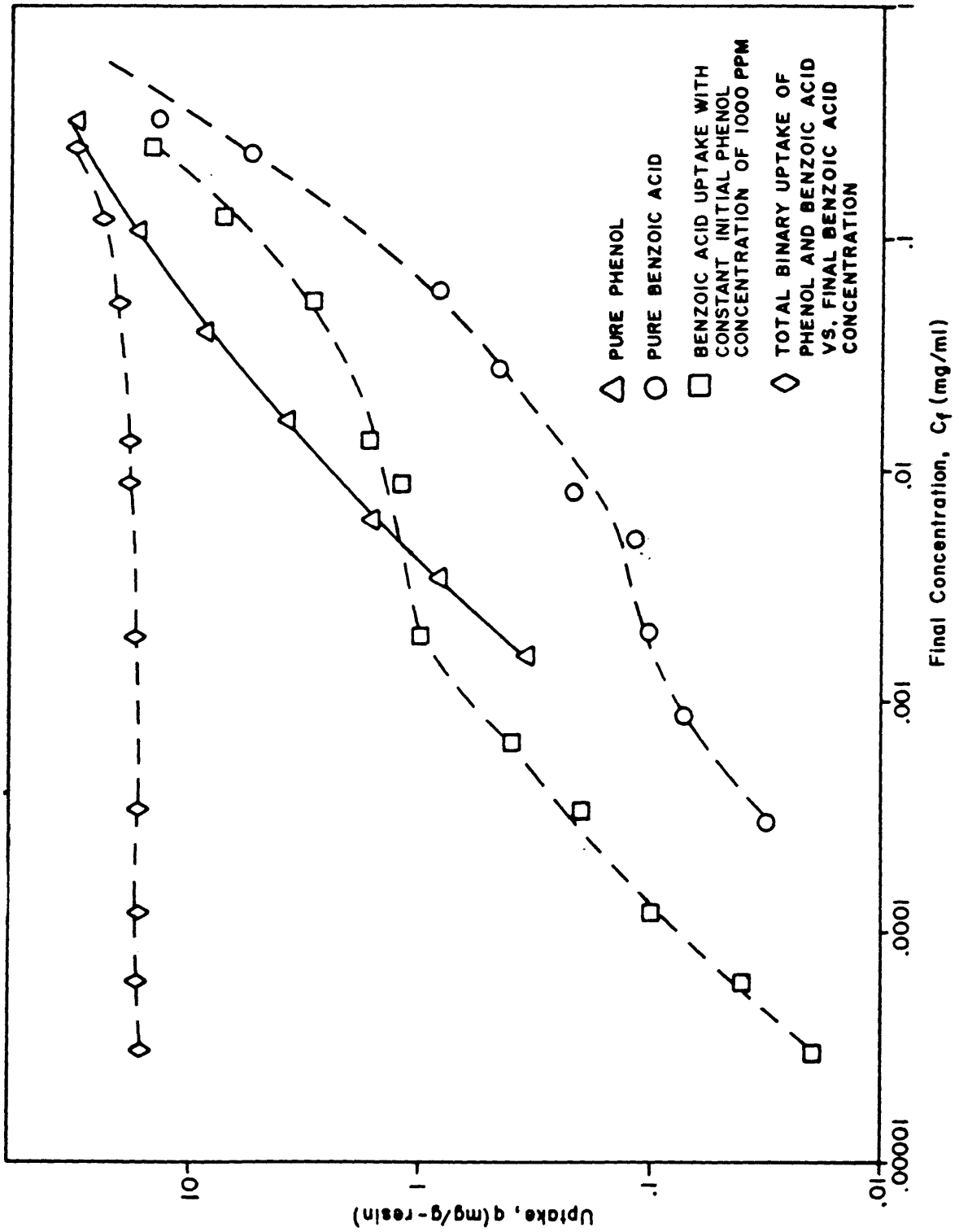


Table 8

Binary Adsorption of Phenol and Benzoic Acid on
Amberlite XAD-8 at 25.°C with Constant Initial
Phenol Concentration

<u>Initial Phenol Conc. mg/l</u>	<u>Initial Benzoic Acid Conc. mg/l</u>	<u>Final Phenol Conc. mg/ml</u>	<u>Final Benzoic Acid Conc. mg/ml</u>	<u>Uptake of Phenol mg/g- resin</u>	<u>Uptake of Benzoic Acid mg/g- resin</u>
1000.1	1007.8	.08977	.24225	17.31074	14.63279
1000.1	500.3	.09776	.12216	17.14792	7.18040
1000.1	205.0	.08752	.05354	17.34489	2.89035
1000.1	101.1	.12404	.01327	16.64607	1.67029
1000.1	71.4	.10957	.00893	16.91564	1.21158
1000.1	52.4	.14884	.00188	16.17036	.99780
1000.1	21.0	.21966	.00066	14.82827	.40172
1000.1	10.5	.12298	.00033	16.66702	.20073
1000.1	7.3	.13097	.00051	16.50728	.13465
1000.1	5.2	.11864	.00012	16.74336	.10028
1000.1	2.1	.12981	.00006	16.54171	.04071
1000.1	1.1	.14962	.00003	16.15787	.02026

Figure 10. Binary Adsorption of Benzoic Acid and Phenol on Amberlite XAD-8 Initial Phenol Concentration Constant at 1000 ppm.



DISCUSSION OF RESULTS

It is evident from the enhancement of benzoic acid adsorption due to the presence of phenol and from the surface coverage calculations that multilayer adsorption may be taking place in both the pure component adsorption and the binary adsorption. In multilayer adsorption, the solute molecules adsorb onto the most energetic sites until the resin surface is saturated (saturation does not necessarily mean 100 percent surface coverage). At this point, the energetics may be such that the solute molecules may begin to adsorb onto already adsorbed molecules instead of onto the remaining resin surface. This phenomenon may result because of a non-homogeneous resin surface with sites of varying adsorptive activity or because of the interaction between molecules on adjacent sites. The flattening of the kinetic data between 40 and 65 hours of contact time could represent the stage at which the surface area of the resin is saturated with phenol molecules.

In order to predict binary adsorption behavior from pure component data, the pure component data must be consistent

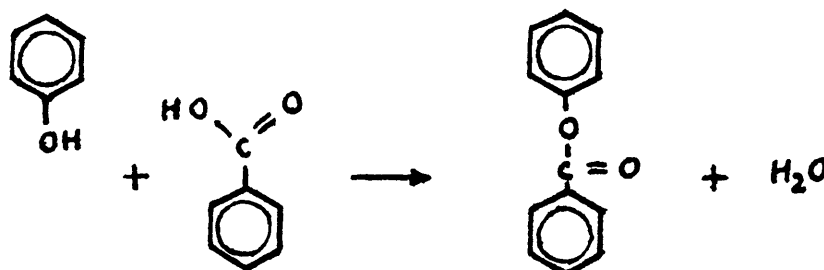
within each component and also with the binary data. This consistency arises from the prediction model that is proposed. The Gibbs equation for adsorption has been useful as a prediction model for binary adsorption in some systems comprised of similar gases or ideal liquids. Kidnay and Myers (1969) state that if a plot of the spreading pressures of the pure components lie along the same curve, then the data shows thermodynamic consistency. The spreading pressure plot of phenol is concave upward whereas, the spreading pressure plot of benzoic acid is concave downward. These curves will not lie along the same curve no matter how the axis of the plots are changed. This system then, does not show thermodynamic consistency by this method.

The fact that the benzoic acid adsorption shows enhancement when the phenol is present indicates that there is more than physical adsorption taking place. No present prediction model that is based purely on physical adsorption may be used to predict binary behavior if enhancement occurs.

The heat of adsorption can vary throughout an adsorption process. The first, most active sites are filled and then the less energetic sites fill up. This is generally accompanied with decreasing heats of adsorption. In multilayer adsorption, however, the higher binding energy of solute molecules adsorbed onto other layers may increase as more surface coverage occurs so that the net result is that

the heats of adsorption may be relatively constant throughout the loading range. When an adsorption process is governed by physical processes such as dipole forces and Van der Waals forces (whether monolayer or multilayer) the heat of adsorption is often close to the heat of condensation in value.

The enhancement may be caused by a reaction between the phenol and benzoic acid to form phenylbenzoate, which precipitates out of solution by crystallizing on the resin. The enhancement might also be explained by a lowering of the dielectric constant of the water due to the presence of the less acidic phenol molecules so that the water is effectively less polar and does not hold the benzoic acid in solution as strongly. The reaction forming the ester is as follows:



This reaction proceeds readily in an aqueous medium at ambient conditions (Bader and Kortowicz, 1953). The ester formed is insoluble in an aqueous medium and may precipitate using the resin as a seed and crystallizing around it. This would give the affect of more material being adsorbed. Since the hydrophobic end of the phenol molecule is adsorbed with the hydrophilic end protruding unattached into the aqueous

phase (Paleos, 1969), it is also possible that the ester is formed on the resin surface after adsorption of phenol. The resin was extracted with methanol, the extract was then concentrated, and presence of the ester was tested for by using thin layer chromatography. The ester was not found by this method.

CONCLUSIONS

The adsorption of phenol and benzoic acid, both as pure components and as a binary, onto Amberlite XAD-8 has been successfully studied. The standard addition method of using radiolabeled solutes in determining concentration changes proved to be successful and allows greater sensitivity in the dilute concentration range than other methods of analysis.

Adsorption has shown to be a good method of secondary cleanup for oil shale retort water. The amberlite XAD-8 resin adsorbs large organic molecules from both polar and organic solvents, and would be useful in retort water cleanup.

The presence of phenol enhances the adsorption of benzoic acid, possibly due to dipole-dipole interactions between the solute molecules. This enhancement benefits the adsorption process and thus the waste water cleanup.

APPENDIX 1

Adsorption Calculations

The calculations involved in getting the adsorption isotherms are computed by a computer program linked to the liquid scintillation counter. Since concentration varies linearly with radioactivity, the final concentration after equilibrium may be calculated as follows:

$$C_f = C_i \left(\frac{\text{cpm}_f}{\text{cpm}_i} \right)$$

where C_f = final concentration, mg/ml

C_i = initial concentration, mg/ml

cpm_f = final solution activity, cpm

cpm_i = initial solution activity, cpm.

By knowing the amount of resin used in the experiment and the volume of solution, the equilibrium uptake may be calculated by:

$$q = \frac{(C_i - C_f) V_s}{r}$$

where q = equilibrium uptake, mg/g-resin

C_i = initial concentration, mg/ml

C_f = final concentration, mg/ml

V_s = solution volume, ml

r = amount of resin used, g.

For Phenol at 25.°C

$$C_i = 9984.5 \text{ ppm} \qquad \text{cpm}_i = 27954$$

$$r = \text{g-resin} = 4.998 \qquad \text{cpm}_f = 10279$$

$$V_s = 95 \text{ ml}$$

$$C_i = 9984.5 \text{ ppm} \left(\frac{\text{mg/l}}{\text{ppm}} \right) \left(\frac{1}{1,000\text{ml}} \right) = 9.9845 \text{ mg/ml}$$

$$C_f = 9.9456 \left(\frac{10,279}{27,954} \right) = 3.6714 \text{ mg/ml}$$

$$q = \frac{(9.9845 - 3.6714)(95)}{4.9998} = 119.954 \text{ mg/g-resin.}$$

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APPENDIX 2

Spreading pressure calculations

Calculation of the spreading pressure is given by:

$$\frac{\pi A}{RT} = \int_0^{p^\circ} \frac{n}{P} dP$$

where

π = spreading pressure

A = specific surface area of adsorbant

R = gas constant

T = absolute temperature

P° = equilibrium pressure for pure i

n = uptake

n° = equilibrium uptake

P = total system pressure.

Because a great deal of dilute region data is needed for this calculation to be accurate, Kidnay and Myers suggest a change in the independent variable from P to n , giving:

$$\frac{\pi A}{RT} = \int_0^{n^\circ} \frac{d \log P}{d \log n} dn$$

The spreading pressure may then be found as a function of the uptake for a pure component by plotting $d \log P / d \log n$

(slope of the adsorption isotherm) versus the uptake and then graphically integrating to get the spreading pressure.

From Figure 2

$$\frac{d \log P}{d \log n} = \frac{d \ln C}{d \ln q} = 1.28$$

for $q = 10$, 25°C

This data is plotted in Figure 4 which is integrated to get:

$$\frac{A\pi}{RT} = \int_0^{10} \frac{d \ln C}{d \ln q} dq = 11.5$$

APPENDIX 3

In Radke's work on the adsorption of propionitrile, 2-propanol, acetone, p-cresol, and p-chlorophenol onto Filtrasorb 300 (Radke and Prausnitz, 1972), he suggests using the following isotherm model to fit his data:

$$\frac{1}{q} = \frac{1}{aC_f} + \frac{1}{bC_f^\beta}$$

where

q = uptake (mg/g-resin)

C_f = final solute concentration

a, b, β = parameters

and where β is constrained to be less than unity.

At low concentrations this model reduces to Henry's law for adsorption. At higher concentrations, the model takes the form of the Freundlich adsorption model. In the special case that β is zero, the model takes the form of the Langmuir adsorption model. Radke's data fits to within 1 percent error of his model.

The parameters in the Radke model may be found by a POWELL algorithm which minimizes functions by conjugate directions. The parameters used in fitting the phenol adsorption data are:

<u>Temp (°C)</u>	<u>a</u>	<u>b</u>	<u>β</u>
0.	.5388	.3935	.3907
25.	.3324	.3015	.4152
70.	.0599	.7005	.6246

APPENDIX 4

Separation Factor Calculations

The separation factor as defined by King is:

$$\alpha_{ij}^S = \frac{X_{ij}/X_{j1}}{X_{i2}/X_{j2}}$$

where $i, j =$ different components
 $X =$ mole, weight, or mass fraction
 $1, 2 =$ products or phases.

If $\alpha_{ij}^S > 1$ component i tends to concentrate in product 1 more than in product 2. The more removed from unity the separation factor is, the better the separation is.

$$\alpha_{BP} = \frac{X_{BA}/X_{PA}}{X_{BL}/X_{PL}}$$

B = benzoic acid

P = phenol

A = adsorbed phase

L = liquid phase

for phenol = 1000 ppm = constant initial concentration

benzoic acid = 1000 ppm

from Table 8

$$\alpha_{BP} = \frac{14.63/17.31}{.2423/.0898} = .313$$

$$\alpha_{PB} = 1/ BP$$

$$\alpha_{PB} = 1/ \underline{.313} = 3.19$$

APPENDIX 5

Error Analysis

An estimate of the random errors associated with the measurement and calculation of the final solute concentration and the uptake can be made from an estimate of the errors involved in the individual parameters. Uncertainties in the measurement of experimental variables are given below:

<u>Experimental Variable</u>	<u>Uncertainty</u>
Weight of solute, w	$\pm .00002$ g
Solution Volume, V_s	$\pm .08$ ml
Final solution activity, cpm_f	$\pm .7\%$ cpm
Initial solution activity, cpm_i	$\pm .7\%$ cpm
Amount of resin, r	$\pm .00005$ g

The final concentration was calculated using the following equation =

$$C_f = \frac{w}{V_s} \left(\frac{\text{cpm}_f}{\text{cpm}_i} \right) \quad (\text{A})$$

Differentiating this equation gives:

$$dC_f = \frac{dw}{V_s} \left(\frac{\text{cpm}_f}{\text{cpm}_i} \right) - \frac{w}{V_s^2} dV_s \left(\frac{\text{cpm}_f}{\text{cpm}_i} \right) + \frac{w}{V_s} \left(\frac{d \text{Cpm}_f}{\text{Cpm}_i} \right) - \frac{w}{V_s} \left(\frac{\text{Cpm}_f}{\text{Cpm}_i^2} \right) d\text{Cpm}_i \quad (\text{B})$$

By representing the derivatives as different values and dividing each term by equation (A) the following is obtained:

$$\frac{\Delta C_f}{C_f} = \frac{\Delta w}{w} + \frac{\Delta V_s}{V_s} + \frac{\Delta \text{cpm}_f}{\text{cpm}_f} + \frac{\Delta \text{cpm}_i}{\text{cpm}_i}$$

The sign on each term has been chosen to yield the maximum error in C_f values. The largest error is at small solute weight. At .100 mg/ml concentration the error is:

$$\frac{\Delta C_f}{C_f} = \frac{.00002}{.01000} + \frac{.08}{100} + .007 + .007 = .0168$$

From this analysis the maximum error due to experimental uncertainty was found to be less than 2 percent at .100 mg/ml concentration. The error was the same for calculation of the uptake.

SELECTED REFERENCES

- Balcomb, K., Colo. Schl.Mines Quarterly, 63 (4), 108 (1968).
- Bader, A.R., and Kontowicz, A.D., Journ. Am. Chem. Soc., 75, 5416 (1953).
- Birks, J.B. Scintillation Counters, McGraw-Hill Co., New York, N.Y. (1953).
- _____, The Theory and Practice of Scintillation Counting, Pergamon Press, New York, NY (1967).
- Burm, B., Personal Communication, EPA Regional Office, Denver, DO (1978).
- Carpenter, H.C., and Sohns, H.W., Colo. Sch. Mines Quarterly, 69 (2), 143 (1974).
- Clarke, C.D., and Armstrong, N.A., Pharm. Jour., Jul. 8, 44 (1972).
- Cook, E.W., Chem. and Ind., (1), 485 (1971).
- Coughlin, R.W., and Tan, R.N., Chem. Eng. Prog. Sym., 64 (90), 207 (1968).
- Crook, E.H., McDonnell, R.P., and McNutty, J.T., Ind. Eng. Chem. Prod. Res. Div., 14 (2), 113 (1975).
- Curran, S.C., Luminescence and the Scintillation Counter, Academic Press, Inc., New York, NY (1953).
- Davankov, A.B., Zvegintseva, G.B., Zubakova, L.B., and Shesterina, N.I., Zhurnal Prikladnoi Khimii, 43 (1), 202 (1970).
- Delaney, R., Colo. Sch. Mines Quarterly, 60(3), 111 (1965).
- Dyer, A., An Introduction to Liquid Scintillation Counting, Heyden & Son, Inc., New York, NY (1974).
- Ely, N., Colo. Sch. Mines Quarterly, 62 (3), 9 (1967).
- Farrier, D.S., Personal communication, L.E.R.C., Laramie, WY, (1977).
- Friederich, R.D., and Mullins, J.C., Ind. Eng. Chem., 11 (4), 439 (1972).
- Fritz, J.S., Ind. Eng. Chem. Prod. Res. Div., 14 (2), 94 (1975).

- Gibbs, R.K., and Himmelblau, D.M., *Ind. Eng. Chem. Fundam.*, 2 (1), 55 (1963).
- Haluska, J.L., and Colver, C.P., *Ind. Eng. Chem. Fundam.*, 10 (4), 610 (1971).
- Horrocks, D.L., Tech. Rep. 1095-NUC-77-1T, Beehman Instruments, Fullerton, CA (1977).
- Hubbard, A.R., *ACS Div. Fuel Chem., Reprints* 16 (1), 21 (1971).
- Iyer, K.P.D., and Wariyar, N.S., *Jour. & Proc. Inst. Chem.*, 38, 221 (1966).
- Jackson, L.P., Poulson, R.E., Spedding, T.J., Phillips, T.E., and Jensen, H.B., Characteristics and Possible Roles of Various Waters Significant to In Situ Oil-Shale Processing, ERDA Pub., L.E.R.C., Laramie, Wy., (1976).
- Junk, G.A., Richard, J.J., Grieser, M.D., Witiak, D., Witiak, J.L., Arguello, M.D., Vick, R., Svec, H.J., Fritz, J.S., and Calder, G.V., *Journ. Chrom.*, 99, 945 (1974).
- Kidnay, A.J., and Myers, A.L., *AIChE Journ.* 12 (5), 981 (1966).
- King, C.J., Separation Processes, McGraw-Hill Co., New York, NY (1971).
- Kipling, J.J., and Wright, E.H.M., *Journ. Col. & Inst. Sci.*, 31 (1), 3382 (1969).
- Kolthoff, I.M., and VanderFoot, E., *Bur Mines Pub.*, 541.183.573: 547.56 (1968).
- Leenheer, J.A., and Huffman, Jr., E.W.D., *Journ. Res., U.S. Geol. Sur.*, 4 (6), 737 (1976).
- Lehninger, A.L., Biochemistry, Worth Publishers, Inc., New York, N.Y. (1975).
- Malcolm, R.L., Thurman, E.M., and Aiken, G.R., A Model for the Prediction of Column Distribution Coefficients for Aqueous Organic Solutes Adsorbed on XAD-8, A Methyl-methacrylate Polymer, USGS, Denver, CO (1977).
- Masel, K.I.T.T.I., *Chem. & Tech. Fuels & Oils*, 10 (5), 401 (1975).
- Mattson, J.S., Mark, Jr. H.B., Malbin, M.D., Weber, Jr., W.J., and Crittenden, J.C., *Journ. Col. & Int. Sci.*, 31 (1), 116 (1969).

- Miller, I., and Freund, J.E., Probability and Statistics for Engineers, Prentice-Hall, Englewood Cliffs, N.Y. (1965).
- Moses, R.J., Colo. Sch. Mines Quarterly, 61 (3), 23 (1966).
- Moriguchi, I., Shizuo, F., and Kaneniwa, N., Chem. Pharm. Bull., 18 (3), 449 (1970).
- Mortimer, R.G., and Clark, N.H., Inc. Eng. Chem. Fundam., 10 (4), 640 (1971).
- Myers, A.L., Ind. Eng. Chem., 60 (5), 45 (1968).
- Myers, A.L., and Prausnitz, J.M., AIChE Journ. 11 (1), 121 (1965).
- Nasipuri, R.N., and Khalil, Saleh A.H., Journ. Pharm. Sci., 63 (11), 1788 (1974).
- Neame, K.D., and Homewood, C.A., Liquid Scintillation Counting, John Wiley & Sons, New York, NY (1974).
- Paleos, J., Journ. Col. Int. Sci., 31 (1), 7 (1969).
- Parkash, S., Fuel Sci. Div., Res. Coun. Alberta, 12, 37 (1974).
- Puri B.R., Bhardwaj, S.S., Kumar, V., and Mahajan, O.P., Journ. Ind. Chem. Soc., 52, Jan. 26 (1975).
- Radke, C.J., "Thermodynamics of Adsorption from Dilute Liquid Solution", Ph.D. Dissertation, Univ. of Calif. at Berkeley (1966).
- Radke, C.J., and Prausnitz, J.M., AIChE Journ. 13 (14), 761 (1972).
- Radke, C.J., and Prausnitz, J.M., Ind. Eng. Chem. Fundam. 11 (4), 445 (1972).
- Reddy, K.A., and Doraiswamy, L.K., Ind. Eng. Chem. Fundam., 6 (1), 77 (1967).
- Rohm and Haas Co., Amberlite XAD Macroreticular Adsorbents, Rohm and Haas Co., Philadelphia, PA (1975).
- Shafroth, S.M., Scintillation Spectroscopy of Gamma Radiation, Gordon & Breach Science Publishers, New York, NY (1967).

- Sharma, S.C., and Fort, Jr., T., Col. & Poly. Sci., 252, 516 (1974).
- Simpson, R.M., The Separation of Organic Chemicals from Water, Rohm and Haas Co., Philadelphia, PA (1972).
- Singh, D.D., Ind. Journ. Chem., 9, De., 1369 (1971).
- Sircar, S., and Myers, A.L., AIChE Journ. 17 (1), 186 (1971).
- Sircar, S., and Myers, A.L., Journ. Phys. Chem., 74 (14), 2828 (1970).
- Sircar, S., Novosad, J., and Myers, A.L., Ind. Eng. Chem. Fundam., 11 (2), 249 (1972).
- Snoeyink, V.L., Weber, Jr., W.J., and Mark, Jr., H.B., Envir. Sci. & Tech., 3 (10), 918 (1969).
- Sparks, F.L., Colo. Sch. Mines Quarterly, 69 (2), 93 (1974).
- Umeyama, H., Nagai, T., and Nogami, H., Chem. Pharm. Bull., 19 (8), 1714 (1971).
- Umeyama, H., Nagai, T., Nogami, H., Chem. Pharm. Bull., 19 (8), 1412 (1971).
- Wiedenhof, N., and Trieling, R.G., Die. Starke, Jan., (4), 129 (1971).
- Zogorski, J.S., and Faust, S.D., Chem. Eng. Prog., 73 (5), 65 (1977).