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ADSORPTION OF PHENOL AND BENZOIC ACID FROM DILUTE AQUEOUS SOLUTION ONTO A MACRORETICULAR RESIN

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Adsorption of Phenol and Benzoic Acid from Dilute Aqueous Solution onto a Macroreticular Resin

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Radiolabeled solutes were used to obtain equilibrium adsorption data for the uptake of benzoic acid and phenol by a macroreticular resin (Amberlite XAD-8) from dilute aqueous solutions. Phenol was studied at 0, 25, and 70°C, and benzoic acid was studied at 25°C. The phenol data, which covered a wide concentration range, was modeled with less than 5% error using a three parameter adsorption equation.

INTRODUCTION

The use of solid adsorbents as a medium for removing trace quantities of organics from waste water has received increased interest because of more demanding environmental restrictions that limit organic concentrations in effluent streams. One area of particular interest is the removal of organics from waters produced when processing fossil fuels. Although it is recognized that various adsorbents can be used to remove a number of organic materials, few systematic adsorption studies over wide concentration ranges have been undertaken; the possible exception is activated carbon. The absence of accurate adsorption data is particularly evident for very dilute aqueous solutions and may be attributed primarily to a lack of analytical sensitivity. Analytical sensitivity can, however, be improved by the use of radioactive tracer techniques with an expected 10^3-10^6 increase in sensitivity over conventional spectroscopic or chromatographic quantitation methods (1). The use of radiolabeled materials and attendant radioanalytical techniques not only supports and augments classical quantification methods but, moreover, contributes a new dimension of experimental possibilities not otherwise attainable with classical methods. An example of this is the increased accuracy of quantifying concentration changes afforded by judicious employment of radiotracer methods. Radiotracer methods are utilized in this work to study the adsorption of benzoic acid and phenol on a macroreticular resin (Rohm and Haas XAD-8) from water.

EXPERIMENTAL

The radioanalytical approach used in these adsorption experiments involved the addition of a small mass of high specific activity radioactive solute to each of the stock solutions of solute made up at varying concentrations. This imparted a uniform and high solute specific activity to each of the stock solutions with negligible change to the final solute concentration. This method provides an equally sensitive and accurate radioanalysis for determining solute concentrations at both high and low levels.

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The net result is that the overall statistical variance and accuracy of the results obtained are the same over the entire concentration range.

Stock solutions with known concentrations of either phenol or benzoic acid were prepared containing a negligible mass of high specific activity radioactive solute. Both solutes were found to have a radiochemical purity greater than 99%. A measured volume of the stock solution was then added to a fixed weight of XAD-8 resin which had been cleaned by exhaustive extraction according to the procedure of Junk *et al.* (2). The slurry was then placed in a constant temperature shaker bath for 144 hr to attain equilibrium. A kinetic study revealed that true equilibrium was reached after 44 hr for benzoic acid and after 104 hr for phenol. After equilibration, the resin was allowed to settle and a supernatant sample was collected and filtered.

Each aqueous sample was radioassayed in triplicate according to the following procedure. Aliquots (1 ml) of the aqueous sample were transferred to glass scintillation vials and admixed with 12 ml of Dimilume-30 (Packard Instrument Company). 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% or less was achieved. Random coincidence monitoring was used to insure that the contribution of counting events not due to radioactivity disintegrations, e.g., chemiluminescence, was less than 0.1%. The counting efficiency was determined for each sample and was used to compute the absolute activity as disintegrations per minute (DPM). 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 was obtained 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 corrected by subtraction of background count rate.

Each scintillation sample was counted twice according to the above procedure and the average DPM result computed. Since each aqueous sample was split for triplicate radioassay, a total of six counts 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%.

RESULTS AND DISCUSSION

Benzoic acid was adsorbed onto the XAD-8 resin at 25°C and the resulting isotherm is shown in Fig. 1. As noted by the figure, the final concentrations ranged over three orders of magnitude and included values from 0.4948 to 0.0003 mg/ml. The uptakes of the resin corresponding to the above final concentrations are 28.904 and 0.032 mg/g resin. The isotherm does not appear to tend to an upper limit in the uptake. The sigmoidal shape of the isotherm with the relatively well-defined knee suggests that multilayer adsorption is occurring. However, if a surface area of 45 Å^2 is assumed for the benzoic acid molecule, the highest surface coverage is only 43%. On this basis, the knee of the isotherm could be attributed to the initiation of a multilayer prior to complete surface coverage of the resin. Alternatively, if the knee of the isotherm does represent the formation of a complete monolayer, then the surface area occupied by a single molecule would be much greater than the above value. The arrangement of the benzoic acid molecule with the plane of the benzene ring and the carboxyl group parallel to the surface

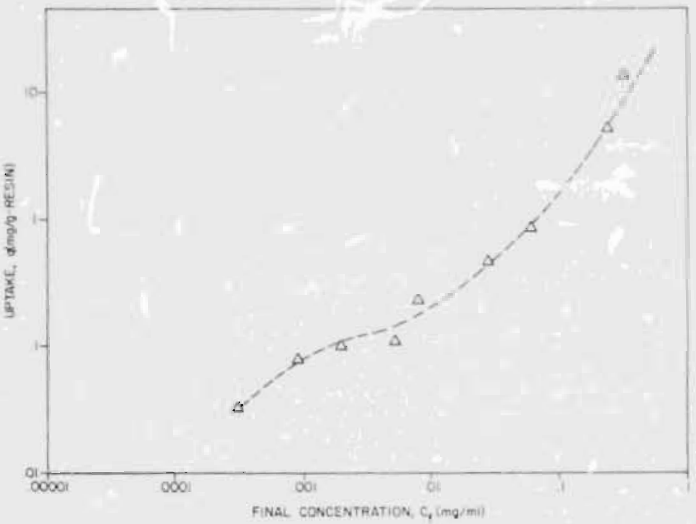

FIG. 1. Equilibrium uptake of benzoic acid on Amberlite XAD-8 at 25°C.

of the adsorbent would require a larger surface area per molecule.

Phenol adsorption isotherms were obtained at 0, 25, and 70°C and are presented in Fig. 2. The isotherms were curve fitted with the three parameter adsorption isotherm model used by Radke and Prausnitz (3) with less than 5% error over the entire concentration range. Their equation is expressed as follows

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

where

q = uptake (mg/g resin),
C_f = final solute concentration (mg/ml),
a, b, β = parameters of the equation to be determined numerically,

and where β is constrained to be less than unity. The parameters in the model of

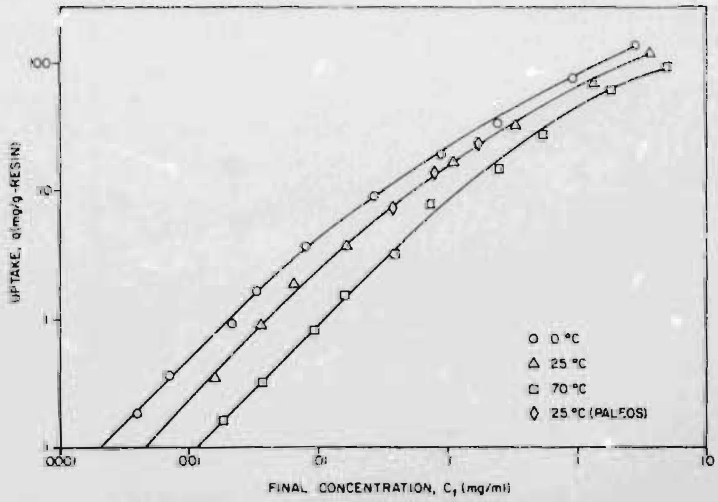

FIG. 2. Equilibrium uptake of phenol on Amberlite XAD-8 at 0, 25, and 70°C.

TABLE I

Curve Fit Parameters for Phenol Adsorption Isotherms

Temperature (°C)	a	b	β
0.	0.5388	0.3935	0.3907
25.	0.3324	0.3015	0.4152
70.	0.0599	0.7005	0.6246

Radke and Prausnitz were found by an algorithm which minimized functions by conjugate directions. The parameters used in fitting the phenol absorption data are given in Table I.

As noted the equilibrium concentrations ranged over four orders of magnitude. Based on a surface area per phenol molecule of 28 Å^2 (5), the maximum uptake of phenol at 25°C corresponds to a surface coverage of the resin of 144%. As noted in Fig. 2, the phenol adsorption data obtained at 25°C by Paleos (4) is in excellent agreement with this study.

Using these isotherms, values for the heat of adsorption were calculated at constant loading from the relationship

$$\frac{\Delta H_s}{R} = -\left[\frac{\partial(\ln C_f)}{\partial(1/T)}\right]_q . \qquad [2]$$

Typical isosteres are shown in Fig. 3. Heats of adsorption calculated over a loading range varying from 0.12% to 120% surface coverage were found to be relatively constant at the value 11.9 Kcal/mole. This compares closely with the heat of condensation, 11.3 Kcal/mole.

The isothermal differential heat of adsorption at the standard state (25°C) can be derived from the Gibbs free energy of adsorption and is given as

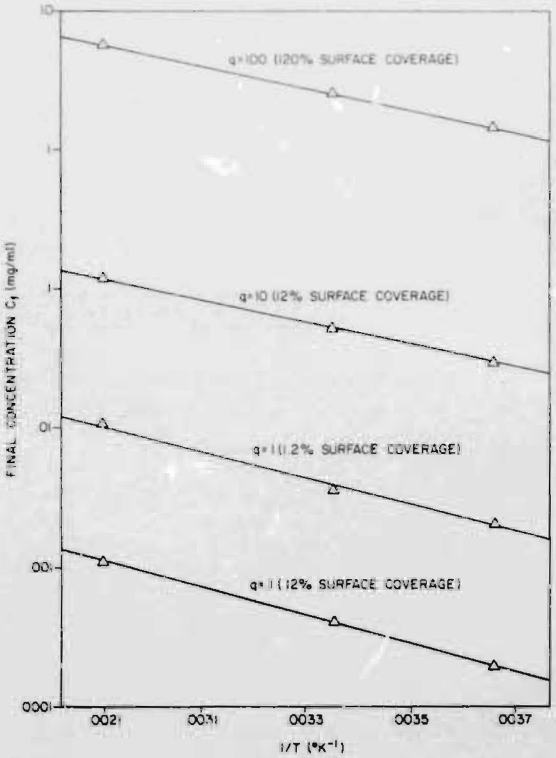

FIG. 3. Heats of adsorption of phenol on Amberlite XAD-8.

$$\Delta H^0 = \Delta G^0 - T(\partial \Delta G^0/\partial T)_c. \quad [3]$$

The standard state of the solute in both the bulk phase and at the interface was taken to be an ideal solution with a concentration of one mole per liter. The standard state change in free energy was calculated from the following equation:

$$\Delta G^0 = -RT \ln (C_s/C_f). \quad [4]$$

where C_s is the concentration on the surface and C_f is the final fluid concentration. An interfacial thickness of 5 Å was used to calculate C_s. The value of C_s/C_f was determined from the slope of the initial part of the adsorption isotherms. The results at 25°C were $\Delta G^0 = -0.53$ Kcal/mole and $\Delta H^0 = -2.88$ Kcal/mole. These small numbers indicate very weak interaction at the surface.

From a comparison of this work with that of Singh (5), it was found that on the basis of surface area, XAD-8 had a much greater adsorption capacity than either Spheron-6 or Graphon (Cabot Corporation of Boston, Mass.). At the maximum phenol concentration studied in this work, the equilibrium uptake of XAD-8 was 8.9×10^{-6} moles/m², whereas for Spheron-6 and Graphon the equilibrium adsorption capacities were 2.1×10^{-6} and 3.2×10^{-6} moles/m², respectively. At 35°C Puri *et al.* (6) found the adsorption capacities of Spheron-6 and Graphon to be 0.1×10^{-6} and 0.32×10^{-6} moles/m², respectively, for an equilibrium concentration of 3.4×10^{-3} moles/liter. This compares to a value of about 2.0×10^{-6} moles/m² for XAD-8.

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