



Project Summary

Predicting Preferential Adsorption of Organics by Activated Carbon

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Preferential adsorption of organic compounds from dilute aqueous solutions onto activated carbon (AC) was studied to develop a comprehensive theoretical basis for predicting adsorption of multicomponent solutes. The research program investigates why some solutes are strong adsorbers, and others weak, and why some solutes displace others during aqueous phase adsorption. The overall objectives were to develop, test, and simplify the theoretical basis for prediction.

The fundamental, multidimensional approach of the solvophobic thermodynamics theory was used to correlate the extent of adsorption for the comprehensive theory with the overall standard free energy change for the association adsorption reaction in solution, and for the simplified theory with the cavity surface area of the solute.

Experimental adsorption isotherms of two homologous series (alkyl phenols and alkyl alcohols) were measured and used to test the theory. Differences resulting from simple structural modifications of solutes were predicted theoretically and confirmed experimentally. Several experimental innovations for equilibrium adsorption studies have been introduced to reduce solute loss by extraneous adsorption and vaporization.

Small negative activation energies for intraparticle pore and surface diffusion of alkyl phenols were also calculated from a temperature study.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see

Project Report ordering information at back).

Background

The ability to predict the effects of even simple structural modifications on the adsorption of organic molecules from dilute aqueous solutions onto AC (or other adsorbents) could be of great value in the design and operation of large-scale commercial water and wastewater treatment plants. Structural modifications such as those found between isomers of the same homologous series are well known to make the difference between benign and toxic compounds. At present, most theoretical approaches either rely on single-solute isotherms originally derived from gas and vapor phase systems to predict mixed-solute isotherms, or they rely on solubility theory. Although Traube and others more than 90 years ago recognized the need to include the solvent interactions, only recently have attempts to quantize these effects been made.

Recent attempts to include the solvent effect in aqueous-phase adsorption include a semi-empirical approach based on partial solubility parameters and some arbitrarily chosen parameters called the net adsorption energy approach. Another approach called the "thick compressed film theory" (or "Polanyi adsorption potential theory," as it is often called) has been used to describe adsorption isotherm behavior. The problem with this three-dimensional adsorbed film model is the difficulty in defining the properties of the film and the need to use "scaling factors" for constructing the so-called characteristic equation.

Objectives

The objectives of this study were:

1. Develop a comprehensive formalism of dilute aqueous-phase adsorption

of organics, including fundamental formulations of all dominant interactions between solute, solvent, and sorbent;

2. Test the use of this formalism to predict a ranking order of adsorption capacity of members of two homologous series;
3. Measure experimentally the equilibrium adsorption isotherms at constant pH and temperature for a statistically significant number of members of two homologous series;
4. Propose and apply certain simplifying assumptions to the comprehensive model that would result, for special cases, in a simplified analytical expression;
5. Compare correlations of adsorption capacity from the comprehensive and simplified theories with those obtained with other independent variables such as the molecular weight, density, index of refraction, molar volume, molar refraction, octanol-water partition coefficient, parachor, and polarizability; and
6. Examine the possibilities of using the derived theory for predicting multicomponent adsorption.

Objective 1 is fundamental to the other objectives. The theoretical formalisms developed during this study were tested both with experimental data obtained from the literature and that suggested in Objective 3. Objective 4 is crucial to the practicability and usefulness of the suggested approach. Objectives 5 and 6 were included because the usefulness of the theory will eventually depend on its ability to rank-order the adsorption of solutes with better predictability (i.e., higher linear coefficients of correlation) than other independent variables, and from multicomponent systems, respectively.

Materials and Methods

Crushed granular activated carbon (PAC) (U.S. Sieve Series No. 200 to No. 400 range and 1031 m²/g) was the major adsorbent used in this study. Comparison of adsorption isotherms of five alkyl phenols on granular activated carbon and on graphitized carbon (89 m²/g) was undertaken. Cleaning procedures of the PAC were an important aspect in obtaining reproducible isotherms.

The adsorbates used included two homologous series of 19 alkyl phenols and 12 aliphatic alcohols all of the highest grade available (>99% purity). Stock solutions of the individual compounds were made up with 0.01M phosphate buffer and stored in covered bottles at pH = 7.0. From

a practical viewpoint, both homologous series are commonly found in surface wastewaters, i.e., alkyl phenols are widely found in coal-conversion process wastewaters and alcohols are found in industrial effluents because of their wide use as solvents and reactants. To minimize extraneous solute-loss and maximize solute/sorbent contact, several innovations have been introduced into the adsorption isotherm procedures in an attempt to improve reproducibility and accuracy and to reduce solute losses.

Thus, completely filled and capped stainless steel tubes containing the adsorbate/adsorbent mixture were rotated 360° end-over-end at 2 rpm for 24 hours at 20 ± 0.5°C. The tubes were then ultracentrifuged at 20,000 rpm for 20 to 30 min at 20°C, thereby spinning down the carbon. The tubes were then opened, and the supernatant was analyzed directly.

Theoretical

General Solvophobic Approach

The solvophobic ($c\phi$) theory describes the tendency of a surrounding solvent medium to influence aggregation or dissociation of those molecules with considerable microsurface areas exposed to the solvent medium.

In the solvophobic treatment, adsorption is considered as a reversible reaction between the adsorbate molecules, S_i , and the activated carbon, C , to form the adsorbed complex, S_iC , at the surface of the carbon, $S_i + C \rightleftharpoons S_iC$. The effect of the solvent on this reaction is obtained by subtracting the standard free energy change for the reaction in the gas phase from that in the presence of the solvent (taking as standard states $X_k \equiv 1$, $p_k \equiv 1$ atmosphere ideal gas). This process results in a net free energy change; $\Delta G_{(\text{solvent effect})}^{\text{net}}$, expressing the effect of the solvent on the association adsorption reaction.

Conceptually, Sinanoglu proposed a two-step dissolution process. First, a hole or cavity needs to be prepared in the solvent to accommodate the solute, carbon, or adsorbed complex "molecule." Second, after the "molecule" is placed into the cavity, it interacts with the solvent. Quantitatively this process is expressed as follows:

$$\begin{aligned} \Delta G_{(\text{solvent effect})}^{\text{net}} = & \\ \Delta G_{(\text{solvent})}^{\text{assoc}} - \Delta G_{(\text{gas})}^{\text{assoc}} = & \\ RT \ln \left[\frac{H_{S_iC}}{k_{S_iC} H_{S_i} H_C} \right] & \quad (1) \end{aligned}$$

or

$$\begin{aligned} \Delta G_{(\text{solvent effect})}^{\text{net}} = & \\ \Delta G_{i,S_iC}^{\text{net}} - \Delta G_{i,S_i}^{\text{net}} - \Delta G_{i,C}^{\text{net}} & \quad (2) \end{aligned}$$

where $k_k^H = p_k/X_k$ is the Henry's constant for the k^{th} species, and j represents each type of interaction such as the cavity, van der Waal's, and electrostatic terms plus two correction terms for polymer mixing and reduced electrostatic effects because of the presence of the solvent, the following expression is obtained from Eq. (1) and (2) for the overall standard free energy change, viz.

$$\begin{aligned} \Delta G_{(\text{solvent})}^{\text{assoc}} - \Delta G_{(\text{gas})}^{\text{assoc}} + & \\ [\Delta G_{\text{cav}} + \Delta G_{\text{vdw}} + \Delta G_{\text{es}} + & \\ \Delta G_{\text{red}}]_{S_iC-S_i-C}^{\text{net}} - RT \ln (RT/P_0V) & \quad (3) \end{aligned}$$

where the last term is called the cratic term and results from an entropy or free volume reduction. $\Delta G_{(\text{solvent})}^{\text{assoc}}$ is related to the experimental equilibrium constant, $K_{\text{solvent},i} \equiv X_{S_iC}/X_{S_i}X_C$, which itself will be related to the experimental adsorption capacity \bar{p}_i for solute S_i later in this analysis. Each term in the square bracket in Eq. (3) can be calculated explicitly from known physiochemical parameters obtained from the literature. Explicit formulae do this and a discussion on the relevance of each term to the adsorption association reaction are presented in Appendix A in the comprehensive report.

For the comprehensive $c\phi$ -model, each of the terms in Eq. (3) is calculated explicitly; for the simplified model, the "thermodynamic microsurface area change of the reaction," ΔA , in the cavity term is assumed to be proportional to the cavity surface area, TSA, of the specific sorbate and homologous series, $\Delta A = g \text{ TSA}$. Thus in this study, $\ln Q^{\circ b}$ is correlated with TSA, where $Q^{\circ b}$ is the initial slope at low solute concentration for the Langmuirian adsorption isotherm. In addition, competitive adsorption as related to surface tension of a multicomponent solution, diffusional kinetics, and a comparison of various isotherm models for use in the Ideal Adsorbed Solution (IAS) theory are all included in the comprehensive report.

Experimental Results

In the comprehensive report, the experimental batch adsorption isotherm results are presented and discussed. After dis-

cussing adsorption sensitivity and the range of solution concentration used, adsorption onto powdered activated carbon (PAC) is compared with adsorption onto graphitized carbon (GC). Kinetic studies are then discussed ipso facto and in connection with the time to reach pseudo-equilibrium and the effects of temperature. Thereafter, both single and multicomponent adsorption results are presented and analyzed with respect to the solvophobic thermodynamic ($c\phi$) approach. Some of these results are presented below.

Kinetic Studies

The time to reach a plateau or pseudo-equilibrium adsorption capacity for phenol, 2-cresol, 2-ethyl phenol, 4-n-propyl phenol, 2-butyl phenol, 2-pentyl phenol, and 2-hexyl phenol is 1, 4, 8, 9, 11, 12, and 14 hours, respectively.

Plots, showing the experimental data points superimposed onto the theoretical curves based on the Freundlich model obtained from Suzuki and Kawazoe, are used to obtain the surface and pore diffusion models.

The results obtained from this procedure are summarized in Table 1; the surface and pore diffusion coefficients for 4-n-propyl phenol are unexplainably too low. The rest of the results follow the expected trend of decreased diffusion rate with increased solute cavity surface area (TSA).

Since $D_e \approx D_b$, the D_e values are within an acceptable range of values, and the D_s values are comparable to previously reported values in the literature. For example, for phenol, Van Vliet et al., using a single parameter approach, report $D_s = 1.24 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ in Filtrasorb 400,* whereas Peel et al., using their branched-pore kinetic model, report $D_s \approx 7.75$ to $9.01 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ for rapid diffusion in the macropores of Filtrasorb 400. 2-Butyl phenol was sorbed onto PAC at four different temperatures, 20 °C, 30 °C, 40 °C, and 50 °C, to determine the effect of temperature on the adsorption dynamics. Both the single parameter surface and pore diffusion models to fit the experimental data, $D_s(t)$ and $D_e(t)$ were obtained and plotted in an Arrhenius plot to obtain the activation energy, E_a . From the plots, E_a values equal to $-2.79 \text{ cal gmole}^{-1}$ and $3.20 \text{ cal gmole}^{-1}$ were obtained for surface and pore diffusion, respectively. Two competing phenomena can be hypothesized; internal diffusion is expected to increase with temperature, while for the exothermic reactions such as adsorption of organics

Table 1. Surface and Pore Diffusion Coefficients Obtained from Adsorption Kinetics

Solute	Molecular weight	Diffusion coefficients, $\times 10^6$		
		Bulk D_b $\text{cm}^2 \text{ sec}^{-1}$	Surface D_s $\text{cm}^2 \text{ sec}^{-1}$	Pore† D_e $\text{cm}^2 \text{ sec}^{-1}$
1. phenol	94.1	9.127	5.26×10^{-4}	8.88
2. 2-cresol	108.2	8.122	4.62×10^{-4}	8.15
3. 4-n-propyl phenol	122.3	7.366	1.28×10^{-4}	2.16
4. 4-ethyl phenol	136.4	6.773	4.36×10^{-4}	8.09
5. 2-butyl phenol	150.2	6.292	3.59×10^{-4}	6.97
6. 2-pentyl phenol	164.3	5.893	3.21×10^{-4}	6.62
7. 2-hexyl phenol	178.4	5.520	2.695×10^{-4}	5.56

onto PAC the reverse is true. The linear plots and the small negative activation energies that result highlight both the competition and the relative importance of the exothermic adsorption reaction.

Single Solute Adsorption

The major experimental effort of this study involved the careful measurement and accumulation of statistically relevant data of single solute aqueous phase adsorption isotherms for two homologous series. The main purpose for doing this is to establish a reliable data base for evaluating the efficacy of the solvophobic thermodynamic treatment in ranking the adsorption intensity of the different members of different homologous series. Homologous series of 19 alkyl phenols and 12 aliphatic alcohols were chosen to represent aromatic and aliphatic organic groups in water, respectively. The adsorption results in terms of $\ln Q^0/b$ versus molecular weight and TSA are summarized in Figs 1 and 2.

One of the major findings shown in Fig 1 is that branched compounds have *lower* adsorbability than linear or normal compounds. For the phenols, however (Fig 2), fragmented compounds (alkyl group distributed around the ring) exhibit *higher* adsorbability. Also above a molecular weight of about 150 D, adsorbability is independent of molecular weight.

Comparison between the goodness-of-fit for correlating adsorbabilities with MW and TSA (i.e., checking the simplified $c\phi$ -model) shows that for 11 alkyl phenols, $r_{mw} = 0.93(7)$ is different from $r_{TSA} = 0.97(5)$ with a confidence of 70%. For all 12 alcohols, $r_{mw} = 0.72$ is different from $r_{TSA} = 0.93$ with a confidence of 95%.

In summary, the adsorption capacity decreases (slope increases) for each isomer of a homologous series with increased branching or decreasing cavity surface area.

By measuring the gas-phase adsorption of the same homologous series of compounds as that measured from the liquid-

phase, $\Delta_{\text{(solvent effect)}}^{\text{net}}$ could be checked. With the study of additional homologous series and the knowledge of the molecular structure and volume of each member, the restriction of adsorption because of steric hinderance, as recently suggested by Benedek (slow adsorption), could be determined. Further work is also necessary to couple the theory to Myers' new characteristic dimensionless adsorption parameter.

With respect to equilibrium adsorption isotherm measurements, the limited data base should be extended to include a comparison of different activated carbons with different pore sizes and surface activities. Adsorption of ionizable homologous groups should also be measured. Competitive adsorption effects should be extended to include additional homologous series. Finally, we recommend that the theory be evaluated for competitive adsorption of some industrial effluent streams, such as coal-based effluents containing many isomers of phenols.

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*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

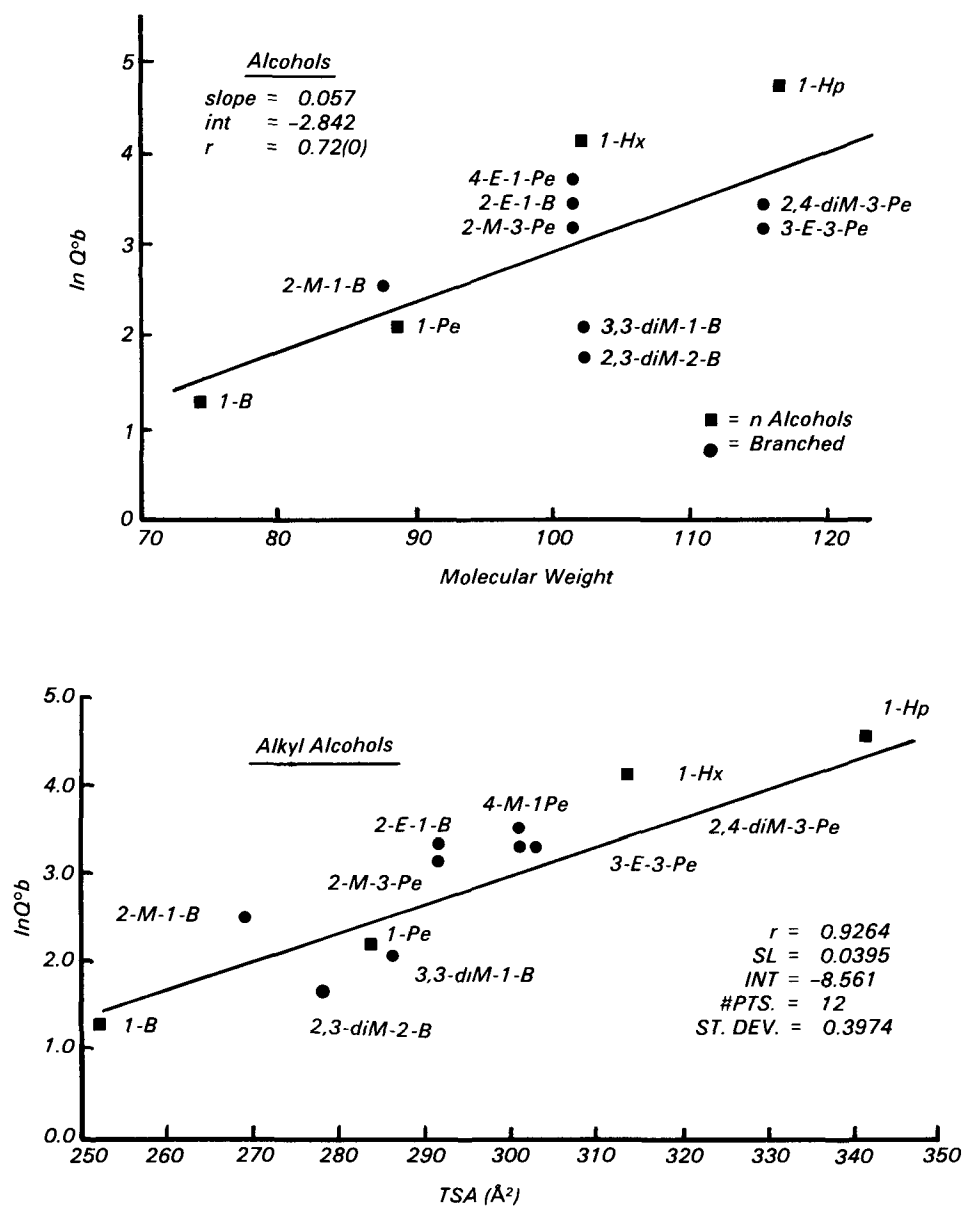


Figure 1. Adsorption ($\ln Q^b$) versus molecular weight (MW) and total cavity surface area (TSA) for linear and nonlinear alkyl alcohols.

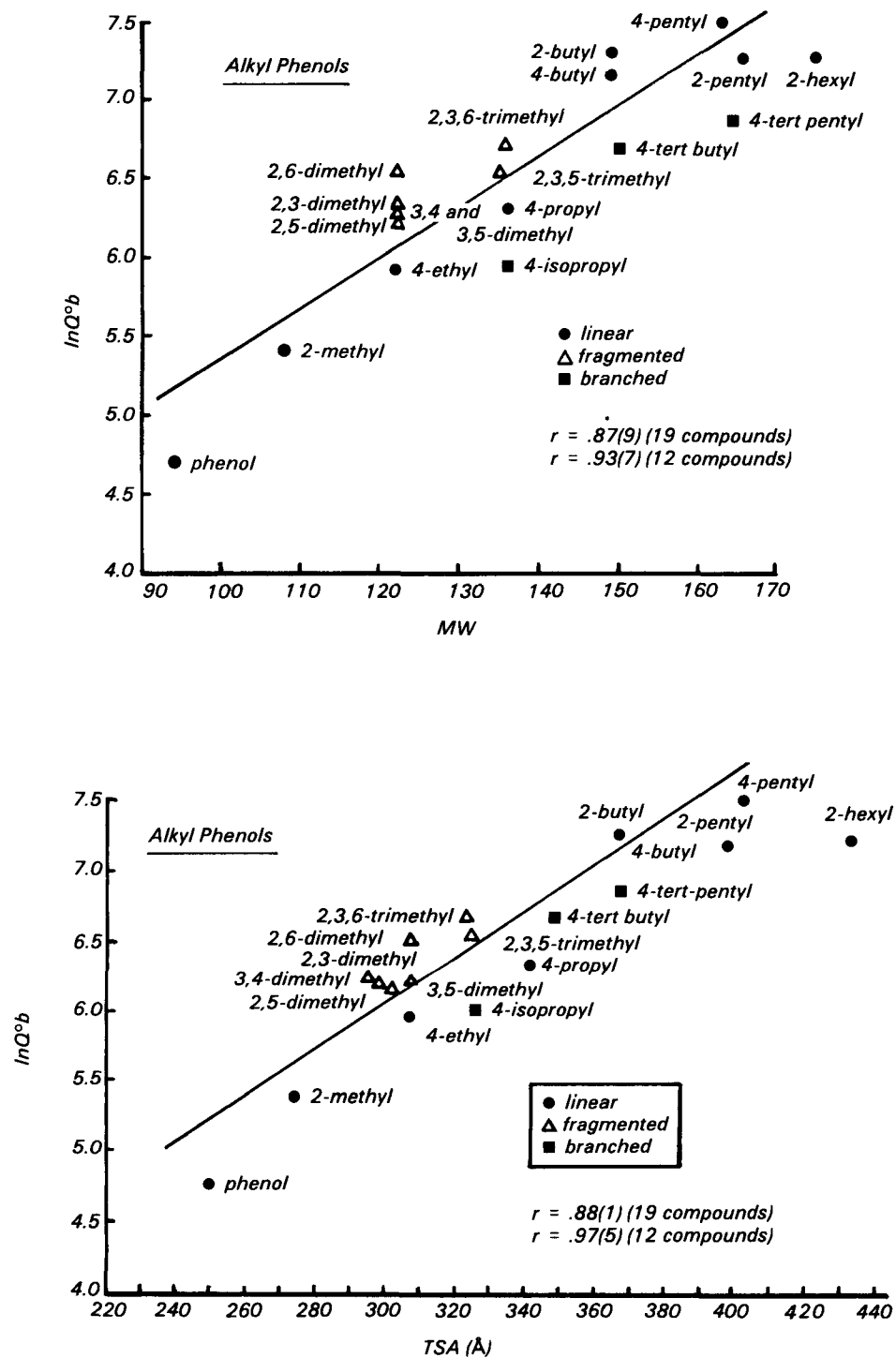


Figure 2. Adsorption ($\ln Q^{\circ b}$) versus molecular weight (MW) and total cavity surface area (TSA) for linear, nonlinear, and fragmented alkyl phenols.

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Richard A. Dobbs is the EPA Project Officer (see below).

The complete report, entitled "Predicting Preferential Adsorption of Organics by Activated Carbon," (Order No. PB 83-222 778; Cost: \$13.00, subject to change) will be available only from:

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