Selective Adsorption of Organic Homologues onto Activated Carbon from Dilute Aqueous Solutions: Solvophobic Interaction Approach

Part IV. Effect of Simple Structural Modifications with Aliphatics

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Preferential adsorption of organic compounds onto activated carbon from dilute aqueous solutions is studied to develop a comprehensive theoretical basis for predicting the adsorption of structurally different isomers for different homologous series. The fundamental multidimensional approach of the solvophobic ($c\phi$) thermodynamic theory is further refined and used to correlate the extent of adsorption for the comprehensive theory with the overall standard net free energy change ($\Delta G^{net}/RT$) for the association-adsorption reaction in solution, and for the simplified theory with the cavity surface area of the solute (*TSA*).

Experimental adsorption isotherms of two homologous series (12 aliphatic alcohols and 21 aliphatic ketones) were measured and used to test and compare the $c\phi$ theory with seven independent parameters characterizing the sorbates. Several experimental innovations for measuring equilibrium adsorption isotherms are introduced to reduce the possible loss of sorbate during the procedure and to provide reproducible and reliable results.

Comparing the coefficients of linear correlation (r), the results for 12 aliphatic alcohols give greater than 99% confidence that the r-values are different for $\Delta G^{net}/RT$ and molecular weight (*MW*). For the 15 aliphatic ketones, greater than 90% confidence interval is obtained for different r-values for *TSA* and *MW*.

These results support the contention that simple structural modifications of aliphatic homologous compounds can be used to predict the effect of solute-solvent-sorbent interactions on adsorption. The $c\phi$ theory can thus be used to rank-order adsorption intensity of these compounds from the aqueous phase onto activated carbon.

SCOPE

During the past century, little effort has been expended in trying to understand the fundamentals underlying the process of adsorption of solutes from a solvent onto a solid sorbent (Miller, 1980a,b). Several simultaneous developments, such as the need to clean our surface water, the development of extremely sensitive analytical techniques, and the wide use of reverse-phase liquid chromatography, have spurred interest in this field.

Most researchers used a phenomenological approach in which equilibrium adsorption models mostly derived from gas- and vapor-phase adsorption, were used to describe adsorption from the liquid phase. This approach either *a priori* ignored the presence of the solvent, assuming that the dominant interaction was between the solute and sorbent, or included the solvent effect without specifying its role quantitatively.

Freundlich (1926), in his classic monograph, describes the first attempts 90 years ago by Traube and others to include the solvent-solute interaction effect through interfacial tension at the solid-liquid interface. Although Defay et al. (1966) updated this approach with a major emphasis on the simplified Gibbs adsorption model, especially under nonequilibrium conditions, a comprehensive interaction theory among solute, solvent, and sorbent is still lacking. Recent attempts to include the solvent-effect in aqueous phase adsorption include a semiempirical approach based on partial solubility parameters called the net adsorption energy approach (McGuire, et al., 1978; McGuire and Suffet, 1980). Unfortunately, the arbitrary choice of the relative values for the acid and base solubility hydrogen bonding parameters is without theoretical justification and renders this approach somewhat capricious (McGuire and Suffett, 1980). With respect to the "thick compressed film theory" (or "Polanyi adsorption potential theory," as it is often called), the basic problem is that the original physical model of a three-dimensional film has been questioned and rejected by many scientists, including none other than Polanyi himself (McBain, 1932). Associated with this is the problem of defining or measuring the adsorbate density, which is needed for plotting or measuring the characteristic curves (Miller, 1980a; Manes, 1980). However, Manes and coworkers (1980) have effectively used this theory with scaling factors to correlate the adsorption of organic liquids and solids from trace concentrations to saturation and to study competitive adsorption of binary and tertiary solute mixtures.

Belfort (1981b) has shown recently that the Polanyi and ideal adsorbed solution theory based on Gibbs' adsorption isotherm have similar thermodynamic structure. Although these approaches provide useful insight with respect to solute-solvent adsorption onto solids, the need exists for a comprehensive formalism of aqueous-phase adsorption including fundamental formulations of all dominant interactions among solute, solvent and sorbent.

The work reported here involves the development of a comprehensive theoretical basis for predicting the preferential adsorption of organic compounds onto activated carbon from dilute aqueous solutions. A detailed analysis of the effect of the solvent on this process yields an expression for the extent of adsorption with no adjustable constants. Branching, cyclization, and position isomerism are automatically accounted for without introducing additional terms or adjustable constants. In principal, the theory incorporates the variation of a wide span of experimental conditions, including a comparison of the adsorption of similar organic compounds on different activated carbons, and comparison of the adsorption of different organic solutes on the same activated carbon. Under *special conditions* and assumptions, simplified analytical expressions result, allowing the prediction of the extent of adsorption as a function of the simple geometric characteristics of the (hydrocarbonaceous moietie(s) of the solute.

The objective of this study is to test and compare the comprehensive $c\phi$ theory and its simplified version with seven independent molecular descriptors characterizing the solute. An experimental database of the aqueous-phase adsorption of two aliphatic homologous groups is obtained for this purpose.

CONCLUSIONS AND SIGNIFICANCE

The solvophobic ($c\phi$) theory is tested using single-solute aqueous-phase adsorption isotherms of two homologous series. Homologous series of alkyl alcohols and alkyl ketones were chosen to represent different aliphatic groups in water. Correlations with adsorption capacity for both the comprehensive and the simplified $c\phi$ theories are compared with similar correlations for other molecular descriptors, including molecular weight, density, index of refraction, molecular volume, and group contribution parameters such as molar refraction (or polarizability), octanol-water partition coefficients, and parachor. For the 12-member alcohol homologous series, the best correlative parameters were the comprehensive $c\phi$ theory parameter, $\Delta G^{net}/RT[r = 0.94(6)]$, the simplified $c\phi$ theory parameter, TSA $[r= 0.92(6)]$, and the octanol-water partition coefficient, $\log P$ $[r = 0.91(1)]$. All the other parameters had correlation coefficients of less than $r < 0.76$. For the 21-member alkyl ketone homologous series, those higher than C_7 fall off the correlation line and adsorption intensity ($lnQ^{o}b$) becomes independent of size or degree of branching. Below this critical value, however, the hypothesis $r_{MW} = r_{TSA}$ can be rejected with 90% probability for the 15 ketones studied.

As part of developing the comprehensive database to test the theory, a new innovative procedure to measure batch adsorption isotherms was developed. The isotherms were measured at constant temperature and pH, and the procedure obviated the potential solute losses associated with the filtration step.

The ability to predict the effects of even simple structural modifications on the adsorption of organic molecules from dilute aqueous solutions onto activated carbon (or other adsorbents) could be of great value in the design and operation of large-scale commercial water and wastewater treatment plants. This capability would assist in gaining a better understanding of competitive adsorption between, and chromatographic elution by different organic solutes during adsorption.

In addition, the usefulness of the $c\phi$ theory extends beyond that of a purely predictive tool. It can provide a comprehensive framework for considering specific contributions to aqueous-phase adsorption, leading to an improved understanding of the entire process. Besides the theoretical analysis, the comprehensive experimental results are self-consistent and can be used as a database for any future model development. Also, the molecular area and volume results, as calculated by the molecular build program, are available *ipso facto* for future use.

As a result of this study, it can be concluded that the solvent plays an important if not dominant role in the adsorption of organics from aqueous solution onto activated carbon. Competitive results (Miller, 1980b; Horvath, et al., 1976) strongly support this contention. The $c\phi$ theory provides a quantitative measure of the individual interaction terms for the solute-solvent-sorbent association reaction. The important counterbalancing terms are the van der Waals' dispersion term and the cavity term. The branched isomers of two aliphatic homologous groups are experimentally used to probe these interactions. Finally, from a practical viewpoint, the simplified $c\phi$ theory together with the molecular-build program can be used with confidence to rank-order single solute aliphatic isomers with respect to their adsorption potential.

INTRODUCTION

During the past decade there has been an intensified effort in the United States to define the performance of activated carbon (AC) for removal of dissolved organics from water supplies. With the development of extremely sensitive analytical techniques and the consequent discovery of potential carcinogenic, mutagenic and teratogenic compounds in drinking water, many researchers have focused on key questions associated with the use of AC in aqueous solutions (Suffet, 1980). The ability to identify and remove toxic compounds from mixtures is one important objective. Often, slight structural changes between isomers make the difference between benign or toxic molecules.

A general comprehensive solution interaction approach, originally developed by Sinanoglu and coworkers (1968, 1969, 1980), was recently adapted to the adsorption of organic homologues from dilute aqueous solutions by Belfort et al. (1979, 1981a). By including solvent effects in the equilibrium adsorption (association) process, this solvophobic theory ($c\phi$) differs from most other equilibrium theories in that the latter were originally derived from gas- and vapor-phase adsorption and thereby *a priori* ignored the presence of the solvent during the adsorption process (Miller, 1980b).

In our preceeding paper (Altshuler and Belfort, 1981), we extended the testing of the solvophobic theory to include the adsorption (data obtained from the literature) of branched aliphatic alcohols and slightly ionized linear carboxylic acids. Correlations from the comprehensive and simplified $c\phi$ theories were compared with correlations of other independent molecular descriptors such as the molecular weight, density, index of refraction, molecular volume, molar refraction, octanol-water partition coefficient, parachor, and polarizability. Total solute surface cavity areas (TSA) were calculated with a newly-developed molecular-build program coupled to Hermann's method of intersecting atomic spheres with appropriate crowding factors (Herman, 1972).

In this paper, we extend the testing of the solvophobic theory to include the adsorption of two comprehensive sets of homologous series of linear and branched aliphatic alcohols and ketones. In contrast to all our previous papers, here we report for the first time our own experimentally measured isotherms. Besides being more comprehensive in number of isomers within a homologous group allowing for better statistical predictions, the data presented here is also internally self-consistent, i.e., the isotherms are measured with similar carbon, water, pH, temperature, duration and range of initial concentrations. In addition, for the first time we compare correlations for adsorbability (lnQ^ob) with the comprehensive $c\phi$ model ($\Delta G^{net}/RT$), with the modified model (TSA), and with other independent variables such as molecular weight, and those listed above for our previous publication. A new molecular-build program is coupled to a new cavity surface area and molecular volume program.

MATERIALS AND METHODS

Adsorbent

Filtrasorb 400 granular activated carbon (Calgon Corp., Pittsburgh, PA) was ground in a jar mill so as to pass through U.S. sieve series #200 (0.074 mm) and to be retained by U.S. sieve series #400 (0.037 mm). The carbon was cleaned with successive washing and supernatant removal. The carbon was then analyzed in a surface area-pore volume analyzer (Model 2100E, Micrometrics Instruments Corp., GA) and the data was fit to a B.E.T. model. The B.E.T. surface area, using N_2 gas, was 1,031 m^2/g, the pore volume was 0.95 cm^3/g, the equivalent particle diameter was 37–74 μm and the bulk density was 0.478 g/cm^3.

The carbon was dried in a vacuum oven (Isotemp No. 281, Fisher Scientific, NY) at 373 K and 3.33×10^3 Pa vacuum for a five-day period. Any extraneous adsorbed organics were volatilized by increasing the temperature to 393.2 K for two days until the weight of the carbon remained constant. The dried carbon was stored in a desiccator until use.

One mg/mL and two mg/mL carbon solutions were prepared using 0.01 M phosphate buffer. These solutions were stored in amber glass bottles for two days to allow for complete wetting before use.

Adsorbates

The ketone compounds were purchased from Supelco (PA) as ketone kits #41 and #42 and the alcohols were obtained from Aldrich Co. (WI). These compounds are graded 99% pure. Stock solutions of these compounds were made with 0.01 M phosphate buffer and were stored in amber glass bottles.

Adsorption Isotherms

During this study, three environmental parameters were held constant; pH, temperature and time. The pH was controlled by using a phosphate buffer at pH 7.0 ± 0.1. The temperature was controlled by conducting the isotherm in a water bath at 293.2 ± 0.5 K. The duration of each experimental isotherm was held constant at 24 hours.

Carbon, solute and buffer were added to 38 mL capped stainless-steel ultracentrifuge tubes (Part No. 301112, Beckman, CA). The carbon dosage was increased from 0 mg/mL to a maximum of 500 mg/mL (depending on the adsorbability of the compound). The tubes were fastened to a rotating shaft and were rotated at 10 rpm for 24 hours while immersed in a water bath at 293.2 K. The tubes were then removed and spun in an ultracentrifuge (Model L8-55, Beckman, CA) at 20,000 rpm for 15 minutes. The remaining solute concentrations, in the supernatant, were measured by TOC (Model 915 A, Beckman, CA). A TOC standard curve, of peak height vs. concentration, was used to compute the final solute concentrations. Stock solutions for TOC standard curve were prepared and refrigerated prior to use.

Kinetic studies were performed on various solutes to confirm that equilibrium was attained in the 24 hour mixing time.

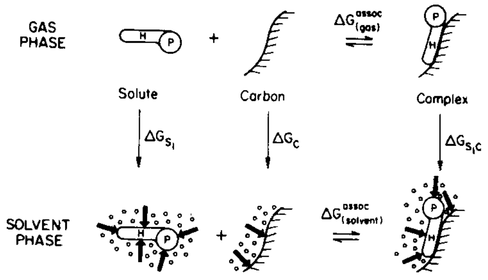

Figure 1. Association-adsorption reaction.

Common statistical tests to determine the significance limits for which coefficients of linear correlation r were different from zero and each other were used.

THEORY

Conceptually, solute adsorption onto activated carbon may be represented by the following reversible association reaction

$$S_i + C \rightleftarrows S_iC \tag{1}$$

where S_i is the adsorbing solute, C is the activated carbon, and S_iC is the adsorbed solute-carbon complex. The equilibrium constant for this reaction, $K_{\text{solvent},i}$ is related to the overall free energy change, $\Delta G^{assoc}_{solvent}$ by

$$\Delta G^{assoc}_{solvent} = -RT\, ln\, K_{\text{solvent},i} \tag{2}$$

The solvophobic theory ($c\phi$) takes into account the effect of the solvent on the above association reaction by considering two hypothetical steps. First, a cavity in the solvent must be created to contain the reacting species. Second, after the gas phase reaction, the "molecules" are placed into the cavities, where each species may interact with the surrounding solvent. This process is depicted in Figure 1.

The effect of the solvent may be calculated from the difference of the free energy changes of the solvent and gas-phase reactions

$$\Delta G^{net}_{\text{solvent effect}} = \Delta G^{assoc}_{solvent} - \Delta G^{assoc}_{gas} \tag{3}$$

In addition, this solvent effect is due to the interaction of each species with the solvent. Therefore,

$$\Delta G^{net}_{\text{solvent effect}} = \sum_j \{\Delta G^{net}_{j,S_iC} - \Delta G^{net}_{j,S_i} - \Delta G^{net}_{j,C}\} \tag{4}$$

where subscript j represents all possible interactions. In previous applications of the solvophobic theory (Sinanoglu, 1968; Halicioglu and Sinanoglu, 1969; Horvath et al., 1976) the interactions considered were cavity formation, van der Waals (and reduction due to presence of a solvent), and electrostatic. Combining Eqs. 3 and 4 gives

$$\Delta G^{assoc}_{solvent} = \Delta G^{assoc}_{gas} + [\Delta G_{cav} + \Delta G_{vdw} + \Delta G_{es}]^{net}_{S_iC-S_i-C} - RT\, ln(RT/P_oV) \tag{5}$$

The free energy change for cavity formation has been calculated (Sinanoglu, 1968) as

$$\Delta G_{cav,i} = \gamma_i A_i \kappa^e_i (1 - W) N \tag{6}$$

where W is given by,

$$W = \left(1 - \frac{\kappa^e_i}{\kappa^s_i}\right)\left(\frac{dln\gamma}{dlnT} + \frac{2}{3} a_i T\right) \cdot \tag{7}$$

The van der Waals' interaction is represented by an effective Kihara potential (a modified Lennard-Jones potential). The term "effective" refers to the fact that it is corrected due to presence of surrounding solvent. This potential is integrated over a discrete solvent layer, then an outer solvent continuum. The resulting approximate equation is (Halicioglu and Sinanoglu, 1969),

$$\Delta G_{vdw,i} \approx -\Delta_i D_i D(0.606Q) \quad (8)$$

where

$$\Delta_i = \frac{1.35\, I_i I}{I_i + I}; \quad D_i = \frac{n_{D,i}^2 - 1}{n_{D,i}^2 + 2} \quad (9, 10)$$

for solute i, nonsubscripted variables refer to the solvent. Also,

$$Q = \nu_i \left[\frac{\bar{\sigma}^6}{(\bar{R} - \bar{l})^9}\left(\frac{t^2}{11} + \frac{t}{5} + \frac{1}{9}\right) - \frac{1}{(\bar{R} - \bar{l})^3}\left(\frac{t^2}{5} + \frac{t}{2} + \frac{1}{3}\right)\right] \quad (11)$$

where

$$t = \frac{\bar{l}}{(\bar{R} - \bar{l})}; \quad R_i = 1.74\left(\frac{3\nu_i}{4\pi}\right)^{1/3}; \quad l_i = R_i\left(\frac{0.24 + 7\omega_i}{3.24 + 7\omega_i}\right) \quad (12\text{–}14)$$

$$\sigma_i = \left(\frac{3\nu_i}{4\pi}\right)^{1/3} \frac{4.64}{3.24 + 7\omega_i} \quad (15)$$

R_i, l_i, and σ_i are the molecular diameter, Kihara parameter, and London parameter, respectively. The overbar variables indicate the mean value of the solute and solvent parameters.

The electrostatic interactions may be estimated by (Horvath et al., 1976),

$$\Delta G_{es,i} = \frac{-N}{2}\frac{\mu_i^2 \mathcal{D}\mathcal{P}}{\nu_i}; \quad \mathcal{D} = \frac{2(\epsilon - 1)}{2\epsilon + 1}$$

$$\mathcal{P} = \left[4\pi\epsilon_0\left(1 - \frac{\mathcal{D}\alpha_i}{\nu_i}\right)\right]^{-1} \quad (16\text{–}18)$$

Substituting Eqs. 6–18 into Eq. 5 gives

$$\begin{aligned}\Delta G_{\text{solvent}}^{\text{assoc}} = \Delta G_{\text{gas}}^{\text{assoc}} + \Bigg[\Delta G_{vdw,S_iC} - \frac{N}{2}\frac{\mu^2{}_{S_iC}}{\nu_{S_iC}} \\ + N\kappa_{S_iC}^e A_{S_iC}\gamma_{w,S_iC}(1 - W_{S_iC})\Bigg] \\ - \left[\Delta G_{vdw,S_i} - \frac{N}{2}\frac{\mu_{S_i}^2}{\nu_{S_i}} + N\kappa_{S_i}^e A_{S_i}\,\gamma_{w,S_i}\,(1 - W_{S_i})\right] \\ - \left[\Delta G_{vdw,C} - \frac{N}{2}\frac{\mu_C^2}{\nu_C} + N\kappa_C^e A_C \gamma_{w,C}(1 - W_C)\right] \\ - RT\, ln(RT/P_oV) \quad (19)\end{aligned}$$

At this point, all of the considered solvent-solute interactions are included in the general Eq. 19. However, further simplification is needed to make the problem tractable.

With respect to the activated carbon surface, essentially two types of interactions are thought to predominate. The first type of surface interaction, which occurs on most of the available surface area (on basal planes) can be characterized by van der Waals' physical interactions, and is apolar in nature. The second type of surface interaction which occurs at the more reactive edges of the microcrystallites, and at surface functional groups, can be characterized by physical (and maybe even chemical) attractive interactions due to electrostatic effects. Although the second type of surface interaction occurs at a small fraction of the total surface area, adsorption differences between different activated carbons is probably the result of their energy potential distributions, and extent of surface functional groups. However, since hydrophobic or apolar interactions play a dominant role in activated carbon adsorption of nonpolar (or nonpolar moieties of) solutes, only the first type of surface interaction discussed above will be considered here.

Considering the carbon surface to be nonpolar, the following assumptions can be made, $\mu_c = 0$ (nonpolar carbon); $\mu_{S_iC} = \mu_{S_i}$ (solute could be polar); $\Delta G_{vdw,S_iC} = \Delta G_{vdw,C}$ (dilute range).

In addition, since the carbon surface is much larger than the solute, then (Horvath et al., 1976)

$$W_{S_iC} = W_{S_i} = W_C \text{ and } \kappa_{S_iC}^e = \kappa_C^e = 1$$

Also per Horvath

$$\kappa_{S_i}^e \approx 1 + (\kappa^e - 1)(V/V_{S_i}) \quad (20)$$

where κ^e is the microscopic cavity factor for pure water, and has a value of 1.277 (Halicioglu and Sinanoglu, 1969).

To simplify the algebra, the molecular volume of the carbon-solute complex S_iC may be expressed as a multiple of the solute molecular volume,

$$\nu_{S_iC} = \lambda\nu_{S_i} \quad (21)$$

where λ is the proportionality constant. For high pressure liquid chromatography, λ was estimated to be approximately 3.7. Since the carbon-solute complex S_iC is much larger than the solute S_i, λ is arbitrarily chosen as $\lambda = 100$ for this work. Previously, it was shown that the actual value of λ has only a very weak effect on $\Delta G_{\text{solvent}}^{\text{assoc}}$ (Belfort, 1981).

Finally, because of the association adsorption reaction of solute S_i onto adsorbent C, the total surface area in contact with the free solvent is reduced by,

$$\Delta A = A_{S_i} + A_c - A_{S_iC} \quad (22)$$

ΔA has been termed "the thermodynamic microsurface area change of reaction" (Sinanoglu, 1980).

Substituting the above assumptions into Eq. 19 gives

$$\begin{aligned}\Delta G_{\text{solvent}}^{\text{assoc}} = \Delta G_{\text{gas}}^{\text{assoc}} - \Delta G_{vdw,S_i} + \frac{N(\lambda - 1)}{2\lambda}\frac{\mu_{S_i}^2}{\nu_{S_i}} \\ - N\gamma\Delta A - N\gamma V^{2/3}(\kappa^e - 1)\frac{A_{S_i}}{V_{S_i}^{2/3}} - RT\, ln\frac{RT}{P_oV} \quad (23)\end{aligned}$$

Equation 23 may be further simplified by noting that in the fifth term on the right hand side, $A_{S_i}/V_{S_i}^{2/3}$ is a constant for a given molecular shape. Therefore, for spherical molecules,

$$A_{S_i} = 4.836\, \nu_{S_i}^{2/3} = 4.836\,(V_{S_i}/N)^{2/3} \quad (24)$$

and Eq. 23 becomes,

$$\begin{aligned}\Delta G_{\text{solvent}}^{\text{assoc}} = \Delta G_{\text{gas}}^{\text{assoc}} - \Delta G_{vdw,S_i} + \frac{N(\lambda - 1)}{2\lambda}\frac{\mu_{S_i}^2}{\nu_{S_i}} \\ - N\gamma\Delta A - 4.836\, N^{1/3}\gamma(\kappa^e - 1)V^{2/3} - RT\, ln\frac{RT}{P_oV} \quad (25)\end{aligned}$$

The free energy change of the association reaction may be related to its equilibrium constant by

$$\Delta G_{\text{solvent}}^{\text{assoc}} = -RT\, ln\, K_{\text{solvent},i} \quad (26)$$

where

$$K_{\text{solvent},i} = x_{S_iC}/(x_{S_i}x_C) \quad (27)$$

for dilute solutions.

Equations 26 and 27 may be rearranged to give,

$$\Delta G_{\text{solvent}}^{\text{assoc}} = -RT\, ln\frac{x_{S_iC}}{x_{S_i}} + RT\, ln\, x_C \quad (28)$$

and therefore,

$$ln\frac{x_{S_iC}}{x_{S_i}} = -\frac{\Delta G_{\text{solvent}}^{\text{assoc}}}{RT} + ln\, x_C \quad (29)$$

or

$$\begin{aligned}ln\frac{x_{S_iC}}{x_{S_i}} = \left\{\frac{-\Delta G_{\text{gas}}^{\text{assoc}}}{RT} + ln\, x_C\right\} \\ + \frac{\Delta G_{vdw,S_i}}{RT} - \frac{N(\lambda - 1)}{2\lambda}\frac{\mu_{S_i}^2}{\nu_{S_i}}\frac{N(\lambda - 1)}{2\lambda RT} \\ + \frac{\gamma}{RT}(N\Delta A + 4.836N^{1/3}(\kappa^e - 1)V^{2/3}) + ln\frac{RT}{P_oV} \quad (30)\end{aligned}$$

or

$$lnQ^ob\ \alpha\ VDW + ES + CAV + CRAT = \Delta G^{\text{net}}/RT \quad (31)$$

where the term in brackets on the righthand side of Eq. 30 is considered constant and omitted from Eq. 31, and $x_{S_iC}/x_{S_i} \equiv Q^ob$, the initial slope at infinite dilution for the Langmiur isotherm with Q^o the capacity term and b the energy term. The relative contribution of each term in Eq. 31 will be discussed later.

TABLE 1. ADSORPTION ISOTHERM MEASUREMENTS FITTED TO LANGMURIAN MODEL FOR ALCOHOLS

Solute	MW	Concentration Range (mmol/L)	No. of Points	Q^o (mmol/g)	b (mmol/L)$^{-1}$	lnQ^o (mmol/g)	lnQ^ob	r
1. 1-butanol	74.1	0.140–0.047	10	0.17(9)	20.2	−1.72(0)	1.2(8)	0.96(0)
2. 2-methyl 1-butanol	88.2	0.190–0.019	10	0.41(1)	30.7	−0.88(9)	2.5(4)	0.98(7)
3. 1-pentanol	88.2	0.133–0.023	10	0.43(7)	19.5	−0.82(7)	2.1(4)	0.98(0)
4. 2,3-dimethyl 2-butanol	102.2	0.151–0.032	13	0.59(8)	9.9	−0.51(4)	1.7(8)	0.99(3)
5. 3,3-dimethyl 1-butanol	102.2	0.108–0.020	11	0.53(4)	14.8	−0.62(8)	2.0(7)	0.97(9)
6. 2-ethyl 1-butanol	102.2	0.204–0.020	11	0.61(6)	45.2	−0.48(5)	3.3(3)	0.96(1)
7. 2-methyl 3-pentanol	102.2	0.139–0.014	14	0.46(5)	50.5	−0.76(6)	3.1(6)	0.99(5)
8. 4-methyl 1-pentanol	102.2	0.180–0.018	12	0.65(7)	51.2	−0.42(1)	3.5(2)	0.99(4)
9. 1-hexanol	102.2	0.161–0.009	10	0.78(0)	79.3	−0.24(9)	4.1(2)	0.98(5)
10. 2,4-dimethyl 3-pentanol	116.2	0.131–0.014	10	0.77(5)	40.6	−0.25(5)	3.4(5)	0.99(0)
11. 3-ethyl 3-pentanol	116.2	0.135–0.018	10	0.65(9)	41.2	−0.41(7)	3.3(0)	0.98(3)
12. 1-heptanol	116.2	0.127–0.005	10	1.03(9)	107.6	−0.03(8)	4.7(2)	0.99(5)

TABLE 2. ADSORPTION ISOTHERM MEASUREMENTS FITTED TO LANGMUIRIAN MODEL FOR KETONES

Solute	Mw	Concentration Range (mmol/L)	No. of Points	Q^o (mmol/g)	$ln\ Q^o$	b (mmol/L)$^{-1}$	$ln\ Q^ob$	r
1. 2-propanone	58.10	0.166–0.103	6	0.13(6)	−1.99(7)	3.2	−0.8(4)	0.61(2)
2. 2-butanone	72.12	0.170–0.030	13	0.28(3)	−1.26(2)	11.4	1.1(7)	0.95(8)
3. 2-pentanone	86.14	0.152–0.010	13	0.37(1)	−0.99(3)	62.4	3.1(4)	0.96(3)
4. 3-pentanone	86.14	0.148–0.016	13	0.33(1)	−1.10(6)	43.7	2.6(7)	0.96(7)
5. 3-methyl-2-butanone	86.14	0.203–0.013	9	0.48(8)	−0.71(8)	10.9	1.6(8)	0.96(7)
6. 2-hexanone	100.16	0.115–0.006	9	0.49(3)	−0.70(8)	77.3	3.6(4)	0.98(3)
7. 4-methyl-2-pentanone	100.16	0.150–0.008	11	0.70(7)	−0.34(6)	37.2	3.2(7)	0.90(2)
8. 2-methyl-3-pentanone	100.16	0.086–0.009	9	0.43(9)	−0.82(4)	39.2	2.8(5)	0.95(0)
9. 3,3-dimethyl-2-butanone	100.16	0.124–0.018	11	0.40(8)	−0.89(5)	32.6	2.5(9)	0.92(8)
10. 2-heptanone	114.19	0.119–0.003	10	0.60(0)	−0.51(1)	203.9	4.8(1)	0.94(6)
11. 3-heptanone	114.19	0.140–0.003	9	0.76(7)	−0.26(5)	232.4	5.2(8)	0.94(7)
12. 4-heptanone	114.19	0.144–0.003	10	0.78(3)	−0.24(4)	317.0	5.5(2)	0.94(8)
13. 4-methyl-2-hexanone	114.19	0.122–0.002	9	0.90(4)	−0.10(1)	91.5	4.4(2)	0.98(4)
14. 5-methyl-2-hexanone	114.19	0.138–0.007	10	0.89(1)	−0.11(5)	96.5	4.4(5)	0.95(3)
15. 2,4-dimethyl-3-pentanone	114.19	0.144–0.007	11	0.97(6)	−0.02(8)	49.5	3.8(8)	0.99(1)
16. 2-octanone	128.22	0.132–0.015	11	1.66(3)	0.50(9)	87.1	4.9(8)	0.99(1)
17. 3-methyl-2-heptanone	128.22	0.122–0.005	10	0.90(5)	−0.09(9)	159.1	4.9(7)	0.96(0)
18. 5-methyl-3-heptanone	128.22	0.092–0.004	9	0.90(5)	−0.09(9)	132.4	4.7(9)	0.98(5)
19. 2-nonanone	142.24	0.135–0.019	11	2.13(7)	0.75(9)	68.9	4.9(9)	0.91(6)
20. 5-nonanone	142.24	0.092–0.015	9	2.12(9)	0.75(5)	73.5	5.0(5)	0.98(1)
21. 2,6-dimethyl-4-heptanone	142.24	0.104–0.017	10	2.14(3)	0.76(2)	90.4	5.2(7)	0.88(1)

RESULTS AND DISCUSSION

The results of the adsorption isotherm experiments for homologous series of alkyl alcohols and ketones are presented in Tables 1 and 2. The data are represented by the Langmuir isotherm parameters, Q^o and b. Where possible, the isotherms of several isomers of the same formula were measured to study the effect of structural modifications of the solute. Many of the isotherms were repeated for confirmational purposes.

Adsorbability is defined here as the slope of the adsorption isotherm at infinite dilution and expressed in Langmuirian terms as lnQ^ob. The value of Q^o is the saturated adsorption capacity as $C \rightarrow C_{sat}$, while the value of b is related to the free energy of adsorption through $\exp(-\Delta G/RT)$.

The physical properties required for calculating ΔG^{net} are listed in Tables 3 and 4. Table 4 also includes calculated values for each term in Eq. 31. A complete consistent set of ionization potential data for the desired compounds was not found in the literature. Therefore a constant ionization potential for each series was assumed. Since the ionization potentials of a homologous series of alcohols varies only between 11.0 eV and 10.0 eV, and approaches 10.0 eV asymptotically as the series is ascended (Vedeneyev et al., 1966), this assumption has a small effect on the adsorbability (lnQ^ob) prediction, but does not introduce a significant error in the correlation slope or coefficients, as shall be seen later.

Surface Area Calculations

The solute total cavity surface areas, *TSA*, were calculated from geometrical considerations. First, the x, y and z coordinates of the solutes' atoms were determined from known bond lengths and angles. These coordinates were then used to construct a set of intersecting spheres with radii equal to the van der Waal's radii of each atom. A spherical probe with the radius of a water molecule (1.5 Å) is then traced around the surface of the spheres, and the resulting surface area and volume is calculated (Richards, 1977). A computer program to carry out these calculations was supplied by G. M. Smith of Merck, Sharp and Dohme.

In comparison with the procedure described above, the calculated *TSA* values did not differ by more than 3% when using the computer optimized surface areas from an energy minimization of the molecular configuration (Woodfield, 1982).

In addition, a value is needed for ΔA, the change in area exposed to solvent as a result of the association reaction. Previous work (Altshuler and Belfort, 1981) estimated ΔA as 20–30% of *TSA*. Thus for this work, a constant value of 25% was used.

Raw Data

Figure 2 is included here for several reasons. First, the fact that although molecular weight is useful as a correlating parameter with

TABLE 3. SOLUTE AND SOLVENT PHYSICAL PROPERTIES

No. Compounds	Molecular weight, MW	Density[a] ρ, g cm -3	Index of[a] refraction n_D	Accentric.[b] factor, ω	Molar refraction, MR cm^3 $mole^{-1}$	Octanol-water partition coefficient[c] log P	Parachor[d] [P]
Aliphatic Alcohols							
1. 1-butanol	74.12	0.8097	1.3993	0.251	22.157	0.87	205.3
2. 2-methyl 1-butanol	88.15	0.8191	1.4107	0.275	26.704	2.17	241.6
3. 1-pentanol	88.15	0.8148	1.4100	0.296	26.804	1.41	245.3
4. 2,3 dimethyl 2-butanol	102.18	0.8226	1.4173	0.251	31.257	1.38	274.2
5. 3,3 dimethyl 1-butanol	102.18	0.8147	1.4138	0.289	31.328	1.51	277.9
6. 2 ethyl 1-butanol	102.18	0.8281	1.4224	0.310	31.382	1.82	281.6
7. 2 methyl 3-pentanol	102.18	0.8239	1.4168	0.299	31.175	1.60	277.9
8. 4 methyl 1-pentanol	102.18	0.8130	1.4154	0.330	31.500	1.82	281.6
9. 1-hexanol	102.18	0.8198	1.4181	0.351	31.417	1.95	285.3
10. 2,4 dimethyl 3-pentanol	116.20	0.8290	1.4250	0.317	35.841	2.01	314.2
11. 3 ethyl 3-pentanol	116.20	0.8445	1.4301	0.304	35.552	2.05	317.9
12. 1-heptanol	116.20	0.8225	1.4241	0.394	36.057	2.49	325.3
Aliphatic Ketones							
1. 2-propanone	58.08	0.7899	1.3588	0.176	16.179	0.24	162.1
2. 2-butanone	72.12	0.8054	1.3788	0.227	12.082	0.30	199.8
3. 2-pentanone	86.14	0.8089	1.3895	0.279	25.215	0.84	238.3
4. 3-pentanone	86.14	0.8138	1.3924	0.275	25.228	0.84	238.3
5. 3 methyl 2-butanone	86.14	0.8051	1.3880	0.247	25.249	0.71	234.6
6. 2-hexanone	100.16	0.8113	1.4007	0.330	29.976	1.38	277.1
7. 4 methyl 2-pentanone	100.16	0.7978	1.3962	0.306	30.179	1.25	273.4
8. 2-methyl 3-pentanone	100.16	0.8106	1.3981	0.299	29.829	1.25	273.4
9. 3,3 dimethyl 2-butanone	100.16	0.8012	1.3952	0.251	29.984	0.94	269.7
10. 2-heptanone	114.19	0.8111	1.4088	0.378	34.791	1.92	317.1
11. 3-heptanone	114.19	0.8183	1.4057	0.369	34.254	1.92	317.1
12. 4-heptanone	114.19	0.8174	1.4069	0.369	34.382	1.92	317.1
13. 4 methyl 2-hexanone	114.19	0.8129	1.4082	0.343	34.669	1.79	313.4
14. 5 methyl 2-hexanone	114.19	0.8119	1.4069	0.352	34.614	1.79	313.4
15. 2,4 dimethyl 3-pentanone	114.19	0.8108	1.4000	0.317	34.138	1.66	309.7
16. 2-octanone	128.21	0.8185	1.4153	0.421	39.250	2.46	354.9
17. 3 methyl 2-heptanone	128.21	0.8218	1.4172	0.383	39.250	2.33	351.2
18. 5 methyl 2-heptanone	128.21	0.8218 (e)	1.4172 (e)	0.392	39.250	2.33	351.2
19. 2-nonanone	142.24	0.8208	1.4210	0.464	43.942	3.00	393.9
20. 5-nonanone	142.24	0.8217	1.4195	0.455	43.761	3.00	393.9
21. 2,6 dimethyl 4-heptanone	142.24	0.8053	1.4120	0.414	43.950	2.74	386.5
Solvent							
1. water	18.0	0.9971	1.3325	0.023			

Footnotes

[a] From (Manufacturing Chemists Assoc., 1966).

[b] Of a non-polar homologue, from (Reid, Prausnitz and Sherwood, 1977).

[c] Calculated from (Leo et. al., 1975).

[d] Calculated from (Quayle, 1953).

[e] Estimated to be same as compound #17.

adsorbability for linear members of a homologous series, it clearly cannot be used for the adsorption of isomers of the same molecular weight. Secondly, the coordinates, plotted in Langmuirian form suggest that this simple model is quite adequate to describe the data especially in the dilute range (i.e., high values of C^{-1}). Thirdly, in addition to the effects of branching, the location of the OH-group on the isomer is shown to affect the adsorbability (inverse slope) of the solute. It will be shown that all these effects are automatically accounted for by the $c\phi$ theory.

Solvophobic Contributions—Alcohols

Figure 3 shows the contributions to the net free energy change for the association reaction of alcohols and the carbon surface, as calculated by Eq. 30. The dominant contribution is due to the van der Waals' dispersion forces. The electrostatic contribution is negligible as expected for nonionizable solutes. However, the theory may be adapted for ionizable solutes (Altshuler and Belfort, 1981). The cratic term (7.21 dimensionless units) due to the reduction of the solvent free volume, is constant for each solute and therefore not shown in Figure 3.

The curves drawn through the calculated points on Figure 3 are for the normal isomer of each formula. Note that branched isomers have an increased net free energy change, indicating decreased adsorption.

Simplified Solvophobic Theory

Although total cavity surface area (TSA) is assumed to be linearly related to the reduced or lost microsurface area (ΔA) due to the association adsorption reaction, this parameter, according to the theory presented here, should only describe the free energy for cavity formation which increases with carbon number in the isomer or decreases with branching for an isomer of constant carbon number. The fact that TSA can be used to universally describe the net free energy $\Delta G^{net}/RT$ is dependent on a recent discovery of Sinanoglu (private communication) that, in addition to $\Delta G_{cav}, \Delta G_{vdw}$, the dominant counteracting term (opposite sign to ΔG_{cav}) in our analysis (Figure 3) is also proportional to TSA. Thus, fortuitously, the difference in free energy ($\Delta G_{vdw} - \Delta G_{cav}$) is also proportional to TSA resulting in, what is termed here, the "simplified $c\phi$ model.'

Test of Theory—Alcohols

The results are plotted as adsorbability (lnQ^ob) vs. MW,TSA,

TABLE 4. SOLUTE PROPERTIES AND SOLVOPHOBIC CONTRIBUTIONS

	MOLECULAR PROPERTIES			ADSORBABILITY	SOLVOPHOBIC FREE ENERGY CHANGE, ΔG/RT[c]				
ADSORBATE	Molecular weight, MW	Cavity Surface area, TSA[a] $Å^2$	Molecular Volume, μ[b] $Å^3$	$\ln(Q^0b)$	VDW	ES	CRAT	CAV	NET
Aliphatic alcohols									
1. 1-butanol	74.12	251.5	152.01	1.29	-19.27	-0.27	7.21	9.39	2.94
2. 2-methyl 1-butanol	88.15	267.2	178.71	2.54	-23.30	-0.23	7.21	9.88	-6.44
3. 1-pentanol	88.15	282.2	179.65	2.14	-25.01	-0.23	7.21	10.34	-7.69
4. 2,3 dimethyl 2-butanol	102.18	274.1	206.27	1.78	-23.32	-0.20	7.21	10.09	-6.22
5. 3,3 dimethyl 1-butanol	102.18	284.0	208.27	2.07	-26.57	-0.20	7.21	10.40	-9.16
6. 2 ethyl 1-butanol	102.18	290.0	204.90	3.33	-28.77	-0.20	7.21	10.58	-11.17
7. 2-methyl 3-pentanol	102.18	290.7	205.94	3.16	-27.50	-0.20	7.21	10.61	-9.88
8. 4-methyl 1-pentanol	102.18	300.4	208.71	3.52	-30.51	-0.20	7.21	10.91	-12.59
9. 1-hexanol	102.18	312.9	206.97	4.12	-32.59	-0.20	7.21	11.30	-14.28
10. 2,4 dimethyl 3-pentanol	116.20	301.2	232.76	3.45	-31.58	-0.18	7.21	10.93	-13.62
11. 3 ethyl 3-pentanol	116.20	302.0	228.49	3.30	-30.29	-0.18	7.21	10.96	-12.30
12. 1-heptanol	116.20	343.6	234.60	4.72	-40.06	-0.17	7.21	12.25	-20.78
Aliphatic Ketones									
1. 2-propanone	58.08	209.6	122.10	-0.84	-11.71	-0.77	7.21	8.09	2.81
2. 2-butanone	72.12	238.7	148.70	1.17	-16.25	-0.64	7.21	8.99	-0.68
3. 2-pentanone	86.14	269.4	176.84	3.14	-21.62	-0.54	7.21	9.94	-5.00
4. 3-pentanone	86.14	267.8	175.77	2.67	-21.30	-0.54	7.21	9.89	-4.73
5. 3 methyl 2-butanone	86.14	258.4	177.67	1.67	-19.22	-0.53	7.21	9.60	-2.94
6. 2-hexanone	100.16	300.9	205.02	3.64	-28.15	-0.46	7.21	10.92	-10.48
7. 4 methyl 2-pentanone	100.16	286.3	208.48	3.27	-25.97	-0.45	7.21	10.47	-8.75
8. 2-methyl 3-pentanone	100.16	287.6	205.19	2.84	-24.96	-0.46	7.21	10.51	-7.71
9. 3,3 dimethyl 2-butanone	100.16	274.3	207.59	2.59	-21.15	-0.46	7.21	10.10	-4.30
10. 2-heptanone	114.19	331.6	233.78	4.81	-35.45	-0.41	7.21	11.88	-16.77
11. 3-heptanone	114.19	330.0	231.73	5.18	-33.76	-0.41	7.21	11.83	-15.14
12. 4-heptanone	114.19	329.3	231.98	5.51	-33.83	-0.41	7.21	11.80	-15.22
13. 4 methyl 2-hexanone	114.19	311.9	233.27	4.42	-31.79	-0.41	7.21	11.26	-13.72
14. 5 methyl 2-hexanone	114.19	318.4	233.55	4.45	-32.61	-0.41	7.21	11.47	-14.35
15. 2,4 dimethyl 3-pentanone	114.19	305.6	233.87	3.88	-28.15	-0.41	7.21	11.07	-10.28
16. 2-octanone	128.21	363.0	260.11	4.98	-43.07	-0.37	7.21	12.85	-23.38
17. 3 methyl 2-heptanone	128.21	345.1	259.07	4.97	-38.67	-0.37	7.21	12.30	-19.53
18. 5 methyl 2-heptanone	128.21	343.8	259.07	4.79	-39.70	-0.37	7.21	12.25	-20.61
19. 2-nonanone	142.24	393.8	287.77	4.99	-51.80	-0.33	7.21	13.81	-31.11
20. 5-nonanone	142.24	392.1	287.45	5.05	-50.38	-0.33	7.21	13.75	-29.75
21. 2,6 dimethyl 4-heptanone	142.24	363.0	293.31	5.27	-43.88	-0.32	7.21	12.85	-24.14

Footnotes:

[a] Calculated from Merck-Sharp & Dohme computer program.

[b] Calculated from density and molecular weight.

[c] Calculated from Eq. 31, with ΔA = 1/4 (TSA); Alcohols, ionization potential = 10.0 eV, dipole moment = 1.8 D, Ketones, ionization potential = 11.0 eV, dipole moment = 2.75 D.

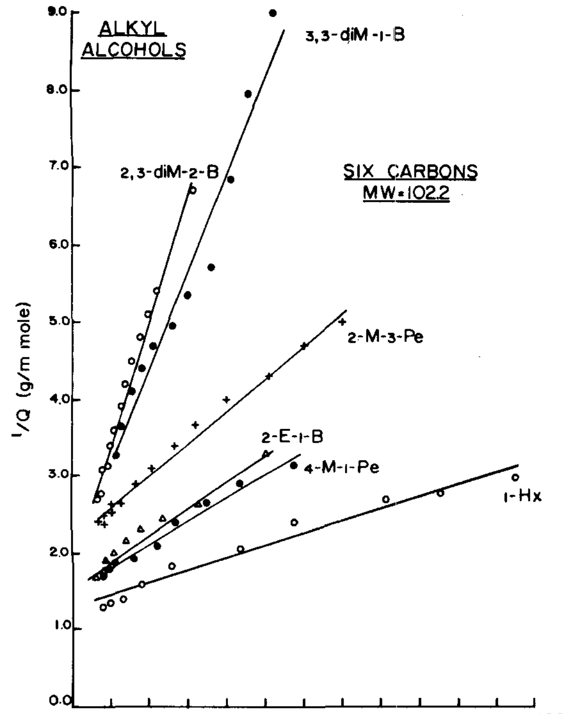

Figure 2. Linear Langmuir isotherms for six-carbon isomers of aliphatic alcohols.

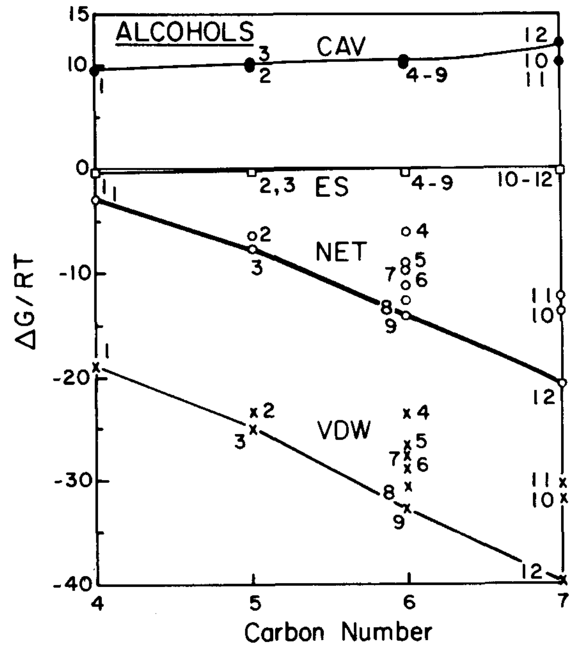

Figure 3. Solvopohobic contributions to $\Delta G^{net}/RT$ for alcohols.

and $\Delta G^{net}/RT$ in Figure 4. Because MW has traditionally been used to estimate the adsorbability, it is included in the analysis for comparison.

As mentioned above, it is generally recognized that adsorption

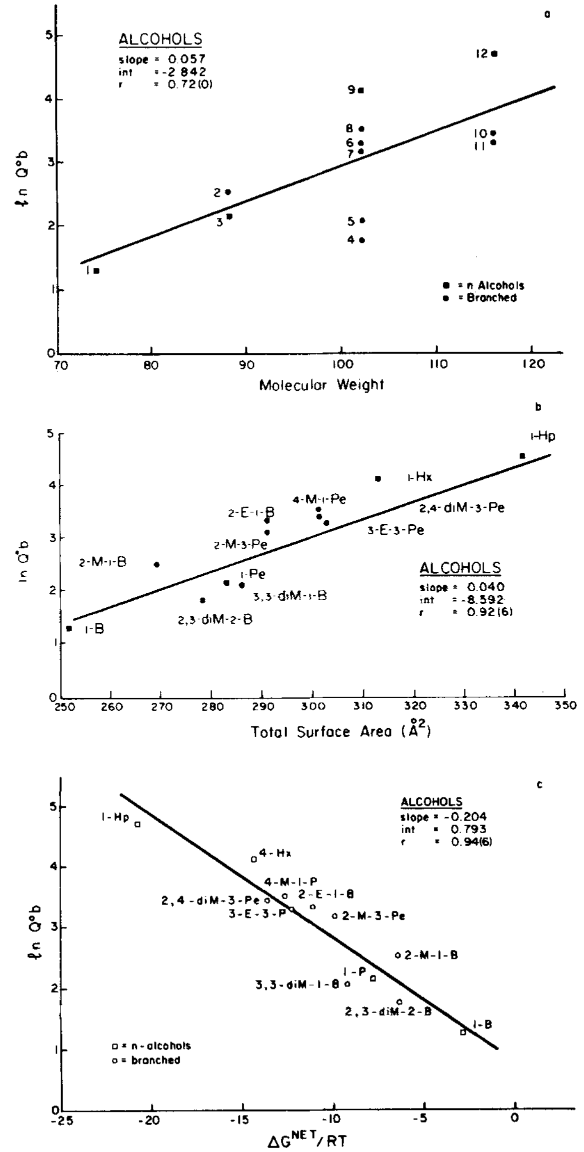

Figure 4. *lnQ°b* as a function of molecular weight, cavity surface area, and $\Delta G^{net}/RT$ for alcohols.

increases with molecular weight. This is true when considering linear members of a homologous series, Figure 4a. However, isomers cannot be distinguished from each other by considering molecular weight only.

Note that in both Figure 4b and c, *TSA* and $\Delta G^{net}/RT$ generally follow the expected trend. Since the surface areas of isomers are different, the correlation coefficient obtained for *TSA* ($r^2 = 0.858$) is higher than that of MW ($r^2 = 0.519$). The highest correlation coefficient ($r^2 = 0.894$) is obtained for $\Delta G^{net}/RT$, which accounts for surface area as well as the other major interactions.

Assumptions

The two main assumptions regarding the physical properties for calculating ΔG^{net} are a constant value of the ionization potential, I, and that the microsurface area change of reaction, ΔA is one quarter of the solute cavity surface area.

Figure 5a compares the results of using an ionization potential of 11.0 eV rather than 10.0 eV which was used in Figure 4c. Since both the slope and the final correlation here are close, the actual value chosen for I has a negligible effect on the final results. Although the choice of ΔA fraction has a larger effect on the absolute magnitude of ΔG^{net}, as shown in Figure 5b, the effect on the final correlation is also negligible ($r = 0.95$ for both cases).

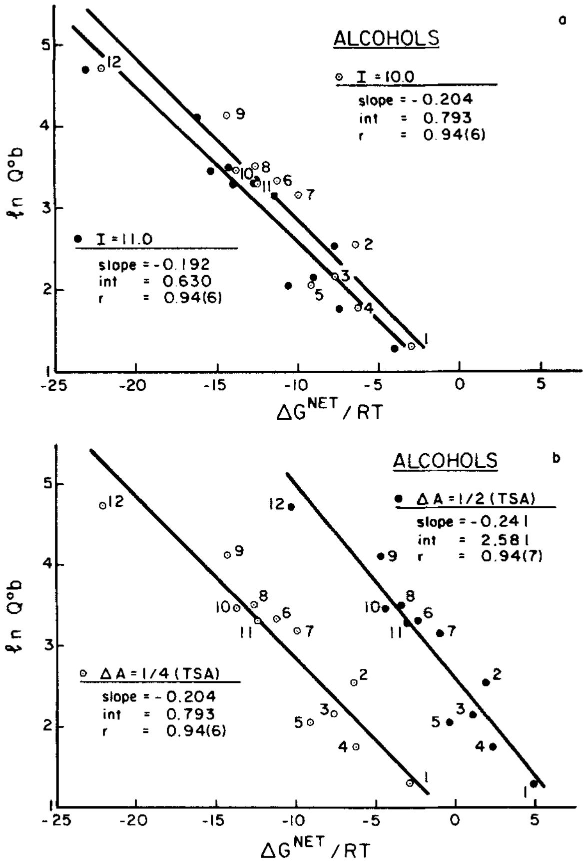

Figure 5. Effect of ionization potential and ΔA and $\Delta G^{net}/RT$.

Molecular Descriptor Correlations

Various parameters that characterize the solvent (water) and solute are needed to calculate the free energy terms in Eq. 31. Thus, a series of solute and solute-solvent molecular descriptors may be correlated with adsorbability *lnQ°b*, to compare then with the $c\phi$ theory. These molecular descriptors are molecular weight, *MW;* density, ρ; index of refraction, n_D; molecular volume, ν; molar refraction, *MR;* parachor, $[P]$; octanol-water partition coefficient, log P; and total cavity surface area, *TSA*.

Molar refraction, *MR*, is a molecular descriptor widely used in quantitative structure-activity relationships (QSAR) (Leo et al., 1969). It is defined by:

$$MR = \frac{MW}{\rho}\left[\frac{n_D^2 - 1}{n_D^2 + 2}\right] \tag{32}$$

and is therefore related to ΔG_{vdw} (Eqs. 8 and 10).

The parachor $[P]$ was developed in the 1920's as a means for calculating molecular volumes. It is defined by:

$$[P] = \gamma^{1/4}\frac{MW}{(\rho_l - \rho_v)} \tag{33}$$

It is not dimensionally correct to consider $[P]$ as a volume. More accurately, the ratio of the parachors of two compounds is equal to the ratio of the molecular volumes under conditions such that the surface tension is equal to unity. Hence the parachor may be thought of as a molecular volume at a corresponding state with respect to surface tension, rather than temperature or pressure (Quayle, 1953).

The octanol-water partition coefficient, log P is the logarithm of the ratio of a solute's concentration in octanol to that in a contacting water phase. It is extensively used in QSAR studies (Leo et al., 1971), and is a measure of the relative hydrophobicity of a solute.

The results of these correlations are presented in Table 5. Of all the correlations for the alcohols, $\Delta G^{net}/RT$ results in the highest

TABLE 5. SOLUTE PARAMETER CORRELATIONS

Group		$\Delta G^{Net}/RT$	MW	π	n_D	ν	MR	$[P]$	Log P	TSA
Aliphatic Alcohols,	$n = 12$									
1 → 12	r^2	0.894	0.519	0.156	0.500	0.771	0.537	0.605	0.714	0.858
	Rank	1	7	9	8	3	6	5	4	2
Ketones	r^2	0.920	0.883	0.662	0.913	0.867	0.778	0.910	0.947	0.952
1 → 15	Rank	3	6	9	4	7	8	5	2	1

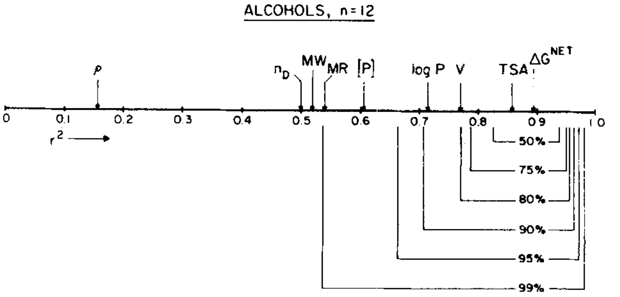

Figure 6. Statistical significance of comparison of correlations with $\Delta G^{net}/RT$.

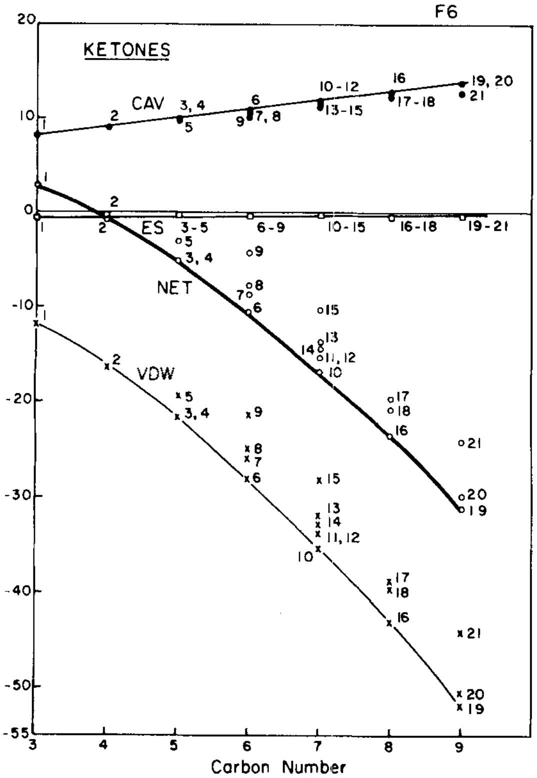

Figure 7. Solvophobic contributions to $\Delta G^{net}/RT$ for ketones.

correlation coefficient. However, the statistical significance of differences in correlation coefficients must be checked. Figure 6 shows the confidence levels at which the hypothesis $r_i = r_{\Delta G^{net}}$ may be rejected. For example, at the 99% confidence level, ΔG^{net} yields a different and higher correlation than ρ, n_D, or MW. However, it cannot be stated that even at the 50% confidence level, TSA and ΔG^{net} yield statistically different values. This substantiates the assumption that TSA represents a useful simplification of the comprehensive solvophobic theory.

All of the ketones examined in this study were monofunctional compounds. As per the results of Abe et al. (1980), molar refraction, molecular weight, molar volume, parachor and the octanol-water partition coefficient all correlated well with the adsorption parameters for the linear ketones.

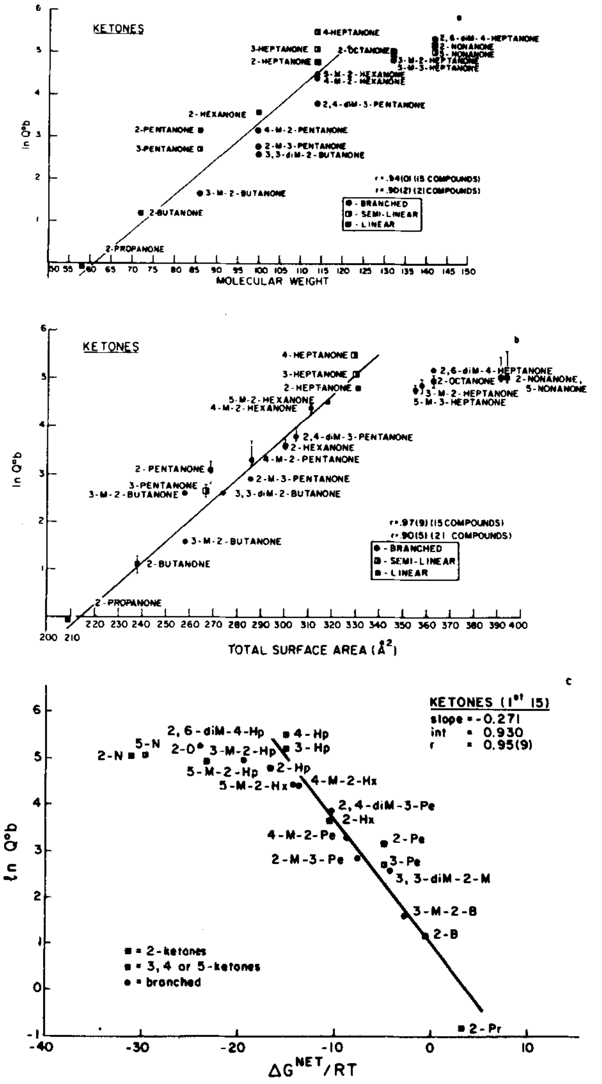

Figure 8. lnQ^ob as a function of molecular weight, cavity surface area, and $\Delta G^{net}/RT$ for ketones.

Abe et al. (1980), studied alcohols, amines, aromatics, esters, ethers, ketones, acids and oxides as a single group. There were nine ketones in this group, two of these nine were branched. For aliphatic monofunctional compounds, these investigators obtained correlations of $r_{MW} = 0.943$, $r_{V_m} = 0.868$, $r_{\text{Log }P} = 0.904$, $r_{MR} = 0.898$, $r_{[P]} = 0.889$, and $r_{n_D} = 0.932$ with adsorbability.

Test of Theory—Ketones

The contributions to ΔG^{net} for the 21 ketones studied show the same trend as the alcohols, Figure 7. However, the adsorption isotherms show a different behavior. When plotted against molecular weight, lnQ^ob appears to level off at a molecular weight of around 114, which corresponds to a seven carbon ketone, Figure 8a. In addition, beyond C_7, the sensitivity in lnQ^ob between isomers appears to have lessened. Both of these observations indicate

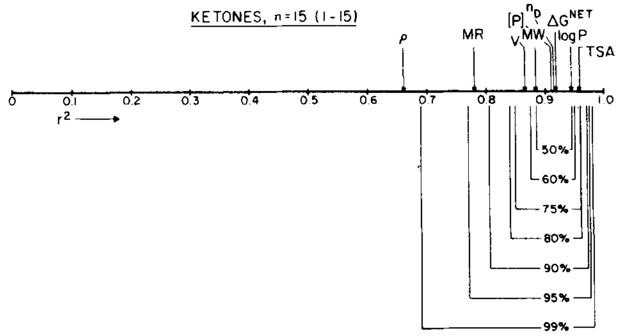

Figure 9. Statistical significance of comparison of correlations with $\Delta G^{net}/RT$.

that there might be steric effects, influencing the larger molecules in reaching the surface of the smaller pores.

Detailed analysis of that data shows that Q^o values increase with molecular weight across the whole range of ketones, while b values decrease, Table 2. Thus, although the saturation values increase, the energy term decreases. These competing effects equalize at $C > C_7$, resulting in an indifferent lnQ^ob with carbon number, TSA, or $\Delta G^{net}/RT$.

Figure 8b shows the relationship of lnQ^ob with total surface area for the aliphatic ketones. The leveling off of the curve starting at heptanone is even more apparent here. The expected relation between the isomers is generally predicted; i.e., the branched isomers show a lower adsorbability than the linear isomers.

Considering lnQ^ob vs. $\Delta G^{net}/RT$ as shown in Figure 8c, the points for the ketones fall close to a straight line, in the expected sequence. In this case, however, TSA results in the highest correlation coefficient (r^2 = 0.95(2), when compared with $\Delta G^{net}/RT$ (r^2 = 0.92(0)), or MW (r^2 = 0.88(3)).

The results of the correlations with lnQ^ob for the parameters studied are listed in Table 5. For those ketones that follow the correlation, Figure 8c; i.e., the first 15 ketones, $\Delta G^{net}/RT$ yields the third best correlation coefficient. However, the differences in correlation coefficients for MW, $[P]$, n_D, and log P are not statistically significant, even at the 50% confidence level, Figure 9. Total surface area, TSA, yields a statistically better correlation then $\Delta G^{net}/RT$ at greater than 75% confidence, and is better than molecular weight at a greater than 90% confidence level.

The above discussion indicates that the solvophobic theory provides a framework to automatically account for changes in adsorbability due to specific solute-solvent interactions resulting from molecular structural changes. Furthermore, the simplified version of the theory provides a useful way of correlating adsorption results.

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NOTATION

A = surface area, A^2
a = coefficient of thermal expansion, cm^3/K
b = Langmuir isotherm parameter
C = solute concentration, mmol/L
D = Clausius-Mosotti function, Eq. 10
$\mathcal{D}$ = electrostatic variable, Eq. 17
G = Gibbs free energy, kcal/mol
I = ionization potential, eV
K = reaction equilibrium constant
l = Kihara parameter, cm^3
log P = logarithm of octanol-water partition coefficient
n_D = index of refraction
MR = molar refraction, cm^3/mol
MW = molecular weight
N = Avogadro's number
$\mathcal{P}$ = electrostatic variable, Eq. 18
P = pressure, kPa
$[P]$ = parachor, Eq. 33
Q = Langmuir isotherm loading, mmol/g
Q' = van der Waals' variable, Eq. 11
Q^o = Langmuir isotherm parameter, mmol/g
R = universal gas constant
R_i = solute diameter, cm^3
T = temperature, K
t = van der Waals' variable, Eq. 12
V = molar volume, cm^3
W = cavity function, Eq. 7
x = mole fraction

Greek Letters

α = polarizability, cm^3
γ = interfacial tension, erg/cm^{-2}
ϵ = solvent dielectric constant
ϵ_o = free space permitivity constant
κ^e = energy correction for curved surface, Eq. 20
κ^s = entropy correction for curved surface, Eq. 7
λ = complex/solute volume ratio
μ = dipole moment, Debyes
ν = molecular volume, A^3
ρ = density, g/cm^3
σ = London parameter, cm^3
ω = accentric factor

Superscripts

assoc = association reaction, Eq. 2
net = sum of all interactions
overbar (-) = mean parameter of solute and solvent

Subscripts

cav = cavity interaction
C = carbon
es = electrostatic interaction
gas = gas phase reaction
i = ith solute
S_i = solute
S_iC = carbon-solute complex
solvent = solvent phase reaction
vdw = van der Waals' interaction
w = water

LITERATURE CITED

Abe, I., K. Hayashi, M. Kitagawa, and T. Urahata, "Adsorptive Mechanism on Activated Carbon in the Liquid Phase," *Bull. Chem. Soc. Jap.*, **53**, 1199 (1980).

Altshuler, G., and G. Belfort, "Selective Adsorption of Organic Homologues onto Activated Carbon from Dilute Aqueous Solutions: III. Branching and Predictions," Am. Chem. Soc. Nat'l Mtg., Atlanta (March 28, 1981).

Belfort, G., "Selective Adsorption of Homologues onto Activated Carbon from Dilute Aqueous Solutions. Solvophobic Interaction Approach: II. Development and Test of Theory," *Chemistry in Water Reuse*, **2**, W. J. Cooper, Ed., Ann Arbor Science, Ann Arbor, MI (1981a).

Belfort, G., "Similarity of Ideal Adsorbed Solution and Potential Theories for Adsorption from a Bulk Phase onto a Solid Surface," *AIChE J.*, **27**, 1021 (1981b).

Defay, R., I. Prigogine, A. Bellemans, and D. H. Everett, Translator, "Surface Tension and Adsorption," John Wiley and Sons, New York (1966).

Freundlich, H., *Colloid and Capillary Chemistry*, Methuen and Co., Ltd. London (1926).

Halicioglu, J., and O. Sinanoglu, "Solvent Effects on Cis-Trans Azobenzene Isomerization," *Ann. N.Y. Acad. Sci.*, **158**, 308 (1969).

Horvath, C., W. Melander, and I. Molnar, "Solvophobic Interactions in Liquid Chromatography with Nonpolar Stationary Phases," *J. Chrom.*, **125**, 129 (1976).

Leo, A., P. Y. C. Jow, C. Silypo, and C. Hansch, "Calculation of Hydrophobic Constant (Log P) from π and f constants," *J. Med. Chem.*, **18**(9), 865 (1975).

Manes, M., "The Polanyi Adsorption Potential Theory and its Applications to Adsorption from Water Solution onto Activated Carbon," *Activated Carbon Adsorption of Organics from Aqueous Phase*, **1**, Ann Arbor Science (1980).

Manuf. Chemists Assoc. Research Project, Chemical Thermodynamics Properties Center, "Selected Values of Properties of Chemical Compounds," Texas A&M University, College Station (1966).

McBain, J. W., *The Sorption of Gases and Vapors by Solids*, George Routledge & Sons, Ltd., London (1932).

McGuire, M. J., I. H. Suffett, and J. V. Radziul, "Assessment of Unit Processes for the Removal of Trace Organic Compounds from Drinking Water," *J. Am. Water Works Assoc.*, **70**, 565 (1978).

McGuire, M. J. and I. H. Suffett, "The Calculated Net Adsorption Energy Concept," *Activated Carbon Adsorption of Organics from the Aqueous Phase*, **1**, Ann Arbor Science (1980).

Miller, S., "Adsorption on Carbon: Solvent Effects on Adsorption," *Environ. Sci. Technol.*, **14**(8), 910 (1980a).

Miller, S., "Adsorption on Carbon: Solvent Effects on Adsorption," *Environ. Sci. Technol.*, **14**(9), 1037 (1980b).

Quayle, O. R., "The Parachors of Organic Compounds," *Chem. Revs.*, **53**, 439 (1953).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill, New York (1977).

Sinanoglu, O., "Solvent Effects on Molecular Associations," *Molecular Associations in Biology*, B. Pullman, Ed., Academic Press, New York 427 (1968).

Sinanoglu, O., "The Solvophobic Theory for the Prediction of Molecular Conformations and Biopolymer Bindings in Solutions with Recent Direct Experimental Tests," *Int. J. Quant. Chem.*, **18**, 381 (1980).

Suffet, I. H., "An Evaluation of Activated Carbon for Drinking Water Treatment," *Am. Water Works Assoc. J.*, **72**(1), 41 (1980).

Sugden, S., "A Relation Between Surface Tension, Density, and Chemical Composition," *J. Chem. Soc.*, **125**, 1177 (1924).

Vedeneyev, V. I., L. V. Gurvich, V. N. Kondrat'yev, and V. A. Medvedev, *Bond Energies, Ionization Potentials and Electron Affinities*, St. Martins Press, New York (1966).

Woodfield, K., "Adsorption of Organic Homologues from Aqueous Solution onto Activated Carbon," Masters Thesis, Rensselaer Polytechnic Institute (1982).

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Characterization of Mixing in Reactor Systems through Analysis of Regional Tracer Dilution Data Obtained with a Gamma Camera

A new approach to the characterization of flow patterns and mixing through analysis of regional tracer dilution data obtained with a gamma camera is presented. Studies performed in a small, two-dimensional, multiple-inlet vessel demonstrate the experimental technique and how data are analyzed to determine the intravessel spatial distribution of fluid deriving from the traced stream. Good agreement is shown between calculated values of the flow distribution and visually observed flow patterns.

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SCOPE

While numerous models have been proposed to characterize fluid mixing in reactor vessels (e.g., Weinstein and Adler, 1967; Nishimura and Matsubara, 1970; Goto et al., 1973; Dudukovic, 1977; Spencer et al., 1980), their assessment has been relatively circumscribed due to the limited availability of relevant and detailed experimental data. Recently, it has been shown that

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