Size-Controlled Capacity and Isocapacity Concentration in Freundlich Adsorption

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ABSTRACT: The Freundlich isotherm is a classic model widely used to analyze the equilibrium of solution-phase adsorption. Further analysis of the adsorption mechanism has, however, been hindered by the empirical nature of the Freundlich isotherm. By deriving the Freundlich isotherm from the Gibbs equation, this study presents a novel interpretation of the classic model with theoretical definitions for model parameters. The new interpretation shows that the inverse of the Freundlich power is linearly correlated with the molecular weight of an adsorbate for congeners with similar chemical structures, revealing a previously unappreciated dependence of adsorption capacity on the molecular size of the adsorbate. The new interpretation also shows a linear correlation between the Freundlich power and the logarithm of the equilibrium constant, exposing the existence of an isocapacity concentration for the adsorption of congeners. The quantitative structure–activity relationships, known as QSARs, represented by these linear correlations are validated using experimental data reported in the literature, including the adsorption of aliphatic alcohols by an activated carbon and the adsorption of aromatic hydrocarbons adsorption by an aquitard soil. These results provide an unprecedented explanatory power to understanding experimental observations of solution-phase adsorption using the Freundlich isotherm.

1. INTRODUCTION

Adsorption occurs when a chemical compound dissolved in an aqueous solution adheres to the surface of a solid material known as the adsorbent. Adsorption is critical for controlling the transport of chemicals in nature as well as their separation and transformation in water and wastewater treatment. An important objective in understanding adsorption is to determine the maximal amount that the compound, known as an adsorbate, can adhere to the adsorbent surface, defining the adsorption capacity q. It is widely accepted that q is controlled by the chemical equilibrium between the adsorbent surface and the aqueous solution through an isothermal relationship with the solution concentration of adsorbate, c. The adsorption isotherm defined by q and c is believed to depend on the molecular properties of adsorbates, indicating the existence of quantitative structure–activity relationships (QSARs) that can link the macroscopic equilibrium to its microscopic mechanism.

Many efforts have been made previously to define QSARs for the adsorption of compounds by solids from solution. To do so, researchers first select a physical model and reduce experimentally obtained values of q and c to a few of model parameters. The parameters are then related to the molecular properties of adsorbates such as solubility, molecular volume, polarity, and bonding characteristics. So far, all QSARs developed using popular models, such as those proposed by Polanyi, Dubinin, and Freundlich, require using a large number of undefined numerical parameters to characterize adsorption potentials and equilibrium constants, therefore limiting the usefulness of QSARs. Establishing QSARs using well-defined parameters requires theoretical advances on the molecular mechanism of solution-phase adsorption.

The Freundlich model is a classical isothermal relationship, first proposed by Saussure and later popularized by Freundlich. The Freundlich isotherm is commonly considered to be an empirical proposition, relating q and c using a power function

\[ q = K_c c^{1/n} \]  

where n is the inverse of power and K_c is the equilibrium constant. In spite of being empirical, the Freundlich model often provides an excellent description of isotherms experimentally obtained for solution-phase adsorption. The superb applicability of the Freundlich isotherm has spurred interests in search for a theoretical basis according to fractal reaction order, multiple-layer adsorption, and surface potential heterogeneity. The introduction of these concepts has not, however, shed much light on how to relate the adsorption capacity with the molecular properties of adsorbates.

The objective of this study is to establish a theoretical foundation for the empirically defined Freundlich isotherm so that the adsorption capacity can be quantitatively related to the molecular properties of adsorbates. Compared to previous

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efforts, the novelty of this study is the recognition that the solution-phase adsorption is predominantly controlled by the capillary effect of surface tension, as described by the phase equilibrium of Gibbsian thermodynamics. According to the Gibbsian interpretation of the Freundlich isotherm, two previously unappreciated results are discovered for solution-phase adsorption, including (1) the linear correlation between the inverse of the Freundlich power, \( n \), and the molecular size of the adsorbate among congeners with similar chemical structures and (2) the linear correlation between the Freundlich power and the logarithm of the equilibrium constant, revealing the existence of an isocapacity concentration (ICC) for the adsorption of congeners. Both correlations are demonstrated using experimental values of \( n \) and \( K_f \) reported in the literature. These results offer new explanatory power to understanding experimental observations of solution-phase adsorption using the classic Freundlich isotherm.

2. RESULTS AND DISCUSSION

The distribution of materials between heterogeneous phases under the influence of surface tension has been extensively analyzed by Gibbs and others. The following results of their analyses are taken as the starting point of this study. First, the internal energy of the surface can only be increased by the absorption of heat, the reception of work, and the addition of materials

\[
\partial U = T \partial S + \gamma \partial A + \sum \mu_i \partial n_i
\]

(2)

where \( U \) is the internal energy, \( T \) is the absolute temperature, \( S \) is the surface entropy, \( \gamma \) is the surface tension, \( A \) is the surface area, \( \mu \) is the chemical potential, \( m \) is the number of moles of a material, and subscript \( i \) enumerates the adsorbate (\( i = \) null), the solid adsorbent (\( i = s \)), and water (\( i = w \)). Second, the assertion of eq 2 indicates that the sum of the remaining three derivatives from the complete differentiation of \( U \) should be zero

\[
S \partial T + A \partial \gamma + \sum m_i \partial \mu_i = 0
\]

(3)

giving a two-dimensional equivalent of the Gibbs–Duhem equation. Third, at equilibrium, the chemical potential for either the adsorbate or water has a single value on the surface and in the solution, allowing the computation of \( \mu_i \) (\( i = \) null or \( w \)) using the solution concentration

\[
\mu_i = \mu_i^\ominus + RT \ln \frac{c_i}{c_i^\ominus}
\]

(4)

where the Plimsoll symbol denotes the reference state of a pure liquid of either the adsorbate or water. Similarly, the chemical potential of the adsorbent is also the same on the surface and in the bulk solid.

The Gibbs equation is obtained from eq 3 with a few simplifications. First, when the solution is dilute, the concentration of water, \( c_w \), is approximately constant, giving \( \partial \mu_w = 0 \). Second, the change of the adsorbate solution concentration should not result in variation of the adsorbent’s chemical potential in the solid, and thus \( \partial \mu_s = 0 \). Third, since temperature is kept constant during the measurement of an isotherm, \( \partial T = 0 \). Taking these conditions into eq 3, the Gibbs equation for adsorption is obtained as

\[
\Gamma = -\frac{\partial y}{\partial \mu}
\]

(5)

where \( \Gamma = n/A \) is the molar density of the adsorbate on the surface. The Gibbs equation indicates that adsorption is a result of reducing surface tension by increasing the chemical potential of the adsorbate. Although the coexistence of the Gibbs equation and the Freundlich isotherm has been well noted since the early development of Gibbsian thermodynamics, it is surprising that no effort has been made to connect the two classic models. Solving the Gibbs equation with an appropriate boundary condition to obtain the Freundlich isotherm is the basic approach used in this study.

The Gibbsian interpretation of the Freundlich isotherm is developed in five steps. First, the development begins with identifying an equation of state for the adsorbent surface according to the conservation of surface area (Section 2.1). Second, the Freundlich isotherm is derived by solving the Gibbs equation using the equation of state (Section 2.2), providing theoretical definitions for the inverse of the Freundlich power, \( n \), and equilibrium constant, \( K_f \). Third, utilizing the new definition of \( n \), a novel QSAR is established between the inverse of the Freundlich power and the molecular size of an adsorbate (Section 2.3), which is then demonstrated using experimentally obtained values of \( n \) reported in the literature. Fourth, using the new definition of \( K_f \), a linear relationship between \( \ln K_f \) and \( 1/n \) is revealed, suggesting the existence of isocapacity concentration for adsorption (Section 2.4). Last, the control of adsorption energetics by surface tension is discussed by comparing chemical potentials on the surface and in the solution (Section 2.5).

2.1. Equation of State for the Surface.

To derive an equation of state for the adsorbent surface in contact with an aqueous solution, eq 2 can be further simplified for adsorption. The addition of an adsorbate to the surface requires the removal of both adsorbent and water from the surface. As shown in Figure 1, since the adsorbate on the surface interacts with both the solid and the solution, the surface defined by the contact of the adsorbent and water (gray and blue blocks in a) is replaced by the adsorbate (pink block in b) after adsorption. The conservation of surface area (black lines in Figure 1a, b) requires

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c01144)

Figure 1. Molecular arrangements at the surface of an adsorbent (gray) in contact with a solution (blue) (a) before and (b) after adsorption, showing the replacement of both adsorbent and water molecules (dark gray and navy blue squares) by an adsorbate molecule (pink square), without changing the surface area at the solid–water interface (black lines). The numbers of adsorbent and water molecules replaced by an adsorbate molecule define stoichiometries \( \nu_a \) and \( \nu_w \), which equal 2 and 4, respectively, in this illustration.
\[ \frac{\partial m}{\partial s} = - \frac{\partial m_w}{\nu_w} = - \frac{\partial m_s}{\nu_s} \quad (6) \]

where \( \nu_w \) and \( \nu_s \) are the numbers of water and adsorbent molecules replaced by an adsorbate molecule, respectively. Taking eq 6 into eq 2 gives
\[ \partial U = T \partial s + \gamma \partial A + \Delta \mu \partial m \quad (7) \]
where the difference in chemical potential is
\[ \Delta \mu = \mu - \nu_w \mu_w - \nu_s \mu_s \quad (8) \]

It is reasonable to assume that the surface entropy, similar to the chemical potential on the surface, has addable contributions from the adsorbate, adsorbent, and water
\[ \partial S = \sum \phi_i \partial m_i \quad (9) \]
where \( \phi_i \) is the molar entropy of \( i \). The material balance described above gives
\[ \Delta s = s - \nu_w s_w - \nu_s s_s \quad (10) \]
Taking eq 10 into eq 7 gives
\[ \partial U = \gamma \partial A + (\Delta \mu + T \Delta s) \partial m \quad (11) \]

Since the sum of chemical potential and the product of molar entropy and temperature is the molar enthalpy
\[ \Delta h = \Delta \mu + T \Delta s \quad (12) \]

Equation 11 is rewritten as
\[ \partial U = \gamma \partial A + \Delta h \partial m \quad (13) \]
where
\[ \Delta h = h - \nu_w h_w - \nu_s h_s \quad (14) \]
accounting for the change of molar enthalpy on the surface by adsorption.

A couple of reasonable assumptions can be made to further develop eq 13. First, the surface density of an adsorbate is assumed to be independent of the surface area
\[ \Gamma = \frac{\partial m}{\partial A} \quad (15) \]
Second, the surface-normalized internal energy is assumed to remain constant
\[ \frac{\partial U}{\partial A} = \gamma_0 \quad (16) \]
Taking eqs 15 and 16 into eq 13 gives an equation of state for the surface
\[ \gamma = \gamma_0 - \Delta h \Gamma \quad (17) \]

Equation 17 shows that surface tension is reduced by adsorption, a well-known experimental fact for the adsorption of surfactants to the surface of a liquid interfacing with a vapor phase.18–20

2.2. Gibbsonian Interpretation of the Freundlich Isotherm. The Freundlich isotherm is obtained by simultaneously solving eqs 5 and 17. Combining the two equations gives
\[ \partial \mu = \Delta h \frac{\partial \Gamma}{\Gamma} \quad (18) \]
by assuming that \( \Delta h \) is independent of the surface density of an adsorbate. Equation 18 can be integrated from the reference state to the state of equilibrium
\[ \int_{\mu_0}^{\mu} \frac{\partial \mu}{\Delta h} = \int_{\Gamma}^{\Gamma_0} \frac{\partial \Gamma}{\Gamma} \quad (19) \]
which gives
\[ \mu = \mu_0 + \Delta h \ln \frac{\Gamma}{\Gamma_0} \quad (20) \]

Since the adsorbate has the same chemical potential on the surface and in the solution at equilibrium, eq 20 is compared to eq 4. After canceling out the chemical potential at the reference state (see below), the following relation is obtained
\[ \ln \frac{\Gamma}{\Gamma_0} = \frac{RT}{\Delta h} \ln \frac{c}{c_0} \quad (21) \]

Provided that \( \varphi \) is the specific surface area that the adsorbent has, \( \Gamma \) can be converted to the adsorption capacity commonly expressed in a unit of mg g\(^{-1}\)
\[ q = \Gamma \varphi \quad (22) \]
Taking eq 22 into eq 21 gives
\[ \ln \frac{q}{q_0} = \frac{RT}{\Delta h} \ln \frac{c}{c_0} \quad (23) \]
where \( q_0 \) is the adsorption capacity at the reference state. Comparing eq 23 to the Freundlich isotherm in eq 1 reveals that they are equivalent under the following conditions
\[ n = \frac{\Delta h}{RT \varphi} \quad (24) \]
and
\[ K_F = \frac{q_0}{(c_0)^{1/n}} \quad (25) \]
Since \( n \) is always greater than zero for solution-phase adsorption, eq 24 indicates that \( \Delta h > 0 \). The increase of enthalpy at the interface is consistent with the understanding that solution-phase adsorption is endothermic21 even through the mechanical energy due to surface tension is simultaneously reduced.

An important condition used in the derivation is that the reference state is the same for the adsorbate on the surface and its counterpart in the solution. For example, when the adsorbate is benzene, the reference state for benzene in the solution is the benzene liquid. Similarly, the derivation also requires the reference of benzene on the surface to be a pure phase in equilibrium with the benzene liquid. Obviously, the pure phase of surface benzene is not a liquid but a solid phase because the two phases are not miscible. This indicates that the reference state is a critical state for the pure adsorbate liquid and the pure adsorbate surface phase. The correct identification of the reference state is crucial to defining the physical meanings of \( q_0 \) and \( c_0 \) (see below).

2.3. Freundlich Power and Adsorbate Size. The Gibbsonian interpretation of \( n \) indicates that the molecular size of an adsorbate is the main determinant of adsorption capacity. This can be seen by combining eqs 14 and 24, giving
\[ nRT = h - (\nu_w h_w + \nu_s h_s) \quad (26) \]
For adsorbates with similar structures, their enthalpies are predominantly controlled by the common functional group and thus \( h \) remains constant among the congener adsorbates. If the adsorbates are dissolved by the same solvent such as water and adsorbed by the same adsorbent, \( h_w \) and \( h_s \) are the same for all of
the congeners. The stoichiometries for surface replacement, \( \nu_{w} \) and \( \nu_{s} \), increase with the increase of an adsorbate’s molecular size. For two-dimensional adsorbates whose molecules can fit entirely on the surface, their molecular sizes can be represented by their molecular weights because the two parameters are linearly correlated. Since both solid and water assume two-dimensional configurations on the surface,\(^{22,23}\) stoichiometries can be replaced by

\[
\nu_{w} = \frac{M}{M_{w}} \quad (27) \\
\nu_{s} = \frac{M}{M_{s}} \quad (28)
\]

where \( M, M_{w}, \) and \( M_{s} \) are the molecular weights of adsorbate, water, and adsorbent, respectively. The molecular weight of the adsorbent is defined, according to the conservation of surface area shown in Figure 1, as the mass of one mole of solid material replaced by one mole of the adsorbate; therefore, \( M_{s} \) increases with the molecular size of the adsorbate and thus its molecular weight. Since \( M_{s} \) is proportional to \( M, \nu_{s} \) in eq 28 is constant. Combining eqs 26 and 27 gives

\[
n = \left( \frac{h}{RT} - \frac{\nu_{h_{s}}}{RT} \right) - \frac{h_{w} M}{RT M_{w}} \quad (29)
\]

indicating a linear correlation between \( n \) and \( M \).

The size-controlled adsorption predicted by the Gibbsian interpretation of \( n \) is demonstrated using the adsorption of aliphatic alcohols by an activated carbon\(^{24}\) and the adsorption of aromatic hydrocarbons by an aquitard soil.\(^{25}\) Both sets of experimental data have been fitted to the Freundlich isotherm in the original reports and are used without modification. As shown in Figure 2, excellent linearity is observed between \( n \) and \( M/M_{w} \).

Figure 2. Linear correlation between the inverse of the Freundlich power, \( n \), and the ratio of the molecular weights of an adsorbate and water, \( M/M_{w} \). Colors: red, aliphatic alcohols adsorbed by an activated carbon (from left to right: 1-propanol, 1-butanol, 1-hexanol, and 1-pentanol); blue, aromatic hydrocarbons by an aquitard soil (from left to right: benzene, naphthalene, fluorene, phenanthrene, and pyrene). Lines are least-squares fits to eq 29 with coefficients of determination of \( R^{2} = 0.99 \).

\( M_{w} \) with \( M_{s} = 18 \text{ g mol}^{-1} \), as predicted by eq 29 but not revealed by the original studies. The least-squares regression estimates \( h_{w} = -0.28 (\pm 0.03) \text{ RT} \) and \( h - \nu_{h_{s}} = 0.76 (\pm 0.15) \text{ RT} \) for the adsorption of aliphatic alcohols and \( h_{w} = -0.058 (\pm 0.005) \text{ RT} \) and \( h - \nu_{h_{s}} = 0.75 (\pm 0.04) \text{ RT} \) for the adsorption of aromatic hydrocarbons (standard deviations in parentheses).

In both examples, the surface molar enthalpy of water is found to be negative with \( h_{w} < 0 \) while the difference of surface molar enthalpy between the adsorbate and the adsorbent is positive with \( h - \nu_{h_{s}} > 0 \). The observation that the surface adsorbate has a higher enthalpy than both surface water and solid is consistent with Einstein’s theory of heat absorption, in which stronger molecular interactions lead to higher heat content before reaching the Dulong–Petit limit.\(^{26}\) In the adsorption system, water and solid molecules at the solid–water interface are replaced by the adsorbate because the latter can interact strongly with the solid.\(^{26}\)

The estimates of \( h - \nu_{h_{s}} \) are identical for the adsorption of aromatic hydrocarbons by the activated carbon and that of aliphatic alcohols by the aquitard soil even though aromatic hydrocarbons are often considered to be hydrophobic and aliphatic alcohols hydrophilic. The equality of \( h - \nu_{h_{s}} \) in the two adsorption systems is, however, consistent with the belief that the adsorption of organic molecules by soils and sediments mostly occurs on the surface of their carbonaceous constituents made of graphitic microcrystals.\(^{27,28}\) The absolute value of \( h_{w} \) associated with the activated carbon is greater than that associated with the aquitard soil, consistent with the expectation that the interaction of water with a carbonaceous adsorbent becomes increasingly unfavorable as the extent of graphitization decreases.

### 2.4. Equilibrium Constant and Isocapacity Concentration

The Gibbsian interpretation of the Freundlich equilibrium constant \( K_{p} \), as shown in eq 25, indicates that \( K_{p} \) is correlated with power 1/\( n \). Equation 25 can be linearized as

\[
\ln K_{p} = \ln q^{\Theta} - \frac{1}{n} \ln c^{\Theta} \quad (30)
\]

The negative correlation of \( K_{p} \) and 1/\( n \) that for \( \ln q^{\Theta} > 0 \) (which can always be achieved by using a small unit), \( K_{p} \) cancels part of the effect that the increase of 1/\( n \) brought about on the adsorption capacity. According to eq 1, an increase of 1/\( n \) (i.e., a decrease of \( n \)) increases \( q \) for any given concentration \( c \) if \( K_{p} \) is constant. Since \( K_{p} \) decreases as 1/\( n \) increases, the increase of adsorption capacity due to the increase of 1/\( n \) is tapered by the simultaneous decrease of \( K_{p} \). This analysis reveals a compensation effect between \( K_{p} \) and 1/\( n \), which has been previously described on an empirical basis according to the Polanyi–Dubinin model of adsorption\(^{24}\) and used to correlate the adsorption of atrazine by different soils.\(^{9,10}\)

The presence of \( K_{p} \) in 1/\( n \) compensation, which has not been previously explained, indicates the existence of an isocapacity concentration under which all related adsorption isotherms exhibit the same capacity. Figure 3a shows the linear correlations between \( \ln K_{p} \) and 1/\( n \), as predicted by eq 30 but not revealed by the original studies, for the adsorption of aliphatic alcohols by the activated carbon and the adsorption of aromatic hydrocarbons by the aquitard soil.\(^{25}\) Adsorbates within a congener series show an ICC because they have the same reference state. For example, a naphthalene can be regarded as two benzene molecules fused together, and thus their liquids have the same mass concentration (or more commonly, density). Isotherms for each set of congeners pass through the same point defined by \( q^{\Theta} \) and \( c^{\Theta} \), where \( c^{\Theta} \) is the isocapacity concentration.

Least-squares regression estimates \( q^{\Theta} = 10^{3.39 (\pm 0.54)} \text{ mg g}^{-1} \) and \( c^{\Theta} = 10^{11.2 (\pm 2.0)} \text{ mg L}^{-1} \) for aliphatic alcohols and \( q^{\Theta} = 10^{4.66 (\pm 0.3)} \text{ mg g}^{-1} \) and \( c^{\Theta} = 10^{8.21 (\pm 0.8)} \text{ mg L}^{-1} \) for aromatic hydrocarbons. The unrealistic values of \( q^{\Theta} \) and \( c^{\Theta} \) indicate that the reference state is a fictional pseudo-thermodynamic state. For real concentrations with \( c < c^{\Theta} \), adsorbates with small 1/\( n \) values
and thus large $K_F$ values have high adsorption capacities, as demonstrated by the isotherms of aliphatic alcohols obtained with the activated carbon in Figure 3b. According to Figure 2, adsorbates with small $1/n$ values and large $K_F$ values have high molecular weights, indicating that large molecules are favored among the congeners in adsorption by the activated carbon and the aquitard soil.

### 2.5. Chemical Potentials on Surface and in Solution.

The Gibbsian interpretation of the Freundlich isotherm is successfully exhibited by both theoretical derivation and experimental support. The physical meaning of adsorption can be further explored by considering the change of enthalpy in the solution during adsorption. This can be done by first assuming that the entropy is predominantly controlled by configurations of mixing

$$S = -nR \ln \frac{n}{n_T}$$  \hspace{1cm} (31)

where $n_T$ is the total moles of the adsorbate and water in the solution. Since the pure adsorbate liquid at the reference state has a zero configurational entropy, the change of molar entropy from the reference state for the adsorbate is computed to be

$$\Delta S = \frac{dS}{dn} = -R \left( \ln \frac{n}{n_T} + 1 \right)$$  \hspace{1cm} (32)

By neglecting the difference of the adsorbate and water in size, $n/n_T$ is replaced by $c/c^\Theta$

$$\Delta S = -R \left( \ln \frac{c}{c^\Theta} + 1 \right)$$  \hspace{1cm} (33)

According to eq 4, the change of chemical potential for the adsorbate at the equilibrium state from the reference state is

$$\Delta \mu = \mu - \mu^\Theta = RT \ln \frac{c}{c^\Theta}$$  \hspace{1cm} (34)

Using eq 12, the change of molar enthalpy can be computed as

$$\Delta h^* = -(\Delta h + \Delta s) = RT$$  \hspace{1cm} (35)

Taking eq 35 into eq 4 gives

$$\mu = \mu^\Theta + \Delta h^* \ln \frac{c}{c^\Theta}$$  \hspace{1cm} (36)

which has the same form as eq 20 for the chemical potential of the adsorbate on the surface. The similarity of the two equations is not surprising because as the surface tension is reduced by adsorption, the surface-normalized mechanical energy is reduced accordingly, transforming into enthalpy to maintain a constant surface-normalized internal energy (cf. eq 16). From this viewpoint, $n$ is the ratio between surface and solution enthalpies for the adsorbate and $nRT$ is the molar heat of adsorption.

### 3. CONCLUSIONS

Each year, thousands of experimental studies on solution-phase adsorption are reported in peer-reviewed publications using the Freundlich isotherm, in conjunction with other classical models such as the Langmuir isotherm and the Dubinin–Radushkevich (DR) isotherm, for data analysis. In spite of their extensive use, the theoretical foundations of these models are still not well established. As a result, model selection is frequently conducted by comparing the coefficients of determination in regression, which often exhibit little difference between different models. More importantly, the statistical approach of model selection yields little insight on how to connect the macroscopic observation with the molecular mechanism through quantitative structure–activity relationships for solution-phase adsorption.

On the basis of Gibbsian thermodynamics, this study tackles the challenge of QSAR development for solution-phase adsorption from a theoretical perspective. In this study, the capillary effect of surface tension on solution-phase adsorption, lacking in Langmuir, DR, and other models developed for gas-phase adsorption, is explicitly recognized for the first time. Accounting for the change of surface tension in adsorption, the Freundlich isotherm is derived by solving the Gibbs equation, which provides theoretical definitions for empirical model parameters $n$ and $K_F$. The Gibbsian interpretation of the Freundlich isotherm results in the discovery of two linear correlations showing the existence of size-controlled capacity and isocapacity concentration in solution-phase adsorption. These correlations are validated using two sets of experimentally obtained parameters reported in the literature. Further validation is currently being performed using experimental data carried out in the author’s laboratory as well as the experimental data that have been published by other investigators in the literature.

It is worth noting that adsorption is also controlled by mass transfer and reaction kinetics in addition to equilibrium. For porous adsorbents such as activated carbon and soil particles, an adsorbate must diffuse through pores and then the stagnant water films near the adsorbent surface even when mixing is provided to homogenize the adsorbate concentration outside the adsorbents. The driving force of these mass transfer steps, as well as the occurrence of adsorption at the adsorbent surface, is regulated by the adsorption capacity. Hence, establishing quantitative relationships for the adsorption capacity and adsorbate molecular properties also provides the necessary and basic knowledge to further understand the molecular control of mass transfer and kinetics in solution-phase adsorption.

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*Figure 3. Isocapacity concentration (ICC) of Freundlich isotherms. (a) Linear correlation between the natural logarithm of the Freundlich prepower parameter $K_F$ expressed in a unit of mg L$^{(1-1/n)}$ g$^{-1}$ and the Freundlich power parameter $1/n$. Colors: colors other than blue, aliphatic alcohols adsorbed by an activated carbon (yellow, 1-propanol; green, 1-butanol; purple, 1-hexanol; orange, 1-pentanol); blue, aromatic hydrocarbons by an aquitard soil (from right to left: benzene, naphthalene, phenanthrene, and pyrene). Lines are least-squares fits to eq 30 with coefficients of determination of $R^2 = 0.98$ (red) and 0.94 (blue), respectively. (b) Freundlich isotherms of aliphatic alcohols showing the ICC.*
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