

Adsorption at Liquid Interfaces: The Generalized Langmuir Isotherm and Interfacial Structure

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The thermodynamics of adsorption of amphiphilic surface-active compounds at the interface between two immiscible liquids is considered. At the interface, these molecules are supposed to replace a few of the adsorbed molecules of both solvents. Classical isotherms of adsorption (Frumkin, Langmuir, Henry) were based on the model of nonpenetrable interface, where an adsorbate can substitute only molecules of one solvent. However, at the interface between two immiscible electrolytes, like nonpolar oil–water interfaces, or liquid membrane amphiphilic molecules can substitute molecules of both solvents; therefore, classical isotherms are not applicable in these cases. The generalization of Langmuir and Frumkin isotherms for permeable and nonpermeable interfaces, known as the Markin–Volkov (MV) isotherm, gives the possibility to analyze adsorption and the interfacial structure in a general case. In the present paper, the adsorption isotherms of pentafluorobenzoic acid at the octane–water interface at various pH were measured by the drop-weight method. The thermodynamic parameters of pentafluorobenzoic acid (PFBA) adsorption at the octane–water interface were found. From the measurements of PFBA adsorption, the structure of the octane–water interface was determined. Substitution of one adsorbed octane molecule requires approximately three adsorbed PFBA molecules. This result shows that the orientation of solvent molecules at the interface is different from the bulk solution. Adsorbed octane molecules have a lateral orientation with respect to the interface. Gibbs free energy of adsorption equilibrium and thermodynamic parameters of PFBA adsorption show that the adsorption of PFBA at the octane–water interface is accompanied by a reduction in the attraction between adsorbed PFBA molecules as the pH decreases to the acidic region.

Introduction

Traditional models for calculation of adsorption isotherms^{1–7} are based on the assumption that surface-active compounds can substitute molecules of only one solvent and cannot penetrate the interface (Figure 1a). Although these models are useful for metal–water interfaces, recent interest has focused on the electrochemistry of amphiphilic compounds, which can penetrate both phases and replace adsorbed molecules of both solvents,^{8–14} for example, water and oil (Figure 1b). Amphiphilic molecules consist of two moieties with opposing properties: a hydrophilic polar head and a hydrophobic tail. We present here a theoretical analysis of the generalized Frumkin adsorption isotherm for surface-active compounds with hydrophilic and hydrophobic groups.

In the present study, we examine the interfacial adsorption of PFBA ($pK_a = 1.48$) in an attempt to understand the adsorptive behavior of nonamphiphilic molecule PFBA with pH-dependent hydrophobic and hydrophilic properties by considering the thermodynamics of adsorption equilibrium at the interface between two immiscible liquids. The adsorption of PFBA at the octane–water interface will be discussed as a model for the adsorption of adsorbate, which penetrates the interface and substitutes adsorbed molecules of both solvents.

Materials and Methods

A system consisting of equal volumes of octane and water was equilibrated for 48 h. All the solutions were prepared with twice-distilled water. Chromatographic grade octane purchased from Fluka was used in the experiments. Reagent grade pentafluorobenzoic acid was bought from Aldrich Chemical Co. Potassium dihydrogen phosphate, sodium hydroxide, and sulfuric acid were “Baker analyzed” reagents.

Various quantities of PFBA were added to water saturated with octane and equilibrated for 48 h with an equal volume of an octane saturated with water. The interfacial tension at the water–octane interface was determined by using the drop-weight method at 22 °C. This method determines the weight and volume of the drop falling from the end of a capillary tube under the force of gravity. The surface tension γ is obtained from the equation:

$$\gamma = \frac{V(d_1 - d_2)fg}{r} \quad (1)$$

where f is a correction factor from the Harkins–Brown table.¹⁵ It is a function of $r/V^{1/3}$ and takes into account the deviation of the drop shape from an ideal sphere. V is the volume of the drop, d_1 and d_2 are the densities of the immiscible liquids, and g is the acceleration due to gravity. The radius of the tip, r , is taken as the radius of the outside wall when the drop covered the bottom of the tip or radius of the inside wall when the liquid

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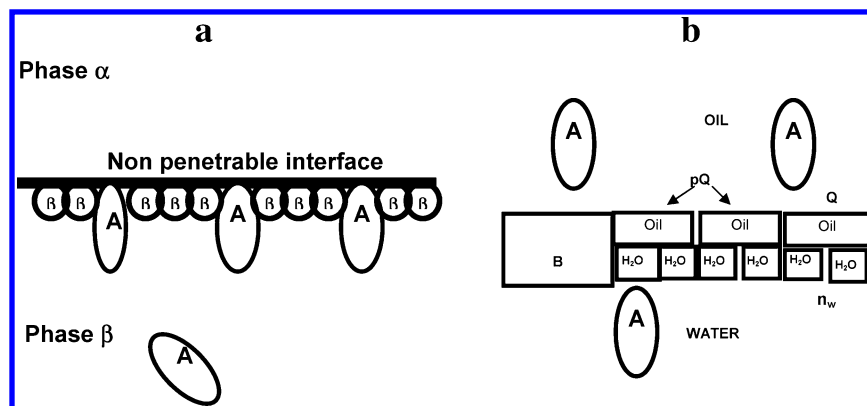


Figure 1. (a) Langmuir model of adsorption of a surfactant substituting adsorbed solvent molecules at the interface without permeation the interface. (b) General structure of the interface with adsorbed monolayer of surfactant B penetrating the interface with substitution of adsorbed molecules of both solvents. Abbreviations: (A) surfactant, (Q) quasimolecule of solvents, (B) p quasimolecules of solvents substituted by one or a group of adsorbate molecules A.

exuded without wetting the bottom of the orifice. The surface tension apparatus consists of a glass capillary tube, 2 cm³ syringe, micrometer, and a container. The internal capillary diameter was about 0.060 cm and the outer one was 0.522 cm. The drop lifetime used to establish adsorption equilibrium was at least 10 min. If the drops form quickly, they will detach prematurely. This early detachment causes errors in the measurement of interfacial tension. Thus, slow drop formation is imperative prior to detachment.

The remarkable accuracy of this method arises from the fact that the surface excess Γ is proportional to the surface activity $d\gamma/dc$, and the relatively small changes of γ due to changes of the concentration of the surface active compound are more important than the absolute values of the interfacial tension.

Two important details of the drop-weight method should be noted. First, it is essential to purify all of the solvents and solutes, including water, to remove all possible impurities, which can reduce interfacial tension. Second, the apparatus must also be assembled so that the influence of vibration is minimized. Otherwise, the drops will detach too soon and erroneous values of interfacial tension will be obtained.

The adsorption of pentafluorobenzoic acid at the octane–water interface is presented as the Gibbs surface excess, Γ . This is determined from the change in the interfacial tension using the Gibbs equation.

Theoretical Basis: Generalized Model

The interface between two immiscible liquids may be considered as a surface solution of surfactant in a special kind of solvent. To calculate the entropy of such a solution, we will adopt a popular lattice model and use lattice statistics, a widely used method for describing surface solutions. However, in the transition from three-dimensional (3-D) to two-dimensional (2-D) geometry one, should be careful enough not to overlook important peculiarities of 2-D solutions.

The solvent molecules do not form a monolayer, but rather a multilayer. Therefore, the transition from 3-D- to 2-D geometry should be specified. Consider molecules of both solvents, which are substituted by a surfactant (Figure 1b). Suppose that these molecules can be assembled into columns consisting of m_o molecules of oil and m_w molecules of water. Suppose that one column of oil molecules matches the n_w molecules of water. This match of 1 oil column and n_w water columns will be considered in what follows as a quasimolecule of solvent Q. These quasimolecules constitute a “monolayer” of solvent. They consist of m_o oil molecules and $n_w m_w$ water molecules.

Designate the molecules of surfactant in the bulk as A, and in the monolayer as B. At the interface, aggregation of surfactant molecules can take place, $rA \rightleftharpoons B$, such as dimerization of porphyrin or pheophytin molecules at the octane–water interface. Let the surfactant B replace p quasimolecules at the interface. Therefore, one can write

$$pQ + rA = B + p(\text{oil}) + pn_w(\text{water}) \quad (2)$$

The chemical potentials for the previous reaction are

$$p\mu_Q^s + r\mu_A^b = \mu_B^s + p\mu_o^b + pn_w\mu_w^b \quad (3)$$

By taking the 2-D solution as ideal, we have:

$$\mu_Q = \mu_Q^{0,s} + RT \ln X_Q^s \quad (4)$$

and

$$\mu_B^s = \mu_B^{0,s} + RT \ln X_B^s \quad (5)$$

In the bulk phase, we have

$$\mu_A^b = \mu_A^{0,b} + RT \ln X_A^b \quad (6)$$

$$\mu_o^b = \mu_o^{0,b} + RT \ln X_o^b \quad (7)$$

$$\mu_w^b = \mu_w^{0,b} + RT \ln X_w^b \quad (8)$$

In all of these equations, X designates the mole ratio of corresponding substances. By substituting these equations into eq 2, one obtains:

$$p\mu_Q^{0,s} + r\mu_A^{0,b} - \mu_B^{0,s} - p\mu_o^{0,b} - pn_w\mu_w^{0,b} + RT \ln \frac{(X_A^b)^r}{(X_o^b)^p (X_w^b)^{pn_w}} = RT \ln \frac{X_B^s}{(X_Q^s)^p} \quad (9)$$

By using the standard Gibbs free energy of adsorption:

$$\Delta_b^s G^0 = \mu_B^{0,s} - r\mu_A^{0,b} + p\mu_o^{0,b} + pn_w\mu_w^{0,b} - p\mu_Q^{0,s} \quad (10)$$

one obtains the adsorption isotherm:

$$\frac{X_B^s}{(X_Q^s)^p} = \frac{(X_A^b)^r}{(X_o^b)^p (X_w^b)^{pn_w}} \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (11)$$

We considered the 2-D solution of surfactant B in the solvent of quasiparticles Q in which the mole ratios were defined as

$$X_B^s = \frac{N_B^s}{N_B^s + N_Q^s}; \quad X_Q^s = \frac{N_Q^s}{N_B^s + N_Q^s} \quad (12)$$

Some authors prefer another set of definitions when real particles in the interface are considered. The equation for this state with real particles A, O, and W becomes:

$$X_A^s = \frac{N_A^s}{N_A^s + N_O^s + N_W^s} \quad (13)$$

$$X_Q^s = \frac{N_Q^s}{N_A^s + N_O^s + N_W^s} \quad (14)$$

$$X_W^s = \frac{N_W^s}{N_A^s + N_O^s + N_W^s} \quad (15)$$

and we can obtain:

$$X_B^s = \frac{X_A^s}{X_A^s + X_O^s}; \quad X_Q^s = \frac{X_O^s}{X_A^s + X_O^s} \quad (16)$$

The adsorption isotherm can then be presented in the form

$$\frac{X_A^s}{(X_Q^s)^p} (X_A^s + X_O^s)^{p-1} = \frac{(X_A^b)^r}{(X_O^b)^p (X_W^b)^{pn_w}} \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (17)$$

In the past, the adsorption isotherm was presented in terms of the fraction θ of the surface actually covered by the adsorbed surfactant.

If we introduce η as the ratio of areas occupied in the interface by the molecules of surfactant and oil, the mole fractions in surface solution can be presented as follows:

$$X_B^s = \frac{\Theta}{\Theta + \eta(1 - \Theta)}; \quad X_O^s = \frac{\eta(1 - \Theta)}{\Theta + \eta(1 - \Theta)} \quad (18)$$

The adsorption isotherm takes the form:

$$\frac{\Theta}{\eta^p (1 - \Theta)^p} [\Theta + \eta(1 - \Theta)]^{p-1} = \frac{(X_A^b)^r}{(X_O^b)^p (X_W^b)^{pn_w}} \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (19)$$

In this isotherm, the mole fractions X_A^b , X_O^b , X_W^b of the components in the bulk solution are presented. In the general case, they must be substituted with activities:

$$\frac{\Theta}{\eta^p (1 - \Theta)^p} [\Theta + \eta(1 - \Theta)]^{p-1} = \frac{(a_A^b)^r}{(a_O^b)^p (a_W^b)^{pn_w}} \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (20)$$

If the molecules B can interact as pairs in the adsorbed layer and the energy of each new particle is proportional to its

concentration, then their chemical potential, μ_B^s , instead of eq 5, should be presented as:

$$\mu_B^s = \mu_B^{s,0} + RT \ln X - 2aRTX \quad (21)$$

where a is so-called attraction constant. Then after some algebra, we obtain the isotherm:⁸⁻¹⁴

$$\frac{\Theta[\eta - (\eta - 1)\Theta]^{p-1}}{\eta^p (1 - \Theta)^p} \exp(-2a\Theta) = \frac{(X_A^b)^r}{(X_O^b)^p (X_W^b)^{pn_w}} \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (22)$$

Recall that η was introduced as the ratio of areas occupied in the interface by the molecule of surfactant to the same of oil, and p was introduced as the number of columns of oil, which could be supplanted with one molecule of surfactant. Therefore, p is a relative size of the surfactant molecule in the interfacial layer. It is reasonable to suppose that:

$$\eta = p \quad (23)$$

If the concentration of surfactant in the solution is not high and the mutual solubility of oil and water is low, then we can use the approximation $X_O^b = X_W^b = 1$, so that the general eq 20 simplifies to:

$$\frac{\Theta[p - (p - 1)\Theta]^{p-1}}{p^p (1 - \Theta)^p} \exp(-2a\Theta) = (X_A^b)^r \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (24)$$

This is the final expression for the isotherm that we will call the amphiphilic or Markin-Volkov (MV) isotherm. It is straightforward to derive classical adsorption isotherms from the MV isotherm (eq 24):

1. The Henry isotherm, when $a = 0$, $r = 1$, $p = 1$, $\Theta \ll 1$:

$$\Theta = X_a^b \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (25)$$

2. The Freundlich isotherm,⁴ when $a = 0$, $p = 1$, $\Theta \ll 1$:

$$\Theta = (X_a^b)^r \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (26)$$

3. The Langmuir isotherm³, when $a = 0$, $r = 1$, $p = 1$:

$$\frac{\Theta}{1 - \Theta} = X_a^b \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (27)$$

4. The Frumkin isotherm,⁵ when $r = 1$, $p = 1$:

$$\frac{\Theta}{1 - \Theta} \exp(-2a\Theta) = X_a^b \exp\left(-\frac{\Delta_b^s G^0}{RT}\right) \quad (28)$$

Therefore, the MV isotherm (eq 24) could be considered as a generalization of the Langmuir and Frumkin isotherms, taking into account the replacement of some solvent molecules with larger molecules of surfactant. Of course, the MV isotherm includes all the features of Langmuir and Frumkin isotherms and displays some additional ones. To elucidate them, it will be convenient to change the variable X_a^b to the relative

concentration $y = X_A^b/X_A^b(\Theta = 0.5)$, where $X_A^b(0.5)$ is the concentration corresponding to the surface coverage $\theta = 0.5$:

$$y = \frac{\Theta[p - (p-1)\Theta]^{p-1}}{(p+1)^{p-1}(1-\Theta)^p} \exp(a - 2a\Theta) \quad (29)$$

This equation gives the coverage fraction θ as a function of relative concentration y , while a and p are the parameters of this isotherm: the former being the attraction constant, and the latter, the size of surfactant. These parameters play an important role because their effect on the shape of MV isotherm is very strong.

While constructing the quasimolecule Q , one inevitable and important question about relationship between the sizes of the molecules arises: is there an exact correspondence between the sizes? If not, then what can one say about the prediction following from the isotherm? An exact correspondence between the solutes and amphiphile molecules cannot be expected with only rare exceptions. This is a standard situation with all isotherms that take into consideration the finite size of molecules beginning with Langmuir isotherm. This effect will manifest itself when we calculate parameter p describing the relationship between the sizes of the molecule with curve fitting of the experimental points. As it will be seen, this parameter happens to be not an integer but rather a fractional number.

MV isotherm (eq 24) analysis can be used for the determination of the interfacial structure. An amphiphilic molecule, which consists of two moieties with opposing properties such as a hydrophilic polar head and a hydrophobic hydrocarbon tail, should be used as an analytical tool located at the interface. Pheophytin a is a well-known surfactant molecule that contains a hydrophobic chain (phytol) and a hydrophilic headgroup. The value of p less than 1.0 indicates that adsorbed molecules of n -octane are parallel to the interface between octane and water.^{8–14} Substitution of one adsorbed octane molecule requires about 4–5 adsorbed pheophytin or chlorophyll molecules. These experimental data are supported by molecular dynamic studies in the systems decane–water, nonane–water, and hexane–water.¹⁶ The structure of both water and octane at the interface is different from the bulk. Octane molecules adsorbed at the interface have an orientation parallel to this interface.

For the first time, the generalized MV isotherm describes the adsorption of amphiphilic and organic molecules with hydrophobic and hydrophilic groups, which can penetrate the liquid–liquid interface and substitute adsorbed molecules of both solvents. Many surfactants can aggregate at the interface, while they exist as monomers in the bulk. For the first time, the generalized MV isotherm describes aggregation of surfactants at the interface and gives the possibility to estimate the aggregation parameter r . All other parameters of Henry, Freundlich, Langmuir, and Frumkin isotherms, such as Gibbs free energy of adsorption equilibrium ΔG_{ads} and interaction constant a are included in the generalized MV isotherm.

Results and Discussion

Pentafluorobenzoic acid is a surface active compound, and hence, when adsorbed, it may considerably reduce the surface tension at the octane–water interface. This property was used to determine the surface excess of pentafluorobenzoic acid, Γ , according to Gibbs.

Figure 2 shows the dependence of interfacial tension at the octane–water interface on the PFBA concentration at different pHs. A gradual reduction of γ in the PFBA concentration range

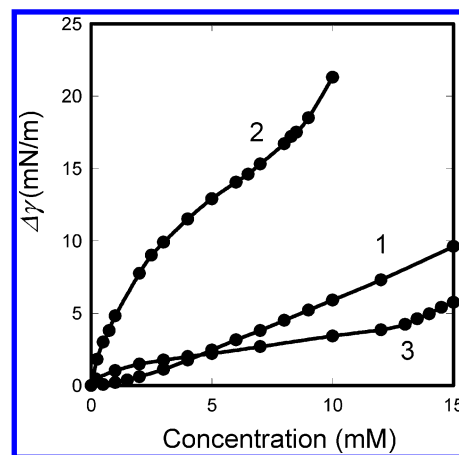


Figure 2. The dependence of surface tension at the octane–water interface on concentration of pentafluorobenzoic acid in the aqueous solution (1) and in the presence of 0.5 M H_2SO_4 (2) or 0.5 M KH_2PO_4 (3).

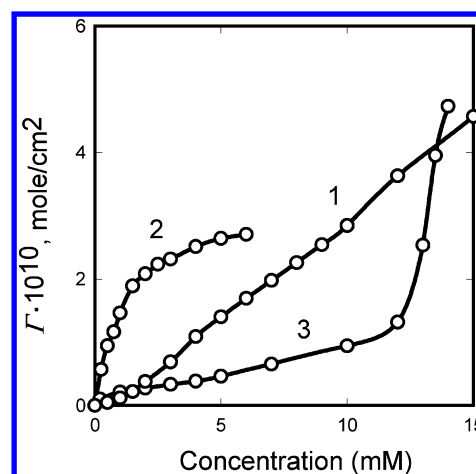


Figure 3. The dependencies of adsorption of pentafluorobenzoic acid at octane–water interface on concentration in the aqueous solution (1) and in the presence of 0.5 M H_2SO_4 (2) or 0.5 M KH_2PO_4 (3).

from 10^{-3} to 10^{-2} M at $\text{pH} = 0.1$ and from 10^{-3} to 4×10^{-2} M at pH from 2 to 5 was observed.

The PFBA isotherms obtained at different pHs using eq 29 are shown in Figure 3. It is apparent from Figure 3, that adsorption isotherms of PFBA at the octane–water interface at various pHs are quite different.

A convenient form of isotherms for comparative purposes is obtained by using the coordinates $y = y(\theta)$. These isotherms are presented in Figure 4. The coordinates $y = y(\Theta)$ are useful for comparing adsorption isotherms of surfactants that have surface activity in different regions of concentration.

The adsorption parameter p and attraction constant a can be calculated from eq 29. The MV isotherm in Figure 4 yields the next PFBA adsorption parameters: $p = 0.301$ and $a = 0.124$ at $\text{pH} 2.1$, $p = 0.416$ and $a = -0.536$ at $\text{pH} 0.1$, and $p = 0.372$ and $a = 0.916$ at $\text{pH} 5$. A p value less than 1.0 indicates that adsorbed molecules of n -octane are parallel to the interface between octane and water. Substitution of one adsorbed octane molecule requires approximately three adsorbed PFBA molecules. These results and our previous study of the adsorption of amphiphilic compounds such as chlorophyll, hydrated oligomer of chlorophyll,^{10,13} and pheophytin¹² correspond to the conclusions of the molecular dynamic study at decane–water interface in ref 16. At the interface, the structure of both water

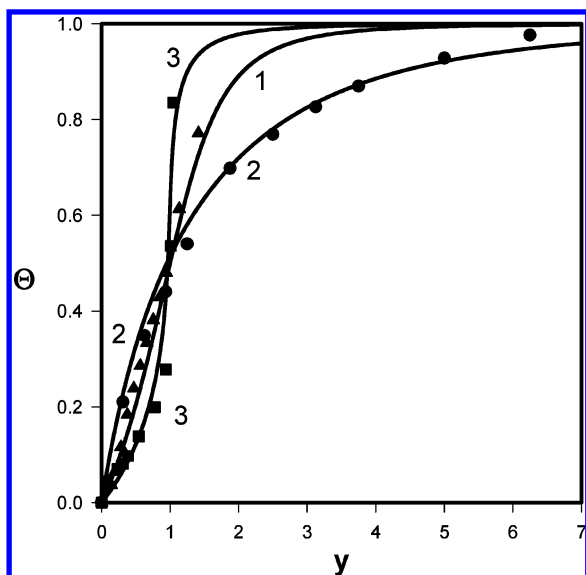


Figure 4. Experimental (points) and theoretical (lines) dependencies of the extent of the surface coverage θ on pentafluorobenzoic acid concentrations in reduced coordinates $y = c/c_{\theta=0.5}$. Medium: PFBA in water (1), PFBA + 0.5 M H_2SO_4 (2), and PFBA + 0.5 M KH_2PO_4 (3).

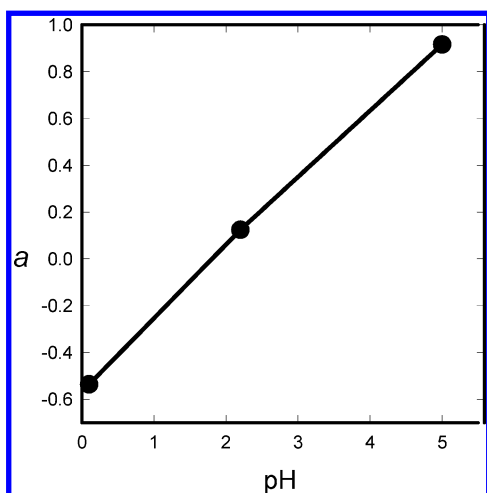


Figure 5. The dependence of attraction constant a between adsorbed at the octane–water interface PFBA molecules on pH.

and octane is different from the bulk. Octane has a lateral orientation with respect to the interface.

The dependence of attraction constant a on pH is shown in Figure 5. The positive value of attraction constant a at pHs higher than pK of PFBA indicates the attractive interaction between adsorbed molecules of PFBA. The negative constant a at the pH below pK indicates repulsion between adsorbed molecules. At $\text{pH} \ll \text{pK}$, neutral PFBA molecules adsorbed at the octane–water interface are present as dipoles oriented in the field of the electric double layer in the same direction. This is the reason repulsive interactions can be observed between adsorbed molecules. When the $\text{pH} \gg \text{pK}$, PFBA is adsorbed at the interface as anions, with COO^- groups oriented to water and screened by the electric double layer of inorganic cations such as H^+ , K^+ , and Na^+ . Benzene rings exhibit van der Waals interaction, so it leads to a positive attraction constant. The influence of the electric double layer can change the pK of PFBA in the adsorbed state compared to the bulk aqueous phase. When the pH is equal to the pK , either attractive or repulsive interactions between adsorbed particles are possible.

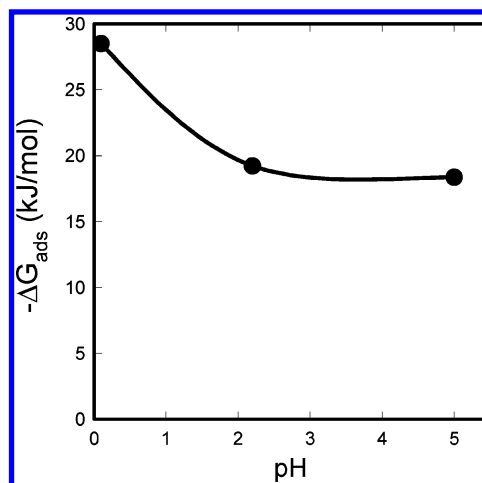


Figure 6. The dependence of Gibbs free energy of adsorption equilibrium of PFBA molecules at the octane–water interface on pH.

By using eq 24, it is possible to calculate the standard Gibbs free energy of adsorption of PFBA at the *n*-octane–water interface. The dependence of ΔG_{ads}^0 on pH is plotted in Figure 6. The absolute value of standard Gibbs free energy decreases with increasing pH. As described above, the higher surface activity of PFBA at the octane–water interface takes place at lower pH.

Elsewhere, the MV or generalized Langmuir isotherm was successfully applied for the study of adsorption at the polarized and nonpolarized nitrobenzene–water, decane–water, and octane–water interfaces in the presence of amphiphilic compounds and for the evaluation of the interfacial structure.^{8–14}

In conclusion, we would like to mention the relationship between the results of classical thermodynamics approach and methods of molecular dynamics. Several liquid–liquid interfaces have been studied by molecular dynamics methods.^{16–22} However, the results strongly depend on the selected model and the model's numerous parameters. Molecular dynamics simulation of interfaces has two goals: to appropriately select the surface tension and solubility parameters that concur with experimental data and to predict characteristics of liquid–liquid interfaces. These preliminary results can provide understanding of the structure of interfaces. Molecular dynamics is a powerful method that gives an important insight into the structure and dynamics of interfaces. In this connection, one can ask if the approach of classical thermodynamics can add something to these data. We believe that it can and it does. As we mentioned above, the results obtained here about the orientation of octane and water molecules at the interface are supported by the molecular dynamics data.^{16,17}

The decane–water interface studied by Van Buuren et al.¹⁶ consisted of 50 decane molecules and 389 water molecules in a two-phase system. There is the difference in the properties of molecules in the bulk solution versus the interface. In bulk solution, water has an unlimited ability to form hydrogen bonds without any special orientation. However at the interfacial layer where there are fewer neighboring water molecules, a given water molecule is limited in its molecular orientation. Van Buuren et al.¹⁶ demonstrated that water molecules tend to orient normal to the interface, while decane assumes a more lateral orientation with respect to the interface.

Michael and Benjamin¹⁷ studied the water–liquid hydrocarbon interface. Their system included 500 water molecules and 108 nonane molecules at $T = 300$ K. The structure of the interface was found to be similar to the water–decane interface,

with a significant lateral ordering of the hydrocarbon molecules at the interface.

Sometimes the results obtained by MD methods are controversial. Wilson and Pohorille¹⁸ studied Na⁺, Cl⁻, and F⁻ ions at the water–vapor interface. They found an asymmetric orientational distribution of water molecules at the pure water–vapor interface. In the more recent paper, Marrink and Marcelja¹⁹ presented a different picture. They claimed that water molecules near an interface tend to order themselves in such a way that configurations with hydrogens pointing outward from the liquid and oxygens inward are slightly more favorable than the other way around.

Marrink and Marcelja¹⁹ also concluded that the energy curves describing sodium and chloride distribution at the interface are very similar, but chloride ions seem to be repelled *more* than sodium ions. This conclusion was questioned in ref 20 based on experimental observations.

This demonstrated that the classical thermodynamic approach still preserves its importance and continue to contribute to our understanding of interfacial phenomena.

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