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Conference Paper

Adsorption from Solution

A. C. Zettlemoyer and F. J. Micale

Center for Surface and Coatings Research, Lehigh University,
Bethlehem, Pa., 18015, U.S.A.

A major problem of the thermodynamic theory of adsorption at the solid/liquid interface is concerned with the definition of the heterogeneous surface in terms of mathematically treatable model. The paper gives a review of the theoretical approaches applied to studies of adsorption from concentrated and diluted binary mixtures.

Experimental work has enjoyed much success since the uniform surface, graphitized carbon blacks became available. Results are described and discussed of measurements of heats of immersion on such surfaces.

INTRODUCTION

The term adsorption is generally used to describe the concentration of a particular component at an interface between two phases. A number of possibilities arises as a result of this definition. For the solid/gas interface, theoretical developments depend upon the adsorption of one component, *i. e.*, the gas molecules, onto the solid surface. The major problem in the development of a thermodynamic theory is concerned with the definition of the usually uncertain, heterogeneous solid surface in terms of a mathematical model. The liquid/liquid and liquid/gas interfaces, however, are more susceptible to theoretical development and interpretation because of the homogeneous nature of the adsorbing surface. The solid/liquid interface, which is the subject matter of this paper, is complicated by the heterogeneous nature of the solid surface as well as the fact that at least two components are involved in competitive adsorption at the solid surface. Although theoretical progress has been relatively slow for the case of the solid/liquid interface, the application of adsorbent carbons to remove coloring matter in solution is one of the oldest technical processes. The technique was noted in the fifteenth century and used by Lowitz, about 1791, to purify raw sugar solutions.

A vast technical literature has grown out of the many studies of adsorption from solution by charcoals and carbon blacks. For the most part the carbon blacks possess rather complicated surfaces because of a multiplicity of residual oxygenated functional groups. These groups produce quite heterogeneous surfaces so that adsorption data are often difficult, if not impossible, to interpret. Beginning in the early 1950's surface chemists and physicists were provided with carbons possessing very uniform surfaces and with sufficient surface areas to yield adequate adsorption data; *i. e.*, the so called graphitized carbon blacks were developed. For a number of investigators, the path was opened toward meaningful theoretical interpretations.

Adsorption from solution can be divided into two categories. One concerns adsorption, *e. g.*, surfactants or polymers, from dilute solution where there

is high specificity for the solute. Binary mixtures of liquids over the entire concentration range form another important type. There are three main types of solution adsorption isotherms as shown in Fig. 1. Type I, often called the Langmuir isotherm, falls into the category of adsorption from dilute solutions

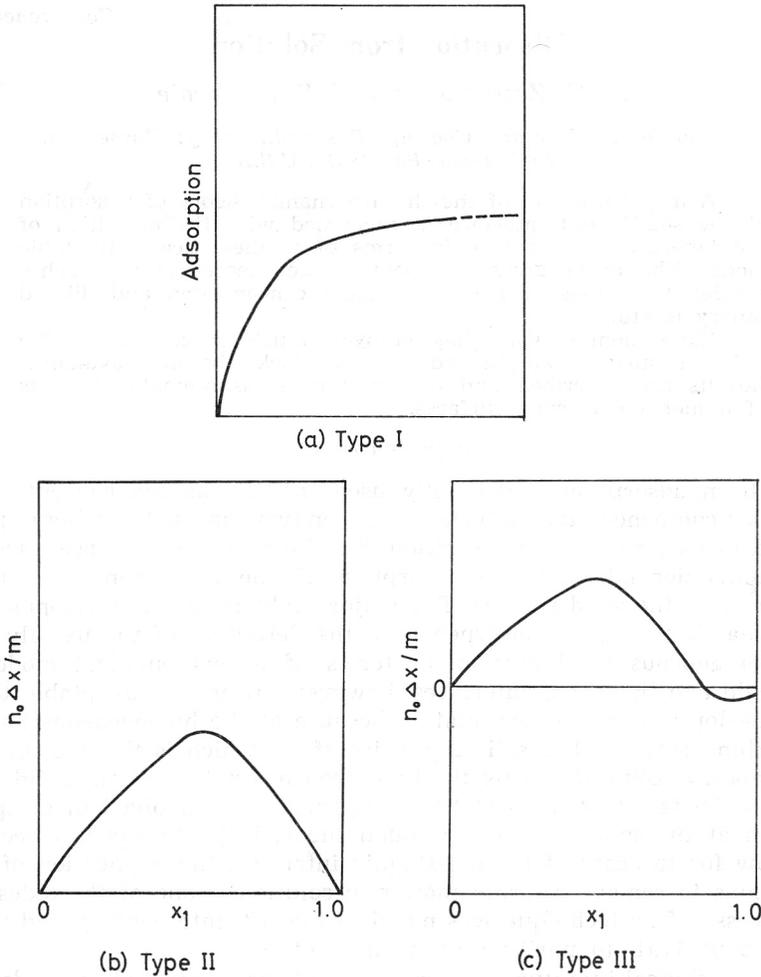


Fig. 1. Solution Adsorption Isotherms.

and is exemplified by limiting or monolayer adsorption. Type II and III isotherms are typical of composite isotherms of two components over their entire concentration range and are distinguishable, as will be seen shortly, by the relative degree of interaction of one component over the other.

Heats of solution adsorption, measured calorimetrically, provide an added approach to the measurement of the isotherms which could lead to much information about the adsorption process. Little has been done, however, with direct calorimetric measurements of heats of interaction of solutions or with the measurements of multi-temperature isotherms.

Adsorption from Binary Mixtures — Theory

Examples of two types of composite isotherms from binary mixtures over the entire concentration range are given in Fig. 1, b and c.

Equation for Composite Isotherm. — Solution adsorption is ordinarily followed by measuring the change in mole fraction of component 1, Δx , from its initial value, x_0 to its equilibrium value, x_1 . Therefore:

$$\Delta x = x_0 - x_1 \tag{1}$$

The total number of moles in the system may be defined:

$$n_0 = n_1 + n_2 + n_1^s m + n_2^s m \tag{2}$$

where n_1 and n_2 are the number of moles of components 1 and 2 in the liquid phase and n_1^s and n_2^s are the number of moles of components 1 and 2 adsorbed per gram of solid. The value of m represents the weight of the added solid adsorbent in grams. Furthermore, by definition:

$$x_0 = \frac{n_1 + n_1^s m}{n_0} \tag{3}$$

$$x_1 = \frac{n_1}{n_1 + n_2} \tag{4}$$

and, combining Equations (1) through (4):

$$\Delta x = \frac{n_1 + n_1^s m}{n_1 + n_2 + n_1^s m + n_2^s m} - \frac{n_1}{n_1 + n_2} \tag{5}$$

or:

$$\Delta x = \frac{m (n_2 n_1^s - n_1 n_2^s)}{n_0 (n_1 + n_2)} \tag{6}$$

Since the mole fraction of component 2, x_2 , may be defined as:

$$x_2 = (1 - x_1) = \frac{n_2}{n_1 + n_2} \tag{7}$$

$$\frac{n_0 \Delta x}{m} = n_1^s (1 - x_1) - n_2^s x_1 \tag{8}$$

Equation (8) is the basic equation of solution adsorption theory. (It appears surprising at first glance.) When the left hand side of Equation (8), $n_0 \Delta x/m$, is plotted as a function of x_1 , this plot is referred to as the composite isotherm. Type II and III isotherms given in Fig. 1 now have meaning in terms of Equation (8). When $n_0 \Delta x/m$ is positive over the entire mole fraction range, then n_1^s must be large with respect to n_2^s , or component 1 adsorbs much more strongly than component 2. When negative values of $n_0 \Delta x/m$ appear, e. g., a Type III composite isotherm, the adsorption of components 1 and 2 are comparable, although one may be larger than the other. Furthermore, the value of $n \Delta x/m$ must be zero at $x_1 = 0$ (where $n_1^s = 0$) and at $x_1 = 1$

(where $n_2^s = 0$); the composite isotherm over its entire range must begin and end at zero apparent adsorption.

Monolayer Hypothesis. — Although a composite isotherm gives limited information about the relative adsorption of each component, the individual isotherms, *i. e.*, n_1^s and n_2^s as a function of concentration, cannot be obtained readily from Equation (8) because it has two unknowns. Several approaches, based on different models, have been advanced in order to evaluate n_1^s and n_2^s . One approach, which might be called the monolayer hypothesis, was suggested by Williams¹ and developed by Elton² and Kipling and Tester³. This theory is based on the assumption that the adsorbed layer is monomolecular and that the surface of the adsorbent is completely covered at all concentrations. This means, in effect, that both components completely wet the surface and that the presence of the surface is not effective beyond the first layer. These assumptions lead to the relationship:

$$\frac{n_1^s}{(n_1^s)_m} + \frac{n_2^s}{(n_2^s)_m} = 1, \quad (9)$$

where $(n_1^s)_m$ and $(n_2^s)_m$ are the number of moles of components 1 and 2, respectively, required to form a complete monolayer per unit weight of solid. The values of $(n_1^s)_m$ and $(n_2^s)_m$ can be estimated from individual vapor adsorption isotherms. If vapor adsorption measurements are not possible, the monolayer moles can be calculated from the specific surface of the adsorbent and from molecular dimensions assuming a suitable orientation of the adsorbed species. By combining Equations (8) and (9), the individual adsorption isotherms can be calculated from the composite isotherms. Figs. 2 and 3 give examples from the literature^{4,5} of Type II and Type III isotherms along with the individual isotherms calculated from the monolayer hypothesis.

Schay and Nagy Approach. — Schay and Nagy^{6,7}, on the other hand, noted that, on many porous adsorbents such as carbon blacks, the composite isotherms often exhibit a long linear decreasing portion extending over a wide range of concentrations. They have suggested that the composition of the adsorbed phase is the same over this entire linear portion. This condition is readily seen by rewriting Equation (8) as:

$$\frac{n_0 \Delta x}{m} = n_1^s - (n_1^s + n_2^s) x, \quad (10)$$

when n_1^s and n_2^s can both be considered to be constant to produce a straight line. Extrapolation of the linear portion of the isotherm to $x = 0$ and $x = 1$ gives values of $(n_1^s)_c$ and $(n_2^s)_c$ which define the composition of the adsorbed phase in the linear portion. From the monolayer values, $(n_1^s)_m$ and $(n_2^s)_m$, for the two components, Schay and Nagy evaluated the mean thickness (number of monolayers) of the adsorbed layer t :

$$t = \frac{(n_1^s)_c}{(n_1^s)_m} + \frac{(n_2^s)_c}{(n_2^s)_m} \quad (11)$$

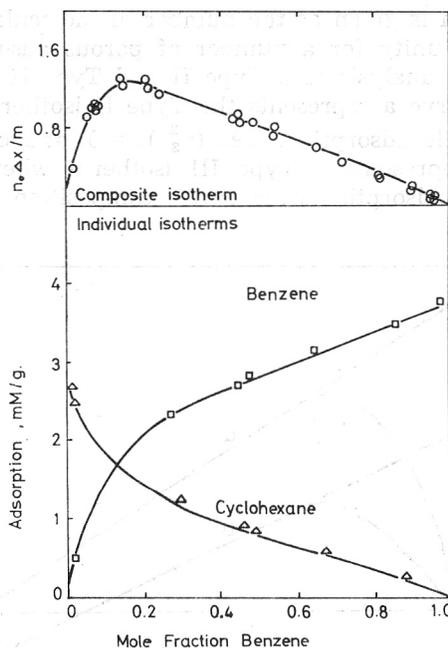


Fig. 2. Composite and Individual Isotherms of Benzene-Cyclohexane on Charcoal. Reprinted from Ref. (4), p. 3819, by courtesy of *J. Chem. Soc.*

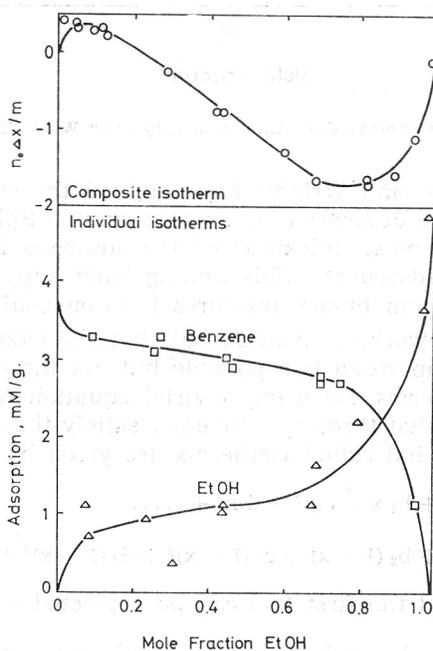


Fig. 3. Composite and Individual Isotherms of Benzene-Ethanol on Charcoal. Reprinted from Ref. (5), p. 4123, by courtesy of *J. Chem. Soc.*

The value of t , which is given as the number of molecular layers, was found to be approximately unity for a number of porous adsorbents. An example of application of this analysis to a Type II and Type III composite isotherm is given in Fig 4. Curve a represents the Type II isotherm where component 2 undergoes very little adsorption, *i. e.*, $(n_2^s)_c = 0$, and component 1 adsorbs strongly. Curve b represents a Type III isotherm where both components undergo comparable adsorption over entire composition range.

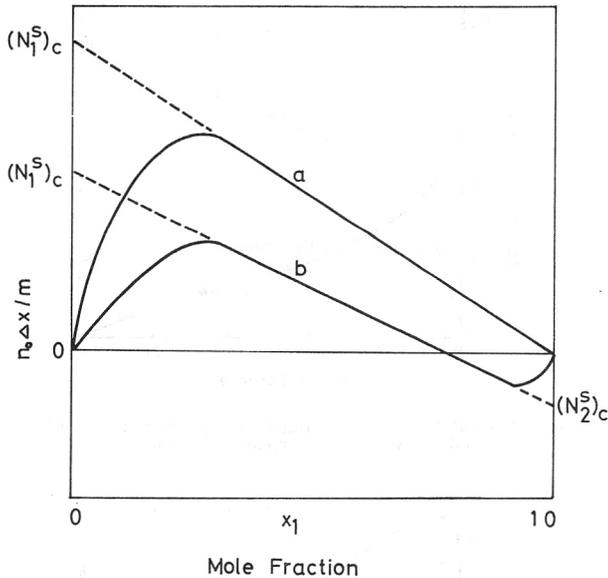


Fig. 4. Composite Isotherms Exhibiting Linearity over Wide Concentration Range.

Cornford, Kipling, and Wright⁸ have applied the concepts of Schay and Nagy to the adsorption of several binary mixtures on Spheron 6 and Graphon. They found that the mean thickness of the adsorbed layer was unity even for these nonporous adsorbents. This finding lends support to the assumption that the adsorption from binary mixtures is often confined to a monolayer.

Cornford and co-workers⁸ pointed out that the existence of an adsorbed layer of constant composition is a possible but not the only condition for the linearity of the isotherms. By using a virial equation for the individual isotherms, they showed that three specific cases satisfy the condition for linearity of the isotherm. The individual isotherms are given by:

$$\begin{aligned} n_1^s &= a_1 + b_1 x + c_1 x^2 + d_1 x^3 + \dots \\ n_2^s &= a_2 + b_2 (1-x) + c_2 (1-x)^2 + d_2 (1-x)^3 + \dots \end{aligned} \quad (12)$$

The terms beyond the first two can be neglected sometimes.

Case 1. If both b_1 and b_2 are zero, $n_1^s = a_1$ and $n_2^s = a_2$, which is the Schay and Nagy condition. This condition has to satisfy an important

thermodynamic criterion. The chemical potentials of component 1 in the solution phase and the adsorbed phase are given by:

$$\begin{aligned} \mu_1^s &= (\mu_1^s)^0 + RT \ln (f_1^s x_1^s), \text{ and} \\ \mu_1^l &= (\mu_1^l)^0 - RT \ln (f_1^l x_1), \end{aligned} \tag{13}$$

where μ_1 and $(\mu_1)^0$ are the chemical potentials of component 1 in the mixture and standard state, respectively; f is the activity coefficient, and the superscripts s and l represent the adsorbed and liquid phase, respectively. At equilibrium $\mu_1^s = \mu_1^l$. The composition of the adsorbed phase will be constant only if changes in $f_1^l x_1$ are compensated by changes in f_1^s . This condition is unlikely to occur in practice.

Case 2. If $b_1 = b_2 = b$, Equation (12) reduces to the form:

$$n_1^s = a_1 + bx \tag{14a}$$

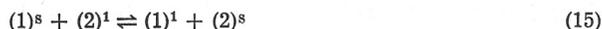
$$n_2^s = a_2 + b - bx \tag{14b}$$

Equations (14 a, b), represent a pair of parallel straight lines and the composite isotherm, which is a resultant of the two, will also be a straight line.

Case 3. If b_1 and b_2 are both small, the composite isotherm will approximate a straight line. Cornford *et al*⁸ have suggested that this situation is likely to occur in the case of systems which are far from being ideal and that possibly the majority of the systems investigated by Schay and Nagy are of this type.

Although extensive experimental work on solution adsorption has been in progress for over 50 years, no satisfactory physical model which enables a vigorous thermodynamic treatment of the process is available. The main reason for the lack of theoretical development in the field is the complexity of the process due to the heterogeneity of most solid surfaces and the lack of knowledge of the various interactions both between the two components and the adsorbent. Recently, however, attempts have been made to define an ideal picture for solution adsorption and to evaluate the thermodynamic properties of real systems in terms of deviations from this ideal picture.

Everett's Approach. — Such an idealized model for the adsorption from binary mixtures has recently been examined in detail by Everett⁹, and the analysis has been extended to adsorption from imperfect solutions¹⁰. In this idealized model, the solution is described in terms of a quasi-crystalline array of plane lattices. The solid is composed of a uniform array of adsorption sites. The adsorption is restricted to a monolayer and the components of the binary mixture are assumed to be of the same size. Everett's theory appears to imply, furthermore, that there should be preferential adsorption for one of the components throughout the entire concentration range for a perfect system. The adsorption is envisaged as an exchange process in which a small amount of component 1 in the adsorbed phase is replaced by an equal amount of the component 2 with change in concentration:



With these assumptions, Everett⁹ has described the adsorption from binary mixtures by means of an equation analogous to the Langmuir adsorption isotherms:

$$\frac{x_1^s x_2}{x_2^s x_1} = K \quad (16a)$$

or:

$$n_1^s = \frac{K n^s x_1}{1 + (K - 1) x_2}, \quad (16b)$$

where n^s is the total number of moles adsorbed, *i. e.*, $n^s = n_1^s + n_2^s$, x_1^s is the mole fraction of component 1 on the surface or $x_1^s = n_1^s / n^s$, x_1 and x_2 are the mole fractions of components 1 and 2 in the liquid phase, and K is a constant given by:

$$K = \exp \left(\frac{\Delta H_A}{RT} - \frac{\Delta S_a}{R} \right), \quad (17)$$

where ΔH_A is the differential heat of adsorption and ΔS_a is the standard differential entropy of adsorption. The value of K determines the strength of adsorption of component 1 by the surface. The differential heat and entropy of adsorption are actually heat and entropy of the exchange process represented by Equation (15).

The composite isotherm equation may now be rewritten by substituting Equation (16b) into Equation (10) and rearranging to put it in its linear form:

$$\frac{x_1 x_2}{n_0 \Delta x/m} = \frac{1}{n^s} \left[x_1 + \frac{1}{(K - 1)} \right]. \quad (18)$$

A plot of the left hand side of Equation (18) as a function of x_1 results in a straight line and n^s and K can be calculated from the slope and intercept. The value of obtaining n^s lies in the fact that solution adsorption data can be used to determine the surface area of the adsorbent by assuming a cross-sectional area for the adsorbate.

Everett⁹ has suggested that the heat of immersion ΔH of a solid by the solution is given most simply by:

$$\Delta H = x_1^s \Delta H_1^0 + x_2^s \Delta H_2^0 \quad (19)$$

where ΔH_1^0 and ΔH_2^0 are the heat of immersion values of the adsorbent in the pure liquids 1 and 2, respectively. Equation (19) may now be combined with Equation (10) and (16b) to yield:

$$\Delta H - (x_1 \Delta H_1^0 + x_2 \Delta H_2^0) = \frac{x_1 x_2}{\left[x_1 + \frac{1}{(K - 1)} \right]} (\Delta H_1^0 - \Delta H_2^0). \quad (20)$$

To test Equation (20), it is necessary to know K , already determined from Equation (18), and to measure ΔH over the entire concentration range. From Equation (20), therefore, a plot of the left hand side against $x_1 x_2 / [x_1 +$

+ (K - 1)] should be linear with a slope ($\Delta H_1^0 - \Delta H_2^0$), which can be directly determined.

Although the number of systems likely to approximate the conditions imposed by this theory is small, a few authors⁹⁻¹³ have attempted correlations with varying degrees of success. The most significant contribution has come from Wright^{12,13} who studied solution adsorption of benzene in a number of different solvents and on a variety of carbon surfaces. The results are presented in Fig. 5 in the form of composite isotherms where the amount adsorbed, $n_0 \Delta x/m$, has been reduced to per unit area, *i. e.*, $\mu\text{-moles}/(\text{meter})^2$, based on BET nitrogen area measurements, so that all six isotherms could be presented on the same graph. The experimental points have been eliminated for the sake of clarity. The results are plotted according to Equation (18) and are given in Fig. 6. The solid lines represent the best fit of the experimental points and the dotted lines the deviation of the data from linearity. Table I identifies the curves in Figs. 5 and 6 and gives the results of calculations according to Equations (18) and (20).

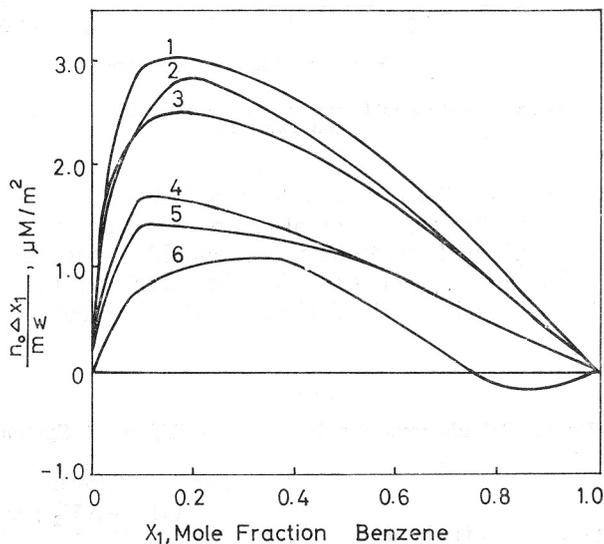


Fig. 5. Composite Isotherms for Benzene in Different Solvent-Adsorbent Systems^{12,13}.

Curve No.	Solvent	Adsorbent
1	Ethylene Dichloride	Graphon
2	Cyclohexane	Coconut Shell Charcoal
3	Cyclohexane	Decolorizing Charcoal
4	Carbon Tetrachloride	Decolorizing Charcoal
5	Carbon Tetrachloride	Coconut Shell Charcoal
6	Ethylene Dichloride	Spheron 6

The results of the benzene-ethylene dichloride adsorption on Graphon and Spheron 6, curves 1 and 6, respectively, indicate that Graphon obeys the requirements for a perfect system while Spheron 6 does not. This conclusion is arrived at by observing the deviation from linearity according to Equation (18), Fig. 6, at a mole fraction of 0.5 for the Spheron 6, while for the Graphon system the line is linear for the entire concentration range. Furthermore, the surface area determinations from the n^s values show reasonably good agreement with the BET nitrogen area for Graphon and poor agreement for

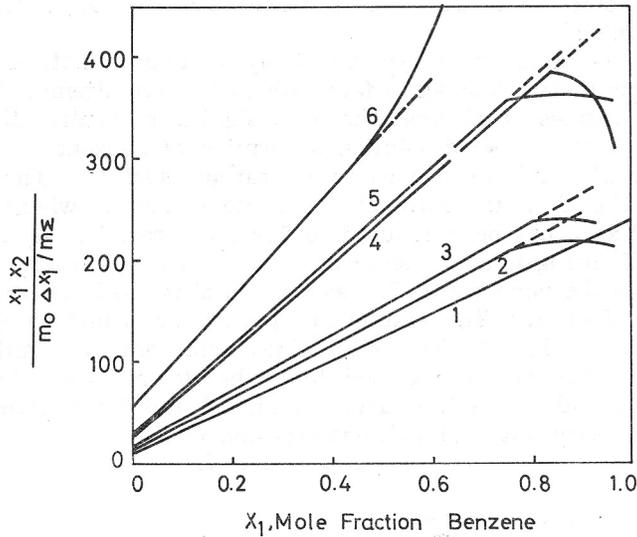


Fig. 6. Composite Isotherms According to Equation (18)^{12, 13}. (Identification of Curves is given in Fig. 5 and Table I).

Spheron 6. The $(\Delta H_1^0 - \Delta H_2^0)$ values in the last column of Table I are too small, practically within experimental error, either to prove or to disprove Equation (20). As explained heretofore, we should expect good agreement with the theory for the homogeneous Graphon surface; the heterogeneous surface of the carbon black provided a poor test adsorbent.

TABLE I
Results of Calculations for Benzene in Different Systems

Curve No.	Solvent	Adsorbent	K	Area of Adsorbent, m ² /g ($\Delta H_1^0 - \Delta H_2^0$) cal/g				Ref.
				Eq. (18)	BET N ₂	Eq. (20)	Measured	
1	Ethylene Dichloride	Graphon	18.5	119	89	0.54	0.97 ± 0.4	(12)
2	Cyclohexane	Coconut Shell Charcoal	19.9	677	593	12.0	10.2 ± 1.5	(13)
3	Cyclohexane	Decolorizing Charcoal	16.4	596	582	7.1	5.9 ± 1.5	(13)
4	Carbon Tetrachloride	Decolorizing Charcoal	16.1	374	582	4.0	3.4 ± 1.5	(13)
5	Carbon Tetrachloride	Coconut Shell Charcoal	18.2	350	593	3.8	3.0 ± 1.5	(13)
6	Ethylene Dichloride	Spheron 6	5	57	119			(12)

Curves 2—5 represent the results for benzene in cyclohexane and carbon tetrachloride on decolorizing charcoal and coconut shell charcoal. Water adsorption results on these adsorbents¹⁴ indicate that the coconut shell charcoal surface was partly covered with a moderate amount of hydrophilic groups and that the decolorizing charcoal had a much higher percentage of surface hydrophilic groups. Fig. 6 shows that all four of these systems obey Equation (18) up to a benzene mole fraction of approximately 0.8. These deviations, however, are expected in view of the chemically heterogeneous nature of the adsorbent surfaces and the slight differences in the sizes of the adsorbing molecules. The surface areas calculated according to Equation (18) show very good agreement with the BET nitrogen areas for the cyclohexane systems and less agreement for the carbon tetrachloride systems. The $(\Delta H_1^0 - \Delta H_2^0)$ values show generally good agreement with the directly measured differences.

The number of ideal systems (and not all of the above approached this state, particularly due to surface heterogeneities) will always remain small. What is more, the technologically important solution is not likely to be nearly ideal. Instead, strong preferential adsorption of one of the components is likely to occur. Such cases will be discussed next.

Adsorption from Dilute Solutions

In the case of dilute solutions, adsorption is treated in manner similar to gas adsorption with the restriction that the adsorption is confined to a monolayer, *i. e.*, Type I isotherm. Multilayer adsorption has been observed in a few cases¹⁵, but generally the solute-adsorbent interactions are not strong enough to overcome the forces extended by the solvent or solution except in the first layer. Equations representing the Langmuir adsorption isotherm have been widely applied to adsorption from solution, but they must be regarded as empirical equations without thermodynamic validity for such multicomponent solutions.

For dilute systems, with high specificity for adsorption of the solute, it is generally assumed for simplicity that the solvent has no influence on the adsorption of the solute. However, even in the case of dilute systems the role of the solvent can be a complicating factor. It is not possible sometimes to exclude the adsorption of the solvent, and it is rather difficult to assess the extent of interaction of the adsorbed solute and solvent. These difficulties are minimized by choosing systems in which the adsorption of the solute from the solution is quite dominant. Accordingly, a polar solvent such as water can be used for adsorption on a low- or medium-energy surface such as Graphon and a nonpolar hydrocarbon solvent for studies on high-energy surfaces such as a metal oxide.

Another problem that confronts the investigator in solution adsorption concerns the particular orientation of the adsorbed solute molecules. In general, it can be said that on high-energy surfaces a molecule is adsorbed through its polar head group, and on a low-energy surface the nonpolar end of the molecule lies on the surface. This picture, however, is oversimplified; the orientation of the adsorbed molecule depends to a large extent on the nature of the polar head group and also on the concentration of the adsorbed species on the surface. For example, it has been shown that on rutile, *n*-propyl alcohol, which can interact with the surface by hydrogen bonding, is adsorbed

through its hydroxyl, the hydrocarbon tail extending into the bulk phase. However, *n*-butyl chloride on the same surface lies flat.

The change in orientation of the same adsorbate, depending on the surface concentration of the adsorbed species, has been demonstrated in the adsorption of sodium dodecyl sulfate (NaDS) on Graphon¹⁶ and is shown in Fig. 7. At low surface concentrations, the isotherm reaches an apparent plateau followed by an increase to a higher plateau with increasing concentration. The interpretation given is that, at low concentrations, the NaDS molecule adsorbs at some equilibrium orientation with a longer length of the hydrocarbon chain in contact with the surface. At some higher concentration, the orientation changes to some new equilibrium position which leads to increased adsorption to a second plateau.

Fig. 7 also shows the effect of Na⁺ ions on the adsorptions of NaDS on Graphon. Sodium ions increase the adsorption of the surfactant. This

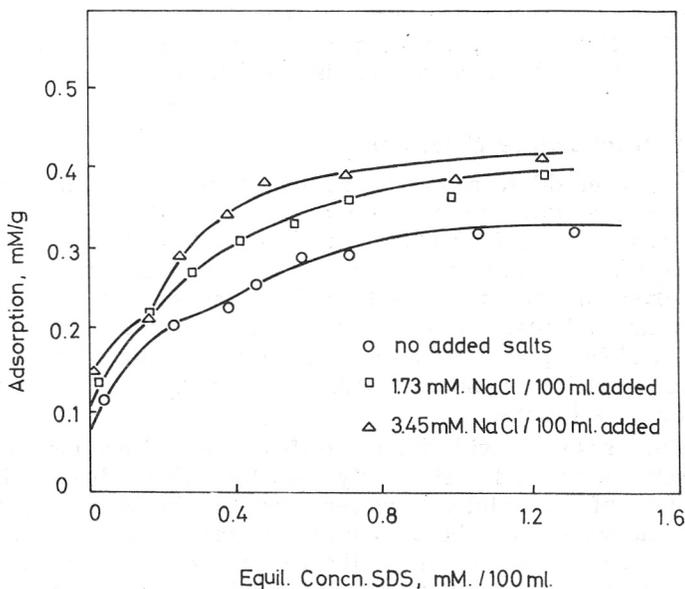


Fig. 7. Adsorption of Sodium Dodecylsulfate onto Graphon. Reprinted from Ref. (16), p. 280, by courtesy of *J. Am. Oil Chemist Soc.*

increase is caused by a decrease in mutual repulsion between head groups. Similar effects have been noted for sodium dodecyl benzene sulfonate on Graphon¹⁶. Based on these results, a model for the Graphon/solution interface has been developed in which the adsorbed surfactant ions have their hydrocarbon chains oriented toward the Graphon surface and the polar head groups oriented toward the bulk aqueous phase. This situation is very similar to spreading at liquid interfaces. The packing densities in such an arrangement can be estimated by applying Davies' equation^{17,18} to the data. This equation takes into account the interionic repulsion and the double-layer formation.

An interesting aspect of solution adsorption is the existence of a relationship between the solubility of a series of compounds and the adsorption at

an interface¹⁹. Hansen and Craig²⁰ have demonstrated that this relationship is indeed quantitative for the adsorption of a series of fatty acids and alcohols on Graphon. When the amount adsorbed per gram of Graphon was plotted against the reduced concentration C/C_0 , where C_0 represents the solubility, the isotherms for a homologous series of compounds were superimposed. This ratio is analogous to relative pressures used in gas adsorption. Two examples are given in Fig. 8 where curve a is indicative of multilayer adsorption and

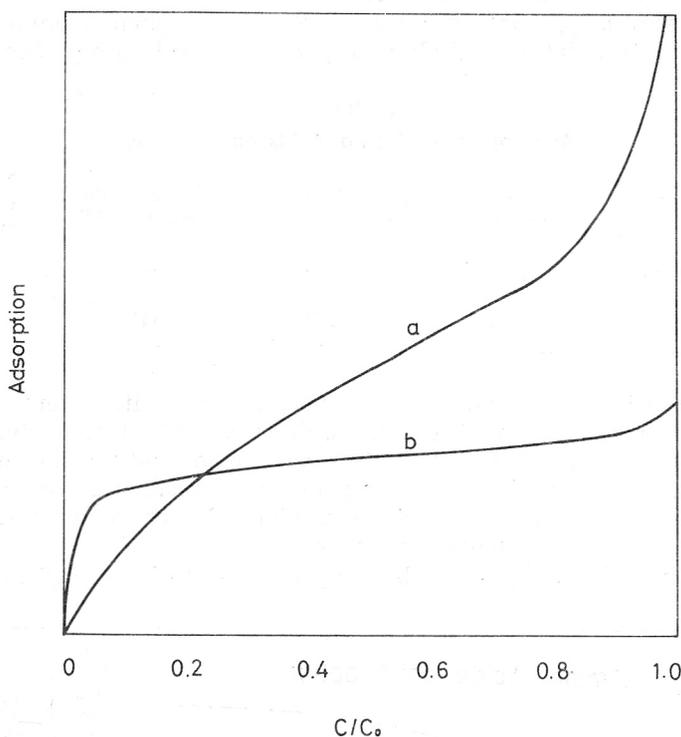


Fig. 8. Adsorption Isotherms at Reduced Concentrations.

curve b is the Langmuir type isotherm usually found for porous solids. The Langmuir and BET equations, both of which were developed for gas adsorption, have sometimes been used to analyze isotherms of this type. The equations, however, can only be used as empirical equations since the constants do not have any physical significance in the case of solution adsorption. Hansen¹⁵ has demonstrated multilayer formation for a number of long chain alcohols on both carbon and graphite surfaces, although the number of adsorbed layers at saturation concentration was found to be small, *i. e.*, three to four layers; in gas adsorption, five to ten layers are common at saturation pressures.

A few words about amino acid adsorption on Graphon might prove of interest. Even though highly important, the surface chemistry of these building blocks of proteins has been little studied. Beyond the adsorption and heat of immersion measurements in our Laboratory, the only other important

measurements that have been found are the surface tensions of solutions of the simple ones reported thirty years ago²¹. The first members of the series, glycine and alanine, behave like inorganic salts and are negatively adsorbed at the air/water interface. Much the same behavior is found at the Graphon/solution interface although alanine is adsorbed at the maximum on an average of one on each seven »benzene rings« on the graphite surface. On the other hand, the apparent monolayer capacity for leucine occurs at a coverage of one on each three surface rings.

It is interesting to contrast the adsorption of DL-phenylalanine with that of DL-tyrosine, the latter including a para hydroxyl group. See Table II.

TABLE II
Adsorption of Amino Acids on Graphon

Amino Acid	Monolayer (millimoles/gm)	Co-area (Å ² /molecule)	Molec. model co-area (Å ²)	Min. conc. for $\theta = 1$, (millimoles/l)
DL-Phenylalanine	0.18	98	104	36
DL-Tyrosine	0.11	163	115	1.9

The adsorption isotherms and thus the monolayer capacities were determined by depletion analysis with differential refractometry²². Fig. 9 gives the adsorption isotherms determined at the isoelectric point and the sketches suggest an explanation for the lower packing of the tyrosine. Tyrosine takes up about 3/2 as much area as the phenylalanine. If each benzene ring at the amino acids sits on a graphite ring, then the lower packing of the tyrosine can be accounted for by hydrogen bonding across one of the graphite hexagons

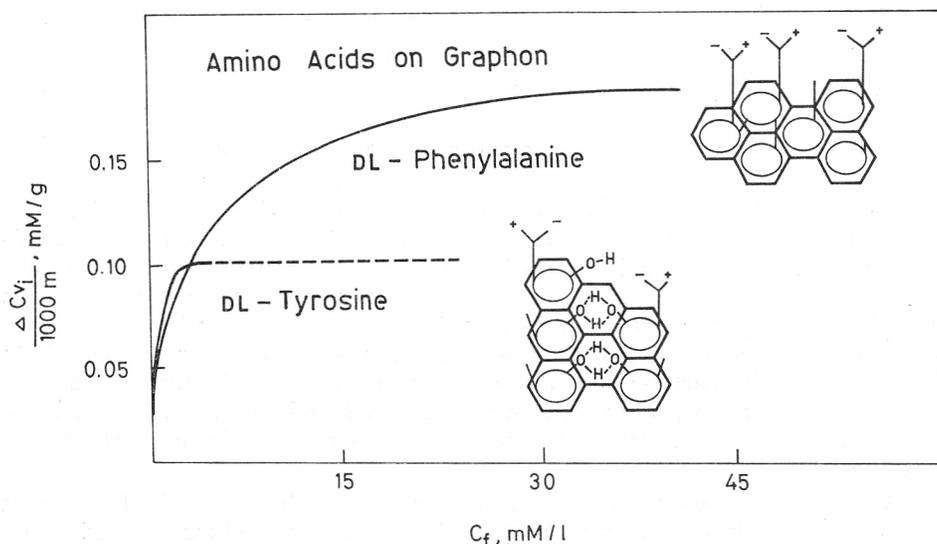


Fig. 9. The adsorption isotherms for DL-phenylalanine and DL-tyrosine onto Graphon. The proposed configuration of these molecules on the Graphon surface explain the 3/2 coverage for tyrosine as due to hydrogen bonding.

as depicted. In addition, the monolayer capacity of the phenylalanine has been confirmed by measurement of heats of immersion which reached a plateau value of 54 ergs/cm² at 0.18 mM adsorbed per gram of Graphon anywhere above 36 mM/l. For tyrosine, the plateau value was rather high at 127 ergs/cm² at 0.11 mM adsorbed per gram above 1.9 mM/l. concentration.

The fact that the tyrosine reached monolayer adsorption at a much lower concentration than the phenylalanine is in accord with its lower solubility limit: 1.44 *versus* 85.4 mM/l.

Heats of Immersion into Solutions

When a solid surface is immersed in a solution which exerts no chemical or solvent action, some of the solute is adsorbed thereby diluting the solution. Generally, the solute is not adsorbed to the complete exclusion of the solvent. The surface enthalpy of the solid, thus, is replaced by the interfacial enthalpies arising from adsorption of solvent and solute. In addition, interfaces are established between these new adsorbed phases and the remaining solution. If it is assumed that the interactions between molecules in the adsorbed phase are of the same order as for those in solution, the heat of wetting for the process can be formulated in terms of surface and interfacial enthalpy changes. The total enthalpy change for the wetting process is given²³ by the equation:

$$h_w = \Theta (h_s - h_{s1}) + (1 - \Theta) (h_s - h_{s2}) + \Theta (h_{s1} - h_{1\sigma}) + (1 - \Theta) (h_{s2} - h_{2\sigma}) \quad (21)$$

where $h_w = \Delta H_w / \Sigma$ is the heat of wetting per unit area, Θ is the surface coverage, $\Theta (h_s - h_{s1})$ is the enthalpy contribution for the formation of the first adsorbed layer, $\Theta (h_s - h_{1\sigma})$ is the enthalpy contribution for the formation of the interface between adsorbed solute and solution, and $(1 - \Theta) (h_s - h_{s2})$ and $(1 - \Theta) (h_{s1} - h_{2\sigma})$ are the enthalpy changes for the adsorption of first layer of water molecules and the formation of the interface between these molecules and the solution.

On simplification, Equation (21) reduces to:

$$h_w = \Theta h_{s1} + (1 - \Theta) h_{s2} + \Theta h_{1\sigma} + (1 - \Theta) h_{2\sigma} \quad (22)$$

The total heat of immersion obtained by calorimetry, on the other hand, is given by:

$$\Delta H_1 = \Delta H_w + \Delta H_D + \Delta H_M + \Delta H_B \quad (23)$$

where the subscripts W, D, M, and B refer to the separate contributions of wetting, dilution of the solution with respect to one component, demicellization when it occurs, and bulb-breaking plus accessory events. The contribution due to demicellization arises only in the case of surfactants above their critical micelle concentration. ΔH_D , ΔH_M , and ΔH_B can all be determined by separate experiments, allowing the evaluation of h_w .

The above concepts have been verified for the system Graphon-*n*-butanol from aqueous solution²³. The value of h_{s1} was determined as the difference between the heat of immersion of a clean Graphon surface and one covered with a monolayer of butanol. The value of $h_s + h_{2\sigma}$ was assumed to be the same as for the heat of immersion of a Graphon surface covered with a monolayer of adsorbed butanol molecules into a solution in equilibrium with this surface.

ΔH_D and ΔH_M were determined experimentally and were quite small. The calculated and experimental heats of immersion are plotted in Fig. 10. The excellent agreement between the calculated and experimental values provides some verification of the validity of the simplified assumptions employed in

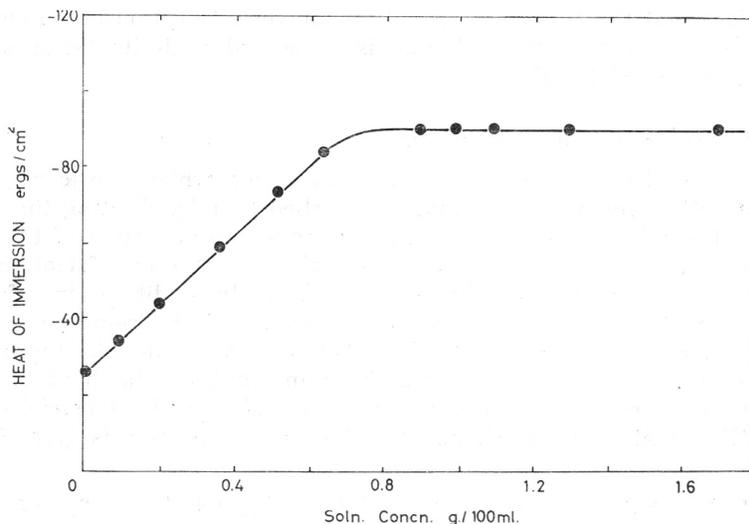


Fig. 10. Heats of Immersion of Graphon in Aqueous *n*-Butyl Alcohol Solutions. Reprinted from Ref. (21), p. 396, by courtesy of *J. Phys. Chem.*

deriving Equation (22). Specifically, there appears to be no special interactions between the adsorbed butanol and water molecules, and the suggestion is made that the individual adsorbates occur in patches.

The heat of immersion technique deserves further exploitation in the study of solution adsorption.

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IZVOD

Adsorpcija iz otopina

A. C. Zettlemoyer i F. J. Micale

Osnovni problem teorije adsorpcije na površini čvrstog tijela je nemogućnost pronalazjenja definiranog matematičkog modela za heterogenu čvrstu površinu, kao i u činjenici da se na granici čvrsto/tekuće uvijek radi o kompetitivnoj izmjeni jedne adsorbirane komponente za drugu. Kao model za eksperimentalno proučavanje i razvoj teorija adsorpcije odlično služe površine grafitiziranih čađa, koje imaju jednoličnu, dovoljno veliku specifičnu površinu potrebnu za mjerenja. Razmatra se teorija adsorpcije iz binarnih smjesa, kako iz koncentriranih, tako i iz razrijeđenih otopina. Kao eksperimentalna metoda koja pruža najveće mogućnosti određivanja energetskih odnosa pri adsorpciji, kao i pri određivanju koncentracija pojedinih vrsta u adsorbiranom sloju, opisana je metoda mjerenja toplina kvašenja.

CENTER FOR SURFACE AND COATINGS
RESEARCH, LEHIGH UNIVERSITY,
BETHLEHEM Pa., USA