

THERMODYNAMICS OF MULTI-SOLUTE ADSORPTION FROM DILUTE AQUEOUS SOLUTIONS

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Abstract—Experimental adsorption data at 20°C are given for six dilute aqueous bi-solute systems adsorbing on activated carbon

The three-parameter Toth adsorption isotherm gives good representation of the data for aqueous single-solute adsorption. Using the thermodynamic ideal-adsorbed-solution method, total and partial adsorptions are calculated for the bi-solute systems, agreement with experimental data is good. Prediction for total adsorption is within about 2–10% and for adsorption of individual components within about 3–20%. In the prediction calculations only single-solute data are used.

A new three-parameter adsorption isotherm is presented. This new isotherm also represents the single-solute data well. For bi-solute systems where dissociation is negligible, calculated individual adsorptions agree with experiment within 2%.

Systematic deviations between calculated and observed results may be due to the acidities of the solutes. In the future, adsorption experiments should be done under controlled pH conditions.

INTRODUCTION

Adsorption onto activated carbon provides a possible technique for purification of industrial wastewaters. Design of a large-scale adsorption column requires, in addition to rate data, information on equilibrium properties, commonly called "adsorption isotherms". We are concerned here with the calculation of adsorption equilibria for multi-solute adsorption, that is, for dilute aqueous solutions containing two (or more) organic solutes that adsorb on the carbon surface. We require that equilibrium adsorption data are available for each single-solute aqueous system. Our task is to predict equilibrium adsorption for the multi-solute aqueous system without using any multi-solute data.

Several years ago, Radke and Prausnitz[1] presented a thermodynamic method for predicting aqueous multi-solute adsorption equilibria from single-solute adsorption data. This method, which utilizes the concept of an ideal solution, proposed by Myers and Prausnitz[2], is useful for engineering design because the experimental effort required to obtain multi-solute adsorption data is much larger than that required to obtain single-solute adsorption data. The thermodynamic method is based on a minimum of assumptions, it is not derived from a specific molecular model but follows from thermodynamic arguments appropriate to dilute solutions.

EXPERIMENTAL

The experimental method is essentially the same as that given in an earlier publication[3]. A commercial activated carbon, B10, from Lurgi (Frankfurt/Main) was used as the adsorbent. Before use, the carbon was boiled in dilute hydrochloric acid to remove acid-soluble impurities, it was then washed with distilled water and subsequently extracted with water for four weeks in a Soxhlet apparatus. Finally, it was dried at 110°C for two days and then was kept in a desiccator containing silica-gel. The physical properties of the carbon are shown in Table 1.

The adsorbates studied are the aqueous bi-solute systems: phenol/*p*-nitrophenol, *p*-chlorophenol/*p*-nitrophenol, *p*-nitrophenol/benzoic acid, *p*-chlorophenol/phenyl acetic acid, *o*-phenylphenol/*p*-nitrophenol and 2,4-dichlorophenol/dodecyl benzol sulfonic acid.

Table 1 Physical properties of activated carbon B10

Equivalent particle radius (mm)	0.62
Particle density (g/cm ³)	0.5
Pore volume (cm ³ /g)	
Total	1.5
Micro (100 Å or less)	0.77
Macro (more than 100 Å)	0.73
BET surface area (m ² /g)	1400–1500

Data have also been obtained for all single-solute systems

The particular binary mixtures were selected because they are representative of the organic contaminants that frequently must be removed from water, and because they exhibit different adsorption equilibrium behavior. An additional criterion for selection was that the desired combinations of solutes can be easily analyzed. The solutions were prepared with deionized water, purified with activated carbon [specific conductivity $< 10^{-6} (\Omega\text{-cm})^{-1}$].

The concentrations of the individual organic solutes were determined using ultraviolet spectrophotometry. With the bi-solute systems it was necessary to measure the absorbance at two different wavelengths. The concentration of each solute was then obtained by solving the corresponding Lambert-Beer equations.

Adsorption equilibria were obtained by contacting known weights of carbon with 200-ml aliquots of a given solution in 250-ml glass bottles. Prior to use, the carbon was degassed under vacuum. The adsorption equilibria in the low concentration range (0.01–0.1 mmole/l) were determined using powdered activated carbon to ensure that a representative sample of carbon was obtained.

The bottles were placed on a gyratory shaker and agitated for 3–4 days at 20°C.

After equilibrium was obtained, a sample was taken from each bottle. Prior to analysis, it was filtered through a 0.45- μ -membrane filter to remove any suspended carbon.

The amount of each solute adsorbed on the carbon at equilibrium was calculated from the mass balance equation.

Tables 2–16 give equilibrium data for single-solute and bi-solute systems.† The experimental data at 20°C cover, approximately, the concentration range 5×10^{-4} to 10 mmole/l for the phenol/*p*-nitrophenol system, 5×10^{-4} to 10^{-1} mmole/l for the *o*-phenylphenol/*p*-nitrophenol system and 10^{-1} to 10 mmole/l for the other four systems.

Adsorption equilibria for single-solute systems were obtained, approximately, over the concentration range 5×10^{-4} to 10 mmole/l except for the ortho-phenylphenol system where the range was 5×10^{-5} to 10^{-1} mmole/l.

For the system 2,4-dichlorophenol/dodecyl benzol sulfonic acid, the experimental uncertainty is within $\pm 10\%$. Other measured values were found to be reproducible within $\pm 3\%$.

MATHEMATICAL REPRESENTATION OF SINGLE-SOLUTE DATA

The thermodynamic method for predicting multi-solute adsorption equilibria requires reliable single-solute data, for convenience in calculation, it is desirable that these data be represented accurately by a relatively simple mathematical equation (adsorption isotherm). However, not only must the equation represent the data within experimental uncertainty but, in addition, the equation must satisfy a necessary thermodynamic boundary

condition at very low surface coverage the equation must show that the adsorption of the solute (per unit mass of adsorbent) is proportional to the solute's concentration in the (aqueous) liquid. This boundary condition is Henry's law.

Because the surface of activated carbon is highly heterogeneous, extremely low concentrations are required to attain the Henry's law region. Due to experimental difficulties with activated carbon, the Henry's law region is almost never reached experimentally. Therefore it is difficult to obtain a meaningful fit of experimental single-solute data using an equation which, in the limit of very low concentrations, reduces to Henry's law.

A popular adsorption isotherm for single-solute systems is that proposed by Freundlich about sixty years ago. This empirical isotherm, suitable for highly heterogeneous surfaces [4], often represents well typical adsorption data over a restricted range of concentrations. At vanishing concentrations, Freundlich's equation does not approach Henry's law. It is often found that when Freundlich's equation is fit to adsorption data at high and intermediate concentrations, it provides a poor fit for adsorption data at low concentrations.

To fit the experimental single-solute data, we considered several equations that have been proposed in the literature. The equation of Freundlich was rejected because it does not obey the necessary boundary condition at vanishing concentrations. The Dubinin-Radushkevitch equation [5] was also rejected for the same reason. The Langmuir equation obeys the correct boundary condition but, because it is intended for homogeneous surfaces, it is not capable of giving a good representation of the data considered here. Finally, the five-parameter interpolation equation of Newman, used by Radke [6], was also rejected because in most practical cases, single-solute data are not sufficiently plentiful to justify use of five parameters for one single-solute system at one temperature.

Attention was initially restricted to three single-solute adsorption isotherms. Each of these reduces to Henry's law at very low concentrations and each contains three adjustable parameters. They are

Toth equation [7]

$$n_i = n_i^\infty c_i (b + c_i^M)^{-1/M} \quad (1)$$

Redlich-Peterson equation [8]

$$n_i = K_1 c_i (1 + K_2 c_i^a)^{-1} \quad (2)$$

Three-parameter Newman equation [6]

$$n_i = [(Ac_i)^{-1} + l(Bc_i^l)^{-1}] \times [(Ac_i)^{-1} + (Bc_i^l)^{-1}]^{-2} \quad (3)$$

In these equations, n_i is the millimoles of component i adsorbed per gram of adsorbent, c_i is the concentration of component i in millimoles per liter and all other letters denote empirical constants. The quantity n_i^∞ , also an empirical parameter, indicates a fictitious maximum adsorption, viz. that achieved when $c_i \rightarrow \infty$.

†These tables are not reproduced here but are available upon request to the authors at Karlsruhe.

The equation of Toth is sometimes written in an equivalent form

$$n_i = n_i^\infty (c_i/a) [1 + (c_i/a)^M]^{-1/M} \quad (1a)$$

where $a = b^{1/M}$ has units of millimoles per liter

The Redlich-Peterson equation[8] approaches Freundlich's equation at large concentration. In a slightly different form, it was used also by Radke[6]

Table 17 shows how well the three equations fit the single-solute data. For each system and for each equation, all final experimental data were used and, using a least-squares data reduction method, the three parameters were obtained to minimize the deviation between calculated and experimental adsorption.

It is clear that eqns (1) and (12) give the best representation for all systems although the goodness-of-fit is not strongly different from that obtained with the other equations. Table 18 gives the parameters for eqn (1), Table 22 gives the parameters for eqn (12)

coverage and is related to the differential enthalpy of adsorption Q by

$$\delta = d \exp - Q/RT \quad (5)$$

where d is a constant, T is the absolute temperature and R is the gas constant

For a heterogeneous surface, Q is not constant but depends strongly on the surface coverage. Toth shows that, subject to certain approximations, the Langmuir equation is still applicable provided δ is given by

$$\delta = k \exp - \bar{Q}/RT \quad (6)$$

where \bar{Q} is the integral enthalpy of adsorption and where \bar{Q} , however, is a function of n_i . The problem now is to specify this dependence. Toward that end, Toth introduces a dimensionless quantity Ψ defined by

$$\Psi = \frac{d \ln c_i}{d \ln n_i} - 1 \quad (7)$$

Table 17 Absolute relative percent deviations for fit of single-solute adsorption data at 20°C†

Solute	Equation			
	1	2	3	12
Phenol	1.9	6.7	11.5	12‡
<i>p</i> -Nitrophenol	1.1	2.0	7.6	0.9
<i>p</i> -Chlorophenol	3.4	4.8	8.0	3.2
2,4-Dichlorophenol	1.5	1.3	5.3	1.3
Benzoic acid	2.2	4.5	6.4	4.2
Phenyl acetic acid	3.6	4.0	3.9	4.3
<i>o</i> -Phenyl phenol	1.4	1.6	3.8	2.1
Dodecyl benzol sulfonic acid	3.2	4.5	9.6	3.7

$$\dagger \text{Absolute relative percent deviation} = \frac{100}{N} \left(\sum_N \frac{|n_{\text{calc}} - n_{\text{exp}}|}{n_{\text{exp}}} \right)$$

‡See footnote on Table 22

Table 18 Parameters in Toth's equation on active carbon at 20°C

Solute	n_i^∞	$10^2 b$	$10^2 M$
	(mmoles/g)	(mmoles/g) ^M	
Phenol	14.15	32.11	14.78
<i>p</i> -Nitrophenol	11.91	14.94	10.72
<i>p</i> -Chlorophenol	9.09	17.31	14.84
2,4-Dichlorophenol	33.15	14.66	6.42
Benzoic acid	10.87	25.44	18.00
Phenyl acetic acid	32.48	27.19	8.95
<i>o</i> -Phenyl phenol	17.20	11.48	7.23
Dodecyl benzol sulfonic acid	1.91	6.27	19.47

TOTH'S EQUATION

Toth's work[7], published in the East European literature, is little known in the West. Toth has considered only adsorption of gases but his ideas can be extended to adsorption of solutes from dilute aqueous solutions.

Toth starts with the Langmuir equation

$$n_i = n_i^\infty c_i (\delta + c_i)^{-1} \quad (4)$$

For a homogeneous surface, δ is independent of surface

For a Langmuir isotherm (homogeneous surface)

$$\Psi = \frac{c_i}{\delta} \quad (8)$$

but for an arbitrary heterogeneous surface the relation between ψ and c_i is more complex.

Therefore, if experimental data can be obtained to determine Ψ , it should be possible to obtain some information on \bar{Q} ; the advantage is that Ψ can be found

from isothermal adsorption data whereas a direct experimental determination of \bar{Q} requires either calorimetry (difficult experimentally) or else differentiation with respect to temperature of several adsorption isotherms (low accuracy)

If Freundlich's isotherm is substituted into eqn (7), Ψ is a constant, independent of c . Upon examining adsorption data on heterogeneous surfaces, Toth finds that typical experimental results fall between the limits set by the (homogeneous) Langmuir isotherm and the Freundlich isotherm. Toth suggests a function of the form

$$\Psi = \alpha c_i^\beta \quad (9)$$

where α and β are constants. When we set $\alpha = 1/b$ and $\beta = M$, integration of eqn (7) gives Toth's equation, eqn (1). In that integration Toth uses the boundary condition $n_i \rightarrow n_i^\infty$ when $c_i \rightarrow \infty$

For Langmuir's equation, $\beta = 1$ and for Freundlich's equation $\beta = 0$. If Henry's law were to hold for all concentrations, α would have to be zero.

Since Ψ can be obtained easily from experimental adsorption data obtained at one temperature, it may be useful for studying the suitability of various proposed adsorption isotherms.

Figures 1-4 show the adsorption data and function Ψ (calculated from experimental data) for four of the single-solute systems studied here. Similar results are obtained for the remaining systems. It is evident that Toth's assumption (eqn 9) provides a satisfactory approximation.

MULTI-SOLUTE CALCULATIONS

Calculations for multi-solute adsorption were performed for six aqueous bi-solute systems at 20°C. These are shown in Table 19. Details of the calculation need not be repeated here since the method used is exactly that of Radke and Prausnitz[1] which, in turn, follows from the earlier work of Myers and Prausnitz[2]. All calculations were performed using the CDC 6400 computer, a copy of the program is available upon request to the Berkeley authors. Integration of the Toth equation to obtain the surface pressure was done numerically because analytical integration, while possible[7], is tedious.

Table 19 shows that, except for the last system, the thermodynamic method provides a good technique for calculating total adsorption. Calculations for adsorption of individual solutes (in a multi-solute system) are not quite as good but still remarkable considering that only

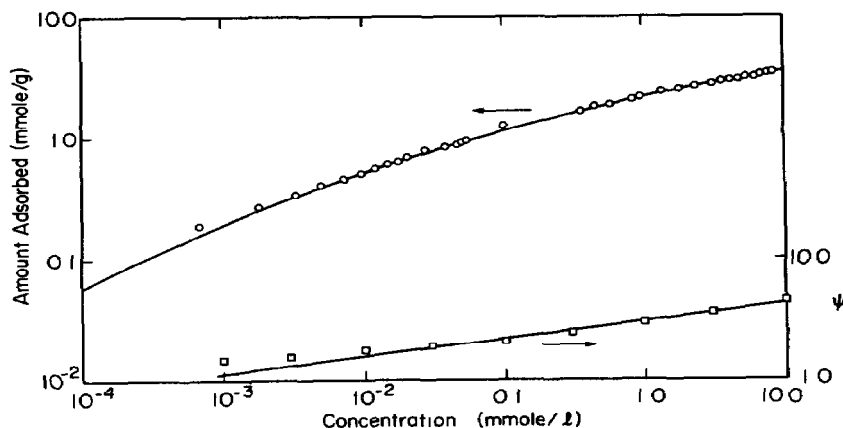


Fig 1 Adsorption isotherm of phenol from water

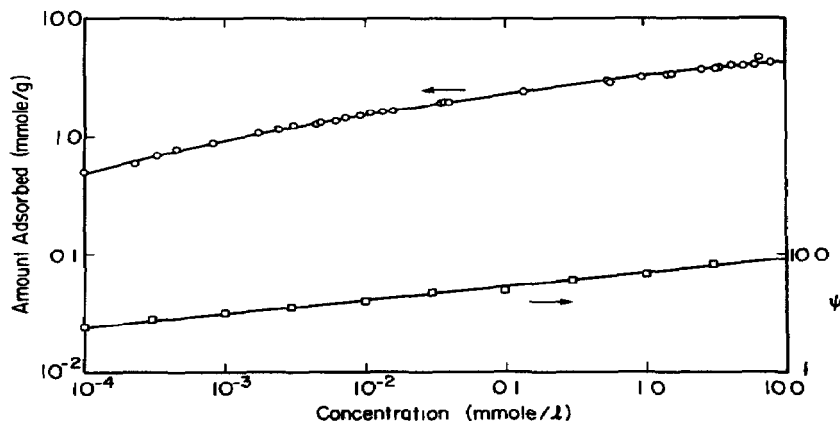


Fig 2 Adsorption isotherm of para-nitrophenol from water Equation (1)

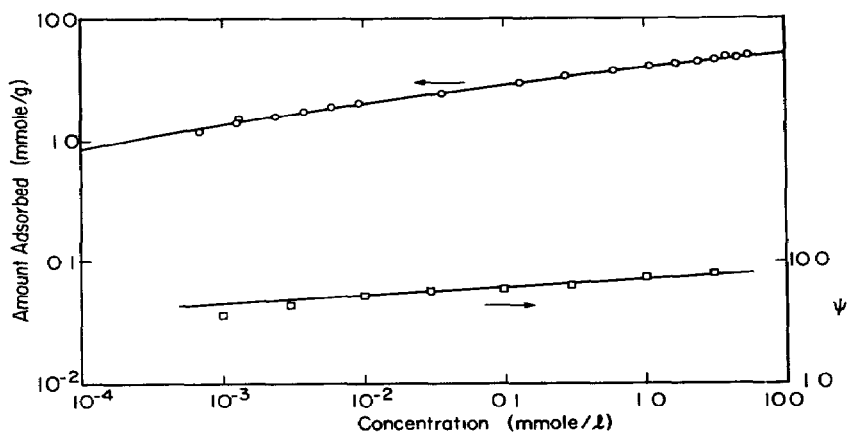


Fig 3 Adsorption isotherm of 2,4-dichlorophenol from water

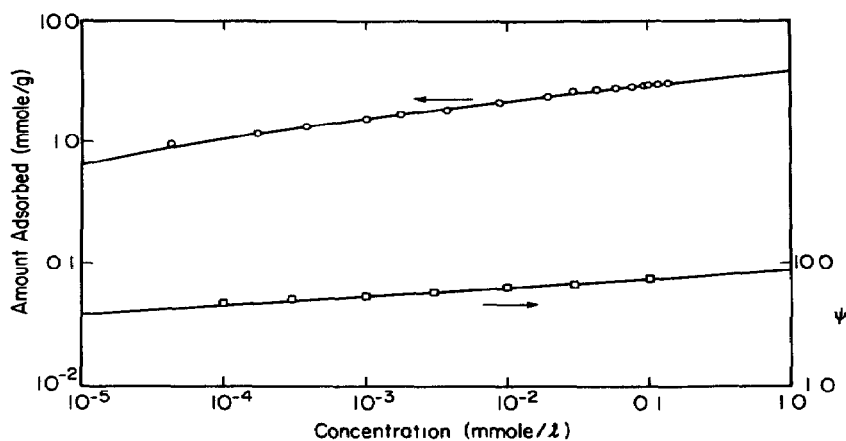


Fig 4 Adsorption isotherm of ortho-phenylphenol from water

Table 19 Prediction of multi-solute adsorption at 20°C using Toth's isotherm

Solutes	No of expt l points	Total adsorption		Av Absolute % difference in individual solute adsorption§
		Av relative % difference†	Av absolute difference (mmoles/g)‡	
Phenol/ <i>p</i> -nitrophenol	230	2.9	0.07	2.8
<i>p</i> -Nitrophenol/ <i>p</i> -chlorophenol	64	3.6	0.12	3.2
<i>p</i> -Nitrophenol/benzoic acid	64	4.9	0.17	15.3
<i>p</i> -Chlorophenol/phenyl acetic acid	64	4.0	0.12	7.4
<i>p</i> -Nitrophenol/ <i>o</i> -phenyl phenol	45	6.6	0.16	8.0
2,4-dichlorophenol/dodecyl benzyl sulfonic acid	16	11.0	0.38	21.5

$$\dagger \frac{100}{N} \sum_{i=1}^N |(n_{T \text{ calc}} - n_{T \text{ exp}})| / n_{T \text{ exp}}$$

$$\ddagger \frac{1}{N} \sum_{i=1}^N |n_{T \text{ calc}} - n_{T \text{ exp}}|$$

$$\S \frac{100}{N} \sum_{i=1}^N |z_{i \text{ exp}} - z_{i \text{ calc}}|$$

n_T total millimoles adsorbed calc calculated exp experimental N No of measurements z_i mole fraction of component i in adsorbed phase (water-free basis)

Table 20 Direction of deviations from experimental results

System	Solutes 1 and 2†	Calc total adsorption	Calc mole fraction (on surface) of more acidic component	$P_{K1} - P_{K2}$
I	Phenol/ <i>p</i> -nitrophenol	slightly low	OK	2.8
II	<i>p</i> -Chlorophenol/ <i>p</i> -nitrophenol	slightly low	OK	2.2
III	<i>p</i> -Nitrophenol/benzoic acid	low	low	3.0
IV	<i>p</i> -Chlorophenol/phenyl acetic acid	low	low	5.1
V	<i>o</i> -Phenyl phenol/ <i>p</i> -nitrophenol	low	low	2.7
VI	2,4-Dichlorophenol/dodecyl benzol sulfonic acid	high	low	5.2

†More acidic solute is solute 2

single-solute (no bi-solute) data were used in the calculations

Table 20 gives the direction in which the calculated adsorption differs from experiment. Deviations between calculated and observed results are not random. For systems I–V, calculated total adsorptions are lower than those found experimentally while for system VI, they are higher. Deviations are small for systems I and II but, for systems III–VI, a noticeable bias exists. In systems III–V, the calculated results are consistently low, and in system VI they are consistently high. The remaining two systems are adequately predicted by the ideal-solution model.

In the absence of more detailed data, it is not possible to explain why the observed results differ from those calculated using the ideal-solution method. However, it may be useful to consider a speculation leading to a possible explanation. Towards that end, we note that there are large differences in the acidities of the solutes.

Table 21 shows the dissociation constants for each solute, also, the last column of Table 20 gives the P_K difference between the lesser and the more acidic solute for each solute pair.

For systems I and II, the solutes have low acidity and, although $P_{K1} - P_{K2}$ is appreciable, there is little effect because the acidities, while different, are very small, for these systems, the ideal-solution method gives good results. For the remaining systems, $P_{K1} - P_{K2}$ is also appreciable but, more important, the acidities of the solutes are now much larger. For these systems, the

calculated surface mole fraction of the more acidic component is consistently lower than that observed. It appears, therefore, that the nature of the surface is such that it distinguishes between components of different acidities.

Due to what appears to be a systematic effect of acidity on adsorption, it will be useful to obtain experimental adsorption data for the various organic solutes (and their mixtures) under controlled pH conditions. It has been reported previously [9] that adsorption is pH dependent, fortunately the pH dependence can be determined with relatively simple adsorption experiments by adding to the aqueous solution small amounts of a strong acid (e.g. HNO_3) or strong base (e.g. NaOH).

A brief discussion of thermodynamic consistency in bi-solute adsorption is given in the Appendix.

A NEW ADSORPTION ISOTHERM

Active carbon is characterized by a highly heterogeneous surface. Highest energy sites are filled first so that the heat of adsorption declines rapidly with increased surface coverage. The isosteric heat of adsorption has the form

$$q_{st} - q_{st}^0 = -Cn_i^p \quad (10)$$

where $0 < p < 1$ and q_{st}^0 is the isosteric heat for the solute at the limit of zero surface coverage. The constants C and p can be related to the distribution of energy sites on the surface by an integral transformation of the adsorption isotherm [10]. For example, a value of $p = 0$ corresponds to a uniform surface for which all sites have the same energy. It can be shown [11] from thermodynamics that the adsorption isotherm corresponding to eqn (10) is

$$\ln c_i = \ln n_i - \ln H + kn_i^p \quad (11)$$

or

$$c_i = \frac{n_i}{H} e^{kn_i^p} \quad (12)$$

p is a constant, H and k are functions of temperature only

$$C = -RT^2 \frac{dk}{dT} \quad (13)$$

$$q_{st}^0 = -RT^2 \frac{d \ln H}{dT} \quad (14)$$

Table 21 Acidities of solutes in water at 25°C†

Solute	$P_K \ddagger$	
Phenol	10	<div style="display: flex; align-items: center; justify-content: center;"> <div style="border-left: 1px solid black; height: 100px; margin: 0 10px;"></div> <div style="writing-mode: vertical-rl; transform: rotate(180deg);"> rising acidity </div> </div>
<i>o</i> -Phenyl phenol	9.9	
<i>p</i> -Chlorophenol	9.4	
2,4-Dichlorophenol	7.8	
<i>p</i> -Nitrophenol	7.2	
Phenyl acetic acid	4.3	
Benzoic acid	4.2	
Dodecyl benzol sulfonic acid	2.6	

†Kortüm G., Vogel W. and Andrussov K., *Dissociation Constants of Organic Acids in Aqueous Solutions* Butterworths, London 1961.

‡ $P_K = -\log_{10} K$, $K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$, $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

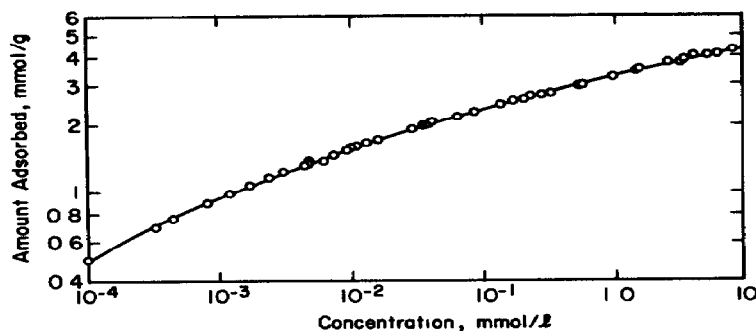


Fig 5 Adsorption isotherm of para-nitrophenol from water Equation (12)

The spreading pressure π caused by loading of the solute on area A is

$$\frac{\pi A}{RT} = n_i + \frac{kp}{(p+1)} n_i^{p+1} \quad (15)$$

The reference state for spreading pressure, $\pi = 0$, is the solid adsorbent immersed in pure water

Equation (12) is an isotherm for adsorption of dilute solutes on heterogeneous surfaces Table 22 presents constants derived for eqn (12) using least-squares data reduction Deviations between calculated and observed adsorption for single-solute systems are shown in Table 17 As shown by this table, the new isotherm represents the data as well as the Toth equation

A comparison of the experimental points with eqn (12) is shown for *p*-nitrophenol in Fig 5 The average relative percentage difference is 1% for a total of 43 experimental points A comparable fit of eqn (12) was obtained for phenol

For *p*-chlorophenol, phenyl acetic acid and benzoic acid, there are fewer experimental points than for phenol and *p*-nitrophenol Moreover, the scatter in the experimental data is larger so that the average relative percentage difference between eqn (12) and the data is about 3–5%

The most carefully studied solute pair was *p*-nitrophenol + phenol, for which 230 experimental points were obtained Figure 6 shows individual isotherms for adsorption of *p*-nitrophenol in the presence of various starting concentrations of phenol Figures 7 and 8 present data for adsorption of phenol in the presence of

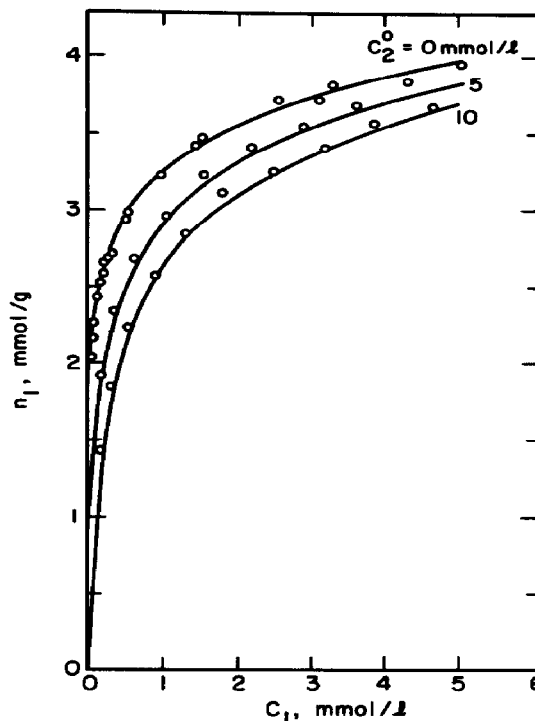


Fig 6 Adsorption of para-nitrophenol(1) from water at various starting concentrations of phenol(2)

p-nitrophenol These figures show that the presence of phenol barely affects the adsorption of *p*-nitrophenol, whereas the uptake of phenol is much reduced by the addition of *p*-nitrophenol The solid lines were calculated

Table 22 Constants in eqn (12) for adsorption from aqueous solution on active carbon at 20°C

Solute	H l/g	k (mmoles/g) ^{-p}	10 ² p
Phenol†	6.812×10^4	8.497	25.00
<i>p</i> -Nitrophenol	1.586×10^5	5.329	60.00
<i>p</i> -Chlorophenol	4.677×10^3	2.959	80.00
2,4-Dichlorophenol	5.199×10^5	5.088	61.51
Benzoic acid	1.248×10^4	4.738	50.00
Phenyl acetic acid	7.659×10^3	5.608	47.06
<i>o</i> -Phenyl phenol	1.085×10^6	4.522	78.03
Dodecyl benzol sulfonic acid	1.651×10^4	5.987	137.2

†For phenol another equation is needed in the range $2.59 < n < 5.6$ mmol/g where $c = 0.007297 n^{5.802}$

Table 23 Prediction of multi-solute adsorption at 20°C using the new adsorption isotherm

Solute pairs	No of expt'l points	Av relative % difference in individual solute adsorption†
<i>p</i> -Nitrophenol/phenol	230	2
<i>p</i> -Nitrophenol/ <i>p</i> -chlorophenol	64	2
<i>p</i> -Nitrophenol/benzoic acid	64	21
<i>p</i> -Chlorophenol/phenyl acetic acid	64	17

$$\dagger \frac{100}{N} \sum_{i=1}^N |n_{i,calc} - n_{i,exp}| / n_{i,exp}$$

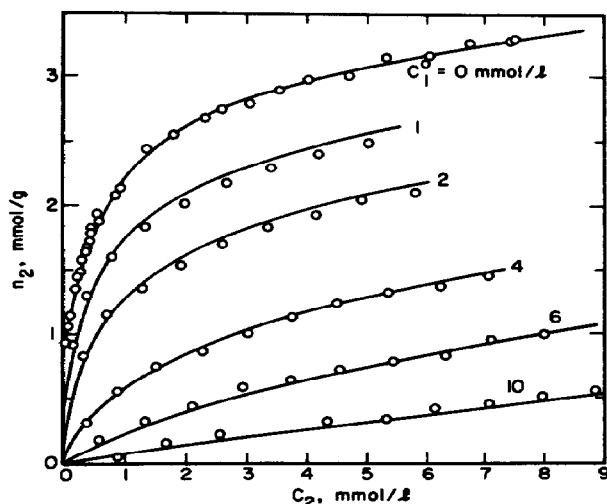


Fig 7 Adsorption of phenol(2) from water at various starting concentrations of para-nitrophenol(1) High coverage region

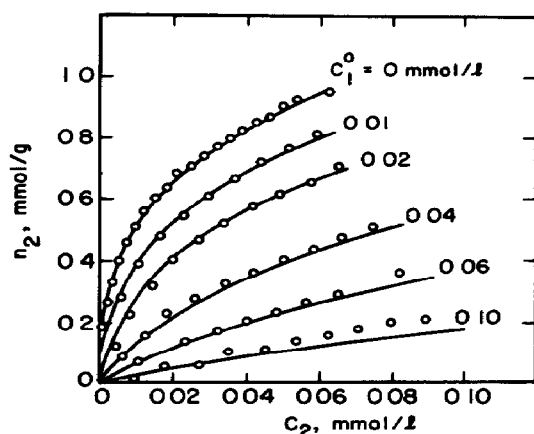


Fig 8 Adsorption of phenol(2) from water at various starting concentrations of para-nitrophenol(1) Low coverage region

by ideal-adsorbed-solution theory and agreement is remarkable the average relative percentage difference is 2%. The reason for the highly unsymmetrical behavior is that the relative distribution coefficient for *p*-nitrophenol on carbon in the presence of phenol varies from 30 at high coverage to nearly 100 at low coverage

Comparable agreement between ideal-adsorbed solution theory and experiment was observed for the solute pair *p*-nitrophenol + *p*-chlorophenol. For the other pairs of solutes, much larger errors were observed, these are summarized in Table 23. Moreover, these errors are systematic in that the calculated surface mole fraction of the more acidic component is always lower than that observed.

Referring to Table 21, it appears that solutes with $P_K > 7$ obey ideal-adsorbed-solution theory almost quantitatively but solutes with $P_K < 7$ (phenyl acetic acid, benzoic acid) exhibit large deviations. Since the latter solutes are partially dissociated even at the high range of concentration above 1 mmol/l, it is likely that the discrepancies are caused by dissociation effects rather than nonidealities in the adsorbed phase.

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APPENDIX

Thermodynamic consistency of binary solute adsorption data

The time required for attainment of equilibrium after an adsorbent is added to a solution is several days or weeks [12], even when the solution containing the adsorbent is agitated. Therefore, it is important to check for thermodynamic consistency.

Consider binary-solute adsorption the Gibbs adsorption isotherm is

$$Ad\pi = n_1 d\mu_1 + n_2 d\mu_2 \quad (A1)$$

For dilute solutes which obey Henry's law in the bulk phase

$$\frac{Ad\pi}{RT} = n_1 d \ln c_1 + n_2 d \ln c_2 \quad (\text{A2})$$

For any closed path,

$$\oint (n_1 d \ln c_1 + n_2 d \ln c_2) = 0 \quad (\text{A3})$$

because π is a state function. Consider a locus of constant total bulk concentration through the binary-solute regime starting with c_1 at zero and ending with c_2 at zero

$$c_1 + c_2 = c = \text{constant} \quad (\text{A4})$$

Then,

$$\frac{A(\pi_1 - \pi_2)}{RT} = \int_{c_1=0}^c \left[\frac{n_1}{c_1} - \frac{n_2}{c_2} \right] d c_1 \quad (\text{A5})$$

The left-hand side of this equation is evaluated from single-solute data and the right-hand side is an integration of the binary-solute data along the locus of constant total bulk concentration. If the mixed solutes obey ideal-adsorbed-solution-theory, eqn (A5) is satisfied automatically. However, eqn (A5) is a valid test of thermodynamic consistency even if the solutes form nonideal solutions in the adsorbed phase.

If experimental data satisfy the integral consistency test in eqn (A5) but do not agree with the predictions of ideal-adsorbed-solution theory, activity coefficients in the adsorbed phase can be calculated. For a particular binary-solute isotherm, the first step is to locate loci of constant π by integrating the differential equation

$$n_1 d \ln c_1 + n_2 d \ln c_2 = 0 \quad (\text{A6})$$

between the limits of the single solutes. The end points of the integration establish standard states (n_i^0, c_i^0) for each locus of constant π . Activity coefficients are obtained from

$$\gamma_i = \frac{c_i}{c_i^0 x_i} \quad (\text{A7})$$

x_i = mole fraction of adsorbed species i

We define an excess Gibbs energy

$$g^e = RT[x_1 \ln \gamma_1 + x_2 \ln \gamma_2] \quad (\text{A8})$$

and an area change upon mixing

$$\left(\frac{1}{n}\right)^e = \frac{1}{n} - \left[\frac{x_1}{n_1^0} + \frac{x_2}{n_2^0} \right] \quad (\text{A9})$$

The excess Gibbs energy is a function of spreading pressure as well as composition, and it can be shown that these two excess functions are related by

$$\frac{\partial(g^e/RT)}{\partial(\pi A/RT)} = \left(\frac{1}{n}\right)^e \quad (\text{A10})$$

The excess functions are zero for experimental data which obey ideal-adsorbed-solution theory. Experimental binary-solute data which are sufficiently extensive and accurate enough to be tested by eqn (A10), have not yet been measured. However, the experimental data can be subjected to an integral thermodynamic consistency test according to eqn (A3) using empirical equations for representing the mixture data as proposed earlier[3]

$$n_1 = \frac{a_1 c_1^{b_{11}+b_{12}}}{c_1^{b_{11}} + a_{12} c_2^{b_{12}}} \quad (\text{A11})$$

$$n_2 = \frac{a_2 c_2^{b_{21}+b_{22}}}{c_2^{b_{22}} + a_{21} c_1^{b_{21}}} \quad (\text{A12})$$

Table A1 Data for the integral thermodynamic consistency test

System†	a_1^\ddagger	b_1	b_{11}	a_{12}	b_{12}	a_2	b_2	b_{22}	a_{21}	b_{21}	c_1, c_2^i (mmole/l)	c_1^u, c_2^u (mmole/l)	D (%)
I	2.16	0.23	0.77	14.0	0.70	3.25	0.13	1.0	0.0185	1.2	0.2	4.0	0.19
II	3.10	0.15	0.90	1.90	0.93	3.25	0.13	0.96	0.29	1.0	0.2	4.0	0.78
III	3.25	0.13	0.90	0.31	1.04	3.05	0.20	0.90	1.80	0.81	0.2	4.0	1.97
IV	3.10	0.15	0.65	0.25	0.67	2.20	0.21	0.49	1.65	0.64	0.2	4.0	0.47
V	4.33	0.15	0.81	0.12	1.07	4.18	0.22	0.64	5.9	0.65	0.002	0.04	2.20
VI	3.86	0.12	0.39	0.48	0.25	1.41	0.05	0.57	1.16	0.37	0.2	4.0	3.90

†More acidic solute is solute 2

‡In using the constants the liquid and surface phase equilibrium concentration are respectively, millimoles per liter and millimoles per gram

The constants for the six bi-solute systems are shown in Table A1

For the consistency test one can choose the following closed path within the validity range of eqns (A11) and (A12)

$$(c_1^l, c_2^l) \xrightarrow{J_1} (c_1^u, c_2^l) \xrightarrow{J_2} (c_1^u, c_2^u) \xrightarrow{J_3} (c_1^l, c_2^u) \xrightarrow{J_4} (c_1^l, c_2^l)$$

where the superscripts *l* and *u* denote the lower and the upper concentrations, respectively as shown in Table A1 for each mixture

With the integrals

$$J_1 = \int_{c_1^l}^{c_1^u} \frac{a_1 c_1^{b_{11}+b_{11}-1}}{c_1^{b_{11}} + a_{12}(c_2^l)^{b_{12}}} dc_1$$

$$J_2 = \int_{c_2^l}^{c_2^u} \frac{a_2 c_2^{b_{22}+b_{22}-1}}{c_2^{b_{22}} + a_{21}(c_1^u)^{b_{21}}} dc_2$$

$$J_3 = \int_{c_1^l}^{c_1^u} \frac{a_1 c_1^{b_{11}+b_{11}-1}}{c_1^{b_{11}} + a_{12}(c_2^u)^{b_{12}}} dc_1$$

$$J_4 = \int_{c_2^l}^{c_2^u} \frac{a_2 c_2^{b_{22}+b_{22}-1}}{c_2^{b_{22}} + a_{21}(c_1^l)^{b_{21}}} dc_2$$

the clockwise integral (A3) becomes

$$J_1 + J_2 - J_3 - J_4 = 0 \quad (\text{A13})$$

This integral is zero only for perfect data. We define the percent deviation *D*

$$D = \frac{|J_1 + J_2 - J_3 - J_4|}{|J_1| + |J_2| + |J_3| + |J_4|} 100 \quad (\text{A14})$$

Table A1 shows calculated values of *D*. The results indicate that the experimental data are thermodynamically consistent within the accuracy of the experiment.