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Thermodynamics of Multi-Solute Adsorption from Dilute Liquid Solutions

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The thermodynamics of ideal dilute solutions is applied toward establishing a method for predicting multi-solute adsorption using only data for single-solute adsorption from dilute liquid solution. The method is similar to that proposed by Myers and Prausnitz for adsorption of gas mixtures.

Experimental adsorption data for activated carbon at 25°C are reported for dilute aqueous solutions containing acetone and propionitrile, and *p*-chlorophenol and *p*-cresol. Calculated and experimental results are in excellent agreement for the first system and in fair agreement for the second system. It appears that the ideal dilute-solution theory for predicting multi-solute adsorption is most reliable for those systems where solute adsorption loading is moderate. When solute adsorption loading is large, the simplifying assumptions in the theory must be relaxed to allow for solute-solute interactions on the surface. The method presented here is simple to use and provides good approximations for engineering design.

Recent studies indicate the economic feasibility of purifying industrial and municipal waste waters by adsorption on activated carbon (*1*, *2*). Adsorption equilibria for mixtures of organic pollutants are required for design of these purification processes. To reduce experimental work, it is desirable to predict the adsorption of mixed organic solutes in dilute aqueous solution employing only experimental

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data from single-solute adsorption. In this paper we extend the method of Myers and Prausnitz (3) for mixed-gas adsorption to multi-solute adsorption from dilute liquid solution.

In spite of its industrial importance, little attention has been given to the thermodynamics of multi-solute adsorption from liquid solution. Amiot (*4*) and Kolthoff and van der Groot (5) report a few experimental data for adsorption of binary solutes from aqueous solution but neither one attempts prediction of the mixture results. Ockrent (*6*) and, more recently, Weber and Morris (*7*) employ the Langmuir mixture model to predict two-solute adsorption. These authors fit single-solute isotherms with the two-parameter Langmuir equation and, using these parameters, calculate multi-solute adsorption. The difficulty with this approach is two-fold: first, the Langmuir equation does not provide an adequate fit for many single-solute isotherms. Second, the Langmuir mixture model violates the Gibbs adsorption equation and consequently is thermodynamically inconsistent (*8*).

It is desirable to establish a procedure for calculating multi-solute adsorption equilibria which is not restricted to a specific theoretical model. Such a procedure, applicable to dilute solutions, is described here. It is based on an exact formulation of the thermodynamics of adsorption from dilute solution; when this formulation is coupled with well-defined assumptions, it is a direct extension of the method proposed earlier (3) for mixed-gas adsorption. The next four sections present the derivation. The reader interested only in the calculation procedure and the results should proceed to the paragraph preceding Equation (24).

THERMODYNAMIC FRAMEWORK

As shown by Gibbs (*9, 10*), the solution-solid interfacial region can be considered as a separate two-dimensional phase. If the solid is assumed to be inert and to possess a specific surface area identical for all adsorbates, then the differential of the Helmholtz energy of the adsorbed phase, designated by superscript *a*, is given by

$$dA^a = -S^a dT + \sigma d\mathcal{A} + \sum_i \mu_i^a dn_i^a + \mu_s^a dn_s^a \qquad (1)$$

where subscript *i* represents solute and subscript *s* represents solvent. The interfacial tension is indicated by σ, and $\mathcal{A}$ stands for the area of the solution-solid interface. The amount of solid adsorbed does not appear in Equation (1) because the Gibbs dividing surface is chosen in such a manner that the adsorption of solid is zero.

By Euler's theorem, Equation (1) can be integrated to give

$$A^a = \sigma\mathcal{A} + \sum_i \mu_i^a n_i^a + \mu_s^a n_s^a \qquad (2)$$

Differentiation of Equation (2) and comparison with Equation (1) lead to the Gibbs isothermal adsorption equation

$$-\mathcal{A}d\sigma = \sum_i n_i^a d\mu_i^a + n_s^a d\mu_s^a \quad (\text{constant } T) \qquad (3)$$

We anticipate the result that at equilibrium the chemical potentials of the adsorbed and liquid phases are identical. Hence the isothermal Gibbs-Duhem equation can be written as

$$\sum_i c_i d\mu_i^a + c_s d\mu_s^a = 0 \quad (\text{constant } T) \qquad (4)$$

where c_i and c_s are the bulk liquid concentrations of solute *i* and solvent *s* in moles per unit volume. [The small effect of pressure on liquid phase properties is neglected in Equation (4)]. Substitution of Equation (4) into Equation (3) gives the desired result which is valid over the entire solute concentration range

$$-\mathcal{A}d\sigma = \mathcal{A}d\pi = \sum_i n_i^m d\mu_i^a \quad (\text{constant } T) \qquad (5)$$

where the summation is over solute species only. The spreading pressure π is defined as the difference between the interfacial tension of the pure solvent-solid interface and that of the solution-solid interface at the same temperature

$$\pi \equiv \sigma_{\text{pure solvent-solid}} - \sigma_{\text{solution-solid}} \qquad (6)$$

The quantity n_i^m is an invariant adsorption of solute *i* (*10*) defined by

$$n_i^m \equiv n_i^a - \frac{c_i}{c_s} n_s^a \qquad (7)$$

Moles of solute and solvent adsorbed n_i^a and n_s^a are defined as Gibbs surface excess quantities (*9, 10*), relative to that dividing surface which makes the adsorption of solid zero. The invariant adsorption n_i^m, being independent of the location of the Gibbs dividing surface, is measurable without experimentally specifying the position of that dividing surface. Appendix A shows that in dilute solution n_i^m can be approximated by measuring the solute concentration decrease Δc_i caused by contacting a solution of known concentration and known volume *V* with a known mass of adsorbent:

$$n_i^m = V\Delta c_i \qquad (8)$$

Because of the approximate nature of Equation (8) we restrict our attention to dilute solutions. Since only invariant adsorptions of solute species appear in Equation (5), the adsorbed phase can be treated as though it were solvent free. This simplification provides helpful analogies between the adsorbed phase and three-dimensional phases. Thus Equation (5) is analogous to the isothermal Gibbs-Duhem equation with area and spreading pressure replacing volume and pressure.

It is useful to define an adsorbed-phase fugacity f_i^a according to (*11*)

$$d\mu_i^a = RTd \ln f_i^a \quad (\text{constant } T) \qquad (9)$$

and

$$\lim_{\pi \to 0} \frac{f_i^a}{z_i \pi} = 1 \quad (\text{constant } T) \qquad (10)$$

where the adsorbed-phase mole fraction is defined by

$$z_i = \frac{n_i^m}{\sum_i n_i^m} = \frac{n_i^m}{n_T^m} \qquad (11)$$

The adsorbed-phase fugacity is two-dimensional and has the same units as the spreading pressure π. Henry's law for adsorption results from the substitution of Equations (9), (10), and (11) into Equation (5). Equation (10), therefore, expresses the reasonable assumption that Henry's law for adsorption holds in the limit of zero concentration.

THE IDEAL ADSORBED PHASE

When solute species adsorb simultaneously from dilute solution at constant temperature and spreading pressure, we propose that the adsorbed phase forms an ideal solution. Thus, we assume that the fugacity f_i^a at constant temperature and spreading pressure is proportional to the mole fraction z_i

$$f_i^a(T, \pi, z_i) = z_i f_i^{ao}(T, \pi) \qquad (12)$$

where f_i^{ao} is the fugacity that single solute i exerts when it adsorbs singly from dilute solution at the same temperature and spreading pressure as those of the mixture. The superscript o denotes single-solute adsorption. Equation (12), for a two-dimensional system, is analogous to the well-known Lewis fugacity rule for a three-dimensional system. Equation (12) becomes exact as $z_i \rightarrow 1$. Just as the Lewis fugacity rule provides a good approximation at low densities, Equation (12) is most reliable when solute adsorption is small.

Equation (12) has the physical consequence that the total invariant adsorption n_T^m, at a given temperature and spreading pressure, is a function only of the adsorbed-phase composition z_i and the invariant adsorptions of the single solutes n_i^{mo} at the same temperature and spreading pressure. To verify this statement we rewrite Equation (5)

$$\frac{\mathcal{A}}{n_T^m} = \sum_i z_i \left(\frac{\partial \mu_i^a}{\partial \pi} \right)_{T,z_i} \tag{13}$$

For an ideal adsorbed phase Equations (5), (9), and (12) give

$$\left(\frac{\partial \mu_i^a}{\partial \pi} \right)_{T,z_i} = \left(\frac{\partial \mu_i^{ao}}{\partial \pi} \right)_T = \frac{\mathcal{A}}{n_i^{mo}} \tag{14}$$

Substituting Equation (14) into Equation (13) yields finally

$$\frac{1}{n_T^m} = \sum_i \frac{z_i}{n_i^{mo}} \quad (\text{constant } T, \pi) \tag{15}$$

where n_i^{mo} is the invariant adsorption of solute i if it adsorbs singly from solution at the same T and π as those of the mixture. Equation (15) for a two-dimensional system is analogous to Amagat's law of additive volumes for a three-dimensional system. It indicates that the total invariant adsorption is determined by the adsorptions of the single solutes at identical values of spreading pressure and temperature. Equation (15) provides one of two relationships of the ideal dilute-solution theory for calculating multi-solute equilibria. The second relationship results from considering the equilibria between the adsorbed and liquid phases.

PHASE EQUILIBRIA

If a mixture of solutes is in equilibrium with an adsorbent, the chemical potential of solute i in the adsorbed phase is equal to that in the liquid phase.

$$\mu_i^a = \mu_i^l \tag{16}$$

The chemical potential of the adsorbed phase depends on temperature, spreading pressure, and composition as measured by the mole fraction z_i. For this chemical potential we write the integral form of Equation (9) and we substitute the ideality assumption of Equation (12)

$$\mu_i^a(T, \pi, z_i) = \mu_i^{ao}(T, \pi) + RT \ln z_i \tag{17}$$

For single-solute adsorption the intensive variables T and π fix the concentration c_i^o in the dilute liquid phase. Thus, for μ_i^{ao} in Equation (17) we substitute

$$\mu_i^{ao} = \mu_i^{lo}[T, c_i^o(\pi)] = \mu_i^{l*}(T) + RT \ln c_i^o(\pi) \tag{18}$$

where superscript * denotes the ideal dilute-solution (Henry's law) standard state of the liquid phase. No activity coefficient is required in Equation (18) when the liquid solution is dilute. The concentration $c_i^o(\pi)$ refers to solute i when that solute adsorbs singly from solution at the same temperature and spreading pressure as those of the mixture. c_i^o has a similar interpretation to n_i^{mo} since experimental single-solute isotherms determine n_i^{mo} as a function of c_i^o.

In a dilute liquid mixture at constant temperature, μ_i^l is a function only of c_i, the concentration of i in that mixture. (Small pressure effects are neglected.) Therefore, the right side of Equation (16) becomes

$$\mu_i(T, c_i) = \mu_i^{l*}(T) + RT \ln c_i \tag{19}$$

Again, no activity coefficient is needed in Equation (19) when attention is restricted to dilute solutions. Equations (16) to (19) lead to the second relationship of ideal dilute-solution theory for calculating multi-solute equilibria

$$c_i = c_i^o(\pi) z_i \quad (\text{constant } T) \tag{20}$$

or

$$c_T x_i = c_i^o(\pi) z_i \quad (\text{constant } T) \tag{21}$$

where x_i is the solvent-free mole fraction of solute i and c_T is the total concentration of all solutes in the liquid phase. Equations (15) and (21) provide the basis for predicting multi-solute equilibria from data on single-solute adsorption from dilute solution.

We note that Equation (21) is analogous to the result for mixed-gas adsorption; when P/RT is substituted for c_T and P_i^o/RT for c_i^o, we recover the equation for prediction of mixed-gas adsorption given by Myers and Prausnitz (*3*):

$$P x_i = P_i^o(\pi) z_i \quad (\text{constant } T) \tag{22}$$

EVALUATION OF SPREADING PRESSURE

To use Equations (15) and (21) spreading pressures must be known for the various singly-adsorbing solutes in the mixture. These spreading pressures can be evaluated from Equation (5) by

$$\pi(c_i^o) = \frac{RT}{\mathcal{A}} \int_0^{c_i^o} \frac{n_i^{mo}(c_i^o)}{c_i^o}\, dc_i^o \quad (\text{constant } T) \tag{23}$$

Experimental single-solute isotherms are used to construct a curve of n_i^{mo}/c_i^o as a function of c_i^o and the area under this curve determines π. Since experimental single-solute information determines π, no theoretical model is needed to describe the adsorption equilibria.

The integration indicated in Equation (23), however, begins at zero solute concentration. Therefore, experimental data must be available over the range of loading from zero to n_i^{mo} in order to calculate π accurately. To reduce the error in determining π, Kidnay and Myers (*12*) recommend integration of the curve $d \ln c_i^o / d \ln n_i^{mo}$ versus n_i^{mo}.

CALCULATION OF MULTI-SOLUTE EQUILIBRIA

Isothermal multi-solute equilibria are calculated by substituting concentration for pressure and then following the procedure outlined by Myers and Prausnitz (*3*). This procedure is briefly illustrated below for two-solute equilibria; extension to the multicomponent case is straightforward.

1. Experimental isotherm data are integrated according to Equation (23) giving the spreading pressure for each single solute

$$\pi_1 = f_1(c_1^o) \tag{24}$$

$$\pi_2 = f_2(c_2^o) \tag{25}$$

2. The equilibrium relationships [Equation (21)] are written

$$c_T x_1 = c_1^o z_1 \tag{26}$$

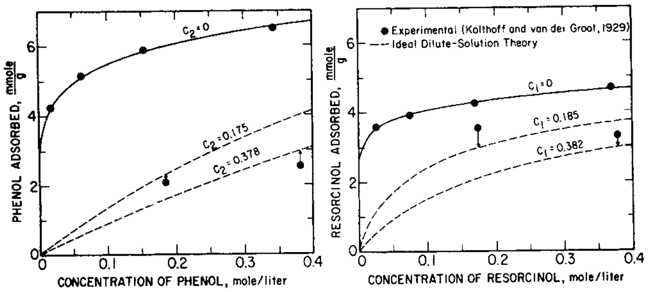

Fig. 1. Adsorption from aqueous multi-solute system: Phenol (1)-Resorcinol (2) at 20°C.

$$c_T x_2 = c_2^o(1 - z_1) \tag{27}$$

3. Since single-solute concentrations c_i^o are defined at the same spreading pressure as that of the mixture,

$$\pi_1 = \pi_2 = \pi \tag{28}$$

4. For given values of c_T and x_1 (or equivalently, c_1 and c_2), the above five equations determine the remaining five variables π_1, π_2, z_1, c_1^o, and c_2^o.

5. The total invariant adsorption can now be calculated using single-solute isotherm data and Equation (15). Invariant adsorption of each solute species in the mixture follows by mass balance

$$n_1^m = n_T^m z_1 \tag{29}$$

and

$$n_2^m = n_T^m(1 - z_1) \tag{30}$$

If an integrable analytic form can be found for the single-solute isotherm, the above procedure, which is a trial-and-error calculation of z_1, can be done conveniently with an electronic computer; our experience indicates that a Newton-Raphson iteration scheme converges rapidly. For two-solute mixtures it is possible to use the graphical method described by Myers and Prausnitz (3).

RESULTS

Kolthoff and van der Groot (5) report experimental data for four mixtures of phenol and resorcinol adsorbing from dilute aqueous solution onto charcoal at 20°C. Figure 1 shows predicted results for this system. Solid lines are single-solute isotherms; dotted lines are calculated by ideal dilute-solution theory. The arrows designate predicted loading of the corresponding experimental mixture points.

Since Kolthoff and van der Groot do not present single-solute data in the low concentration region, the calculated lines are based on arbitrary extrapolations to zero solute concentration; unfortunately, the calculations are sensitive to such extrapolations. The average deviation between predicted and experimental loading is 15% for the three highest concentrations; the lowest concentration was not calculated because of an apparent typographic error in the reported resorcinol concentration. It is difficult to assess the accuracy of the mixture calculation because no experimental error limits are given by Kolthoff and van der Groot. Experimental results given for the phenol-resorcinol mixture are typical of those available in the literature: only a few single-solute and mixture data are reported over a small range of loading. In addition, for multi-solute adsorption the ratio of solute concentrations investigated is near unity, whereas deviations between calculated and experimental results are more likely when the two solutes are present in widely different concentrations. Therefore, although agreement with experimental data for phenol-resorcinol mixtures is satisfactory, this system does not provide a quantitative test of ideal dilute-solution theory.

To test adequately the theory, we studied experimentally two aqueous two-solute systems: acetone-propionitrile and *p*-cresol–*p*-chlorophenol, adsorbing from dilute solution on a commercial activated carbon (Calgon Corporation Filtrasorb 300; specific surface area = 1000 m^2/g) at 25°C. Concentrations from 5×10^{-5} to 10^{-1} molar were measured by a gas chromatograph with a flame ionization detector. Below 5×10^{-5} molar, *p*-cresol and *p*-chlorophenol single-solute concentrations were analyzed with a Beckmann D.U. spectrophotometer after conversion of the phenols to phenolates by sodium hydroxide. Experimental procedures and detailed data are given elsewhere (*13*).

Figures 2 and 3 show predicted results for several acetone-propionitrile mixtures. Again, solid lines are single-solute isotherms, and dotted lines are calculated by ideal dilute-solution theory. Nineteen experimental mixture points were measured over a three-decade range in concentration and a two-decade range in loading; only one point per calculated line is shown because it was not possible to control the final solute concentrations. Since single-solute isotherm data begin at loadings which are close to the region where Henry's law for adsorption holds, there is little error in the evaluation of spreading pressure. Agreement between predicted and experimental results is excellent, even for concentration ratios of eight; the average deviation for amounts of acetone and propionitrile adsorbed is 3% while the average deviation in the total amount adsorbed is 2.5%. These deviations are within the 4% estimated experimental error. Thus, for small organic molecules which do not exhibit extensive loadings, ideal

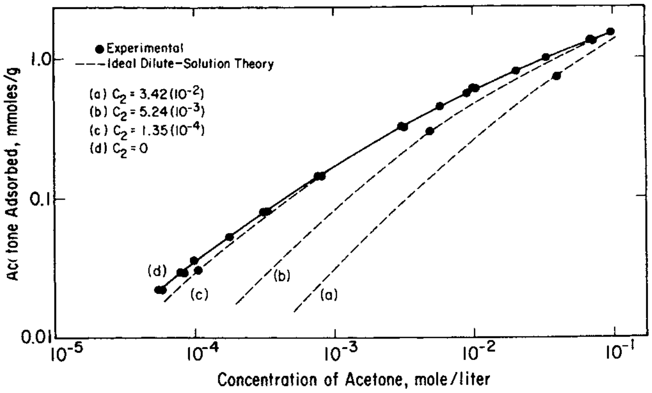

Fig. 2. Adsorption from aqueous multi-solute system: Acetone (1)-Propionitrile (2) at 25°C.

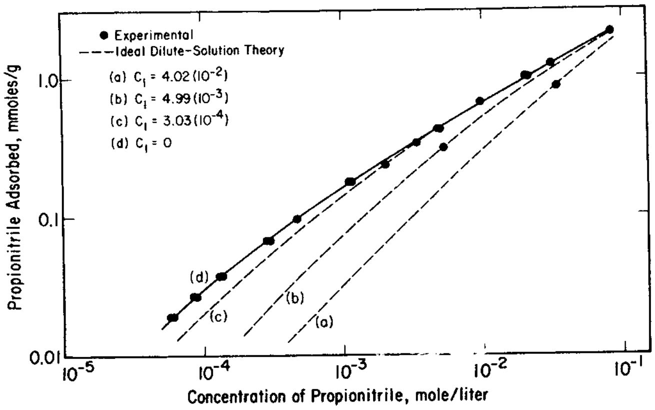

Fig. 3. Adsorption from aqueous multi-solute system: Acetone (1)-Propionitrile (2) at 25°C.

dilute-solution theory appears to provide excellent quantitative prediction of two-solute adsorption.

Figures 4 and 5 compare predicted and experimental results for several *p*-cresol–*p*-chlorophenol mixtures. Here a four-decade range in concentration covers only one decade in loading. For the 29 experimental mixture points, there is a 10% average deviation in the amounts of *p*-cresol and *p*-chlorophenol adsorbed and a 5% average deviation in the total loading. Maximum deviations of 25% occur at concentrations ratios near ten. These deviations are not within the 7% estimated experimental error. Corrections due to nonideality in the bulk liquid prove to be negligible at these low concentrations. Because adsorption in this system is strong, however, correction for adsorbed-phase nonideality is indicated. This nonideality can be included by defining an activity coefficient for the adsorbed phase

$$\gamma_i^a(T, \pi, z_i) = \frac{f_i^a}{z_i f_i^{ao}} \tag{31}$$

If the concentration dependence of γ_i^a is expressed by a one-parameter Margules equation

$$\ln \gamma_1^a = \alpha z_2^2 \quad \text{and} \quad \ln \gamma_2^a = \alpha z_1^2 \tag{32}$$

then α may be determined by minimizing the percentage errors between predicted and experimental loadings. A value of $\alpha = -0.46$ reduces the average error in the loadings of *p*-cresol and *p*-chlorophenol to 4%.

The significant difference between the behavior of the acetone-propionitrile system and that of the *p*-cresol–*p*-chlorophenol system is the higher loadings in the latter. The highest total loading measured in the acetone-propionitrile system is about 1.5 mmole/g whereas this same number corresponds to about the lowest total loading measurable in the *p*-cresol–*p*-chlorophenol system. Interactions between adsorbed-phase species rise with increasing loading. Therefore, it appears that ideal dilute-solution theory gives excellent results for systems where adsorption is moderate, while deviations due to adsorbed-phase nonideality may be expected when adsorption is extensive.

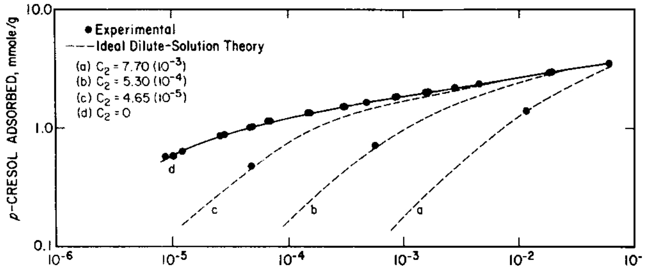

Fig. 4. Adsorption from aqueous multi-solute system: *p*-Cresol (1)—p-Chlorophenol (2) at 25°C.

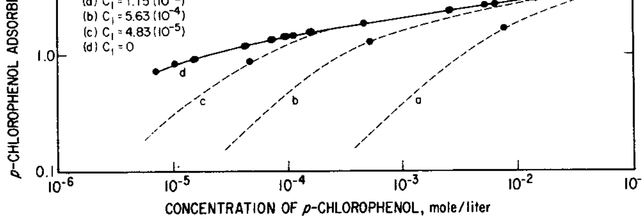

Fig. 5. Adsorption from aqueous multi-solute system: *p*-Cresol (1)—*p*-Chlorophenol (2) at 25°C.

CONCLUSIONS

Ideal dilute-solution theory provides a convenient procedure for predicting two-solute adsorption from dilute solution. No mixture data are required for this theory, nor is there any restriction on whether the solutes are above or below their melting points, or whether or not they are miscible in all proportions with the solvent. Single-solute isotherms, however, are required at low loadings because spreading pressure calculations are sensitive to data obtained in this region. Extension to multi-solute systems and to mixed-solvent systems is straight-forward. For volatile organic solutes, such as acetone and propionitrile adsorbing from water, ideal dilute-solution theory is in excellent agreement with experimental results. For more strongly adsorbing solutes, such as *p*-cresol and *p*-chlorophenol, predicted results deviate somewhat but not excessively from experiment, especially at high concentration ratios because of nonidealities in the adsorbed phase. The need for adsorbed-phase activity coefficients in these systems is due to the higher loadings that occur. This conclusion is analogous to that of Henson and Kabel (*14*), who showed that the ideal-solution method of Myers and Prausnitz (3) for mixed-gas adsorption, although reliable at low coverages, shows systematic deviations from experiment at high coverages.

To permit accurate concentration measurements with gas-liquid chromatography, this work considered binary systems with chemically similar components. Therefore, additional systems containing solutes which adsorb strongly and which are chemically dissimilar must be studied to obtain information on adsorbed-phase interactions. For engineering work, however, ideal dilute-solution theory provides a useful technique for estimating multi-solute adsorption from dilute liquid solution.

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NOTATION

$\mathcal{A}$ = surface area of adsorbent
A^a = Helmholtz free energy of adsorbed phase
c_i = liquid-phase concentration of solute i
$c_i^o(\pi)$ = liquid-phase concentration of single-solute i at spreading pressure π
f_i = fugacity of solute i
m = mass of adsorbent
m_i = liquid-phase molality of solute i
n_i^a = moles of solute i adsorbed (defined relative to the solid)
n_i^c = invariant adsorption of solute i (based on concentration change), Equation (A5)
n_i^m = invariant adsorption of solute i (based on molality change), Equation (7)
R = gas constant
S^a = entropy of adsorbed phase
T = absolute temperature
V = volume of solution
$\overline{v}_i$ = liquid-phase partial molar volume of solute i
x_i = liquid-phase solvent-free mole fraction of solute i
z_i = adsorbed-phase invariant mole fraction of solute i

Greek Letters

α = constant in adsorbed-phase activity coefficient equation, Equation (32)
γ_i^a = adsorbed-phase activity coefficient

μ_i = chemical potential of solute i
π = spreading pressure
σ = interfacial tension

Superscripts

a = adsorbed phase
c = invariant adsorption, Equation (A5)
l = liquid phase
m = invariant adsorption, Equation (7)
o = single-solute
t = total
$^\circ$ = standard state of liquid phase (Henry's law)

Subscripts

i = solute i
s = solvent
T = total

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APPENDIX A

The Invariant Adsorption

In this appendix the invariant adsorption n_i^m of solute i is related to the measurable quantity $V\Delta c_i/m$ (sometimes written as x/m). Experimental data give the solute concentration decrease Δc_i caused by contacting a solution of known solute concentration and known volume V with a known mass of adsorbent m. We write $V\Delta c_i$ as

$$V\Delta c_i = n_i^t - c_i V \qquad \text{(A1)}$$

where n_i^t is the total moles of solute contacted with the solid adsorbent. From a material balance

$$n_i^t = n_i^a + n_i^l \qquad \text{(A2)}$$

and

$$n_s^t = n_s^a + n_s^l \qquad \text{(A3)}$$

where superscript l denotes bulk liquid phase. If partial molar volumes of solutes $\overline{v}_i$ and solvent $\overline{v}_s$ vary little over the concentration decrease Δc_i, the initial volume of the solution is given by

$$V = \sum_i n_i^t \overline{v}_i + n_s^t \overline{v}_s \qquad \text{(A4)}$$

Combination of Equations (A1) to (A4) gives the desired result:

$$V\Delta c_i = n_i^a - c_i\left(\sum_i n_i^a \overline{v}_i + n_s^a \overline{v}_s\right) \equiv n_i^c \qquad \text{(A5)}$$

where n_i^c is a different invariant adsorption of solute i defined by Equation (A5). n_i^c is also independent of the location of the Gibbs dividing surface; it is the invariant adsorption n_i^c which is actually measured in this work.

To relate the two invariant adsorptions n_i^m and n_i^c we substitute Equation (A5) into Equation (7) of the text

$$n_i^m = n_i^c + c_i\left(\sum_i n_i^a \overline{v}_i + n_s^a \overline{v}_s - \frac{n_s^a}{c_s} \right) \qquad \text{(A6)}$$

Next, Equation (A4), written in the form $\sum_i c_i\overline{v}_i + c_s\overline{v}_s = 1$, is combined with Equation (A6):

$$n_i^m = n_i^c + \frac{c_i}{c_s\overline{v}_s}\left[\left(1 - \sum_i c_i\overline{v}_i\right)\left(\sum_i n_i^a \overline{v}_i + n_s^a \overline{v}_s\right) - n_s^a \overline{v}_s\right] \qquad \text{(A7)}$$

Substitution of Equation (A5) yields finally

$$n_i^m = n_i^c \left[1 - \frac{c_i}{c_s} \sum_j \frac{\overline{v}_j n_j^c}{\overline{v}_s n_i^c} \right] \qquad \text{(A8)}$$

where the summation is over all j solute species. In dilute solution the second term of Equation (A8) is much less than unity:

$$\lim_{\text{all } c_i \to 0} \frac{c_i}{c_s} \sum_j \frac{\overline{v}_j n_j^c}{\overline{v}_s n_i^c} << 1 \qquad \text{(A9)}$$

With the approximation of Equation (A9) we recover Equation (8) of the text. Therefore, Equation (A9) serves as a definition of the dilute-solution approximation of ideal dilute-solution theory.

The quotients $n_i^m/\mathfrak{A}$ and $n_i^c/\mathfrak{A}$ are sometimes given the symbols $\Gamma_i^{(s)}$ and $\Gamma_i^{(v)}$; they are two of several surface concentrations that may be defined (*15* to *17*). Since both invariant adsorptions n_i^m and n_i^c are independent of the location of the Gibbs dividing surface, they are, therefore, consistent with the particular dividing-surface convention chosen in this work.

Extension of Theory to Higher Concentrations

To extend ideal dilute-solution theory to higher concentrations requires a quantitative measurement of the invariant adsorption n_i^m in the concentration region where the approximation of Equation (A9) is not valid. A straightforward argument shows that n_i^m can be related to the experimental quan-

TABLE 1. EMPIRICAL PARAMETERS FOR SINGLE-SOLUTE ISOTHERMS AT 25°C

° Solute	A	B	C	l	m
acetone	0.506649	0.465834	——	0.441502	——
propionitrile	0.475672	0.393168	——	0.521769	——
p-cresol	123.0233	7.5452	−9.6644	0.209991	13.2924
p-chlorophenol	193.4210	9.3566	−21.6057	0.184523	17.3461

° c_i° [=] mmole/liter.

$$n_i^{\circ\circ} = \frac{V\Delta c_i^\circ}{m} \text{ [=] mmole/g.}$$

tity $V_{(\mathrm{pure})s}\rho_{(\mathrm{pure})s}\,\Delta m_i/m$ where Δm_i is the molality decrease caused by contacting a solution of known molality and solvent mass $V_{(\mathrm{pure})s}\rho_{(\mathrm{pure})s}$ with a known mass m of adsorbent. The symbols $V_{(\mathrm{pure})s}$ and $\rho_{(\mathrm{pure})s}$ indicate the volume and mass density of the solvent. We write $V_{(\mathrm{pure})s}\rho_{(\mathrm{pure})s}\Delta m_i$ as

$$V_{(\mathrm{pure})s}\rho_{(\mathrm{pure})s}\Delta m_i = n_i^t - M_s\, m_i\, n_s^t \qquad \text{(A10)}$$

where M_s is the molecular weight of the solvent, and m_i is the solute, liquid-phase molality. Since $M_s m_i = c_i/c_s$, substitution of Equations (A2) and (A3) into Equation (A10) gives

$$V_{(\mathrm{pure})s}\rho_{(\mathrm{pure})s}\Delta m_i = n_i^a - \frac{c_i}{c_s}\, n_s^a \qquad \text{(A11)}$$

or finally by Equation (7) of the text:

$$V_{(\mathrm{pure})s}\rho_{(\mathrm{pure})s}\Delta m_i = n_i^m \qquad \text{(A12)}$$

Thus n_i^m can be measured at all solute concentrations by the experimental quantity $V_{(\mathrm{pure})s}\rho_{(\mathrm{pure})s}\Delta m_i$.

TABLE 2. EXPERIMENTAL RESULTS FOR AQUEOUS MULTI-SOLUTE SYSTEM: ACETONE (1)—PROPIONITRILE (2) AT 25°C

c_1 mole/liter	c_2 mole/liter	*n_1^c (exp) mmole/g	n_1^c (calc) mmole/g	n_2^c (exp) mmole/g	n_2^c (calc) mmole/g	n_T^c (exp) mmole/g	n_T^c (calc) mmole/g
5.52E†-5	7.46E-5	0.0192	0.0180	0.0199	0.0206	0.0391	0.0385
6.14E-5	7.71E-5	0.0191	0.0197	0.0198	0.0210	0.0389	0.0407
1.06E-4	1.35E-4	0.0308	0.0301	0.0320	0.0322	0.0628	0.0622
1.12E-4	1.46E-4	0.0307	0.0312	0.0319	0.0340	0.0626	0.0652
3.03E-4	2.32E-3	0.0378	0.0379	0.263	0.256	0.301	0.294
3.17E-4	2.34E-3	0.0378	0.0394	0.264	0.256	0.302	0.296
3.25E-4	3.89E-4	0.0644	0.0663	0.0672	0.0667	0.132	0.133
1.42E-3	1.58E-3	0.161	0.159	0.169	0.158	0.330	0.317
1.42E-3	1.61E-3	0.161	0.159	0.169	0.160	0.329	0.319
1.43E-3	1.60E-3	0.161	0.160	0.169	0.159	0.330	0.319
2.09E-3	3.84E-4	0.250	0.246	0.0390	0.0399	0.289	0.286
2.17E-3	3.85E-4	0.251	0.251	0.0392	0.0395	0.290	0.291
4.99E-3	5.24E-3	0.291	0.299	0.307	0.313	0.598	0.611
5.06E-3	5.31E-3	0.288	0.300	0.305	0.316	0.593	0.615
7.41E-3	2.42E-2	0.237	0.236	0.900	0.909	1.14	1.15
7.52E-3	2.47E-2	0.236	0.237	0.896	0.920	1.13	1.16
2.79E-2	7.59E-3	0.802	0.804	0.251	0.259	1.05	1.06
4.00E-2	3.44E-2	0.715	0.755	0.822	0.872	1.54	1.63
4.02E-2	3.42E-2	0.717	0.758	0.834	0.867	1.55	1.62

* $n_i^c = V\Delta c_i/m$.

† $E^n = 10^n$.

TABLE 3. EXPERIMENTAL RESULTS FOR AQUEOUS MULTI-SOLUTE SYSTEM: *p*-CRESOL (1)—*p*-CHLOROPHENOL (2) AT 25°C

c_1 mole/liter	c_2 mole/liter	*n_1^c (exp) mmole/g	n_i^c (calc) mmole/g	n_2^c (exp) mmole/g	n_2^c (calc) mmole/g	n_T^c (exp) mmole/g	n_T^c (calc) mmole/g
4.21E†-5	4.36E-5	0.476	0.431	0.848	0.821	1.32	1.25
4.83E-5	4.65E-5	0.475	0.461	0.848	0.817	1.32	1.28
3.86E-4	1.04E-3	0.407	0.322	1.73	1.71	2.14	2.03
3.95E-4	1.05E-3	0.410	0.326	1.73	1.71	2.14	2.03
4.24E-4	1.13E-3	0.408	0.328	1.73	1.72	2.14	2.05
4.24E-4	1.13E-3	0.410	0.328	1.73	1.72	2.14	2.05
4.82E-4	4.60E-4	0.707	0.664	1.27	1.25	1.98	1.92
5.63E-4	5.30E-4	0.708	0.679	1.27	1.26	1.98	1.94
7.74E-4	4.94E-3	0.279	0.193	2.42	2.27	2.70	2.46
7.76E-4	5.06E-3	0.280	0.190	2.42	2.28	2.70	2.47
8.03E-4	2.20E-3	0.461	0.356	1.95	1.87	2.41	2.23
8.04E-4	2.23E-3	0.466	0.353	1.95	1.88	2.41	2.23
8.85E-4	2.44E-3	0.460	0.360	1.95	1.90	2.41	2.26
9.04E-4	9.10E-4	0.796	0.691	1.43	1.37	2.23	2.06
9.41E-4	6.05E-3	0.280	0.201	2.42	2.34	2.70	2.54
9.80E-4	6.39E-3	0.279	0.201	2.41	2.36	2.69	2.57
1.02E-3	1.03E-3	0.796	0.702	1.44	1.39	2.23	2.09
1.12E-3	3.44E-3	0.463	0.352	1.94	2.02	2.40	2.37
1.68E-3	3.37E-4	1.42	1.46	0.714	0.579	2.13	2.04
1.68E-3	3.39E-4	1.42	1.46	0.711	0.580	2.13	2.04
1.72E-3	3.39E-4	1.42	1.47	0.713	0.572	2.13	2.04
2.81E-3	6.08E-4	1.56	1.55	0.790	0.653	2.35	2.21
2.87E-3	6.19E-4	1.56	1.56	0.791	0.652	2.35	2.21
5.22E-3	4.22E-4	2.12	2.07	0.452	0.317	2.57	2.38
5.41E-3	3.25E-3	1.28	1.24	1.46	1.36	2.73	2.60
5.75E-3	3.46E-3	1.27	1.25	1.46	1.37	2.72	2.62
1.08E-2	7.18E-3	1.41	1.38	1.66	1.58	3.08	2.96
1.08E-2	7.14E-3	1.41	1.39	1.66	1.57	3.08	2.96
1.15E-2	7.70E-3	1.40	1.40	1.66	1.60	3.05	3.00

* $n_i^c = V\Delta c_i/m$.

† $E^n = 10^n$.

TABLE 4. EFFECT OF ADSORBED PHASE NONIDEALITY— MULTI-SOLUTE SYSTEM: *p*-CRESOL (1)—*p*-CHLOROPHENOL (2) AT 25°C

c_1 mole/liter	c_2 mole/liter	* n_1^c (exp) mmole/g	** n_1^c (w act) mmole/g	n_2^c (exp) mmole/g	n_2^c (w act) mmole/g	n_T^c (exp) mmole/g	n_T^c (w act) mmole/g
4.21E†-5	4.36E-5	0.476	0.476	0.848	0.807	1.32	1.28
4.83E-5	4.65E-5	0.475	0.506	0.848	0.806	1.32	1.31
3.86E-4	1.04E-3	0.407	0.408	1.73	1.64	2.14	2.05
3.95E-4	1.05E-3	0.410	0.412	1.73	1.64	2.14	2.05
4.24E-4	1.13E-3	0.408	0.415	1.73	1.65	2.14	2.07
4.24E-4	1.13E-3	0.410	0.416	1.73	1.65	2.14	2.07
4.82E-4	4.60E-4	0.707	0.722	1.27	1.21	1.98	1.94
5.63E-4	5.30E-4	0.708	0.738	1.27	1.23	1.98	1.97
7.74E-4	4.94E-3	0.279	0.270	2.42	2.21	2.70	2.48
7.76E-4	5.06E-3	0.280	0.267	2.42	2.22	2.70	2.49
8.03E-4	2.20E-3	0.461	0.452	1.95	1.80	2.41	2.25
8.04E-4	2.23E-3	0.466	0.449	1.95	1.81	2.41	2.26
8.85E-4	2.44E-3	0.460	0.459	1.95	1.83	2.41	2.29
9.04E-4	9.10E-4	0.796	0.761	1.43	1.33	2.23	2.09
9.41E-4	6.05E-3	0.280	0.281	2.42	2.28	2.70	2.56
9.80E-4	6.39E-3	0.279	0.281	2.41	2.31	2.69	2.59
1.02E-3	1.03E-3	0.796	0.774	1.44	1.35	2.23	2.12
1.12E-3	3.44E-3	0.463	0.453	1.94	1.95	2.40	2.40
1.68E-3	3.37E-4	1.42	1.41	0.714	0.658	2.13	2.06
1.68E-3	3.39E-4	1.42	1.41	0.711	0.659	2.13	2.07
1.72E-3	3.39E-4	1.42	1.42	0.713	0.652	2.13	2.07
2.81E-3	6.08E-4	1.56	1.50	0.790	0.735	2.35	2.24
2.87E-3	6.19E-4	1.56	1.51	0.791	0.736	2.35	2.24
5.22E-3	4.22E-4	2.12	1.99	0.452	0.412	2.57	2.40
5.41E-3	3.25E-3	1.28	1.28	1.46	1.37	2.73	2.65
5.75E-3	3.46E-3	1.27	1.30	1.46	1.38	2.72	2.69
1.08E-2	7.18E-3	1.41	1.44	1.66	1.59	3.08	3.03
1.08E-2	7.14E-3	1.41	1.44	1.66	1.58	3.08	3.03
1.15E-2	7.70E-3	1.40	1.46	1.66	1.61	3.05	3.06

* $n_i^c = \Delta c_i/m$.
† $E^n = 10^n$.
** w act = calculated with activity coefficient $\ln \gamma_1 = -0.46(1 - z_1)^2$.

At higher concentrations liquid-phase solute activity coefficients must be included in Equations (18) and (19) of the text; liquid-phase activity coefficients can be independently measured. It is likely that at higher concentrations the adsorbed phase will also become nonideal. In this case adsorbed-phase activity coefficients are required in Equation (17). Unfortunately, adsorbed-phase activity coefficients cannot be independently measured. The present method, therefore, may be of limited usefulness for predicting multi-solute adsorption at higher solute concentrations.

APPENDIX B

Empirical Equations

Empirical equations are chosen to fit single-solute data within experimental error, to be linear in the limit of zero solute concentration, and to be analytic in the integral expression for spreading pressure. As suggested by John Newman, acetone and propionitrile isotherms are fit by the three-parameter form (solid lines in Figures 2 and 3 of the text):

$$n_i^{mo} = \frac{\dfrac{1}{Ac_i^o} + \dfrac{l}{Bc_i^{ol}}}{\left(\dfrac{1}{Ac_i^o} + \dfrac{1}{Bc_i^{ol}}\right)^2} \tag{B1}$$

Equation (B1) integrates to the following analytic expression for spreading pressure:

$$\frac{\pi_i \mathfrak{A}}{RT} = \frac{Ac_i^o}{\left(1 + \dfrac{Ac_i^{o(1-l)}}{B}\right)} \tag{B2}$$

For the *p*-cresol and *p*-chlorophenol isotherms, Equation (B1) does not provide an adequate fit. Therefore, it is modified to the five-parameter form (solid lines in Figures 4 and 5 of the text):

$$n_i^{mo} = \frac{\dfrac{1}{Ac_i^o} + \dfrac{l}{Bc_i^{ol}}}{\left(\dfrac{1}{Ac_i^o} + \dfrac{1}{Bc_i^{ol}}\right)^2} + Cc_i^o \exp(-mc_i^o) \tag{B3}$$

The corresponding expression for spreading pressure from Equation (B3) is

$$\frac{\pi_i \mathfrak{A}}{RT} = \frac{Ac_i^o}{\left(1 + \dfrac{Ac_i^{o(1-l)}}{B}\right)} - \frac{C}{m}\left[\exp(-mc_i^o) - 1\right] \tag{B4}$$

Parameters A, B, C, l, and m are obtained by minimizing the sum of squares of the percentage deviation in loading. A University of California Computer Center Library subroutine, designated as POWELL, calculates the minimum by the method of conjugate directions. When concentration is expressed in mmole/liter and loading in mmole/g, values of the parameters are given in Table 1. These parameters should not be used to extrapolate isotherms beyond 0.1 molar concentration.

Experimental Mixture Data

Tables 2 and 3 give experimental mixture data and ideal dilute-solution theory results for the acetone-propionitrile system and the *p*-cresol–*p*-chlorophenol system. Table 4 indicates the effect of correcting the *p*-cresol-*p*-chlorophenol mixture for adsorbed-phase nonideality with a one-parameter Margules expression. Single-solute experimental data are given in Chapter 2 of (*13*).

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