Prediction of Adsorption at Liquid-Solid Interface from Adsorption Isotherms of Pure Unsaturated Vapors

Adsorption from liquid mixtures can be predicted from the adsorption isotherm of the pure unsaturated vapor, measured for each component of the liquid mixture. The theory gives analytical expressions for adsorption from liquids corresponding to Type I (finite capacity) and Type II (multilayer adsorption) vapor isotherms. The free energy of immersion of the adsorbent in the pure liquid adsorbate is the essential parameter for either type of adsorption. Predictions based upon the assumption of an ideal adsorbed solution are compared with experimental data on adsorption from liquid mixtures.

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SCOPE

If a liquid mixture is contacted with a solid adsorbent, the composition of the mixture changes. The magnitude of the change depends upon the selectivity of the adsorbent for the components of the mixture. This change in composition and its variation with the composition of the bulk liquid is called the liquid adsorption isotherm.

If a pure vapor is contacted with a solid adsorbent, some of the gas is adsorbed. The amount adsorbed at equilibrium increases with the pressure of the gas, from zero pressure up to the saturation vapor pressure. The amount adsorbed as a function of pressure is called the gas adsorption isotherm.

The scope of this article is to show that adsorption from liquid mixtures can be fully explained in terms of the gas adsorption isotherms of its components.

CONCLUSIONS AND SIGNIFICANCE

The selectivity of an adsorbent for the components of a liquid solution may be inferred from the adsorption of the same components from gases, that is, liquid adsorption isotherms can be predicted from gas adsorption isotherms.

Surface excess isotherms for adsorption from liquid solutions are divided into two classes, depending upon the type of vapor isotherm: Type I (finite capacity) and Type II (multilayer formation).

For Type I vapor isotherms the constants are the saturation capacity (m) and the free energy of immersion (ϕ^s). If it is assumed that the adsorbed phase forms an ideal solution, the surface excess for adsorption from liquids is given by Equation (18) in terms of these constants for adsorption from gases. Predictions of this kind are shown in Figures 7, 8, and 9.

For Type II vapor isotherms the constants are the free energy of immersion (ϕ^s) and the constants in the Frenkel-Halsey-Hill slab theory of multilayer adsorption. The surface excess for adsorption from liquids is given by Equation (42), which has not yet been tested.

The adsorption isotherms in Figures 7 and 8 exhibit strong negative deviations from Raoult's law for the adsorbed solutions of benzene + cyclohexane and benzene + n-heptane. The adsorbed solution of cyclohexane + n-heptane obeys Raoult's law.

The principal significance of this work is that it provides a method of studying the nonideality of adsorption from liquids in terms of constants measured independently (from gas adsorption isotherms). If no experimental data on adsorption from liquids are available, then gas adsorption isotherms may be used to predict liquid adsorption isotherms. These predictions, since they are based upon the assumption of an ideal adsorbed solution, are not in quantitative agreement with experiment but may be useful for design calculations (see Figures 7 and 8).

It has been shown that adsorption from liquid mixtures may be calculated using data on adsorption from unsaturated vapors of the same mixture (Myers and Sircar, 1972). Adsorption from the vapor mixture, in turn, may be predicted using data on the pure vapor isotherms in conjunction with the assumption of an ideal adsorbed solution (Sircar and Myers, 1972). It follows that one can predict adsorption isotherms for liquid mixtures using only the isotherms for the pure, unsaturated vapors.

It is interesting that this procedure cannot be reversed to predict vapor isotherms using data for adsorption from liquids because different kinds of vapor isotherms can produce the same liquid isotherm.

For reasons that will become apparent, equations for vapor isotherms are divided into two classes: Type I (finite capacity at saturation) and Type II (multilayer formation).

THEORY

The object is to derive an expression for the surface excess (n_i^e) of i'th component adsorbed from a liquid solution, which is defined by (Kipling, 1965):

$$n_i^e = n^0(x_i^0 - x_i) \tag{1}$$

where n^0 is the initial number of moles of bulk liquid (per unit mass of adsorbent) and $\Delta x_i = (x_i^0 - x_i)$ is the change in the mole fraction of i'th component when the adsorbent is immersed in the liquid.

It is easy to show by means of a material balance (Kipling, 1965) that Equation (1) may be written in terms of the properties of the adsorbed phase (identified by a prime symbol):

$$n_i^e = n'(x_i' - x_i) \tag{2}$$

The next step is to define similar quantities for adsorption from gas mixtures. Let the individual isotherms measured for equilibrium adsorption from a gaseous mixture be $n_i' = n_i'(P, y_i)$. y_i stands for the composition of the vapor mixture and n_i' is the number of moles of component i adsorbed per unit mass of adsorbent. The total number of moles adsorbed is $n' = \Sigma n_i'$. For a given vapor composition, n_i' is a function of pressure $[0 < P < P^s]$. The saturation pressure of the vapor is $P^s = P^s(y_i)$. We define the surface excess for adsorption from a vapor mixture (n_i^{ev}) using the same Equation (2) that applies to adsorption from liquids. x_i' is the mole fraction of i'th component in the adsorbed phase. Since there is no bulk liquid in equilibrium with the unsaturated vapor, x_i is defined as the mole fraction of i'th component that would be in equilibrium with vapor of composition y_i at saturation. That is, $x_i(y_i)$ is the liquid-vapor equilibrium measured independently of the adsorption experiment.

Since both surface excess variables (n_i^{ev} and n_i^e) are defined by the same Equation (2), it follows that (Myers and Sircar, 1972):

$$n_i^e = \lim_{P \to P^s} (n_i^{ev}) \tag{3}$$

Adsorption from liquid mixtures may be calculated by Equation (3) using data on adsorption from unsaturated vapors of the same mixture. The next step is to predict adsorption from the vapor mixture (n_i^{ev}) using data on the pure vapor isotherms. For this purpose it is assumed that the adsorbed mixture forms an ideal adsorbed solution. At low surface coverage the standard state for the pure adsorbates is the surface potential or, as it has been called in the past, the spreading pressure (Myers and Prausnitz, 1965). In the region of high surface coverage corresponding to near-saturation of the vapor, mixing at constant surface potential is undefined; the correct standard state is the reduced surface potential (Sircar and Myers, 1972)

$$\phi_r = \frac{\phi}{\phi^s} = \frac{\phi_i^*}{\phi_i^s}$$

where the asterisk refers to pure adsorbate and ϕ^s is the value of ϕ at saturation. ϕ^s is finite even in the case of multilayer adsorption (Cassel, 1944). In the limit as the vapor approaches saturation, $P \to P^s$, $\phi \to \phi^s$, $\phi_i^* \to \phi_i^s$ and $\phi_r \to 1$.

The surface potential is obtained from the Gibbs adsorption isotherm (Myers and Prausnitz, 1965):

$$- d\phi = \Sigma\, n_i' d\mu_i' \tag{4}$$

For a pure adsorbate and the usual subatmospheric pressure of interest, Equation (4) may be integrated to get

$$- \frac{\phi_i^*}{RT} = \int_0^{P_i^*} \frac{n_i^*}{P}\, dP \tag{5}$$

The reference state is the clean adsorbent $[\phi = 0$ at $n' = 0]$. Therefore the pretreatment of the adsorbent must be the same for the mixture as for the pure adsorbates. The value of the surface potential at saturation, called the free energy of immersion (ϕ^s), is

$$- \frac{\phi_i^s}{RT} = \int_0^{P_i^s} \frac{n_i^*}{P}\, dP \tag{6}$$

Thus $\phi_i^*(P_i^*)$ and ϕ_i^s are obtained from the pure vapor isotherm.

The equations describing an ideal adsorbed solution are (Sircar and Myers, 1972):

$$P y_i = P_i^* x_i' \exp\left[\frac{- \phi_r(\phi^s - \phi_i^s)}{n_i^* RT}\right] \quad (i = 1, 2, \ldots, N_c) \tag{7}$$

and

$$\frac{1}{n'} = \sum \frac{x_i'}{n_i^*} \tag{8}$$

All pure-adsorbate properties in Equations (7) and (8) are measured at the same value of $\phi_r = \phi_i^*/\phi_i^s$. Equation (7) equates the fugacity in the vapor (left-hand side) to the fugacity in the adsorbed phase (right-hand side). These equations are analogous to Raoult's law (Denbigh, 1966) for vapor-liquid equilibrium. The exponential factor in Equation (7) is analogous to the Poynting correction and Equation (8) is analogous to the equation for zero volume change upon forming a liquid solution from its components.

y_i and x_i are related by the vapor-liquid equilibrium condition:

$$P^s y_i = P_i^s \gamma_i x_i \qquad (i = 1, 2, \ldots, N_c) \tag{9}$$

The left-hand side is the fugacity in the vapor at saturation and the right-hand side is the fugacity in the bulk liquid. The activity coefficients are established by independent measurements of vapor-liquid equilibria.

The mole-fraction constraint equation for the adsorbed phase is

$$\Sigma\, x_i' = 1 \tag{10}$$

for the vapor phase

$$\Sigma\, y_i = 1 \tag{11}$$

The summation, here and elsewhere, is over the N_c components of the adsorbed mixture. Consider, specifically, the case of a binary mixture ($N_c = 2$). It is seen from these equations that n_i^{ev} is a function of 17 variables $\{x_1, x_2, \gamma_1, \gamma_2, n_1^*, n_2^*, P_1^*, P_2^*, \phi_r, \phi^s, x_1', x_2', y_1, y_2, P, P^s, n'\}$. The last 7 of these variables may be eliminated from Equation (2) by the set of 7 Equations (7) to (11) to obtain

$$n_1^{ev} = \frac{x_1 x_2 (1 - K)}{\dfrac{x_1}{n_1^*} + K \dfrac{x_2}{n_2^*}} \tag{12}$$

where

$$K = \frac{P_{r1}\gamma_2^*}{P_{r2}\gamma_1^*} \exp\left[\frac{\phi_r(\phi^s - \phi_2{}^s)}{n_2{}^*RT} - \frac{\phi_r(\phi^s - \phi_1{}^s)}{n_1{}^*RT}\right] \quad (13)$$

and

$$P_{ri}{}^* = \frac{P_i{}^*}{P_i{}^s} \quad (14)$$

There are left 10 variables $\{x_1, x_2, \gamma_1, \gamma_2, n_1{}^*, n_2{}^*, P_1{}^*, P_2{}^*, \phi_r, \phi^s\}$ of which two $\{x_1, \phi_r\}$ are independent. Substitution of Equation (12) in (3) gives

$$n_1{}^e = \lim_{\phi_r \to 1} \left\{ \frac{x_1 x_2(1 - K)}{\dfrac{x_1}{n_1{}^*} + K\dfrac{x_2}{n_2{}^*}} \right\} \quad (15)$$

where

$$K = \frac{\gamma_2}{\gamma_1} \exp\left[\frac{(\phi^s - \phi_2{}^s)}{n_2{}^*RT} - \frac{(\phi^s - \phi_1{}^s)}{n_1{}^*RT}\right] \quad (16)$$

so that the surface excess is a function of x_1 only.

The behavior of the limit in Equation (15) depends upon whether the adsorption is Type I, for which $n_i{}^*$ at saturation is finite, or Type II, for which $n_i{}^*$ at saturation tends to infinity. Zeolites and microporous adsorbents such as silica gel give Type I isotherms; adsorbents without micropores such as graphitized carbon, titanium oxide, and metals give Type II isotherms.

TYPE I ISOTHERMS

The capacity at saturation is

$$\lim_{P_{ri} \to 1} (n_i{}^*) = m_i \quad (17)$$

m_i, sometimes erroneously called the monolayer capacity of the adsorbent, is the number of moles adsorbed in the micropores at saturation. If none of the adsorbates are excluded from the pores because of stearic effects, then m_i is approximately proportional to the liquid density of the adsorbate. This follows from the observation that the volumetric capacity of a porous adsorbent is constant according to Gurvitsch's rule (Gurvitsch, 1915).

Equations (15) and (17) give

$$n_1{}^e = \frac{x_1 x_2(1 - K)}{\dfrac{x_1}{m_1} + K\dfrac{x_2}{m_2}} \quad (18)$$

where

$$K = \frac{\gamma_2}{\gamma_1} \exp\left[\frac{(\phi^s - \phi_2{}^s)}{m_2RT} - \frac{(\phi^s - \phi_1{}^s)}{m_1RT}\right] \quad (19)$$

K, which is a function of composition, may be obtained as follows: ϕ^s is related to the composition of the bulk liquid by the Gibbs adsorption isotherm (Sircar and Myers, 1970):

$$n_1{}^e = -\,a_1 x_2 \frac{1}{RT}\frac{d\phi^s}{da_1} \quad (20)$$

where $a_1 = \gamma_1 x_1$ is the activity of component 1 in the bulk liquid solution. The activities in the bulk liquid are related by the Gibbs-Duhem equation (Denbigh, 1966):

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0 \quad (21)$$

Substitution of Equations (18), (19), and (21) into (20) followed by integration gives

$$\gamma_1 x_1 e^{\left(\frac{\phi^s - \phi_1{}^s}{m_1RT}\right)} + \gamma_2 x_2 e^{\left(\frac{\phi^s - \phi_2{}^s}{m_2RT}\right)} = 1 \quad (22)$$

Given the constants m_1, m_2 and $(\phi_1{}^s - \phi_2{}^s)$ and the bulk-phase activity coefficients (γ_1, γ_2), Equations (22), (19), and (18) are solved sequentially for the variables $\phi^s(x_1)$, $K(x_1)$, and $n_1{}^e(x_1)$. Since the solution of Equation (22) for ϕ^s is implicit, it is not possible to write an explicit equation for $n_1{}^e$ except for special cases which are considered below.

Another approach is to eliminate the free energy of immersion (ϕ^s) by substituting Equations (18), (19), and (21) into (20) to get a differential equation for K:

$$\frac{d \ln K}{dx_1} = \left[\frac{(m_2 - m_1)(1 - K)\left(1 + \dfrac{d \ln \gamma_1}{d \ln x_1}\right)}{(x_1 m_2 + K x_2 m_1)}\right] - \frac{1}{x_2}\left(\frac{d \ln \gamma_1}{dx_1}\right) \quad (23)$$

Equation (23) may be integrated numerically to get $K(x_1)$ and $n_1{}^e(x_1)$ is then given by Equation (18). The boundary conditions (not independent) are

$$K = \gamma_2{}^\infty \exp\left(\frac{\phi_1{}^s - \phi_2{}^s}{m_2RT}\right) \qquad (\text{at } x_1 = 1) \quad (24)$$

$$K = \frac{1}{\gamma_1{}^\infty} \exp\left(\frac{\phi_1{}^s - \phi_2{}^s}{m_1RT}\right) \qquad (\text{at } x_1 = 0) \quad (25)$$

where $\gamma_i{}^\infty$ is the bulk-phase activity coefficient of component i in the limit of infinite dilution. Here, as before, the relation for $n_1{}^e$ is not explicit. Several interesting special cases that give an explicit equation for $n_1{}^e$ are considered next.

Nonideal Bulk Solution, $m_1 = m_2 = m$

From Equation (19),

$$K = \frac{\gamma_2}{\gamma_1} \exp\left(\frac{(\phi_1{}^s - \phi_2{}^s)}{mRT}\right) \quad (26)$$

Substitution of Equation (26) in (18) gives an explicit equation for $n_1{}^e$. It is interesting to determine the effect of nonidealities upon the shape of the adsorption isotherm. For a regular solution in which

$$\ln \gamma_1 = q x_2{}^2$$
$$\ln \gamma_2 = q x_1{}^2$$

the surface excess is plotted on Figure 1 for solutions varying from strong positive deviations from Raoult's law $(q = 2)$ to strong negative deviations from Raoult's law $(q = -2)$. Since $|\phi_1{}^s| > |\phi_2{}^s|$, component 1 is adsorbed preferentially at all concentrations for an ideal bulk solution $(q = 0)$. Figure 1 shows that sigmoidal isotherms may be explained by nonidealities in the bulk solution.

Ideal Bulk Solution, $m_1 \neq m_2$

For ideal bulk solutions $(\gamma_i = 1)$ of unequal densities $(m_1 \neq m_2)$ Equation (23) reduces to

$$\frac{d \ln K}{dx_1} = \frac{(m_2 - m_1)(1 - K)}{(x_1 m_2 - K x_2 m_1)} \quad (27)$$

Rearranging

$$\frac{dx_1}{dK} - \frac{(m_2 - K m_1)x_1}{K(1 - K)(m_2 - m_1)} = \frac{m_1}{(1 - K)(m_2 - m_1)} \quad (28)$$

Equation (28), which is linear and first order in x_1, may be integrated to get $x_1(K)$. Using the boundary condition from Equation (24), integration of Equation (28) gives

$$x_1 = \frac{K}{1-K}\left[\left(\frac{e^{\frac{\phi_1^s-\phi_2^s}{RT}}}{K^{m_1}}\right)^{\frac{1}{m_1-m_2}} - 1\right] \quad (29)$$

Equation (29) is the function $x_1(K)$; the inverse relation $K(x_1)$ may be substituted in Equation (18) to get the adsorption isotherm, $n_1^e(x_1)$.

It is not possible to deduce the ratio m_1/m_2 from the shape of the surface excess isotherm. For example, Figure 2 shows the surface excess for $\Delta\phi/RT = 1.5$, $m_1 = 1.2$ and $m_2 = 0.8$ calculated by Equations (18) and (29). The same isotherm is given by Equation (31) for $\Delta\phi/RT = 1.5$, $m_1 = m_2 = 2.05$. Although the average value of m is 1.0 in the first case and 2.05 in the second case, the adsorption isotherms nearly coincide. This surprising result shows that the ratio m_1/m_2 must be determined independently if the surface excess isotherm is to be interpreted properly (it was mentioned previously that m is proportional to the density of the pure liquid if there is no stearic hindrance to adsorption).

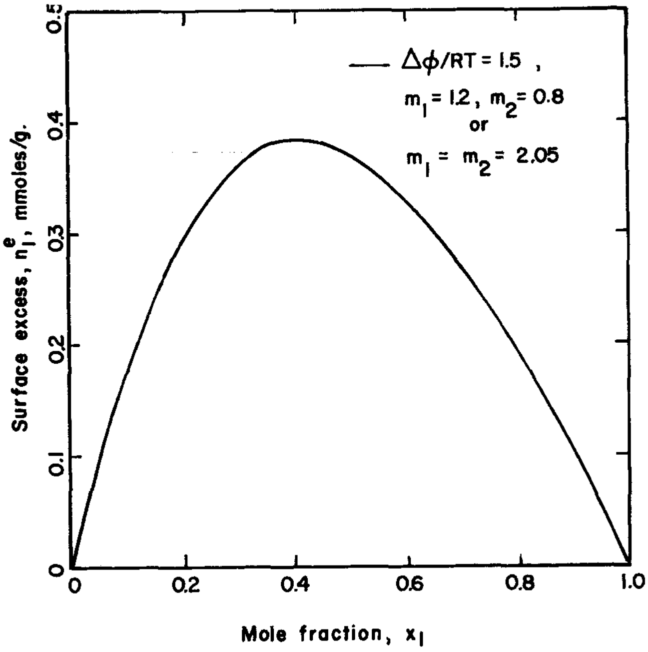


Fig. 2. Effect of differences in saturation capacities upon surface excess isotherm.

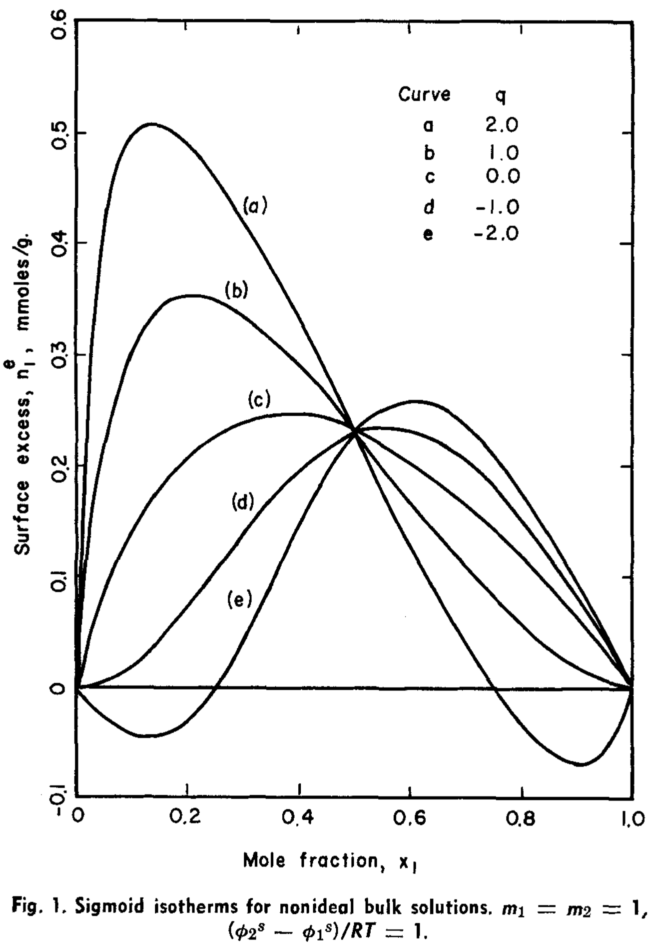


Fig. 1. Sigmoid isotherms for nonideal bulk solutions. $m_1 = m_2 = 1$, $(\phi_2^s - \phi_1^s)/RT = 1$.

Ideal Bulk Solution, $m_1 = m_2 = m$

From Equation (19)

$$K = e^{\left(\frac{\phi_1^s-\phi_2^s}{mRT}\right)} \quad (30)$$

so that K is a constant. Equation (18) reduces to

$$n_1^e = \frac{m x_1 x_2 (1-K)}{x_1 + K x_2} \quad (31)$$

If component number 1 is preferentially adsorbed, then $|\phi_1^s| > |\phi_2^s|$ and $K < 1$. The maximum value of n_1^e,

$$(n_1^e)_{\max} = \frac{m(1-K)}{(1+\sqrt{K})^2}$$

is located at

$$x_1 = \frac{\sqrt{K}}{1+\sqrt{K}} < \frac{1}{2}$$

Unfortunately very few solutions satisfy the assumptions upon which this simple equation is based. Sigmoidal isotherms cannot be explained by Equation (31).

Adsorption of Dilute Solutes

If component number 1 is preferentially adsorbed so that $|\phi_1^s| >> |\phi_2^s|$ and $K << 1$, then in the region of high concentration where x_1 and x_2 are of the same order of magnitude Equation (18) reduces to

$$n_1^e = m_1 x_2 \quad (32)$$

The surface excess isotherm is linear in mole fraction with an apparent y-intercept equal to m_1 (at $x_1 = 0$). The interesting region is that of low concentration of solute where $x_1 << 1$ for which Equation (18) reduces to

$$n_1^e = \frac{\left(m_2 \frac{1}{K}\right)x_1}{1 + \left(\frac{m_2}{m_1}\frac{1}{K}\right)x_1} \quad (33)$$

where K is given by Equation (16). Equation (33) has the form of the Langmuir adsorption isotherm when $m_1 = m_2$ (Sircar et al., 1970). If the solute (component number 1) is only slightly soluble in the solvent (component number 2) then γ_1^∞ is large; for example, for water in hydrocarbon solvents γ_1^∞ is of the order of 10^4.

TYPE II ISOTHERMS

For multilayer adsorption the value of the activity coefficient in the adsorbed phase approaches the value of the activity coefficient in the bulk phase in the limit as the amount adsorbed tends to infinity. Here it is assumed that both phases, adsorbed and bulk, are ideal.

For Type II isotherms

$$\lim_{\phi_r \to 1} P_{ri}^* = 1$$

and

$$\lim_{\phi_r \to 1} n_i^* = \infty$$

From Equation (13)

$$\lim_{\phi_r \to 1} K = \lim_{\phi_r \to 1} \left(\frac{P_{r1}^*}{P_{r2}^*} \exp \left[\frac{\phi_r(\phi^s - \phi_2^s)}{n_2^* RT} - \frac{\phi_r(\phi^s - \phi_1^s)}{n_1^* RT} \right] \right) = 1 \quad (34)$$

Therefore, according to Equation (15)

$$n_1^e = \lim_{\phi_r \to 1} \frac{[x_1 x_2 (1-K)]}{\left[\dfrac{x_1}{n_1^*} + \dfrac{K x_2}{n_2^*} \right]} = \frac{0}{0} \quad (35)$$

Equation (34) shows that K is a function of P_{ri}^*, n_i^* and ϕ_r for a fixed value of composition. In order to apply L'Hôpital's rule to the limit in Equation (35), the functions $P_{ri}^*(\phi_r)$ and $n_i^*(\phi_r)$ are needed. These functions depend upon the nature of the multilayer adsorption isotherms for the pure vapors.

The B.E.T. theory of multilayer adsorption incorrectly predicts that the free energy of immersion is infinitely large (Hill, 1960). The simplest acceptable theory of multilayer adsorption is the Frenkel-Halsey-Hill slab theory (Young and Crowell, 1962):

$$\ln P_{ri}^* = \frac{-\beta_i}{(n_i^*)^r} \quad (36)$$

where $r > 1$ and $\beta > 0$. The theoretical value of r is 3 but values in the range $2 < r < 3$ have been reported for experimental data (Young and Crowell, 1962). The surface potential calculated by insertion of Equation (36) into (5) is

$$\frac{1}{n_i^*} = \left[\frac{(1-\phi_r)(r-1)}{(\beta_i r)} \left(\frac{-\phi_i^s}{RT} \right) \right]^{\frac{1}{r-1}} \quad (37)$$

Substituting Equation (37) in (36):

$$P_{ri}^* = \exp \left\{ -\beta_i \left[\frac{(1-\phi_r)(r-1)}{(\beta_i r)} \left(\frac{-\phi_i^s}{RT} \right) \right]^{\frac{r}{r-1}} \right\} \quad (38)$$

After substitution of Equations (37) and (38) into (35), an application of L'Hôpital's rule yields

$$n_1^e = \frac{\lim\limits_{\phi_r \to 1} \dfrac{d}{d\phi_r} [x_1 x_2 (1-K)]}{\lim\limits_{\phi_r \to 1} \dfrac{d}{d\phi_r} \left[\dfrac{x_1}{n_1^*} + \dfrac{K x_2}{n_2^*} \right]} = \frac{-x_1 x_2 \left[C \left(\dfrac{\phi^s - \phi_2^s}{RT} \right) - \left(\dfrac{\phi^s - \phi_1^s}{RT} \right) \right]}{x_1 + C x_2} \quad (39)$$

where C, a dimensionless constant, is

$$C = \left[\frac{\beta_1 \phi_2^s}{\beta_2 \phi_1^s} \right]^{\frac{1}{r-1}} \quad (40)$$

ϕ^s in Equation (39), which is a function of composition, may be calculated by substituting Equation (39) into (20); integration then gives

$$\phi^s (C-1) + \phi_1^s - C\phi_2^s = \frac{C(\phi_1^s - \phi_2^s)}{x_1 + C x_2} \quad (41)$$

Substitution of Equation (41) in (39) gives the adsorption isotherm

$$n_1^e = \frac{C \left[\dfrac{\phi_2^s - \phi_1^s}{RT} \right] x_1 x_2}{(x_1 + C x_2)^2} \quad (42)$$

If component number 1 is preferentially adsorbed, then $|\phi_1^s| > |\phi_2^s|$. The maximum value of n_1^e from Equation (42)

$$(n_1^e)_{\max} = \frac{1}{4} \left(\frac{\phi_2^s - \phi_1^s}{RT} \right)$$

is located at

$$x_1 = \frac{C}{C+1}$$

Equation (42) for Type II isotherms should be compared with Equation (31) for Type I isotherms. These equations may be generalized in the form

$$n_1^e = \frac{C_1 x_1 x_2}{(x_1 + C_2 x_2)^\alpha} \quad (43)$$

where $\alpha = 1$ for Type I isotherms and $\alpha = 2$ for Type II isotherms.

One cannot deduce the character of the vapor isotherm (Type I or Type II) from the adsorption isotherm for the liquid mixture. This is apparent from Figure 3, upon which is plotted Equation (31) based upon vapor adsorption of Type I and Equation (42) based upon vapor adsorption of Type II. The two isotherms nearly coincide.

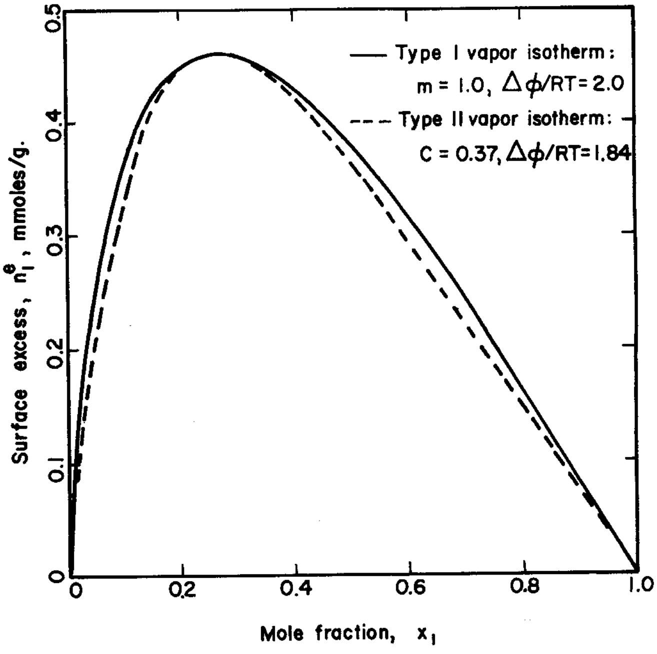
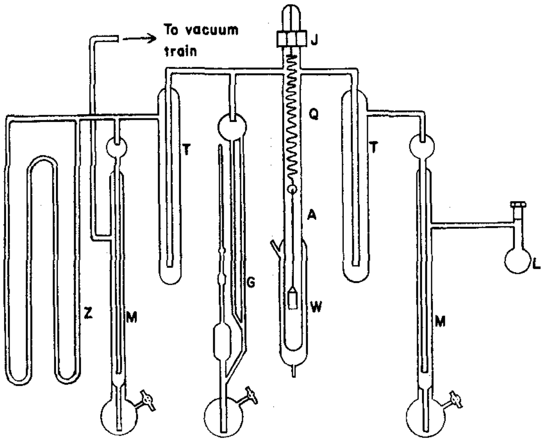


Fig. 3. Comparison of surface excess isotherms for Types I and II vapor isotherms.



Legend:

A - Adsorption chamber
G - McLeod gauge
J - Glass-glass joint
L - Liquid sample
M - Mercury cut off
Q - Quartz spring
T - Trap
W - Water jacket
Z - Zimmerli manometer

Fig. 4. Schematic diagram of vapor adsorption apparatus.

EXPERIMENT

Surface excess isotherms for three binary liquid mixtures (benzene + cyclohexane, benzene + *n*-heptane and cyclohexane + *n*-heptane) adsorbed on silica gel at 30°C were measured previously (Sircar and Myers, 1970). The objective here is to measure the adsorption from pure, unsaturated vapors of these materials (benzene, cyclohexane, and *n*-heptane) on the same adsorbent at the same temperature.

Chemicals

The chemicals were Spectroquality reagents obtained from Matheson, Coleman and Bell Company. The silica gel, supplied by the Davison Chemical Co., was reactivated by heating it to 430°C for 6 to 8 hours under vacuum.

Apparatus

A gravimetric adsorption apparatus was designed for measuring adsorption from condensable vapors. The special features of the apparatus are the absence of stopcocks and a temperature control to prevent condensation of vapors. A schematic diagram of the apparatus is shown on Figure 4. The main components are the vapor supply flask (L) containing the liquid adsorbate, the water-jacketed adsorption chamber (W), a McLeod gauge (G), a Zimmerli type manometer (Z), mercury cutoffs (M), and a vacuum train consisting of a liquid nitrogen trap, a mercury diffusion pump and a mechanical vacuum pump. A quartz bucket containing a weighed amount of the adsorbent was suspended inside the adsorption chamber by a helical spring (Q). The amount adsorbed was determined from the elongation of the spring (spring constant = 0.1006 mm/mg); the elongation was measured with a filar eye piece microscope (resolution = 0.002 mm). The temperature of the water circulated through the jacket was controlled within ± 0.01°C.

Pressures less than 10 mm of Hg were measured with the McLeod gauge; pressures greater than 10 mm of Hg were measured with the Zimmerli manometer.

The apparatus, except for the feed supply flask and the vacuum train, was enclosed in an air bath. The temperature of the air bath was maintained slightly higher than the temperature of the adsorption measurements in order to prevent condensation of vapors near their saturation pressure.

Procedure

After removal of dissolved gases by heating under vacuum, the feed supply flask was disconnected from the rest of the apparatus using the mercury cutoff. The apparatus was evacuated and the adsorbent was regenerated in situ by heating with an infrared lamp at 400 to 450°C for 6 to 8 hours. Vapor was then introduced and allowed to equilibrate with the adsorbent. Equilibrium, as indicated by constancy of the elongation of the spring, was attained within a few minutes. It was assumed that equilibration was complete after a period of 45 to 60 minutes, after which the equilibrium pressure was read. This procedure was repeated for successive adsorption points up to saturation of the vapor.

Desorption measurements were made to check the reversibility of the isotherms. The pressure inside the adsorption chamber was reduced by connecting and cooling the vapor supply flask.

RESULTS

The adsorption isotherms for benzene, cyclohexane, and *n*-heptane vapors on silica gel at 30°C are given in Tables 1, 2, and 3 and are plotted on Figure 5. The low-coverage

TABLE 1. ADSORPTION OF BENZENE VAPOR ON SILICA GEL AT 30°C

P mm Hg	*n* mmol/g	*P* mm Hg	*n* mmol/g
0.226	0.478	19.90	3.151*
0.520	0.732	28.20	3.446
0.890	0.906*	35.5	3.608
1.490	1.170	41.1	3.708*
2.510	1.385	55.2	3.757
2.87	1.484*	66.1	3.794
4.20	1.731	81.6	3.832
6.10	1.949	94.0	3.862
8.95	2.294	100.7	3.872
12.90	2.678	107.3	3.890
17.80	3.043		

TABLE 2. ADSORPTION OF CYCLOHEXANE VAPOR ON SILICA GEL AT 30°C

P mm Hg	*n* mmol/g	*P* mm Hg	*n* mmol/g
0.500	0.149	19.80	2.127
0.690	0.186*	20.50	2.191*
0.93	0.230	25.90	2.467
1.15	0.269	31.10	2.741*
1.69	0.348	36.7	2.811
3.30	0.529	49.6	2.932
5.81	0.830	73.1	2.992*
8.00	1.070*	82.9	3.012
9.35	1.190	93.8	3.028
11.70	1.469	109.8	3.052
17.10	1.905		

TABLE 3. ADSORPTION OF *n*-HEPTANE VAPOR ON SILICA GEL AT 30°C

P mm Hg	*n* mmol/g	*P* mm Hg	*n* mmol/g
0.041	0.111	8.40	1.956
0.069	0.150	11.60	2.130
0.290	0.346	12.40	2.150*
0.510	0.495	20.7	2.288
0.89	0.680*	32.9	2.330
1.08	0.751	46.1	2.360
2.10	1.028	48.8	2.366*
4.60	1.498	55.2	2.379
6.50	1.781*		

* Desorption point.

data are plotted on Figure 6.

The free energy of immersion was calculated from the vapor isotherms using Equation (6) and is reported in Table 4. These are Type I isotherms; the saturation capacity (m) is also reported in Table 4.

The vapor and liquid adsorption isotherms may be compared for thermodynamic consistency. Differences in free energy of immersion may be calculated from Equation (20), which gives upon integration:

$$\frac{\phi_2^s - \phi_1^s}{RT} = \int_{x_1=0}^{1} \frac{n_1^e}{\gamma_1 x_1 x_2}\, d(\gamma_1 x_1) \qquad (44)$$

Differences in free energies of immersion calculated by Equation (44) using the experimental data on surface excess are reported in Table 5. These may be compared with the differences obtained from the vapor isotherms (from Table 4). There is a discrepancy of 9% in the values of $\Delta\phi$ obtained by the two different methods. This discrepancy is within the estimated experimental error of 5% ($\Delta\phi$ is the difference of two numbers of the same magnitude).

The vapor isotherms were used to predict the liquid isotherms by means of Equations (22), (19), and (18) solved sequentially as explained previously. Bulk phase activity coefficients are available (Sircar and Myers, 1970). The prediction (solid line) is compared with experimental data for the benzene + cyclohexane system on Figure 7, which shows that the agreement is not quantitative. The prediction shown on Figure 7 is based upon the assumption of an ideal adsorbed solution. The experimental data may be interpreted quantitatively in terms of nonidealities in the adsorbed phase; for this system the adsorbed solution exhibits strong negative deviations from Raoult's law ($\gamma = 0.8$ at equimolar composition).

The same result was obtained for the benzene + n-heptane system (see Figure 8). Here, as before, the assumption of an ideal adsorbed solution is not in quantita-

TABLE 4. FREE ENERGY OF IMMERSION AND SATURATION CAPACITY FOR ADSORPTION ON SILICA GEL AT 30°C

Adsorbate	Free energy of immersion, ϕ^s/RT mmol/g	Saturation capacity, m mmol/g
benzene	−14.52	3.91
cyclohexane	−7.90	3.06
n-heptane	−7.90	2.37

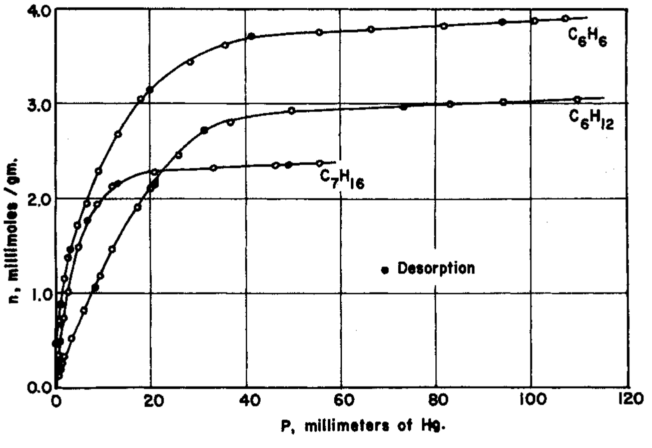


Fig. 5. Adsorption isotherms of benzene, cyclohexane, and n-heptane on silica gel at 30°C.

TABLE 5. DIFFERENCES IN FREE ENERGIES OF IMMERSION

	$\frac{\phi_1^s - \phi_2^s}{RT}$, mmol/g	
Mixture	From liquid isotherms, Equation (44)	From vapor isotherms Table 4
benzene (1) + cyclohexane (2)	−7.20	−6.62
benzene (1) + n-heptane (2)	−7.20	−6.62
cyclohexane (1) + n-heptane (2)	0.0	0.0

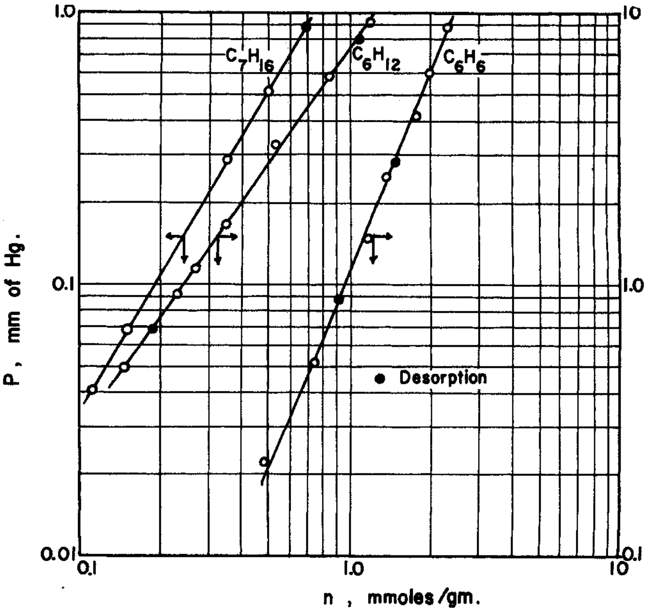


Fig. 6. Adsorption isotherms at low pressure of benzene, cyclohexane, and n-heptane on silica gel at 30°C.

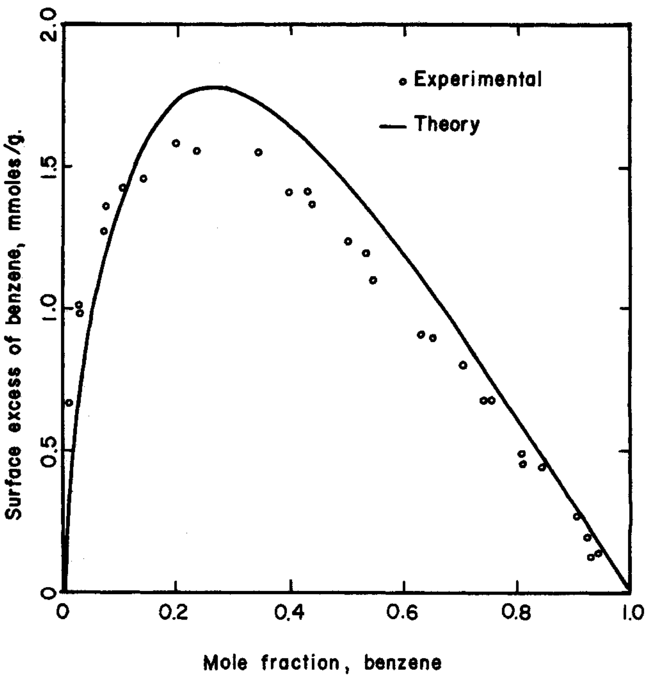


Fig. 7. Surface excess of benzene adsorbed on silica gel from liquid mixture of benzene + cyclohexane at 30°C.

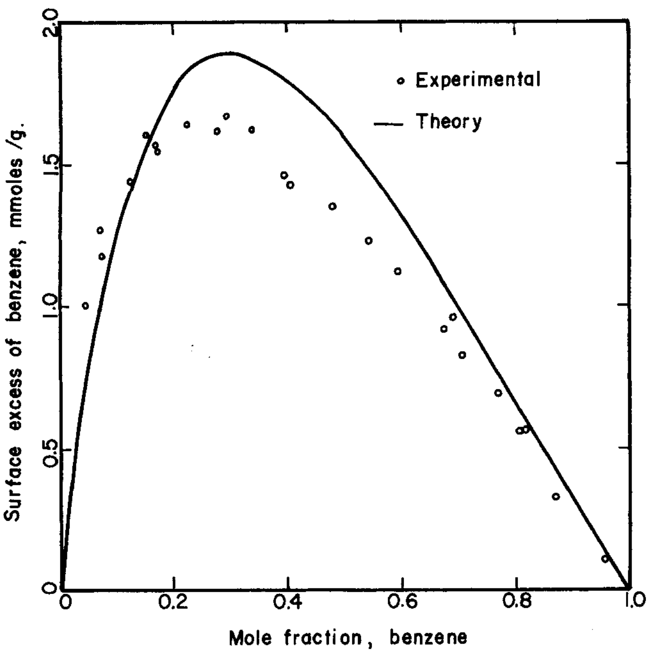


Fig. 8. Surface excess of benzene adsorbed on silica gel from liquid mixture of benzene + n-heptane at 30°C.

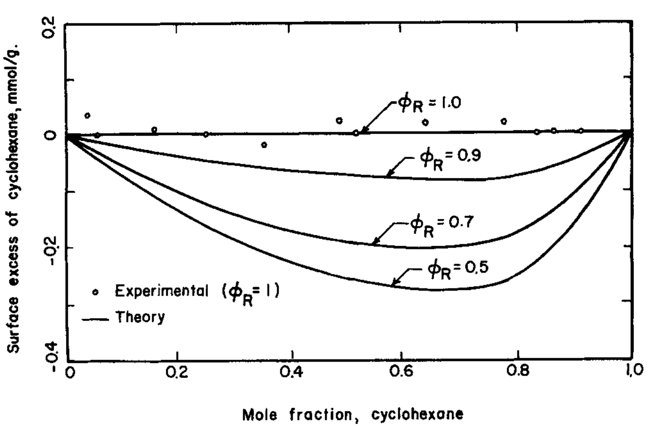


Fig. 9. Surface excess of cyclohexane adsorbed on silica gel from liquid mixture of cyclohexane + n-heptane at 30°C.

tive agreement with the observed data. The adsorbed solution, like the benzene + cyclohexane system, shows strong negative deviations from Raoult's law ($\gamma = 0.8$ at equimolar composition).

The free energies of immersion of the silica gel in cyclohexane and n-heptane are equal. The prediction of Equations (18), (19), and (22) is that $n_1^e = 0$ at all concentrations; this prediction is in quantitative agreement with the experimental results on Figure 9. It is interesting that silica gel adsorbs n-heptane in preference to cyclohexane from the vapor mixture but shows no preference for either adsorbate at saturation. This change in selectivity is a consequence of the crossing of the vapor isotherms (see Figure 5).

ACKNOWLEDGMENT

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NOTATION

a = activity
C = constant, Equation (40)
K = defined by Equations (13), (16), (19), (26), and (30)
m = number of moles adsorbed at saturation
n_i' = number of moles of i'th component in adsorbed phase
n_i^* = number of moles of pure i'th adsorbate in adsorbed phase
n_i^e = surface excess of i'th component
P = pressure
P^s = pressure of bulk liquid at saturation
P_r = reduced pressure = P/P^s
P_i^* = pressure of pure i'th adsorbate
R = gas constant
r = a constant, Equation (36)
T = absolute temperature
x_i' = mole fraction of i'th component in adsorbed phase
x_i = mole fraction of i'th component in bulk liquid phase
y_i = mole fraction of i'th component in vapor phase

Greek Letters

α = constant, Equation (43)
β = constant, Equation (36)
γ_i = activity coefficient of i'th component in bulk liquid
ϕ = surface potential
ϕ^s = free energy of immersion
ϕ_r = reduced surface potential = ϕ/ϕ^s
ϕ_i^* = surface potential of pure i'th adsorbate

Subscripts

1 = component no. 1
2 = component no. 2
i = i'th component

Superscripts

$'$ = adsorbed phase
$*$ = pure adsorbate
s = value at saturation

Note: the variables m, n and ϕ refer to unit mass of adsorbent

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