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S. Sircar[a]; A. L. Myers[b]
[a] AIR PRODUCTS AND CHEMICALS, INC. ALLENTOWN, PENNSYLVANIA [b] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF PENNSYLVANIA PHILADELPHIA, PENNSYLVANIA

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REVIEW

Liquid Adsorption Operations: Equilibrium, Kinetics, Column Dynamics, and Applications

S. SIRCAR

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PENNSYLVANIA 18105

A. L. MYERS

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA 19104

Abstract

Separation and purification of liquid mixtures by adsorption has become an important unit operation in the chemical industry. Design of adsorbers requires information on both adsorption equilibrium and kinetics. The amount of each species adsorbed at equilibrium is the *surface excess*, which is usually measured experimentally. Analytical equations for the surface excess in bulk and dilute solutions account for differences in molecular size and surface heterogeneity. Experimental equilibrium data can be tested for thermodynamic consistency. The rate of adsorption depends upon the structure of the internal surface of the adsorbent particle, pore diffusivities of the adsorbates, and mass transfer coefficients for the external film. The dynamical behavior of adsorption columns is modeled using equilibrium and kinetic data by simultaneous solution of the partial differential equations for the mass balance of each solute. Industrial adsorption processes for separating bulk liquid mixtures and for removing trace impurities from liquids are designed for continuous or semicontinuous operation.

INTRODUCTION

Separation and purification of multicomponent liquid mixtures by *adsorption* on solid *adsorbents* has become an important unit operation in

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the chemical industry. Typical applications are: removal of trace contaminants such as color-, taste-, or odor-producing compounds from liquids; drying of hydrocarbons; treatment of municipal and industrial wastewaters; and bulk separation of various hydrocarbon and carbohydrate mixtures (see Industrial Applications section). Because of differences in intermolecular forces between the components of the liquid mixture (called the *adsorbates*) and the solid adsorbent, certain adsorbates become concentrated at the solid surface. The creation of a surface phase with a composition different from that of the surrounding bulk liquid provides a basis for separation.

The reverse process by which the adsorbed molecules are removed from the solid adsorbent is called *desorption*. Desorption constitutes an integral part of every practical separation because the adsorbent must be reused.

Ad(de)sorption can by physical or chemical. *Physisorption* is characterized by weak molecular interactions between the adsorbate and the solid. It is governed primarily by: the size and shape of the adsorbate molecules, the polarity of the adsorbates and the adsorbent, and the porous structure of the solid. In *chemisorption*, a stronger chemical bond is formed due to electron sharing or transfer between the adsorbate and the adsorbent.

Because of their complexity, liquid–solid molecular interactions cannot generally be predicted. However, the phenomenon of adsorption from liquids can be analyzed in considerable depth using experimentally measured properties of the adsorption systems, in a manner similar to that for gas adsorption which has been covered previously (*1*). The following discussion is a panoramic survey of the key topics in adsorption from liquids.

ADSORPTION EQUILIBRIUM

The extent of equilibrium adsorption of component i from a multicomponent liquid mixture of N components ($i = 1, 2, \ldots, N$) is given by the *surface excess* (n_i^e) for each component (*2*). n_i^e is measured by comparing the bulk concentration (c_i) or mole fraction (x_i) of component i before contact with the solid adsorbent (c_i^0 or x_i^0) and after attainment of equilibrium (c_i or x_i). In terms of mole fractions:

$$n_i^e = n^0[x_i^0 - x_i] \qquad (i = 1, 2, \ldots, N) \tag{1}$$

where n^0 is the total amount (moles) of liquid mixture contacted with unit amount of solid.

n_i^e is a function of x_i and the system temperature T. It is usually a very weak function of the system pressure (*3*). It follows from Eq. (1) that

$$n_i^e = 0 \qquad \text{(for a pure liquid)} \tag{2}$$

$$\Sigma\, n_i^e = 0 \qquad \text{(for a mixture)} \tag{3}$$

Thus, adsorption from a pure liquid is not a meaningful measurement, contrary to the case for adsorption of a pure gas (*1*). For adsorption from liquids, the simplest nontrivial case of interest is a binary liquid mixture. The surface excess ($n_1^e = -n_2^e$) is a measure of the *competition* of the two liquids for accessible adsorption sites on the surface of the solid. Zero surface excess means that both species adsorb with equal strength so there is no separation effect. Physically, n_i^e is the amount of component i adsorbed (n_i) *in excess* of the amount of that component which would be present in the adsorbed phase if its composition and density were the same as that of the equilibrium bulk liquid phase (*2*):

$$n_i^e = n_i - x_i\, \Sigma\, n_i \tag{4}$$

Both n_i^e and n_i are expressed in specific terms, e.g., in moles of adsorbate per gram of solid.

n_i^e is approximately equal to n_i only when component i is present in very dilute concentration ($x_i \ll 1$) and is adsorbed very strongly compared to the other species present (*4*). It is, however, customary to define a selectivity (s_{ij}) of adsorption by

$$s_{ij} = n_i x_j / n_j x_i \tag{5}$$

Component i is adsorbed preferentially relative to component j if $s_{ij} > 1$.

It is not necessary to know the absolute amount adsorbed in order to write material balances, rate equations, and equilibrium relationships for adsorption systems. Design equations can and should be based upon the surface excess variable rather than the absolute amount adsorbed.

The functionality $n_i^e(x_i)$ for a given temperature is called the *surface excess isotherm*. For a binary liquid mixture, these isotherms can be "U" or "S" shaped, as shown in Figs. 1 and 2, respectively. One component of the mixture is adsorbed preferentially at all concentrations in the case of a U-

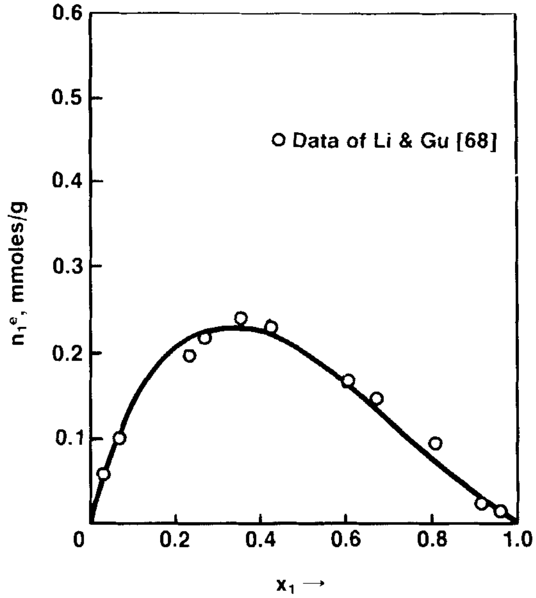

FIG. 1. Adsorption of toluene (1) from bromobenzene (2) on silica gel at 20°C.

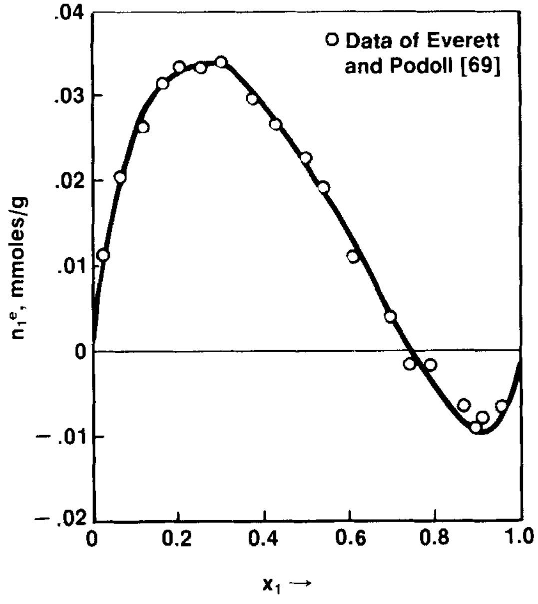

FIG. 2. Adsorption of benzene (1) from dichloroethane (2) on graphon at 0°C.

shaped isotherm, but a reversal of preference occurs at some intermediate (azeotropic) concentration for an S-shaped curve.

For adsorption of a dilute solute of limited solubility $(0 \leqslant x_i \leqslant x_i^s)$ from a liquid solvent on a porous adsorbent, the solute isotherm is usually analogous to the Type I Brunauer classification for gas adsorption (*5*), as shown in Fig. 3. This type is actually a U-shaped isotherm truncated at the upper limit of x_i. Dilute solute isotherms having a Type II shape (*5*) have been observed for nonporous adsorbents (*6*).

MODEL ISOTHERMS

Bulk Liquid Mixtures

The distinguishing feature between adsorption from liquids and adsorption from gases is that, in the former case, the adsorbent surface is always completely covered with adsorbate molecules. For a porous adsorbent, the pores are filled with liquid. This observation (*7*) has

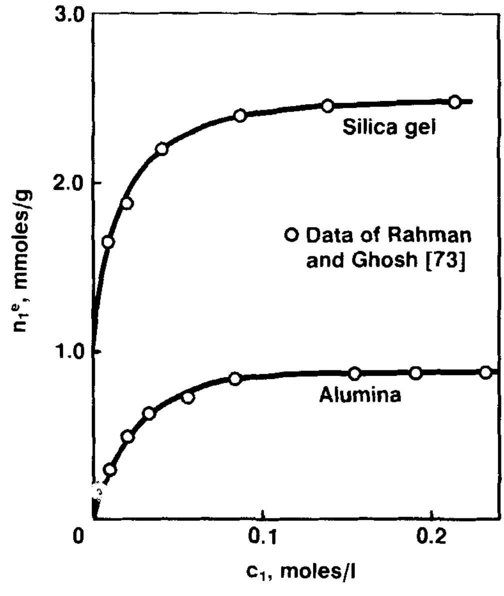

FIG. 3. Adsorption of dilute pyridine from *n*-heptane on silica gel and alumina at 30°C.

prompted the development of a "monolayer or pore-filling" (MPF) mechanism of adsorption from liquids (*8*). An expression for n_i^e can be derived (*9, 10*) using this model for the adsorption of a binary liquid mixture which is nonideal in the bulk phase:

$$n_i^e = \frac{m_1[sa_1x_2 - a_2x_1]}{sa_1 + \beta a_2} \tag{6}$$

where

$$s = s_0[sa_1 + a_2]^{(\beta-1)/\beta} \tag{7}$$

and

$$s_0 = e^{(\phi_2^0 - \phi_1^0)/m_1RT} \tag{8}$$

m_i is the monolayer or pore-filling capacity of ith pure adsorbate, β is the ratio (m_1/m_2), and a_i is the activity of component i in the bulk liquid phase at equilibrium. s is the binary selectivity, defined by

$$s = n_1a_2/n_2a_1 \tag{9}$$

s_0 is the value of s at the limit of infinite dilution of component 1 $(x_1 \rightarrow 0)$. ϕ_i^0 is the surface potential [9] for adsorption of pure liquid i at the temperature (T) of the isotherm. R is the gas constant. The difference in surface potentials is given by (*9*):

$$\frac{(\phi_2^0 - \phi_1^0)}{RT} = \int_{a_1=0}^{1} \frac{n_1^e}{a_1x_2}\,da_1 \tag{10}$$

Equations (6)-(8) are based upon the assumption that the adsorbed (but not the bulk) phase forms an ideal solution (*10*). The model, however, can be extended to include the effect of nonideality in the adsorbed phase (*9*). Other models for liquid adsorption like the "phase exchange reaction model" (*11, 12*) yield similar expressions for n_1^e.

Equation (7) shows that s is a strong function of a_i and β. s is a constant $(= s_0)$ only when the adsorbate molecules are the same size (equal values of m_i). The MPF capacities are related by

$$\frac{m_i}{m_j} = \left[\frac{v_j}{v_i}\right]^{2/3} \quad \text{(monolayer adsorption)} \tag{11a}$$

$$= \left[\frac{v_i}{v_i}\right] \quad \text{(pore-filling model)} \qquad (11b)$$

v_i is the molar volume of *i*th pure liquid. Equation (11b) is known as Gurvitch's rule (*5*) and is valid for most porous adsorbents providing that there is no molecular sieving effect which allows a smaller molecule to enter pores inaccessible to larger species.

Selection of capacities m_i for use in Eq. (6) may be critical (*13, 14*). An independent estimation of m_i from pore volume or surface area data is recommended.

Extension of the MPF model to describe adsorption from multicomponent ($N > 2$) mixtures is also available (*15*).

Adsorbent Heterogeneity

Most adsorbents of practical interest are energetically heterogeneous, and this factor plays an important role in determining the behavior of the surface excess isotherms. Many models and theories have been proposed to account for adsorbent heterogeneity (*16, 17*). One simple model (*14, 18*) that gives an analytical expression for the surface excess assumes that the adsorbent is composed of a distribution of homogeneous patches or sites, each of which is characterized by a selectivity parameter s_0 given by Eq. (8). The overall surface excess can then be estimated by integrating over the contributions of individual sites (*19*):

$$n_1^e = \int_{s_0=0}^{\infty} (n_1^e)_h \lambda(s_0) ds_0 \qquad (12)$$

$(n_1^e)_h$ is a homogeneous surface excess isotherm, such as Eq. (6). $\lambda(s_0)$ is the probability density function for s_0. Both the gamma $[\lambda(s_0) = k(s_0)^n \exp(-\alpha s_0)]$ and the uniform $[\lambda(s_0) = k]$ distribution functions have been used (k, α, and n are constants). The gamma function yields the following isotherm for equal-sized adsorbates (*18*):

$$n_1^e = m[x_2 - \theta \exp(\theta) E_{n+1}(\theta)] \qquad (13)$$

where $\theta = \alpha a_2/a_1$ and $E_{n+1}(\theta)$ is the exponential integral of order $(n + 1)$. Analytical expressions for n_1^e have also been derived for unequally sized adsorbates (*10*). The solid lines in Figs. 1 and 2 show the fit of Eq. (13) to experimental data.

n_i^e is fairly insensitive (*10*) to the choice of the distribution function, given a particular model for the local isotherm. This observation applies as well to gas adsorption (*20*). Surface heterogeneity can be responsible for the formation of an S-shaped isotherm, even when both the bulk liquid and adsorbed phases are ideal (*10, 14, 18*), as in Fig. 2. The homogeneous MPF model cannot predict this behavior unless there are nonidealities in the adsorbed phase. Since both U- and S-shaped isotherms can be interpreted in terms of either adsorbed phase nonidealities or energetic heterogeneity (*21*), experimental methods for studying these properties independently are needed.

Dilute Solutes

The most frequently used equation for describing the adsorption of a dilute solute of limited solubility from a solvent is the Freundlich equation (*8, 22–24*):

$$n_i^e = k_i(c_i)^{1/q_i} \qquad (q_i \geqslant 1) \tag{14}$$

where k_i and q_i are constants for a given solute, and c_i is its bulk concentration. An isotherm of this form is usually evidence of surface heterogeneity (*25*), and it has been derived using Eq. (6) as a local isotherm (*26*). Figure 4 shows examples of the fitting of data by Eq. (14). The domain of its applicability is usually limited to one or two decades of change in concentration. The Freundlich equation has the flaw that it has the incorrect limit at very low coverage, and thus is not recommended for extrapolation. Another commonly used isotherm for dilute single solutes has the form of the Langmuir equation for pure gas adsorption (*5*). It may be derived (*26*) as a limiting case $[x_1 \ll 1]$ of Eq. (6):

$$n_1^e = \frac{(m_2 s_0 \gamma_1^\infty) x_1}{1 + [s_0 \gamma_1^\infty (2 - \beta)/\beta] x_1} \tag{15}$$

γ_1^∞ is the bulk-phase activity coefficient of the solute at the limit of infinite dilution ($x_1 \rightarrow 0$).

Multicomponent Dilute Solutes

Empirical equations are often used for adsorption of multicomponent dilute solutes from a single solvent. An example is (*27, 28*):

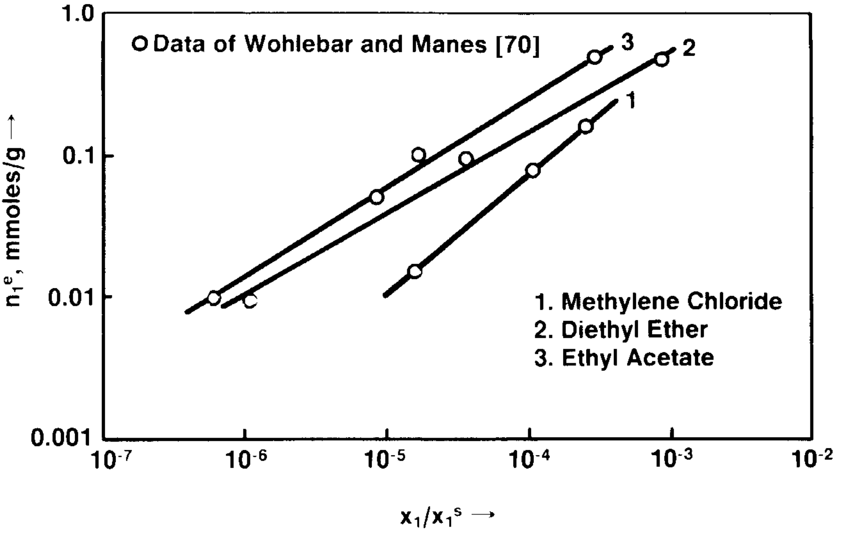

FIG. 4. Adsorption of single, dilute hydrocarbon solutes from water onto activated carbon at 25°C.

$$n_i^e = \frac{a_{i0} x_i^{b_{i0}}}{c_i + \Sigma a_{ij} x_j^{b_{ij}}} \tag{16}$$

where a_{i0}, b_{i0}, c_i, a_{ij} and b_{ij} are constants and the summation ($i = 1, 2, \ldots N$) is over the N solutes present. For single solutes Eq. (16) can be made to reduce, for certain values of the constants, to either the Freundlich or Langmuir equations.

Isotherms for adsorption of different, pure solutes of limited miscibility from the same solvent on a particular adsorbent can be correlated by a theory of correspondence (*29*), which gives the following universal isotherm:

$$\frac{m_1 RT \ln [x_1/x_1^s]}{(\phi_2^0 - \phi^s)} = f[n_1^e/n_1^{es}] \tag{17}$$

where Component 1 is the solute and Component 2 is the solvent. n_1^{es} and ϕ^s are, respectively, the values of n_1^e and the surface potential for adsorption of the liquid mixture (ϕ) at the limit $x_1 \rightarrow x_1^s$. f is a universal function of the fractional coverage (n_1^e/n_1^{es}) and is independent of the nature of the solute. ($\phi_2^0 - \phi^s$) can be obtained by:

$$\frac{(\phi_2^0 - \phi^s)}{RT} = \int_0^{x_1^s} \frac{n_1^e}{x_1} dx_1 \tag{18}$$

Isotherms for different solutes can be estimated from that of a reference solute using Eq. (17) and a single experimental point for the solute of interest. Figure 5 illustrates the ability of Eq. (17) to coalesce isotherms into a single curve. Theories are needed which estimate the quantity $(\phi_2^0 - \phi^s)$, so that predictions of adsorption can be made entirely from reference isotherms.

Dilute multisolute isotherms can be calculated from the ideal adsorbed solution model (*30*) if experimental data for each solute–solvent pair is available. The model assumes ideal mixing in the adsorbed phase at constant relative surface potential $(\phi - \phi_s^0)$ and temperature:

$$\Sigma (n_i^e/n_i^{e*}) = 1 \tag{19}$$

$$c_i = c_i^* [n_i^e/\Sigma n_i^e] \tag{20}$$

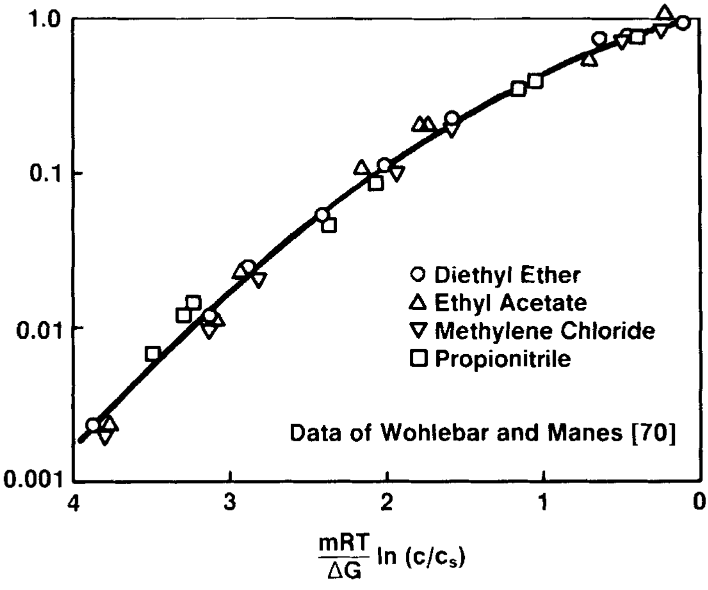

FIG. 5. Application of correspondence theory to isotherms for adsorption of various solutes from water on activated carbon at 25°C. *f* is the fractional loading of the adsorbent.

where n_i^e and c_i are, respectively, the surface excess and the concentration of ith solute in the multisolute mixture. ϕ_s^0 is the surface potential for adsorption of the pure solvent at T. The asterisks refer to the standard state: n_i^{e*} and c_i^* are, respectively, the surface excess and concentration of ith solute in the *binary* (single solute + solvent) system at the same relative surface potential $(\phi - \phi_s^0)$ and temperature as that of the multisolute mixture. The relative surface potential is obtained from the integral:

$$\frac{(\phi - \phi_s^0)}{RT} = -\int_0^{c_i^*} \frac{n_i^{e*}}{c_i^*}\,dc_i^* \tag{21}$$

$$n_i^{e*} = n_i^{e*}(c_i^*) \tag{22}$$

where Eq. (22) is the single-solute isotherm in functional notation.

For a multisolute system containing j solutes ($i = 1, 2, \ldots, j$), there are $(3j + 1)$ unknowns, viz, n_i^e, n_i^{e*}, c_i^* and $(\phi - \phi_s^0)$. Equations (19)-(22) provide $(3j + 1)$ independent equations relating these variables, so a unique solution exists. The theory provides approximations good enough for engineering design when the solute loadings are low; an example is given in Table 1 for a binary solute system (*30*).

An analytic adsorption isotherm for a multisolute system has been derived (*74*) using Eq. (14) as the single-solute isotherm in conjunction with Eqs. (19)-(22):

TABLE 1
Surface Excess Isotherms for Adsorption of Dilute *p*-Cresol (1) and *p*-Chlorophenol (2) from Water on Activated Carbon at 25°C

$c_1 \times 10^5$ mol/L	$c_2 \times 10^5$ mol/L	n_1^e (mmol/g)		n_2^e (mmol/g)	
		expt	calc	expt	calc
4.21	4.36	0.476	0.431	0.848	0.821
38.6	104	0.407	0.322	1.73	1.71
77.4	494	0.279	0.193	2.42	2.27
102	103	0.796	0.702	1.44	1.39
287	61.9	1.56	1.56	0.79	0.653
541	325	1.28	1.24	1.46	1.36
1080	718	1.41	1.38	1.66	1.58

$$c_i = \left[\frac{n_i}{\Sigma n_i}\right]\left[\frac{\Sigma(n_i q_i)}{K_i q_i}\right]^{q_i} \tag{14b}$$

Thus the bulk concentration of each solute is given explicitly in terms of the loading and the single-solute constants of Eq. (14). The summation is over the *solutes* present in the mixture.

ADSORPTION THERMODYNAMICS

The thermodynamics of adsorption from liquid mixtures is well developed [31–34]. Some of the most useful results are summarized below.

Thermodynamic Consistency Test

The surface excess isotherms for a set of binary liquid mixtures comprised of any three adsorbates must obey the integral consistency test dictated by Eq. (10). Thus for adsorption of 1–2, 2–3, and 3–1 binary mixtures, one has:

$$(\phi_2^0 - \phi_1^0) + (\phi_3^0 - \phi_2^0) + (\phi_1^0 - \phi_3^0) = 0 \tag{23}$$

Each of the three terms of Eq. (23) can be evaluated with Eq. (10) using surface excess data for the appropriate binary mixture. This requirement places a constraint on the parameters of any model for adsorption from liquid mixtures. Table 2 gives an example of the use of this test (*31*).

TABLE 2
Integral Thermodynamic Consistency Test for Adsorption of Binary Mixtures on Silica Gel at 30°C

	$(\phi_2^0 - \phi_1^0)/RT$ (mmol/g)
Benzene (1) + cyclohexane (2)	7.20
n-Heptane (1) + benzene (2)	−7.20
Cyclohexane (1) + *n*-heptane (2)	0.00
Sum	0.00

Temperature Coefficient of Surface Excess

For an ideal ($a_i = x_i$) binary liquid mixture (*32*):

$$\left(\frac{\partial n_1^e}{\partial T}\right)_{x_1} = \left(\frac{x_1 x_2}{RT^2}\right)\left(\frac{\partial \Delta H}{\partial x_1}\right)_T \tag{24}$$

where ΔH is the heat of immersion (a negative quantity) of the adsorbent in a liquid mixture of equilibrium composition x_1. Since the absolute magnitude of the heat of immersion is usually greater for the preferentially adsorbed species (#1), n_1^e typically decreases with increasing temperature at fixed composition. According to the MPF model, ΔH for an ideal liquid mixture of molecules of equal size is:

$$\Delta H = \frac{s_0 x_1 \Delta H_1^0 + x_2 \Delta H_2^0}{s_0 x_1 + x_2} \tag{25}$$

where ΔH_i^0 is the heat of immersion of the adsorbent in pure *i*th liquid. Expressions for the temperature coefficient of surface excess, and for the heat of immersion, can also be derived for molecules of unequal size (*32*). The heat of immersion $\Delta H(x_1)$ can be measured directly by calorimetry; Fig. 6 shows an example. The highly nonlinear shape of this curve is predicted by Eq. (25).

Vapor-Liquid Adsorption Analogy

For microporous adsorbents, the surface potential for adsorption of a pure liquid (ϕ_i^0) is equal to that for adsorption of its vapor (ϕ_i^{vs}) at the limit $P \rightarrow P_i^s$, where P_i^s is the vapor pressure of the saturated liquid at the same temperature. It follows (*33, 34*) that:

$$\frac{\phi_i^0}{RT} = \frac{\phi_i^{vs}}{RT} = -\int_0^{P_i^s} \frac{n_i^v}{P}\,dP \tag{26}$$

where $n_i^v(P)$ is the experimental isotherm for adsorption of the pure vapor at the temperature of interest. Equation (26) provides a link between adsorption of vapors and liquids; Table 3 shows an example (*34*).

The relationship between adsorption from liquids and their vapors can be more easily understood by defining a surface excess (n_i^{ev}) for

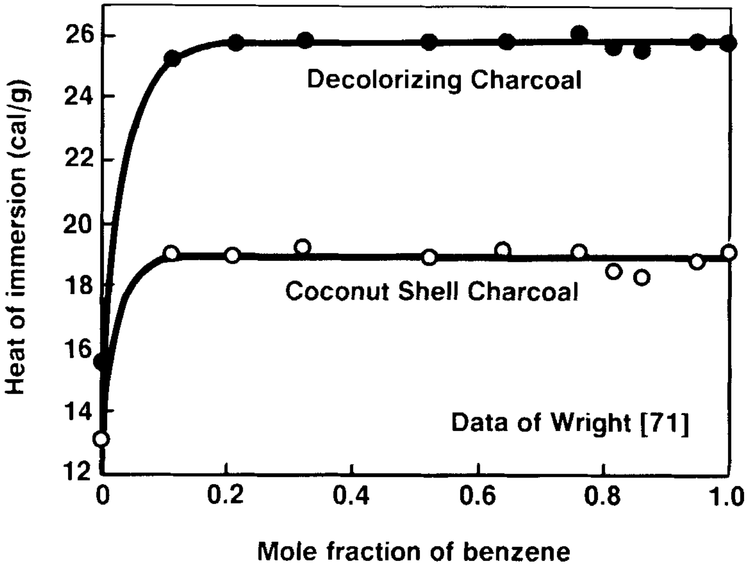

FIG. 6. Heat of immersion of charcoals in benzene + cyclohexane mixtures at 30°C.

adsorption of the ith component from a vapor mixture of mole fraction y_i:

$$n_i^{ev} = n_i^v - x_i \Sigma n_i^v \tag{27}$$

where x_i refers to the mole fraction in the bulk liquid mixture which is in equilibrium with the vapor at the same temperature. It follows from the vapor–liquid analogy that:

$$n_i^e = \lim_{P \to P^S} n_i^{ev} \tag{28}$$

For a given vapor mixture of composition y_i, let the pressure increase isothermally to its dew point. This occurs at the saturation pressure P^s, when the vapor is in equilibrium with bulk liquid of composition x_i. Equation (28) then provides a means of calculating n_1^e for liquids from adsorption isotherms of the vapor mixture. The latter, in turn, can be estimated from the pure-vapor isotherms (*35*, *36*). Thus it is feasible to estimate n_1^e from unsaturated vapor isotherms of the individual components (*13*, *33*); Fig. 7 shows an example of such a prediction.

TABLE 3
Vapor–Liquid Adsorption Analogy for Benzene + Cyclohexane on Silica Gel at 30°C

	ϕ_1^s/RT (vapor) (mmol/g)	ϕ_2^s/RT (vapor) (mmol/g)	$(\phi_2^0 - \phi_1^0)/RT$ (liquid) (mmol/g)
Benzene (1)	−14.5		
Cyclohexane (2)		−7.9	
Benzene (1) + cyclohexane (2)			7.2

$$(\phi_2^s - \phi_1^s)/RT = -7.9 - (-14.5) = 6.6 \text{ mmol/g}$$

$$(\phi_2^0 - \phi_1^0)/RT = 7.2 \text{ mmol/g}$$

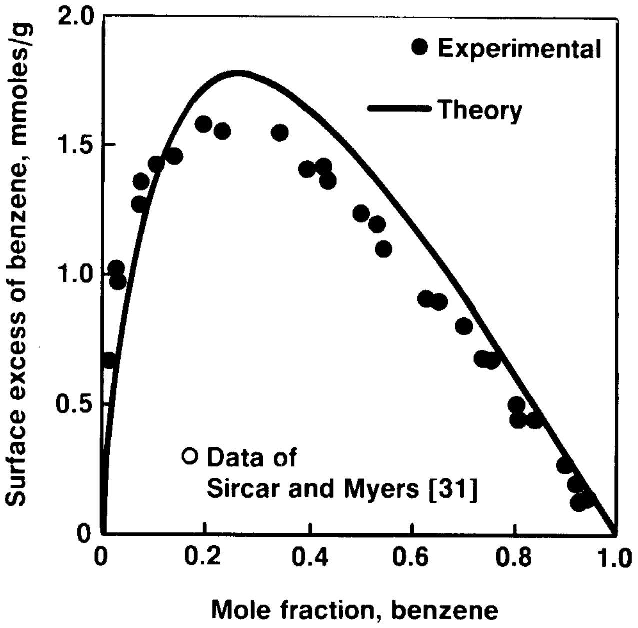

FIG. 7. Prediction of surface excess isotherm of benzene (1) + cyclohexane (2) mixtures on silica gel at 30°C, using data on adsorption of pure vapors.

Type I pure-vapor isotherms lead to surface excess isotherms (*13*) which are of the form of Eq. (6), which has also been derived from statistical thermodynamics for molecules of equal size (*37*).

ADSORPTION KINETICS

The actual physisorption process is usually very fast, but the measured rate of adsorbate uptake from liquid mixtures by porous adsorbents can be slow due to resistances against mass transfer from the bulk liquid to the adsorption sites. The same mass transfer considerations apply to desorption. The rates are controlled by:

(a) Liquid film resistance at the outer surface of the adsorbent particles
(b) Internal diffusional resistance of the liquid-filled pores
(c) Resistance to internal diffusion for transport of adsorbate molecules on the adsorbent surface

The pore (b) and surface (c) diffusional resistances operate in parallel while the external film (a) forms a resistance in series with (b) and (c). The film resistance depends upon the properties of the liquid mixture, the adsorbent particle size, and the surface roughness, as well as on the degree of agitation in the liquid–solid interface. On the other hand, the internal resistances are a function of the porous structure of the adsorbent, its particle size, and the energetic heterogeneity of the adsorbent surface. Thus, unlike equilibrium adsorption, which can be studied without defining the exact structure of the adsorbent or the mechanism of adsorption, kinetic studies require detailed information about pore geometry and surface properties in order to estimate mass transfer coefficients and diffusivities from experimental uptake data. The kinetics of ad(de)sorption from liquids is usually much slower than that from gases.

The internal pore structures of most industrial adsorbents are very complex and ill defined. It is customary to define average pore (D_{pi}) or surface (D_{si}) diffusivities for each adsorbate i of the mixture in kinetic models. Values for these diffusivities are often treated as constants but they can be concentration dependent or be affected by the presence of other adsorbates, thus increasing the complexity of the problem (38–41).

Several review papers have been published on the batch kinetics of adsorption from liquids (*28, 42, 43*). The simplest model is for isothermal adsorption of a dilute ($n_1^e = n$) single solute from a finite bath of liquid mixture into spherical adsorbent particles of radius R. For the case when all three resistances mentioned above are present, the mass balance equations are:

Overall Solute

$$\frac{dn}{dt} = -n^0 \frac{dc}{dt} \tag{29}$$

Solute Balance in Adsorbent Particle

$$\varepsilon_p \frac{\partial}{\partial t} [c_p(r,t)]_r + \rho_p \frac{\partial}{\partial t} [n_p(r,t)]_r = -\frac{D_p \varepsilon_p}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial c_p}{\partial r} \right]_t - \frac{D_s \rho_p}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial n_p}{\partial r} \right]_t \tag{30}$$

$$n(t) = (3/R^3) \int_0^R n_p(r,t) r^2 dr \tag{31}$$

Initial and Boundary Conditions

$$-\varepsilon_p D_p \left[\frac{\partial c_p}{\partial r} \right]_{r=R} - \rho_p D_s \left[\frac{\partial n_p}{\partial r} \right]_{r=R} = k_f [c(t) - c_p(R,t)] \tag{32}$$

$$\left[\frac{\partial c_p}{\partial r} \right]_{r=0} = \left[\frac{\partial n_p}{\partial r} \right]_{r=0} = 0 \tag{33}$$

$$c_p(r,0) = c^* \qquad (t < 0) \tag{34}$$

$$c = c^0 \qquad (t = 0) \tag{35}$$

Equilibrium Isotherm

$$n_p = n_p(c_p) \tag{36}$$

A batch kinetic test is performed by changing the bulk liquid concentration (c) of the solute from c^* to c^0 at time $t = 0$ and then monitoring $c(t)$. c decreases with time until equilibrium is reached. The rate of adsorption of the solute per unit amount of adsorbent, dn/dt, can be measured by Eq. (29), which follows from Eq. (3). Equation (30) is a transient solute balance based on a Fickian diffusion mechanism in an adsorbent particle, where n_p and c_p are, respectively, the specific amount of solute adsorbed and its concentration within the pores at radius r of the particle and at time t. ε_p is the void fraction of the pores and ρ_p is the particle density. The first and second terms on the right-hand side of Eq. (30) account for pore and surface diffusion, respectively, of the solute within the adsorbent particle.

Equation (31) gives the total specific amount adsorbed at time t. The boundary condition of Eq. (32) accounts for the solute flux at the particle surface ($r = R$), which is determined by the external film mass transfer resistance k_f. Equation (33) describes the symmetry of the concentration and adsorbate loading profiles at the center of the particle ($r = 0$).

Equilibrium is assumed to exist between the liquid and adsorbed phases within the pores, and Eq. (36) is a functional notation for an adsorption isotherm such as Eqs. (14)-(16). Equations (30)-(36) are solved simultaneously to obtain $n(t)$ or dn/dt, which can then be compared with experimental uptake data (Eq. 29) in order to estimate the adsorbate diffusivities.

The model can be simplified by assuming that one or two resistances dominate. Even then, numerical solutions of the equations are needed for realistic nonlinear adsorption isotherms. Analytical solutions are available for the case when either pore or surface diffusion are the controlling mechanisms and the adsorption isotherm is linear or irreversible (*42, 44*). Other more complicated models which include bi-disperse pore structure (macro- and micropores) have also been proposed (*45, 46*). Simplified models based on a linear-driving-force mechanism for mass transfer and a lumped mass transfer coefficient have also been used (*47*). An example of batch kinetic data for a single dilute solute is illustrated in Fig. 8.

Only a few batch kinetic studies of dilute, multisolute adsorption have been performed (*28*), and there are none for bulk liquids.

Correlations for the estimation of the mass transfer coefficient k_f of the external film are available (*48, 49*). However, the methods for estimating D_{pi} or D_{si} for dilute solutes are based upon simplified models (*39, 44, 49, 50*). It is difficult to determine unequivocally the actual transport mechanism from experimental uptake data using models (*41*) but there are nevertheless strong indications of the existence of concentration-dependent surface diffusion for many systems (*50, 51*).

The assumption of isothermal adsorption from liquid mixtures is often valid because of the large heat capacity of the liquid, although such an assumption cannot generally be made for adsorption of gases (*1*).

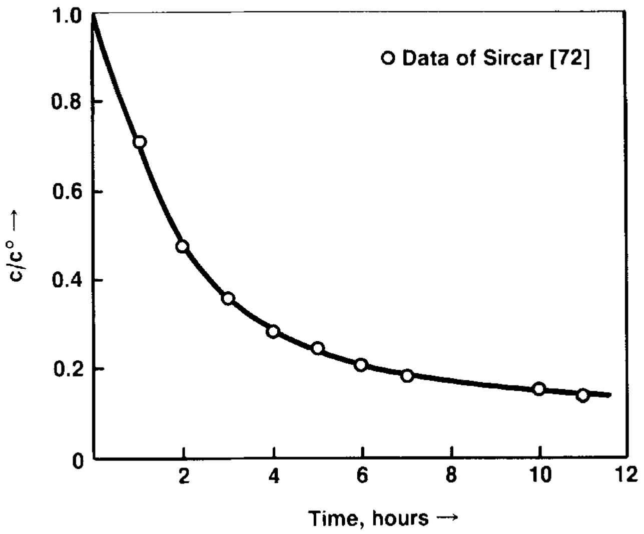

FIG. 8. Batch kinetics for adsorption of dilute water from cyclohexane on 3A-zeolite at 21°C.

COLUMN DYNAMICS

Adsorption

Most separations and purifications of liquid mixtures by adsorption are carried out in packed columns. Therefore, column dynamics of ad(de)sorption is a major concern for the design and optimization of separation processes.

The simplest case of adsorption arises when a feed containing a single, dilute solute (Component 1) is passed through an isothermal, isobaric column initially saturated with pure solvent (Component 2). A mass transfer zone (MTZ) is formed and moves down the column as feed is introduced continuously. Eventually the zone emerges at the outlet of the column, after the adsorbent in the bed equilibrates with the solute in the feed so that no additional adsorption is possible. The effluent concentration profile of the solute (c versus t) is called the *breakthrough curve.* Figure 9 shows typical transient profiles within the column for a single solute, and Fig. 10 is an experimental breakthrough curve.

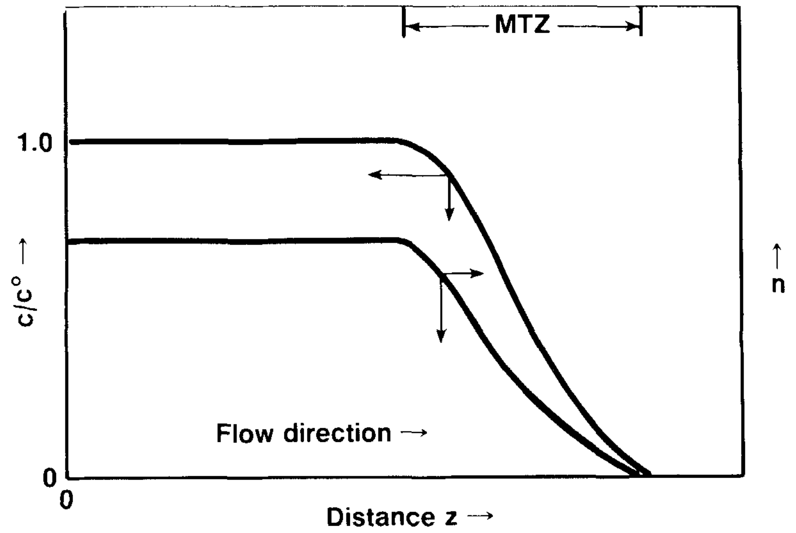

FIG. 9. Schematic diagram of column profiles for concentration (*c*) and loading (*n*) of single, dilute solutes.

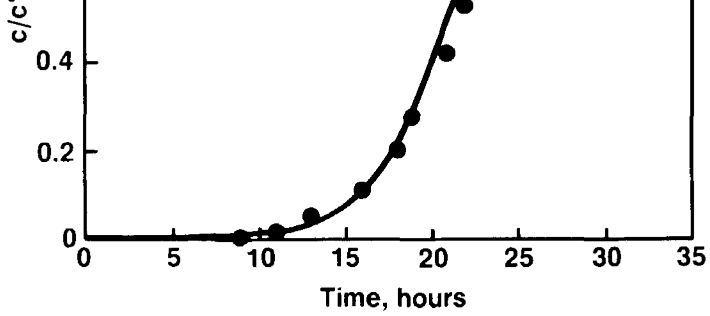

FIG. 10. Breakthrough curve for adsorption of dilute *p*-chlorophenol from water on activated carbon column. The solid line is the calculated result for a mass transfer model in which the external film and surface diffusion control the kinetics.

The size and shape of the MTZ depend on the adsorption kinetics and equilibrium, the nature of the packing in the column, and the feed flow rate. The zone can expand (proportionate pattern) or retain its size (constant pattern) as it moves through the column. Although there is no established criterion for the formation of constant-pattern zones, they are favored by solute isotherms which are more concave toward the concentration axis (large value of q in Eq. 14), by fast adsorption kinetics and by long columns.

Several MTZ's are formed inside a column when a multisolute feed is adsorbed, as shown in Fig. 11 for a dilute bisolute system in which Component 1 is more strongly adsorbed than Component 2. Experimental bisolute breakthrough data are given in Fig. 12. One interesting characteristic of multisolute adsorption is that the liquid-phase concentration of the more weakly adsorbed species may exceed that in the feed, both within the column and in the breakthrough curve. This rollover effect arises from displacement of the weakly adsorbed solute by the more strongly adsorbed species as the MTZ of the latter propagates through the column.

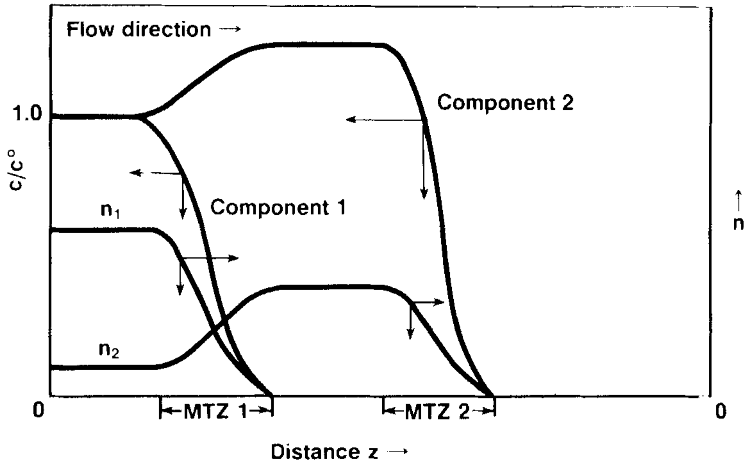

FIG. 11. Schematic diagram of column profiles of concentration and loading for a dilute, bisolute adsorption system.

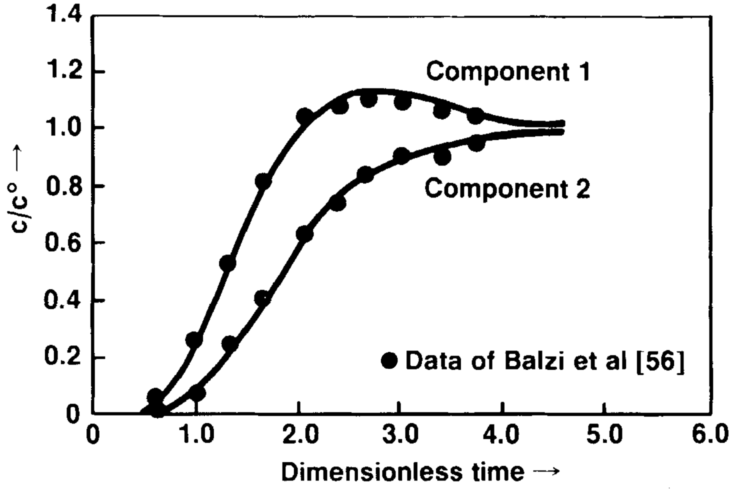

FIG. 12. Breakthrough curves for adsorption of dilute 2-butanol (1) and *t*-amyl alcohol (2) from water on a column of activated carbon. The solid lines were calculated using a mass transfer model in which the external film and pore diffusion control the kinetics.

Desorption

Desorption of one or more adsorbed components from a column can be achieved by purging the column with a liquid which adsorbs only weakly. Purge desorption is the only effective heatless method for liquids because the effect of pressure is almost negligible. (However, the reduction of column pressure is a common mode of desorption for gases (*1*)). The purge liquid can be heated to facilitate the desorption process. Other thermal desorption techniques are described later.

Mathematical Models

Isothermal ad(de)sorption from liquids may be analyzed by simultaneous solution of the partial differential equations describing the mass balance for each adsorbate present in the column in terms of their adsorption equilibrium and kinetic properties, and in conjunction with the initial and boundary conditions for the column. Numerous models have been proposed (*42, 52*). For the simple case of adsorption of a single, dilute solute of concentration c^0 from a solvent in a column of length L

which is initially solute-free and which is packed with spherical adsorbent particles of radius R, the solute mass balance in the column is:

$$\varepsilon\left[\frac{\partial c}{\partial t}\right]_z + \rho_b\left[\frac{\partial n}{\partial t}\right]_z = -Q\left[\frac{\partial c}{\partial z}\right]_t \tag{37}$$

where $c(z,t)$ and $n(z,t)$ are, respectively, the concentration of the solute in the bulk liquid phase and the specific amount adsorbed at distance z from the entrance of the column ($z = 0$) and at time t. ε is the void fraction in the column and ρ_b is the bulk density of the adsorbent. Q is the flow rate of the liquid mixture per unit (empty) cross-sectional area of the column. Equation (37) neglects axial dispersion of the solute in the bulk liquid and adsorbed phases.

The local rate of adsorption in the column $[\partial n/\partial t]_z$ is determined by the adsorption mechanism. If the kinetics are controlled by external film, pore, and surface diffusional resistances, then $n(z,t)$ is related to $c(z,t)$ by Eqs. (30)–(33) and (36). The variables n_p and c_p are in this case functions of z, r, and t. The characteristics of the solute in the MTZ, $c(z,t)$, or in the breakthrough curve, $c(L,t)$, can then be calculated by solving Eqs. (30)–(33), (36), and (37) with the initial and boundary conditions for the column, for example: $c(z,0) = 0$, $c(0,t) = c^0$, and $c_p(z,r,0) = 0$.

The solution can be simplified by assuming a LDF model for the local rate of adsorption:

$$\left[\frac{\partial n}{\partial t}\right]_z = k[n^* - n] \tag{38}$$

$n^*(z,t)$ is the specific amount of solute adsorbed in equilibrium with the local concentration $c(z,t)$ and k is a lumped mass transfer coefficient.

The partial differential equations describing the column dynamics must be solved numerically, except for the special cases of linear adsorption isotherms (*42, 52*) or constant-pattern zone formation for the LDF model (*53, 54*). Considerable amounts of computation time may be necessary. Studies have shown that the results are often more sensitive to the equilibrium isotherms than to the mass transfer resistances (*55*).

Column dynamics for adsorption of dilute bi- or trisolute systems with complex equilibrium isotherms like Eq. (16) have been studied for the case of pore and surface diffusion resistances (*56, 57*). Diffusivities of the solute were measured by batch kinetic tests for each solute–solvent pair in the mixture, or by column data on breakthrough curves for the single solutes.

The dynamics of ad(de)sorption in laboratory or industrial columns may also be influenced by liquid maldistribution, channeling, and nonuniform particle size distribution [58]. These factors can affect the scale-up and optimization of column design.

ADSORBENTS

A large variety of solid adsorbents are available for commercial separation and purification of liquid mixtures, including inorganic adsorbents like silica gels, aluminas, and zeolites; carbonaceous solids like activated carbons produced from various coal, petroleum, or vegetable sources; and polymeric adsorbents. A wide spectrum of pore sizes, surface areas, surface polarity, and chemical properties are exhibited by these adsorbents, which have the ability to separate many different classes of liquid mixtures. An extensive literature on the preparation, structure, and activation of adsorbents has been published (*59–61*). Separation is normally based on the selectivity at equilibrium, but zeolites and carbon molecular sieves possess the ability to separate liquid mixtures by exclusion on the basis of the size and shape of the adsorbate molecules (*62*). New adsorbents or modifications of older ones to improve separation performance are continuously being developed.

INDUSTRIAL APPLICATIONS

Trace Impurity Removal

By far the most frequently used industrial application of liquid adsorption has been the removal of trace impurities from products or waste streams. Two major industrial processes are:

Drying of liquid hydrocarbons
Removal of trace organic compounds from water or other organic liquids

The adsorption step is accomplished in a fixed bed at near ambient temperature, and desorption is achieved by draining the column and heating it with a hot gas or steam. Transferring the spent adsorbent elsewhere for thermal regeneration is a common practice. The spent adsorbent may also be regenerated *in situ* by chemical, biochemical or vacuum procedures.

The treatment of potable and municipal and industrial wastewater by carbon adsorption has grown into a multifaceted business. A vast technology on the subject has been developed (*24, 63, 64*). The complexity of these processes can be appreciated by the fact that the feed stream entering an adsorber may contain innumerable contaminants, many of them unknown. Furthermore, the types and concentrations of impurities as well as flow rates often vary with time.

Bulk Separation

Although the traditional use of adsorption has been for purification of streams in which the solute is present in concentrations of parts per million, bulk mixtures (for example, 20% A and 80% B) can also be separated by adsorption. The feed is contacted with a fixed bed of adsorbent to produce a product stream rich in the more weakly adsorbed component. The column is then purged with a liquid eluent to remove the more strongly adsorbed substance. The eluent is in turn separated from the desorbed stream by conventional means of separation such as distillation and recycled. Separation of the eluent from the product stream may also be necessary.

Liquid adsorption is being applied to separations of liquid mixtures which are difficult or expensive by traditional methods. These include separations requiring azeotropic or extractive distillation, vacuum distillation, and fractional crystallization. Much higher separation efficiency can be achieved by adsorption in some of these cases (*65*). The key commercial processes for bulk liquid separations by adsorption are:

n-Paraffins from naphtha, kerosene and gas oils
Olefins from paraffins
p-Xylene from other C_8-aromatics
m,p-Crysol from the crysol isomers
Fructose from glucose

Simulated moving-bed adsorbers have been designed for these separations (*65*). The feed and eluent injection points into the fixed bed, as well as the various effluent withdrawal points from the bed, are changed periodically in a sequential manner to create the effect of a continuous, countercurrent liquid–solid adsorber (*66, 67*).

Countercurrent flow can be achieved in a multistage fluidized bed containing perforated distributor plates and no downcomers. Controlled downward flow of the resin through the holes in the plates is achieved by cycling the liquid feed (*75*).

Despite an enormous amount of basic research and development on adsorption from liquid mixtures, basic understanding of the technology still offers a challenge to scientists and engineers because of its complexities. More fundamental work is necessary to quantify and predict the effects of energetic heterogeneity of adsorbents, multicomponent liquid–solid molecular interactions, and transport mechanisms in porous solids. At the engineering level, the development of sound design procedures for established and new separation schemes is needed.

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