

COMPUTER ALGORITHM AND GRAPHICAL METHOD FOR CALCULATING ADSORPTION EQUILIBRIA OF GAS MIXTURES

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Key Words: Adsorption, Mixtures, Equilibrium, Gas, Computer

Adsorption equilibria of gas mixtures are predicted from single-gas isotherms that obey the Toth equation by a graphical procedure. Since the design of gas adsorbers requires repetitive calculations, a fast-converging algorithm has been designed for execution on a computer. Predicted adsorption isotherms agree very well with experimental data at low and moderate surface coverage.

Introduction

Separation and purification of gaseous mixtures by adsorption is becoming a standard unit operation in the chemical industry, comparable in importance to the traditional techniques of distillation and extraction. The engineering design of gas adsorption operations requires information on both adsorption equilibrium and kinetics.⁴⁾ Measurement of the equilibrium amount adsorbed from a pure gas is a straightforward experiment based upon standard volumetric or gravimetric methods. However, adsorption from gas mixtures is more difficult to measure because:

1. The composition of the adsorbed phase must be determined indirectly by a material balance.
2. Considerable care must be exercised to ensure that mixture measurements are made under equilibrium conditions.
3. A large number of experimental points are needed to characterize each system due to the fact that for isothermal, binary adsorption there are two independent variables (P, y_1). By way of comparison, there is only one independent variable (y_1) for isothermal, binary vapor-liquid equilibrium.

A complete, thermodynamically consistent study of the isothermal adsorption of a binary mixture may require a year or more of work. Consequently, mixture equilibria are often predicted from the pure-gas isotherms by thermodynamic methods.¹⁾

A typical set of equilibrium data³⁾ is shown in Fig. 1 for the adsorption of pure propylene and ethylene on carbon molecular sieve MSC-5A at 323.15 K. Isobaric

adsorption of the gas mixture at the same temperature is shown in Fig. 2. At very low surface coverage where there is no competition for surface area, the mixture isobars are linear in composition. The highly non-linear behavior observed in Fig. 2 is a result of competition between propylene and ethylene for available surface; at equal fugacity ($y_1=0.5$) propylene displaces ethylene on a majority of the occupied sites.

Because of the experimental difficulties mentioned above, reliable methods are needed to predict multi-component adsorption (Fig. 2) using pure-gas isotherms (Fig. 1). A summary of the basic equations is followed by a graphical solution and an algorithm

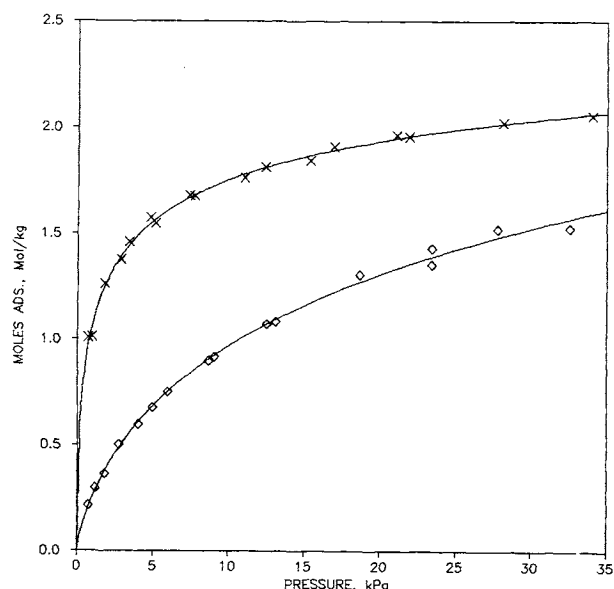


Fig. 1. Single-gas adsorption isotherms of propylene (x) and ethylene (◇) on carbon molecular sieve MSC-5A at 323.15 K. Points are experimental data³⁾ and solid lines are Eq. (8) with constants from Table 1.

Received January 11, 1986. Correspondence concerning this article should be addressed to A. L. Myers.

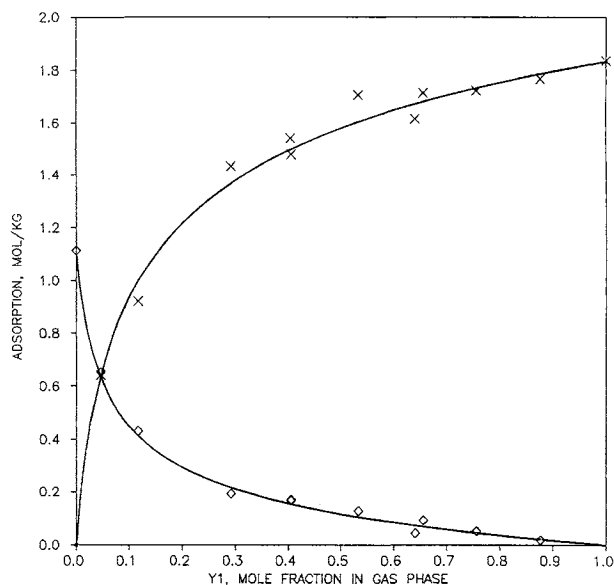


Fig. 2. Mixed-gas adsorption isotherms of propylene (x) and ethylene (◇) on carbon molecular sieve MSC-5A at $T = 323.15$ K, $P = 13.575$ kPa. Points are experimental data³⁾ and solid lines are calculated using the algorithm in Fig. 5 with constants from Table 1.

suitable for implementation on a computer.

Theory

Ideal adsorbed solution (IAS) theory for mixed-gas adsorption² is based upon the experimental pure-gas isotherms:

$$n_i^0 = n_i^0(P_i^0) \quad (1)$$

where the superscript 0 refers to pure-gas adsorption at the reference state, and Eq. (1) is functional notation for the fact that n_i^0 is some function of P_i^0 . Assuming a perfect-gas mixture and an ideal adsorbed solution, equality of fugacity in both phases requires that:

$$Py_i = P_i^0 x_i \quad (2)$$

where P is pressure, x_i and y_i are mole fractions of component i in the adsorbed and gas phases, respectively, and P_i^0 is the adsorbate vapor pressure. Eq. (2) is corrected for imperfect gas behavior at high pressure by the insertion of fugacity coefficients (ϕ_i) calculated from second virial coefficients or an equation of state. The adsorbed phase is assumed to form an ideal solution because there is no simple correlation between activity coefficients in the adsorbed phase and activity coefficients measured for bulk liquid mixtures.

Integration of the adsorption isotherm yields the spreading pressure Π :

$$\psi = \int_{P=0}^{P_i^0} \frac{n_i^0}{P} dP \quad (3)$$

$\psi \equiv (\Pi A/RT)$, and A is the specific surface area of the adsorbent. ψ and n_i^0 have units of mol/kg. The inverse of Eq. (3) is needed to calculate adsorbate vapor pressures at a given value of ψ :

$$P_i^0 = P_i^0(\psi) \quad (4)$$

Equation (4), like Eq. (1), uses functional notation. Finally, the mole fractions in the adsorbed phase must sum to unity:

$$\sum_{i=1}^N x_i = 1 \quad (5)$$

For a gas mixture of N components, Eqs. (1), (2), (4) and (5) comprise a total of $(3N+1)$ equations. Given the state of the mixture $\{P, y_i\}$, there are $(3N+1)$ unknowns $\{n_i^0, P_i^0, x_i, \psi\}$ so that a unique solution exists.

After the adsorbed-phase composition is obtained by solving the above set of equations, the loadings $\{n_i\}$ of components of the mixture are calculated from an equation for ideal mixing in the adsorbed phase:²⁾

$$n_t = \frac{1}{\sum (x_i/n_i^0)} \quad (6)$$

$$n_i = n_t x_i \quad (7)$$

where $n_t = \sum n_i$ is the total amount adsorbed expressed in mol/kg of solid.

The details of the solution depend upon the functional form of the equation adopted to fit the experimental data, Eq. (1). One successful three-constant equation for adsorption on high-area surfaces like activated carbon and zeolites is that of Toth:⁵⁾

$$n = mP[b + P^t]^{-1/t} \quad (8)$$

The constants $\{m, b, t\}$ are different for each gas and vary with temperature.¹⁾ For example, Eq. (8) is plotted on Fig. 1 (solid lines) using constants from Table 1, which were obtained by minimizing $\sum (\Delta_i^2)$, where $\Delta_i = (n_{\text{calc}} - n_{\text{exp}})_i$. The average of the error $|\Delta_i|$ is less than 0.02 mol/kg.

Graphical Method for Prediction of Mixed-Gas Adsorption

The dimensionless spreading pressure (ψ/m) calculated from Eq. (12) below is plotted in Fig. 3 as a function of fractional surface coverage ($\theta = n/m$) for various values of the parameter t of the Toth equation. This graph is designed for making quick estimates of gas adsorption equilibria. The procedure is illustrated by an example in which a point in Fig. 2 is calculated using the constants in Table 1.

The pressure is 13.575 kPa. Choose an arbitrary value of spreading pressure, e.g. $\psi/m_1 = 1.0$. From Fig. 3 read $\theta_1 = 0.4$, so $\psi = m_1 = 2.9431$ mol/kg.

Table 1. Constants of Eq. (8) for adsorption of propylene and ethylene on carbon molecular sieve MSC-5A at 323.15 K

Gas	m [mol/kg]	b [kPa] ^t	t
Propylene(1)	2.9431	0.3944	0.3283
Ethylene(2)	4.7087	2.1941	0.3984

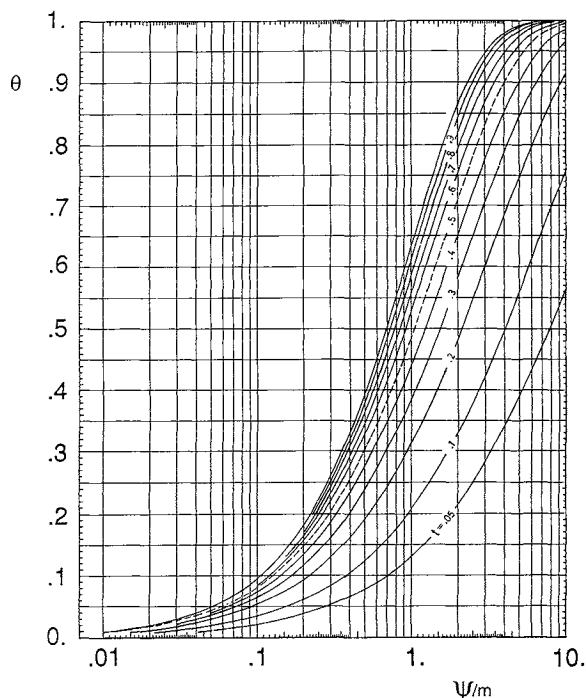


Fig. 3. Dimensionless spreading pressure (ψ/m) as a function of θ for various values of parameter t of the Toth equation.

Therefore $\psi/m_2 = (2.9431/4.7087) = 0.625$ and, again from Fig. 3, $\theta_2 = 0.32$. The inverse of Eq. (8):

$$P = b^{1/t} \theta (1 - \theta)^{-1/t}$$

gives the pressure of the reference state in terms of $\theta = n/m =$ dimensionless amount adsorbed. It follows that:

$$P_1^0 = (0.3944)^{(1/0.3283)} (0.40) (1 - 0.40)^{(0.3283)} (-1/0.3283) = 1.43 \text{ kPa}$$

$$P_2^0 = (2.1941)^{(1/0.3984)} (0.32) (1 - 0.32)^{(0.3984)} (-1/0.3984) = 28.9 \text{ kPa}$$

$$n_1^0 = \theta_1 m_1 = (0.40)(2.9431) = 1.177 \text{ mol/kg}$$

$$n_2^0 = \theta_2 m_2 = (0.32)(4.7087) = 1.507 \text{ mol/kg}$$

By Eq. (2), $\sum P y_i = P = \sum P_i^0 x_i = (P_1^0 x_1 + P_2^0 x_2)$ so

$$x_1 = (P - P_2^0) / (P_1^0 - P_2^0) = (13.575 - 28.9) / (1.43 - 28.9) = 0.558$$

$$y_1 = P_1^0 x_1 / P = (1.43)(0.558) / (13.575) = 0.059$$

Then, from Eqs. (6) and (7), the amount adsorbed is:

$$1/n_t = (0.558)/(1.177) + (0.442)/(1.507) = 0.767 \text{ kg/mol}$$

$$n_t = 1/0.767 = 1.30 \text{ mol/kg}$$

$$n_1 = n_t x_1 = (1.30)(0.558) = 0.73 \text{ mol/kg}$$

$$n_2 = n_t x_2 = (1.30)(0.442) = 0.57 \text{ mol/kg}$$

The calculated amounts adsorbed at $P = 13.575 \text{ kPa}$ and $y_1 = 0.059$ agree with the experimental data plotted in Fig. 2. Another point may be obtained by repeating the procedure for a new value of ψ . If the assumed value of ψ does not generate values of P_i^0 which bracket P , then another value of ψ is selected (P_i^0 increases with ψ).

Computer Calculations of Mixed-Gas Equilibria

For the design of gas adsorption operations in which repetitive equilibrium calculations are necessary, the following IAS algorithm derived for the Toth equation converges for a binary mixture point in 1 s on a computer with a speed of 0.1 MFLOPS (FLOPS = floating point operations per second). The functions α_i , β_i , γ_i , δ_i are required:

$$n = \alpha_i(P) = m_i P (b_i + P^{t_i})^{-1/t_i} \quad (10)$$

$$P = \beta_i(n) = b_i^{1/t_i} (n/m_i) [1 - (n/m_i)^{t_i}]^{-1/t_i} \quad (11)$$

$$\psi = \gamma_i(P) = m_i \left[\theta - \frac{\theta}{t_i} \ln(1 - \theta^{t_i}) - \sum_{k=1}^{\infty} \frac{\theta^{(kt_i+1)}}{kt_i(kt_i+1)} \right] \quad (12)$$

where

$$\theta = P(b_i + P^{t_i})^{-1/t_i}$$

$$P = \delta_i(\psi/m_i) \quad (13)$$

Equation (10) is the Toth equation and Eq. (11) is its inverse. Eq. (12) is obtained by substituting Eq. (10) into (3), expressing the integrand as a series and integrating term-by-term, followed by some algebraic manipulation. The series in Eq. (12) converges for $0 \leq \theta < 1$. A suitable convergence criterion is that successive estimates of the sum should differ by less than 10^{-8} . Equation (13), which is the inverse of Eq. (12), is solved by Newton's method using the algorithm in Fig. 4. Convergence to the solution, $G=0$, is based upon the observation that the derivative $G' = dG/dP = \theta/P$.

For the case when the state of the gaseous mixture is specified by the pressure and gas-phase composition $\{P, y_i\}$, the IAS solution is given in Fig. 5. Convergence is fast because Newton's method is used to solve the equation $F = \sum x_i - 1 = 0$ for ψ . The derivative of F is $F' = dF/d\psi = -P \sum [y_i / (n_i^0 P_i^0)]$.

Predictions based upon this algorithm are shown by the solid lines in Fig. 2. Constants were taken from Table 1. The average error $|\Delta_i|$ is only 0.03 mol/kg and

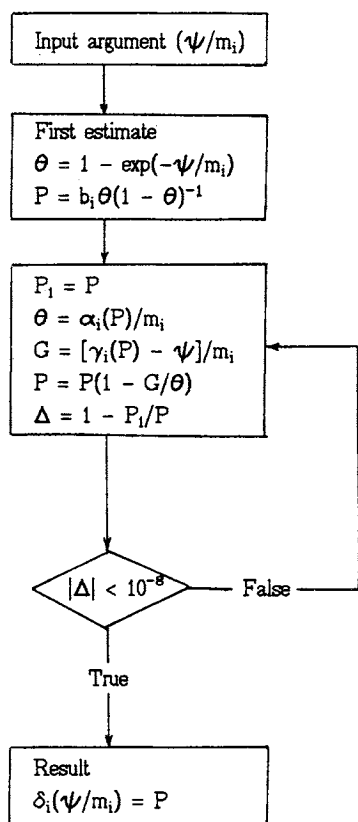


Fig. 4. Algorithm for computing inverse function $P = \delta_i(\psi/m_i)$ of Eq. (13). Subscripts i refer to the i -th component and the equality sign ($=$) stands for an assignment in FORTRAN or PASCAL languages.

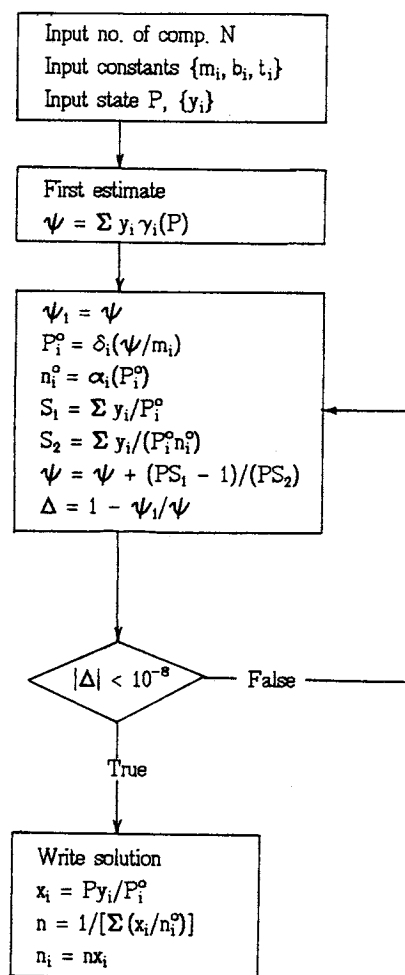


Fig. 5. IAS calculation for Toth equation. For notation see Fig. 4 and Eqs. (10)–(13). Summations are over the N components present.

shows no systematic deviation from the experimental points. The surface coverage in this case is about half of the saturation value. At higher coverage, systematic deviations between IAS predictions and experiment are possible.⁶⁾

We determined parameters of the Toth equation for a large number of systems⁶⁾ and these may be used to estimate mixed-gas adsorption. If measurements are available for more than one temperature, interpolation and cautious extrapolation procedures have been developed to predict the effect of temperature upon the amount adsorbed.¹⁾

Nomenclature

A	= specific surface area	[m ² /kg]
b	= constant in Eq. (8)	[—]
F	= function $F(\psi) = \sum x_i - 1$	[—]
G	= function defined in Fig. 4	[—]
m	= specific amount adsorbed at saturation	[mol/kg]
n	= specific amount adsorbed	[mol/kg]
n_i^0	= specific amount of component i adsorbed at standard state	[mol/kg]
P	= pressure	[kPa]
P_i^0	= adsorbate vapor pressure of component i at standard state	[kPa]
R	= gas constant	[—]
T	= absolute temperature	[K]
t	= constant in Eq. (8)	[—]

x_i	= mole fraction of i 'th component in adsorbed phase	[—]
y_i	= mole fraction of i 'th component in gas phase	[—]
α	= function, Eq. (10)	[—]
β	= function, Eq. (11)	[—]
γ	= function, Eq. (12)	[—]
δ	= function, Eq. (13)	[—]
Δ	= error, $(n_{\text{calc}} - n_{\text{expt}})$	[mol/kg]
θ	= n/m , fractional surface coverage	[—]
Π	= spreading pressure	[N/m]
ϕ	= gas-phase fugacity coefficient	[—]
ψ	= $\Pi A / RT$	[mol/kg]

<Subscripts>

i	= refers to component i
t	= refers to total for all components

<Superscripts>

$_0$	= refers to standard state for pure gas
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EFFECT OF HYDROPHOBICITY OF EXTRACTANT ON EXTRACTION KINETICS OF COPPER WITH *N*-8-QUINOLYLSULFONAMIDE

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Key Words: Extraction, Stripping, Kinetics, Hydrophobicity, Membrane Extractor, Copper, Hollow Fiber, *N*-8-Quinolylsulfonamide, LIX 34

Using four kinds of alkylbenzene-substituted *N*-8-quinolylsulfonamides of different alkyl-chain length and their copper chelate complexes, kinetic studies concerning the extraction of copper with extractant and the stripping of copper with sulfuric acid were carried out in a membrane extractor using a hollow fiber.

It was found that the interfacial reaction between the adsorbed copper complex (CuR_{ad}^+) and the adsorbed extractant (HR_{ad}) is a rate-controlling step among the interfacial reaction steps of the extraction and stripping processes, regardless of the alkyl-chain length of the extractants, and that the reaction rate constant of the rate-controlling step is proportional to the equilibrium constant of this reaction for each of the four kinds of extractants.

The validity of a diffusion model with the interfacial reaction was confirmed by agreement of the observed extents of copper extracted and stripped with those calculated over a wide range of experimental conditions.

Introduction

Extractants used for metal extraction in hydro-metallurgical processes are generally amphiphile, having a hydrophobic long alkyl chain to lower the solubility loss into water and a hydrophilic coordinating group to metal. Due to this property, the extractant exhibits interfacial activity and is adsorbed at the oil-water interface. It is well known that the interfacial reaction between the adsorbed extractant and metal very strongly influences the extraction rate.^{1-3,5,6)} However, no systematic investigation concerning the influence of interfacial activity of extractant on the extraction kinetics has been carried out so far.

In a previous paper,⁷⁾ it was reported that the distribution and interfacial adsorption equilibria of five kinds of alkylbenzene-substituted *N*-8-quinolylsulfonamides (henceforth RphSAQ, abbreviated as HR) having different alkyl-chain length were examined. It was found that the equilibrium constants

of the distribution and the interfacial adsorption of these extractants between the aqueous and organic solutions were remarkably affected by the hydrophobicity of the extractant.

In the present study, using the same RphSAQ as those used in the previous paper,⁷⁾ the extraction and stripping rates of copper were measured in a membrane extractor consisting of a hollow fiber. The experimental results were analyzed by a diffusion model for metal extraction with an interfacial reaction, taking account of the velocity distributions of the aqueous solution in the inner part of the hollow fiber and the organic solution in the annulus between the inner surface of the glass tube and the outer surface of the hollow fiber.⁹⁾ The influence of the hydrophobicity of the extractant on the extraction kinetics was examined quantitatively.

1. Experimental

Four kinds of RphSAQ — *N*-8-quinolyl-*p*-*n*-octadecylbenzenesulfonamide, $\text{nC}_{18}\text{H}_{37}\text{phSAQ}$ (henceforth $\text{nC}_{18}\text{phSAQ}$), $\text{nC}_{12}\text{phSAQ}$, $\text{C}_{12}\text{phSAQ}$ and nC_6phSAQ , and their copper chelate complexes (ab-

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