Linear Algebraic Solution for Multicomponent Adsorption on Porous Media

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Adsorption has been used for many years to separate liquid mixtures. For process development and design, it would be useful to have an equilibrium, multicomponent model based on pure-component properties and surface excess data that is directly soluble. A thermodynamic monolayer model that incorporates nonidealities in the bulk liquid and the adsorbed phase is that of Minka and Myers (1973). The model gives predictions for multicomponent adsorption equilibria from binary isotherms. Multicomponent surface excess data, adsorbed phase activity coefficients, and selectivities are predicted from experimental, binary isotherms and pure-component capacities.

Analytical solutions of the model equations relating selectivities to multicomponent surface excess data and pure-component capacities have been obtained for two and three component mixtures (Minka and Myers, 1973), and a numerical solution has been given for k components (Myers, 1989).

This work describes an exact solution for the same monolayer model for k components. One experimental point for a multicomponent system yields the composition of the adsorbed phase and component loadings at that point, but not at other points. The solution is not predictive and cannot be used for interpolation or extrapolation. However, if multicomponent surface excess and pure-component capacity data are available, selectivities and component loadings can be calculated directly. Adsorbents can be evaluated using equilibrium data and the solution formulae. The exact solution is simple to use and is therefore an improvement over the existing numerical method.

Model

For k adsorbable components at equilibrium, the total millimoles of adsorbed material per gram of adsorbent is (Larionov and Myers, 1971):

$$n' = \left[\sum_{i=1}^{k} \frac{x_i'}{(n_i')^\circ} \right]^{-1} \tag{1}$$

The surface excess of the ith component is:

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

where $\sum_{i=1}^{k} n_i^e = 0$. The selectivity of component i relative to component j is:

$$S_{ij} = \frac{x_i' x_j}{x_j' x_i} \tag{3}$$

where $S_{ii} = 1$, $S_{ji} = 1/S_{ij}$, and $S_{ij} = S_{im} S_{mj}$. Combining Eq. 3 and $\sum_{i=1}^{k} x_i' = 1$ gives:

$$x_j' = \frac{x_j}{\sum_{i=1}^{k} x_i S_{ij}} = \frac{x_j / S_{ij}}{\sum_{m=1}^{k} x_m / S_{im}} \tag{4}$$

Combining Eqs. 1-4 and $\sum_{j=1}^{k} x_j = 1$ gives (Minka and Myers, 1973):

$$n_i^e = \frac{\sum_{j=1}^{k} x_i x_j (1 - 1/S_{ij})}{\sum_{j=1}^{k} x_j / [S_{ij} (n_j')^\circ]} \tag{5}$$

Myers has given a numerical solution for x_i' $(i = 1, \ldots, k)$, (Myers, 1989).

The existence and structure of an exact solution to the equations are shown as follows. Substitution of the expression for n' from Eq. 1 into the definition from Eq. 2 gives:

$$0 = x_i' - n_i^e \cdot \sum_{j=1}^{k} x_j' / (n_j')^\circ - x_i \tag{6}$$

These equations are linear in x_i' and an exact solution exists for x_i' in terms of x_i, n_i^e, and $(n_i')^\circ$.

Reformulation and solution of the equations in terms of selectivities are appropriate for adsorbent evaluation and comparison. Rearranging Eq. 5 gives:

$$x_i = \sum_{j=1}^{k} \xi_{ij} \phi_{ij} \tag{7}$$

where

$$\underline{\underline{\phi}} \equiv \underline{\underline{S}}^T \tag{8}$$

and

$$\xi_{ij} \equiv \frac{n_i^e x_j}{(n_j')^\circ} + x_i x_j \tag{9}$$

Each element of matrix $\underline{\underline{\phi}}$ can be written in terms of ratios of elements of any single row or column of $\underline{\underline{\phi}}$:

$$\phi_{ij} = \phi_{mj}/\phi_{mi} = \phi_{in}/\phi_{jn} \tag{10}$$

Let vector $\underline{\psi}(m)$ be the mth row of $\underline{\underline{\phi}}$:

$$\psi_j(m) \equiv \phi_{mj} \tag{11}$$

where $\psi_m(m) = 1$. Combining Eqs. 7, 10 and 11 gives:

$$\psi_i(m) \cdot x_i = \sum_{j=1}^{k} \xi_{ij} \cdot \psi_j(m) \tag{12}$$

or

$$\underline{\underline{A}}(m)\underline{\psi}(m) = \underline{b}(m) \tag{13}$$

where

$$\underline{\underline{A}}(m) = \left[\begin{array}{cc:c:c} (\xi_{11} - x_1) & \xi_{12} & \xi_{1m} & \xi_{1k} \\ \xi_{21} & (\xi_{22} - x_2) & \xi_{2m} & \xi_{2k} \\ \hdashline \xi_{m1} & \xi_{m2} & 0 & \xi_{mk} \\ \hdashline \xi_{k1} & \xi_{k2} & \xi_{km} & (\xi_{kk} - x_k) \end{array}\right] \tag{14}$$

and

$$\underline{b}(m) = \left[\begin{array}{c} 0 \\ 0 \\ \hdashline (x_m - \xi_{mm}) \\ \hdashline 0 \end{array}\right] \tag{15}$$

If matrix $\underline{\underline{V}}(m)$ is defined as:

$$\underline{\underline{V}}(m) \equiv \underline{\underline{A}}^{-1}(m) \tag{16}$$

then the elements of $\underline{\psi}(m)$ are:

$$\psi_i(m) = V_{im}(x_m - \xi_{mm}), \quad \text{for} \quad i \neq m \tag{17}$$

and $\psi_m(m) = 1$. Finally,

$$\phi_{ij} = \psi_j(m)/\psi_i(m) = V_{jm}/V_{im} \tag{18}$$

and

$$S_{ij} = V_{im}/V_{jm} \tag{19}$$

for $\{i, j\} = 1, \ldots, k$.

Therefore, the selectivity of the adsorbent for component i relative to component j is equal to the ratio of the ith to the jth elements of any column of $\underline{\underline{V}}(m)$. The result is identical when the selectivity is obtained using pairs of elements from any column of $\underline{\underline{\phi}}$.

Usage

Experimental data were obtained for adsorption of compounds A, B and C. Estimates of pure component capacities for $A(1)$, $B(2)$, and $C(3)$ are 2.90, 2.44, and 2.11 mmol/g adsorbent, respectively.

Use of the solution method is illustrated with the set of data given in Table 1. Substituting liquid mole fractions, capacities, and surface excesses into Eq. 9 gives:

$$\underline{\underline{\xi}} = \begin{bmatrix} 0.0227 & 0.0929 & 0.111 \\ 0.0479 & 0.182 & 0.203 \\ 0.0407 & 0.146 & 0.153 \end{bmatrix} \tag{20}$$

If $m = 1$,

$$\underline{\underline{A}}(1) = \begin{bmatrix} 0.0000 & 0.0929 & 0.111 \\ 0.0479 & -0.239 & 0.203 \\ 0.0407 & 0.146 & -0.315 \end{bmatrix} \tag{21}$$

and

$$\underline{\underline{V}}(1) = \begin{bmatrix} 11.3 & 11.3 & 11.3 \\ 5.80 & -1.12 & 1.32 \\ 4.14 & 0.937 & -1.10 \end{bmatrix} \tag{22}$$

Selectivities are: $S_{12} = V_{11}/V_{21} = 1.95$, $S_{13} = V_{11}/V_{31} = 2.73$, and $S_{23} = V_{21}/V_{31} = 1.40$. Substituting these values and the equilibrium liquid concentrations into Eq. 4 gives the adsorbed-phase concentrations: $x_1' = 0.223$, $x_2' = 0.433$, and $x_3' = 0.344$. These concentrations and Eq. 1 give component capacities for A, B, and C of 4.16, 9.58, and 8.73% (g/g adsorbent), respectively. The total capacity of the adsorbent is 22.47%.

Discussion

With this approach, adsorbent evaluation and comparison

Table 1. Experimental Data for Adsorption of *A*, *B*, and *C*

	Initial Liquid Mole Fraction	Equilibrium Liquid Mole Fraction	Surface Excess (mmol/g Adsorbent)
A	0.1230	0.1113	0.2675
B	0.4218	0.4205	0.0298
C	0.4552	0.4682	−0.2973

are straightforward. Equilibrium adsorption experiments are conducted with selected adsorbents over a range of loadings. The zero-loading limit for equilibrium adsorption yields liquid-phase concentrations corresponding to the concentrations of effluent from a continuous adsorption bed at its saturation capacity. Consequently, the solution equations are used to calculate selectivities and capacities in the limit of zero loading. The adsorbent that exhibits the optimal combination of selectivity and capacity for a compound of interest can thus be readily identified.

It was demonstrated that multicomponent selectivities and capacities can be calculated directly from experimental liquid-phase concentrations, surface excess data, and pure component capacities. The method is not predictive. It cannot be used for interpolation or extrapolation to concentrations or temperatures for which experimental data do not exist. When data are available, however, the exact solution is an improvement over existing numerical methods.

Notation

k = number of components

n° = total millimoles of initial liquid per gram of adsorbent

n_i^e = surface excess of component i (mmol/g adsorbent)

$(n_i')^\circ$ = adsorption capacity for pure component i (mmol/g adsorbent)

n' = total millimoles of material adsorbed per gram of adsorbent

S_{ij} = selectivity of adsorbent for component i relative to component j

x_i = mole fraction of component i in bulk liquid at equilibrium

x_i° = mole fraction of component i in initial liquid

x_i' = mole fraction of component i in adsorbed phase

Literature Cited

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