Prediction of Multicomponent Liquid Adsorption Equilibria

A new method of predicting adsorption equilibria for multicomponent liquid solutions on solids has been developed which combines the thermodynamic and kinetic treatments of liquid adsorption. Multicomponent equilibria can be predicted using parameters obtained from binary adsorption data. The method requires the adsorbent capacities, the bulk and surface phase activity coefficients, and the binary adsorption equilibrium constants. The calculation procedure is simpler than other available methods. Predictions are made for the mixture of benzene, ethyl acetate, and cyclohexane on activated carbon at 303 K. The predictions are in quantitative agreement with published experimental data for this system.

P. E. Price, Jr. and R. P. Danner
Department of Chemical Engineering
Pennsylvania State University
University Park, PA 16802

Introduction

Adsorption at the solid-liquid interface involves the preferential accumulation of one or more components of a liquid mixture at the surface of a solid. This phenomenon forms the basis for many industrial operations, including separation and purification of chemical products, treatment of wastewater, and others. Clearly, there exists a need for developing an understanding of adsorption processes beyond the recognition of empirical results. Of particular interest is the development of a theory for adsorption from multicomponent solutions, since most industrial processes involve such solutions.

The theoretical treatment of equilibrium adsorption from multicomponent liquid solutions on solids has progressed considerably in recent years. An excellent review of the subject is given by Borowko and Jaroniec (1983). A major objective in the development of the theory is the ability to predict ternary and higher order adsorption equilibria over the entire concentration range using parameters obtained from adsorption data for the constituent binary mixtures. Two successful approaches to this problem have appeared in the literature. The first was the thermodynamic treatment of Minka and Myers (1973). In their theory the authors assume that the adsorbent is energetically homogeneous and that both the adsorbed and bulk phases are nonideal. They predicted ternary adsorption data that were in quantitative agreement with experimental data. A major drawback to their theory, however, is the complexity of the required calculations.

An alternative approach based on consideration of the kinetics of adsorption from liquid solutions onto heterogeneous solids has been suggested by Jaroniec et al. (1981). This method requires adsorption data for only two of the three constituent binary mixtures to predict adsorption equilibria for ternary systems. However, the assumptions that both the adsorbed and bulk phases are ideal and that the sizes of all adsorbed molecules are identical, limit the accuracy of the predictions. A major advantage of the method is the simplicity of the required calculations.

In this paper, we present a hybrid approach that maintains the accuracy of the thermodynamic treatment while having the computational simplicity of the kinetic method. The method draws from both the thermodynamic treatment of Minka and Myers and the kinetic approach of Jaroniec et al. Predicted equilibrium adsorption excesses for the system of benzene, ethyl acetate, and cyclohexane on activated carbon at 303 K are in quantitative agreement with experimental data published by Minka and Myers.

The method is significant in that it provides an accurate but computationally simple technique for predicting multicomponent adsorption on solid surfaces where both the bulk and adsorbed phases are nonideal. This is of practical importance because complex experimental studies of multicomponent adsorption can be replaced by relatively straightforward experimental studies of binary mixtures.

Theoretical Development

In treating liquid adsorption systems, we first assume that upon addition of the solid adsorbent, a solution initially contain-

P. E. Price, Jr. is now with the Department of Chemical Engineering and Materials Science, University of Minnesota.

ing a total of n^o moles of liquid can be divided into an adsorbed (surface) phase and a bulk (liquid) phase containing n^s and n^l moles, respectively. A total mass balance on the system requires that:

$$n^o = n^l + n^s \tag{1}$$

From this we can define the experimental variable most often used to characterize liquid adsorption, the surface excess. The surface excess is determined by the change in concentration in the bulk solution upon addition of the solid adsorbent:

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

where n^o denotes the total number of moles in the liquid solution per unit mass of adsorbent, x_i^o is the mole fraction of component i in the solution prior to addition of the solid adsorbent, and x_i^l is the mole fraction of component i in the bulk liquid after addition of the adsorbent.

We will treat the adsorbed phase as having constant composition throughout. Furthermore, we will assume that the adsorbent is microporous and that the volume of the adsorbed phase is fixed. As reported by Minka and Myers (1973), the condition for complete filling of the adsorbed phase volume in such systems gives:

$$\frac{1}{n^s} = \sum \frac{x_i^s}{m_i} \tag{3}$$

where m_i is the molar capacity of the adsorbent for the pure component i. The capacity m_i is given by the amount of the ith component adsorbed from the pure vapor at saturation.

Assuming that the rule of Gurvitsch (1915) is valid, we have:

$$m_i = \frac{V_p}{V_i} \tag{4}$$

where V_p is the micropore volume and V_i is the molar volume of component i.

If the adsorbed phase is of uniform concentration, then Eq. 1, combined with a mass balance on any component i, allows the excess adsorption to be expressed as:

$$n_i^e = n^s(x_i^s - x_i^l) \tag{5}$$

Finally, from Eq. 2 it can readily be shown that:

$$\Sigma n_i^e = 0 \tag{6}$$

From a kinetic viewpoint, one can write an equation for the exchange of molecules between the adsorbed and liquid phases:

$$r_{ji}(i)^l + (j)^s \rightleftharpoons r_{ji}(i)^s + (j)^l \tag{7}$$

where (i) and (j) represent the ith and jth components in the liquid (l) and adsorbed (s) phases, respectively. The stoichiometric coefficient, r_{ji}, is the ratio of the molar volumes of adsorbates j and i. r_{ji} is introduced to satisfy the condition that the volume of the adsorbed phase is constant and always filled.

The rate of exchange in Eq. 7 as the system approaches equilibrium has been given by Dabrowski (1983) for monolayer adsorption on nonporous, heterogeneous adsorbents in nonflow systems:

$$\frac{d\theta_{i,k}^s}{dt} = \kappa_k^a(\theta_i^l\gamma_i^l)^{r_{ji}}(\theta_{j,k}^s\gamma_{j,k}^s) - \kappa_k^d(\theta_{i,k}^s\gamma_{i,k}^s)^{r_{ji}}(\theta_j^l\gamma_j^l) \tag{8}$$

where κ_k^a and κ_k^d are the rate constants for adsorption and desorption onto the kth surface site, respectively; θ_i^l and θ_j^l are the equilibrium liquid phase volume fractions of component i and j; γ_i^l and γ_j^l are the corresponding activity coefficients; $\theta_{i,k}^l$ and $\theta_{j,k}^l$ are the volume fractions of components i and j on the kth surface site; and $\gamma_{i,k}^s$ and $\gamma_{j,k}^s$ are the activity coefficients of the adsorbed phase on the kth surface site.

From Eq. 8, Dabrowski (1983) derived the adsorption equilibrium constant for binary systems:

$$K_{ij} = \left[\frac{(\gamma_j^l\theta_j^l)}{(\gamma_i^l\theta_i^l)^{r_{ji}}}\right]\left[\frac{(\gamma_i^s)^{r_{ji}}(\theta_i^s)^{r_{ji}/c}}{(\gamma_j^s)(\theta_j^s)^{1/c}}\right] \tag{9}$$

where the volume fractions θ_i^s and θ_j^s, and the activity coefficients γ_i^s and γ_j^s are average values for the entire adsorbed phase. c is the heterogeneity parameter which describes the shape of a quasi-Gaussian distribution function that characterizes the topography of adsorption sites on a heterogeneous adsorbent. It must lie in the range of zero to one, where $c = 1$ denotes a homogeneous surface. Dabrowski and Jaroniec (1985) have discussed the application of the above equation to binary systems at length.

Simplified versions of Eq. 9 have been discussed by several researchers, including Everett (1973) and Jaroniec et al. (1981). The various simplifying assumptions have included ideality of one or both phases, homogeneity of the adsorbent, and equality of molecular sizes.

Since Dabrowski (1983) considered systems where the adsorbed phase is restricted to a monolayer (i.e., the adsorbent area is fixed), and we are considering the similar situation where the adsorbed phase volume is fixed, we shall assume that the above equation can be extended to adsorption systems involving microporous adsorbents with homogeneous adsorbed phases. Equation 9 becomes:

$$K_{ij} = \left[\frac{(\gamma_j^l\theta_j^l)}{(\gamma_i^l\theta_i^l)^{r_{ji}}}\right]\left[\frac{(\gamma_i^s\theta_i^s)^{r_{ji}}}{(\gamma_j^s\theta_j^s)}\right] \tag{10}$$

Using Eq. 4, r_{ji} for the microporous system can be determined according to:

$$r_{ji} = \frac{V_j}{V_i} = \frac{m_i}{m_j} \tag{11}$$

Equation 10 is the kinetic contribution to our hybrid adsorption model. In order to make use of this equation, some method must be available for determining the surface phase activity coefficients.

One can also examine the adsorption equilibrium from a thermodynamic viewpoint. At equilibrium, the fugacities of each component in the bulk and adsorbed phases can be equated. Minka and Myers used this approach to derive the following

equation:

$$\gamma_i^s = \frac{x_i^l \gamma_i^l}{x_i^s} \exp\left[\frac{(\phi - \phi_i^o)}{m_i RT}\right] \tag{12}$$

where ϕ_i^o is the free energy of immersion in the pure liquid, and ϕ is the free energy of immersion in the mixture.

Equation 12 is used in conjunction with the Gibbs-Duhem equation and the Gibbs adsorption isotherm to determine the adsorbed phase activity coefficients. The appropriate forms of these equations were given by Minka and Myers (1973). These equations can be used to derive Eq. 16, shown below.

Implementation of the Model

In their review, Borowko and Jaroniec (1983) listed the systems for which multicomponent adsorption data had been experimentally measured over the entire concentration range. Also, in a recent paper by Goworek et al. (1985), ternary adsorption data for three more systems were published, although these appear to correspond to systems listed as unpublished in the previous reference. Despite the growing number of such systems that have been studied, the data published by Minka and Myers (1973) remain the most complete tabular adsorption data for a ternary system and its constituent binaries available in the literature. For this reason, and because they showed their data to be thermodynamically consistent using the method of Sircar and Myers (1971), we have used their data to demonstrate the application of our new method.

To make use of Eq. 10 in characterizing adsorption systems, the molar capacities of the adsorbent for the pure components m_i, the liquid phase activity coefficients γ_i^l, and the adsorbed phase activity coefficients γ_i^s must be known.

The adsorbent capacities are determined from the vapor phase adsorption of the pure components at saturation. The adsorbent capacities for the system of interest are given in Table 1 (Table 6 of Minka and Myers, 1973).

Liquid phase activity coefficients are, in general, determined from vapor-liquid equilibrium data and enthalpy of mixing data. Table 2 (Table 7 of Minka and Myers, 1973) shows the parameters for the Redlich-Kister activity coefficient model for the bulk phase. The Redlich-Kister equations for the activity coefficients in a binary mixture at constant temperature (Prausnitz, 1969) are:

$$\ln \gamma_1 = a^{(1)} x_2^2 + b^{(1)} x_2^3 + c^{(1)} x_2^4 + d^{(1)} x_2^5 \tag{13}$$

$$\ln \gamma_2 = a^{(2)} x_1^2 + b^{(2)} x_1^3 + c^{(2)} x_1^4 + d^{(2)} x_1^5 \tag{14}$$

where

$$a^{(1)} = A + 3B + 5C + 7D \qquad a^{(2)} = A - 3B + 5C - 7D$$

$$b^{(1)} = -4(B + 4C + 9D) \qquad b^{(2)} = 4(B - 4C + 9D)$$

$$c^{(1)} = 12(C + 5D) \qquad c^{(2)} = 12(C - 5D)$$

$$d^{(1)} = -32D \qquad d^{(2)} = 32D$$

Activity coefficients for the adsorbed phase must be calculated using the binary adsorption data. Combining Eqs. 2 and 3 leads, after some algebraic manipulation, to the following expression (Minka and Myers, 1973) for the adsorbed phase composition:

$$x_1^s = \frac{m_1(m_2 x_1 + n_1^e)}{m_1 m_2 + n_1^e(m_1 - m_2)} \tag{15}$$

Minka and Myers also gave the following equations for determining the activity coefficients of the adsorbed phase. First, the difference in the free energies of immersion is calculated by integrating the Gibbs adsorption isotherm (Larionov and Myers, 1971) using the isothermal Gibbs-Duhem equation for a binary system (Prausnitz, 1969) and Eq. 5:

$$\frac{\phi - \phi_1^o}{RT} = -\int_{x_1^l=1}^{x_1^l} \frac{n_1^e}{x_1^l x_2^l \gamma_1^l} d(\gamma_1^l x_1^l) \tag{16}$$

Then, from Eq. 12, the activity coefficients are given by:

$$\gamma_1^s = \frac{x_1^l \gamma_1^l}{x_1^s} \exp\left[\frac{(\phi - \phi_1^o)}{m_1 RT}\right] \tag{17}$$

$$\gamma_2^s = \frac{x_2^l \gamma_2^l}{x_2^s} \exp\left[\frac{(\phi - \phi_2^o)}{m_2 RT}\right] \tag{18}$$

Activity coefficients calculated using these equations can then be used to regress activity coefficient model parameters. The surface phase Redlich-Kister parameters for the three mixtures of interest are shown in Table 2.

Correlation of Binary Mixtures

For binary solutions, Eq. 10 can be written in the linear form:

$$\ln\left[\frac{\theta_2^s \gamma_2^s}{(\theta_1^s \gamma_1^s)^{r_{21}}}\right] = \ln K_{21} + \ln\left[\frac{\theta_2^l \gamma_2^l}{(\theta_1^l \gamma_1^l)^{r_{21}}}\right] \tag{19}$$

Table 1. Saturation Capacities on Activated Carbon

Adsorbate	m mol/kg
Benzene	5.48
Ethyl acetate	4.95
Cyclohexane	4.30

Table 2. Constants for Redlich-Kister Equation for Binary Mixtures at 303 K

Parameter	Benzene (1) + Ethyl Acetate (2)	Benzene (1) + Cyclohexane (3)	Ethyl Acetate (2) + Cyclohexane (3)
	Liquid Phase		
A	0.1151	0.5328	1.2206
B	0.0309	0.0519	−0.0226
C	0.0000	0.0000	0.0000
D	0.0000	0.0000	0.0000
	Surface Phase		
A	−0.4245	−0.8169	0.1531
B	0.1949	0.6429	0.5503
C	−0.0567	−0.1333	−0.3004
D	0.0862	0.0181	−0.2526

where

$$K_{21} = \frac{1}{K_{12}} \tag{20}$$

The liquid phase volume fractions are related to the liquid phase mole fractions by the equations:

$$\theta_1^l = \frac{x_1^l}{x_1^l + r_{21}(1 - x_1^l)}$$
$$\theta_2^l = 1 - \theta_1^l \tag{21}$$

Similarly, the surface phase volume fractions are related to the surface phase mole fractions by the equations:

$$\theta_1^s = \frac{x_1^s}{x_1^s + r_{21}(1 - x_1^s)}$$
$$\theta_2^s = 1 - \theta_1^s \tag{22}$$

Equation 5 can be rearranged to give the surface phase mole fraction in terms of the liquid phase mole fraction, the surface phase capacity, and the surface excess:

$$x_1^s = \frac{n_1^e}{n^s} + x_1^l \tag{23}$$

The experimental surface excess vs. liquid phase mole fraction data can now be used with the above equations to determine the adsorption equilibrium constants. Using Eqs. 19–23 and Eq. 3, K_{12} is determined by minimizing the function:

$$S = \Sigma[n_{1,\text{exp}}^e(x_1^l) - n_{1,\text{calc}}^e(x_1^l, n^s, K_{12})]^2 \tag{24}$$

where S is the sum of the squared differnces between the experimental and correlated surface excess values. For this work, the IMSL (1983) routine ZXSSQ was used to determine the optimal equilibrium constants.

Table 3 contains the optimal adsorption equilibrium constants for each of the binary mixtures of benzene and ethyl acetate, benzene and cyclohexane, and ethyl acetate and cyclohexane on activated carbon at 303 K, as well as the sum of the squared deviations of the correlated and experimental surface excesses, S. Figures 1 through 3 show the experimental data originally reported by Minka and Myers and the model correlations of the binary excess isotherms. The model provides very reasonable correlations of all three binary systems. The fits are similar to those obtained by Minka and Myers using their theory.

Table 3. Optimal Adsorption Equilibrium Constants for Binary Mixtures

Liquid Mixture			
Comp. 1	Comp. 2	K_{21}	S
Benzene	Ethyl acetate	0.4895	0.003
Benzene	Cyclohexane	0.2646	0.013
Ethyl acetate	Cyclohexane	0.5954	0.022

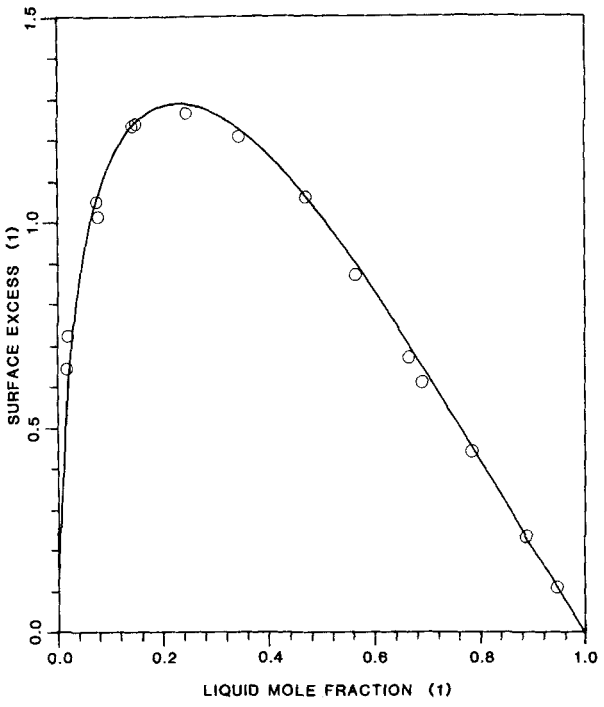

Figure 1. Surface excess correlation of benzene in mixture of benzene (1) and ethyle acetate (2) on activated carbon at 30°C.
O experimental data of Minka and Myers (1973)

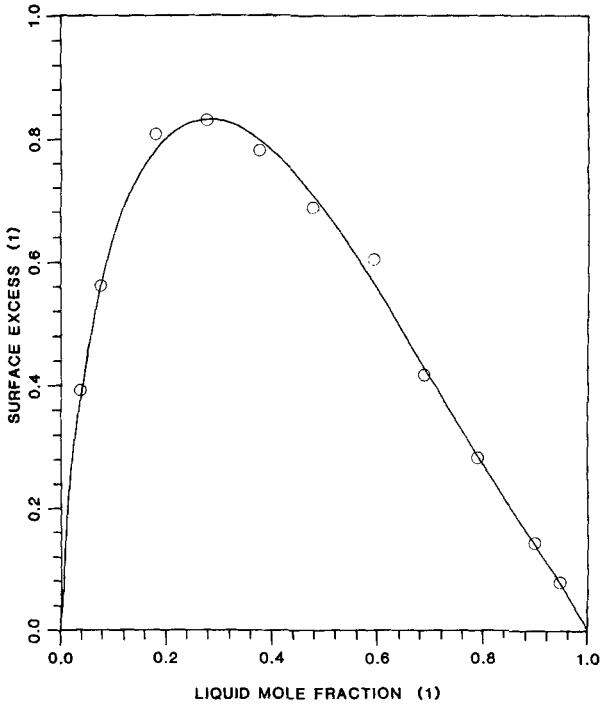

Figure 2. Surface excess correlation of benzene in mixture of benzene (1) and cyclohexane (2) on activated carbon at 30°C.
O experimental data of Minka and Myers (1973)

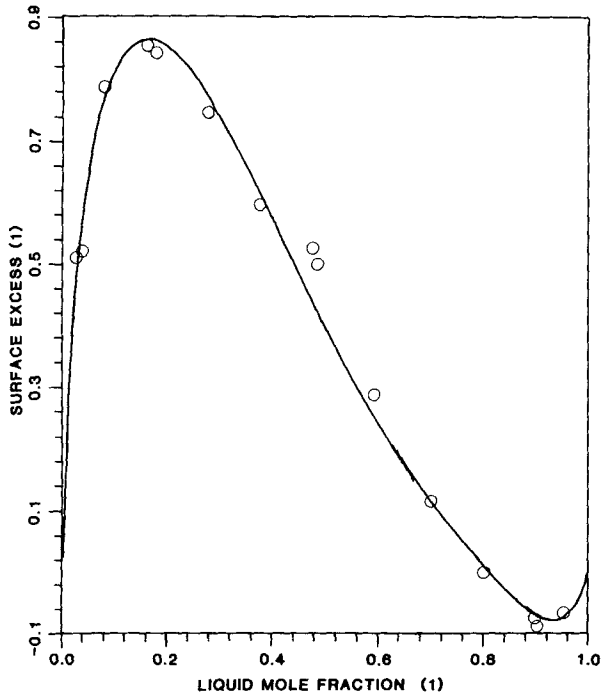

Figure 3. Surface excess correlation of ethyl acetate in mixture of ethyl acetate (1) and cyclohexane (2) on activated carbon at 30°C.

O experimental data of Minka and Myers (1973).

Prediction of Ternary Adsorption Equilibria

In considering ternary systems, we first assume that only binary interactions are significant. Thus, to predict the equilibria in a ternary system we need only consider two of the binary phase exchange processes. Data for all three binary mixtures are required, however, to predict the activity coefficients in the ternary mixtures, see the Appendix. Considering two simultaneous exchange reactions, Eq. 10 leads to the set of linear equations:

$$\ln\left[\frac{\theta_3^s\gamma_3^s}{(\theta_i^s\gamma_i^s)^{r_{3i}}}\right] = \ln K_{3i} + \ln\left[\frac{\theta_3^l\gamma_3^l}{(\theta_i^l\gamma_i^l)^{r_{3i}}}\right] \quad i = 1, 2 \tag{25}$$

where

$$K_{3i} = \frac{1}{K_{i3}} \tag{26}$$

The liquid phase volume fractions for the ternary system are related to the liquid phase mole fractions by the equations:

$$\theta_i^l = \frac{x_i^l}{\sum_{j=1}^{3} r_{ji}x_j^l} \quad i = 1, 2, 3 \tag{27}$$

Similarly, the equations relating surface phase volume and mole fractions are:

$$\theta_i^s = \frac{x_i^s}{\sum_{j=1}^{3} r_{ji}x_j^s} \quad i = 1, 2, 3 \tag{28}$$

We also note that:

$$x_1^s + x_2^s + x_3^s = 1 \tag{29}$$

The procedure for predicting surface excess values for a given liquid phase composition is as follows:

1. Determine the liquid phase activity coefficients at the composition of interest. Calculation of activity coefficients for ternary systems using the Redlich-Kister model is described in the Appendix.
2. Calculate the righthand sides of the equations given by Eq. 25 using the above activity coefficients, the adsorption equilibrium constants determined from the binary adsorption data, and Eq. 27. This gives two equations for the unknown adsorbed phase volume fractions and activity coefficients.
3. The equations that relate the surface phase volume and mole fractions, given by Eq. 28, as well as the Redlich-Kister expansions for the surface phase activity coefficients in the ternary mixture, can be substituted into the two equations generated in step 2. These two equations and Eq. 29 give three equations for the three unknown adsorbed phase mole fractions. Two of the equations are nonlinear and therefore some iterative solution scheme is required. We have used Brent's algorithm (More and Cosnard, 1980) for these calculations primarily because it was readily available as a FORTRAN subroutine in the literature.
4. The various surface excesses can then be calculated from Eq. 5 where the number of moles in the adsorbed phase, n^s, is given by Eq. 3.

Table 4 contains the predicted adsorption excess values and the experimental and predicted excess values reported by Minka and Myers for the system of benzene, ethyl acetate, and cyclohexane on activated carbon at 303 K. The average absolute difference between experimental data and values predicted using the proposed method is 0.014. This is slightly less than the difference of 0.015 between the experimental excesses and those predicted by Minka and Myers. Our proposed method does not require the numerical integration required by the Minka and Myers method. Hence, the calculations are considerably easier, and computation times are much less.

The predictions shown in Table 4 were based on the adsorption equilibrium constants for the binary systems of benzene and cyclohexane, and ethyl acetate and cyclohexane. However, predictions can be made by considering any of the three possible pairs of binary equilibrium constants. The other two combinations were also examined, and the predictions were of similar accuracy.

Extension to Multicomponent Mixtures

The prediction of adsorption equilibria for higher order systems using only binary parameters should be possible if ternary and higher order interactions are not significant. Consider an n component mixture. There will be $n - 1$ independent exchange reactions involving the nth component and the other components in the system. Thus, Eq. 10 will lead to the set of equations:

$$\ln\left[\frac{\theta_n^s\gamma_n^s}{(\theta_i^s\gamma_i^s)^{r_{ni}}}\right] = \ln K_{ni} + \ln\left[\frac{\theta_n^l\gamma_n^l}{(\theta_i^l\gamma_i^l)^{r_{ni}}}\right] \quad i = 1, 2, \ldots, n-1 \tag{30}$$

Table 4. Adsorption of Ternary Mixtures of Benzene (1), Ethyl Acetate (2), and Cyclohexane (3) on Activated Carbon at 303 K

Liquid Mol Frac.		Surface Excess					
		Benzene			Ethyl Acetate		
			Calc.			Calc.	
x_1	x_2	Exp.	Hybrid Model	Minka and Myers (1973)	Exp.	Hybrid Model	Minka and Myers (1973)
0.087	0.841	0.576	0.557	0.560	−0.582	−0.574	−0.580
0.130	0.075	0.960	0.973	0.990	0.283	0.297	0.295
0.176	0.675	0.708	0.706	0.714	−0.656	−0.632	−0.638
0.252	0.515	0.705	0.728	0.737	−0.450	−0.492	−0.500
0.291	0.115	0.947	0.955	0.970	0.154	0.145	0.145
0.410	0.199	0.718	0.744	0.758	−0.058	−0.046	−0.050
0.510	0.126	0.720	0.701	0.715	−0.033	−0.018	−0.020
0.615	0.230	0.487	0.482	0.492	−0.250	−0.234	−0.240
0.719	0.117	0.387	0.398	0.405	−0.107	−0.102	−0.105
0.759	0.157	0.313	0.318	0.324	−0.172	−0.177	−0.180
0.857	0.072	0.218	0.214	0.219	−0.094	−0.083	−0.084

where

$$K_{ni} = \frac{1}{K_{in}} \tag{31}$$

and

$$\sum_{i=1}^{n} x_i^s = 1 \tag{32}$$

Equations relating the volume and mole fractions of the liquid and surface phases and equations for the adsorbed phase activity coefficients in the multicomponent mixture must be substituted into Eq. 30. These equations, together with Eq. 32, give n equations that can be solved simultaneously for the n unknown absorbed phase mole fractions at a specified liquid composition. Once the surface phase mole fractions have been determined, the surface excess values can be calculated using Eqs. 3 and 5.

An appropriate model must be selected that will allow activity coefficients for the multicomponent mixture to be calculated using only parameters for the constituent binary mixtures.

Discussion

The proposed method provides a very convenient way to correlate binary adsorption data and predict ternary excess adsorption values. The most difficult part of the method is the determination of the surface phase activity coefficients using Eqs. 16–18. Since experimental data are available only at discrete points, there will be some degree of uncertainty in the evaluation of the integral in Eq. 16.

One possible method of avoiding this problem is to simultaneously regress the parameters for the surface phase activity coefficient model and the K_{ij} during the minimization of Eq. 24. This was done for the three binary mixtures examined herein. We found that the optimal Redlich-Kister parameters determined in this way corresponded very closely to the parameters reported by Minka and Myers (Table 2). This suggests that the activity coefficients, as incorporated into the kinetic model, are consistent with the standard thermodynamic activity coefficients.

If one can evaluate Eq. 16 over the entire composition range, then K_{ij} can be determined directly. Substituting Eqs. 17, 18, 21, and 22 into Eq. 10, substituting this result into Eq. 20, and taking the limits as the mixture approaches the pure components leads to the following two expressions:

$$\lim_{x_1^s \to 1} K_{21} = \exp\left[\frac{(\phi_1^o - \phi_2^o)}{m_2 RT}\right] \tag{33}$$

and

$$\lim_{x_2^s \to 1} K_{21} = \left\{\exp\left[\frac{(\phi_1^o - \phi_2^o)}{m_1 RT}\right]\right\}^{r_{21}} \tag{34}$$

Either of these expressions can be used in conjunction with the difference in free energies of immersion of the binary components and the pure-component adsorbent capacities to determine K_{21}. Table 5 contains the differences in free energies of immersion reported by Minka and Myers, the values for K_{21} calculated using the above expressions, and the values regressed from the adsorption data. It is clear that the values calculated using the above equations are in excellent agreement with the regressed values. Hence, depending on the quality and quantity of experimental data, it may be preferable to determine the binary adsorption equilibrium constants either by regression or by using the above equations after determining the differences in free energies of immersion.

In their discussion of adsorption from binary systems, Dabrowski and Jaroniec (1985) suggest that mole fractions may be substituted for volume fractions in the kinetically derived equi-

Table 5. Binary Adsorption Equilibrium Constants

Liquid Mixture		$\frac{\phi_1^o - \phi_2^o}{RT}$	K_{21}	K_{21}
Comp. 1	Comp. 2	mol/kg	Eq. 33	Eq. 24
Benzene	Ethyl acetate	−3.53	0.4901	0.4895
Benzene	Cyclohexane	−5.68	0.2669	0.2646
Ethyl acetate	Cyclohexane	−2.21	0.5981	0.5954

librium expression when the ratio of molecular sizes, r_{ji}, is in the range of 0.8 to 1.2 with only a slight decrease in the model's accuracy. We examined the effect of this assumption on the hybrid model correlations and predictions for the system of benzene, ethyl acetate, and cyclohexane on activated carbon at 303 K. The binary correlations were virtually identical to the correlations made using volume fractions. The ternary predictions at individual points varied to a greater degree, although the average absolute difference between experimental and predicted surface excess values was only 0.016.

The assumption that mole fractions can be substituted for volume fractions in the equilibrium expression is tantamount to assuming that all of the adsorbate molecules have identical sizes. Retaining the molecular size ratio power term in the expression would appear to contradict this assumption. Our results, however, suggest that this assumption introduces little additional error, while significantly reducing the calculational complexity of the method.

It can be shown that by substituting Eqs. 12, 20, 21 and 22 into Eq. 10, the adsorption equilibrium constant, K_{ij}, is a function of composition except when $r_{ij} = 1$ or when the bulk and surface phase compositions are the same. We believe that many systems that do not meet these requirements can be accurately characterized using a constant K_{ij}. Dabrowski and Jaroniec (1985) have shown this to be possible for various systems using the heterogeneous form of the kinetic model.

Acknowledgment

We gratefully acknowledge the financial support provided by the Frontiers of Separations Program of the Exxon Research and Engineering Co. We also appreciate the comments by Prof. E. U. Schlünder, Universität Karlsruhe, West Germany.

Notation

A, B, C, D = parameters for Redlich-Kister activity coefficient model
K_{ij} = adsorption equilibrium constant
m_i = adsorbent capacity for pure component i, mol/kg
n^o = number of moles in bulk liquid before addition of solid adsorbent
n^l = number of moles in bulk liquid at equilibrium
n^s = number of moles in adsorbed phase at equilibrium
n_i^e = surface excess of ith component, mol/kg
r_{ji} = ratio of molar volume of component j to molar volume of component i
R = gas constant = 8.314 J/mol · K
T = absolute temperature, K
x_i^o = mole fraction of component i in liquid prior to addition of solid adsorbent
x_i^l = mole fraction of component i in bulk liquid after addition of solid adsorbent
x_i^s = mole fraction of component i in adsorbed phase after addition of solid adsorbent
V_i = molar volume of component i, m^3/mol
V_p = micropore volume of adsorbent, m^3/kg

Greek letters

γ_i^l = activity coefficient of component i in bulk liquid
γ_i^s = activity coefficient of component i in adsorbed phase
κ^a = adsorption rate constant
κ^d = desorption rate constant
ϕ = free energy of immersion of adsorbent in liquid solution, J/kg
ϕ_i^o = free energy of immersion of adsorbent in pure liquid i, J/kg
θ_i^l = volume fraction of component i in bulk liquid
θ_i^s = volume fraction of component i in surface phase

Subscripts and superscripts

i, j = ith and jth components
k = kth adsorption site
l = bulk liquid phase
s = adsorbed phase

Appendix: Determination of Activity Coefficients for Ternary Mixtures

In the appendix to their paper, Minka and Myers gave the following expression for the activity coefficient of component 1 in a ternary solution:

$$\begin{aligned}\ln \gamma_1 = {} & x_2(1 - x_1)[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 \\ & + D_{12}(x_1 - x_2)^3] + x_3(1 - x_1)[A_{13} + B_{13}(x_1 - x_3) \\ & + C_{13}(x_1 - x_3)^2 + D_{13}(x_1 - x_3)^3] - x_2x_3[A_{23} \\ & + 2B_{23}(x_2 - x_3) + 3C_{23}(x_2 - x_3)^2 + 4D_{23}(x_2 - x_3)^3] \\ & + x_1x_2(2x_2 + x_3)[B_{12} + 2C_{12}(x_1 - x_2) \\ & + 3D_{12}(x_1 - x_2)^2] + x_1x_3(2x_3 + x_2)[B_{13} \\ & + 2C_{13}(x_1 - x_3) + 3D_{13}(x_1 - x_3)^2]\end{aligned}$$

This equation is based on the assumption that the ternary interaction terms in the Redlich-Kister expansion for a three-component system are negligible. Expressions for the activity coefficients for components 2 and 3 are obtained by rotation of the subscripts. For example, the activity coefficient for component 2 is obtained by the above expression where the subscript 1 has been replaced by 2, the subscript 2 is replaced by 3, and the subscript 3 is replaced by 1.

Literature cited

Borowko, M., and M. Jaroniec, "Current State in Adsorption from Multicomponent Solutions of Nonelectrolytes on Solids," *Adv. Colloid Interface Sci.*, **19,** 137 (1983).

Dabrowski, A., "Theoretical Studies on the Adsorption from Nonideal Binary Liquid Mixtures on Heterogeneous Surfaces Involving Difference in Molecular Sizes of Components," *Monat. Chem.*, **114,** 875 (1983).

Dabrowski, A., and M. Jaroniec, "Characterization of Solid-Liquid Adsorption Systems by Using Gaussian Energy Distribution," *Mat. Chem. Phys.*, **12,** 339 (1985).

Everett, D. H., "Adsorption at the Solid/Liquid Interface: Nonaqueous Solutions," *Colloid Science: Specialist Periodical Reports,* Chemical Soc., London, **1,** ch. 2 (1973).

Goworek, J., J. Oscik, and R. Kusak, "Adsorption of Benzene Derivatives from Binary and Ternary Solutions in Benzene and *n*-Heptane on Silica Gel," *J. Colloid Interface Sci.*, **103,** 392 (1985).

Gurvitsch, L., *J. Phys. Chem. Soc. Russ.*, **47,** 805 (1915).

IMSL Library Reference Manual, IMSL, Houston, TX (1983).

Jaroniec, M., J. Oscik, and A. Derylo, "Correlation between Adsorption Parameters Characterizing Binary and Ternary Liquid Mixtures on Heterogeneous Solid Surfaces," *Acta Chim.*, **106,** 257 (1981).

Larionov, O. G., and A. L. Myers, "Thermodynamics of Adsorption from Nonideal Solutions of Nonelectrolytes," *Chem. Eng. Sci.*, **26,** 1,025 (1971).

Minka, C., and A. L. Myers, "Adsorption from Ternary Liquid Mixtures on Solids," *AIChE J.*, **19,** 453 (1973).

More, J. J., and M. Y. Cosnard, "BRENTM: A Fortran Subroutine for the Numerical Solution of Systems of Nonlinear Equations," *ACM Trans. Math. Software,* **6,** 240 (1980).

Prausnitz, J. M., *Molecular Thermodynamics of Fluid-Phase Equilibria,* Prentice-Hall, Englewood Cliffs, NJ (1969).

Sircar, S., and A. L. Myers, "A Thermodynamic Consistency Test for Adsorption from Binary Liquid Mixtures on Solids," *AIChE J.*, **17,** 186 (1971).

Manuscript received Dec. 27, 1985, and last revision received Sept. 10, 1986.