# Adsorption from Ternary Liquid Mixtures on Solids

The theory of adsorption from binary liquid mixtures on solids is extended to an arbitrary number of components. An equation for the surface excess is derived in terms of the free energy of immersion of the adsorbent, the capacity of the adsorbent at saturation, and activity coefficients in the bulk and adsorbed phases.

Experimental data are reported for adsorption from binary and ternary liquid mixtures of benzene, ethyl acetate, and cyclohexane on activated carbon at 30°C. These systems exhibit nonidealities in the adsorbed phase. The theory provides accurate estimates of adsorption from the ternary mixture using data for adsorption from binaries.

**CHARLES MINKA and ALAN L. MYERS**

**School of Chemical Engineering**
**University of Pennsylvania**
**Philadelphia, Pennsylvania**

## SCOPE

Although there have been numerous experimental studies of adsorption from binary liquid mixtures (Kipling, 1965), most industrial separations of materials are concerned with multicomponent solutions. It should be possible to predict adsorption from multicomponent liquid mixtures (ternary and higher) in terms of adsorption from pairs of liquids. For example, estimation of adsorption from a ternary mixture ($A + B + C$) would be based upon data for adsorption from the binaries ($A + B$), ($B + C$), and ($A + C$). The most important application is the special case of two dilute solutes (say, $A$ and $B$) in a solvent ($C$), but this development is not restricted to the dilute region.

## CONCLUSIONS AND SIGNIFICANCE

Quantitative agreement between theory and experiment was obtained for adsorption from a ternary liquid mixture of benzene, ethyl acetate, and cyclohexane on activated carbon at 30°C. The system is nonideal in both bulk and adsorbed phases. This result suggests that multicomponent adsorption may be predicted from binary adsorption.

Significance of this work lies not only in reducing the study of multicomponent adsorption to the study of adsorption from binary solutions but also in the generality of the theory, which is applicable to nonideal adsorption from nonideal solutions at all compositions.

## THEORY

Surface excess is the measure of adsorption from liquid mixtures (Kipling, 1965). The object is to derive an equation for surface excess for the case of multicomponent adsorption in terms of variables that can be obtained from binary-solution adsorption.

### Thermodynamic System

The thermodynamic system consists of a liquid phase (adsorbate) and an insoluble solid phase (adsorbent). The variable of interest is the isothermal change in the composition of the bulk liquid when the solid adsorbent is immersed in the liquid mixture and equilibrium is established.

### Assumptions

The basic assumption is that the original liquid solution consisting of a total of $n^0$ moles may be divided after the establishment of equilibrium into two phases: an adsorbed phase containing $n'$ moles and a bulk phase containing $n$ moles so that

$$n^0 = n + n' \tag{1}$$

For nonporous adsorbents upon which molecules adsorb in multiple layers, the assumption is weak because neither $n$ and $n'$ can be measured unless additional assumptions such as the validity of the B.E.T. theory (Brunauer, Emmett and Teller, 1938) are introduced. For microporous adsorbents, on the other hand, $n'$ may be estimated by

$$\frac{1}{n'} = \sum \frac{x_i'}{m_i} \tag{2}$$

where $m_i$ is the capacity of the pores in moles for pure $i$'th liquid, given by the amount adsorbed from the vapor of that liquid at saturation. Equation (2) is based upon the reasonable assertion that the volume change is zero when the solution is formed in the micropores from the pure liquids. Furthermore, according to Gurvitsch's rule (Gurvitsch, 1915), $m_i$ is approximately proportional to the bulk liquid density of the adsorbate.

Equations (1) and (2) are the critical assumptions. These assumptions, as shown below, lead to Equation (10) for adsorption from multicomponent liquid solutions.

### Surface Excess

The surface excess is obtained by measurements of the isothermal change in the composition of the bulk liquid ($\Delta x$) when the solid adsorbent is immersed in the liquid mixture:

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Correspondence concerning this paper should be addressed to A. L. Myers.

$$n_i^e = n^0(x_i^0 - x_i) \qquad (3)$$

$x_i^0$ and $x_i$ are the mole fractions of $i$'th component before and after, respectively, immersion of the adsorbent in the liquid.

Equation (1) is a material balance on the total number of moles of liquid. Using Equation (1) and a material balance on the $i$'th component of the mixture, Equation (3) may be written in terms of properties of the adsorbed phase (identified by a prime symbol):

$$n_i^e = n'(x_i' - x_i) \qquad (4)$$

Equation (4) shows that the surface excess is the amount of $i$ adsorbed less the amount of $i$ that would be adsorbed if the composition of the adsorbed phase were the same as that of the bulk liquid.

The efficiency of an actual separation process depends upon two factors: the degree of approach to equilibrium and the effectiveness of the separation of the bulk liquid from the solid adsorbent after the contacting operation. The separation efficiency is defined in terms of the difference in concentrations of the adsorbed and bulk phases ($\Delta x$). The value of $\Delta x$ given by Equation (4) is the ideal value corresponding to complete removal of the bulk liquid from the adsorbent.

It follows from Equation (3) that

$$\Sigma\, n_i^e = 0 \qquad (5)$$

In the special case of strongly adsorbed solutes for which $x_i' >> x_i$, we see from Equation (4) that $n_i^e \simeq n'x_i'$. For this special but important case, the surface excess is simply the amount adsorbed.

### Phase Equilibria

The adsorbed-phase variables $n'$ and $x_i'$ in Equation (4) cannot be measured directly. $n'$ is estimated by Equation (2) and $x_i'$ is calculated from bulk-phase properties using the basic equation of phase equilibrium

$$f_i' = f_i \qquad (6)$$

The fugacity in the bulk phase ($f_i$) is (Prausnitz, 1969)

$$f_i = P_i^s \gamma_i x_i e^{\left[\frac{v_i^s(P-P_i^s)}{RT}\right]} \qquad (7)$$

Similarly the fugacity in the adsorbed phase ($f_i'$) is (Larionov and Myers, 1971)

$$f_i' = P_i^s \gamma_i' x_i' e^{\left[\frac{-(\phi-\phi_i^0)}{m_i RT}\right]} \qquad (8)$$

where $\phi_i^0$ is the free energy of immersion of the adsorbent in the pure liquid and $\phi$ is the free energy of immersion in the mixture. $\phi$ is the product $\sigma A$, or surface tension × specific area of the adsorbent. For a solid-liquid interface we prefer to call this quantity the free energy of immersion ($\phi$) for two reasons: first, surface area has no meaning for microporous adsorbents and second, the familiar heat of immersion (Young and Crowell, 1962) is related to $\phi$ by the Gibbs-Helmholtz equation (Sircar et al., 1972)

For most adsorption systems the pressure is subatmospheric and the exponential term in Equation (7) may be set equal to unity with negligible error. Equations (6) to (8) then give

$$\gamma_i x_i = \gamma_i' x_i' e^{\left[\frac{-(\phi-\phi_i^0)}{m_i RT}\right]} \qquad (9)$$

### General Equation for Surface Excess

The variables $n'$ and $x_i'$ are eliminated from Equation (4) using Equations (2) and (9). The result, after some algebraic manipulation, is

$$n_i^e = \frac{\Sigma\, x_i x_j (1 - K_{ij})}{\Sigma\, x_j K_{ij}/m_j} \qquad (10)$$

where

$$K_{ij} = \frac{\gamma_i'\gamma_j}{\gamma_j'\gamma_i} \exp\left[\frac{(\phi-\phi_j^0)}{m_j RT} - \frac{(\phi-\phi_i^0)}{m_i RT}\right] \qquad (11)$$

$K_{ij}$ is a function of composition. The activity coefficients in the adsorbed phase ($\gamma_i', \gamma_j'$) are functions of the composition of the adsorbed phase ($x_j'$), which is a known function of bulk-phase composition ($x_j$):

$$x_j' = \frac{x_j K_{ij}}{\Sigma\, x_j K_{ij}} \qquad (12)$$

The summation in Equations (10) and (12) are over $j$; $j = 1, 2, \ldots, n$. The quantity $K_{ij}$ has the following properties:

$$\begin{aligned} K_{ij} &= 1 \qquad (i = j) \\ K_{ij} &= 1/K_{ji} \\ K_{ij} &= K_{ip}K_{pj} \end{aligned} \qquad (13)$$

The free energy of immersion ($\phi$) is also a function of composition and is obtained by integrating the Gibbs adsorption isotherm (Larionov and Myers, 1971):

$$-\,d\phi = \Sigma\, n_i' d\mu_i \qquad (14)$$

Since Equation (10) is not explicit in terms of the bulk-phase composition, the use of Equations (10) to (14) for calculation of surface excess requires further discussion.

### Ternary Liquid Solution

For a ternary liquid solution we note from Equation (5) that

$$n_1^e + n_2^e + n_3^e = 0 \qquad (15)$$

Two excess quantities must be determined; the third is given by Equation (15). From Equation (10),

$$\begin{aligned} n_1^e &= \frac{x_1x_2(1-K_{12}) + x_1x_3(1-K_{13})}{x_1/m_1 + x_2K_{12}/m_2 + x_3K_{13}/m_3} \\ n_2^e &= \frac{x_1x_2(1-K_{21}) + x_2x_3(1-K_{23})}{x_1K_{21}/m_1 + x_2/m_2 + x_3K_{23}/m_3} \end{aligned} \qquad (16)$$

where

$$\begin{aligned} K_{12} &= \frac{\gamma_1'\gamma_2}{\gamma_2'\gamma_1} \exp\left[\frac{(\phi-\phi_2^0)}{m_2RT} - \frac{(\phi-\phi_1^0)}{m_1RT}\right] \\ K_{13} &= \frac{\gamma_1'\gamma_3}{\gamma_3'\gamma_1} \exp\left[\frac{(\phi-\phi_3^0)}{m_3RT} - \frac{(\phi-\phi_1^0)}{m_1RT}\right] \\ K_{21} &= 1/K_{12} \\ K_{23} &= K_{13}/K_{12} \end{aligned} \qquad (17)$$

We consider next the calculation of free energy of immersion ($\phi$). The chemical potentials in the bulk liquid are related by the isothermal Gibbs-Duhem equation (Prausnitz, 1969)

$$x_1 d\mu_1 + x_2 d\mu_2 + x_3 d\mu_3 = 0 \qquad (18)$$

From Equation (4),

$$n_i' = n_i^e + n' x_i \qquad (i = 1, 2, 3) \qquad (19)$$

Substitution of Equations (15) to (19) into (14) followed by algebraic rearrangement gives

$$d\phi = \frac{x_2(1-K_{12})d\mu_2 + x_3(1-K_{13})d\mu_3}{\dfrac{x_1}{m_1} + \dfrac{x_2K_{12}}{m_2} + \dfrac{x_3K_{13}}{m_3}} \tag{20}$$

Integrating along the path $x_3/x_2 =$ constant,

$$\frac{\phi-\phi_1^0}{RT} = \int_{x_1=1}^{x_1} \frac{x_2(1-K_{12})\left(\dfrac{d\ln\gamma_2}{dx_1} - \dfrac{1}{1-x_1}\right) + x_3(1-K_{13})\left(\dfrac{d\ln\gamma_3}{dx_1} - \dfrac{1}{1-x_1}\right)}{\dfrac{x_1}{m_1} + \dfrac{x_2K_{12}}{m_2} + \dfrac{x_3K_{13}}{m_3}}\, dx_1 \tag{21}$$

The variables $K_{12}$ and $K_{13}$ in Equation (21) are functions of the values of the activity coefficients in the adsorbed phase [Equation (17)] which in turn are functions of the composition of the adsorbed phase. According to Equation (12)

$$x_1' = \frac{x_1}{x_1 + x_2K_{12} + x_3K_{13}}$$

$$x_2' = \frac{x_2K_{12}}{x_1 + x_2K_{12} + x_3K_{13}} \tag{22}$$

After numerical integration of Equation (21) for $\phi(x_1, x_2)$, the surface excess is given by Equations (15) to (17).

### Ternary Liquid Solution, Special Cases

The numerical integration of Equation (21) may be avoided under certain special conditions. If the adsorbed phase is ideal ($\gamma_i' = 1$), Equation (16) becomes

$$n_1^e = \frac{a_1 - x_1\,[a_1 + a_2K_{12}' + a_3K_{13}']}{\dfrac{a_1}{m_1} + \dfrac{a_2K_{12}'}{m_2} + \dfrac{a_3K_{13}'}{m_3}} \tag{23}$$

where $a_i = \gamma_i x_i$ is the activity in the bulk solution and

$$K_{12}' = \exp\left\{\frac{(\phi-\phi_2^0)}{m_2RT} - \frac{(\phi-\phi_1^0)}{m_1RT}\right\}$$

$$K_{13}' = \exp\left\{\frac{(\phi-\phi_3^0)}{m_3RT} - \frac{(\phi-\phi_1^0)}{m_1RT}\right\} \tag{24}$$

Integration of Equation (21) gives

$$a_1 e^{\left[\frac{\phi-\phi_1^0}{m_1RT}\right]} + a_2 e^{\left[\frac{\phi-\phi_2^0}{m_2RT}\right]} + a_3 e^{\left[\frac{\phi-\phi_3^0}{m_3RT}\right]} = 1 \tag{25}$$

Equation (25) is solved implicitly for $\phi(x_1, x_2)$. If the bulk phase obeys Raoult's law ($\gamma_i = 1$), Equation (23) becomes

$$n_1^e = \frac{x_1x_2(1-K_{12}') + x_1x_3(1-K_{13}')}{x_1/m_1 + x_2K_{12}'/m_2 + x_3K_{13}'/m_3} \tag{26}$$

$K_{12}'$ and $K_{13}'$ are constants, independent of composition, only for the special case when $m_1 = m_2 = m_3$.

### Binary Liquid Solution

For a binary liquid solution of component nos. 1 and 2, the calculation of surface excess is similar to that for a ternary but the equations are simpler ($x_3 = 0$). Properties needed for the calculation are: difference of free energies of immersion in the pure liquids [$(\phi_1^0 - \phi_2^0)/RT$]; the capacities of the adsorbent [$m_1, m_2$]; activity coefficients in the bulk liquid [$\gamma_1(x_1)$, $\gamma_2(x_2)$]; activity coefficients in the adsorbed phase [$\gamma_1'(x_1')$, $\gamma_2'(x_2')$].

First the free energy of immersion is obtained by numerical integration [see Equation (21)]:

$$\frac{\phi-\phi_1^0}{RT} = -\int_{x_1=1}^{x_1} \frac{(1-K_{12})}{\gamma_1\left[\dfrac{x_1}{m_1} + \dfrac{x_2K_{12}}{m_2}\right]}\, d(\gamma_1x_1) \tag{27}$$

where

$$K_{12} = \frac{\gamma_1'\gamma_2}{\gamma_2'\gamma_1}\exp\left\{\frac{(\phi-\phi_2^0)}{m_2RT} - \frac{(\phi-\phi_1^0)}{m_1RT}\right\} \tag{28}$$

and

$$x_1' = \frac{x_1}{x_1 + x_2K_{12}} \tag{29}$$

Then the surface excess is given by

$$n_1^e = \frac{x_1x_2(1-K_{12})}{\dfrac{x_1}{m_1} + \dfrac{x_2K_{12}}{m_2}}$$

$$n_2^e = -\,n_1^e \tag{30}$$

This calculation for the case of binary solutions has been described previously (Larionov and Myers, 1971).

## EXPERIMENT

We designed an experiment to test Equation (16) for adsorption from a ternary liquid mixture of benzene + ethyl acetate + cyclohexane on activated carbon. The selectivity of the adsorbent for these liquids decreases in the order benzene, ethyl acetate, cyclohexane. The constants in Equation (16) were derived from experimental data for adsorption from pairs of the same liquids using the procedure to be described.

### Experimental Procedure

The surface excess was measured by Equation (3). A binary or ternary solution of known amount ($n^0$) and composition ($x_i^0$) was prepared for each experimental point. A known quantity of freshly regenerated adsorbent was added to the solution in a screw-capped Erlenmeyer flask. The amounts of liquid and adsorbent were measured gravimetrically. Equilibrium, as evidenced by independence of the measurements and the order of contact of the liquids, was obtained by shaking the flask in a water bath for 15 to 20 hours. The temperature of the bath was thermostatically controlled at 30 ± 0.1°C. Compositions of binary solutions were determined refractometrically. Compositions of ternary solutions were obtained by a combination of refractive index and density measurements; calibration curves are given by Chao (1956). Standard solutions were prepared to check the accuracy of the analysis; the error in the measurement of the composition of the ternary solution is about ± 0.2 mole %.

### Chemicals

Chemicals were spectroquality reagents obtained from Matheson, Coleman and Bell Company. The activated carbon was furnished by the Pittsburgh Activated Carbon Company (Type BPL 4 × 10), surface area, 1,100 $m^2/g$ by BET ($N_2$) method). The carbon was outgassed at 200°C under vacuum for 8 hours.

### Thermodynamic Consistency Test

Surface excess as a function of composition is reported in Tables 1 to 4. The experimental points for the binary solutions are plotted on Figures 1, 2, and 3. Binary data were checked for thermodynamic consistency using the method of Sircar and Myers (1971). The test, summarized in Table 5, requires that the sum of integrals for the binaries be zero. The actual sum is about 1% of the value of the largest integral. Therefore the data are consistent within the accuracy of the experiment.

## ANALYSIS OF RESULTS

The theory, Equation (16), calls for the capacity of the adsorbent ($m_i$), activity coefficients in the ternary solution for the bulk phase and for the adsorbed phase, and differences of free energies of immersion in the pure liquids (Table 5).

Table 1. Adsorption of Liquid Mixtures of Benzene (1) and Cyclohexane (2) on Carbon at 30°C

| mmoles/g $n_1^e$ | $x_1$ |
|---|---|
| 0.642 | 0.019 |
| 0.723 | 0.021 |
| 1.051 | 0.077 |
| 1.014 | 0.079 |
| 1.233 | 0.143 |
| 1.239 | 0.152 |
| 1.264 | 0.246 |
| 1.207 | 0.346 |
| 1.061 | 0.470 |
| 0.872 | 0.565 |
| 0.669 | 0.667 |
| 0.609 | 0.692 |
| 0.441 | 0.783 |
| 0.233 | 0.888 |
| 0.107 | 0.945 |

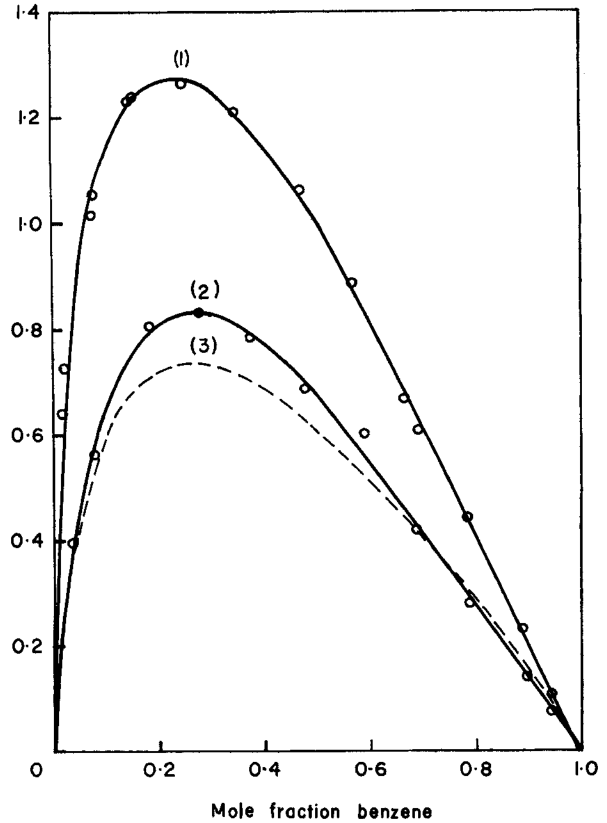

Fig. 1. Adsorption of benzene on activated carbon at 30°C from (1) benzene + cyclohexane, (2) benzene + ethyl acetate, (3) benzene + cyclohexane + ethyl acetate with equimolar amounts of cyclohexane and ethyl acetate in bulk. Solid lines: Equation (30) for binaries. Circles: experimental points for binaries. Dashed line: Equation (16) for ternary.

### Absorbent Capacity

The capacity of the adsorbent at saturation was obtained from adsorption isotherms for the pure vapors (Bruzzi, 1972). The values, given in Table 6, obey Gurvitch's rule within 4%.

Table 2. Adsorption of Liquid Mixtures of Benzene (1) and Ethyl Acetate (2) on Carbon at 30°C

| mmoles/g $n_1^e$ | $x_1$ |
|---|---|
| 0.394 | 0.039 |
| 0.561 | 0.080 |
| 0.809 | 0.183 |
| 0.832 | 0.278 |
| 0.782 | 0.376 |
| 0.686 | 0.479 |
| 0.603 | 0.592 |
| 0.416 | 0.688 |
| 0.281 | 0.790 |
| 0.143 | 0.898 |
| 0.079 | 0.947 |

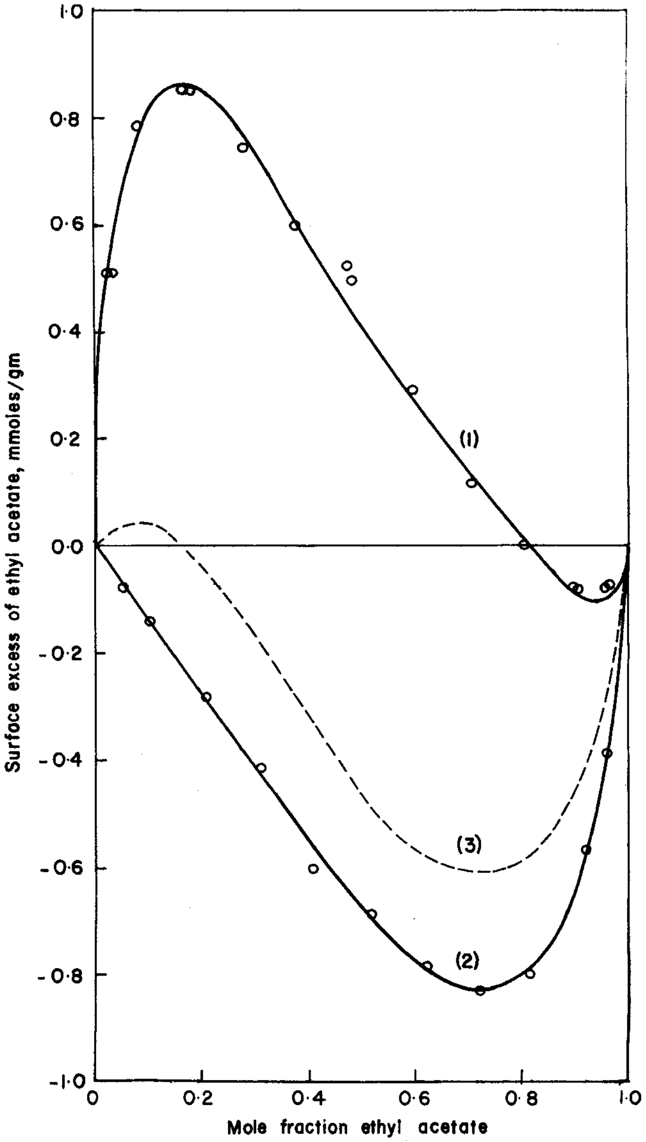

Fig. 2. Adsorption of ethyl acetate on activated carbon at 30°C from (1) ethyl acetate + cyclohexane, (2) ethyl acetate + benzene, (3) ethyl acetate + cyclohexane + benzene with equimolar amounts of cyclohexane and benzene in bulk. Solid lines: Equation (30) for binaries. Circles: experimental points for binaries. Dashed line: Equation (16) for ternary.

### Activity Coefficients of Binary Solutions in the Bulk Phase

Activity coefficients for binary solutions in the bulk phase were obtained from isobaric vapor-liquid equilibrium data (Chao, 1956) and from enthalpy of mixing data (Ratman et al., 1962). Constants of the Redlich-Kister equation (Prausnitz, 1969—see Appendix) for these data at 30°C are reported in Table 7. All three binaries have positive deviations from Raoult's law, ranging from small positive deviations for ethyl acetate + benzene to large positive deviations from ethyl acetate + cyclohexane.

### Activity Coefficients of Binary Solutions in Adsorbed Phase

Activity coefficients of binary solutions in the adsorbed phase were derived from data in Tables 1 to 3 as follows: for a binary solution ($x_3 = 0$), combination of Equations (29) and (30) gives the composition of the adsorbed solution

$$x_1' = \frac{m_1(m_2 x_1 + n_1^e)}{m_1 m_2 + n_1^e(m_1 - m_2)} \tag{31}$$

The free energy of immersion, from an integration of Equation (14) using Equations (18) and (19) with $x_3 = 0$, is

$$\frac{\phi - \phi_1^0}{RT} = -\int_{x_1=1}^{x_1} \frac{n_1^e}{x_1 x_2 \gamma_1}\, d(\gamma_1 x_1) \tag{32}$$

Then from Equation (9),

$$\begin{aligned} \gamma_1' &= \frac{x_1}{x_1'}\,\gamma_1 \exp\left(\frac{\phi - \phi_1^0}{m_1 RT}\right) \\ \gamma_2' &= \frac{x_2}{x_2'}\,\gamma_2 \exp\left(\frac{\phi - \phi_2^0}{m_2 RT}\right) \end{aligned} \tag{33}$$

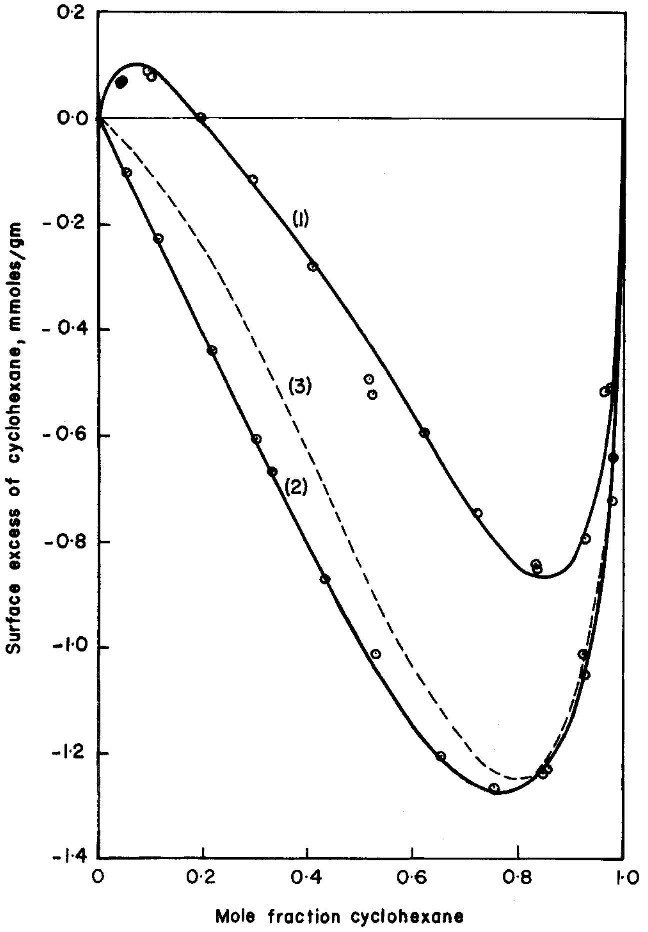

Fig. 3. Adsorption of cyclohexane on activated carbon at 30°C from (1) cyclohexane + ethyl acetate, (2) cyclohexane + benzene, (3) cyclohexane + ethyl acetate + benzene with equimolar amounts of ethyl acetate and benzene in bulk. Solid lines: Equation (30) for binaries. Circles: experimental points for binaries. Dashed line: Equation (16) for ternary.

TABLE 3. ADSORPTION OF LIQUID MIXTURES OF ETHYL ACETATE (1) AND CYCLOHEXANE (2) ON CARBON AT 30°C

| mmoles/g<br>$n_1^e$ | $x_1$ |
|---|---|
| 0.510 | 0.028 |
| 0.520 | 0.039 |
| 0.787 | 0.079 |
| 0.852 | 0.163 |
| 0.840 | 0.179 |
| 0.747 | 0.278 |
| 0.599 | 0.378 |
| 0.525 | 0.477 |
| 0.499 | 0.485 |
| 0.288 | 0.593 |
| 0.116 | 0.702 |
| 0.000 | 0.801 |
| −0.075 | 0.898 |
| −0.087 | 0.904 |
| −0.068 | 0.951 |
| −0.065 | 0.953 |

TABLE 4. ADSORPTION OF TERNARY MIXTURES OF BENZENE (1), ETHYL ACETATE (2) AND CYCLOHEXANE (3) ON CARBON AT 30°C

| | | mmoles/g | | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $n_1^e$(exp.) | $n_1^e$(calc.) | $n_2^e$(exp.) | $n_2^e$(calc.) |
| 0.087 | 0.841 | 0.576 | 0.560 | −0.582 | −0.580 |
| 0.130 | 0.075 | 0.960 | 0.990 | 0.283 | 0.295 |
| 0.176 | 0.675 | 0.708 | 0.714 | −0.656 | −0.638 |
| 0.252 | 0.515 | 0.705 | 0.737 | −0.450 | −0.500 |
| 0.291 | 0.115 | 0.947 | 0.970 | 0.154 | 0.145 |
| 0.410 | 0.199 | 0.718 | 0.758 | −0.058 | −0.050 |
| 0.510 | 0.126 | 0.720 | 0.715 | −0.033 | −0.020 |
| 0.615 | 0.230 | 0.487 | 0.492 | −0.250 | −0.240 |
| 0.719 | 0.117 | 0.387 | 0.405 | −0.107 | −0.105 |
| 0.759 | 0.157 | 0.313 | 0.324 | −0.172 | −0.180 |
| 0.857 | 0.072 | 0.218 | 0.219 | −0.094 | −0.084 |

TABLE 5. INTEGRAL THERMODYNAMIC CONSISTENCY TEST OF BINARY ADSORPTION ISOTHERMS AT 30°C. NOTATION IS BENZENE (1), ETHYL ACETATE (2) AND CYCLOHEXANE (3)

| Binary mixture | Differences in free energy of immersion, cal/g |
|---|---|
| 1-2 | $\phi_1^0 - \phi_2^0 = -3.53$ |
| 1-3 | $\phi_3^0 - \phi_1^0 = 5.68$ |
| 2-3 | $\phi_2^0 - \phi_3^0 = -2.21$ |
| | Sum $= -0.06$ |

TABLE 6. CAPACITY OF CARBON ADSORBENT

| Liquid | m, mmol/g |
|---|---|
| Benzene | 5.48 |
| Ethyl Acetate | 4.95 |
| Cyclohexane | 4.30 |

Given the experimental isotherms $n_1^e(x_1)$ in Tables 1 to 3, activity coefficients in the bulk liquid ($\gamma_i$) from Table 7, and the capacity ($m_i$) in Table 6, calculation of activity coefficients in the adsorbed phase is straightforward. After numerical integration of Equation (32), activity coefficients in the adsorbed phase as a function of its composition $[\gamma_1'(x_1'), \gamma_2'(x_2')]$ were calculated from Equations (31) and (33). Results are plotted in Figures 4 to 6. These activity coefficients for the adsorbed phase show a complex variation with composition and there is no obvious relationship with the nonideal behavior observed in the bulk liquid solutions.

Constants of the Redlich-Kister equation (Prausnitz, 1969) for these activity coefficients are reported in Table 7.

### Prediction of Surface Excess in Ternary Solution

Values of surface excess for ternary solutions were calculated by Equation (16) and are compared in Table 4 with the experimental data. Predictions are based entirely upon binary data: adsorbent capacity in Table 6, differences of free energies of immersion in Table 5, and activity coefficients in bulk and adsorbed phases in Table 7. Activity coefficients of ternary solutions, both in the bulk phase and in the adsorbed phase, were calculated from binary data using the procedure described in the Appendix. Integration of Equation (21) was carried out using a fourth-order Runge-Kutta procedure (Carnahan, 1969). Table 4 shows that the average of the absolute value of the difference between experimental and predicted points is 0.015 mmole/g. This difference lies

TABLE 7. CONSTANTS OF REDLICH-KISTER EQUATION (SEE APPENDIX) FOR BINARY MIXTURES AT 30°C

| | | Benzene (1)— Ethyl Acetate (2) | Benzene (1)— Cyclohexane (3) | Ethyl Acetate (2)— Cyclohexane (3) |
|---|---|---|---|---|
| Bulk Phase | A | 0.1551 | 0.5328 | 1.2206 |
| | B | 0.0309 | 0.0519 | −0.0226 |
| | C | 0 | 0 | 0 |
| | D | 0 | 0 | 0 |
| Adsorbed 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 |

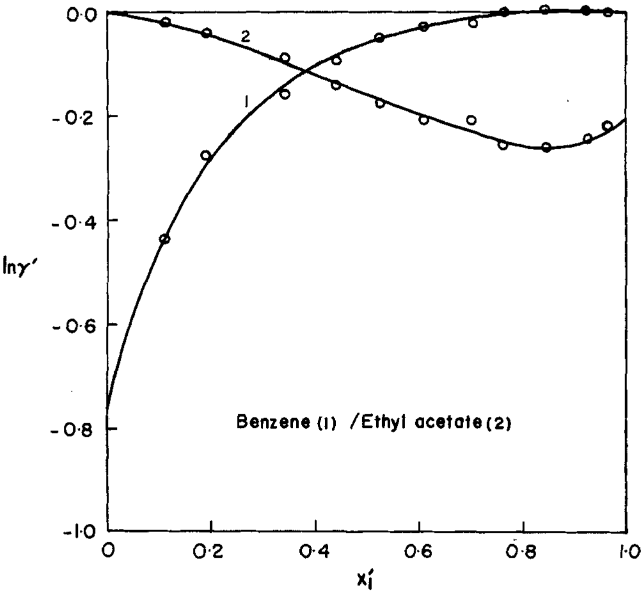

Fig. 4. Activity coefficients in adsorbed phase for binary solution of benzene + ethyl acetate. Circles: experimental points. Solid lines: Redlich-Kister equation using constants in Table 7.

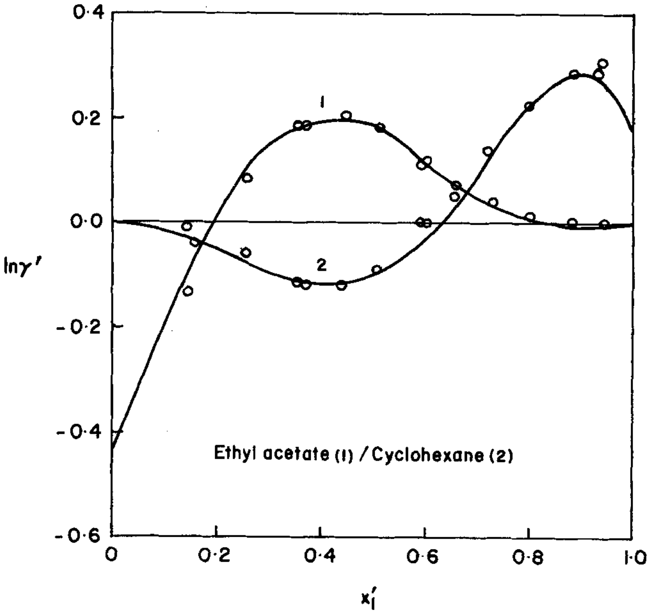

Fig. 5. Activity coefficients in adsorbed phase for binary solution of ethyl acetate + cyclohexane. Circles: experimental points. Solid lines: Redlich-Kister equation using constants in Table 7.

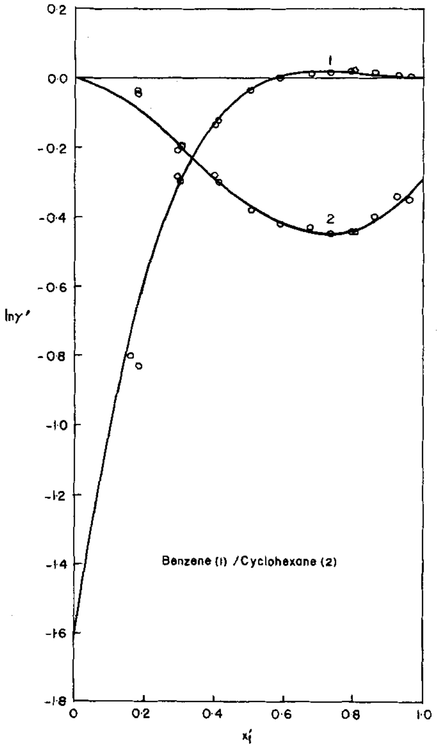

Fig. 6. Activity coefficients in adsorbed phase for binary solution of benzene + cyclohexane. Circles: experimental points. Solid lines: Redlich-Kister equation using constants in Table 7.

within the estimated experimental error for surface excess, and therefore the theory is in quantitative agreement with the observed data.

## DISCUSSION

Since the experimental points confirm Equation (16), it may be used to study the behavior of the ternary system along various loci. In Figures 1 to 3 is plotted the surface excess of, say, component $A$ as a function of its mole fraction in bulk solution for binary mixtures of $A$-$B$ and $A$-$C$. The solid line is Equation (30) and the circles are the experimental points in Tables 1 to 3. The dashed line is Equation (16) for the surface excess of component $A$ adsorbed from a ternary solution of $A$-$B$-$C$ on the locus $x_B = x_C$. At fixed mole fraction of any component, the variation of its surface excess with composition is highly nonlinear. The most unexpected result is found in Figure 1: for cyclohexane and ethyl acetate in equimolar amounts, the surface excess of benzene is less for the ternary (dashed line) than for either binary (solid lines). Thus for a given mole fraction of benzene in bulk, the surface excess of benzene goes through a minimum as the molar ratio of cyclohexane/ethyl acetate increases.

## ACKNOWLEDGMENT

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## NOTATION

$a$ = activity
$f$ = fugacity
$K_{ij}$ defined by Equation (11)
$K_{ij}'$ defined by Equation (24)
$m$ = capacity of adsorbent, moles/g
$n^0$ = number of moles in bulk liquid before contact with adsorbent
$n$ = number of moles in bulk liquid at equilibrium
$n'$ = number of moles in adsorbed phase
$n_i^e$ = surface excess of $i$'th component, Equation (3)
$P$ = pressure
$P^s$ = vapor pressure of saturated liquid
$R$ = gas constant
$T$ = absolute temperature
$v_i^s$ = molar volume of saturated liquid
$x_i^0$ = mole fraction of $i$ in bulk liquid before contact with adsorbent
$x_i$ = mole fraction of $i$ in bulk liquid at equilibrium
$x_i'$ = mole fraction of $i$ in adsorbed phase

### Greek Letters

$\gamma_i$ = activity coefficient of $i$'th component in bulk liquid
$\gamma_i'$ = activity coefficient of $i$'th component in adsorbed phase
$\mu$ = chemical potential
$\phi$ = free energy of immersion of adsorbent in liquid solution
$\phi_i^0$ = free energy of immersion of adsorbent in pure $i$'th liquid

### Subscript and Superscript

$i$ = $i$'th component
$'$ = adsorbed phase

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## APPENDIX. CALCULATION OF ACTIVITY COEFFICIENTS IN TERNARY SOLUTIONS

The basic assumption is that the excess free energy of the ternary solution ($\Delta g^e{}_{123}$) is equal to the sum of excess free energies of its constituent binaries ($\Delta g^e{}_{12}$, $\Delta g^e{}_{23}$, $\Delta g^e{}_{13}$):

$$\Delta g^e{}_{123} = \Delta g^e{}_{12} + \Delta g^e{}_{23} + \Delta g^e{}_{13}$$

Activity coefficients are obtained using the relationship (Chao, 1956)

$$\ln \gamma_1 = \frac{\Delta g^e{}_{123}}{RT} + \frac{\partial}{\partial x_1}\left[\frac{\Delta g^e{}_{123}}{RT}\right]_{x_2} - x_1 \frac{\partial}{\partial x_1}\left[\frac{\Delta g^e{}_{123}}{RT}\right]_{x_2} - x_2 \frac{\partial}{\partial x_2}\left[\frac{\Delta g^e{}_{123}}{RT}\right]_{x_1}$$

The Redlich-Kister equation (Prausnitz, 1969) for the excess Gibbs free energy of a binary mixture of components 1 and 2 is

$$\frac{\Delta g^e{}_{12}}{RT} = x_1 x_2 \left[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + D_{12}(x_1 - x_2)^3\right]$$

It follows that the activity coefficient of component no. 1 in ternary solution is given by

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

Similar expressions are obtained for $\ln \gamma_2$ and $\ln \gamma_3$. Constants of the Redlich-Kister equation for binary adsorbed and bulk solutions of the liquids benzene, ethyl acetate, and cyclohexane at 30°C are reported in Table 7.

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