# Thermodynamic Properties of Adsorbed Mixtures of Benzene and Cyclohexane on Graphitized Carbon and Activated Charcoal at 30 °C

Experimental data at 30°C are reported for the adsorption of mixtures of benzene and cyclohexane on two types of carbon surface: graphitized carbon and activated charcoal. The properties of the adsorbed solution approach those of bulk liquid at vapor saturation for graphitized carbon, but not for activated charcoal. The mixtures adsorbed on graphitized carbon are nonideal, and the deviations from ideality increase with surface coverage. For activated charcoal, the adsorbed mixtures are nearly ideal at all coverages. Mixture behavior for both adsorbents can be predicted without using experimental data for the adsorbed mixtures.

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## SCOPE

Work on theories for adsorption from mixtures may be divided into two major categories: (1) extension of equations derived for adsorption of pure gases and (2) thermodynamic methods. The advantage of the first group is that analytical equations are well-suited to calculations on a digital computer. Unfortunately, the equations proposed so far do not fit the experimental data for the pure gases, and predictions for mixtures are generally poor.

Thermodynamic methods have the advantage that they are not based on any particular adsorption model. In order to use these methods, it is assumed that the adsorbed solution is ideal. The only information required is the adsorption isotherm of each pure gas. The theory of ideal adsorbed solutions (IAS) (Myers and Prausnitz, 1965) has been successful in multicomponent adsorption equilibria for a wide variety of systems. The disadvantage of the thermodynamic approach is that the equations for the mixture equilibria are not explicit. Graphical methods are often used. However, a recent paper by Tien (1981) has shown how the IAS method may be used in computer calculations of breakthrough curves by approximating the pure-component isotherm piecewise with a Freundlich isotherm.

Because of the extensive use of IAS, it is necessary to test its applicability. The aim of this work is to obtain experimental data which will give an insight into the nature of adsorbed solutions and lead to better predictions of adsorption from multicomponent mixtures.

## CONCLUSIONS AND SIGNIFICANCE

We measured the adsorption of a mixture of benzene and cyclohexane on two types of surfaces: graphitized carbon and activated charcoal. A summary of our findings is given in Table 1.

It is not surprising that the nonideality of a solution adsorbed on a homogeneous, nonporous surface like graphitized carbon should approach bulk liquid behavior in the limit as the vapor approaches saturation and several layers of molecules are adsorbed. However, for adsorption on a microporous adsorbent like activated charcoal, there is no reason to expect a corresponding behavior at saturation because the number of molecules in the pores is too small to simulate bulk liquid properties. Experimental results indicate that solution behavior is close to ideal for adsorption in micropores, even at fairly high surface coverage.

It has been pointed out often that it is impossible to apply the concept of an ideal adsorbed solution (IAS) at high coverage when the standard state of the weakly adsorbed species must be estimated by an unjustified extrapolation of its spreading pressure. Here we have shown that this problem may be resolved by using the reduced spreading pressure, rather than the spreading pressure itself, to define the standard state. In this way, the mixture adsorption isotherm may be predicted from low coverage up to vapor saturation.

We have found that mixture behavior for both types of adsorbent, nonporous and microporous, may be predicted without using experimental data for the adsorbed mixture. However, these findings are for one mixture and similar studies of other systems are needed to test the generality of our results.

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The adsorption equilibria of mixed gases can be described in terms of solution thermodynamics. Such a treatment was first advanced by Butler (1932) for the case of the liquid-vapor interface. This approach was applied later to adsorption of gas mixtures on solids (Arnold, 1949; Myers and Prausnitz, 1965; Cook and Basmadjian, 1965; Sircar and Myers, 1973).

In order to calculate adsorption from multicomponent mixtures, it is necessary to know the activity coefficients for the components of the adsorbed solution. It has been found that many adsorbed mixtures obey Raoult's law, even though the same mixtures in the bulk liquid phase are nonideal. Therefore, for a particular adsorbent, the adsorption of any mixture can be predicted using Raoult's

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TABLE 1. SUMMARY OF RESULTS FOR ADSORPTION OF MIXTURES OF BENZENE AND CYCLOHEXANE

| | Adsorbent | |
|---|---|---|
| Property | Graphitized Carbon | Activated Charcoal |
| Type of surface | Homogeneous, nonporous | Heterogeneous, microporous |
| Surface area, $m^2/g$ | 10 | 1100 |
| Type of adsorption | Multilayer | Filling of micropores |
| Amount adsorbed at saturation | Infinite | Finite |
| Composition of adsorbed phase at saturation | Approaches bulk liquid composition | Unrelated to bulk liquid composition |
| Solution behavior at low surface coverage | Ideal | Ideal |
| Solution behavior at high surface coverage | Approaches bulk liquid nonideality | Ideal |

law in combination with the adsorption isotherms of the pure gases. This serendipitous result is very useful for the design of adsorptive separation processes, because experiments to measure mixed-gas adsorption are time-consuming and expensive.

Because of the widespread use of Raoult's law to predict the adsorption of gas mixtures, it is important to test its range of applicability. We measured the activity coefficients of adsorbed mixtures of benzene and cyclohexane from low surface coverage to pressures near vapor saturation. This particular mixture was selected because the bulk liquid forms a nonideal solution. The equilibria were measured on two adsorbents: a microporous, heterogeneous solid (activated charcoal) and a non-porous solid (graphitized carbon). The first adsorbent is widely used commercially and the second has theoretical importance because of its nearly homogeneous surface.

## EXPERIMENTAL

### Apparatus

The apparatus was designed to measure adsorption of vapors from low pressure to near condensation. A schematic diagram is shown on Figure 1. Mercury cutoffs and greaseless Teflon valves were used to prevent solution of vapors in stopcock grease. Condensation of vapors in cooler parts of the apparatus was prevented by enclosing it in a plexiglas chamber, which was thermostatically controlled at the temperature of the adsorption isotherm. The adsorption system had a volume of about 6 L in order to meet the requirement for measurement at constant gas composition. A vapor circulation system was provided to ensure that the gas in contact with the adsorbent had the same composition as the bulk vapor.

The vapor supply system consisted of a 75 $cm^3$ flask and 20-L glass bottle. A liquid mixture of known composition was introduced into the flask, which was then outgassed and evaporated into the bottle. The mercury cutoffs were designed to allow evacuation of the supply system independently of the adsorption system.

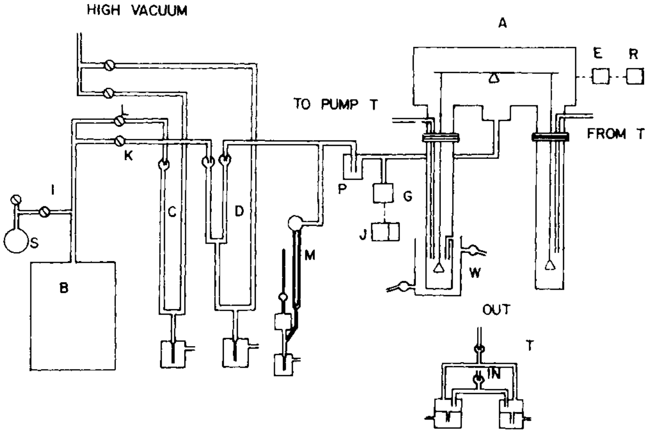

**Figure 1. Schematic diagram of vapor adsorption apparatus. A: electrobalance; B: vapor mixing reservoir; C,D: mercury cutoff; E: balance electronic unit; G: manometer head; I,K,L: teflon valve; J: manometer electronic unit and recorder; M: McLeod gauge; P: trap; R: balance recorder; S: vapor supply bottle; T: circulation pump; W: water bath.**

Pressures below 10 Pa were measured by a McLeod gauge and higher pressures were measured with a capacitance manometer manufactured by MKS Instruments, Inc.

A Cahn electrobalance was used to weigh directly the amount of vapor adsorbed on the adsorbent. A good description of this balance is available (Cahn, 1964). Adsorbent sample and tare weights were contained in cylindrical quartz buckets which were suspended from the balance with 0.1 mm diameter Nichrome wire. The electrobalance is extremely sensitive to outside disturbances. Spurious changes in weight caused by static charges were eliminated by coating the outside of the hang-down tubes with an anti-static compound.

The temperature of the water bath around the sample hang-down tube was controlled to ± 0.01 C. The gas circulation system consisted of two automatic Toepler pumps connected in parallel. The pumps were operated one-half cycle apart to maintain a nearly continuous flow of the gas. The vacuum system consisted of a three-stage mercury diffusion pump in series with a mechanical vacuum pump.

### Procedure

Because of buoyancy effects, zero drift of the balance, and other noises affecting weight measurements, it was necessary to make blank runs prior to the adsorption experiment. Blank runs were carried out like actual measurements in all respects except that nonporous, nonadsorbing glass beads were substituted for the adsorbent. It was found that blank corrections were less than 0.5% of the amount of gas adsorbed.

After the blank runs, a sample of 230 mg of graphite or 20 mg of charcoal was placed into the sample pan of the electrobalance. The adsorbent was degassed at room temperature under a vacuum of $10^{-2}$ Pa for 6 hours, after which it was heated to its final regeneration temperature, 400°C for graphite and 300 C for charcoal. After 12 hours of regeneration the heating mantle was removed and the adsorbent was allowed to cool to room temperature under vacuum. A fresh sample of adsorbent lost about 10 percent of its original weight during degassing.

After outgassing the adsorbent, a constant temperature water bath was placed around the sample hangdown tube. The vapor was then introduced into the adsorption section and the approach to equilibrium was followed directly by observing the balance recorder. Equilibrium was attained with 20 to 30 minutes for the graphite and within 2 to 3 hours for charcoal.

Desorption measurements were carried out to check the reversibility of the isotherms. A liquid nitrogen bath was placed around flask S. The cooling caused freezing of vapors in the supply system which acted as a vacuum pump.

### Materials

The properties of the adsorbents are given in Table 2. Benzene and cyclohexane were spectroquality reagents obtained from Matheson, Coleman and Bell. Prior to use, they were dried by adsorption on a molecular sieve.

### Results

We measured the adsorption at 30°C of benzene and cyclohexane, as well as mixtures of these gases, on two adsorbents: graphitized carbon and activated charcoal.

The isotherms for graphitized carbon are shown on Figure 2 (low pressure region) and Figure 3 (high pressure region) for the pure gases and four compositions of the gas mixture. At high and low coverage benzene adsorbs

TABLE 2. PROPERTIES OF ADSORBENTS

| | Adsorbent | |
|---|---|---|
| Property | Graphitized Carbon | Activated Charcoal |
| Structure | Nonporous | Microporous |
| Surface area, $m^2/g$ ($N_2$, B.E.T. method) | 10 | 1100 |
| Pore volume, $cm^3/g$ | — | 0.95 |
| Particle diameter, $\mu m$ | 0.34 | 1000 |
| Bulk density, $g/cm^3$ | 0.61 | 0.40 |
| Trade name | Sterling MT-D5 | Filtrasorb 400 |
| Manufacturer | Cabot Corp., Bellerica, MA | Calgon Corp., Pittsburgh, PA |

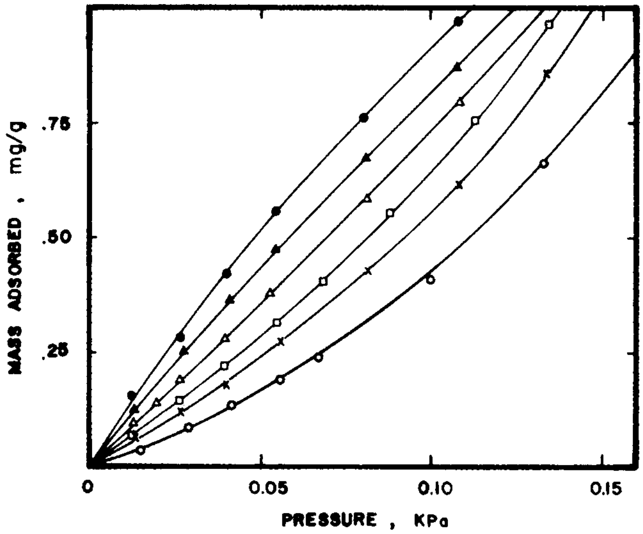

Figure 2. Adsorption for benzene(1), cyclohexane(2) and their mixtures on graphitized carbon at 30 C, low pressure region. ●: pure benzene; X: $y_1 = 0.1525$; □: $y_1 = 0.2999$; △: $y_1 = 0.5016$; ▲: $y_1 = 0.8500$; O: pure cyclohexane.

more strongly, but there is an intermediate region from 0.2 to 3.2 kPa where more cyclohexane than benzene is adsorbed. Thus the pure benzene and pure cyclohexane isotherms cross each other twice as the pressure increases. It is seen on Figure 3 that the isotherm at high coverage for the mixture does not lie between the isotherms for the pure gases. This is evidence for nonideal behavior in the adsorbed phase and will be discussed later. The other mixture isotherms, which are not drawn on Figure 3, are similar to the one shown. The cyclohexane isotherm has a positive second derivative at low pressure (Figure 2), which is considered typical of adsorption on a homogeneous surface. However, the benzene isotherm does not show the expected point of inflection below monolayer coverage, an observation that has been made before (Isirikyan and Kiselev, 1961). At high surface coverage the cyclohexane isotherm shows a weak second step indicative of the formation of a second layer of adsorbed molecules.

The experimental results for activated carbon are shown on Figure 4 (low coverage) and Figure 5 (high coverage). At low coverage the adsorption isotherms for the pure gases nearly coincide; only one of the mixture isotherms lying between this pair is drawn on Figure 4. At high coverage the benzene adsorbs considerably more strongly than cyclohexane. No hysteresis was observed up to the highest pressure studied (about $P_r = 0.9$). Although the rise of the isotherms near saturation (15.83 kPa for benzene and 16.19 kPa for cyclohexane) shows evidence of multilayer formation for filling of the larger pores, the amount of gas adsorbed at saturation (511 mg/g of benzene and 416 mg/g of cyclohexane) is fairly well defined by an extrapolation of the experimental data to $P_r = 1$. This is in contrast to the

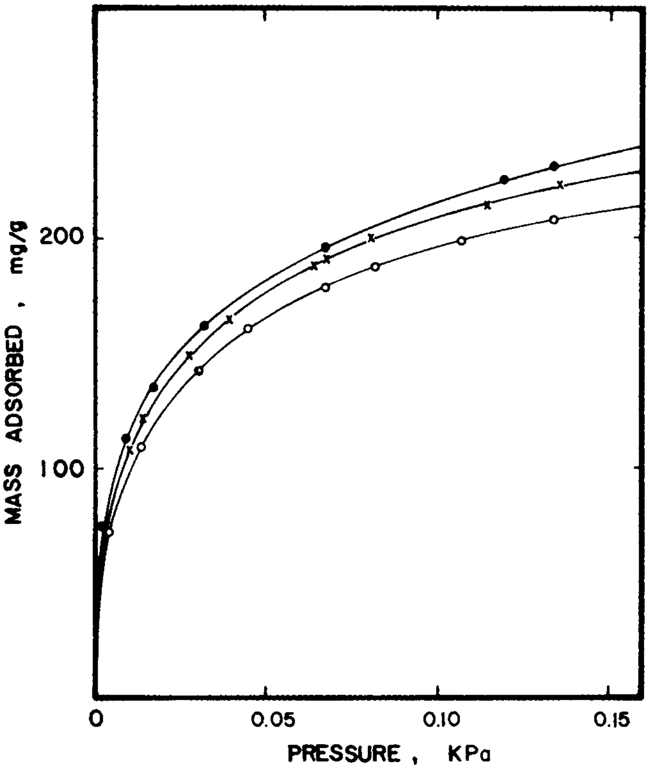

Figure 4.. Adsorption for benzene(1), cyclohexane(2) and one mixture on activated charcoal at 30°C, low pressure region. ●: pure benzene; X: $y_1 = 0.5018$; O: pure cyclohexane.

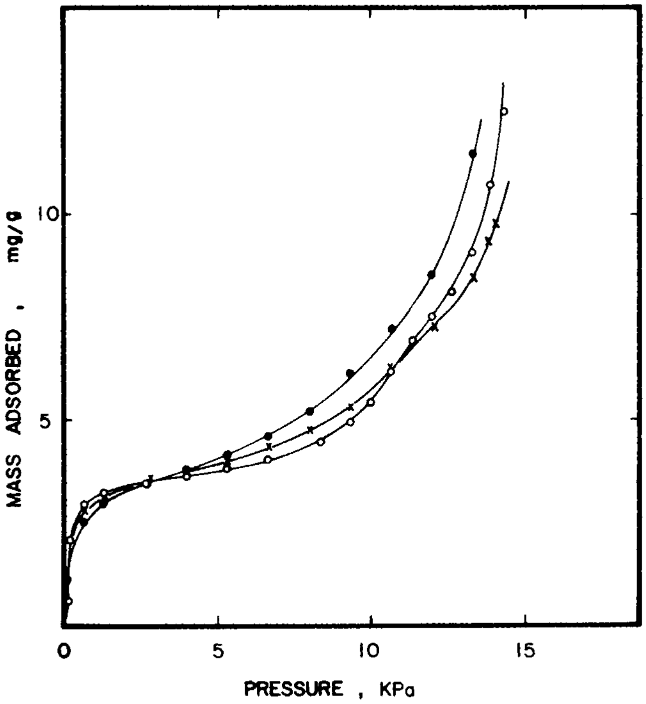

Figure 3. Adsorption for benzene(1), cyclohexane(2) and one mixture on graphitized carbon at 30°C, high pressure region. ●: pure benzene; X: $y_1 = 0.1525$; O: pure cyclohexane.

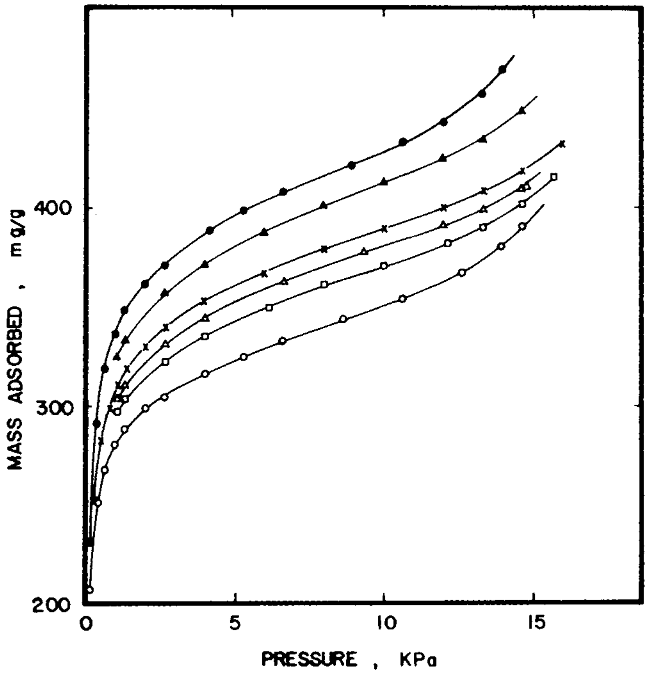

Figure 5. Adsorption for benzene(1), cyclohexane(2) and their mixtures on activated charcoal at 30°C, high pressure region. ●: pure benzene; □: $y_1 = 0.2063$; △: $y_1 = 0.3021$; X: $y_1 = 0.5018$; ▲: $y_1 = 0.7988$; O: pure cyclohexane.

adsorption on nonporous graphitized carbon, for which the amount adsorbed approaches infinity at saturation (Figure 3).

The composition of the adsorbed phase was calculated as follows. For both adsorbents, the mass of gas adsorbed per unit mass of adsorbent ($m$) was measured gravimetrically as a function of pressure ($P$) and gas phase composition ($y_1$):

$$m = m(P,y_1) \tag{1}$$

The number of moles of gas adsorbed ($n$) depends upon the molecular weight ($M$) of the adsorbed mixture:

$$n = \frac{m}{M_1x_1 + M_2(1 - x_1)} = \frac{m}{M} \tag{2}$$

The adsorbed phase composition $x_1 = x_1(P,y_1)$ was not measured experimentally, but was calculated using the thermodynamic method proposed by van Ness (1969). The calculation is based upon the Gibbs adsorption isotherm for a binary gas mixture:

$$d(\Pi A/RT) = n(x_1 d\ln Py_1 + x_2 d\ln Py_2) \tag{3}$$

This equation contains the assumption that the gas phase obeys the perfect gas law so that the fugacity of each gas may be replaced by its partial pressure ($Py_i$). The assumption is valid because the pressure does not exceed 15 kPa. Equation 3 is valid even if there are nonidealities or deviations from Raoult's law in the adsorbed phase. The partial derivatives of the Gibbs adsorption isotherm for the two independent variables ($P$ and $y_1$) are:

$$\left[\frac{\partial(\Pi A/RT)}{\partial y_1}\right]_P = n\left[\frac{x_1}{y_1} - \frac{(1 - x_1)}{(1 - y_1)}\right] \tag{4}$$

$$\left[\frac{\partial(\Pi A/RT)}{\partial P}\right]_{y_1} = \frac{n}{P} \tag{5}$$

Substitution of Eq. 2 into Eqs. 4 and 5 gives a set of first order partial differential equations which can be solved for the two unknowns, $(\Pi A/RT)$ and $x_1$. The boundary conditions are the function $(\Pi A/RT) = f(P)$ for the pure gases at $y_1 = 0$ and $y_1 = 1$ and

$$(\Pi A/RT) = 0 \ (\text{at } P = 0) \quad (0 \leq y_1 \leq 1) \tag{6}$$

The results of the calculation, details of which are given in the Appendix, are the tabulated functions:

$$x_1 = x_1(P,y_1) \tag{7}$$

$$\Pi A/RT = \Pi A/RT(P,y_1) \tag{8}$$

The adsorbed phase composition for graphitized carbon is plotted on Figure 6. The dashed line is the vapor-liquid equilibrium (VLE) curve, which exhibits an azeotrope at 48 mol % benzene. At very low coverage there is no azeotrope in the adsorbed phase; in fact, benzene adsorbs much more strongly than cyclohexane at all concentrations in the sub-monolayer region. However, the relative strength of adsorption of cyclohexane increases in the monolayer region, so that at high coverage the adsorbate-gas equilibrium rapidly approaches azeotropic conditions (the 45-degree line of Figure 6). Note that the adsorbed phase composition approaches that of the liquid phase more rapidly at high concentration of benzene, where benzene is the heavy component in both phases.

For activated carbon, the composition of the adsorbed phase does not approach the liquid composition at saturation. As shown on Figure 7, benzene is adsorbed more strongly than cyclohexane at low surface coverage. However, the preference of the charcoal for benzene increases with pressure, which is the opposite of the effect observed for graphitized carbon. The separation factor $(x_1y_2/x_2y_1)$ of benzene relative to cyclohexane increases from 1.5 at low coverage to 2.9 at high coverage. These values may be compared to a relative separation factor of 4 for graphitized carbon at low surface coverage.

### Thermodynamic Consistency

The mixture adsorption data described above are thermodynamically consistent because the adsorbed phase compositions were calculated using the Gibbs adsorption isotherm. The procedure is analogous to binary VLE measurements where the composition of the vapor is not measured, but is calculated by an integration of the Gibbs-Duhem equation.

The single vapor isotherms were tested for thermodynamic consistency with liquid adsorption data (Myers and Sircar, 1972):

$$\int_{x_1=0}^{1} \frac{n_1^e}{\gamma_1 x_1 x_2}\, d(\gamma_1 x_1) = \int_{P=0}^{P_1^s} \frac{n_1^0}{P}\, dP - \int_{P=0}^{P_2^s} \frac{n_2^0}{P}\, dP \tag{9}$$

The integral on the left-hand-side was evaluated from surface excess measurements ($n_1^e$) of adsorption from liquid solutions of mole fraction $x_1$, using standard methods (Minka and Myers, 1973). $\gamma_1$ is the activity coefficient of benzene in the liquid phase, which is known from VLE data. The integrals on the right-hand-side were evaluated using the data for the pure gas isotherms plotted on Figures 4 and 5. It was necessary to extrapolate the spreading pressure from $P_r = 0.9$ to saturation. The result of this calculation was:

$$\Delta\left(\frac{\Pi A}{RT}\right) = 5.9 \simeq 30.7 - 24.3 \text{ (mmol/g)} \tag{10}$$

These numerical results for Eq. 9 are consistent within an error of 2% for the spreading pressure integrals.

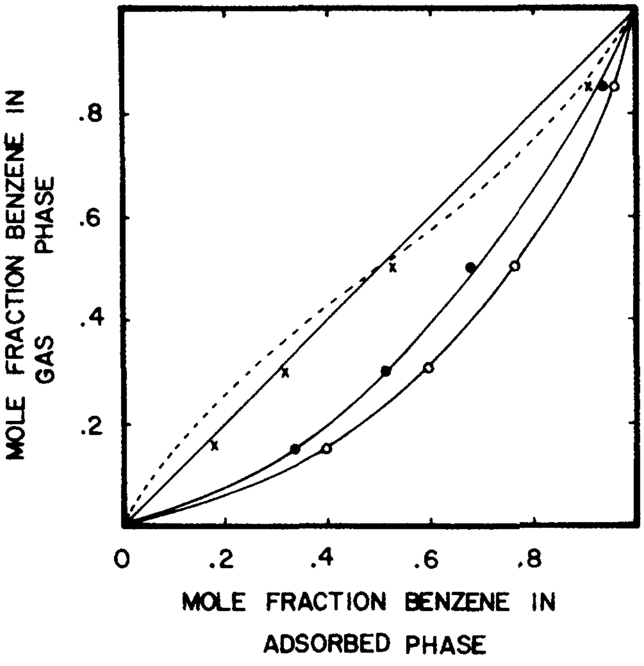

**Figure 6. Vapor-adsorbed phase equilibria of benzene and cyclohexane on graphitized carbon at 30°C. O: $P$ = 0.067 kPa; ●: $P$ = 0.133 kPa; X: $P$ = 10.7 kPa. Dashed line: VLE.**

### THEORY

Activity coefficients in the adsorbed phase ($\gamma_i$) are defined by (Myers and Prausnitz, 1965):

$$Py_1 = P_1^0\gamma_1 x_1 \tag{11}$$

$$Py_2 = P_2^0\gamma_2 x_2 \tag{12}$$

An ideal adsorbed solution (IAS) is the special case when $\gamma_i = 1$ for all components. The vapor pressures of the pure adsorbates ($P_i^0$) are measured at equal values of spreading pressure ($\Pi$) and vary from zero up to the pressure of the saturated vapor. The activity coefficients are a function of composition and can be calculated from the excess Gibbs free energy of the adsorbed phase ($\Delta g^e$):

$$\ln\gamma_i = \left[\frac{\partial(n\Delta g^e/RT)}{\partial n_i}\right]_{T,\Pi} \tag{13}$$

In addition to the variation with composition, the activity coefficients vary with spreading pressure:

$$\left[\frac{\partial(\Delta g^e/RT)}{\partial(\Pi A/RT)}\right]_{T,x_1} = \left(\frac{1}{n}\right)^e \tag{14}$$

where the excess quantity $(1/n)^e$ is defined by:

$$\left(\frac{1}{n}\right)^e = \left(\frac{1}{n}\right) - \sum_i \frac{x_i}{n_i^0} \tag{15}$$

Equation 15 is analogous to the equation for excess volume in VLE. The free energy of an adsorbed mixture should obey certain boundary conditions:

$$\lim_{P\to 0}\left(\frac{\Delta g^e}{RT}\right) = 0 \tag{16}$$

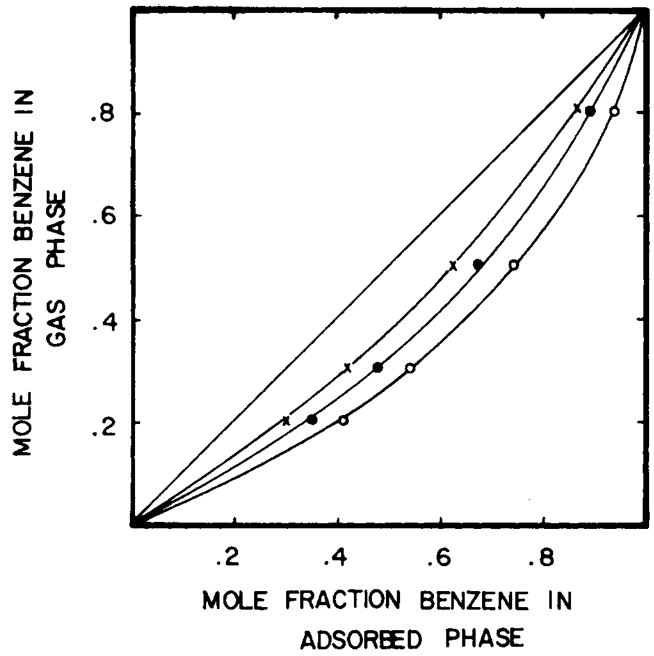

Figure 7. Vapor-adsorbed phase equilibria of benzene and cyclohexane on activated charcoal at 30°C. X: $P = 0.27$ kPa; ●: $P = 1.33$ kPa; O: $P = 13.3$ kPa.

$$\lim_{P\to P^s}\left(\frac{\Delta g^e}{RT}\right)=\left(\frac{\Delta g^e}{RT}\right)_{\text{liquid}} \tag{17}$$

Equation 16 follows from the requirement that an adsorbed solution should be ideal at the limit of zero surface coverage where the adsorbed molecules do not interact. Equation 17 applies to multilayer adsorption on nonporous adsorbents, but not necessarily to microporous adsorbents like active charcoal and molecular sieves for which the adsorbed solution at saturation may be composed of only 20 molecules.

## DISCUSSION

The experimental data were analyzed to determine the extent of nonideal behavior in the adsorbed solution. For graphitized carbon, we found that the adsorbed solution was ideal at low surface coverage and nonideal at high coverage. The experimental data can be described by the following equation:

$$\frac{\Delta g^e}{RTx_1x_2}=0.5\left[\frac{\Pi}{\Pi^{\text{sat}}}\right] \tag{18}$$

where the two spreading pressures, $\Pi$ and $\Pi^{\text{sat}}$, are measured at the same adsorbed phase composition. The value of 0.5 for $\Delta g^e/RTx_1x_2$ is that for the bulk liquid solution at 30°C. Thus, Eq. 18 obeys the limits imposed by Eqs. 16 and 17. Equation 14 applied to Eq. 18 gives a constant excess of reciprocal amount adsorbed at each composition of the adsorbed phase:

$$\left(\frac{1}{n}\right)^e=\frac{0.5}{(\Pi^{\text{sat}}A/RT)}x_1x_2 \tag{19}$$

At low surface coverage $(1/n)^e$ is negligible compared to $(1/n)$.

The mixture adsorption isotherms were calculated using Eqs. 11–13, 15, 18 and 19 and are shown on Figure 8 for high coverage at the equimolar vapor composition. At low coverage, where $\Delta g^e$ is small, the experimental data indicate that the adsorbed solution is ideal. However, at high coverage, the prediction of IAS (dashed line on Figure 8) is in poor agreement with the data. Thus the behavior of the adsorbed solution is small positive deviations from Raoult's law, which increase from zero at low coverage to the value for VLE at saturation. It is noted that the application of Eq. 18 requires VLE data but no experimental data for the adsorbed mixture.

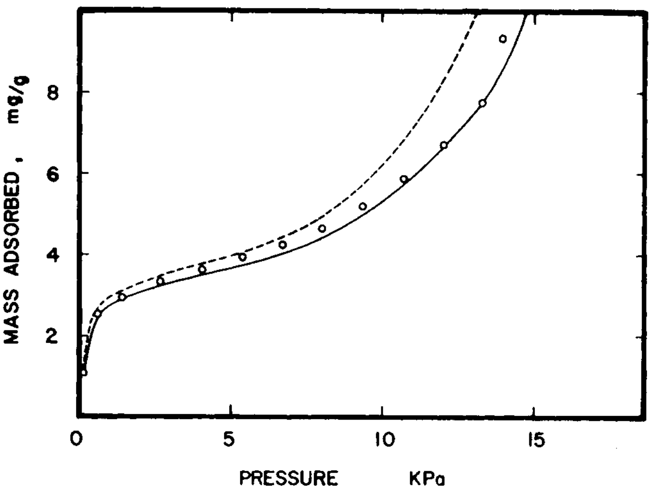

Figure 8. Prediction of adsorption isotherm for benzene and cyclohexane on graphitized carbon at 30°C. O: experimental points, $y_1 = 0.5016$; solid line: calculated by Eq. 18; dashed line: IAS.

Although we have shown only the equimolar mixture isotherm at $y_1 = 0.5016$, the other three mixture isotherms give similar results. The average absolute deviation of the predicted isotherms from the experimental data (30 points) is 3%.

For activated carbon we encounter a problem in trying to interpret the experimental data using activity coefficients. The problem is similar to that found in VLE when one component is supercritical, so that its standard state in the condensed phase is undefined. The analogy in adsorption occurs when the mixture spreading pressure is above the saturation spreading pressure of the weakly adsorbed component. In this case the standard state (adsorbate vapor pressure $P_i^0$) and the activity coefficients are undefined. This difficulty can be surmounted by defining a new standard state which is approximately equivalent to IAS at low coverage but well defined at high coverage. This new standard state (Sircar and Myers, 1973) is the reduced spreading pressure:

$$\Pi_r=\frac{\Pi}{\Pi^{\text{sat}}} \tag{20}$$

The properties of the standard state $(P_i^0, n_i^0)$ are measured at equal values of $\Pi_r$ and a "Poynting" correction is applied to the vapor pressure so that the Gibbs adsorption isotherm is satisfied:

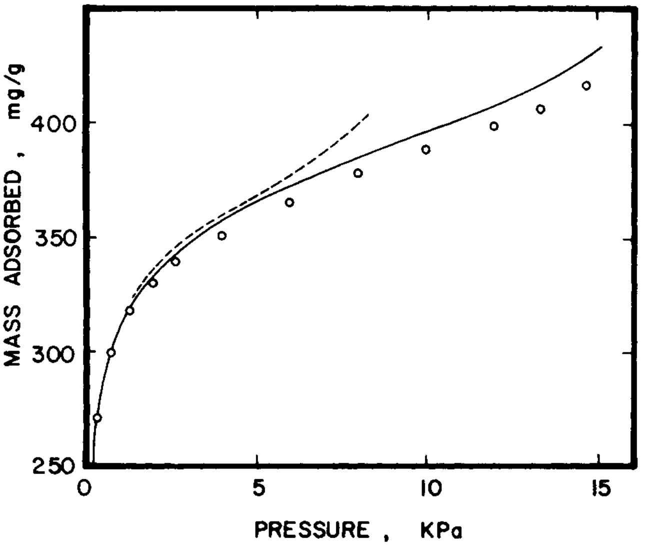

Figure 9. Prediction of adsorption isotherm for benzene and cyclohexane on activated charcoal at 30°C. O: experimental points, $y_1 = 0.5018$; dashed line: IAS, equal spreading pressures; solid line: IAS, equal reduced spreading pressures.

$$f_i^0 = P_i^0 \exp\left[\frac{(\Pi - \Pi_i^0)A}{n_i^0 RT}\right] \qquad (21)$$

where $\Pi$ is the spreading pressure of the mixture and $\Pi_i^0$, $P_i^0$ and $n_i^0$ refer to the fixed value of $\Pi_r = \Pi_i^0/\Pi_i^{sat}$ for the components of the mixture. $f_i^0$ replaces $P_i^0$ in Eqs. 11 and 12.

For activated charcoal at low coverage there is no ambiguity about the standard state and we found that the mixture data could be predicted by the usual procedures of IAS. At high coverage the standard states of equal spreading pressures are undefined when $P_r$ exceeds about 0.5, as shown by the dashed line for IAS on Figure 9. However, using the concept of equal reduced spreading pressure, we found good agreement (within 2%) of IAS with the observed data at $y = 0.5018$. The other three mixture isotherms are not plotted, but the average absolute deviation of IAS (with standard states defined by reduced spreading pressure) for 31 experimental points was 1.2%.

## NOTATION

$A$ = surface area per unit mass of adsorbent
$f_i^0$ = fugacity of $i$'th component at standard state, Eq. 21
$\Delta g^e$ = molar excess Gibbs free energy
$M$ = molecular weight of adsorbed mixture
$M_i$ = molecular weight of $i$'th component
$m$ = mass of mixture adsorbed per unit mass of adsorbent
$n$ = total moles adsorbed per unit mass of adsorbent
$n_i$ = moles of $i$'th component adsorbed per unit mass of adsorbent
$n_i^0$ = moles of $i$'th component adsorbed at standard state, per unit mass of adsorbent
$n_i^e$ = surface excess of $i$'th component per unit mass of adsorbent
$P$ = pressure
$P_r$ = reduced pressure, $P/P^s$
$P_i^s$ = vapor pressure of $i$'th component
$P_i^0$ = pressure of $i$'th component at standard state
$R$ = gas constant
$T$ = absolute temperature
$x_i$ = mole fraction of $i$'th component in adsorbed phase
$y_i$ = mole fraction of $i$'th component in gas phase

### Greek Letters

$\gamma_i$ = activity coefficient of $i$'th component
$\Pi$ = spreading pressure of adsorbed phase
$\Pi^{sat}$ = spreading pressure at saturation
$\Pi_i^0$ = spreading pressure of $i$'th component at standard state

## APPENDIX

The following equations are written for constant temperature. For an isothermal, binary mixture there are two thermodynamic degrees of freedom. The experimental data are the mass of gas adsorbed per unit mass of adsorbent ($m$) and the independent variables are pressure ($P$) and mole fraction in the vapor phase ($y_1$). Six isotherms were measured, two for the pure gases ($y_1 = 0$ and $y_1 = 1$) and four for the mixture (each at constant $y_1$). The pressure was divided into intervals as follows:

| $P$, mm Hg | $\Delta P$, mm Hg |
|---|---|
| $0 < P < 1$ | 0.1 |
| $1 < P < 10$ | 1.0 |
| $10 < P < 100$ | 10.00 |

Values of $m(P)$ at $P_i, P_{i+1} \ldots$ were obtained by a spline interpolation of the experimental data, holding $y_1$ constant. The values of the unknowns $(\Pi A/RT)$, n and $x_1$ at the pressure $P_{i+1}$ were obtained by means of simultaneous iteration on the values of $x_1$ at the four vapor compositions as follows: Given the values of $(\Pi A/RT)$, $n$ and $x_1$ from the previous iteration at $P_i$, guess values of $x_1$ at $P_{i+1}$ were used to calculate the molecular weight of the mixture in the adsorbed phase:

$$M = M_1 x_1 + M_2(1 - x_1)$$

For the first guess, the values of $x_1$ at $P_i$ are used. The spreading pressure is obtained by integration of Eq. 5:

$$\left(\frac{\Pi A}{RT}\right)_{i+1} = \int_{P_i}^{P_{i+1}} \frac{m}{MP}\, dP + \left(\frac{\Pi A}{RT}\right)_i \qquad (\text{constant } y_1)$$

The integrand is evaluated at $P_{i+1}$ and the interval $\Delta P = (P_{i+1} - P_i)$ is divided into ten parts for an integration by Simpson's rule. The ordinates at the intermediate points in the interval are obtained by a spline interpolation of the integrand $(m/MP)$ using the known values at $P_{i+1}, P_i, P_{i-1}, \ldots$ A third or fourth order polynomial is used to fit $(\Pi A/RT)$ as a function of $y_1$ at $P_{i+1}$, using four values of $(\Pi A/RT)$ for the mixture and two values for the pure gases. Then new values of $x_1$ are calculated from Eq. 4 rearranged in the form:

$$x_1 = y_1 + \frac{y_1(1 - y_1)M}{m}\left[\frac{\partial(\Pi A/RT)}{\partial y_1}\right]_{P=P_{i+1}}$$

These four values of $x_1$ at $P_{i+1}$ are compared with the previous guess values and iteration is continued until successive values agree within ±0.0001.

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