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Manuscript received February 10, 1964; revision received May 11, 1964; paper accepted May 12, 1964.

Binary Liquid-Phase Adsorption Equilibria

JOHN F. WALTER and EDWARD B. STUART

University of Pittsburgh, Pittsburgh, Pennsylvania

At present a number of empirical models exist describing binary liquid-phase adsorption equilibria. Vermeulen (*1*) reviewed a number of empirical liquid-phase correlations. Some of these correlations are analogies of common gas-phase adsorption isotherm equations, such as the Freundlich, Langmuir, and B.E.T. isotherm equations. Another correlating equation was offered by Stuart and Coull (*2*). Perhaps the most commonly used correlating equation is known as the Gibbs-Duhem isothermal-isobaric equation (*3, 4*):

$$\frac{y}{1-y} = \alpha \frac{x}{1-x} \qquad (1)$$

The relative adsorptivity is determined empirically and is sometimes assumed to be constant. Although most of these correlating equations have semitheoretical bases, they are all used empirically and for the most part do not provide insight into effects of variation in molecular properties, temperature, pore diameter, and adsorbent properties.

With the discovery by London of dispersion forces, the forces causing physical adsorption are reasonably well understood. These forces are discussed and summarized by de Boer (*5*). As de Boer shows and as will be discussed again in the following, the attractive potential energy for an adsorbate molecule to an adsorbent is proportional to the inverse cube of the separation distance. In the case of porous adsorbents, these forces are also dependent upon the pore structure, such as pore diameter or curvature, and surface composition. It is often stated that physical adsorption should be independent of the adsorbent used; this is not strictly true. Variations in the ionization poten-

J. F. Walter is presently with the Westinghouse Electric Corporation, Bettis Atomic Power Laboratory, Pittsburgh, Pennsylvania.

tial, polarizability, and number densities of various adsorbents should cause similar variations in the adsorption forces and consequently in the adsorption capacities. This type of information is generally not available for most common adsorbents.

THEORY

In the following, a model describing liquid-phase adsorption is developed, which is based on thermodynamic considerations and an approximate adsorbate-adsorbent interaction model.

This model is a quasi steady state approach based on the thermodynamic fact that at equilibrium the escape tendencies of each component in each phase are equal. This approach was initially proposed by Stuart (2); however, a more detailed description of the parameters involved leads to a different result. The initial phase of the theoretical development is the same as that of Stuart (2) and will not be reproduced here. Stuart considered the adsorbed phase to be the entire pore space. This assumes multilayer adsorption on the pore surface and filling of the remainder of each pore with a mixture whose composition is that of the outside liquid. The assumptions made in this derivation are as follows.

1. The partial molal volumes are equal to the molal volumes in each phase. This implies ideal solutions in both the adsorbed and liquid phases.
2. The adsorbent consists of cylindrical, smooth surface capillaries.
3. The liquid free volumes for both components of the liquid are equal. For hydrocarbons where Trouton's rule applies, the entropy of condensation is a constant. Frank (6, 7) showed that the free volumes of molecules having the same entropy of vaporization are equal.

From these assumptions and thermodynamic considerations of equilibrium, Stuart derived the following equation:

$$\ln\left[\frac{\frac{y}{1-y}}{\frac{x}{1-x}}\right] = \frac{2}{RT}\left[\frac{a_{iy}}{V_{iy}} - \frac{a_{jy}}{V_{jy}} - \frac{a_{ix}}{V_{ix}} + \frac{a_{jx}}{V_{jx}}\right] \quad (2)$$

The cohesive energy as defined by Hildebrand (8) is

$$E = -\frac{a}{V}$$

As is shown by Stuart (2), the cohesive energy in a cylindrical capillary of diameter D can be corrected to zero curvature (planar surface) by the relationship

$$\left(\frac{a_y}{V_y}\right)_{\text{capillary}} = \frac{a_o}{V_c}\left(\frac{D}{D-\delta}\right)^2 = E_o\left(\frac{D}{D-\delta}\right)^2 \quad (3)$$

Equation (2) becomes

$$\ln\left[\frac{\frac{y}{1-y}}{\frac{x}{1-x}}\right] = \frac{2}{RT}\left[-E_{io}\left(\frac{D}{D-\delta_i}\right)^2 + E_{jo}\left(\frac{D}{D-\delta_j}\right)^2 - \frac{a_{ix}}{V_{ix}} + \frac{a_{jx}}{V_{jx}}\right] \quad (4)$$

The term a_{ix}/V_{ix} represents the cohesive energy of molecules of component i relative to the bulk liquid phase. The following classical assumption is used:

$$a_{ix} = \sqrt{a_{ii}a_x} \quad (5)$$

The term a_x is given by

$$\sqrt{a_x} = x\sqrt{a_{ii}} + (1-x)\sqrt{a_{jj}}$$

Therefore, Equation (5) is

$$a_{ix} = \sqrt{a_{ii}a_{jj}} + (a_{ii} - \sqrt{a_{ii}a_{jj}})\,x = a_{ij} + x(a_{ii} - a_{ij}) \quad (6)$$

As is discussed by Hildebrand (9), $\sqrt{a_{ii}a_{jj}}$ is an upper limit on the magnitude of this interaction, and a closer approximation for molecules of different diameters is given by

$$a_{ij} = \left[\frac{4d_id_j}{(d_i+d_j)^2}\right]^3\sqrt{a_{ii}}\sqrt{a_{jj}} \quad (7)$$

In a similar manner a_{jx} is given by

$$a_{jx} = \sqrt{a_{jj}a_x} = a_{jj} + x(a_{ij} - a_{jj}) \quad (8)$$

Substituting Equations (6) and (8) into Equation (4), one obtains

$$\ln\left[\frac{\frac{y}{1-y}}{\frac{x}{1-x}}\right] = \frac{2}{RT}\left[-E_{io}\left(\frac{D}{D-\delta_i}\right)^2 + E_{jo}\left(\frac{D}{D-\delta_j}\right)^2 + \frac{a_{jj}}{V_{jx}} - \frac{a_{ij}}{V_{ix}} + x\left(\frac{a_{ij}}{V_{jx}} + \frac{a_{ij}}{V_{ix}} - \frac{a_{jj}}{V_{jx}} + \frac{a_{ii}}{V_{ix}}\right)\right] \quad (9)$$

The first two terms on the right-hand side of Equation (9) represent the cohesive energies of the two components in the adsorbed phase. These energies will now be related to a molecular potential energy model.

For nonpolar molecules the potential energy of interaction is given by

$$\phi(r) = \frac{B'}{r^{12}} - \frac{C'}{r^6} - \frac{D'}{r^8} - \frac{E'}{r^{10}} \quad (10)$$

The first term represents the very strong short range repulsion force which arises from the interpenetration of electronic clouds. The second term is due to induced dipole dispersion effects; the third term is due to induced dipole-induced quadrupole, and the fourth term is due to induced quadrupole-induced quadrupole dispersion effects. Since, in the range of distance r associated with adsorption, the first and last two terms counterbalance each other, a common approximation (5) is to write

$$\phi(r) = \frac{C_i'}{r^6} \quad (11)$$

Equation (11) represents the interaction between one adsorbate molecule and one molecule of adsorbent. In order to obtain the attractive energy $\phi(r)$ between one molecule of adsobate and all the molecules of an adsorbent, the individual adsorbent molecule contributions are summed. As is discussed by Polyanyi and London (10), this summation may be approximated for a plane surface by integration to obtain the following:

$$\phi(r) = -\frac{N_g\,\pi\,C_i'}{6r^3} \quad (12)$$

Equation (12), therefore, represents the potential energy of a single adsorbate molecule relative to an infinite planar adsorbent of number density N_g in molecules per cubic centimeters. In Equation (12) C_i' is related to the

polarizabilities and characteristic optical dispersion frequencies of the component i and the adsorbent molecules. Since these quantities are not generally known for the adsorbent, C_i' must be approximated. When a molecule of component i is adsorbed on an adsorbent molecule, the energy evolved is given by

$$\Delta H_{ai} = \frac{C_i'}{\delta_m^6} \tag{13}$$

Similarly, when a molecule of component i condenses to another molecule of component i, the heat evolved (heat of condensation) is

$$\Delta H_{Li} = \frac{C_i}{\delta_m^6} \tag{14}$$

With the assumption that the minimum distances of approach for adsorption and condensation are the same, C_i' can be written as

$$C_i' = C_i \frac{\Delta H_{ai}}{\Delta H_{Li}} \tag{15}$$

Although it has been assumed that the minimum distance of approach for the adsorbed and condensed phases are equal, if Equation (15) included a ratio of minimum distances of approach to the sixth power, both components should have such a correction. As indicated in Equation (4), the cohesive energy difference is involved, and these corrections would tend to offset one another. In addition C_i may be written in terms of the pure liquid component van der Waals constant a_{ii} as follows:

$$a_{ii} = 2\pi N^2 \int_{\delta_i}^{\infty} \frac{C_i}{r^6} r^2\, dr = \frac{2\pi}{3} \frac{N^2 C_i}{\delta_i^3} \tag{16}$$

Therefore, Equation (15) may be expressed as

$$C_i' = \frac{3}{2} \frac{a_{ii}}{\pi N^2} \delta_i^3 \frac{\Delta H_{ai}}{\Delta H_{Li}} \tag{17}$$

Equation (12) becomes

$$\phi(r) = -\frac{a_{ii}}{4N^2} N_g (\delta_i)^3 \frac{\Delta H_{ai}}{\Delta H_{Li}} \left(\frac{1}{r^3}\right) \tag{18}$$

Consider an arbitrary surface σ of the adsorbent. In a unimolecular layer on this surface, the number of component i molecules which could be adsorbed is σ/σ_i, where σ_i is the area of one molecule of component i. The energy associated with one of these molecules in the first layer is

$$\phi_i^1 = -\frac{a_{ii} N_g}{4N^2} \frac{\Delta H_{ai}}{\Delta H_{Li}} \frac{\sigma}{\sigma_i} \tag{19}$$

This result does not include a term for the energy contribution due to adsorbate-adsorbate interaction since, as is shown in Equation (4), the cohesive energy difference is involved, and this interaction term tends to cancel.

With the assumption of a closely packed arrangement of spherical molecules, the distance from the surface to the second layer is $\delta_i + 0.707\ \delta_i$. The energy associated with one of these molecules in the second layer is

$$\sigma_i^2 = -\frac{a_{ii} N_g}{4N^2} \frac{\Delta H_{ai}}{\Delta H_{Li}} \frac{\sigma}{\sigma_i} \left(\frac{1}{1 + 0.707}\right)^3 \tag{20}$$

In the n^{th} layer, the energy is

$$\sigma_i^n = -\frac{a_{ii} N_g}{4N^2} \frac{\Delta H_{ai}}{\Delta H_{Li}} \frac{\sigma}{\sigma_i} \left(\frac{1}{1 + 0.707\ (n-1)}\right)^3 \tag{21}$$

The cohesive energy per mole of adsorbate on the arbitrary surface σ is, therefore

$$E_{io} = N \sum_{n=1}^{\infty} \phi_i^n = -\frac{a_{ii} N_g}{4N} \frac{\Delta H_{ai}}{\Delta H_{Li}} \frac{\sigma}{\sigma_i} \sum_{n=1}^{\infty} \left(\frac{1}{1 + 0.707\ (n-1)}\right)^3 \tag{22}$$

This latter summation converges to 1.353. Therefore, Equation (22) becomes

$$E_{io} = -0.3382 \frac{a_{ii} N_g}{N} \frac{\sigma}{\sigma_i} \frac{\Delta H_{ai}}{\Delta H_{Li}} \tag{23}$$

Similarly for component j, the cohesive energy is

$$E_{jo} = -0.3382 \frac{a_{jj} N_g}{N} \frac{\sigma}{\sigma_j} \frac{\Delta H_{aj}}{\Delta H_{Lj}} \tag{24}$$

Substituting Equations (23) and (24) into Equation (9), one obtains

$$\ln \left[\frac{\frac{y}{1-y}}{\frac{x}{1-x}}\right] = \frac{2}{RT}\left[0.3382 \frac{N_g}{N}\left(a_{ii} \frac{\sigma}{\sigma_i} \frac{\Delta H_{ai}}{\Delta H_{Li}} \left(\frac{D}{D-\delta_i}\right)^2 - a_{jj} \frac{\sigma}{\sigma_j} \frac{\Delta H_{aj}}{\Delta H_{Lj}} \left(\frac{D}{D-\delta_j}\right)^2\right) + \frac{a_{jj}}{V_{jx}} - \frac{a_{ij}}{V_{ix}} + x\left(\frac{a_{ij}}{V_{jx}} + \frac{a_{ij}}{V_{ix}} - \frac{a_{jj}}{V_{jx}} - \frac{a_{ii}}{V_{ix}}\right)\right] \tag{25}$$

When one chooses the arbitrary area σ as the cross-sectional area of component i and writes $\rho_i = 1/V_i$, Equation (25) becomes

$$\ln \left[\frac{\frac{y}{1-y}}{\frac{x}{1-x}}\right] = \frac{2}{RT}\left[0.3382 \frac{N_g}{N}\left(a_{ii} \frac{\Delta H_{ai}}{\Delta H_{Li}} \left(\frac{D}{D-\delta_i}\right)^2 - a_{jj} \frac{d_i^2}{d_j^2} \frac{\Delta H_{aj}}{\Delta H_{Lj}} \left(\frac{D}{D-\delta_j}\right)^2\right) + a_{jj} \rho_j - a_{ij} \rho_i + x\,(a_{ij} \rho_j + a_{ij} \rho_i - a_{ii} \rho_i - a_{jj} \rho_j)\right] \tag{26}$$

When one factors out ρ_i, Equation (26) can be written as

$$\ln \left[\frac{\frac{y}{1-y}}{\frac{x}{1-x}}\right] = \frac{2\rho_i}{RT}\left[0.3382 \frac{N_g}{N\rho_i}\left(a_{ii} \frac{\Delta H_{ai}}{\Delta H_{Li}} \left(\frac{D}{D-\delta_i}\right)^2 - a_{jj} \frac{d_i^2}{d_j^2} \frac{\Delta H_{aj}}{\Delta H_{Li}} \left(\frac{D}{D-\delta_j}\right)^2\right) + B + Cx\right] \tag{27}$$

where

$$B = a_{jj}\,(\rho_j/\rho_i) - a_{ij}$$

$$C = a_{ij}\,(1 + \rho_j/\rho_i) - a_{ii} - a_{jj}\,(\rho_j/\rho_i)$$

For binary systems with molecular diameters which are small when compared with the pore diameter D, Equation (27) can be reduced to

$$\ln \left[\frac{\frac{y}{1-y}}{\frac{x}{1-x}}\right] = \frac{2\rho_i}{RT}\left[\frac{A}{\rho_i} + B + Cx\right] \tag{28}$$

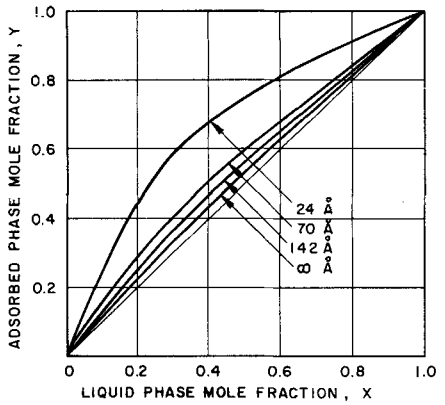


Fig. 1. Effect of variation of pore diameter. Benzene-cyclohexane system on silica gel at 25°C.

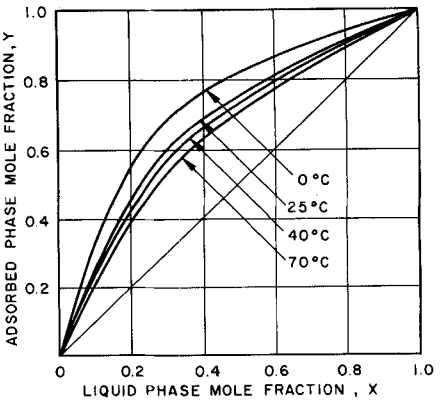


Fig. 3. Effect of variation of adsorption temperature. Benzene-cyclohexane system on silica gel. Pore diameter is 24Å.

where

$$A = 0.3382 \frac{N_g}{N} \left(\frac{D}{D - \delta_{avg}} \right)^2 \left[a_{ii} \frac{\Delta H_{ai}}{\Delta H_{Li}} - a_{jj} \frac{d_i^2}{d_j^2} \frac{\Delta H_{aj}}{\Delta H_{Lj}} \right] = \left(\frac{D}{D - \delta_{avg}} \right)^2 A_\infty$$

$$\delta_{avg} = \frac{\delta_i + \delta_j}{2}$$

For many binary systems, the ratio ρ_j/ρ_i shows little or no variation with temperature. In addition, the van der Waals constants a_{ii} and a_{jj} show a small decrease with increase in temperature. Since B and C in Equation (28) involve differences in the van der Waals constants and molal density ratios, these constants would show negligible variation with temperature over a reasonable temperature range.

Interestingly, this model gives the isothermal-isobaric Gibbs-Duhem equation

$$\frac{y}{1-y} = \alpha \frac{x}{1-x}$$

where α is given by

$$e^{\frac{2\rho_i}{RT}\left[\frac{A}{\rho_i} + B + Cx\right]}$$

As stated earlier, the relative adsorptivity α was found empirically to be constant in some cases and was a function of the liquid concentration in other cases. If the relative adsorptivity is constant, a log-log plot of $y/1 - y$ vs. $x/1 - x$ should give a straight line with slope 1 and intercept log α. The equation developed above includes this situation as a special case (that is, $C = 0$) but also permits other shapes to the log $y/1 - y$ vs. log $x/1 - x$ curves depending entirely on the liquid properties.

COMPARISON OF THEORETICAL PREDICTIONS AND EXPERIMENTAL DATA

In order to test and demonstrate further the usefulness of the theoretical model developed above, theoretical predictions for the benzene-cyclohexane-silica gel and for the isooctane-toluene-silica gel and silica-alumina systems are discussed in this section. In the first subsection, the effects of varying pore diameter, heat of benzene adsorption, and temperature are predicted for the benzene-cyclohexane silica gel system. In addition, a comparison of experimental data and a predicted equilibrium curve is made. In the second subsection, similar predictions for the isooctane-toluene-silica-alumina and silica gel systems are tested against experimental equilibrium data.

Benzene-Cyclohexane-Silica Gel Predictions

In Figures 1, 2, and 3, the effects of variation of pore diameter, average heat of benzene adsorption, and adsorption temperature are shown. These predictions are based on Equation (28) and the literature data summarized in the description of parameter.

In Figure 1, the effect of variation in pore diameter for the benzene-cyclohexane system adsorbed on hydrated silica gel is shown. Investigation of Equation (28) reveals that the existence of an azeotrope (compositions of both phases are equal) may be determined by the pore diameter. That is when

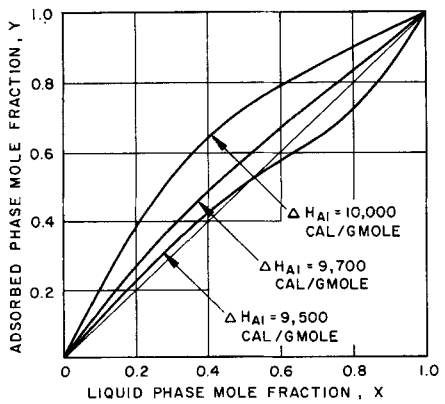


Fig. 2. Effect of variation of average heat of benzene adsorption. Benzene-cyclohexane system on silica gel at 25°C. Pore diameter is 70Å. ΔH_{AJ} = 8,860 cal./g. mole.

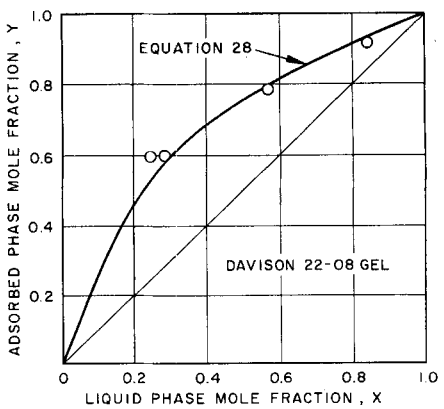


Fig. 4. Comparison of predicted and measured data of Mair (4). Benzene-cyclohexane system on silica gel at 25°C.

Table 1. Adsorbent Parameters for Data of Eagle and Scott (3) and Mair (4)

Adsorbent identif.	Manuf.	Composition	Pore volume, ml./g.	sq. m./g.	Pore diameter, Å.
SA-4	Socony	9% alumina	0.395	388	40.7
1	Davison	Silica gel	0.350	630	22.2
22-08	Davison	Silica gel	0.430	700	24.0

$$\left(\frac{D}{D-\delta_{avg}}\right)^2 \frac{A_\infty}{\rho i} = -B - Cx_a$$

or

$$x_a = \left(\frac{D}{D-\delta_{avg}}\right)^2 \frac{A_\infty}{\rho i\, C} + \frac{B}{C}$$

x_a = azeotropic composition

an azeotrope will exist. The values of A_∞, B, and C may be such that x_a might have a value between 0 and 1.0 depending upon D. For the benzene-cyclohexane-hydrated silica gel system, the values of A_∞, B, and C in Equation (28) are such that no azeotrope is predicted. The effect of surface hydroxyl group concentration on the average heat of adsorption is much more pronounced. Since hydrogen bonding is postulated (*24*) for the unsaturated cyclic hydrocarbons such as benzene, the result of a constant cyclohexane heat of adsorption and varying benzene average heats of adsorption is presented. The profound effect of a small change in the average benzene heat of adsorption is shown in Figure 2. The center curve for ΔH_{ai} = 9,700 cal./g. mole represents the literature prediction for hydrated silica gel. In this figure a change of 500 cal./g. mole results in a change from very marked benzene adsorption to an azeotrope with rather marked cyclohexane adsorption. In Figure 3, increase in adsorption temperature results in less selective adsorption. This result has been generally observed. Benzene-cyclohexane-silica gel predictions were prepared for the adsorption data of Mair (*4*). The prediction and data points of Mair are shown in Figure 4. Mair's silica gel had an average pore diameter of 24 Å. The remainder of the literature data used in this prediction are listed in Table 1.

Isooctane-Toluene-Silica-Alumina or Silica Gel Predictions

One of the assumptions used in the derivation of Equation (28) was that the partial molal volumes of two components equaled the mole volumes. This assumption strongly implies that the solution of the two components must be ideal. Since isooctane and toluene form a typical nonideal system (*11*), the isooctane-toluene adsorption equilibria on silica gel and silica-alumina adsorbents were predicted in order to demonstrate further the usefulness of Equation (28). Eagle and Scott (3) measured the equilibrium adsorption at 23.9°C. for isooctane-toluene on a sample of silica gel and on a silica-alumina sample (9% alumina, 91% silica gel). The adsorbent parameters were measured by butane adsorption and were corrected to nitrogen isotherms by Stuart and Coull (2). These adsorbent parameters are listed in Table 1.

Table 2. Toluene-Isooctane System

Parameter	Isooctane value	Toluene value	Source
$a\left(\frac{\text{cal. cc.}}{\text{mole g. sq.}}\right)$	19.37×10^4	16.37×10^4	computed from the critical temperature and pressure
T_c (°C.)	271.2	320.8	(*12*)
P_c (atm.)	25.5	41.6	(*12*)
ρ (g./ml.)	0.6926	0.8611	(*13*)
d_i (Å.)	6.89	—	(*14*)
d_j (Å.)	—	5.38	(*15*)
$\Delta H_a \frac{\text{K. cal.}}{\text{g. mole}}$	12.7	—	(*16*)
$\Delta H_a \frac{\text{K. cal.}}{\text{g. mole}}$	—	12.9	(*17*)
$\Delta H_a \frac{\text{K. cal.}}{\text{g. mole}}$	8.395	9.079	(*18*)

Table 3. Mole Density in Gram-Moles Per Cubic Centimeter

Temp., °C.	C_6H_6	C_6H_{12}	Source
0	0.0115	0.00949	(*25*) and molecular weights
25	0.0112	0.00923	
40	0.0110	0.00906	
70	0.0106	0.00875	

The literature values of the necessary parameters for the isooctane-toluene system are listed in Table 2.

In the prediction for the silica gel sample (Davison 1) a surface molecular weight of the gel of 69.07 (see descriptive parameters) was assumed. In the prediction for the silica-alumina system, the adsorbent was assumed to be 91% silica gel (molecular weight 69.07) and 9% alumina in the form aluminum oxide · $3H_2O$ (molecular weight 155.99). This latter molecular form for alumina is suggested by Weiser (*19*). The heats of adsorption listed in Table 2 are for silica gel. These same values were used in the prediction for the silica-alumina adsorbent. The predictions, y vs. x curves, for these two adsorbents and isooctane-toluene are shown in Figure 5. The prediction for the silica-alumina adsorbent shows the greatest deviation from the experimental data. However, considering the inconsistencies of the literature data for this adsorbent, the agreement is considered satisfactory.

DISCUSSION

The agreement between the predicted and measured isooctane-toluene isotherms (Figure 5) is, perhaps, much better than should be expected for this typically nonideal system. In addition, the agreement between the predictions and the adsorption data of Mair is again better than one might expect from the assumptions and simplifications made in the development of this model. Such assumptions as ideal solutions in both phases, no adsorbate-adsorbate interaction, and the approximations associated with the interaction potential model should perhaps lead to only qualitative results. This in itself would be a distinct ad-

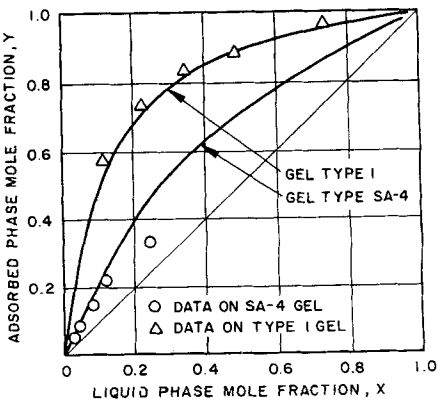


Fig. 5. Comparison of predicted and measured data of Eagle and Scott (3). Toluene-isooctane on gel samples at 23.9°C.

vantage, in that prediction of the effects of changes in various parameters, such as temperature, pore diameter, heat of adsorption, etc., could be made. In addition the form of an empirical correlation (two constant without the temperature effect, three constant with the temperature effect) is suggested. However, the agreement between pure predictions and measured data strongly suggested that the limitations of the deriving assumptions and approximations are minimized. This conclusion appears quite reasonable when it is noticed that the theoretical model involves the differences of the adsorbed-phase cohesive energies for the two components. Thus, the errors introduced by neglecting adsorbate-adsorbate interaction, by assuming ideal solutions, and by simplifying the molecular interaction potentials tend to negate one another.

CONCLUSION

Equation (28) is proposed to predict binary, liquid-phase, adsorption equilibria. This equation includes the effects of the molecular parameters pertinent to binary, liquid-phase adsorption in cylindrical smooth pore adsorbents. These parameters are: adsorbent properties, pore diameter, adsorbent composition; adsorbate properties, heats of adsorption, molecular diameters, intermolecular forces, density; temperature; liquid-phase concentration. The results of this testing are sufficiently good to suggest further testing of this model on other adsorbate-adsorbent systems. Even if this model is not entirely successful in predicting binary, liquid, adsorption equilibria for some system, it would still suggest a useful empirical form. In addition, the use of this model empirically would permit extrapolation of adsorption data with variation in temperature, pore diameter, heat of adsorption, etc.

DESCRIPTION OF ADSORBENT AND ADSORBATE PARAMETERS FOR THE BENZENE-CYCLOHEXANE-SILICA GEL SYSTEM

The Minimum Distance of Approach δ

Van Voorhes (20) measured the adsorbed monolayer thickness of benzene and cyclohexane as 2.9 and 2.4 Å, respectively. However, several adsorbed layers will exist. Equation (22) represents the summation of the contributions of the various layers to the overall cohesive energy. The series in Equation (22) converges to a value of 1.353. This implies that the adsorbate acts, on the average, as if it were at a distance from the surface of 1.353 times the monolayer thickness. Therefore

$$\delta = 1.353 \times (\text{monolayer thickness})$$

Thus, δ for benzene and cyclohexane, respectively, are 3.9 and 3.2 Å. The value of δ_{avg} is, therefore, 3.6 Å.

Silica Gel Number Density

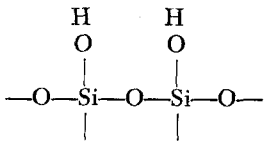
The adsorbent number density is difficult to establish. This number density (molecules per cubic centimeters) is given by

$$N_g = \frac{(\text{adsorbent density}) \times (\text{Avagadro's number})}{\text{adsorbent molecular weight}}$$

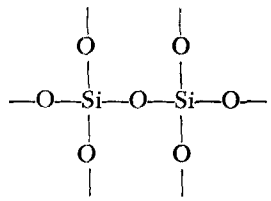
TABLE 4. LITERATURE VALUES OF MOLECULAR DIAMETERS DIAMETER IN ANGSTROM UNITS.

C_6H_6 Component i	C_6H_{12} Component j		Reference
5.7	6.1		(27)
5.3	6.1		(28)
5.5	6.1	average values	

Silica gel has an absolute density of 2.2 g./cu. cm. (references 21 and 22). The molecular weight of silica gel is more difficult to define. At the surface of the silica gel both Iler (23) and Kiselev (24) conclude that the surface is completely covered with hydroxyl groups as follows:



This gives a surface molecular form which is $SiO_2 \cdot (1/2H_2O)$ (molecular weight 69.07). Iler (23) concludes that the bulk structure of silica gel is composed of continuous bonds of the following type:



This would suggest that the molecular form of the gel is SiO_2 (effective molecular weight 60.06). When one considers the proximity of the surface to the adsorbate, the surface composition probably dominates. Therefore, the molecular weight of hydrated silica gel is assumed to be 69.07.

Heats of Adsorption and Liquefaction

The average heat of adsorption ΔH_a is proportional to the square root of the heat of condensation ΔH_L or

$$\Delta H_a = k\sqrt{\Delta H_L}$$

Furthermore, from Trouton's principle (26) the latent heat of condensation can be expressed as a linear function of temperature over a small region of temperature. By using the heat of condensation data for benzene and cyclohexane given in reference 18, the following linear equations for the variation of heat of condensation with temperature are obtained:

$$\Delta H_L = 12{,}026 - 13.35T \text{ (Benzene)}$$

$$\Delta H_L = 11{,}271 - 11.38T \text{ (Cyclohexane)}$$

Therefore, the ratio of the average heat of adsorption to the heat of condensation is given by

$$\frac{\Delta H_{ai}}{\Delta H_{Li}} = \frac{k_1}{\sqrt{12{,}026 - 13.35T}} \quad \text{(Benzene)}$$

$$\frac{\Delta H_{aj}}{\Delta H_{Lj}} = \frac{k_2}{\sqrt{11{,}271 - 11.38T}} \quad \text{(Cyclohexane)}$$

The constants k_1 and k_2 can be evaluated from the heat of adsorption at one temperature. Van Voorhes (28) measured the heats of wetting of 1,740 and 1,000 cal./g. mole for benzene and cyclohexane, respectively, on silica powder at 26°C. Since Van Voorhes reported a pore diameter of 236 Å. based on a Kelvin radius from nitrogen adsorption, his diameters were corrected to an equivalent cylindrical volume-area diameter of 191 Å. This reduction in diameters was typical for Kelvin vs. cylindrical volume-area measurements for similar silicas. These heats of wetting, or average net heats of adsorption, were corrected to zero curvature with the diameter correction as in Equation (3).

TABLE 5. VAN DER WAALS CONSTANT, a, IN CALORIES-CUBIC CENTIMETERS PER GRAM-MOLES SQUARED $\times 10^{-4}$

Temp., °C.	van der Waals Constant C_6H_6	van der Waals Constant C_6H_{12}	Source
0	68.41	80.37	extrapolated from data at 25° and 40°C.
25	67.04	79.25	(29)
40	66.22	78.52	(29)
70	65.00	76.78	(29)
25	64.43	71.58	(30)
T_c & P_c	45.4	52.0	(31)

The above values were calculated from experimental data at the temperatures indicated. The last listing was obtained from the critical pressures and temperatures and are included for comparative purposes only.

By adding the heat of liquefaction at 26°C. to these heats of wetting, the corrected average heats of adsorption at zero curvature of benzene and cyclohexane at 26°C. are determined to be 9,680 and 8,860 cal./g. mole, respectively. With the average heats of adsorption used to evaluate k_1 and k_2, the following are obtained:

$$\frac{\Delta H_{ai}}{\Delta H_{Li}} = \frac{108}{\sqrt{12{,}026 - 13.35T}} \quad \text{(Benzene)}$$

$$\frac{\Delta H_{aj}}{\Delta H_{Li}} = \frac{99.5}{\sqrt{11{,}271 - 11.38T}} \quad \text{(Cyclohexane)}$$

The Molecular Diameters

The molecular diameters for benzene and cyclohexane obtained from the literature are given in Table 4.

The molecular diameters appear in Equation (28) as the ratio of their squares. This term arose from consideration of the ratios of the apparent areas of benzene to cyclohexane. With the average values of the data in Table 4, the ratio of the squares is

$$\left(\frac{d_i}{d_j}\right)^2 = 0.8129$$

The van der Waals Force Constants

In Table 5 the van der Waals force constants for benzene and cyclohexane are computed from literature data.

NOTATION

a = van der Waals force constant
D = pore diameter in Å.
d = molecular diameter in Å.
E = cohesive energy in cal./g. mole
ΔH_a = average heat of adsorption in cal./g. mole, the average heat of adsorption is defined as the heat of wetting plus the heat of condensation
ΔH_L = heat of liquefaction in cal./g. mole
N = Avogadros number
N_g = number density of the adsorbent in molecules/cc.
n = number of adsorbed layers
R = gas constant
r = distance between interacting molecules or adsorbate molecule and surface in Å.
T = absolute temperature in °K.
V = molal volume in cc./g. mole or capillary volume when with subscript c
x = mole fraction of component i in the liquid phase
y = mole fraction of component i in the adsorbed phase (pore space)
α = relative absorptivity
ρ = molal density in g. mole/cc.
σ = an area in Å.^{2}
δ = minimum distance of aproach in Å.

Subscripts

i = component i
j = component j
x = bulk liquid phase
y = adsorbed phase (pore space)
o = planar surface
c = capillary space
∞ = planar surface

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Manuscript received September 30, 1963; revision received March 19, 1964; paper accepted March 20, 1964.