Liquid-phase Adsorption Equilibria

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A correlating equation for liquid-phase adsorption equilibria, including the effects of temperature and pore diameter, is presented, together with a derivation of the equation ascribing the equilibration process of physical adsorption to van der Waal's forces. The derivation is based on the effect of temperature and surface configuration on the concentration of adsorbate at the surface. The correlating equation was tested with experimental data for the benzene-cyclohexane-silica-gel system and the toluene-isooctane–silica-gel system. Temperatures ranged between 23.9° and 99°C. and the pore diameters between 20.7 and 149.5 Å.

Equilibrium data are unimportant in the design of percolation or contact adsorption equipment, and in decolorizing solutions the low concentration of the component to be removed allows the use of excess adsorbent, but with the advent of countercurrent liquid-phase contacting as described by Eagle and Scott (*9*), a greater need exists for more liquid-phase–equilibrium data.

Karnofsky (*18*) has suggested that the design of an adsorption percolation or chromatographic column may be based on the concentrations in the pores or immobile phase as a function of liquid concentrations. Mair (*23*) has correlated static equilibrium data with kinetic data in a packed column for a number of hydrocarbon binary solutions. Weatherford (*30*), using static equilibrium data, has predicted the concentrations of effluents in the chromatographic separation of a benzene-cyclohexane mixture on alumina.

Eagle and Scott (*10*), reporting on equilibrium data used on a mixture of aromatic and kerosene distillates, found that this polycomponent system could be treated as a simple binary system, in the design of adsorption columns for separating aromatics from nonaromatics, similar to the key-component method used in polycomponent–distillation-column design.

EFFECT OF TEMPERATURE AND SURFACE CONFIGURATION

From a chemical engineering viewpoint, fundamental theories on phase equilibria are useful in that they reduce the amount of experimental data needed for design calculations. It is sufficient but not necessary that the theory describe the mechanism of equilibration. A contribution to engineering adsorption theory could be made if the effect of one or more of the variables could be correlated for liquid-phase selective adsorption.

The Brunauer-Emmett-Teller equation has been very successful in representing the adsorption of single gases and vapors (*5*). Lewis and others (*20*) have correlated vapor-phase adsorption capacities for a binary system with the adsorption capacities of the pure components, and a correlation of liquid-phase adsorption capacity with nitrogen or butane surface areas has been presented by Rescorla (*29*) and Mair (*22*). The latter work, which was intended to facilitate surface-area measurements, is based on a single temperature and a constant concentration of the starting binary solution.

To aid in the design of fractionation equipment, it would be desirable to be able to estimate the effect of the operating variables of temperature, pressure, and adsorbent properties. The intrinsic pressures in a liquid are very large compared with the operating-pressure variation; consequently the effect of pressure was not studied. The two variables chosen were surface configuration and temperature.

Silica gel was chosen as the adsorbent because its high adsorption capacity and industrial importance (*9, 10, 15, 21, 23*) increase the usefulness of equilibrium data based on it. Three commercial types of silica gel were studied: Davison 912, 922, and 70. Gels 912 and 922 differed only in their particular size range; gel 70 had a larger average pore diameter.

The choice of a liquid binary was based partially on industrial interest in aromatic-nonaromatic separation (*9, 10, 15, 23*). The benzene-cyclohexane system has the additional advantage of having similar molecular dimensions, which decreases the problem of selectivity by a screening effect alone.

Since the range of data was limited, the correlating equation presented here was checked by supplementary data from the literature. The experimental data were taken at three temperatures, 33°, 52.6°, and 77°C., three different silica gels with two average pore diameters being used, for the complete concentration range of a benzene-cyclohexane binary solution. The literature data used included four isotherms from 23.9° to 99°C., two additional silica gels and a silica-alumina gel, and the toluene-isooctane system.

PRESENT THEORIES ON ADSORPTION

The adsorption of a vapor increases with pressure at constant temperature, and at a high temperature the volume adsorbed is small since the adsorption process is exothermic. When both the adsorbed volume and pressure are low, an equation analogous to Henry's Law will represent the data, and so

$$G' = kp \qquad (1)$$

At higher adsorption capacities the volume adsorbed is a power function of the pressure and is expressed as

TABLE 1

SUMMARY OF ADSORBENT PROPERTIES AND CORRELATING CONSTANTS

Adsorbent type	Adsorbent source	Pore Volume cc./g.	Surface Area sq. m./g.	Pore Diam., D Å	Mesh Size	ξ	d Å	k °K	ψ °K	Lit. cited
				Benzene-cyclohexane system						
912	Davison	0.429	698.8	24.6	28–200	5.92	14.5	54.2	77.5	This Work
922	Davison	0.429	698.8	24.6	-200	5.92	14.5	54.2	77.5	This Work
70	Davison	1.088	290	149.5	24–250	1.22	14.5	54.2	77.5	This Work
22–08 (a)	Davison	0.43	700	24	-200	6.39	14.5	54.2	77.5	*23*
1 (b)	Davison	0.350	630	22.2	28–200	8.32	14.5	54.2	77.5	*10*
				Toluene-isooctane system						
61 (b)	California Res.	0.304	587	20.7	10–14	11.15	14.5	54.2	31.0	*10*
1 (b)	Davison	0.350	630	22.2	28–200	8.32	14.5	54.2	31.0	*10*
SA-4 (b)	Socony	0.395	388	40.7	6–10	2.41	14.5	54.2	31.0	*10*

(a) This gel is equivalent to Davison No. 922.

(b) Pore volumes and surface areas originally obtained from butane isotherms are corrected to nitrogen values to correspond to gels 922, 912, and 70.

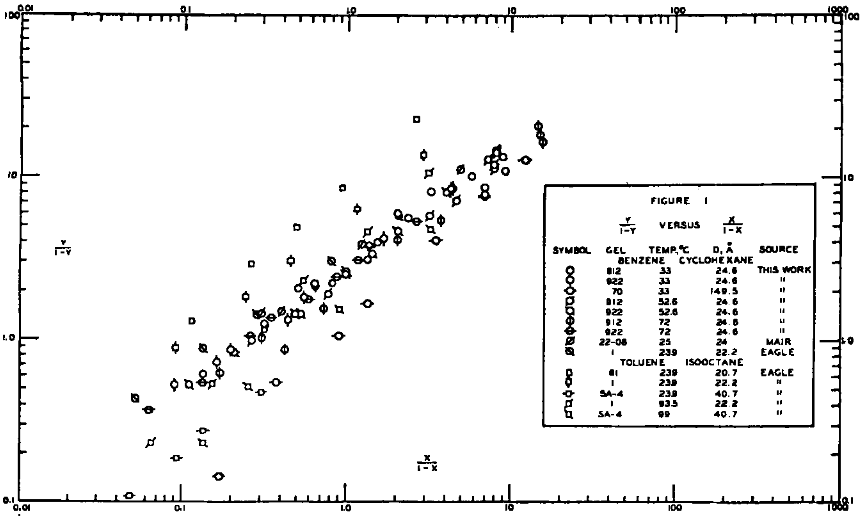

Fig. 1—Experimental data showing mole ratio in adsorbed phase vs. mole ratio in bulk phase.

$$G' = k'p^{1/n} \tag{2}$$

where n is greater than 1. Equation (2) was developed by Freundlich (*14, 25*) and when obeyed by the system is quite useful for engineering calculations because of its simplicity. It can be used to correlate data from a liquid-phase adsorption process when used in the following form

$$G = k'x^{1/n'} \tag{3}$$

Zeldowitsch (*32*) added flexibility to the vapor-phase Freundlich Equation (2) by empirically representing the constants k' and n as functions of temperature:

$$\frac{1}{n} = \frac{T}{T_F} : \log k' = b_1T + b_2 \tag{4}$$

where T is the temperature of adsorption and T_F a limiting temperature. Above T_F

$$\frac{1}{n} = 1 : \log k' = b_3 + \frac{b_4}{T} \tag{5}$$

Polanyi, who advanced a theory based on the assumption that adsorption was a physical process and that the adsorbed phase was many layers thick (*24*), defined the adsorption potential as the work done by the adsorption forces in bringing a molecule to a point in the adsorbed state;

$$\epsilon_i = \int_{\delta_x}^{\delta_i} v\,dp \tag{6}$$

Polanyi assumed that an equation of state that describes the effect of temperature and pressure of the gas could be used for the adsorbate. The potential theory also assumes that the potential does not change with temperature, and so

$$\frac{d\epsilon_i}{dT} = 0 \tag{7}$$

Berenyi, calculating ϵ_i as a function of the volume adsorbed, assumed as a first approximation that the vapor behaved as an ideal gas and that the liquid was incompressible. Berenyi's equation is as follows:

$$\epsilon_i = \int_{p_x}^{p_0} \frac{RT}{p}\,dp = RT \ln \frac{p_0}{p_x} \tag{8}$$

Although the Polanyi potential theory does not offer an expression for an adsorption isotherm, the potential theory using a three-dimensional equation of state for the adsorbed phase can account for the temperature dependency of adsorption. Polanyi and Berenyi (*27*) also found empirically that the maximum adsorption potential ϵ_0 was related to the van der Waal's constant a for a single adsorbent as follows:

$$\epsilon_0 = k\sqrt{a} \tag{9}$$

Equation (9) is similar to the expression $(\sqrt{a_a}\sqrt{a_b})$ for attractive potential between two molecules as preposed by Berthelot (*4*).

In the determination of the selective adsorption capacity, or the quantity of more strongly adsorbed component per unit weight of adsorbent, it is assumed that only one component is adsorbed. Experimentally, the adsorbent is added to a binary of known composition. The change in composition of the liquid is recorded and the selective adsorptive capacity is defined as

$$G' = \frac{v}{m}\left[\frac{X_0 - X}{1 - X}\right] \tag{10}$$

where G' is the selective adsorptive capacity in volume of adsorbate per unit weight of adsorbent, v is the volume of the initial solution, m is the weight of adsorbent, and X_0 and X are the initial and final volume fraction of adsorbate respectively.

If the adsorbed phase can be distinctly separated from the equilibrium liquid, it is assumed that the immobile liquid, or liquid in the pore space, constitutes a pseudoadsorbed phase (*11, 30*). For process-design calculations, the equilibrium data are more useful in the form of an x-y diagram (*10, 18*). The adsorbed-phase concentration may be calculated by the following equation:

$$Y = \frac{G' + (V_p - G')X}{V_p} \tag{11}$$

where Y is the volume fraction of strongly adsorbed component in the pore volume, V_p is the pore volume, and G' and X are defined in Equation (10). By use of the liquid densities the equilibrium data may be presented by either weight or mole fractions.

The relative adsorbability α is defined as follows (*23*)

$$\left(\frac{y}{1-y}\right) = \alpha\left(\frac{x}{1-x}\right) \tag{12}$$

where y is the mole fraction of more strongly adsorbed component in the adsorbed phase or pore space, and x is the mole fraction of the same component in the equilibrium liquid.

This definition of α in Equation (12) is analogous to the relative volatility in vapor-liquid equilibrium calculations. It is of interest to note that Eagle (*10*) using Equation (12), correlated benzene cyclohexane data essentially assuming a constant relative adsorbability, while Mair (*23*) records the variation in α with concentration for the same system.

Equation (12) is plotted as in $y/1 - y$ vs. in $x/1 - x$ should give a straight line with a slope of one and, an intercept equal to ln α if α is a constant over the experimental range.

Corrigan and Koble (*7, 19*) have suggested an equation primarily for chemical adsorption but including physical adsorption. By the use of the methods of Hougen and Watson (*17*) Equation (13) is derived relating the concentration of one component on a solid surface to the partial pressures of the binary and the equilibrium constants for the individual adsorption reactions.

$$C_{a1} = \frac{K_a p_a}{(1 + K_a p_a + K_b p_b)} \tag{13}$$

By extending Corrigan's discussion to include a concentration ratio of the two adsorbed components, one obtains,

$$\frac{C_{a1}}{C_{b1}} = \frac{K_a p_a}{K_b p_b} \tag{14}$$

The temperature dependency of K is given by,

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{15}$$

If liquid concentrations are used instead of gas partial pressures in Equation (14) and with logarithms,

$$\ln \frac{C_{a1}}{C_{b1}} = \ln \frac{C_a}{C_a} - \frac{\Delta H_a^0 - \Delta H_b^0}{RT} + \frac{\Delta S_a^0 - \Delta S_b^0}{R} \qquad (16)$$

A comparison of Equation (16) with Equation (3) shows the similarity of the former equation with Freundlich's equation including Zeldowitsch's Equation (5) for the temperature effect.

CORRELATING EQUATION

Assumptions:

1. The correlating equation applies to physical adsorption from the liquid phase.
2. The adsorbed phase concentration is based on the total pore volume.
3. The adsorbed phase follows a three-dimensional equation of state.
4. The attractive potential is not a function of temperature.
5. The pore volume and surface area as calculated with the use of nitrogen adsorption is completely available to the adsorbate.
6. The liquid free volumes for both components of the liquid binary are equal.
7. The mutual attractive potential in the binary is a function of mole fraction similar to Equation (17)
8. The attractive potential between the solid and adsorbate is a function of the pore diameter as defined in Equation (17).
9. The partial molal volumes in both phases are equal to the volumes of the pure components at the temperature and pressure of the phase.

The term physical-adsorption applies to systems in which the heats of adsorption are of the same order of magnitude as the heats of condensation. Further distinction is also made in which the heats of activated or chemical adsorption are comparable to heats of reaction. The heat of adsorption for benzene on silica gel is 8400 cal./g. mole (*7*), and its heat of vaporization is 7550 cal./g. mole.

Mair (*23*) measured adsorptive capacities by allowing a silica gel to come in contact with vapors in equilibrium with a liquid. His adsorptive capacities were reasonably close to the pore volumes as calculated on a similar adsorbent (Davison gel 922).

For pore diameters more than two or three times the diameter of an adsorbate molecule, the adsorbed phase will exist in a multimolecular layer. Brunauer, Emmett, and Teller (*6*) assume that above the initial layer the adsorbate behaves as a liquid with liquid physical properties. Polanyi (*28*) successfully used a three-dimensional equation of state in the potential theory.

In the potential theory, Polanyi (*28*) uses the assumption that the attractive potential is independent of temperature, Equation (7). If a temperature dependency were present, it should be of the same order of magnitude in both the liquid and adsorbed state. The difference in the two potentials is utilized for the equilibrium relationship so that the error introduced should be small.

The simplifying assumption of equal free volume for both components of the binary is partially justified if both components have similar entropies of vaporization (*16*). For hydrocarbons where Trouton's rule holds, this assumption will not introduce an error. Frank (*12, 13*) correlated the entropy of vaporization with the free volume using the spherical cage model.

Aging of an adsorbent or high temperatures may change the pore size of an adsorbent; but for adsorbents with relatively small pores, the specific surface decreases at approximately the same rate. Milligan and Rachford (*26*) found that heating silica gel did not change the distribution or the size of the pores but did reduce their number.

The van der Waals attraction constants for binary systems have been found to follow the relationship (*16*)

$$(a_{a,b})^{1/2} = (a_a)^{1/2} + (a_b)^{1/2}(1 - x) \qquad (17)$$

A thermodynamic criterion for phase equilibria is that a component of a solution has the same chemical potential in each phase

$$\mu_{iy} = \mu_{ix} \qquad (18)$$

where μ_{iy} and μ_{ix} are the chemical potentials of the i, the component in the adsorbed and liquid phase, respectively (*8*). The chemical potential is defined as follows:

$$\mu_{ix} = \int_{P_0}^{P_x} \bar{v}_i \, dp + RT \ln x_i + F_i^0 \qquad (19)$$

where $\bar{v}_i$ is the partial volume of the ith component, P_0 is the standard state pressure of the solution, R is the gas constant, T is the absolute temperature, and x_i the mole fraction of the ith component in either phase, Equation (18) with Equation (19) leads to

$$\frac{y}{x} = \exp\left\{\frac{1}{RT}\left[\int_{P_0}^{P_x} \bar{v}_i \, dp - \int_{P_0}^{P_y} \bar{v}_i \, dp\right]\right\} \qquad (20)$$

where y is the mole fraction of the ith component in the adsorbed phase and P_y the pressure of the adsorbed phase.

Since the adsorbed phase behaves like a highly compressed liquid, Equation (20) may be written as,

$$\frac{y}{x} = \exp\left[\frac{1}{RT}\int_{P_y}^{P_x} \bar{v}_i \, dp\right] \qquad (21)$$

of if $\bar{v}_i$, the partial volume is assumed to be equal to the molal volume of the pure component,

$$\frac{y}{x} = \frac{f_x}{f_y} \qquad (22)$$

In Equation (22) the equilibrium condition, assuming ideal solutions in both phases, states that the concentrations are inversely proportional to their escaping tendencies or fugacities (*8*).

If the volumes are additive in either solution, $\bar{v}_i$ is equal to v_i. If one assumes the liquid equation of state to be,

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \qquad (23)$$

where a and b are constants, the integral in Equation (21) becomes,

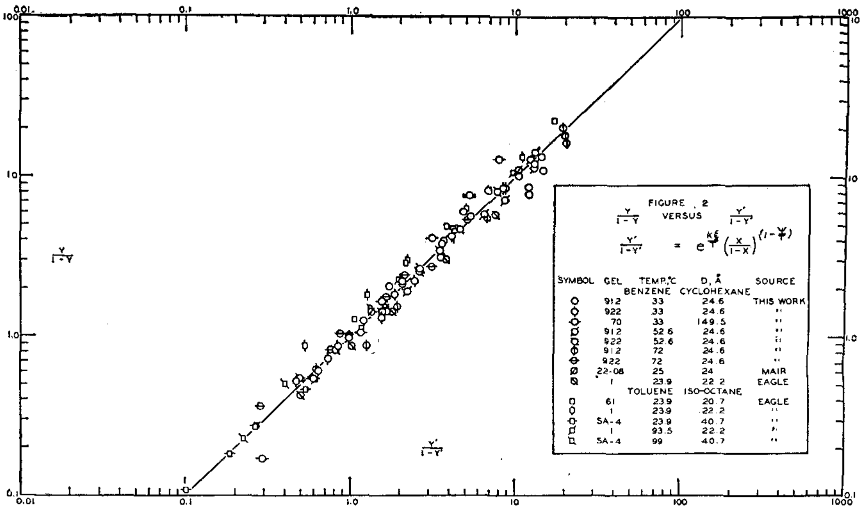

Fig. 2. Correlated data.

$$\frac{1}{RT}\int_{P_y}^{P_x} v_i\,dp \tag{24}$$

$$= \left[\ln\frac{RT}{v_i - b} - \frac{b}{v_i - b} - \frac{2a}{RTv_i}\right]_{v_{iy}}^{v_{ix}}$$

Equation (21) may be written in the form of mole ratios for a binary solution as,

$$\frac{y}{1-y} = \frac{x}{1-x} \tag{25}$$

$$\cdot \exp\left\{\frac{1}{RT}\left[\int_{P_y}^{P_x} v_a\,dp - \int_{P_y}^{P_x} v_b\,dp\right]\right\}$$

where v_a and v_b are volumes of component A and B at the conditions in each phase.

Using Equation (24) in (25) and taking logarithms of both sides of the resulting equation give the following:

$$\ln\frac{\dfrac{y}{1-y}}{\dfrac{x}{1-x}} = \ln\left[\frac{v_b - b_b}{v_a - b_b}\right. \tag{26}$$

$$\left. + \frac{b_a(v_b - b_b)}{b_b(v_a - b_b)} + \frac{2a_b}{RTv_b} - \frac{2a_a}{RTv_a}\right]_{v_y}^{v_x}$$

It is assumed that constants a and b are functions of composition since the proper representation of the volume of each component at the pressure of each phase should include a variation of attractive force per unit area represented by a, and minimum volume represented by b. The free volume for the liquid is given approximately by the equation

$$(v - b) = v_f \tag{27}$$

where b is the van der Waal's constant in Equation (23). As stated in the previous section, the free volumes for liquids having the same entropy of vaporization should be equal (*12*, *13*).

Since most nonpolar compounds follow Trouton's rule, $\Delta H_{LV}/T = \Delta S_{LV} =$ constant and for nonpolar liquids Equation (26) reduces to,

$$\ln\left(\frac{y}{1-y}\right)\left(\frac{1-x}{x}\right) - \left[\frac{b_{ax}}{b_{bx}} - \frac{b_{ay}}{b_{by}}\right.$$

$$\left. - \frac{2}{RT}\left(\frac{a_{ax}}{v_{ax}} - \frac{a_{bx}}{v_{bx}} + \frac{a_{by}}{v_{by}} - \frac{a_{ay}}{v_{ay}}\right)\right] \tag{28}$$

the interaction constants for both components will be the same so that Equation (28) becomes,

$$\ln\left(\frac{y}{1-y}\right)\left(\frac{1-x}{x}\right) \tag{29}$$

$$= \frac{2}{RT}\left[a_y\left(\frac{1}{v_{ay}} - \frac{1}{v_{by}}\right) - a_x\left(\frac{1}{v_{ax}} - \frac{1}{v_{bx}}\right)\right]$$

The attractive force constant in the adsorbed phase, a_y, is dependent on the attractive force of the solid surface and of the liquid.

Comparing the thermodynamic equation of state,

$$P + T\left(\frac{\partial p}{\partial T}\right)_v - \left(\frac{\partial E}{\partial v}\right)_T \tag{30}$$

with Equation (23)

$$\left(\frac{\partial E}{\partial v}\right)_T = \frac{a}{v^2} \tag{31}$$

where the cohesive energy is defined as,

$$E = -\frac{a}{v} \tag{32}$$

If the attractive potential energy between the adsorbate and the surface, ϕ is divided by the effective volume, v_e,

$$\frac{\phi}{v_e} = -\frac{a}{v_e^2} \tag{33}$$

the result is a potential-energy density term having the dimensions of force per unit area.

To account for varying pore or capillary curvature, the attractive force per unit area may be referred to a plane surface equivalent.

With the assumption of an effective distance, d, from the surface of the adsorbent, the attractive force per unit of surface area for a flat plane is,

$$\frac{a_y}{v_{ep}^2} = \frac{a_y}{d^2} \tag{34}$$

The attractive force per unit area in a capillary of radius r is,

$$\frac{a_0}{v_{ec}^2} = \left(\frac{a_0}{d^2}\right)\left(\frac{2r}{2r - d}\right)^2 \tag{35}$$

Equating the terms for attractive force per unit area and solving for a_y result in:

$$a_y = a_0\left(\frac{2r}{2r - d}\right)^2 = a_0\left(\frac{D}{D - d}\right)^2 \tag{36}$$

where a_0 is a measure of the attractive force between the binary liquid at composition y and the adsorbent corrected to zero curvature.

Substitution of Equation (36) in Equation (29) gives the following

$$\ln\left(\frac{y}{1-y}\right)\left(\frac{1-x}{x}\right) \tag{37}$$

$$= \frac{2}{RT}\left[\left(\frac{D}{D-d}\right)^2 a_0\Delta\rho_y - a_x\Delta\rho_x\right]$$

where $\Delta\rho_y$ and $\Delta\rho_x$ are the density differences of the adsorbed components and liquid components, respectively.

The attractive force constant, a_0, in the adsorbed phase will be a function of y. Since the solid has a constant volume fraction in the combination of adsorbed binary and surface, a_0 should not vary greatly with composition.

The constant a_x shows a variation of approximately 10% over the composition range studied for the system benzene-cyclohexane (*31*). Assuming a_x to be constant with composition leads to an equation of the following form,

$$\ln\left(\frac{y}{1-y}\right) = \ln\left(\frac{x}{1-x}\right) + M \tag{38}$$

where

$$M = \frac{2}{RT}\left[\left(\frac{D}{D-d}\right)^2 a_0\Delta\rho_y - a_x\Delta\rho_x\right]$$

Equation (38) indicates that a plot of ln $(y/1 - y)$ vs. ln $(x/1 - x)$ at a constant temperature would give a straight line with a slope of plus one and an intercept equal to M. Figure 1 shows that the isotherms have slopes less than one, and the slope does not correlate with the pore radius. If a_x is a weak function of ln $(x/1 - x)$, Equation (38) may be written as,

$$\ln\left(\frac{y}{1-y}\right) = \ln\left(\frac{x}{1-x}\right)$$

$$\cdot\left[1 - \frac{\psi}{T}\right] + \frac{\xi_k}{T} \tag{39}$$

where

$$\psi = \frac{2a_x\Delta\rho_x}{R\ln\left(\dfrac{x}{1-x}\right)}$$

$$\xi = \left(\frac{2r}{2r-d}\right)^2 = \left(\frac{D}{D-d}\right)^2$$

$$k = \frac{2a_0\Delta\rho_y}{R}$$

In exponential form Equation (39) becomes

$$\left(\frac{y}{1-y}\right) = e^{\xi k/T}\left(\frac{x}{1-x}\right)^{1-\psi/T} \tag{40}$$

Equation (40) indicates that liquid-phase data may be correlated by obtaining constants k, ψ, and d for the binary system on an adsorbent which has an average pore diameter D.

To calculate the constants for a system, a log-log plot of equilibrium data can be made at a minimum of two temperatures or pore diameters, from which the slope and intercept can then be determined. The log of the intercept is called C and the slope M, then the constants are,

$$C = \frac{\xi k}{T} \tag{41}$$

$$M = 1 - \frac{\psi}{T} \tag{42}$$

A plot of M vs. $1/T$ gives ψ since

$$C = \frac{\left(\dfrac{D}{D-d}\right)^2 k}{T} \tag{43}$$

rearranging

$$\left(\frac{CT}{k}\right)^{1/2} = \frac{D}{D-d} \tag{44}$$

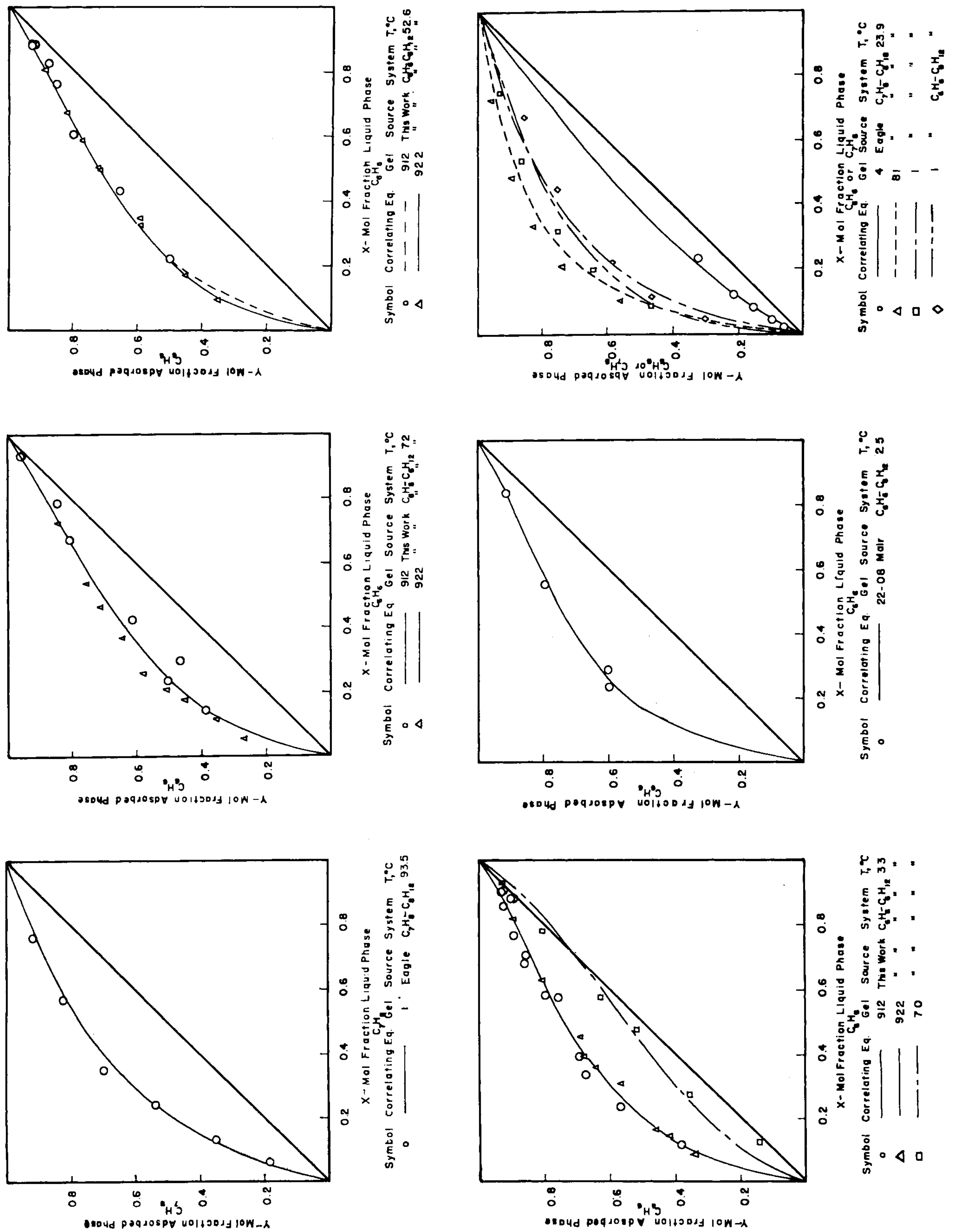

Fig. 3. Mole-fraction curves comparing experimental and predicted equilibrium data.

and

$$\frac{1}{D} = \frac{1}{d} - \frac{1}{d}\left(\frac{k}{CT}\right)^{1/2} \qquad (45)$$

A plot of $1/D$ vs. $(1/CT)^{1/2}$ is made. The slope equal to $(-k^{1/2}/d)$ and the intercept is $1/d$.

COMPARISON WITH EXPERIMENTAL DATA

1. Benzene-Cyclohexane System*

The fit of the experimental data to Equation (40) can be shown by Figures 2 and 3. The correlating constants are in Table 1.

For the benzene-cyclohexane system, the data according to Mair *et al.* (*23*) as well as Eagle and Scott (*10*) were correlated with the use of Equation (47). A range of temperatures 23.9°C. to 72°C. was included in the correlation, and the pore size ranged from 24 to 149 Å. The average per cent deviation between the calculated and observed values was 3.16%.

To better check the suitability of Equation (40), the data on the toluene-isooctane system as presented by Eagle and Scott (*10*) were correlated. The average deviation, or calculated minus experimental adsorbed-phase concentration, was 7.0%.

The pore diameters reported by Eagle and Scott (*10*) were calculated with a butane volume and a surface area. The butane surface area has been found to give surface areas approximately 30% too low compared with nitrogen adsorption areas (*5*). The pore diameters used in the correlation were calculated on the basis of the corrected surface area, see Table 1.

The solution densities were obtained from the measurements of Wood and Austin (*31*) and the pore volumes were measured with the nitrogen adsorption equipment and method of Brunauer, Emmett, and Teller (*1, 6*). Pore-size distribution of the silica gels was also checked by the method of Barrett, Joyner, and Halenda (*2, 3*). The pore-size determination showed a peaked distribution for the silica gels so that no correction was necessary to account for the fraction of pores too small to admit a benzene molecule.

CONCLUSIONS

Liquid-phase adsorption equilibrium data for a binary on a silica-alumina adsorbent can be correlated with the use of the equation

$$\left(\frac{y}{1-y}\right) = e^{\xi k/T}\left(\frac{x}{1-x}\right)^{(1-\psi/T)}$$

From the restrictions on the derivation and systems tested, the correlation is limited to van der Waal's or physical adsorption, to binary systems with similar free volumes for both components, and to the definition of the adsorbed phase having a volume equal to the total pore volume.

NOTATION

a = van der Waals attractive force constant
b, b_1, b_2, b_3, b_4 = constants
C = molecular concentrations, and constant defined in Equation (41)
d = correlating constant
D = adsorbent pore diameter
E = energy content
f = fugacity
G, G' = weight and volume adsorbed respectively
H = enthalpy
K = reaction equilibrium constant
k, k' = constants
M = constant defined in Equation (42)
m = weight of adsorbent
n, n' = constants
P = total pressure
p = partial pressure
r = pore radius
R = gas constant
S = entropy
T = temperature
v = volume
V_p = pore volume
x = mole fraction of adsorbate in solution
X = volume fraction in solution
y = mole fraction of adsorbate in pore space
Y = volume fraction in pores

Greek Letters

α = relative adsorbability Equation (12)
δ = densities of solution Equation (6)
Δ = difference
ϵ = adsorption potential
μ = chemical potential
ρ = densities of solution components
ϕ = attractive potential
ψ = correlating constant Equation (39)
ξ = $(D/D - d)^2$

Subscripts

o = initial state prior to adsorption
a = component a in phase
b = component b in phase
ec = effective curved value
ep = effective planar value
i = point i within adsorbed phase
1 = active sites on adsorbent surface
LV = liquid to vapor phase change
p = pore space
x = liquid phase, nonadsorbed phase in Equation (8)
y = adsorbed phase

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