Correlating Criteria for Liquid-Phase Adsorption

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A correlating equation for selective adsorption in the liquid phase has been extended to predict accurately the benzene-cyclohexane equilibrium data on silica gel. Gel pore diameters range from approximately 25 to 150 Å. and temperatures between the boiling and freezing points of the pure components.

The ability to select the best adsorbent and conditions for the most effective separation of a particular system of liquid components can yield real savings in time and manpower. Before chromatographic columns, percolation columns, or other types of countercurrent liquid-phase contacting equipment can be designed, the knowledge of the optimum conditions for separation is absolutely necessary. Whether the operation involves separation of organic liquids or merely decoloration, there is a definite need for data which indicate the effects of pore diameter and system temperature on separation efficiency. The utility of an expression relating these factors was recently shown when Weatherford (8) and Somers (6) successfully used the equation proposed in this paper in predicting wave-front compositions for the separation of benzene and cyclohexane on silica gel and alumina in chromatographic columns.

An equation was suggested by Stuart and Coull (7) by which one could predict equilibrium data for a particular system for all liquid-phase temperatures and pore diameters after a measurement of only four equilibrium points. This present work is an extension and modification of the original equation and its application.

EXPERIMENTAL PROCEDURE

The container for the equilibrium solution and adsorbent was a dried 125-ml. Erlenmeyer flask fitted with a 24/40 ground-glass top. There were two outlets from the top, one fitted with a serum cap and the other having a No. 1 tapered stopcock. The activation of the gel was conducted by placing 5 g. of adsorbent in the flask and heating at 550°F. for 15 hr. While it was at this temperature the top was inserted into the flask with the serum cap in place and the stopcock closed to ensure as little contamination from gas or moisture as possible. The unit was cooled under vacuum.

About 10 g. of a premixed solution of pure benzene and cyclohexane (R.I. ± 0.00005) was placed in the flask. By inserting an 18-gauge, 6-in. syringe needle attached to a 30-cc. medicinal syringe filled with about 15 cc. of solution through the serum cap to a position above this gel and depositing the solution.

The solution in the flask assembly was placed in a constant-temperature bath at a predetermined temperature and gently agitated by means of a wrist-action shaker for at least 30 min. Clear samples were then removed from the slurry by inserting a syringe needle fitted with a syringe filter through the serum cap to withdraw about a cubic centimeter of liquid. The sample was placed in a refractometer at 33°C., and the refractive index was determined. From data by Stuart and Coull (7) the benzene concentration was determined. At least three identical readings were taken from each flask before a run was considered complete. Descriptive dimensional parameters of the silica gels studied are shown in Table 1.

EQUILIBRIUM EQUATIONS

When a binary solution is shaken with a solid adsorbent, one of the components may be preferentially adsorbed, resulting in a decrease in the mole fraction of the component in solution. The adsorption may take place in one of the following ways

1. One component will be adsorbed on a single layer in the adsorbent pore, and the rest of the pore will be filled with equilibrium binary solution.
2. Both components will be adsorbed in a single layer and the remaining pore volume filled with solution.
3. Both components will be adsorbed in multilayers with the degree of selectivity decreasing as the distance from the surface is increased.

Jones and Mill (3) have advocated the use of the multilayer concept in analyzing data. However this method involves the use of partial molar volumes in the adsorbed phase, and as such quantities are extremely difficult to determine experimentally, discussion will be confined to monolayer adsorption only.

On the basis of the adsorption of one component, Eagle and Scott (2) suggested the use of adsorption capacity in calculating the weight of this adsorbed component:

$$G = \frac{W_s(X_o - X)}{W_a(1 - X)} \qquad (1)$$

Assuming that all the adsorption takes place in a monolayer and that the rest of the pore is filled with binary solution, one may calculate the over-all

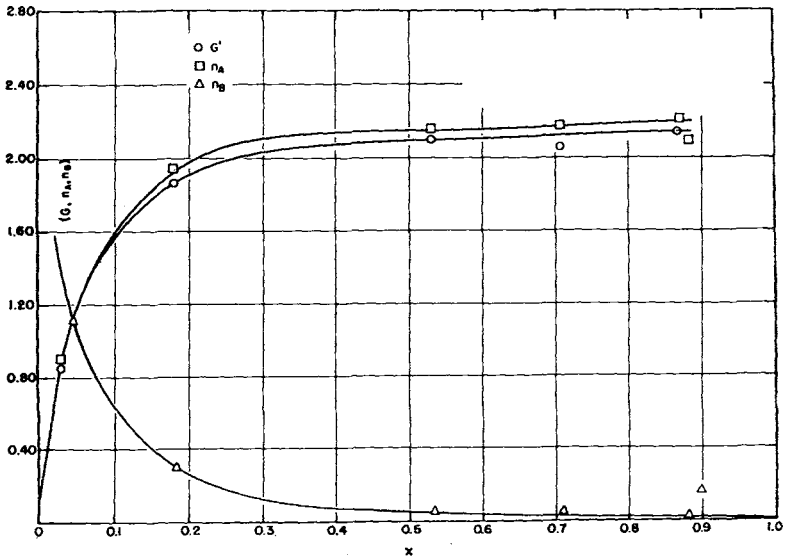

Fig. 1. Adsorption (G, n_A, n_B), moles benzene adsorbed per gram of adsorbent x, mole from benzene in equilibrium liquid: benzene-cyclohexane-silica gel (No. 922) at 8.0°C.

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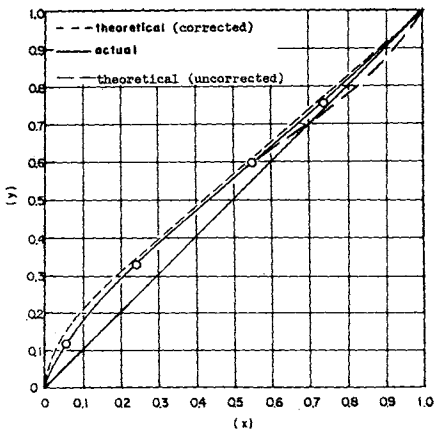

Fig. 2. Mole fraction of benzene in adsorbed phase (y) vs. mole fraction of benzene in equilibrium phase (x): benzene-cyclohexane-silica gel (No. 70) at 8.0°C.

TABLE 1. ADSORBENT PROPERTIES

	Silica gel No. 922	Silica gel, 70 Å.	Silica gel No. 70
Pore volume, cc./g.	0.429	0.562	1.0876
*Surface area, sq. m./g.	698.8	321.0	290.0
Average pore diameter, Å.	24.6	70.0	149.5
Mesh size	—200	100-200	+10

* B.E.T. method.

TABLE 2.

Pore diameter, Å.	Azeotrope mole fraction
24.6	1.000
30.0	0.980
32.0	0.917
40.0	0.865
70.0	0.710
149.5	0.690

composition of all the liquid in the pore using

$$Y = \frac{G + \left(V_p - \frac{G}{\rho_b}\right)\rho_x X}{G + \left(V_p - \frac{G}{\rho_b}\right)\rho_x} \quad (2)$$

When the correlating equation (Stuart equation) was used to predict equilibrium data for gels having diameters over 30Å.; an inversion in selectivity, that is an azeotrope, was predicted to occur at higher mole fractions, as shown in Table 2.

The actual data interpreted by the use of the G-factor concept indicated no such change in selectivity. This lack of agreement between estimated values and actual equilibrium data was attributed either to inaccurate interpretation of equilibrium data by the equations above or to an error in the correlating equation.

TABLE 3. BENZENE-CYCLOHEXANE-SILICA GEL NO. 922
(Equilibrium Data Taken at 8°C.)

Weight of solution, g. W_s	Refractive index Before	Refractive index After	Weight fraction benzene after X	Weight of silica gel, g. No. 922 W_a	Selective adsorption, g. benzene / g. gel G	n_A, m.-moles / g.	n_B, m.-moles / g.	G', m.-moles / g.
12.3245	1.4224	1.4203	0.0279	7.7477	0.0663	0.895	1.168	0.850
10.7102	1.4332	1.4281	0.1729	7.7730	0.1452	1.927	0.295	1.862
11.3801	1.4531	1.4509	0.5160	4.3716	0.1624	2.142	0.052	2.082
12.6449	1.4682	1.4652	0.6934	0.2200	0.1592	2.149	0.044	2.041
12.4305	1.4817	1.4802	0.8629	8.6170	0.1652	2.179	0.010	2.118

A more realistic interpretation of the data was undertaken by assuming the adsorption of both components in a single layer. Such a relationship was suggested empirically by Williams (9) and later adopted by Kipling and Tester (4):

$$\frac{n}{W_a}(x_o - x) = \frac{n\,\Delta x}{W_a} = n_A(1-x) - n_B x \quad (3)$$

The essential unknowns in this equation are n_A and n_B; they can be determined only by solving this equation simultaneously with a second equation.

If the adsorption took place in a monolayer, the following equation could be used as a second relationship between n_A and n_B to solve the Williams equation:

$$n_A A_A + n_B A_B = S_T \quad (4)$$

By combining Equations (3) and (4) with the mole-fraction form of Equation (1) one obtains

$$n_A = \frac{\frac{n\,\Delta x}{W_a(1-x)} + \frac{S_T}{A_B}\left(\frac{x}{1-x}\right)}{1 + \frac{A_A}{A_B}\left(\frac{x}{1-x}\right)} = \frac{G' + \frac{S_T}{A_B}\left(\frac{x}{1-x}\right)}{1 + \frac{A_A}{A_B}\left(\frac{x}{1-x}\right)} \quad (5)$$

From these equations one may calculate the molal concentration in the monolayer:

$$y_{(m)} = \frac{n_A}{n_A + n_B} \quad (6)$$

Robert (5) determined the area of an adsorbed benzene molecule, and Blackburn, Kipling, and Tester (1) measured the ratio of the adsorbed areas of cyclohexane and benzene. With these data and the surface area of the adsorbent, a corrected concentration in the pore was calculated by means of the following relationship:

$$(y'_m) = \frac{n_A + \left[V_P - \frac{M_{(m)}(n_A + n_B)}{(\rho_x)_m}\right]\rho_x \frac{x}{M_x}}{n_A + n_B + \left[V_P - \frac{M_{(m)}(n_A + n_B)}{(\rho_x)_m}\right]\frac{\rho_x}{M_x}} \quad (7)$$

Figure 1 and Table 3 show the comparative calculated values of n_A, n_B, and G for a typical system.* It is apparent from these data that the two methods of calculation are almost identical and that the original interpretation of equilibrium data was correct.

CORRELATING EQUATIONS

Stuart and Coull (7) proposed the following equation as a means of correlating liquid-phase adsorption-equilibrium data:

$$\left(\frac{y}{1-y}\right) = e^{\xi k/T}\left(\frac{x}{1-x}\right)^{\left(1-\frac{\psi}{T}\right)} \quad (8)$$

In logarithmic form this may be written as

$$\ln\left(\frac{y}{1-y}\right) = \ln\left(\frac{x}{1-x}\right)\left[1 - \frac{\Psi}{T}\right] + \frac{\xi k}{T} \quad (9)$$

where

$$\Psi = \frac{2\,a_x\,\Delta\rho_x}{R \ln\left(\frac{x}{1-x}\right)} \quad (10)$$

$$\xi = \left(\frac{D}{D-d}\right)^2 = \left(\frac{2r}{2r-d}\right)^2 \quad (11)$$

$$k = \frac{2\,a_o\,\Delta\rho_y}{R} \quad (12)$$

where a_x is a measure of the attractive force (attractive force constant) between molecules of both components and the equilibrium binary solution, a_o is a measure of the force of attraction between the solid and a binary solution at composition y, $\Delta\rho_x$ and $\Delta\rho_y$ are

* Data pertaining to all of the gels studied are filed with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., as document 6263 and may be obtained for $3.75 for photoprints or $2.00 for 35-mm. microfilm.

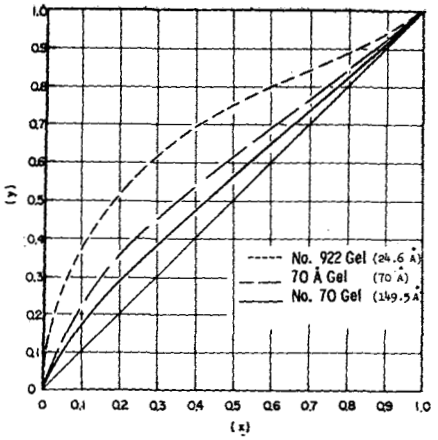

Fig. 3. Equilibrium data as a function of pore diameter: benzene-cyclohexane-silica gel (No. 922) at 8.0°C.

the density differences of the adsorbed components and equilibrium liquids, a_y is the attractive force constant between both components and the adsorbate, and d is an effective distance between the adsorbent surfaces and the adsorbed layer of molecules.

The term a_x has been viewed as a weak function of $\ln (x/1-x)$, and a_y is dependent on y, the over-all concentration of benzene in the adsorbed phase. The terms a_y and a_o may be related as follows:

$$a_y = a_o\left(\frac{D}{D-d}\right) = \xi a_o \text{ or } \frac{a_y}{a_o} = \xi \tag{13}$$

Equation (8) may be used for predicting equilibrium data by making a log-log plot of $y/1-y$ vs. $x/1-x$ and determining the slope and intercept. Calling the slope M and the intercept C, one obtains

$$C = \frac{\xi\ k}{T} \tag{14}$$

and

$$M = 1 - \frac{\Psi}{T} \tag{15}$$

A plot of M vs. $1/T$ yields Ψ; this factor requires the use of only two equilibrium points at one temperature.

Values of d and k are determined as follows:

$$C = \frac{\xi\ k}{T} = \frac{\left(\frac{D}{D-d}\right)_k^2}{T} \tag{16}$$

and

$$\left(\frac{CT}{k}\right)^{1/2} = \frac{D}{D-d} \tag{17}$$

then

$$\frac{1}{D} = \frac{1}{d} - \frac{1}{d}\left(\frac{1}{CT}\right)^{1/2} \tag{18}$$

A plot of $1/D$ vs. $(1/CT)^{1/2}$ is made from data obtained at a minimum of either two pore diameters or temperatures. This requires at least four equilibrium points. It is advisable however when establishing a completely new system that two temperatures and two pore sizes be investigated. Values for the constants for the benzene–cyclohexane–silica gel system were determined Stuart (7).

Table 4. Adsorbent Constants

Constants	Silica gel No. 922	Silica gel 70 Å.	Silica gel No. 70
d, Å.	14.5	14.5	14.5
ξ	5.932	1.590	1.226
k, °K.	54.2	54.2	54.2
ψ_1, °K.	77.5	71.70	55.37
ψ_2, °K.	77.5	20.52	15.82
$\xi k/\psi_1$	4.2	1.20	1.20
$\xi k/\psi_2$	4.2	4.20	4.20

At smaller pore diameters the above form of the equation as originally derived and applied predicts equilibrium data satisfactorily. However with larger diameter gels the equations will predict azeotropes at higher benzene concentrations.

This faulty indication of azeotropes was corrected by altering the $\xi k/\Psi$ factor above and below benzene concentrations of 50%. This is done by first determining the $(\xi k)/\Psi$ factor as originally suggested by Stuart and Coull (7). If the correlation is to be applied below a mole fraction of strongly adsorbed component of 0.50, the $(\xi k)/\Psi$ ratio must be equal to a value of at least 1.2. If it is less, the Ψ constant is adjusted to bring the ratio up to 1.2. If the correlating equation is to be applied to data above 0.50, the $(\xi k)/\Psi$ ratio must be equal to 4.2. Again if the calculated values are less, then the Ψ factor is reduced accordingly. Figure 2 shows the results of adjustment on actual data for a typical gel. Table 4 lists the constants used for all the gels.

A partial theoretical justification for the adjustment of the $(\xi k)/\Psi$ ratio is based on the comparative attractive force between surface and solution. It may be seen from Figure 3 that the adsorption capacity, or the attractive force between the surface and a molecule, falls off for gels above 25Å. in diameter. Further it would seem that this force becomes very low for adsorption in macropores (pores over 100 Å.). Therefore the effects of the relative cohesive energy densities of the adsorbed phases on a molecule would become more important as the diameter increased. In terms of the previously mentioned attractive force constants a relationship between these two energy terms would be

$$\frac{f\ (\text{cohesive energy density of adsorbate})}{f\ (\text{cohesive energy density of solution})} = \frac{f\ (a_y)}{f\ (a_x)} \tag{19}$$

In terms of Stuart constants

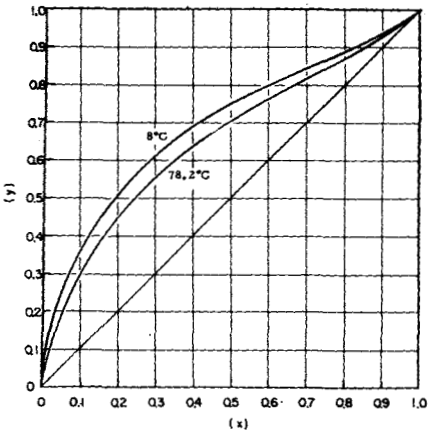

Fig. 4. Variation of equilibrium data with temperature: silica gel (No. 922).

$$\frac{\xi\ k}{\Psi} = \frac{\left(\frac{D}{D-d}\right)_k}{\Psi} = \frac{a_y/a_o(2a_o\,\Delta\rho_y/R)}{2a_x\,\Delta\rho_x/R\ln\frac{x}{1-x}} = \frac{f(a_y)}{f(a_x)}\cdot\phi(x) \tag{20}$$

Since a_x is a function of $\ln(x/1-x)$, it is felt that this partially negates the effect of $\phi(x)$ and yields

$$\frac{\xi\ k}{\Psi} = \frac{f(a_y)}{f(a_x)} \tag{21}$$

It would seem reasonable then that when $a_o \to a_x$, the ratio of $(\xi k)/\Psi$ must be greater than 1.

TEMPERATURE EFFECTS

The work of Stuart and Coull was extended to include temperatures covering the entire range between the boiling and freezing points of the pure liquids. The effect of temperature on equilibrium data for a typical gel is shown in Figure 4.

SUMMARY AND CONCLUSIONS

It is shown that for the benzene–cyclohexane–silica gel system the concept of monomolecular adsorption in a single layer followed by pore filling with equilibrium solution is as valid as the assumption of bimolecular adsorption. A correlating equation has been proposed which can satisfactorily predict equilibrium data for the benzene-cyclohexane system and similar systems for adsorption on adsorbents over a wide pore-diameter range. The equation relates only to liquid adsorption and includes the effects of tempera-

ture. A theoretical mechanism for the adsorption-based cohesive-energy-density differences is suggested.

NOTATION

A = liquid component A, the more highly adsorbed component (benzene in this case)
A_A = effective area occupied by a mole of component A in a monolayer (sq. m./g.)
A_B = effective area occupied by a mole of B in a monolayer (sq. m./g.)
a_o = attractive force constant between components and adsorbent surface
a_x = attractive force constant between binary solution and components
a_y = attractive force constant between binary solution and pore
B = liquid component B, component (cyclohexane in this case)
C = Stuart slope of $\ln y/1-y$ vs. $\ln x/1-x$
D = adsorbent pore diameter, Å.
d = constant in Stuart equation
G = selective adsorption capacity (g. of component A adsorbed/g. of adsorbent)
G' = moles of component A adsorbed /g. of adsorbent
k = constant in Stuart equation
M = Stuart intercept of plot $\ln y/1-y$ vs. $\ln x/1-x$
$M_{(m)}$ = average molecular weight of binary solution in monolayer
$M_{(x)}$ = average molecular weight of equilibrium solution
n = moles of total original solution
n_A = moles of component A adsorbed /g. of adsorbent
n_B = moles of component B adsorbed/g. of adsorbent
R = universal gas constant
r = pore radius, Å.
S_T = adsorbent surface area, sq. m./g.
T = temperature, °K.
V_p = adsorbent pore volume cc./g.
W_s = weight of original solution, g.
W_a = adsorbent weight, g.
X = equilibrium weight fraction of adsorbed component (bulk solution)
X_o = weight fraction of stronger adsorbed component in original solution
x = equilibrium mole fraction of adsorbed component (bulk solution)
x_o = mole fraction of more highly adsorbed component in original solution
Y = weight fraction of component A in equilibrium solution
$y_{(m)}$ = mole fraction of component A in monolayer calculated by the use of Williams equation
$y'_{(m)}$ = equilibrium mole fraction of component A in the pore as calculated by the Williams equation

Greek Letters

ξ = constant in Stuart equation
ρ_b = density of benzene, g./cc.
$\rho_{x(m)}$ = density of binary mixture in monolayer, g./cc.
ρ_x = density of equilibrium solution, g./cc.
$\Delta\rho_x$ = density differences between the equilibrium liquid components, g./cc.
$\Delta\rho_y$ = density difference between adsorbate components, g./cc.
Ψ = constant in Stuart equation

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Calculation Procedures for Binary Batch Rectification

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A rigorous mathematical description, consisting of differential-difference equations, is presented for binary batch rectification in the plate type of column. Two approaches are taken to solving these equations for the condition of constant reflux ratio: an integration by numerical means employing an IBM 650 computer, and a hand calculation procedure that involves trial-and-error computation of batch-rectification curves, which is of interest primarily where high-speed computing equipment is not available.

Enthalpy balances are used to avoid assumption of equal rate of overflow in the tower; weight units are used instead of mole units; means for accounting for holdup in the condenser-accumulator system are described. Criteria of convergence and stability of the numerical solution are presented. The validity of the results of the proposed calculation procedures is substantiated by the close agreement of experimental and calculated batch-rectification curves.

Interest in batch-rectification calculations has grown during recent years, as evidenced by the contributions which have appeared in the technical literature. For a review of most of this work it is recommended that the reader consult the work of Rose and Rose (*1*) and Rose and Johnson (*2*). Rose, Johnson, and Williams (*3*) also give a brief historical outline of many of the accomplishments in the field.

The mathematical model describing batch rectification is inherently very complex even for the case of a binary mixture. Batch-rectification calculation procedures, comparable in rigor to methods for continuous steady state distillation calculations, have therefore led to long and tedious procedures. Simplification for convenience, on the other hand, has tended to restrict applicability of the results to the conditions embodied within the simplifying assumptions. For instance, the use of

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