Anal. Calcd. for $C_{20}H_{21}O_6N$ (371.4): N, 3.8; neut. equiv., 371. Found: N, 3.7; neut. equiv.,[8] 374.

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(8) Obtained by titration in alcohol; *cf.* E. Brand, B. F. Erlanger and H. Sachs, THIS JOURNAL, **74**, 1851 (1952).

DEPARTMENT OF BIOCHEMISTRY
COLLEGE OF PHYSICIANS AND SURGEONS
COLUMBIA UNIVERSITY
NEW-YORK 32, N. Y.

Separation Factors for Expressing the Relative Adsorbabilities of Liquids on Adsorbents[1]

BY ROBERT W. SCHIESSLER AND CARLETON N. ROWE[2]

Separation factors are used as criteria for the evaluation of various fractional separation processes. By analogy to relative volatility in fractional distillation, the adsorption separation factor, α, is defined as the ratio of relative adsorbabilities and may be expressed as

$$\alpha = (N_A/N_B)^a/(N_A/N_B)^l \qquad (1)$$

where

N = mole fraction
A and B = components
a = adsorbed phase
l = liquid phase

Experimental determination of the adsorbed phase composition cannot be made since a completely satisfactory method for the physical separation of the adsorbed and liquid phases has not been found. In consequence, only one application of the separation factor concept to the adsorption of binary liquid mixtures has been found in the literature. Mair, Westhaver and Rossini[3] have reported separation factors for a number of low molecular weight hydrocarbons. These were determined by a rather indirect method through the use of adsorption columns. A lengthy mathematical treatment of the fractionation process and an independent determination of the adsorbent capacity through the vapor phase were required to employ the fractionation data in an expression similar to equation 1.[4]

(1) American Petroleum Institute Research Project 42. Advisory Committee: H. Sutherland (Chairman), E. M. Barber, J. R. Bates, L. C. Beard, Jr., G. H. Denison, L. M. Henderson, R. F. Marschner, L. A. Mikeska and J. H. Ramser.

(2) American Petroleum Institute Research Fellow. Abstracted from an M.S. thesis by Carleton N. Rowe, 1953.

(3) B. J. Mair, J. W. Westhaver and F. D. Rossini, *Ind. Eng. Chem.*, **42**, 1279 (1950).

(4) The separation factor may be expressed[3] in terms of volume fractions by converting equation 1 as

$$\alpha = \frac{(N_A/N_B)^a}{(N_A/N_B)^l} = \frac{(n_A/n_B)^a}{(n_A/n_B)^l} = \frac{\left[\frac{(dv/M)_A}{(dv/M)_B}\right]^a}{\left[\frac{(dv/M)_A}{(dv/M)_B}\right]^l} =$$

$$\frac{(v_A/v_B)^a}{(v_A/v_B)^l} = \frac{(V_A/V_B)^a}{(V_A/V_B)^l}$$

where α, N, A, B, a and l have the meanings stated previously
n = moles
v = volume *as liquid* of a component in either the liquid phase or the adsorbed phase
d = *liquid* density of the pure components
M = molecular weight
V = volume fraction

Separation factors determined by the column method tend to be in error since they generally vary with composition due to non-ideality, and wide composition ranges are covered in the column technique.

The present investigation was undertaken to find a direct and more accurate method for determining adsorption separation factors. Jones and Outridge,[5] and Mair, Westhaver and Rossini[3] have observed that the adsorbent capacity determined by equilibration through the vapor phase·is nearly constant for pure liquids having widely different chemical compositions and properties. This has been confirmed in the present work for activated alumina and silica gel. Table I shows the average adsorbent capacities in cc. adsorbed per gram adsorbent for a number of liquids.

TABLE I

ADSORBENT CAPACITIES

| | Alumina | | Silica gel | |
Liquid	Capacity, cc./g.	Deviation from av., %	Capacity, cc./g.	Deviation from av., %
Methylcyclohexane	0.213	−0.5	0.357	−1.4
n-Heptane	.218	+1.9	.356	−1.7
Benzene	.217	+1.4	.365	+0.8
Cyclohexane	...	...	.349	−3.6
5-*n*-Butylnonane	.209	−2.3	...	...
Water	.211	−1.4	.383	+5.8
Av.	.214	1.5	.362	2.6

Defining the adsorbed phase in terms of the adsorbent capacity,[6,7] an expression may be derived for determining the separation factor in a static system. In the derivation, the assumption is made that the volumes are additive. Let

A = component preferentially adsorbed
V_A^i = vol. fctn. of A in original liquid mixture
V_A^l = vol. fctn. of A in liquid phase at equilibrium
V_A^a = vol. fctn. of A in adsorbed phase at equilibrium
X = vol. of original liquid mixture in cc.
Y = vol. of liquid phase at equilibrium in cc.
W = weight of adsorbent
z = capacity of adsorbent, cc./g.
Z = Wz, total capacity of W g. of adsorbent in cc.

The material balance for component A at equilibrium is

$$V_A^i X = V_A^l Y + V_A^a(X - Y) \qquad (2)$$

but, as previously defined

$$Z = (X - Y) \qquad (3)$$

thus

$$V_A^i X = V_A^l(X - Z) + V_A^a Z \qquad (4)$$

Rearranging

$$V_A^l = (V_A^l - V_A^a)X/Z + V_A^i \qquad (5)$$

Since the separation factor may be determined from volume fractions[4] and since $V_B^a = 1 - V_A^a$, equation 1 reduces to

$$\alpha = V_B^l V_A^a/V_A^l(1 - V_A^a) \qquad (6)$$

(5) D. C. Jones and L. Outridge, *J. Chem. Soc.*, 1574 (1930).

(6) The assumption that the adsorbent capacity determined by vapor phase equilibration is analogous to the adsorbed phase when the adsorbent is immersed in liquid is slightly erroneous due to the reduction of the vapor pressure of the liquid trapped in fine capillaries.[5]

(7) Mair, Westhaver and Rossini[3] used the adsorbent capacity determined through the vapor phase in their estimation of separation factors from column data.

Substituting equation 5 in equation 6, recalling that $V_A^1 + V_B^1 = 1$, and subtracting 1 from both sides for simplification

$$\alpha - 1 = \frac{(V_A^1 - V_A^1)X}{V_A^1[V_B^1 Z - (V_A^1 - V_A^1)X]} \tag{7}$$

Equation 7 is an expression of the separation factor in terms of readily determined quantities.

Error due to any non-additivity in volume can be reduced by employing an experimentally-determined density–composition curve to find the value for X used in equation 7.

Expressions similar to equation 7 may be derived using mole fraction or weight fraction, but both involve the density of a liquid mixture having the composition of the adsorbed phase. Assuming density to be linear with composition, or experimentally determining a density–composition curve, it is possible to calculate the separation factor using either mole fraction or weight fraction, but the equations are more complex. From the nature of the separation factor expression, any non-additivity in volume will lead to the same error, independent of the method of expressing the compositions.

A comparison of separation factors determined by the column method and the static method can be made for n-hexane/benzene mixtures on silica gel. Mair, Westhaver and Rossini[3] have determined separation factors for this hydrocarbon pair by the use of the column method. These values are shown graphically in Fig. 1. Equilibria data for the same hydrocarbon pair and the same type adsorbent (Davison Chemical Corporation, No. 22-08, "through 200 mesh") in a static system have been reported by Lombardo.[8] From these data we have calculated separation factors, also plotted in Fig. 1.
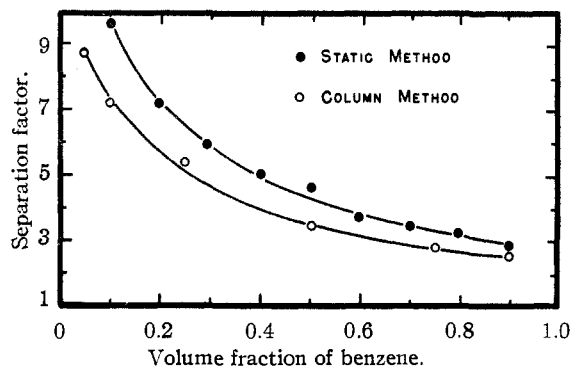

Fig. 1.—Separation factors for benzene/n-hexane mixtures.

The results indicate that the separation factors determined by the static method are higher than those determined by the column method. Since both methods assume additivity in volumes, and since both methods define the adsorbed phase in terms of the adsorbent capacity as determined by equilibration through the vapor phase, any deviations from these two assumptions could not account for the differences between the two curves. Due to the broad composition range covered in the column method, involving a broad range of separation factors, it is believed that the separation factors

determined by the static method are more accurate. Furthermore, the attainment of equilibrium was determined experimentally in the static method, and must be assumed in the column method.

Experimental

The experimental work consisted of determining the adsorbent capacities listed in Table I.

Adsorbents.—Activated alumina (Alcoa, F-20 grade, 80–200 mesh) was pretreated by heating to 200° for 16 hours in a 10 mm. i.d. column with passage of a slow stream of nitrogen gas through the column. Silica gel (Davison Chemical Corporation, No. 11-08-08-01, 28–200 mesh) was heated to 175° for 20 hours in the same apparatus.

Test Liquids.—Table II lists the liquids, their sources, refractive indices and vapor pressures at room temperature. Methylcyclohexane was purified by distillation in a helix packed column of 35–40 plates at a reflux ratio of 15/1 and passed over silica gel. Cyclohexane was passed over silica gel twice before use. The distilled water was boiled to remove any dissolved gases.

TABLE II

TEST LIQUIDS

Liquid	Source	$n^{25}D$	Approx. v.p. at 25°, mm.
Methylcyclo-hexane	Phillips, Tech. Grade, 95 mole % pure	1.4213[a]	48.0
Cyclohexane	Eastman, Practical	1.4236[a]	96.0
n-Heptane	Pure, Westvaco	1.3851	49.0
Benzene	Phillips, 99.97% pure	1.4976	95.2
Distilled water	Laboratory	1.3321	23.8
5-n-Butylnonane	API Project 42 Penn. State	1.4246	0.2

[a] Refractive index following purification.

Procedure for Determining Adsorbent Capacity.—The pretreated adsorbent was placed in a weighed covered Petri dish, and then dish and contents were weighed to the nearest ±0.0001 g. to give the weight of the adsorbent. The Petri dish and adsorbent were placed in a desiccator along with pure liquid in another open Petri dish. The desiccator was evacuated until the vapor pressure of the liquid was approached. The desiccator was then sealed and equilibration allowed to proceed. At 24-hour intervals, the adsorbent plus adsorbate was weighed to the nearest ±0.0001 g. until no increase in weight was observed. The weight of the adsorbate divided by the density of the liquid at room temperature gave the volume of the liquid adsorbed.

A Study of the Quantitative Dinitrophenylation of Amino Acids and Peptides

BY W. A. SCHROEDER AND JOANN LEGETTE

During an investigation of peptides in partial hydrolysates of gelatin,[1] the method of Sanger[2] has been used not only for the identification of the N-terminal amino acids but also for the identification and estimation of the other amino acids of the peptides. According to this method, the dinitrophenyl (DNP) peptide is completely hy-

(8) R. J. Lombardo, Ph.D. Thesis, The Pennsylvania State College (1951). An equation similar to 5 was employed to determine the composition of the adsorbed phase.

(1) W. A. Schroeder, L. Honnen and F. C. Green, Proc. Nat. Acad. Sci., 39, 23 (1953).
(2) F. Sanger, Biochem. J., 39, 507 (1945).