mined independently, but that both the separation factor and the true selective adsorbent capacity may be determined simultaneously from the experimental data for static liquid–adsorbent systems.

The reported expression[1,2]

$$\alpha - 1 = \frac{(V_A^i - V_A^l)X}{V_A^l[V_B^l Wz - (V_A^i - V_A^l)X]} \quad (1)$$

may be transformed into the form of an equation for a straight line by taking the reciprocal of both sides, and rearranging

$$V_A^l = \frac{V_A^l V_B^l W}{(V_A^i - V_A^l)X} z - \frac{1}{\alpha - 1} \quad (2)$$

A second equation of a straight line is obtained by dividing equation 2 by $V_A^l V_B^l W/(V_A^i - V_A^l)X$

$$\frac{(V_A^i - V_A^l)X}{V_B^l W} = -\frac{(V_A^i - V_A^l)X}{V_A^l V_B^l W}\left(\frac{1}{\alpha - 1}\right) + z \quad (3)$$

If the separation factor, α, and the selective adsorbent capacity, z, are constant with varying initial liquid compositions, then plots of V_A^l *vs.* $V_A^l V_B^l W/(V_A^i - V_A^l)X$ and $(V_A^i - V_A^l)X/V_B^l W$ *vs.* $(V_A^i - V_A^l)X/V_A^l V_B^l W$ will give straight lines from which the separation factor and the selective adsorbent capacity may be determined from the slope or the intercept, depending on the equation used.

The equations were tested experimentally using binary mixtures of several pure hydrocarbons in static systems. For each binary used several compositions were employed, using only 1 to 2 g. of adsorbent and 1 to 2 cc. of liquid mixture. The compositions were determined by refractive index, using a refractometer with a precision of ±0.00005 and an experimental refractive index–composition diagram. Both activated alumina (Alcoa, F-20) and silica gel (Davison, 28-200 Mesh) were employed as adsorbents.

An example of the constancy of the separation factor and the adsorbent capacity is illustrated in Fig. 1 in which the data for toluene–*n*-heptane mixtures on alumina are plotted. Deviation from linearity at higher concentrations of toluene is within the limits of precision. Equation 3 is less reliable due to increased sensitivity. In Fig. 1, the values obtained for the separation factor and the selective adsorbent capacity are 7.70 ± 0.67 and 0.062 ± 0.003 cc./g., respectively.

The results for the separation of low molecular weight hydrocarbon pairs on alumina and silica gel strongly indicate that the method is an improvement over previous attempts[1,3] to define and determine the true selective adsorbent capacity of the adsorbents for the liquids presented to them. The separation factors found are constant with composition, a fact not revealed by previous methods, and these separation factors should be the true values since only initial and equilibria data are needed.

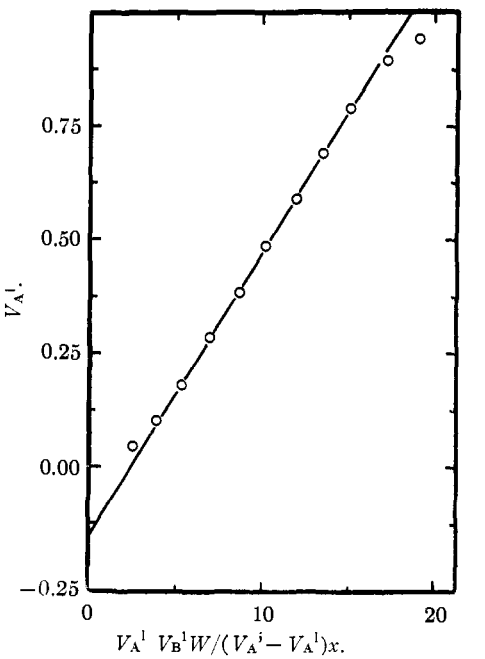

Fig. 1.—Results of equation 2 with *n*-heptane–toluene mixtures on activated alumina.

The detailed results for adsorbents and liquid binaries already examined will be the subject of a separate publication. The investigation is being continued.

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(2) α = adsorption separation factor
A = component preferentially adsorbed
V_A^i = vol. fctn. of A in original liq. mixt.
V_A^l = vol. fctn. of A in liq. phase at equil. $V_B^l = 1 - V_A^l$
X = vol. of original liq. mixt. in cc.
W = weight of adsorbent
z = selective capacity of adsorbent, cc./g.

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

THE PREPARATION OF STANNANE

Sir:

In the course of an investigation of the reduction of tin in acid solution with aqueous sodium borohydride, an unexpectedly large quantity of stannane was obtained. On the basis of the behavior of elements in the neighboring groups toward this reagent, it was expected that the reduction product would be principally metallic tin, with the possibility of a small amount of the hydride. Instead, yields of stannane as high as 84% were obtained from the borohydride reduction of tin(II) chloride in 0.6 *N* hydrochloric acid solution.

The only efficient method of preparation of stannane heretofore available was the reduction of tin(IV) chloride in ether by means of lithium aluminum hydride.[1] Those methods of preparation involving reduction of tin salts in aqueous solution by metals or metal alloys[2] or electrolytic

(1) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

(2) F. Paneth and K. Fürth, *Ber.*, **52**, 2020 (1919); F. Paneth, A. Johannsen and M. Matthies, *ibid.*, **55**, 769 (1922); I. Alimarin and Arest-Yakubovich, *C.A.*, **31**, 6573 (1937).

reduction[3] are inefficient and give only small yields.

In a typical preparation, 50 ml. of a solution 0.6 *N* in hydrochloric acid of tin(II) chloride containing 0.46 mmole of tin were introduced into a reaction flask connected to a series of traps suitable for the collection of the condensable products. The reaction system was swept with nitrogen, and the nitrogen stream was maintained throughout the reduction. From a dropping tube, 20 ml. of a 5% aqueous sodium borohydride solution were added over a period of 20 minutes. At this point the reduction was considered complete. The produced gases were passed through a trap held at −23° to remove most of the water vapor and through a trap kept at −196° to collect the stannane. The crude product was purified by fractionation through a trap maintained at −112°. The yield of stannane was 0.39 mmole or 84% based on the amount of tin taken.

The product was identified by its vapor pressure at −105° (39 mm.) and at −78° (198 mm.), values which are in agreement with those reported by Paneth.[4] The identification was verified by permitting 0.75 mmole of stannane to decompose into the elements. After seven days the decomposition was judged complete and 1.27 mmoles of hydrogen were found compared to 1.50 mmoles expected for stannane.

It has been observed that the yield of the hydride is dependent upon the acid concentration, the effect of which is still being investigated, and upon the concentration of tin. This latter effect is illustrated by the following data:

Mg. of tin per ml. of soln.	Yield of stannane, %
11	9
6	18
4	25
3	37
1	84

By an analogous reaction small but significant yields of bismuthine have been obtained. The preparation of these hydrides and those of related elements is under continuing study.

(3) F. Paneth and E. Rabinowitsch, *Ber.*, **57B**, 1877 (1924).

(4) F. Paneth, W. Haken and E. Rabinowitsch, *ibid.*, **57B**, 1898 (1924).

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RECEIVED JANUARY 15, 1954

THE SYNTHESIS OF PROTOPORPHYRIN FROM δ-AMINOLEVULINIC ACID IN A CELL-FREE EXTRACT[1]

Sir:

We have recently reported that δ-aminolevulinic acid can replace the two substrates, "active" succinate and glycine for porphyrin synthesis.[2] In order to investigate porphyrin synthesis in greater detail we have begun to fractionate duck red blood cell preparations which we have previously demonstrated are capable of synthesizing protoporphyrin *in vitro*. We have found that not only can homogenized duck erythrocyte preparations synthesize protoporphyrin from δ-aminolevulinic acid but that a soluble cell-free extract of the duck red blood cell can effect the synthesis. It can be seen from Table I, that the supernatant fluid obtained on high speed centrifugation (12×10^3 to 100×10^3 *g*) is almost as active as the homogenate and that even a lyophilized preparation of the cell-free extract still retains its synthetic activity. On the other hand, although the whole red blood cell or a gently hemolyzed preparation of duck erythrocytes can synthesize protoporphyrin from glycine and succinate,[3-5] the ability to convert these substrates to protoporphyrin is lost on disruption of the structure (Table I). It would appear that on homogenization the functional activity of only those enzymes that are involved in the condensation of succinate with glycine is lost.

TABLE I

COMPARISON OF C^{14} ACTIVITIES OF HEMIN SYNTHESIZED FROM δ-AMINOLEVULINIC ACID-5-C^{14} (0.05 MC./MM.) AND SUCCINIC ACID-2-C^{14} (0.05 MC./MM.) IN DIFFERENT RED BLOOD CELL PREPARATIONS[a]

Expt.	Substrate, acid	Red cell preparation	C^{14} activity in hemin sample, c.p.m.
1	Succinic (0.05 mM.)[b]	Hemolyzed	390
	Succinic (0.05 mM.)[b]	Homogenized	7
2	δ-Aminolevulinic (0.013 mM.)	Hemolyzed	4300
	δ-Aminolevulinic (0.013 mM.)	Homogenized	4500
3	δ-Aminolevulinic (0.009 mM.)	Homogenized	2200
	δ-Aminolevulinic (0.009 mM.)	Supernatant (12 × 10^3 *g*)	1600
	δ-Aminolevulinic (0.009 mM.)	Supernatant (47 × 10^3 *g*)	1600
	δ-Aminolevulinic (0.009 mM.)	Supernatant (100 × 10^3 *g*)	1500
4	δ-Aminolevulinic (0.009 mM.)	Supernatant (12 × 10^3 *g*)	2000
	δ-Aminolevulinic (0.009 mM.)	Lyophilized prepn.	1500

[a] Each preparation represented 25 ml. of duck blood and prepared as previously described.[3,4] [b] Plus 0.33 mM. of non-radioactive glycine.

Further proof that δ-aminolevulinic acid is indeed the precursor for porphyrin synthesis was obtained by degrading a hemin sample synthesized from δ-aminolevulinic acid-5-C^{14}.[6,7] The δ-carbon atom of the latter compound should label the same carbon atoms of protoporphyrin as those which we have previously found arise from the α-carbon atom of glycine[6] since the latter carbon atom is the

(1) This work was supported by grants from the National Institutes of Health, United States Public Health Service (RG-1128(C5)), from the American Cancer Society on the recommendation of the Committee on Growth of the National Research Council, and from the Rockefeller Foundation.

(2) D. Shemin and C. S. Russell, THIS JOURNAL, **76**, 4873 (1953).

(3) D. Shemin, I. M. London and D. Rittenberg, *J. Biol. Chem.*, **173**, 799 (1948); **183**, 757 (1950).

(4) D. Shemin and S. Kumin, *ibid.*, **198**, 827 (1952).

(5) I. M. London and M. Yamasaki, *Federation Proc.*, **11**, 250 (1952).

(6) J. Wittenberg and D. Shemin, *J. Biol. Chem.*, **185**, 103 (1950).

(7) D. Shemin and J. Wittenberg, *ibid.*, **192**, 315 (1951).