experiments carried out on proteins dissolved in aqueous media, when h/m is less than 1 and $d - \rho$ is less than 0.01, a value for the unsolvated molecular weight, M, within about 3% of the correct value should be obtained. Whenever $(h/m)\ (d - \rho)$ exceeds 0.01, unsolvated molecular weights of proteins determined by means of equation 10 will be too low by 3% or more.

When allowance is made for the differences in symbols, it is evident that equation 9 divided by equation 10 yields the equation derived previously by Lansing and Kraemer[7] for sedimentation equilibrium. Their equation 9 applies to the case of sedimentation equilibrium in a ternary system where the solute combines with only one of the other two components. In the same paper, of course, Lansing and Kraemer showed that the molecular weight of solute determined by sedimentation equilibrium of a dilute binary solution was virtually independent of solvation. Just as Lansing and Kraemer's equation 9 in no way contradicts their own equation 7, our treatment is in no way inconsistent with theirs.

Summary

The effect of hydration on the density correction of sedimentation constants is considered. Equations are presented to show the influence of hydration and a comparison is made between these new equations and the equation of Svedberg and Pedersen which is shown to represent a special case. Calculations involving previously published data show errors due to neglecting hydration ranging from 5 to 26% in an extreme case.

BERKELEY, CALIF.
PITTSBURGH, PENNA.
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[7] Lansing and Kraemer, THIS JOURNAL, **58**, 1471 (1936).

NOTES

Synthesis of C^{14}-Sodium Cyanide from Carbon Dioxide[1]

BY B. BELLEAU[2] AND R. D. H. HEARD

The two methods in current use for the conversion of radiocarbonate to radiocyanide, namely, the interaction[3] of $C^{14}O_2$, NH_3 and K in a sealed tube at 620°, and the fusion of $BaC^{14}O_3$ with sodium azide,[4] have in our experience proved to be tricky, inconvenient and distinctly limited in size [see also[5]]. Just recently an improved synthesis has been reported by Abrams[5]; $C^{14}O_2$ is reduced with magnesium to elementary carbon, which is then converted in 60–70% over-all yield to cyanide by treatment with ammonia at 1000°. The desirability of producing radiocyanide by simple organic reactions not requiring high temperature or pressure techniques prompted the adaptation of the following sequence of reactions.

$$\underset{\text{I}}{(C_6H_5)_3CNa} \xrightarrow[90\%]{C^{14}O_2} \underset{\text{II}}{(C_6H_5)_3CC^{14}OOH} \xrightarrow[95\%]{SOCl_2\ \text{then}\ NH_4OH}$$

$$\underset{\text{III}}{(C_6H_5)_3CC^{14}ONH_2} \xrightarrow[97\%]{P_2O_5} \underset{\text{IV}}{(C_6H_5)_3CC^{14}N} \xrightarrow[90\%]{\text{Na, EtOH}} \underset{\text{V}}{(C_6H_5)_3CH} + \underset{\text{VI}}{NaC^{14}N}$$

Triphenylmethylsodium (I)[6] carbonates[7] readily to the crystalline triphenylacetic acid II. The corresponding amide III,[8] prepared in the usual way through the acid chloride,[8] dehydrates smoothly to the nitrile IV, which, because of the pronounced electrophilic properties of the component groups facilely undergoes[9] hydrogenolysis to triphenylmethane (V) and cyanide (VI) rather than hydrogenation to triphenylethylamine. A consistent yield of 90% or better has been achieved in each of the steps, with the over-all realization of 68 to 72% of $NaC^{14}N$ from $BaC^{14}O_3$. The purification of intermediates is not necessary.

The method offers several worthwhile advantages: (a) in one convenient reaction, a gaseous low molecular weight starting material ($C^{14}O_2$; m. w., 46) leads to a solid high molecular weight product (II, m. w., 290, m. p., 267°); (b) it is equally adaptable to a micro- or a macroscale; and, (c) other useful one carbon compounds such as formate, methylamine, etc., may be obtainable directly (in the course of exploration).

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[2] Quebec Scientific Research Bureau Bursar. Contributed in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Cramer and Kistiakowsky, *J. Biol. Chem.*, **137**, 547 (1941); Loftfield, *Nucleonics*, **1**, No. 3, 54 (1947).

[4] Adamson, THIS JOURNAL, **69**, 2564 (1947).

[5] Abrams, *ibid.*, **71**, 3835 (1949).

[6] Renfrow and Hauser, *Org. Syntheses*, Col. Vol. II, 607 (1943).

[7] Schlenk and Marcus, *Ber.*, **47**, 1666 (1914).

[8] Schmidlin and Hodgson, *ibid.*, **41**, 445 (1908).

[9] Biltz, *Ann.*, **296**, 253 (1897).

Experimental

Triphenylacetic Acid-1-C^{14} (II).—The apparatus, assembled with $^{14}/_{20}$ standard taper joints, consisted of a 10 ml. generator flask and a 100 ml. reaction vessel, each equipped with a separatory funnel and interconnected through a drying tube (Drierite) with a stopcock on the reaction vessel side. The vacuum line, also with stopcock, led from the reaction vessel.

Ten and seven-tenths millicuries of $BaC^{14}O_3$ in 600 mg. of total barium carbonate were introduced into the generator flask, and the system was swept free of atmospheric gases with dry nitrogen fed through the generator separatory funnel. After partial evacuation, the carbon dioxide was liberated by the dropwise addition of 30% perchloric acid and frozen (liquid air) into the reaction vessel. The latter was then isolated from the rest of the system, the liquid air bath removed, and 30 ml. (1.2 molar proportions) of a 0.1 *N* solution of triphenylmethyl sodium (I)[6] in ether was added immediately and rapidly from the separatory funnel. It is essential that oxygen be excluded from I in the course of preparation and manipulation, in accordance with the technique described by Renfrow and Hauser.[6] The reaction vessel was then brought to room temperature, and the contents were shaken vigorously for two minutes. On removal from the system, an equal volume of 10% ammonia was added, and the ethereal phase was extracted twice again with dilute ammonia. The combined alkaline solutions, after one ether wash, were acidified to precipitate from 780 to 800 mg. (90-92% yield) of triphenylacetic acid-1-C^{14} (II), melting at 267° and exhibiting a specific radioactivity of 12.5 million counts per mg. per min., as determined in the windowless flow gas counter operating at approximately 40% efficiency. Schlenk and Marcus[7] report m. p. 267° for the C^{12} product obtained in unstated yield through the same reaction.

Triphenylacetamide-1-C^{14} (III).—The acid II (800 mg.) in purified thionyl chloride (5 ml.) was refluxed 2.5 hours. After evaporation to dryness in vacuum on the bath, the solid acid chloride was pulverized under 10 ml. of concentrated ammonia and let stand for 30 minutes when the amide was collected and dried (780 mg., melting at 246-248° in agreement with the literature).[8]

Triphenylacetonitrile-1-C^{14} (IV).—The amide III (780 mg.) in dry toluene (15 ml.) was heated under reflux for 50 hours with 5 g. phosphorus pentoxide. After addition of water, the aqueous phase was separated and washed four times with benzene. The combined organic extracts were dried over potassium hydroxide, and the solvents distilled to yield 730 mg. of crude IV as a brownish crystalline residue melting at 115-125°. Recrystallization from dilute acetone raised the m. p. to the reported[10] 127-128°.

Other dehydrating agents were found to be less satisfactory. Oxalyl chloride failed to effect the conversion, and phosphorus pentachloride gave a lower yield than phosphorus pentoxide. While the yield with thionyl chloride was excellent, the product was contaminated with traces of a tenacious sulfur-containing impurity which remained in the final cyanide.

Sodium Cyanide-C^{14} (VI).—The crude nitrile IV (730 mg.) in 9.5 ml. of dry ethanol contained in a 50-ml. standard taper flask fitted with a sealed-in gas inlet tube (closed) was refluxed with 1 g. of sodium added in ten portions over a period of 30-40 minutes. As a precautionary measure to prevent the loss of any free hydrogen cyanide at the beginning of the reaction, the effluent gases from the reflux condenser were passed through sodium hydroxide solution. At the end of the operation, the aqueous alkali from the trap was added to the reaction mixture [when triphenylmethane (V) precipitates], and the vessel was fitted to a dropping funnel carrying a gas exit tube from the interior of the system to the distillation condenser, the outlet from which protruded below the surface of the receiving 1 *N* sodium hydroxide solution (20% excess). The apparatus was swept with a slow stream of nitrogen introduced through the inlet tube to the reaction vessel, and excess dilute sulfuric acid was added dropwise from the separatory funnel. The contents of the flask were then boiled gently until approximately 15 ml. of distillate had collected. A slight turbidity in the latter was cleared by one washing with ether, and the alkaline solution was made to known volume and an aliquot was taken for titration of its cyanide content by the usual argentimetric method. For storage, the solution was taken to dryness in vacuum at room temperature.

In many runs, each from 600 mg. of barium carbonate and without purification of the intermediates, the yields of $NaC^{14}N$ ranged from 103 to 109 mg. (68-72%).

DEPARTMENT OF BIOCHEMISTRY
McGILL UNIVERSITY
MONTREAL, CANADA

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[10] Vorländer, *Ber.*, **44**, 2468 (1911).

A Derivation of the Concentration Distribution Equation for the Craig Counter Current Apparatus

BY ROBERT M. BOCK[1]

The development of the Craig counter-current distribution apparatus, with subsequent successful application to widely varied problems of separation, isolation and identification, has created a need for an equation which relates the distribution coefficient of a solute with the solute concentration in any tube, *r*, after *n* transfers have been completed. This equation has been obtained from consideration of the terms of a binomial expansion of degree *n* and by drawing an analogy between diffusion and the distribution process.[2]

It is the purpose of this note to present a derivation of the concentration distribution equation based solely upon probability considerations.

We shall discuss a system of a solute and two mutually saturated immiscible phases, where the solute has a linear distribution coefficient, *K*, between the phases. The coefficient, *K*, is defined as Y/X, where Y and X are the equilibrium solute concentrations in the upper and lower phases, respectively. Then, if *n* be the number of transfers performed, *r* the number of the tube under consideration, and if we give our attention to one molecule in tube number 0, we can derive the expression for the probability that this molecule will be in the tube *r* after *n* transfers.

The probability that the molecule will be in the upper (mobile) phase at the time a transfer occurs is equal to the ratio of the equilibrium amount of solute in the upper phase to the total amount of solute present in the tube.

Letting the amount of solute present in tube number 0 at the start of the procedure be one arbitrary unit and denoting the ratio of the volumes, V_1 and V_2, of the upper and lower phases by Z, we see that the probability of successful transfer, p, which is the same as the probability of being in the mobile phase, is given by

$$p = V_1Y/(V_1Y + V_2X)$$

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[1] Public Health Service Research Fellow of the National Heart Institute.

[2] Williamson and Craig, *J. Biol. Chem.*, **168**, 687 (1947).