at the boiling point of the alcohol over an open flame. To prevent a possible loss of the monomeric α-vinylthiophene through polymerization in the dehydrating flask, 0.1% hydroquinone was added to the alcohol before dehydration. The temperature of the vapor rose rapidly to 100° and then gradually to 130–135° and remained at this latter temperature until the dehydration was completed. α-Vinylthiophene is a water-like liquid having a styrene-like odor with the following constants: d^{20}_4 1.0429, $n^{23.4}D$ 1.5612.

α-Vinylthiophene polymerizes at room temperature to a yellowish transparent resin characterized by flexibility despite apparent hardness. The polymer obtained after ninety days was softened by toluene, cyclohexanol, thiophene and acetone at 25° but did not dissolve in any of these solvents. The polymer dissolved slowly in boiling cyclohexanol. Further work is in process on the thermal polymerization of α-vinylthiophene with special reference to degree of polymerization and average molecular weights of the polymer samples.

The 2-thienylmethylcarbinol from which the α-vinylthiophene was obtained was prepared according to the Meerwein–Ponndorf–Verley reduction[1] method: 70.08 g. (0.555 mole) of pure 2-acetylthiophene obtained by fractionally distilling a sample of the ketone as originally supplied by the Socony–Vacuum Laboratories, New York, N. Y., and utilizing the fraction which distilled at 89–90° (9 mm.) in the oxidation–reduction reaction, gave a yield of 44.16 g. (0.344 mole) of the secondary alcohol. Previous work[2] on the preparation of the carbinol reported yields of approximately 47% in contrast to a rectified yield of about 62% for this investigation. During the reduction of the ketone with aluminum isopropylate in dry isopropyl alcohol, the yield of acetone is used as an index of the reaction progression. Kuhn and Dann carried the reaction for only three hours, at which time the acetone test reagent (0.1% solution of 2,4-dinitrophenylhydrazine[3] still gave positive results indicating an incomplete reduction. The present investigation carried the reduction to a negative acetone test after a reaction time of five and one-half hours.

The reaction mixture was gently heated between 82–84° in an oil-bath at 107°. The vapor temperatures varied between 77–81°, becoming progressingly higher at the end of the reaction.

The carbinol is a water-white oil becoming yellowish upon standing and has a pleasantly sweet odor. It was separated from the by-products of the reaction by fractionation in a 10-cm. semimicro Widmer spiral distillation column and that portion which distilled at 88–89° (6 mm.) was used in the preparation of α-vinylthiophene. Additional constants found on 2-thienylmethylcarbinol were as follows: d^{20}_4 1.0926, $n^{23.4}D$ 1.5419. Two by-products were removed before the alcohol distilled over during the fractionation: 2 ml. of a floral-odor substance distilled at 38–40° (12 mm.), $n^{23}D$ 1.4922, and 5.5 ml. of a second substance at 75–78° (12 mm.), $n^{23}D$ 1.4862. Approximately 8 ml. of residue remained in the distillation flask.

(1) Roger Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

(2) von Richard Kuhn and Otto Dann, *Ann.*, **547**, 293–299 (1941).

(3) Lund, *Ber.*, **70**, 1520 (1937).

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THE CHARACTERISTIC SHEAR VALUE: A COEFFICIENT OF THIXOTROPIC BREAKDOWN

Sir:

In a recent article[1] equations for thixotropic breakdown in suspensions have been given. For the conditions that (1) the down-curves intersect at a common point and that (2) the up-curve also passes through the common point, the equation of the upcurve can be expressed in the form

$$U/M = \ln k - \ln (\sigma - \sigma_0) \qquad (1)$$

where U is the plastic viscosity, σ is the rate of shear with the subscript 0 referring to the common point, M is the "coefficient of thixotropic breakdown with varying rates of shear," and k is a constant. Based upon eq. 1 Green and Weltmann have introduced a new coefficient, V, designated the "coefficient of thixotropic breakdown when the yield value (f) changes with variation in the plastic viscosity (U)," and given by

$$V = -\,\mathrm{d}f/\mathrm{d}U \qquad (2)$$

This writer wishes to point out that eq. 2 is independent of eq. 1 and that the coefficient V is simply the rate of shear corresponding to the common point. Consider a series of straight lines intersecting the force axis at various points $f_1, f_2, \ldots, f_n$ and passing through a common point whose coördinates of force and rate of shear are f_0 and σ_0, respectively. Then the slope or plastic viscosity of each line is given by

$$U = (f_0 - f)/\sigma_0 \qquad (3)$$

By differentiating eq. 3 and rearranging, one obtains

$$\sigma_0 = -\,\mathrm{d}f/\mathrm{d}U \qquad (4)$$

Thus from eqs. 2 and 4 it is seen that V is equal to σ_0.

In Green's[1] treatment of the problem V was obtained from a series of equations and substitutions from which the following relationships were taken: $V = 2/MJ$, $J = 2S/MC\omega_0$, and $C = S/\ln (R_c/R_b)$. Condensing the various constants

$$V = \frac{\omega_0}{\ln (R_c/R_b)} \qquad (5)$$

For a rotational viscometer in which the separation of the cylinders is small, the average rate of shear can be obtained by assuming a linear velocity gradient between the cylinders, *viz.*

(1) H. Green and R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed.*, **18**, 167 (1946).

$$\bar{\sigma} = \frac{dv}{dr} = \frac{r d\omega}{dr} \qquad (6)$$

Integrating eq. 6 between limits R_b to R_c and $\omega = 0$ to $\omega = \omega$, one obtains

$$\bar{\sigma} = \frac{\omega}{\ln (R_c/R_b)} \qquad (7)$$

A comparison of eqs. 5 and 7 again shows that V is equal to σ_0. By substituting the numerical values for the dimensions of the viscometer cylinders[2] in eq. 7, one obtains good agreement between eqs. 4 and 7 from the data of Table I.[1]

(2) H. Green and R. N. Weltmann, *J. Applied Phys.*, **15**, 417 (1944).

A change in time does not affect the yield value but alters the plastic viscosity as a logarithmic function of time.[3] Thus the force coördinate of the points of intersection of the downcurves from different top rates of shear will vary with time but the rate of shear coördinate will be a constant. Therefore, it is proposed here to refer to the constant V or σ_0 as the "Characteristic Shear" value for the particular material.

(3) R. N. Weltmann, *J. Applied Phys.*, **14**, 343 (1943).

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NEW BOOKS

Acetanilid. A Critical Bibliographic Review. By MARTIN GROSS, M.D., Research Assistant (Assistant Professor), Laboratory of Applied Physiology, Yale University. Hillhouse Press, New Haven, Conn., 1946. 155 pp. 16 × 24 cm. Price, $3.00.

The very promising developments in the field of synthetic analgesics during recent years, in particular the discovery of synthetic compounds which equal or exceed morphine in potency, and possibly in clinical usefulness, have reawakened interest in this subject. In view of this progress, the preparation of a series of Monographs of the Institute for the Study of Analgesics and Sedative Drugs is especially welcome at this time. The subject of this review is the first volume in the series; salicylates, antipyrin, bromides and phenacetin will be dealt with in subsequent volumes.

In "Acetanilid" there is presented a critical bibliographical survey of the history, physico-chemical properties, metabolism, therapeutic uses, pharmacology, toxicology and tolerance of the drug. Because of the very extensive use of acetanilid, especially as an ingredient of a great variety of proprietary preparations, unbiased opinion relative to its toxicity is of paramount importance. This subject, as well as the question of habituation or addiction, has been given lengthy and careful consideration. The bibliography and author index includes seven hundred and sixty-three references. It seems to the writer that this monograph is to be recommended to those interested in the field because of the interesting and thorough treatment of the subject.

F. F. BLICKE

Advances in Protein Chemistry. Vol. II. Edited by M. L. ANSON, Continental Foods, Hoboken, and JOHN T. EDSALL, Harvard Medical School, Boston. Academic Press, Inc., 125 East 23rd Street, New York, N. Y., 1945. xiii + 443 pp. 15.5 × 23.5 cm. Price, $6.50.

The second volume of Advances in Protein Chemistry contains 11 reviews on various subjects of interest to the protein chemist. The discussions include proteins as they occur in nature as components of biological systems (copper proteins, mucoids and glycoproteins, wheat gluten), the estimation of amino acids by chemical and bacterial growth methods, the determination and reactivity of special groupings (reactions with formaldehyde, terminal amino acids and protein denaturation), the amino acid content of food proteins, the relation of protein nutrition to antibody formation and the implications of X-ray diffraction data on protein structure.

Most of these articles are of high quality, all have been written by authors who are actually working in the special field they describe. Unfortunately space does not permit every one of these contributions to be dealt with adequately so that for discussion only a few points can be singled out, in line with this reviewer's particular interests and bias.

Under the ambitious title "Analytical Chemistry of Proteins" Martin and Synge have compiled, unfortunately not alphabetically, about 800 assorted references to work of the last 15 years. Only chromatographic and ionophoretic methods have been treated in detail. Martin and Synge feel that it would be a great advance if editors insisted on the results of amino acid analysis being expressed in terms of amino acid N per 100 g. of total N in the protein. This reviewer rather hopes that results will continue to be reported as grams of amino acid (or of amino acid residue) yielded per 100 g. of protein. In addition, the figures could be presented in the manner suggested by the British authors.

The present state of our knowledge of the microbiological assay of amino acids is covered in an excellent, well organized review by E. E. Snell. Pertinent information is assembled in sixteen concise tables. The theoretical foundation of micro bioassays is by no means understood. It is apparent, nevertheless, that these techniques, in spite of their simplicity, are capable of yielding results whose accuracy compares with that of reliable chemical methods. The rapid development of microbiological methods during the past two years makes it understandable that many chemists still view them with suspicion. Snell's review will certainly help to overcome some of these doubts.

The identification of terminal amino acids in peptides and proteins is discussed by S. W. Fox. This timely review should prove valuable since much additional work on this important subject will no doubt be carried out in the future with the aid of new reagents.

The extensive literature on the reactions of formaldehyde with amino acids and proteins has been condensed by French and Edsall into a model review. All the pertinent information has been critically and lucidly discussed, although a vast number of reports, particularly technical ones, had to be omitted from consideration.

Research workers and students in many branches of science will look forward with anticipation to subsequent volumes of the Advances in Protein Chemistry, in which the Editors have promised us extensive and critical discussions of recent advances in the physical chemistry of amino acids, peptides and proteins.

ERWIN BRAND