dioxide[4] would indicate that it must occur at least as a transitory species. One might expect, moreover, a marginal stability for the monomer since the isoelectronic molecule chlorine dioxide does not dimerize to an appreciable extent. The reducing action of dithionite can now be pictured as proceeding simply by loss of an electron to any suitable acceptor with formation of sulfur dioxide.

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(4) H. B. van der Heijde, *Rec. trav. chim.*, **72**, 95 (1953).

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## NON-AQUEOUS SOLUTIONS OF SODIUM DESOXYRIBOSE-NUCLEATE

*Sir:*

Present hypotheses[1] concerning the structure of sodium desoxyribose nucleate (DNA) are based entirely on experiments with the hydrated polymer. Consequently, the extent to which water itself participates in stabilizing the structure has remained uncertain or ignored. We have discovered that it is possible to prepare solutions of DNA in a number of organic solvents[2] by dialysis and this communication concerns the novel properties of DNA in absolute ethanol.

Two different samples of calf thymus DNA, samples A and SB11B, prepared according to the method of Simmons[3] were used.[4] Dialysis of pure water solutions of DNA against increasing concentrations of ethanol yielded stable absolute ethanol solutions whose light scattering and sedimentation behavior indicates a drastic change of configuration at constant molecular weight. The comparison of macromolecular properties of sample SB11B in ethanol and 0.2 *M* NaCl in water (Table I) deserves further comment. The measured molecular weights in 0.2 *M* NaCl and ethanol differ by 15%. This is within the limits of experimental error.[7] On the other hand, the change in the radius of gyration is tremendous, especially when it is recalled that DNA is more extended in pure water than in 0.2 *M* NaCl.[8] As a consequence of this molecular collapse, ethanol solutions of DNA demonstrate little concentration dependence of the sedimentation constant and no hypersharpening of the sedimentation boundary. In addition, the intrinsic viscosity undergoes a fifty-fold decrease.

TABLE I

PROPERTIES OF CALF THYMUS DNA (SAMPLE SB11B)

| | 0.2 *M* NaCl[a] | 100% Ethanol |
|---|---|---|
| Molecular weight[b] | $7.7 \times 10^6$ | $6.6 \times 10^6$ |
| Radius of gyration, $A$[b] | 3000 | 980 |
| Sedimentation constant, $[S_{20,w}]_{c=0}$ | 21 | 65 |

[a] From reference (5). [b] From light scattering. For discussion of the averages determined for these quantities by the double extrapolation of reciprocal scattering to zero angle and concentration, see reference (6).

Two additional experiments are of interest: the first (Fig. 1) follows the change of sedimentation constant of sample SB11B in ethanol–water mixtures of varying composition. The change of

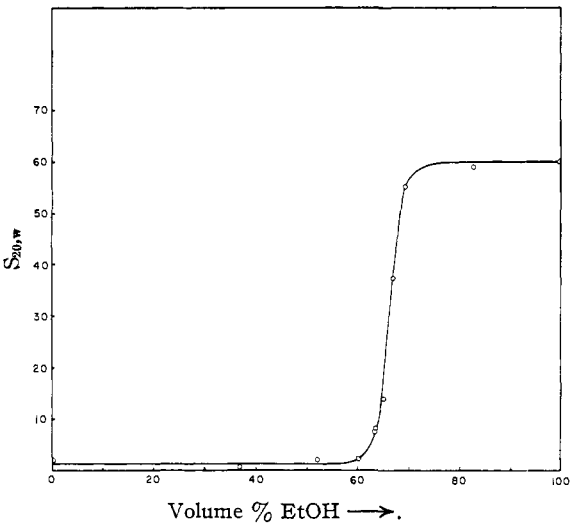


Fig. 1.—Sedimentation constant of DNA, sample SB11B, in ethanol–water mixtures as a function of solvent composition. The solute concentration varies between 0.06 and 0.13%.

DNA configuration is shown to occur rather sharply at about 65% ethanol content. It is not accompanied by the increase in ultraviolet absorption associated with denaturation.[9] The second experiment shows that the ethanol configuration change is essentially reversible with respect to size and shape. The light scattering of sample A in .2 *M* NaCl before and after dialysis[10] against 100% ethanol was compared. Molecular weights of 5.2 and 4.9 million, radii of gyration of 2060 and 1830 Å. and $s_{20,w}$ in 0.03% solution of 11.5 and 13.1, respectively, were obtained. While the redialyzed DNA is not as highly extended as the native material, a very closely similar structure has been reformed. This contrasts sharply with the irreversible change of shape produced by heating aqueous solutions.[5,11] It would be of interest to establish whether the ethanol configuration change is also reversible with respect to biological activity.

Further evidence[5] against the interrupted chain

(1) F. H. C. Crick and J. D. Watson, *Proc. Roy. Soc.*, **A223**, 80 (1954).

(2) The solubilities of a large number of proteins and DNA in organic solvents have also been investigated by E. D. Rees and S. J. Singer, *Arch. Biochem. Biophys.*, in press.

(3) N. Simmons, Atomic Energy Commission Report UCLA 184.

(4) Sample SB11B was the generous gift of Professor Paul Doty, which we gratefully acknowledge. It had been prepared by Dr. Simmons according to his method.

(5) P. Doty and S. Rice, *Biochim. Biophys. Acta*, **16**, 447 (1955).

(6) H. Benoit, *J. Polymer Sci.*, 11, 507 (1953).

(7) Not only must the uncertainty of the double extrapolation to zero angle and concentration be considered, (especially in ethanol), but in addition the two measurements were made on different instruments, introducing the absolute calibrations as a source of divergence.

(8) J. W. Rowen, *Biochem. Biophys. Acta*, **10**, 391 (1953).

(9) R. Thomas, *ibid.*, **14**, 231 (1954).

(10) The dialyzed sample was submitted to the following series of steps: exhaustive dialysis against water was followed by dialysis against increasing concentrations of ethanol, redialysis against increasing concentrations of water, and a final dialysis of this aqueous solution against 0.2 *M* NaCl.

(11) S. Zamenhof, H. Alexander and G. Leidy, *J. Exptl. Med.*, **98**, 373 (1954).

theory of DNA structure[12] is provided by the constancy of molecular weight throughout the structural changes which we have described. In addition, however, we are led to wonder whether the observed phenomena do not point to the participation of water in stabilizing the structure of DNA. With this end in view, we are investigating the behavior of DNA in a variety of organic solvents with different hydrogen-bonding characteristics.

(12) C. A. Dekker and H. K. Schachman, *Proc. Nat. Acad. Sci.*, **40**, 89 (1954).

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## SEGREGATION COEFFICIENTS OF VARIOUS IMPURITIES IN A SILICON TETRAIODIDE MATRIX

*Sir:*

The demand for transistors and other semiconductor devices has stimulated considerable research in the preparation of ultra-pure silicon. It was found that zone-refining techniques[1] were inadequate for the removal of certain impurities, *e.g.*, boron, in a silicon matrix,[2] and it was decided to approach the problem by preparing a suitable compound of silicon, subjecting this to such purification techniques as recrystallization, sublimation, and zone purification and ultimately decomposing it to elemental silicon. Thermodynamic calculations indicated that of the four tetrahalides, silicon tetraiodide decomposed most readily and that it lent itself best to zone-melting techniques because of its relatively high melting point (121.5–122.5°). Furthermore, it could be expected that the segregation coefficients for the various impurities in silicon tetraiodide would differ from those found in silicon.

Silicon tetraiodide was prepared by passing iodine vapor over Coleman and Bell Company ninety-eight per cent. pure silicon at 800° and the product was then crystallized from toluene. This material was used to fill Pyrex ampoules nine millimeters in diameter and thirty centimeters long. It was then densified, the tube sealed, and zone-purification was effected by vertical passage at the rate of five centimeters an hour. The zone width was two and one-half centimeters, and the temperature of the molten zone was about 135°. A small molten zone was passed through the charge only once in order to maintain impurities at spectrographically detectable levels. Spectrographic analyses of the successive two and one-half centimeter zones permitted preliminary calculations to be made based on Pfann's original equation.[1] The results of these calculations gave plots of $C/C_0$ *versus* $x/l$ (where $C$ is the concentration of an impurity in a solid frozen from a mother zone, $C_0$ is the mean concentration of the impurity before zone refining, $x$ is the distance that the zone has traveled along the tube, and $l$ is the zone length) which indicated that certain impurities can be efficiently removed by this technique. In the case of boron where the concentration level was below the limit of spectrographic detectability, a mathematical extrapolation was employed based on the minimum spectrographically detectable concentration found. Using this value in conjunction with the expression:

$$C_z = K[C_0 + (C_{z-1}/K - C_{z-1})]$$

where $C_z$ is the concentration of an impurity frozen into the $z$th zone, $C_{z-1}$ is the concentration of the impurity frozen into the previously frozen zone, $k$ is the segregation coefficient of the impurity, and $C_0$ is as described above, the maximum value for the $k$ of boron was determined. The values of the $k$'s determined for various metallic impurity species in the $SiI_4$ matrix are: boron, 0.16 ± 0.07, aluminum, 0.88 ± 0.04, sodium, 0.07 ± 0.01, magnesium, 0.58 ± 0.06, copper 0.63 ± 0.05.

It is apparent from the above that the impurities listed can be removed to levels below the one part per million range by a suitable number of passes. Work on this project, and the method and/or methods of preparing pure silicon tetraiodide, as well as the preparation of the elemental silicon, is continuing.

(1) W. G. Pfann, *Trans. AIME, J. Metals*, **194**, 747 (July, 1952).
(2) J. A. Burton, *Physica*, **20**, 845 (Nov., 1954).

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## GLUCOSIDURONIC ACID SYNTHESIS BY β-GLUCURONIDASE IN A TRANSFER REACTION

*Sir:*

Certain biological phenomena have been correlated with the activity of the enzyme β-glucuronidase. Among these are glucuronidogenesis,[1] action of gonadal hormones,[2,3,4,5] human cancer,[6,7,8] genetic control in mouse tissues,[3,9,10] and effects of pituitary interstitial cell stimulating hormone.[11] In attempts to arrive at an interpretation of the function of the enzyme *in vivo*, we have found it difficult to explain the findings on the basis of a purely hydrolytic action of the enzyme or its simple reversal. It was postulated that β-glucuronidase participates as a member of a multicomponent system concerned with glucosiduronic

(1) W. H. Fishman, *J. Biol. Chem.*, **136**, 229 (1940).
(2) W. H. Fishman, *ibid.*, **159**, 7 (1947).
(3) W. H. Fishman and M. H. Farmelant, *Endocrinology*, **52**, 536 (1953).
(4) A. L. Beyler and C. M. Szego, *ibid.*, **54**, 323, 334 (1954).
(5) W. H. Fishman, in "Vitamins and Hormones," Vol. IX, Academic Press, New York, N. Y., 1951, p. 213.
(6) W. H. Fishman, A. J. Anlyan and E. Gordon, *Cancer Research*, **7**, 808 (1947).
(7) W. H. Fishman and R. Bigelow, *J. Natl. Cancer Inst.*, **10**, 1115 (1950).
(8) W. H. Fishman, S. Green, F. Homburger, S. C. Kasdon, H. E. Nieburgs, G. McInnis and E. R. Pund, *Cancer*, **7**, 729 (1954).
(9) A. G. Morrow, E. M. Greenspan and D. M. Carroll, *J. Natl. Cancer Inst.*, **10**, 657 (1949).
(10) L. W. Law, A. G. Morrow and E. M. Greenspan, *ibid.*, **12**, 909 (1952).
(11) W. H. Fishman, G. Benjamin and S. Green, *J. Clin. Endocrinol.*, **15**, 876 (1955).