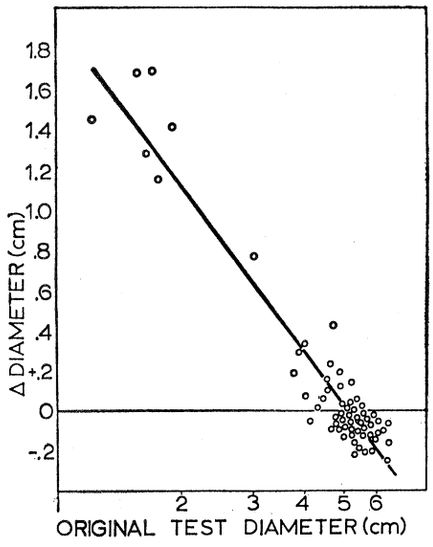

Fig. 1. Diameter changes (Δ diameter) of marked sea urchins in the experimental pool. The regression equation is $y = -2.77\ x + 1.97$, where x is the original diameter in logarithms and y is the change in diameter. Time is 1 year from June 1964 to June 1965.

parts are involved in the estimate of size, the fact that the animals shrink suggests that calcite was resorbed. The general growth of echinoid tests by addition of material around individual plates has long been known (*6*). Resorption of plates at the peristome has been experimentally determined in cidarids (*7*), and a highly precise deposition and resorption in spines has been suggested (*8*). Mechanisms for reworking calcite are obviously present and could lead to controlled decreases in test size.

In 1963, large numbers of newly settled animals were observed. By following these during the year, I knew that the small individuals collected from the control pool and marked in 1964 were all 1 year old. Size distributions were constructed from samples from the control pool during the summers of 1964 through 1966. Animal densities exceeded 200 individuals per meter squared, and sampling consisted of simply collecting all individuals within a small area and measuring one diameter with vernier calipers. Distributions for all 3 years were distinctly bimodal. Graphic analysis (*9*) was used to determine means and standard deviations of the distribution (Table 1).

The growth equation which can be derived from the regression in Fig. 1 is:

$$-x_t^{2.77} + x_t + 1.97 = x_{t+1} \quad (1)$$

where t is years and x is test diameter in centimeters. If in Eq. 1 x equals 1.65 cm and t equals 1 year (Table 1), then test diameters of urchins 2 years old would be 3.02 cm; those of 3-year-olds, 3.66 cm; and those of 10-year-olds, 4.95 cm.

Shifts in the modes of the 1963 class (Table 1) indicate mean sizes of 2.44 cm for 2-year-old urchins and 3.50 cm for animals 3 years old; these values are in general agreement with the sizes suggested from marking. Settling was apparently poor from 1964 to 1966; so the first mode, even in 1966, represented an almost pure 1963 class. The underestimate of the true mean of the 1963 class in 1966 is accordingly considered to be insignificant. Because of the agreement between growth of small marked animals and apparent growth of small animals in the control pool, I conclude that marking did not seriously affect the growth of small individuals. It would also then be expected that growth of larger individuals would not be affected by marking. The apparent shift of the second mode in the size distributions from 1964 to 1965 (Table 1) is much greater than that observed for marked animals of comparable sizes, as is the decrease from 1965 to 1966. Differences between large individuals in the experimental and control pools could be simply artifacts due either to sampling or to the graphic method of determination of mean size. It is also possible that there are environmental differences or that marking affects large animals differently than it does small ones. The latter explanation, however, appears to be unlikely. General growth form of *S. purpuratus*, as indicated by Walford's method (*10*), with size at $t + 1$ plotted as a function of size at t, is unlike graphs which can be drawn for other urchins (*1*), fish (*10, 11*), or pelecypods (*12*).

An implication of shrinking in large animals is that periods of decrease in size may be interspersed with periods of net gain, when environmental conditions change from year to year. Perhaps sea urchins grow to the limit allowed by the environment and adjust as the environment fluctuates.

The growth of animals in this study indicates that *S. purpuratus* may attain an age of at least 10 years. If settling observed since 1963 was normal, the large standing populations must represent recruitment over many years; the average age is possibly more than 10 years. The growth equation and the suggested relationship between size and age must of course be considered as representative only for the period 1964 to 1965 at the high area of Sunset Bay having eel grass; they cannot be considered as the only ones possible for this urchin.

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Stabilization of Hydrated Electrons in Irradiated Frozen Sugar Solutions

Abstract. *Yields of free radicals in irradiated aqueous solutions of saccharides at 77°K are larger and qualitatively different from those observed in the components alone. In addition, a blue color results only with the solution. The mechanism proposed to explain the observations is the stabilization of hydrated electrons by the solute.*

Irradiation of frozen solutions of sucrose and the monomers forming it—fructose and glucose—results in phenomena which are specific to the solution and which do not occur in either the solvent or solute alone. The electron spin resonance spectrum exhibits a strong narrow single line in addition to the absorption due to the components by themselves. Irradiation effects on the

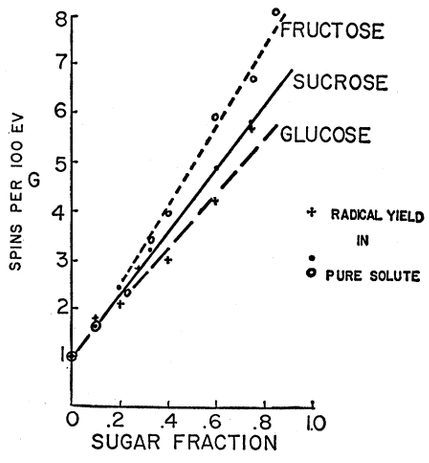

Fig. 1. Free-radical yield per 100 ev. Absorbed energy as a function of solution composition. Dose, 10^5 rads; temperature, 77°K.

components have been extensively reported (*1*). The irradiated solution also has a brilliant blue color which likewise does not occur in the components individually.

The samples were irradiated by a cobalt-60 source (12,000 curies) and observed at 77°K. The yield of stable unpaired electron spins was determined for sugar concentrations from 0 to 100 percent by weight (Fig. 1). This yield is substantially greater than would be the case if the spectra resulting from the two components were added independently. The narrow line width of the added spectrum component contributes to the striking contrast between the absorption derivative spectrum of the solution and that obtained from the corresponding amount of components (Fig. 2). These traces refer to a solution in which the ratio of sucrose to water is 1 to 4. The line width of the strong line did not appear to vary with solution concentration.

The irradiation dose received by the samples observed in Figs. 1 and 2 was 10^5 rads. At this dose, the free-radical yield is a linear function of dose received. Increasing the dosage results in a departure from linearity according to the relation:

$$\text{Unpaired spins per gram of sample} = 3 \times 10^{18} [1 - \exp(-D/10^6)]$$

where D is the dose in rads. The maximum concentration corresponds to one unpaired spin for every 10^4 molecules of solution. In view of the fact that each molecule has an equally likely chance of being damaged, it is clear that the amount of saturation is not due to the limited number of molecules available to produce free radicals. A pairing of spins, or a relaxation of the radicals back to the normal state equilibrating with the rate of production, is more apt to be the cause. The latter explanation was shown to be invalid when the spectrum was found to be stable over an 8-hour period with the samples in the dark. Under ordinary room illumination, the color and the sharp line in the spectrum disappeared within 2 hours. The spectrum then resembled a combination of the spectra for the components individually.

Raising the temperature above 124°K resulted in the disappearance of the blue color and the sharp line. This is the same temperature at which the spectrum of free radicals in irradiated ice disappears. In view of the mutual presence and absence of the strong narrow line characteristic of the solution and the color, it is reasonable to assume that they are related.

The observed behavior was similar to phenomena reported by Blandamer *et al.* for frozen solutions of alkali-metal hydroxide (*2*). Such behavior is perhaps due to the stabilization of the hydrated electron (H_2O^-) at low temperatures by the solute. This radical, which is formed when water is irradiated, is extremely reactive and has a lifetime on the order of 10^{-13} second at room temperature. Pulsed radiolysis has yielded light-absorption spectra, with a peak in the long wavelength region of the visible spectrum. This absorption spectrum is similar to that reported for the irradiated solutions of alkali-metal hydroxide and would explain the blue color observed in the sugar solution (*3*). Blandamer *et al.* (*4*) propose a model in which the negative hydrated electron is trapped in a cavity set up within the polar solvent and solute molecules which are so oriented that their positive poles are directed toward the electron. The repulsion between the positive poles of the molecules forces them apart, and a cavity is formed in which the electron is trapped.

The concentration of solvated electrons in solutions of alkali metals in liquid ammonia is proportional to the solute concentration. However, concentrations of 0.01 mole per liter result in pairing of one-half of the spins, and consequently these spins are not observed in the electron spin resonance spectra (*5*). This is a concentration of approximately 10^{-4} spin per molecule and is consistent with the magnitude of the spectrum for irradiated sugar solutions.

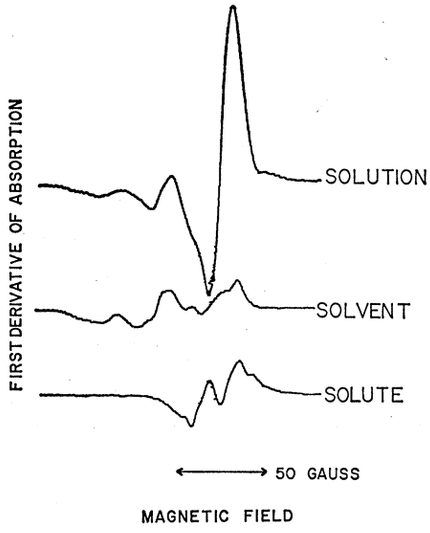

Fig. 2. Electron spin resonance spectrum for solution and individual components. First derivative of absorption plotted against magnetic field (ratio of sucrose to water, 1 : 4). Dose, 10^5 rads; temperature, 77°K.

Our observations are similar in optical behavior and electron spin resonance spectra both qualitatively and quantitatively to those of other workers mentioned in the references. However, although previous work involved ionic solutes, organic solutes may also exhibit this behavior. In general, organic compounds do not exhibit it, although a similar effect was observed with choline chloride and soluble starch. The characteristics of sugar molecules and a few other substances which appear to stabilize the solvated electron at low temperature are not yet understood.

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