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Visual Autoclaving Studies of Hydrothermal Changes in Sugar Solutions

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Visual autoclaving studies of hydrothermal changes have so far been restricted to inorganic compounds.[1] Lately it occurred to us that an extension of the studies to organic compounds might add to our information on hydrothermal changes. Sugars were chosen because they resemble inorganic compounds as regards their behavior towards solvents; that is, they are easily soluble in water but not in organic solvents. By such a choice, we were able to find a new mode of the concentration dependence of hydrothermal changes.

Sugars. Commercial saccharose, dextrose, and levulose of the best grade were used. Solutions of various concentrations were put into 5 tubes of Pyrex glass (dia. 10 mm). They were evacuated with a water-jet pump, sealed, and subjected to visual autoclaving. Solutions with concentrations of 0.4M, 0.1M, 0.04M, 0.01M and 0.004M were autoclaved up to 230°C in 1.5 hr, and the resulting changes were observed. Coloration took place in each solution at a certain temperature, which rose with a decrease in the concentration. Reproducibility of the values of the coloration temperature was within ±3 °C. Levulose underwent the change most easily. Above the coloration temperature, a deepening in color took place with a rise in the temperature, followed by a coagulation of the particles which separated from the solution. All the 0.4M solutions turned into two phases, a dark precipitate and a brown liquid. The sugar appeared to be charred in water.[2] The changes became less marked with a decrease in concentration, all the 0.004M solutions turning brown with hardly any precipitate. The onset of coloration of each 0.4M solution took place at a temperature slightly higher (2—8 °C) than that of the corresponding solid sugar observed when heated in an open glass tube.

The results are shown in Fig. 1. The concentration range of the solutions being great, it was necessary to reduce the scale for representation. For this, the average inter-solute distance was used instead of the logarithm of the concentration. This was found to be effective also for giving an intuitive picture of a non-dissociated solution. If we put r=inter-solute distance and c=molar concentration, their relation is given by[3]

$$r = 12/\sqrt[3]{c} \qquad (1)$$

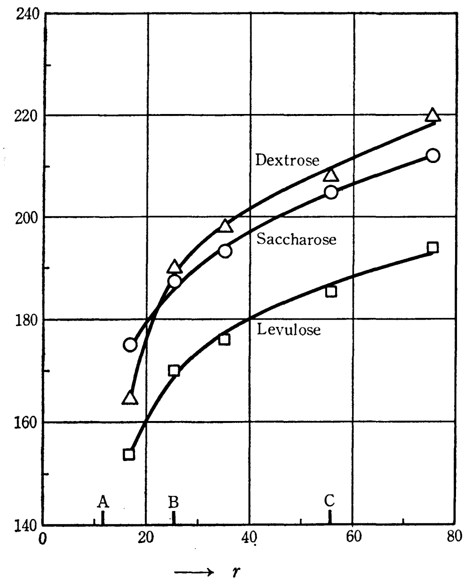

Fig. 1. Concentration dependence of coloration temperature
T=coloration temperature in °C.
r=average inter-solute distance in Å
Points A, B, and C correspond to 1M, 0.1M, and 0.01M, respectively.

The concentration dependence of the coloration temperature T is given in terms of the curve T *vs.* r. The area above the curve represents the zone in which the solution undergoes changes, while that under the curve is the zone in which the solution remains stable. The concentration dependence here is in contrast to the case of electrolytes (hydrolysis), where a high concentration makes the solution stable.

Equation (1) can be obtained as follows. We assume that solute particles are of equal size and are not dissociated. Let us take the case in which 6.02×10^{23} (Avogadro's number) particles are distributed uniformly in a space of 1 liter volume. The inter-solute distance, say l, can be taken as a unit distance corresponding to one molar solution. For its evaluation we replace the problem with one of packing. Suppose that a volume of 1 liter is closely packed with 6.02×10^{23} spheres of equal size; then the distance between the centers of the nearest neighbors, or the diameter of the

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[1] For the principal achievements attained by visual autoclaving, see T. Katsurai and K. Sone, This Bulletin, **41**, 519 (1968).

[2] The precipitate obtained from 0.4 M levulose was subjected to electron-diffraction study. The diffraction pattern indicated that the precipitate consists of dielectric and polymerized matter differing from electro-conductive carbon. The precipitate seems to be formed by the hydrothermal polymerization of levulose. We owe this information to Dr. Shigeto Yamaguchi, National Institute for Research in Inorganic Materials.

[3] This formula was found to be useful also for obtaining the empirical formula for the optimum concentration in hydrothermal precipitation; T. Katsurai, This Bulletin, **44**, 3207 (1971). The applicability of Formula (2) can be extended to a case where we have a solvent only. If we put l=10.3 Å (tetrahedral packing) and c=55.3 (number of moles of water in 1 liter), we obtain r=2.70 Å, which agrees with the distance between water molecules experimentally obtained; T. T. Wall and D. F. Hornig, *J. Chem. Phys.*, **43**, 2084 (1965).

sphere, gives the required value. It is not unique, but differs according to the mode of packing.

Mode of packing	l in Å
Closest	13.3
Cubic	11.8
Tetrahedral	10.3

Since the concentration (number of solute particles in unit volume) is inversely proportional to the third power of the inter-solute distance, we obtain the following relation for the conversion of concentration into inter-solute distance:

$$r = l/\sqrt[3]{c} \tag{2}$$

For our present purpose, the value 12 is taken as an approximation of the average (11.8Å) of the three values of l. We thus obtain Eq. (1). This can be taken for granted when we consider the fluctuation of the positions of the solute particles.

Some modifications in the experimental procedure should be added:[4] (a) for the simultaneous observation of the changes taking place in the 5 tubes, it is advantageous to keep the circular disk supporting the sealed tubes rotating and the ring burner below the disk fixed; (b) the appropriate r.p.m. of the disk is 3, and (c) the tubes are tilted 30° from the direction of gravity. This makes the circulation of the stream in the solution caused by heating smoother, and the shock given to the test tube caused by contingent bumping smaller.

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[4] T. Katsurai, *Kolloid-Z.*, **170**, 57 (1960), Fig. 1.