Light Scattering Properties of Acacia Catechuic Acid. Effects of Urea and Temperature

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Synopsis

Association of acacia catechuic acid (ACA) molecules was established in ethanol–water medium.[2] This association was further tested in pure aqueous medium as well as by using urea in increasing amounts in aqueous solutions. The $5M$ urea depressed the molecular weight to 2.82×10^6, as against 5.04×10^6 in aqueous solution of NaCl or KCl. This reduction has been explained as due either to rupture of the molecule itself or dissociation of molecules which normally remain associated in water. The diminution of root-mean-square end-to-end distance in urea from 323 mμ in water[3] to 290 mμ has also been attributed to the disaggregation of the associated molecules. To test this point further, the effect of increasing the temperature was next studied. The molecular weight was observed to be lower at higher temperature (actual value at 47°C was nearly half the original value at 28°C). This considerable reduction positively points to a dissociation of the molecule which was first suspected in our study with urea. The root-mean-square end-to-end distance also diminished to a certain extent, but not so much as the molecular weight. This has been explained as due to the stretching of the molecule when the solvent behaves as a better solvent at higher temperature.

INTRODUCTION

Acacia catechu is a gum plant, commonly known as "Khair" in India. Although it is widely distributed in the country, it has not been much utilized due to lack of precise knowledge of its chemistry. The preliminary structure[1] of this gum was first elucidated by Hulyalkar, Ingle and Bhide. They obtained D-galactose, L-arabinose, D-rhamnose, and D-glucuronic acid on acid hydrolysis of the gum. Acacia catechuic acid (ACA) is an acid polysaccharide obtained by the electrodialysis of the gum *Acacia catechu* and replacement of the cations by hydrogen ions. Previous investigations[2] of this gum acid in ethanol–water mixture revealed the possibility of association between its molecules. In the present investigation this point has been tested further, particularly to determine in what form, whether monomerized, dimerized, or any other associated form, the ACA molecules exist in pure aqueous medium.

Water, as already known, is a highly polar medium which can form hydrogen bonds with the OH groups of the polysaccharides. Naturally, the light scattering measurements of ACA were considered necessary in the

presence of water alone, the results of which were discussed elsewhere.[3,4] The present investigation was performed in two parts as follows.

PART I: EFFECT OF UREA

The ability of urea to reduce aggregation in aqueous polymer solutions through hydrogen bond rupture is well known.[5] Consequently, the mol. wt. of a sample of ACA was investigated in aqueous urea solutions. At low concentrations of urea, the behavior was almost similar to that of ACA in plain water.[2] A slight effect began to be manifested by increasing the urea concentration to $3M$. The effect became prominent and interesting when the concentration was gradually changed to $5M$. On further increasing the urea concentration above $5M$, no further notable change was observed. Hence the data of these experiments in $5M$ urea–water solutions only are presented here.

The absolute refractive index of $5M$ urea–water solution (n_0) was determined with the help of a Pulfrich refractometer correct up to 5 places. The value of n_0 turned out to be 1.38500. The differential refractive index increment ($n - n_0$) was, however, determined with a Brice Phoenix differential refractometer maintaining a temperature of 28°C, where n is the refractive index of ACA solution in $5M$ urea. From the knowledge of both of these quantities, the value of the constant H was determined:

$$H = \frac{32\pi^3 n_0^2 (n - n_0)^2}{3N\lambda^4 c^2}$$

where N is the Avogrado number, λ is the wavelength of the light used, and c is the concentration of the solution. The recorded value of H was equal to 6.14×10^{-6} (compared to 5.74×10^{-6} with water[2]).
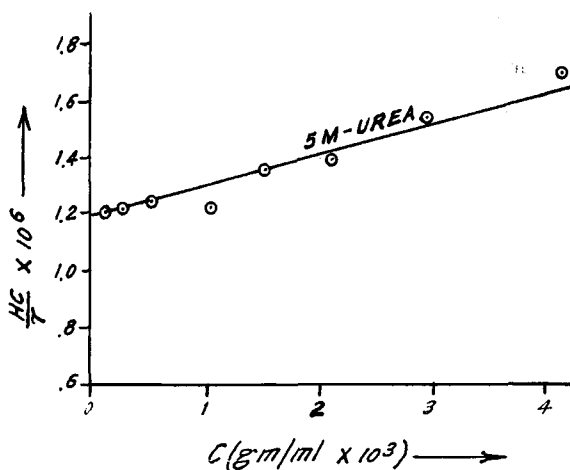

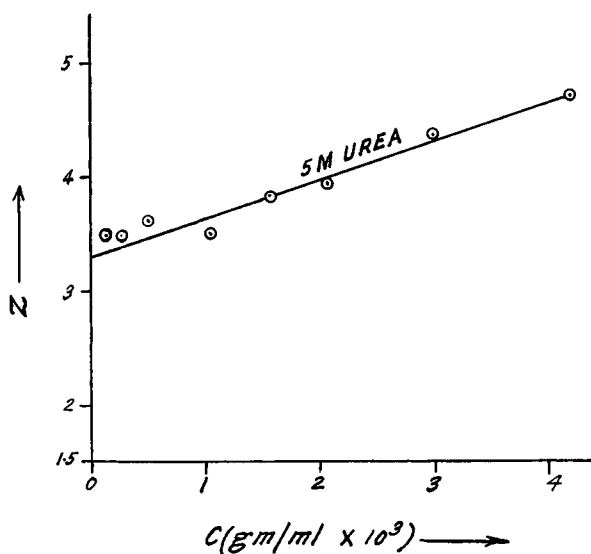Fig. 1. Variation of Hc/τ with concentration in $5M$ urea ($H = 6.140 \times 10^{-6}$).

Fig. 2. Variation of dissymmetry with concentration in $5M$ urea.

The value of turbidity and dissymmetry for $5M$ urea–water solvent were found considerably higher than those when only water was used as solvent. The net values of turbidity and dissymmetry were calculated as usual after subtracting the values obtained for the urea–water solvent.

The plot of Hc/τ versus C in $5M$ urea–water solvent yields a straight line (Fig. 1). The slope of the straight line when extrapolated to zero concentration gives the apparent molecular weight as 0.83×10^6 which needs further correction for dissymmetry and depolarization. When the correction for the dissymmetry of scattering is made, the value of the molecular weight amounts to 2.82×10^6. The depolarization effect, being very small, was not taken into account.

The intrinsic dissymmetry value was found to be 3.3 from the Z versus C plot (Fig. 2). The corresponding root-mean-square end-to-end distance was 290 mμ (compared to 323 mμ when only water was used as a solvent).

It is quite obvious from the above results that the molecular weight of ACA reduces to about 50% (2.82×10^6 in place of 5.04×10^6 in aqueous solution of sodium and potassium salts) when a $5M$ urea–water mixture was used as solvent. The root-mean-square end-to-end distance has also reduced to some extent, although not in the same proportion as the molecular weight. This reduction in the molecular weight may be due either to the breakage of a single molecule into parts or due to dissociation of molecules which ordinarily remain associated by hydrogen bonds or weak Van der Waals forces. The root-mean-square end-to-end distance, however, was not much reduced perhaps due to the good solvent behavior of the urea–water mixture, as evident from the high positive values of the second virial coefficient (Fig. 1).

PART II: EFFECT OF TEMPERATURE

In the preceding part, the experimental results revealed the two possibili-
ties in which ACA molecules may remain in aqueous solution, viz., either
monomerized or in the associated forms.   In order to assess which of the
states is more probable, a study of the effect of temperature on the light
scattering behavior of ACA was considered necessary.

Barry and Halsey[6] observed the breakage of large aggregates of the poly-
mer locust bean gum in aqueous solution through rupture of the hydrogen
bonds by elevating the temperature of the polymer solution.   The experi-
ments were performed at two different temperature, viz., 28°C and 47°C,
dissolving the ACA in 0.25N KCl; and after neutralizing, the ACA with
NaOH.   Such a medium for ACA was chosen because its molecular weight
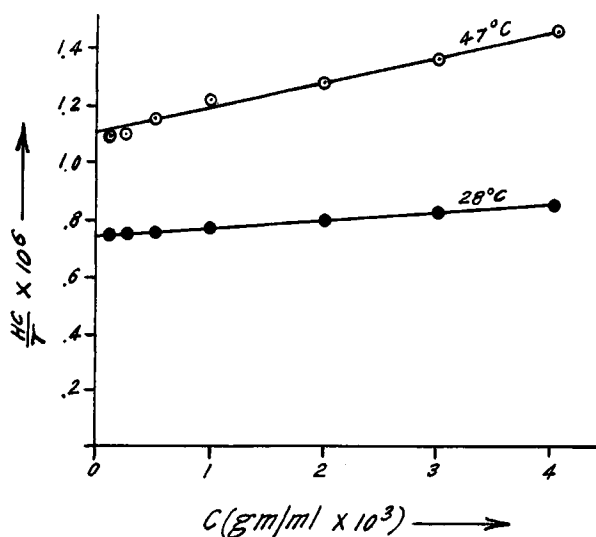could not be ascertained correctly with pure water as solvent.

Fig. 3. Variation of Hc/τ with concentration in 0.025N KCl ($H = 5.744 \times 10^{-6}$).

The constancy of the temperatures was maintained with the help of a
thermostat and specially designed glass coils fitting into the experimental
cell and other accessories.

The plots of Hc/τ versus C and Z versus C for 28°C and 47°C are repre-
sented in Figures 3 and 4, respectively.   The plots of Hc/τ versus C for
both temperatures yielded linear graphs.   From the intercepts of these
straight lines, the respective values of molecular weights were calculated.
After making corrections for dissymmetry of scattering, the values for the
molecular weights were 5.08×10^6 and 2.55×10^6 (vide the value 2.82
$\times 10^6$ in 5M urea–water solvent) at temperatures of 28°C and 47°C, re-
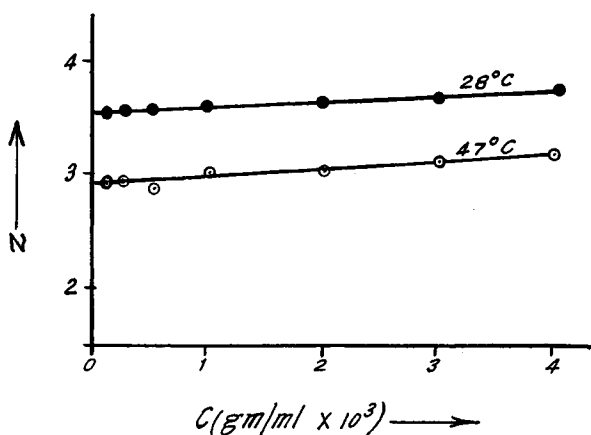spectively.   Depolarization was negligible and therefore was not taken into
account.

Fig. 4. Variation of dissymmetry with concentration in 0.025N KCl.

The experiment was repeated after about 24 hr for the same set of solutions bringing the temperature back to 28°C, but the molecular weight was found to remain unchanged, i.e., 2.55×10^6. This proved that the process was irreversible. The root-mean-square end-to-end distances at 28°C and 47°C were equal to 305 mμ and 260 mμ, respectively. The slope of the Hc/τ versus C plot at 47°C was greater than that at 28°C which indicated that the solvent behavior of 0.025N KCl at the former temperature was better than the latter.

It is known that an increase in temperature decreases the effect of intermolecular and intramolecular attractive forces. The temperatures, therefore, should have pronounced effect on the chemical potential of polymer solutions. The effect was quantitatively given by the Flory and Krigbaum equations.[7] Usually the solvent property improves with the increase of temperature, and even a bad solvent may become a good solvent at higher temperatures.

From the above discussion we find that the molecular weight was reduced to half its original value at 28°C when the temperature was raised to 47°C. It is interesting to note here that the values of the molecular weight for the ACA in 5M urea–water solvent and that in 0.025N KCl solution at 47°C agreed almost within experimental error. Since it is very unlikely that any covalent links had been broken by the rise in temperature, this finding probably gives support to the second possibility that the ACA remains, on the average, a hydrogen-bonded dimeric structure in aqueous solution which has been dissociated by the rupture of hydrogen bonds. The observation that the molecular weight was almost halved by the rise in temperature to 47°C, while the root-mean-square end-to-end distance changed slightly for the same rise, may be understood in the light of one or both of the following factors playing an influence in these cases:

1. As already mentioned, rise in temperature affects the quality of the solvent favorably, and the associated molecules being detached from each

other at high temperature find the solvent better suited for their stretching both in the presence of urea as well as at high temperature in its absence. This conclusion is also supported by higher and similar slopes observed in Hc/τ versus curves.

2. The other possibility is that associated molecules are, on the average, probably dimers, associated with each other at an inclination (as opposed to straight-chain association) which on dissociation to simple portions have lengths different from the root-mean-square end-to-end distance of the associated molecules.

References

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