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VISCOMETRIC AND LIGHT SCATTERING STUDIES ON AZRECHTIC ACID

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Abstract—Results are reported for viscometric and light scattering studies on azrechtic acid (ARA) in pure aqueous medium, in 0·02 N KCl and in a mixture of 0·02 N KCl, $CaCl_2$, $MgCl_2$. The investigations reveal the polyelectrolyte character of the azrechtic acid molecule. The corrected average value of the molecular weight from light scattering measurements is $1{\cdot}7 \times 10^6$. Assuming the polydisperse random coil as a suitable model for ARA molecules, the root-mean-square end-to-end distances have been calculated as 2570 Å in water, 1410 Å in 0·02 N KCl and 1180 Å in a mixture of 0·02 N KCl, $CaCl_2$, $MgCl_2$. The contraction of the molecules in the presence of neutral salts has been attributed to partial reduction of electrostatic repulsion due to similarly charged ions.

INTRODUCTION

Azadirechta indica, commonly known as Neem, is widely cultivated throughout India and its gum has been well known for its medicinal value for many centuries. It occurs in nature as a complex polysaccharide containing various cations, viz. Ca, Mg, K and Na. Mukherjee and Shrivastava [1] reported that the gum, on acid hydrolysis, yields L-arabinose, L-fucose, D-galactose and D-glucuronic acid. Very little is known regarding the fine structure or the physical properties [2] of the gum. The conductivity and pH of azrechtic acid have been investigated in detail by Kulshrestha [3]. The pK_a of the acid has been found to be 4·4.

It is noted that when the pH of the acid is plotted against the logarithm of concentration, a straight line is obtained satisfying the equation $\mathrm{pH} = D + E \log C$ where D (2·96) and E ($-0{\cdot}85$) are constants and C is the concentration. It is further observed that the pH with dilution also follows the expression $\mathrm{pH} = A_1 C^a$ where A_1 (2·96) and a ($-0{\cdot}1009$) are constants.

In the present investigation, attention is focussed on studying the polyelectrolyte behaviour of the acid using viscometric and light scattering techniques.

VISCOMETRIC STUDY

Azrechtic acid (ARA) has been prepared in the laboratory by electrodialysis in the presence of mineral acid as previously mentioned [3]. The viscosity of the acid has been studied using an Ostwald's viscometer at different concentrations keeping the temperature at 28°; the results are presented in Figs. 1 and 2.

From Fig. 1, it is evident that the reduced viscosity, η_{sp}/C, sharply increases with dilution, definitely indicating its polyelectrolyte character. This behaviour could be explained on the basis of the folding chain theory of polyelectrolytes in conjunction with the electrostatic repulsion which increases with dilution. The following formula for the reduced viscosity due to Fuoss [4] could be applied.

$$\eta_{sp}/C = \frac{A}{1 + B\sqrt{C}}. \tag{1}$$

The constant A is related to the size of the polyelectrolyte and B is a measure of the electrostatic repulsion. Plotting the reciprocal η_{sp}/C against $\sqrt{C}$ yields a linear graph (see Fig. 2). The reciprocal of the intercept equals A (0·525) and the slope yields the value of B (1·95).

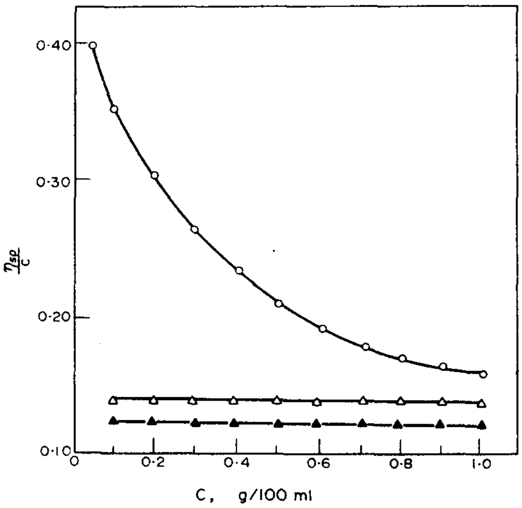

Fig. 1. Reduced viscosity vs concentration of ARA. Medium: ○—Water; △—0·02 N KCl; ▲—0·02 N KCl + $CaCl_2$ + $MgCl_2$.

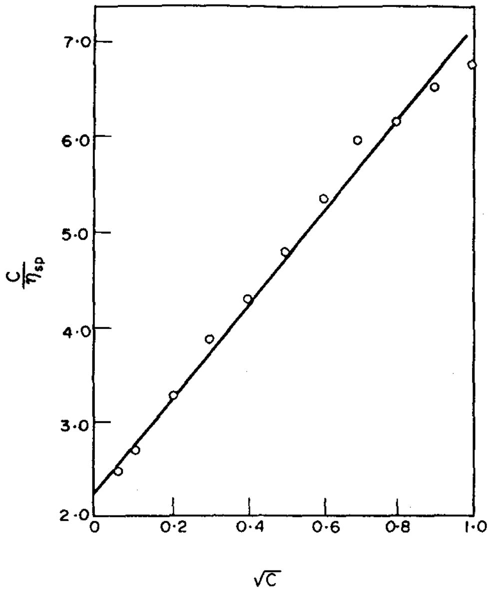

Fig. 2. Reciprocal reduced viscosity vs $\sqrt{C}$ for ARA solution.

When ARA is dissolved in solutions of 0·02 N KCl and 0·02 N KCl, $CaCl_2$, $MgCl_2$, respectively, the values for reduced viscosity do not vary appreciably with concentration. In both the cases, the plot of η_{sp}/C against C gives a straight line (see Fig. 1). This interesting behaviour in the presence of added salts could be explained thus.

In a polymer solution, the field of the polyions attracts counterions. The addition of neutral salts, viz. KCl, $CaCl_2$ and $MgCl_2$ increases the number of counterions. The solvent between polymer molecules now contains, in addition to the counterions, simple ions of both charges which act as electrostatic screens against long-range forces.

It may be pointed out here that the screening action is only partial and is incomplete for the salt concentrations used. In fact, for complete elimination of the electrostatic repulsion, much higher salt concentrations (about 0·08 N KCl) have been found necessary. Hence the electrostatic repulsion between the charges are expected to be reduced though not completely eliminated.

The straight line plot for η_{sp}/C against C in the presence of 0·02 N KCl could be interpreted thus. In 0·02 N KCl medium, the polymer is in a constant ionic strength solution, independent of polymer concentration. Hence its configuration is not concentration dependent, as in the case of pure water. On changing to a mixed salt solution (i.e. $K^+ + Mg^{2+} + Ca^{2+}$) where the ionic strength is greater, the value of η_{sp}/C decreases. This is probably due to the increased screening action of the charges on the polyelectrolyte or specific interactions of Ca^+ or Mg^{2+} with the polymer or both.

LIGHT SCATTERING STUDY

The ARA solution was prepared and clarified by repeated filtration through sintered glass (No. 4). The scattering measurements were made at −45°, −90°, −135° and 0° angles in a Brice Phoenix Light scattering photometer using a semi-octagonal dissymmetry cell. The detailed experimental technique has been discussed elsewhere [5]. The wavelength of the unpolarized light used was 4356 Å. The specific refractive increment of the solution was measured in a Brice Phoenix differential refractometer maintaining temperature at 28°.

The molecular weight M was calculated from the Debye [6] equation:

$$\frac{HC}{\tau}.P(90) = \frac{1}{M} + 2BC.P(90), \qquad (2)$$

where C is the concentration in g/ml, τ is the net value of turbidity, B is the interaction constant and $P(90)$ is the particle scattering factor at 90°. The quantity H is given by

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

where n_0 is the refractive index of the solvent, n is that of solution, λ is the wavelength of the incident light in cm, N is the Avogrado number.

Plots of HC/τ against C and dissymmetry Z against C are shown in Figs. 3 and 4, respectively. The plot of HC/τ against C for ARA in aqueous solution exhibits a typical polyelectrolyte behaviour, the curvature introducing an uncertainity in the extrapolation to zero concentration resulting in an uncertain determination of the molecular weight. It appears that a linear plot of HC/τ vs C can be expected for the acid if sufficent K^+, Ca^{2+} and Mg^{2+} ions be added to reduce at least

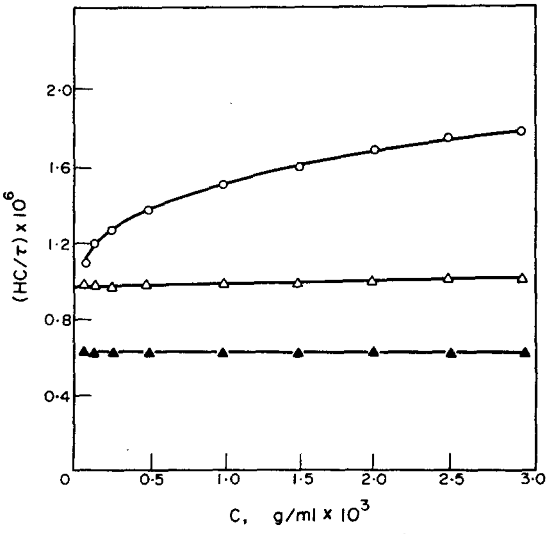

Fig. 3. Variation of HC/τ with concentration. ○—Water; △—0·02 N KCl; ▲—0·02 N KCl + $CaCl_2$ + $MgCl_2$.

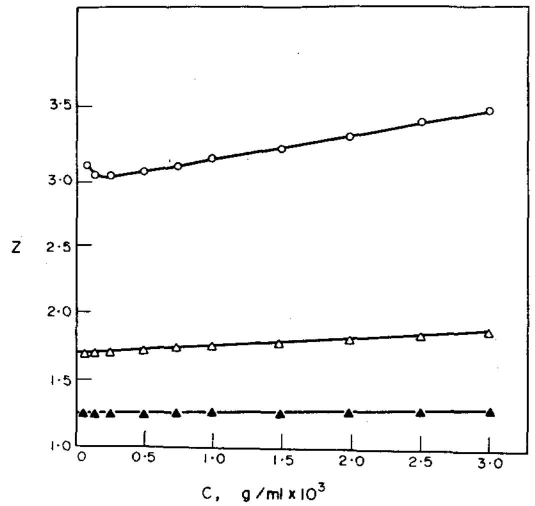

Fig. 4. Variation of dissymmetry with concentration. ○—Water; △—0·02 N KCl; ▲—0·02 N KCl + $CaCl_2$ + $MgCl_2$.

partially the effect of charges on the macro-ion. For this purpose, the scattering measurements were made in 0·02 N KCl and in a mixture of 0·02 N solutions of KCl, $CaCl_2$ and $MgCl_2$. A linear graph resulted in each case, although the slopes differed to some extent. The graph for ARA in the presence of the mixture shows smaller slope and is almost parallel to the abscissa.

The molecular weight was calculated from the value of HC/τ extrapolated to zero concentration from the linear graphs so obtained for 0·02 N KCl. The calculated value of the molecular weight is $1{\cdot}1 \times 10^6$ but further correction is needed for dissymmetry of the scattering and also depolarization. The dissymmetry values of ARA in water, in 0·02 N KCl and in a mixture of 0·02 N KCl, $CaCl_2$, $MgCl_2$ were extrapolated to zero concentration. Assuming ARA to be a polydisperse macromolecule of random coil type [7], the intrinsic dissymmetry in 0·02 N KCl was calculated for the correction factor. The molecular weight after this correction is $1{\cdot}6 \times 10^6$. The fluorescence and depolarization were found to be negligible and were not taken into account. The molecular weight calculated from the linear graph of HC/τ vs C for 0·02 N(KCl + $CaCl_2$ + $MgCl_2$) is $1{\cdot}8 \times 10^6$. The mean value of the molecular weight is thus $1{\cdot}7 \times 10^6$.

The statistical dimensions of the ARA molecule in aqueous solution in the presence or absence of the neutral salts can be determined from the corresponding intrinsic dissymmetry values. It appears that the root-mean-square end-to-end distance of the macromolecule is 2510 Å in water, 1410 Å in 0·02 N KCl and 1180 Å in the aqueous medium of 0·02 N (KCl + $CaCl_2$ + $MgCl_2$). The small molecular dimensions, determined from scattering measurements in the presence of salt solutions, indicate that considerable contraction of the acid molecule occurs in the presence of common ions, due to partial reduction of electrostatic repulsion between the charges on the polyelectrolyte. Although the strength of both salt solutions are equal, yet the contraction in molecular size when dissolved in the mixture of 0·02 N (KCl + $CaCl_2$ + $MgCl_2$) is greater than when dissolved in 0·02 N KCl. This is probably due to the presence of divalent ions, viz. Ca and Mg, which appeared to possess greater screening power [8] than the monovalent ion, K.

It can be concluded from both the viscometric and light scattering studies that the ARA molecules are polyelectrolyte in character and undergo contraction when placed in a medium containing neutral salts having common ions.

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