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Aloke Chattopadhyay
Department of Chemistry,
S.B. College, Bagati, Mogra,
Hooghly, West Bengal, India

Correspondence
Aloke Chattopadhyay
Department of Chemistry,
S.B. College, Bagati, Mogra,
Hooghly, West Bengal, India

Studies on involvement of backbone of a polymer to bind cupric ion at lower pH

Aloke Chattopadhyay

Abstract
Aqueous solution of guargum-*graft*-acrylamide (G-g-Am) and cupric nitrate solution mixture forms a green mass when pH is raised from acidic medium by adding ammonium hydroxide. UV spectral study indicates at lower pH interaction may take place between–$CONH_2$ group of G-g-Am and Cu^{2+}. At this pH, interaction is loose. Ultrasonic study indicates, ultrasonic attenuation from pH=>4 to pH=>6 is abnormal probably due to peculiar absence of involvement of backbone of polymer in the association below pH=>6.

Keywords: Polymer, cupric ion binding, loose association, ultrasound, ultraviolet spectra.

1. Introduction
Guargum is a water soluble natural polymer and has good industrial use [1]. Its structure is relatively known (fig.1). Aqueous solution of guargum has poor biodegradation resistance [2]. When polycrylamide side chains are grafted on guargum, resulting graft copolymer becomes considerable biodegradation resistant and efficient flocculent for metallic ions [2]. Aqueous solution of guargum-*graft*-acrylamide (G-g-Am) and cupric nitrate solution mixture forms green mass at pH≥6 [3] when ammonium hydroxide is added. It has been reported that–COOH group from side chain for G-g-Am [3] and –OH group from backbone for G-g-Am [4] are expected to take part to bind Cu^{2+} at pH≥6. In this present investigation, whether involvement of backbone in case of polymer – cupric ion interaction below pH=>6 is evident or not, has been studied by ultrasound.

2. Materials and Methods
2.1 Guargum-*graft*-actylamide (G-g-Am)
G-g-Am has been achieved from Rheological Laboratory of I.I.T., Kharagpur, India. Material has been characterized by ESCA and thermal study and has been reported earlier [5].

2.2 Cupric nitrate solution
Cupric nitrate solution has been prepared by dissolving cupric oxide in nitric acid.

2.3 Ultraviolet Spectrophotometric Study
Aqueous solution of G-g-Am has been used to study polymer-metal ion interaction by UV spectrophotometer. Shimadzu spectrophotometer is used for UV spectral study. To record UV spectra for aqueous solution of G-g-Am, water is used as the reference. To record UV spectra for aqueous G-g-Am-metal nitrate solution mixture, corresponding metal nitrate solution has been used as the reference.

2.4 Ultrasonic Experiment
Ultrasonic Interferometer (Mittal Enterprises) has been used for ultrasonic experiment. For ultrasonic experiment, polymer-metal ion mixtures have been prepared by varying the ratio by volume of aqueous G-g-Am and metal nitrate solution. Each of these mixtures are tested by taking in the cell (12 milliliters capacity) which contains a gold plated quartz crystal at the bottom and passing ultrasound, of frequency 5 MHz., through the solution of the cell. The cell is fitted with a small steel plate at the top which can be raised or lowered inside the cell and its relative displacement can be measured by means of a micrometer scale over which supporting arm of the top plate can be moved in upward or downward direction. Relative displacement (d)

for ten successive most likely constructive interferences between incoming and outgoing waves have been measured. Velocity (V) can be calculated in the following way:

$$V = f \times \lambda = \frac{nd}{5 \times 2} \text{ meters/sec.}$$

$$= \frac{10d}{5 \times 2} \text{ meters/sec.}$$

$$= 25d \text{ meters/sec.}$$

Where, f = 5 MHz.

Ultrasonic interferometer is used for checking constructive interference.

3. Results and Discussion

3.1 UV

In the UV spectra for G-g-Am (fig.2), there is considerable absorbance near about at 242.86 nm. Which may be attributed to n → Π^* transition for $-CONH_2$ of polymer. Appearance of a peak near about at 238.93 nm. in the UV spectra for Cu^{2+} / polymer mixture (fig.3) may be due to interaction between $-CONH_2$ and Cu^{2+} at this pH.

3.2 Ultrasound

From ultrasonic experiment, it is obvious that from pH=>6 to pH=>4 nature of plot (fig.4) is in the form of a curve. After this pH, as pH decreases ultrasonic attenuation decreases almost smoothly.

$$\text{Ultrasonic velocity, } V=\sqrt{\frac{E}{\rho}}$$

Where,
E => Elasticity of the medium through which ultrasound is propagating.
P => density of the medium through which ultrasound is propagating.

Fig.4 indicates decrease of ultrasonic attenuation is abnormal from pH=>6 to pH=>4. This indicates below pH=>6, stiffness of the mixture initially decreases abnormally with decrease in pH. So interaction between polymer and Cu^{2+} below pH=>6 may be accompanied by disappearance of involvement of backbone from polymer peculiarly.

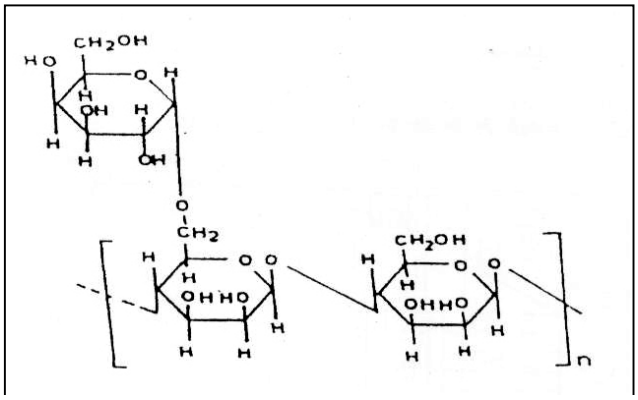

Fig 1: Structure of guargum

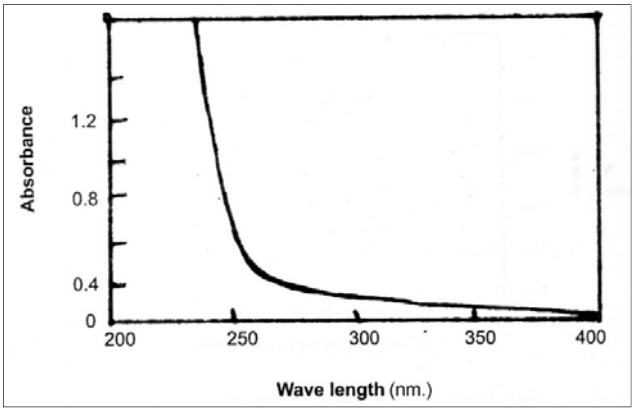

Fig 2: UV absorption spectra for aqueous solution of G-g-Am using water as reference.

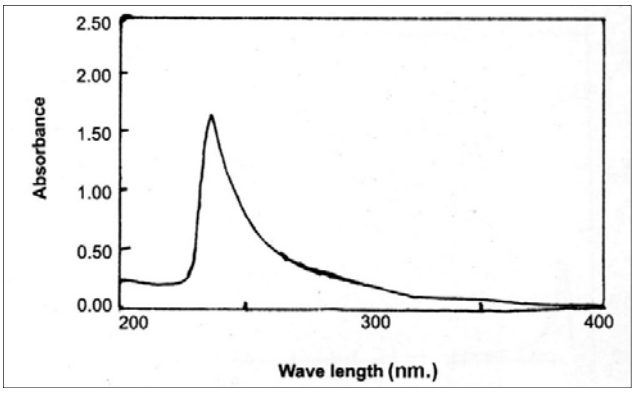

Fig 3: UV absorption spectra for the mixture of G-g-Am and Cu(NO3)2 solutions using Cu(NO3)2 solution as reference.

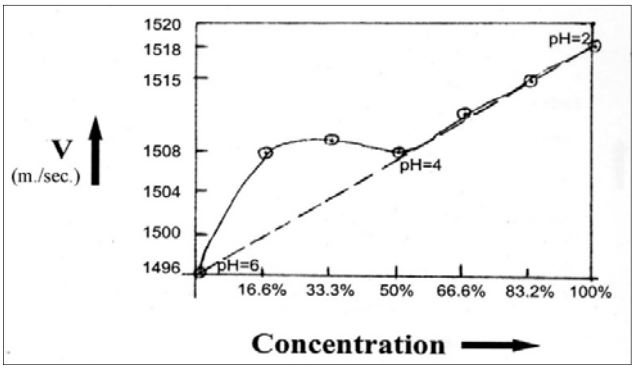

Fig 4: Plot of ultrasonic velocity Vs. concentration of Cu(NO3)2 solution in volume % in the mixture. (-) for experimental curve and (---) for hypothetical non-interaction line.

4. Conclusion

Any sort of loose association is called complexation. For co-ordination compounds, there will be some stability. UV study indicates, at lower pH, $-CONH_2$ group from G-g-Am may interact with Cu^{2+}. At pH≥6, -COOH group from side chain and –OH group from backbone for G-g-Am may have role to bind Cu^{2+} [4]. This is in favour of decrease of stiffness due to peculiar absence of involvement of backbone of polymer at lower pH.

5. Acknowledgement

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6. References

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