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Studies on polyvalent metal ion bound guargum-*graft*-acrylamide

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Abstract

Guargum-*graft*-acrylamide (G-g-Am) is a modified natural polymer. Aqueous solution of G-g-Am is a good flocculent for metallic ions. It can be used to bind Y^{3+}, Ba^{2+} and Cu^{2+} to get a precursor for probable route for preparation of $Y_1 Ba_2 Cu_3 O_{7-x}$ ceramic oxide superconductor. Complex formation for Y^{3+} or Ba^{2+} or Cu^{2+} with the polymer in this case has been understood from pH titration, conductometric titration and IR spectral technique. IR spectra shows involvement of $-COO^-$ group from side chain and -OH group from backbone of G-g-Am to bind polyvalent metal ion. From Nakamoto's reference, for binding Cu^{2+}, bidentate chelating nature of $-COO^-$, for binding Ba^{2+} and Y^{3+}, bidentate bridging nature of $-COO^-$ are expected. From charge neutralization, it is possible to understand that two $-COO^-$ (bidentate chelating) to bind Cu^{2+}, four $-COO^-$ (bidentate bridging) to bind Ba^{2+} and six $-COO^-$ (bidentate bridging) to bind Y^{3+} are required. By considering involvement of -OH group from backbone, probable co-ordination number for cupric ion bound G-g-Am (G-g-Am-Cu^{2+}) is 6, for G-g-Am-Ba^{2+} is 6 for G-g-Am Y^{3+} is 8.

Keywords: infrared spectra, polyvalent metal ion binding, graft copolymer, coordination number, ph titration, conductometric titration

1. Introduction

Guargum is a water soluble natural polymer [1]. Its structure is shown in fig.1. Major drawback of guargum is its poor biodegradation resistance [2]. If polyacrylamide side chains are grafted on guargum, resulting graft copolymer becomes considerable biodegradation resistant and efficient flocculent for metallic ions [3]. So, it can be thought that guargum-g-acrylamide (G-g-Am) may be used as a polymer for preparation of $Y_1 Ba_2 Cu_3 O_{7-x}$ ceramic oxide superconductor by polymeric precursor technique [4]. Aqueous solution of G-g-Am binds Y^{3+} at pH near about 9.5 (fig.2), Ba^{2+} at pH near about 12.5(fig.3) and Cu^{2+} at pH near about 6.0(fig.4). IR spectra for G-g-Am-Y^{3+}, G-g-Am-Ba^{2+} and G-g-Am Cu^{2+} indicate involvement of $-COO^-$ group from side chain and $-OH$ group from backbone of G-g-Am for binding polyvalent metal ion [5]. Nakamoto's reference [6-8] and charge neutralization help to understand that coordination number for binding Cu^{2+} is 6, for binding Ba^{2+} is 6 and for binding Y^{3+} is 8.
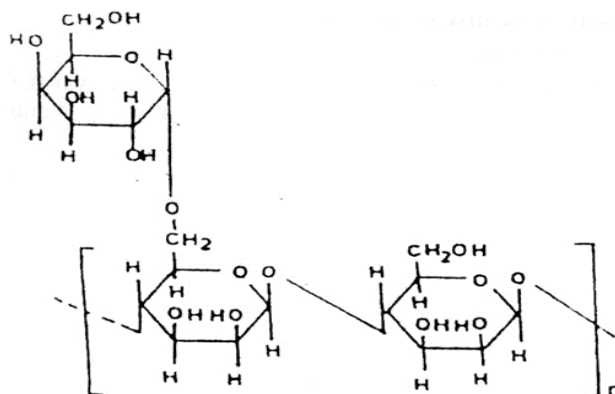
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Fig 1: Structure of guargum

2. Materials and Methods

2.1 Guargum–*graft*-acrylamide (G-g-Am)
Guargum-*graft*-acrylamide used in this present investigation has been achieved from Rheological Laboratory of Materials Science Centre of I.I.T., Kharagpur. For grafting polyacrylamide side chains on guargum, ceric ion initiation method has been adopted [9]. From ESCA study, it was possible to understand that, it contains about 11 atom % nitrogen, 22 atom% oxygen and 68 atom% carbon [10].

2.2. Metal nitrate solutions
Cupric oxide or yttrium oxide is dissolved in nitric acid to get cupric nitrate solution or yttrium nitrate solution. Barium nitrate solution can be prepared by dissolving barium nitrate in distilled water and pH can be lowered by nitric acid.

2.3 Polyvalent metal ion bound G-g-Am
For G-g-Am-Cu^{2+} or G-g-Am-Y^{3+}, aqueous solution of G-g-Am is mixed with cupric nitrate solution or yttrium nitrate solution and pH can be raised by adding ammonia solution. A mass separates which is washed with water for some time and then with methanol for some time. Then it is kept in the oven for drying for IR spectral study. For G-g-Am- Ba^{2+}, aqueous solution of G-g-Am is mixed with barium nitrate solution and pH is raised by adding sodium hydroxide solution. A precipitate – like mass separates which is washed with water for some time and then with methanol for some time. Then it is kept in the oven for drying for IR spectral study.

2.4 G-g-Am-Na^+
Aqueous solution of G-g-Am is mixed with sodium hydroxide solution and the mixture is immediately poured into methanol for precipitation. Precipitate is washed with water for some time and then with methanol for some time. Then it is kept in the oven for drying for IR spectral study.

2.5 pH titration
Beckman model G pH meter has been used for pH titration. For pH titration, alkali solution has been added from the burette.

2.6 Conductometric titration
For conductometric titration, a dip-type cell (Cell constant 1.1) containing platinised platinum electrode has been used. Sodium hydroxide solution has been added from the burette.

2.7 IR spectra
The IR spectra for G-g-Am-Na^+, G-g-Am-Y^{3+}, G-g-Am-Ba^{2+} and G-g-Am-Cu^{2+} have been registered between 4000-200 cm^{-1} with a Perkin-Elmer model 883 spectrometer using potassium bromide pellets.

3. Results and Discussion
pH titration curves are shown in figs 2-4. Conductometric titration curve is shown in fig. 5. IR spectra for G-g-Am-Na^+, G-g-Am-Y^{3+}, G-g-Am-Ba^{2+} and G-g-Am-Cu^{2+} are shown in figs.6-9 respectively. It is very difficult to get idea of co-ordination numbers (C.N.) for different polyvalent metal ions for complex formation, from pH titration or conductometric titration due to probable chance of hydrolysis of polymer (G-g-Am) which will cause problem in determination of number of $-COO^-$ groups required for binding a polyvalent metal ion. So attempt can be made to determine C.N. qualitatively. From IR spectra and Nakamoto's reference [6-8] (fig. 6-9), bidentate chelating mode of $-COO^-$ to bind Cu^{2+} is expected and for

Y^{3+} and Ba^{2+}, bidentate bridging mode of $-COO^-$ is expected. Considering charge neutralization of metal ion, two $-COO^-$ (bindentate chelating) for a Cu^{2+}, four $-COO^-$ (bidentate bridging) for a Ba^{2+} and six $-COO^-$ (bidentate bridging) for an Y^{3+} ion are expected for binding polyvalent metal ion. IR spectra indicates, -OH group from backbone of guargum-g-acrylamide also may bind Cu^{2+} or Ba^{2+} or Y^{3+}. Copper is an element of first transition series. So C.N. greater than 6 is unexpected for Cu^{2+}. Considering two bidentate chelating $-COO^-$ and maximum two -OH groups to bind Cu^{2+}, C.N. 6 is predicted for G-g-Am-Cu^{2+} [11]. IR spectra for G-g-Am-Cu^{2+} and for G-g-Am-Ba^{2+} show almost similar expected relative intensity for -OH stretch bonded to metal ion. So for G-g-Am-Ba^{2+}, C.N. 6 is also expected [12]. Yttrium is an element of second transition series. So C.N. greater than 6 is quite common for Y^{3+}. Moreover, complex of Y^{3+} is a d^o complex. There is literature reference [11] for C.N. 8 for complex of Y^{3+}. Considering six $-COO^-$ (bidentate bridging) and two -OH groups for binding Y^{3+}, C.N. 8 is expected for G-g-Am-Y^{3+}.
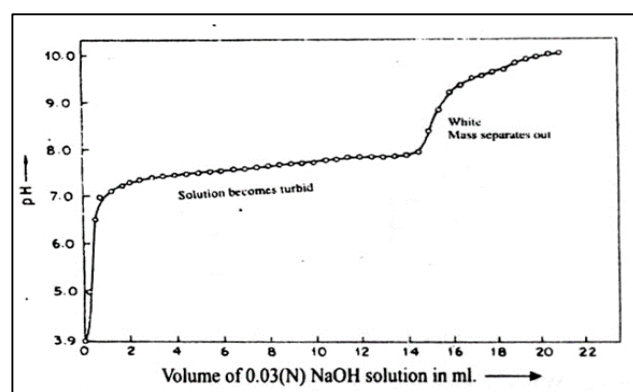
Fig 2: pH titration curve for a mixture of aqueous G-g-Am, $Y(NO_3)_3$ solution and HNO_3, when titrated with NaOH solution
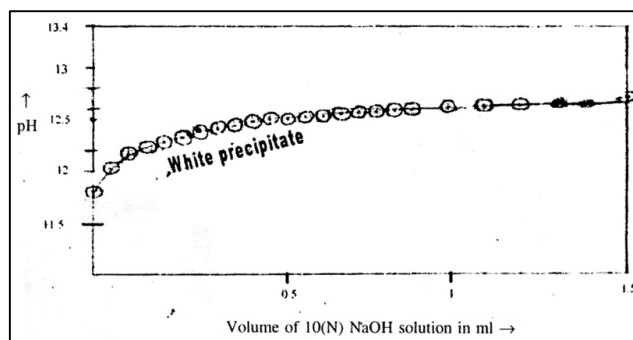
Fig 3: pH titration curve for a mixture of aqueous G-g-Am, $Ba(NO_3)_2$ solution when titrated against NaOH solution
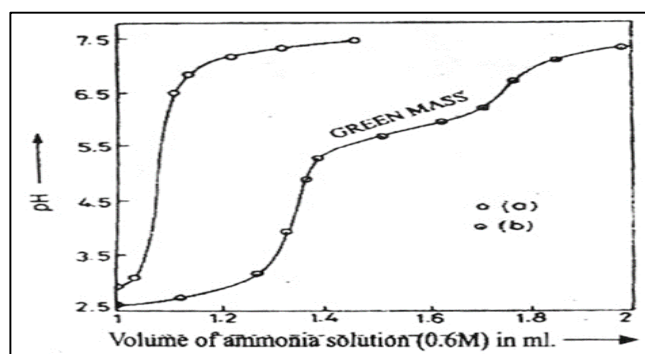
Fig 4: pH titration curve for (a) a mixture of aqueous G-g-Am solution and HNO_3 and (b) a mixture of aqueous G-g-Am $Cu(NO_3)_2$ solution and HNO_3, when titrated against amonia solution.
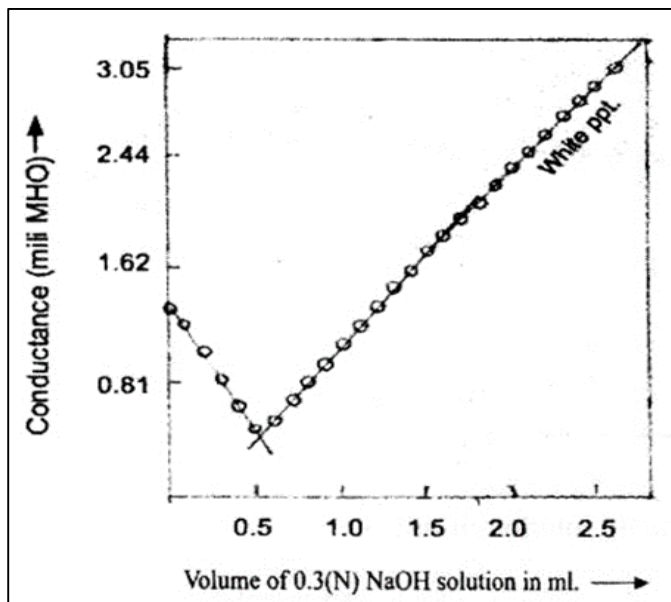
Fig 5: Conductometric titration curve for a mixture of aqueous G-g-Am, Ba(NO3)2 solution and HNO3, when titrated against NaOH solution
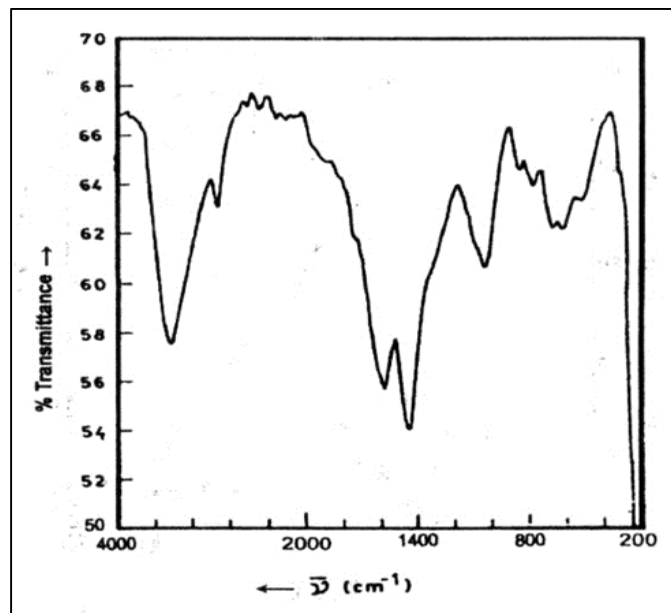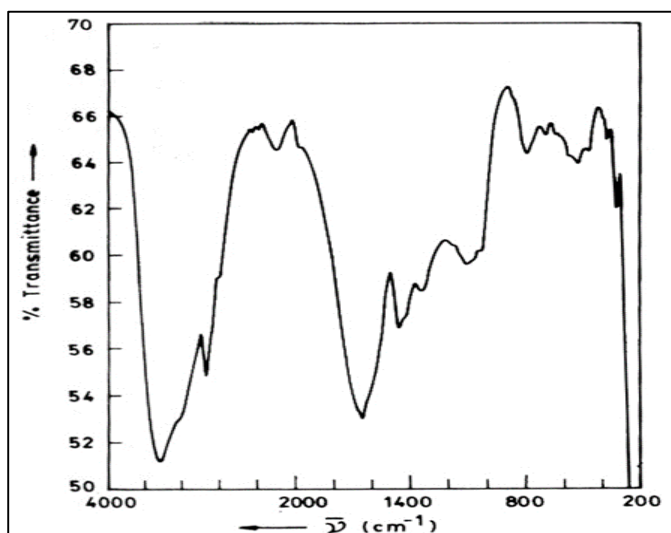

Fig 8: IR spectra for G-g-Am-Ba^{2+}
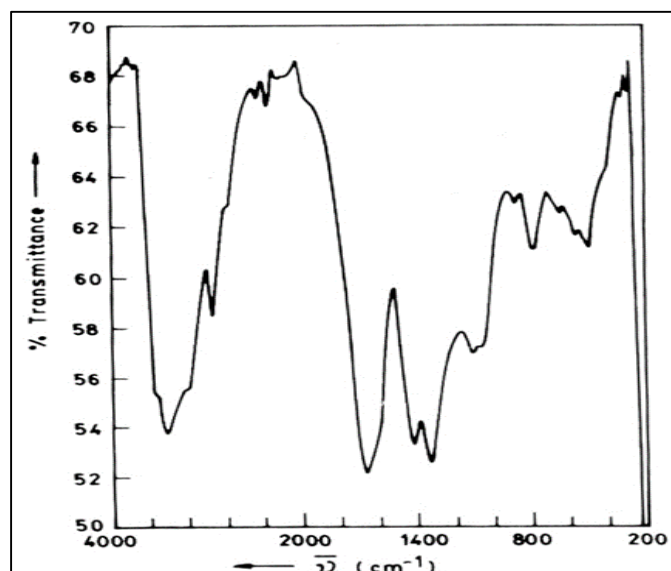

Fig 6: IR spectra for G-g-Am-Na^{2+}

Fig 9: IR spectra for G-g-Am-Cu^{2+}

4. Conclusion

For Cu^{2+} and Ba^{2+}, C.N. 6 is expected from the present study. For C.N.6, geometry is generally octahedral. For Y^{3+}, C.N.8 is expected in this case. For C.N.8, squareantiprismatic or dodecahedral geometry is probable. Y^{3+} (d^0 complex) can show squareantiprismatic geometry [11].

5. Acknowledgement

Fig 7: IR spectra for G-g-Am-Y^{3+}

6. References

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