Group(IV) Metal Halide Chelates of Salicylic Acid-Urea-Formaldehyde Copolymer

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Salicylic acid-urea-formaldehyde (SUF) copolymer in 4:1:4 molar ratio has been synthesized in presence of an acid catalyst. Chelation, metal uptake and distribution ratio of this copolymer with halides of Si(IV), Ge(IV), Sn(IV), Zr(IV) and Ti(IV) have been studied. The polymer and the complexes have been characterized on the basis of elemental analyses and IR spectroscopy. The molar conductances of 10^{-3} M solutions of the complexes in DMF (0.2-0.4 cm^{-1} mol^{-1}) indicate them to be non-ionic. It has been observed that in a group, the metal uptake decreases with increasing atomic number of the metal.

The synthesis, chelation and ion exchange properties of urea-formaldehyde (UF) polymer are well known. A water soluble salicylic acid-formaldehyde (SF) polymer has also been synthesised and its complexes have been prepared. Recently, a terpolymer of salicylic acid (S) and thiourea with trioxane, obtained by reaction in different molar ratios, has been shown to have varying compositions. Patel and coworkers have synthesized salicylic acid-urea-formaldehyde (SUF) copolymer in 3:1:4 molar ratio and studied its properties but they have ignored the possibility of the synthesis of SUF copolymer in 4:1:4 ratio. We have carried out a successful synthesis of SUF copolymer in this ratio and also prepared its chelates with some group(IV) halides. The results are presented in this note.

SiCl₄, SnCl₄, TiCl₄, ZrCl₄ (all BDH), GeCl₄ (Koch Light), salicylic acid, urea (Sarabhai) and formaldehyde (BDH) were used without further purification. The IR spectra (600-4000 cm^{-1}) were recorded on a Perkin Elmer 621 infrared spectrophotometer in KBr. Conductivity measurements were made on a systronics conductivity bridge type 302.

Synthesis of the polymer

The SUF copolymer was synthesized in 4:1:4 molar ratio by condensation of salicylic acid, urea and formaldehyde in presence of 2M hydrochloric acid as catalyst at 100°C. The mixture was refluxed for about 5 hr when condensation occurred. The copolymer was washed with a large amount of water and soxhlet-extracted with ether. It was purified by dissolving in 5% NaOH and reprecipitating with 1:1 (v/v) conc. HCl. Finally, the copolymer was washed with hot water and dried in vacuo at room temperature.

For the determination of the metal uptake, solutions of the same concentration (0.1 M) of metal halides and the copolymer were prepared. A large excess of metal (5-fold) was added to the polymer and the mixture was stirred (~1 hr) till a complex was obtained. The filtrate containing metal halide was precipitated and the metal analysed gravimetrically. It is clear from the results in Table 1 that the metal uptake is maximum in the case of SiCl₄. The quantity of metal uptake is a measure of stability of the chelate and also a measure of the degree of polymerisation.

Distribution of metal ions

The metal contents, both in the complex and in filtrate, were determined. Since all these metal tetrachloride solutions get hydrolysed in presence of acid or alkali, study in presence of a supporting electrolyte at varying pH could not be made. The distribution coefficient (D) was calculated by the formula given below:

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D = \frac{\text{amount of metal ion on the copolymer}}{\text{amount of metal in the solution}} \times \frac{\text{volume of solution}}{\text{weight of copolymer}}
\]

The formation of SUF copolymer by the condensation of salicylic acid, urea and formaldehyde is shown in Scheme 1.

Nitrogen atom in urea links with the formaldehyde and subsequently with salicylic acid eliminating water molecules. One end in urea is left unlinked when a 3:1:4 molar ratio of S, U and F is used. Hence, a 4:1:4 ratio of S, U and F has been taken in the present synthesis in order to complete the reaction and prepare a symmetrical copolymer. The composition of the copolymer has been ascertained by molecular weight.
amides increase the electron density of the carbonyl oxygen, but $\nu_{\text{C}=\text{O}}$ decreases. Hence, it is quite likely that metals are coordinated to carbonyl oxygen rather than the nitrogen atom of urea.

In the present case the substituents at the nitrogen are also likely to increase the electron density at the carbonyl oxygen, thus making it more likely that metal tetrahalides are coordinated with the carbonyl group. Two bands appearing at 1450 and 1490 cm$^{-1}$ are assigned to $\nu_{\text{C} \equiv \text{N}}$ mode; these remain almost unaltered in the complexes. Two strong broad bands at 1620 and 1670 cm$^{-1}$ are assigned to $\nu_{\text{C}=\text{O}}$ mode. They show a decrease of 20 to 50 cm$^{-1}$ in the complexes indicating bonding of C=O group with MX$_4$. A new band has been noted at 1130 cm$^{-1}$ in the complexes which is absent in the polymer; it is an additional evidence of the coordination of C=O group of the urea. The possibility of the coordination of the ester carbonyl group may be ruled out in view of the steric hindrance and hydrogen bonding.

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References