The Effect of Bivalent Metal Ions on Tannin Formaldehyde Reaction

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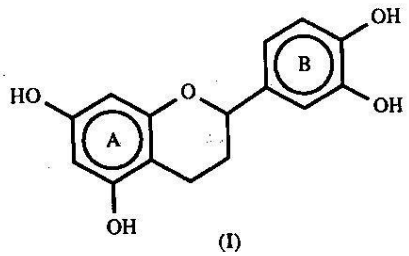
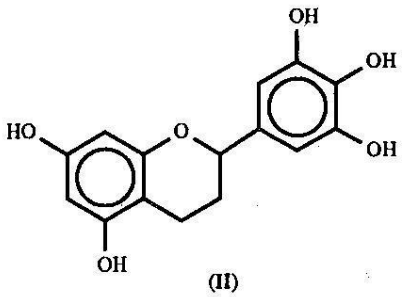
Summary: The catalytic influence of bivalent metal ions on tannin formaldehyde reaction has been investigated, using three different methods (1): Hydroxylamine hydrochloride (2), Viscometry and (3) IR Spectroscopy. The results obtained from the first and third methods are comparable, while a slight deviation in the order of effectivity was observed in the case of second method due to the stability of the intermediate complexes. It was also observed that transition metals catalysed the reaction more effectively than alkaline earth metals.

Introduction

Tannins are composed of a mixture of different phenols [1]. They are divided into two categories [2] (1) condensed (2) and hydrolyzable tannins. Condensed tannins constitute [3] about 90% of the commercial tannins and are composed of flavonoid units. These flavonid structures are in polymeric form which contain two to eleven attached units [4]. In Pinus species [5] the A- ring of flavonoid structure is composed of phloroglucinol while B-ring may be either of catechol (I) or pyrogallol (II).

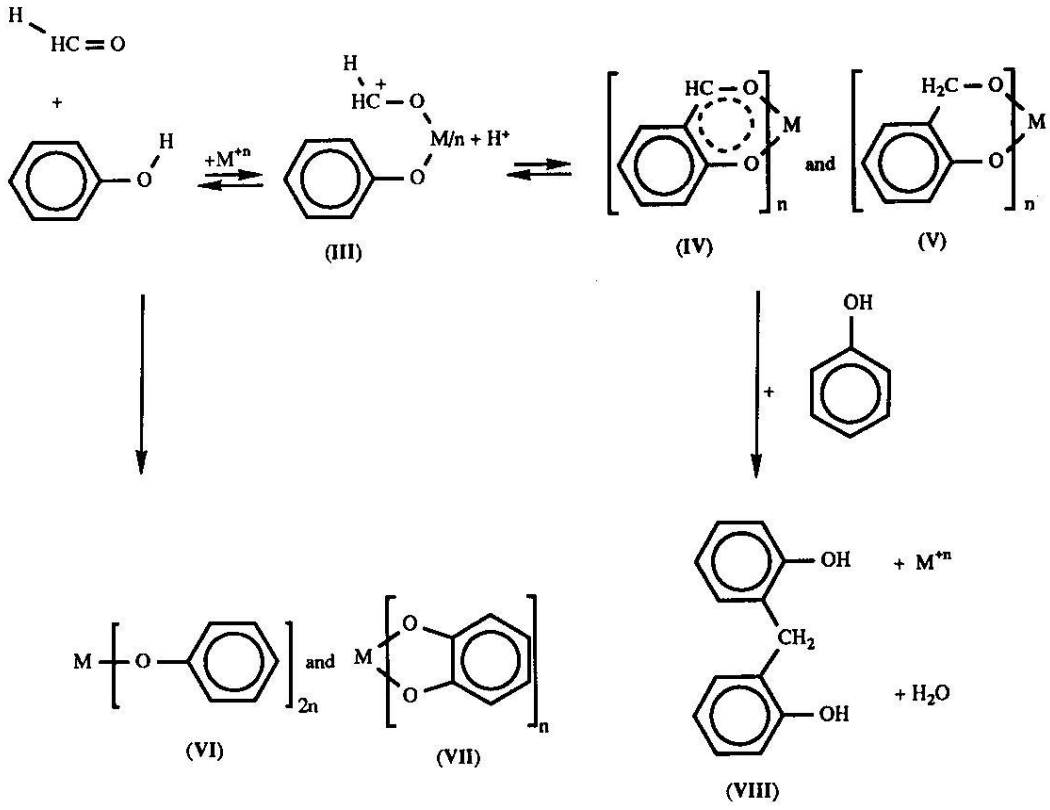


(I)



(II)

Condensed tannins are both chemically and economically more interesting for the preparation of adhesives and resins. Their reaction with formaldehyde is acid as well as base catalyzed [6]. The adhesive prepared at very low pH causes deterioration of wood [3] and also the B-ring of tannin molecule does not participate in the reaction. Whereas at very high pH (> 10) the B-ring takes part in reaction but the reactivity of A-ring is so high that the adhesives prepared have unacceptable short pot life [7].



Scheme - 1

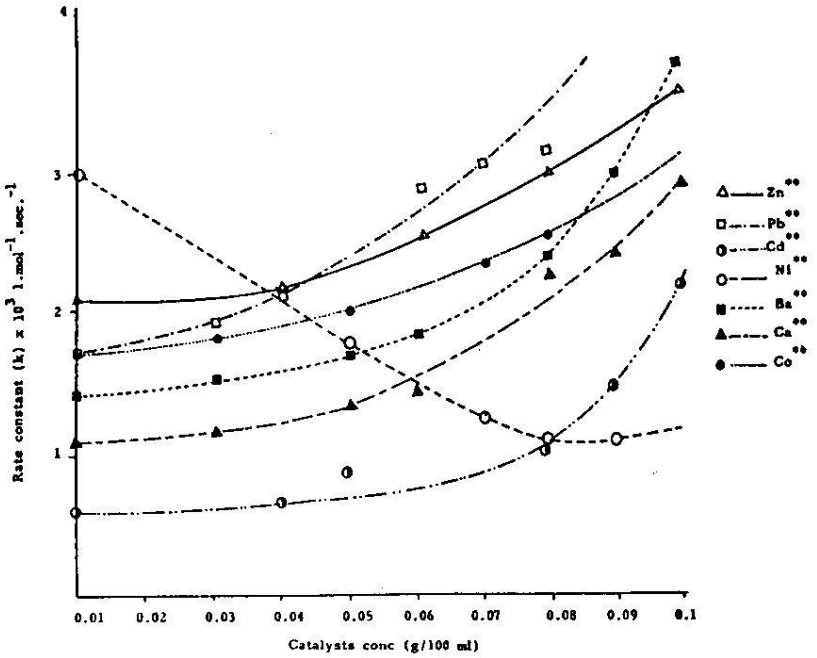
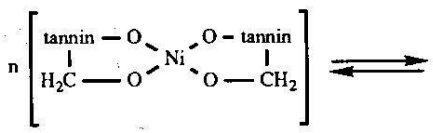


Fig.1: Effect of metal ions on rate constant of tannin-Formaldehyde reaction at different concentrations.

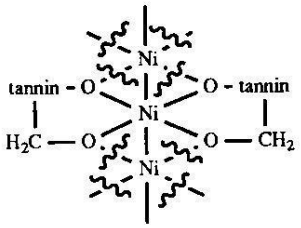
Pb^{++} $>Zn^{++}$ > Co^{++} > Ba^{++} > Ca^{++} $>Cd^{++}$ $>Mg^{++}$

The effectivity of the transition metals may depend upon the following factors.

1. Size of metallic ion.
2. Geometry of intermediate complex (V, IV).
3. Hydration of metal ion.
4. Paramagnetism.



(IX)



(X)

Ca, Ba and Mg are alkaline earth metals while Pb, Zn, Co and Cd are transition metals [13]. If we arrnage the alkaline earth metals according to increasing accelerating effect, the order is:

Mg > Ca > Ba

The increase in effectivity is due to increase in size as well as in metallic character which increases on descending in a periodic group.

Pb^{++} appears to be the most effective catalyst in the present series which may be due to its size and metallic character. Geometry of intermediate complex (IV or V), and hydration of metallic ion may also contribute towards effectivity of metal ions. When the size of metal ion is small, it is completely hydrated by water molecules and resultantly has loss chances to activate the phenol or formaldehyde molecule.

Zn and Co are in the same transition series. The paramagnetic character of Zn is zero while that of Co is 3.87 MB [14]. As the benzene ring has its own magnetic field so the attraction between this ring and Co^{++}, is greater than Zn^{++} and resultantly, the stability of Zn^{++} complex (IV, V) is less than that of Co. In other words Zn^{++} will accelerate the reaction because the complexes it forms are unstable and their rate of exchange in solution is high.

In case of nickel acetate, rate constant decreased with increase of catalyst which may be due to that in bivalent state, nickel exhibits a wide and interesting variety of coordination number and stereochemistry which often exists simultaneously in equilibrium with each other [15]. In coordinating solvent such as water, the planer and octahedral complexes of Ni^{++} exist in equilibrium with each other. In case of tannin molecule, the formation of the following intermediate (IX, X) may be expected:

As the concentration of Ni^{++} increases, the possibility of octahedral complexes increases and resultantly due to its greater size, the retardation of TF reaction increases.

Viscometry

When a polymer is dissolved in a solvent, its frictional character is changed due to considerable difference between mass of solvent and solute molecules. The extent of viscosity increase can be empirically related to the molecular weight of polymer. For this reason viscosity is widely used in determining the molecular mass of macromolecule. Mark-Houwink's equation (3) [16] relates the intrinsic viscosity [η] to weight average molecular weight (M) of a polymer in a specific solvent and at a specific temperature.

$$[\eta] = KM^a \quad (3)$$

The relative effectivity of metal II catalysts on TF reaction inferred from the plot of relative viscosity vs reaction time (Fig. 2) was found to vary in the order:

Co^{++} $>Zn^{++}$ > Ni^{++} $>Ba^{++}$ $>Cd^{++}$ $>Ca^{++}$

Increase in relative viscosity may depend upon two factors:

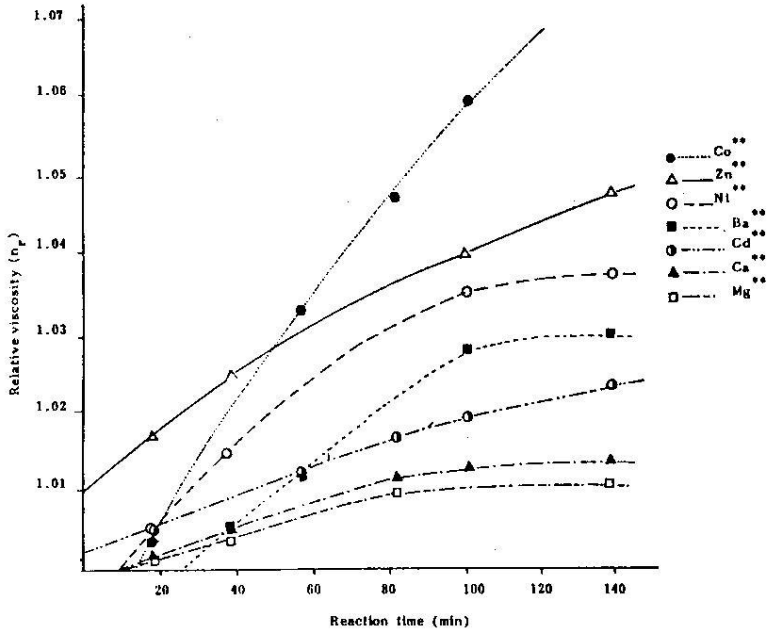


Fig. 2: Effect of metal ions on relative viscosity of tannin-Formaldehyde resin at different intervals of reaction time.

1. Condensation of tannin molecules with formaldehyde (VIII).

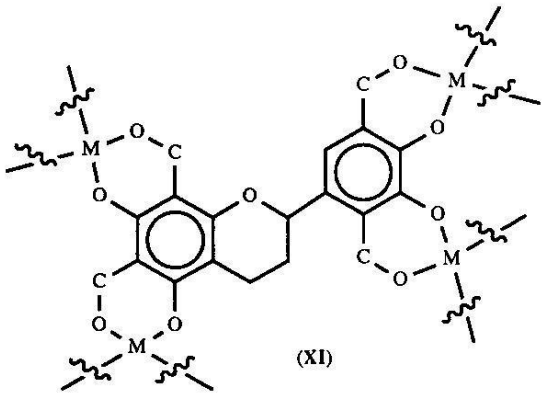
2. Stability of intermediate complexes (IV, V, VII).

Since transition metal ions such as Cu^{++} and Pb^{++} formed stable complexes (VI, VII) in the initial stage of reaction, so the kinetic studies of these metals could not be carried out by viscometry. The increase in viscosity of the reaction mixture was greater in presence of Co as compared to Zn (Fig. 2) and this was due to condensation process as well as stability of intermediate complexes (IV, V). Since Ni is paramagnetic in nature (2.83 MB) and has octahedral structure, it may form comparatively stable complexes, (V, IV, IX, X). Although Cd and Pb are in the same transition series but cadmium tannate particles were not observed in the initial stage of reaction which indicated that the increase in viscosity might be due to condensation process. The increase in viscosity for Ba^{++} was greater than other alkaline earth metals used and the reason might be the same as described earlier.

IR technique

IR studies were carried out for determination of resorcinolic contents of tannin based adhesives [17,18]. The spectra of tannin, metal/tannin and TF resin were recorded to monitor the change that occurred due to the addition of metal acetate to the tannin solution and also during tannin formaldehyde condensation. For this purpose the absorbance ratios of the bands were taken [19] (Fig. 3-6). Copper formed stable etherocyclic complexes which were characterized by decrease of phenolic C-O (1210 cm^{-1}) band as well as by increase of intensity of the ether linkage (1120 cm). The absorbance ratio of some bands increased with progress of teannin formaldehyde reaction using metal ions as catalyst. The increase of absorbance ratio at 780/880 (Fig. 4) showed substitution on benzene ring. The ether linkage absorbance bands [20] (1290, 1120) in tannin spectrum are due to the heterocyclic ring in flavonoid structure (1,2). The increase in absorbance ratio at 1290 and 1120 cm^{-1} (Fig. 5) are due to the equal possibility of the product containing methylene as well as ether linkage (XI).

Methylene groups from heterocyclic ring of tannin molecule and that from sugars (17 - 24 % of the extract) [21] present as impurities in the extract contribute at 1450 cm^{-1}. The absorbance ratio at 1450/880 cm^{-1} increased with progress of reaction (Fig. 6). As one methylene group brings two benzene rings close to each other, so the increase in



(XI)

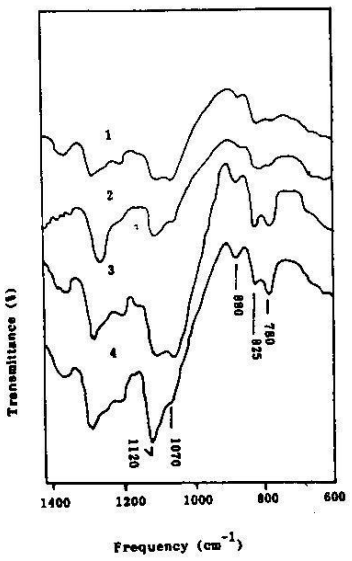


Fig. 3: IR spectra of (1), Tannin (2) Tannin/Copper acetate (3) Tannin/Zinc acetate and (4) Tannin-formaldehyde resin (using zinc acetate as catalyst).

benzene C= C absorbance ratio (Fig. 7) is not unexpected.

Experimental

Hydroxylamine hydrochloride method

i. The standard solution of hydroxylamine hydrochloride was prepared by dissolving 20.0 g of it in distilled water (40 ml) and diluting the soltuion to 400.00 ml with ethanol (99.8%). To this alcoholic solution, 300.0 ml of 0.5 N KOH and 2.5 ml of bromophenol blue solution (0.4 % in 50% ethanol) were added with stirring. The final solution was allowed to stand for 30 min and filtered for experimental use.

ii Tannin solution was prepared in 50 % (v/v) ethanol-water mixture and filtered to remove suspension.

Progress of reaction

Weighed amount (0.01 - 0.10 g) of metal acetate was added to tannin solution (100 ml). It was then stirred and heated to the required temperature (40°C) 1.5 ml of formaldehyde (37-41%) was added to this solution and progress in the reaction was monitored by estimating unreacted formaldehyde at different intervals of time as follows:

A known amount (1 ml) of reaction mixture was taken and poured into flask containing 5 ml of

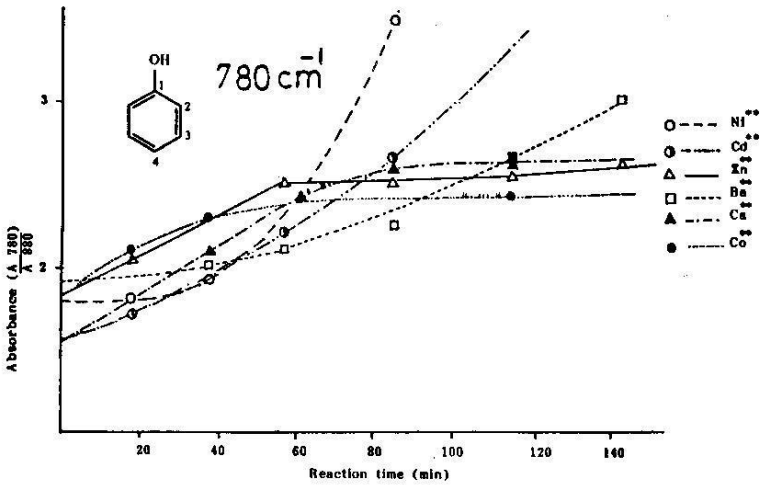


Fig. 4: Effect of metal ions on absorbance ratio (780/880) of Tannin-formaldehyde resin at different intervals of reaction time.

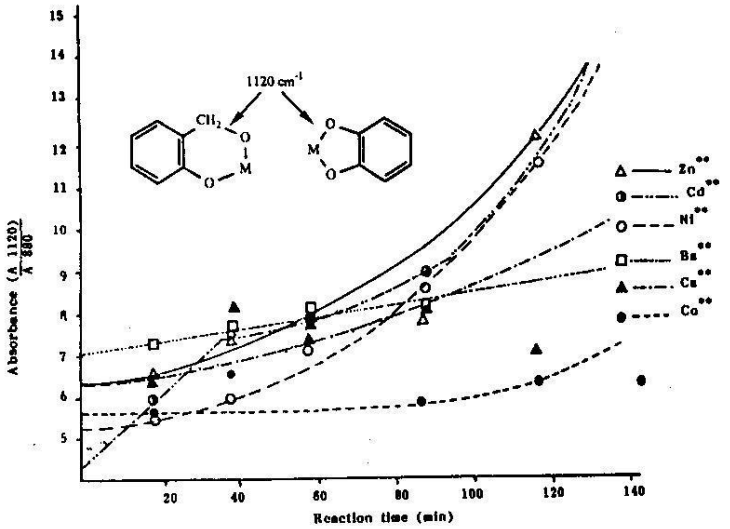


Fig.5: Effect of metals ions on absorbance ratio (A1120/A880) of Tannin-Formaldehyde resin at different time intervals of reaction.

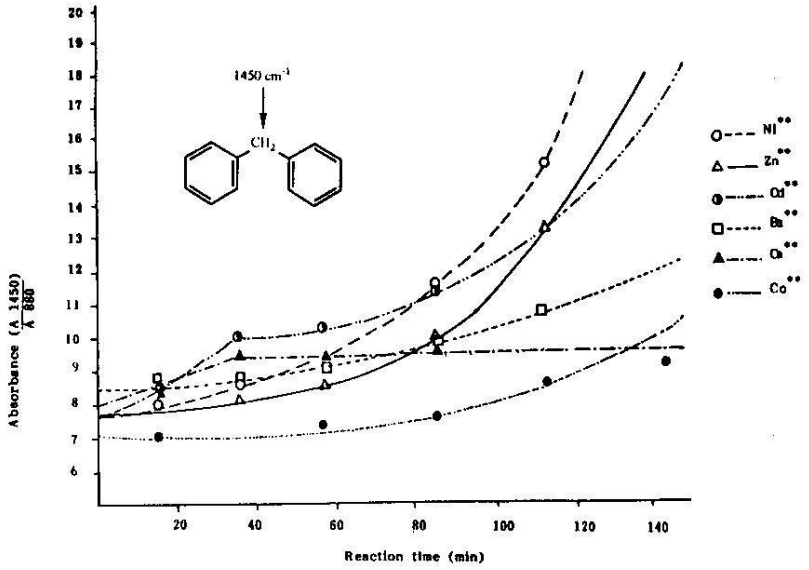


Fig.6: Effect of metals ions on absorbance ratio (A1450/A880) of Tannin-Formaldehyde resin at different intervals of reaction time.

hydroxylamine hydrochloride. The unreacted alkali was titrated against standard solution of HCl. The disappearance of blue colour indicated the end point. The concentration of formaldehyde was determined at different intervals of time from the hydrochloric acid liberated during the reaction.

$$NH_2OH.HCl + HCHO \longrightarrow HCH = NOH + HCl + H_2O$$

Viscometry

Metal acetate (0.1 g) was added to 100 ml of tannin solution (1%). It was continuously stirred and heated till the required temperature was achieved (60°C). The flow time of the solution was measured by Ostwald viscometer (BS/IP/RE) at 25°C before addition of formaldehyde. The 3.0 ml of formaldehyde (37-41%) was added to it. The

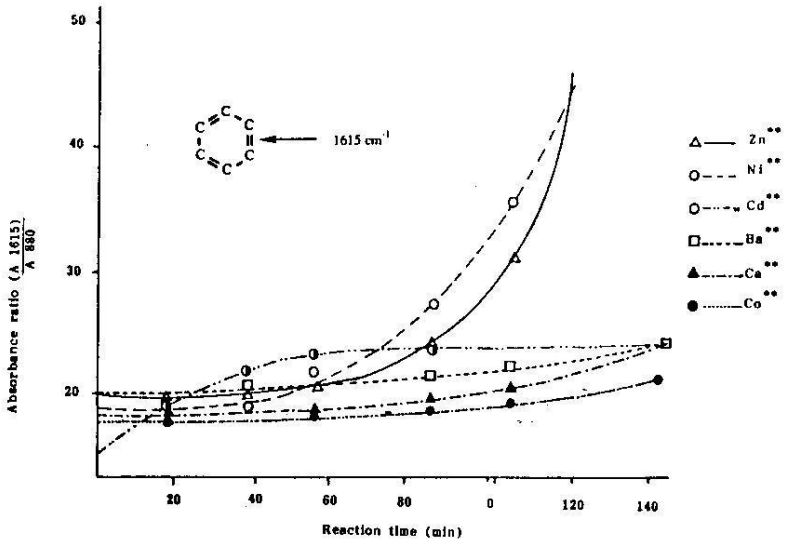


Fig.7: Effect of metal ions on absorbance ratio (1615/880) of Tannin-formaldehyde resin at different intervals of reaction time.

flow time of the reaction mixture was determined at different intervals of time. Relative viscosity (η_r) was determined as follows (1) [16]:

$$\eta_n = \frac{\text{Flow time of reaction mixture of resin}}{\text{flow time of tannin/metal acetate solution}} \quad (1)$$

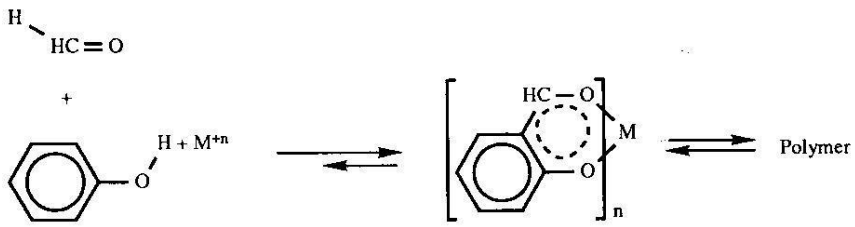
IR technique

Samples of resin were taken at different intervals of reaction time from the reaction mixture used in viscometry and dried at 110°C [22]. IR spectra of these samples were recorded in KBr on Pye-Unicam, SP3-100 IR spectrophotometer. The change in major absorbance frequencies and their ratios with reaction time and catalyst were calculated (Fig. 3-6).

ter catalyst than alkaline earth metals. Ni is the most effective catalyst among the transition metals because in hydroxylamine hydrochloride method, it shows maximum efficiency even at very low concentration (Fig. 1). Zn is the next accelerating transition metal. The efficiency of Cd is greater in the first 35 min of reaction but later on it becomes normal (Fig. 5-7). This unexpected behaviour is due to its size which is greater than other metals, used. The large size of the metal reduces the stress in the etherocyclic ring and the equilibrium of the reaction is shifted to the right in the initial stage.

Pb^{++} and Cu^{++} cannot be used as catalysts because they form stable metal-tannate complexes.

Of all the techniques used, viscometry is comparatively less reliable because the viscosity is not



Conclusion

Results obtained from various techniques indicate that transition metals are comparatively better catalyst than alkaline earth metals. Ni is the most effective catalyst among the transition metals because in hydroxylamine hydrochloride method, it shows maximum efficiency even at very low concentration (Fig. 1). Zn is the next accelerating transition metal. The efficiency of Cd is greater in the first 35 min of reaction but later on it becomes normal (Fig. 5-7). This unexpected behaviour is due to its size which is greater than other metals, used. The large size of the metal reduces the stress in the etherocyclic ring and the equilibrium of the reaction is shifted to the right in the initial stage.

Pb^{++} and Cu^{++} cannot be used as catalysts because they form stable metal-tannate complexes.

Of all the techniques used, viscometry is comparatively less reliable because the viscosity is not only enhanced by condensation process but it may be affected by metal tannate formation (VII). The possibility of formaldehyde evaporation during reaction cannot be completely ignored which may

affect the accuracy of the result, obtained with hydroxylamine hydrochloride method. So IR technique may be considered relatively more reliable than others.

Acknowledgement

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