

# Kinetics of $Ce^{4+}$ /Sodium Sulphite Initiated Polymerisation of Acrylamide.

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Received: 16 November 1993; accepted 19 July 1994

## ABSTRACT

The kinetics of the aqueous polymerisation of acrylamide initiated by the redox pair  $Ce^{4+}$ /sodium sulphite is studied under atmospheric oxygen at  $25 \pm 0.2$  °C. The rate of polymerisation is found to obey the equation:

$$R_p \propto [\text{acrylamide}]^{1.1} [Ce^{4+}]^{1.5} [\text{sodium sulphite}]^{1.3}$$

The effect of temperature, neutral salts, complexing agents and organic solvents on the course of polymerisation is studied and numerical values of the Tudos parameter and retardation constants for retarders like organic solvents are evaluated. The energy of activation is calculated to be 6.90 Kcal/mol from the Arrhenius plot.

## Key Words

acrylamide, Ce (IV), sodium sulphite, polymerisation, retardation.

## INTRODUCTION

$Ce^{4+}$  has long been recognised as a valuable reagent in analytical chemistry [1]. Besides its potential use as a versatile tool in analytical determinations, it has also been widely employed as an initiator in redox and graft polymerisation of a variety of vinyl monomers [2-4]. Although the efficiency of  $Ce^{4+}$  in initiating redox polymerisation is well established in inert atmosphere [5-7], few studies have been made on  $Ce^{4+}$  as an initiator in oxygen atmosphere.

Here the results of kinetics of polymerisation of acrylamide initiated by  $Ce^{4+}$ /sodium sulphite redox pair in atmospheric oxygen are reported. The monomer chosen for the polymerisation

procedure was acrylamide as its polymer has a wide spectrum of applications in the phenomenon of flocculation [8].

## EXPERIMENTAL

### Preparation of Materials

Acrylamide (Robert Johnson, India) was recrystallised twice from methanol (analytical reagent grade) and dried in vacuum over silica gel for a week. Ceric ammonium sulphate (Loba Chemie, India) was used without any further purification and its solution was prepared by the method described in the literature [9]. Sodium

sulphite was of analytical reagent grade (E. Merck, India) and was used as received. Other chemicals used were also of standard grade. Fresh solutions in doubly distilled water were prepared for each run.

### Method

The techniques adopted for polymerisation and molecular weight determination were similar to that described in our other communications [10-14]. The results obtained are quite reproducible and the experimental error lies within 2 percent.

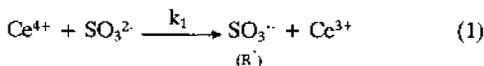
## RESULTS AND DISCUSSION

### Mechanism

The proposed plausible mechanism involves the interaction of Ce<sup>4+</sup> and sulphite ions to produce sulphite ion radicals which consequently initiate polymerisation of monomer (M) as described below:

a: Formation of free radicals

Ce<sup>4+</sup> ions derived from ceric ammonium sulphate react with sulphite ions to generate sulphite ion radicals as follows:

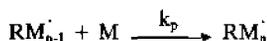
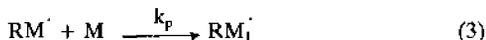


The free radicals (R<sup>·</sup>) so produced in the system initiate polymerisation according to the scheme mentioned below:

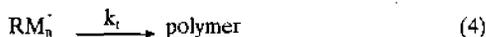
b: Initiation



c: Propagation



d: Termination



This mode of termination is unimolecular in nature and occurs due to the dissolved metal ions or some impurities present in the system.

### Rate Expression

Based on the steady state kinetic assumptions the following rate expression may be derived:

$$R_p = k_p [M] [\text{RM}_n^\cdot] \quad (5)$$

On applying steady state treatment to macroradicals RM<sub>n</sub><sup>·</sup>, we have:

$$R_i = R_t$$

Where RR<sub>i</sub> and RR<sub>t</sub> are the rate of initiation and termination respectively.

$$\text{or } k_i [\text{R}^\cdot] [\text{M}] = k_t [\text{RM}_n^\cdot] \quad (6)$$

$$\text{or } [\text{RM}_n^\cdot] = \left( \frac{k_i}{k_t} \right) [\text{R}^\cdot] [\text{M}]$$

From equations (5) and (6), we have

$$R_p = \left( \frac{k_p k_i}{k_t} \right) [\text{M}]^2 [\text{R}^\cdot] \quad (7)$$

Now to determine the concentrations of free radicals R<sup>·</sup>, steady state assumptions are applied according to which

$$\begin{aligned} \frac{d}{dt} [\text{R}^\cdot] &= 0 = k_i [\text{Ce}^{4+}] [\text{SO}_3^{2-}] - k_t [\text{R}^\cdot] [\text{M}] \\ \text{or } [\text{R}^\cdot] &= \frac{k_i [\text{Ce}^{4+}] [\text{SO}_3^{2-}]}{k_t [\text{M}]} \quad (8) \end{aligned}$$

On substituting the value of [R<sup>·</sup>] in equation (7), we have:

$$R_p = \left( \frac{k_p k_i}{k_t} \right) [\text{Ce}^{4+}] [\text{SO}_3^{2-}] [\text{M}]$$

Since Ce<sup>4+</sup> and sulphite ions are derived from ceric ammonium sulphate (CAS) and sodium sulphite, respectively, we may write:

$$R_p \propto [\text{CAS}] [\text{Sodium Sulphite}] [\text{Monomer}] \quad (9)$$

Equation (9) is in partial agreement with the experimental outcome and the deviations regarding

the order with respect to redox components shall be explained later on.

### Monomer Dependence

When the concentration of monomer varies between the range  $5.0$  to  $9.0 \times 10^{-2}$  mol/L, the initial rate of polymerisation and percentage conversion increase as shown in Figure 1. The

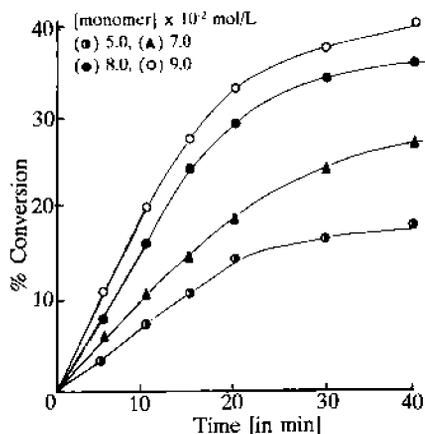


Figure 1. Dependence of the initial rate of polymerisation and percentage conversion on varying monomer concentration at fixed  $[Ce^{4+}] = 5.0 \times 10^{-2}$  mol/L,  $[SO_3^{2-}] = 5.0 \times 10^{-2}$  mol/L,  $25 \pm 0.2$  °C.

increase observed is due to the fact that on increasing monomer concentration in the studied range, the availability of monomer molecules in the propagation step increases which results in a rise in the initial rate and percentage conversion. The order with respect to monomer has been calculated to be 1.1 as obtained from double logarithmic plot (Figure 2) which is slightly greater than the unity value given in the rate expression. The slightly higher value of exponent observed may be attributed to the increased viscosity of the medium as pointed out elsewhere [15]. This first order occurrence with respect to monomer is a common observation in redox polymerisation.

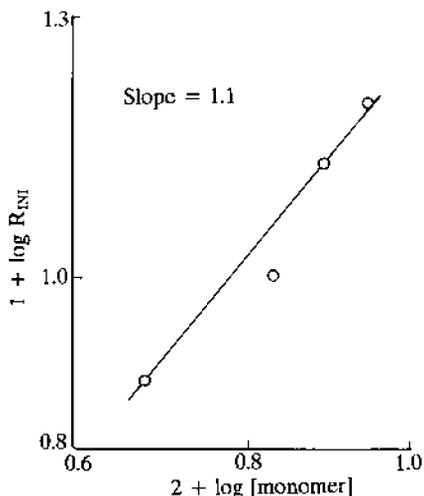


Figure 2. Double logarithmic plot drawn between the initial rate of polymerisation  $R_{INI}$  (in % conversion per minute) and monomer concentration. Slope = 1.1.

### Redox Component Dependence

Both the initial rate and percentage conversion increase on increasing the concentration of initiator ( $Ce^{4+}$ ) and activator (sodium sulphite) in the range  $4.0$  to  $7.5 \times 10^{-2}$  mol/L and  $4.0$  to  $8.0 \times 10^{-2}$  mol/L, respectively. The observed increase is quite obvious as increased concentration of initiator and activator results in a rapid rate of the free radical generation step (eq.1) and, therefore, the initial rate of polymerisation and percentage conversion increase. From double logarithmic plots (Figure 3) the exponent values to initiator ( $Ce^{4+}$ ) and activator (sodium sulphite) have been found to be 1.5 and 1.3, respectively which are higher than the unity values of the derived rate expression.

In redox polymerisation the value of exponent to initiator varies between 0.5 and 1.0 depending on the mode of termination the macroradicals undergo. The exponent shifts from 0.5 towards 1.0 as the termination changes from a bimolecular to unimolecular one. In the present case the exponent observed is 1.5 which is not a

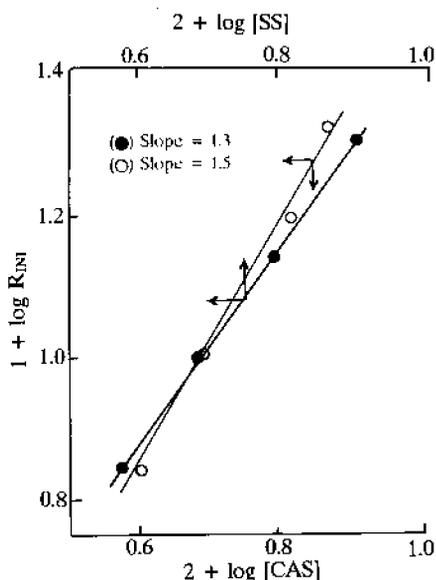
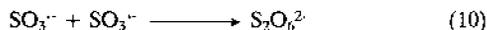


Figure 3. Double logarithmic plots drawn between the initial rate of polymerisation  $R_{INI}$  (in % conversion per minute) and initiator concentration and activator concentrations. Slope = 1.5 and 1.3, respectively.

common finding in redox polymerisation. The explanation for such a higher order may be attributed to the fact that while studying the polymerisation of acrylamide by  $Ce^{4+}$  ions alone, Toru et al. [16] suggested a complex formation between  $Ce^{4+}$  ions and acrylamide on the basis of IR studies. This complex further dissociates to yield initiating free radicals. In the present case also, it may be possible that some  $Ce^{4+}$  ions are complexed with acrylamide molecules and this complex under the existing experimental conditions may not produce free radicals (if free radicals were produced in such a way, certainly there would have been some polymer formation even in the absence of sulphite ions, however, this observation is absent in the present work). In this way, the actual concentration of  $Ce^{4+}$  ions taking part in the radical generation step remains less than the added

concentration. This may be the reason for the occurrence of order higher than unity with respect to  $Ce^{4+}$  concentration.

In case of the exponent to the activator (sodium sulphite) the observed value of 1.3 is higher than unity which may be due to some side reactions occurring in the system of the type shown below:



The higher value of order with respect to activator is uncommon in redox polymerisation. As in most of the redox systems the order varies between 0.5 to unity.

#### Temperature Effect

Upon varying the temperature of the reaction medium in the range 25 to 50 °C, both the initial rate and percentage conversion are found to increase. The increase observed is obvious as a rise in temperature results in a rapid rate of free radical generation (eq.1) which consequently brings about an increase in the initial rate and percentage conversion. From the Arrhenius plot the energy of activation has been calculated to be 6.90 Kcal/mol as shown in Figure 4.

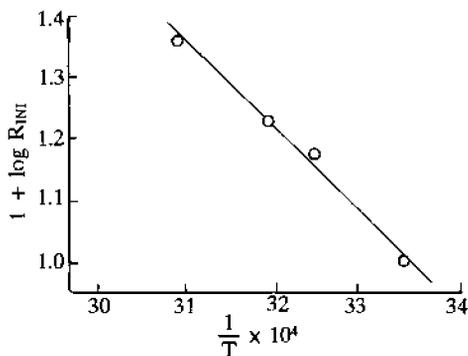


Figure 4. Arrhenius plot drawn between  $\log R_{INI}$  and  $1/T$  with  $E_a = 6.90$  Kcal/mol.

#### Salt Effect

To observe the effect of variation in ionic strength

of the reaction medium on the polymerisation procedure, various electrolytes in equimolar amounts were added. The effect of cations and anions have been studied by addition of sulphates of alkali metals and halides of potassium to the reaction medium. It is clear from Figure 5 that both the initial rate and percentage conversion fall in a specific way.

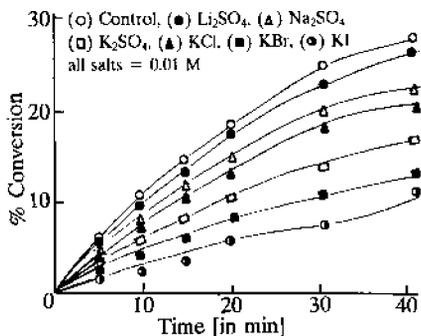


Figure 5. Effect of addition of various salts on the initial rate of polymerisation and percentage conversion fixed [monomer] =  $7.0 \times 10^{-2}$  mol/L,  $[Ce^{4+}] = 5.0 \times 10^{-2}$  mol/L,  $[SO_3^{2-}] = 5.0 \times 10^{-2}$  mol/L,  $25 \pm 0.2$  °C.

In case of cations, the depression in rate percentage conversion is observed in increasing order as follows:



In the same way the increasing order of depression of initial rate and percentage conversion due to anionic addition is given by:



The cause of depression may be attributed to the following reasons:

- Added electrolytes dissociate in the reaction medium and the ions so produced cause an interference with the normal polymerisation procedure resulting in a fall in the initial rate and percentage conversion.

- Added cations and anions may form ion

couples with  $SO_3^{2-}$  and  $Ce^{4+}$  ions in the medium and thus reducing their concentration in the radical generation step (in eq.2).

- Added electrolytes may also cause a change in the ionic strength of the medium which also effects the polymerisation course in some way.

### Complexing Agent Effect

The effect of addition of complexing agents like EDTA on polymerisation rate has been studied by adding sodium salt of EDTA to the reaction medium which results in a fall in the initial rate and percentage conversion. The reason for this behaviour is quite clear as chelation of  $Ce^{4+}$  ions by EDTA molecules will prevent  $Ce^{4+}$  ions from participating in a radical generation step and therefore, the initial rate and percentage conversion will decrease.

### Retarder (Solvents) Effect

The commercial importance of stabilisers and antioxidants have drawn the attention of researchers particularly Bird and Russell [17], Tudos [18-20] and Pospisil [21] in particular have made significant contributions in the field of kinetics and the mechanism of retarded or inhibited polymerisation.

The retarding influence of toluene [22] and chalcone [23] on  $Ce^{4+}$  initiated polymerisation has been studied. We have undertaken the study to observe the retarding behaviour of organic solvents in  $Ce^{4+}$ /sodium sulphite initiated polymerisation of acrylamide. For quantitative evaluation of retarding behaviour of retarders, kinetic parameters like  $\beta$  (known as Tudos parameter) given by Tudos [18] and retardation constant I [24] have been calculated.

Scheme proposed by Tudos:



Where M, R and Z are monomer, chain carrier and retarder respectively. If the rate of initiation is assumed to be constant then the Tudos parameter  $\beta$  may be given as:

$$\beta = \mu k_5 X^{1/2} / 2 (w_1 k_4)^{1/2} = \phi X^{1/2} Z \quad (15)$$

Here  $\mu$  = stoichiometry of the hydrogen abstraction reaction.

$$\text{Now } \phi = \frac{1}{2} \left( \frac{W_{ST}}{W} = \frac{W}{W_{ST}} \right) \quad (16)$$

Here, W = rate of retarded polymerisation

$W_{ST}$  = rate of unretarded polymerisation

X = initial concentration of retarder

Thus with the help of equations (15) and (16),  $\beta$  may be calculated.

### Retardation Constant I

For calculation of retardation constant I, the following equation would be helpful as derived elsewhere.

$$(M)_0 = \frac{(w)_0}{I \left[ \frac{1}{(DP)} - \frac{R_p}{(DP)_p} \right]} \quad (17)$$

(Since unimolecular termination mechanism has been proposed, factor 2 in the original formula from the denominator has been replaced by 1.) Here, the different terms have their usual significance as previously described [24].

The effect of organic solvents such as various alcohols on the polymerisation rate has been studied by adding 5% (V/V) organic solvents to the reaction medium. It is clear from Figure 6 that both the initial rate and percentage conversion so observed have been well explained in our previous reports by the hydrogen abstraction mechanism. The quantitative effect of retardation has been summarised in Table 1 in terms of the Tudos parameter  $\beta$  and retardation constant I.

### CONCLUSIONS

Acrylamide is polymerised in air by the redox system Ce<sup>4+</sup>/sodium sulphite via a free-radical type mechanism. The order of the polymerisation reaction with respect to monomer and redox components in each case is greater than unity and

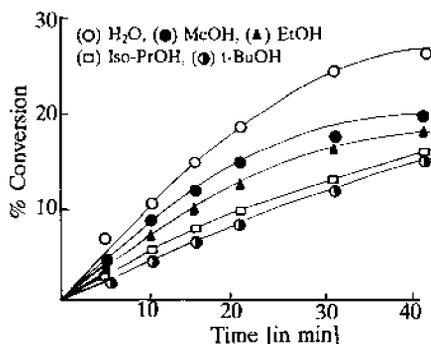


Figure 6. Effect of addition of various organic solvents on the initial rate of polymerisation and percentage conversion at fixed [monomer] =  $7.0 \times 10^{-2}$  mol/L, [Ce<sup>4+</sup>] =  $5.0 \times 10^{-2}$  mol/L, [SO<sub>3</sub><sup>2-</sup>] =  $5.0 \times 10^{-2}$  mol/L,  $25 \pm 0.2$  °C.

thus forms a typical type of a redox system. The rate of polymerisation is lowered by the addition of chelating agent like EDTA, inorganic salts and water miscible organic solvents. The retardation constants and the Tudos parameter for the solvents have also been calculated.

Table 1. Quantitative effect of retarding behaviour of organic solvents in redox polymerisation of acrylamide.

Retarder	Tudos parameter $\beta^a \times 10^2$	Retardation constant $I^b \times 10^4$
Methanol	1.21	1.15
Ethanol	1.25	2.69
Isopropanol	1.77	4.94
t-Butanol	2.35	9.87

a. Calculated from equations (15) and (16).

b. Calculated from equations (17).

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