Asian Journal of Chemistry Vol. 9, No. 4 (1997), 763–768

Polymerisation of Acrylamide initiated by Ce(IV)-Iminodiacetic acid Redox system

K.E.N. NALLA MOHAMED
Post Graduate Department of Chemistry
Khadir Mohideen College, Adirampattinam-614 701, India

Polymerisation of acrylamide initiated by ceric ammonium sulphate Ce(IV) in combination with iminodiacetic acid (IDA) has been investigated in aqueous solution. Polymerisation behaviour as a function of the concentration of Ce(IV), IDA and acrylamide as well as temperature have been studied. The polymerisation is initiated by the radical produced from the decomposition of the complex formed between Ce(IV) and IDA. The rate of polymerisation is found to be first order with respect to the concentration of monomer and complex. The complex formation constant (K) and disproportionation constant (k_d) of Ce(IV)-IDA chelated complex are evaluated and they are 9.043×10^2 and 2.096×10^{-3} respectively. The effect of excess of Ce(IV), mineral acid and complex (initiator) concentrations were studied. The R_p value gradually increases to a maximum and then dercreases with increase of complex concentration. The kinetic parameters involved were determined.

INTRODUCTION

Aqueous polymerisation is a free radical chain process in which free radicals are produced. Ceric ion redox systems are extensively used as the initiators for vinyl polymerisation. The reducing agents used in the redox systems along Ce(IV) commonly are acids[1, 2] alcohols,[3–6] aldehydes,[7] ketones,[8, 9] thiols,[10] sulphur compounds,[11, 12] amines,[13] carbohydrates,[14, 15] thiourea[16] etc. Weng-Cheng *et al.*[17] used an aminopolycarboxylate ligand EDTA and Ce(IV) for the polymerisation of acrylamide. The reducing agent is well known to be the initiator fragment in the intiation reaction. The mechanism of the initiation suggested is that the reducing agent reacts with ceric ion to form a complex intermediate and subsequently decomposes to the free radical. This free radical is initiating polymerisation. The complex formation constant (K) as well as disproportionation constant (k_d) are evaluated. In our study along with Ce(IV) the reducing agent used is an aminopolycarboxylic acid—iminodiacetic acid (IDA) which contains one secondary nitrogen atom and two carboxylic groups. Ce(IV)-IDA is an effective initiator in aqueous polymerisation. In this work, the kinetics of the aqueous polymerisation of acrylamide initiated by Ce(IV)-IDA redox pair is investigated in detail.

EXPERIMENTAL

The reaction mixture containing sulphuric acid, the monomer acrylamide, ceric ammonium sulphate and iminodiacetic acid is deaerated with nitrogen and kept in a constant temperature water bath at 40°C. During polymerisation, the rate of monomer disappearance is followed by bromometric method and the rate of disappearance of Ce(IV) by volumetry with iron(II), using ferroin indicator. The studies are carried out by varying monomer, complex, Ce(IV) and sulphuric acid concentrations and also by varying temperature. The complex formation is supported by absorption spectra. All the reagents used in this work are the purest available, mostly BDH (AnalaR) or E. Merck (GR) or Aldrich (AR) products.

RESULTS AND DISCUSSION

Polymerisation Reaction

The polymerisation of acrylamide initiated by Ce(IV)-IDA in an aqueous solution occurred at 40°C at measurable rate. No induction period was observed under deaerated condition but there was an induction period in the aerated condition. This showed that the polymerisation was initiated by free-radicals produced by the above complex system. The rate of polymerisation (R_p) decreased and the percentage conversion of monomer increased regularly with increase of time.

Generation of IDA free radical

Iminodiacetic acid is a chelating agent.[13] Therefore Ce(IV)-IDA complex (C) pair is formed. The complex decomposed to give Ce(III), IDA$^\bullet$ and H^+. The radical produced IDA is initiating the polymerisation reaction.

$$\mathrm{Ce(IV) + IDA} \overset{K}{\rightleftharpoons} \underset{\text{Complex C}}{\mathrm{(Ce(IV) - IDA)}} \tag{1}$$

$$\underset{\text{Complex C}}{\mathrm{(Ce(IV) - IDA)}} \xrightarrow{k_d} \underset{R'}{\mathrm{IDA^\bullet}} + \mathrm{Ce(III)} + \mathrm{H^+} \tag{2}$$

Evaluation of Formation constant (K) and disproportionation Constant (k_d)

To evaluate K and k_d the rate of disappearance of Ce(IV) in the polymerisation experiment in which the concentration of the ligand is varied keeping Ce(IV) as constants (Table-2, Fig. 2). We have followed the method of Wen-Cheng *et al.*[14] for calculation of K and k_d by using the equations (1) and (2).

$$\frac{1}{k_d K}\frac{1}{[\mathrm{IDA}]}+\frac{1}{k_d}=\frac{[\mathrm{Ce(IV)}]}{-d[\mathrm{Ce(IV)}]/dt}$$

where K is formation constant and k_d is disproportionation constant (Table 1). From our experiment it is evaluated that K is 9.043×10^2 and k_d is 2.096×10^{-3} in this system.

TABLE-1
EVALUATION OF FORMATION CONSTANT (K) AND DISPROPORTIONATION CONSTANT (k_d)
Ce(IV)-IMINODIACETIC ACID-ACRYLAMIDE SYSTEM

[M] = 0.15 mol dm^{-3}, [Ce(IV)] = 2.0×10^{-3} mol dm^{-3},
(H^+) = 0.1 mol dm^{-3}, Temperature 40°C

[IDA] × 10^3 mol dm^{-3}	$\frac{1}{[IDA]} \times 10^2$	$\frac{-d[Ce(IV)]}{dt} \times 10^6$ mol dm^{-3} s^{-1}	$\frac{[Ce(IV)]}{-d[Ce(IV)]/dt}$
0.5	20.00	1.3000	1538.0
0.7	14.28	1.5975	1252.9
0.9	11.11	1.9280	1037.3
1.1	9.09	2.1200	943.1
1.3	7.69	2.3375	856.6
1.5	6.66	2.4250	824.7
1.7	5.86	2.4960	802.9
1.9	5.26	2.5500	784.3

Plot: $\frac{1}{[IDA]}$ *vs.* $\frac{[Ce(IV)]}{-d[Ce(IV)]/dt}$

$K = 9.043 \times 10^2$, $K_d = 2.096 \times 10^{-3}$

TABLE-2
VARIATION OF TEMPERATURE
Ce(IV)-IMINODIACETIC ACID-ACRYLAMIDE SYSTEM

[M] = 0.15 mol dm^{-3}, [IDA] = [Ce (IV)] = 2.5×10^{-3} mol dm^{-3}, [H_2SO_4] = 0.05 mol dm^{-3}

Temp. K	$10^3 \frac{1}{T} K^{-1}$	$10^6 R_p$ mol $dm^{-3}s^{-1}$	$5 + \log R_p$
298	3.356	7.124	0.8527
303	3.300	11.032	1.0426
308	3.247	17.512	1.2433
313	3.195	25.875	1.4828
318	3.145	45.406	1.6571
323	3.098	72.137	1.8515

Effect of monomer and complex concentrations on R_p

The polymerisation reaction is carried out by varying the monomer concentration from 0.025 mol dm^{-3} to 0.3 mol dm^{-3}, keeping [Ce (IV)] = [IDA] = 2.5×10^{-3} mol dm^{-3}, $H_2SO_4 = 5 \times 10^{-2}$ mole dm^{-3} for 20 min. at 40 ± 0.5°C. The value of log [M] is plotted against log R_p and shown in Fig. 1. It is evident from the graph that the order of monomer disappearance is about one. The first order dependence of [M] can be explained by assuming (i) no involvement of monomer in the radical production, (ii) the growing polymer radicals undergo combination with monomer for termination. The polymerisation expt. is also carried by varying the complex concentration in the above experiment, (Fig. 1). This is also in accordance with the following reaction scheme derived.

$$R_p = \frac{k_p k_i k_d}{k_t}[C][M]$$

where k_i, k_p and k_t are constants of initiation, propagation and termination, respectively.

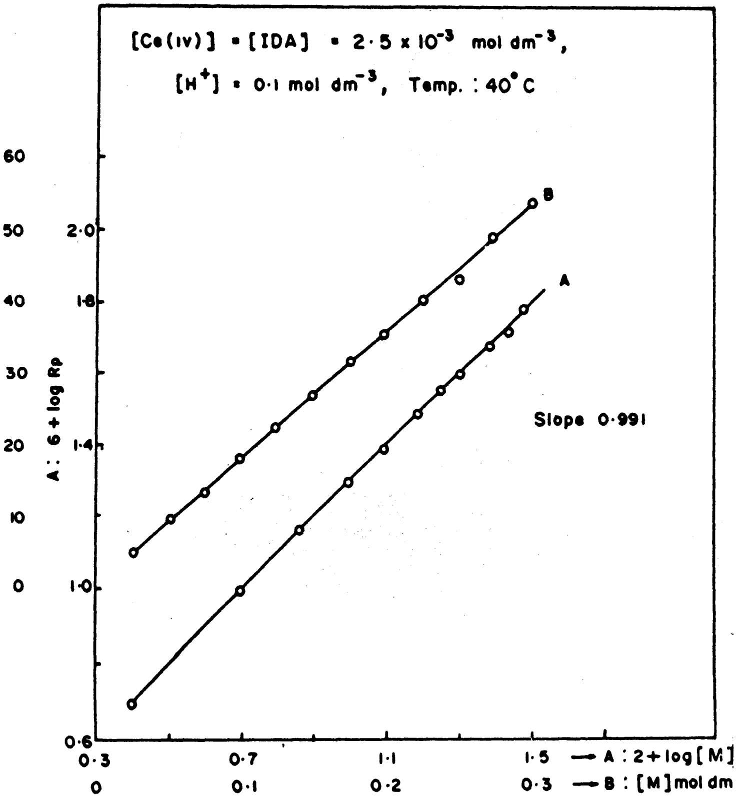

Fig. 1. Variation of monomer concentration
Ce(IV)-Iminodiacetic acid-Acrylamide system
Plot: A: log R_p *vs.* log [M], B: R_p *vs.* [M]

Effect of excess of Ce(IV) on R_p

The Ce(IV) concentration is varied from 1×10^{-4} mol dm^{-3} to 2×10^{-3} mole dm^{-3} keeping the ligand concentration at 1×10^{-3} mol dm^{-3}. This concentration ratio [IDA]/[Ce(IV)] ranged from 0.1 to 2.0 (Fig. 2). As this ratio is increased from 0.1 to 1.0 the R_p increases gradually and reaches a maximum value. Beyond the ratio 1.0 no increase in R_p is observed. This shows that as the ratio is less the Ce(IV) ions being present in large excess are involved in the termination process and hence the R_p is significantly low. Moreover as the ratio [IDA]/[Ce (IV)] is nearly equal to one such termination process is insignificant and the R_p is maximum. The complex concentrations also increase as the ratio is increased which is reflected in the increasing R_p values. Beyond the ratio 1.0 the R_p is constant showing no influence of excess of ligand concentration on R_p. Similar result is noticed in Ce(IV)-lactic acid[5] and Ce(IV)-citric acid[18] systems. Contrarily, Pramanick *et al.*[16] in Ce(IV)-thiourea system reported that the R_p value increased with the ratio [TU] [Ce(IV)] from 0.1 to 0.9 but after 1.0 the R_p value decreased. (where TU is Thiourea).

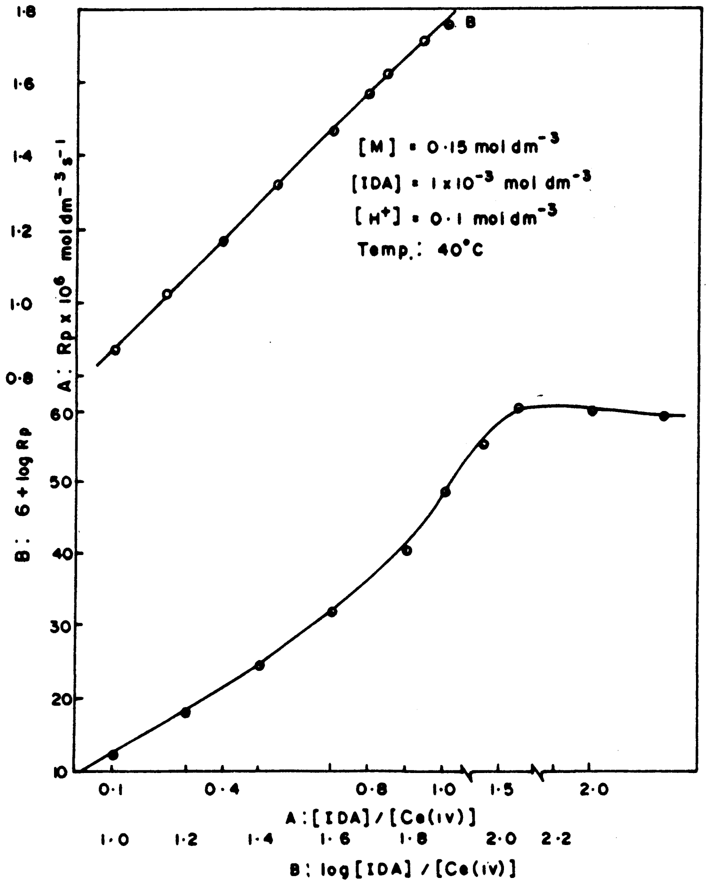

Fig. 2. Effect of excess of Ce(IV) on rate of polymerisation Ce (IV)-Iminodiacetic acid-Acrylamide system.
Plots: A: [IDA]/[Ce (IV)] *vs.* R_p
B: 2 + log [IDA]/[Ce (IV)] *vs.* 6 + log R_p

Effect of mineral acid on polymerisation reaction

The aminopolycarboxylate ligands gradually lose protons as the pH is increased. The pK values of IDA are 2.54 and 9.12.[19] At low pH values, the ligand is protonated and hence the complex formation of Ce(IV) is not effective.

Moreover as pH value increase the Ce(IV) ions gets olated by OH^- ions which is unfavourable for complex formation. The rate of polymerisation is determined for monomer solution containing varied concentration of sulphuric acid. It is noticed that R_p is maximum at $[H^+] = 0.075$ mol dm^{-3}. This shows that Ce(IV) complexed with IDA is a better initiator at this concentration than the uncomplexed Ce(IV) or olated Ce(IV).

Variation of Temperature

The temperature is varied from 298 K to 323 K. As the temperature is increased the R_p is also increased and follows the Arrhenius relations (Table-2). The activation energy is estimated from the slope of the plot between log R_p and 1/T K^{-1}. The activation energy for this system is 73.8 kJ mol.

REFERENCES

1. G.S. Mishra, P.S. Bassi and S.L. Abrol, *Indian J. Chem.*, **22A**, 286 (1983).
2. Sarac Abdul Kadir Sezhi, Goemen Ayrena and Basaram Behil, *J. Solution Chem.*, **9**, 901 (1990).
3. K. Riaz Ahmed, Q. Anwardeen and L.V. Natarajan, *Makromol. Chem.*, **179**, 1193 (1978).
4. N. Mohanty, B. Pradhan and M.C. Mohanta, *J. Macromol. Sci. Chem.* **A16**, 1413 (1983).
5. G.S. Misra and J.I. Khatib, *Colloid Polym., Sci.*, **261**, 188 (1983).
6. K. Nageswar Rao, S. Sondu, B. Sethuram and T. Navneeth Rao, *Polym. Bull.*, **2**, 43 (1980).
7. S.V. Subramanian and M. Santappa, *Makromol. Chem.*,**112**, 1 (1968).
8. R. Anuradha, P. Swoyam, B. Singh and M. Santappa, *J. Polym. Sci, Chem. Ed.*, **16**, 391 (1978).
9. K. Nageswar Rao, B. Sethuram and T. Naveneeth Rao, *Indian J. Chem.*, **19A**, 259 (1980).
10. S. Lenka and P.L. Nayak, *Colloid Polym. Sci.*, **260**, 1114 (1982).
11. R.K. Samal, M.C. Nayak, G. Panda, G.V. Subramaniyan and D.P. Dass, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 53 (1982).
12. G.S. Mishra and S.N. Bhattacharya, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 131 (1982).
13. S.K. Saha and A.K. Chaudhuri, *J. Polym. Sci.*, **A1**, 797 (1972).
14. N.P. Pachi and B.C. Singh, *Colloid Polym. Sci.*, **261**, 390 (1983).
15. ________, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 299 (1983).
16. D. Pramanick and A.K. Chatterjee, *Eur. Polym. J.*, **17**, 239 (1981).
17. Wen-Cheng Hsu, Jen-Feng Kuo and Chuh-Jung Chen, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 2459 (1992).
18. P. Ibrahim Shahib, K. Sahul, P.G. Diss, Ph.D. Thesis, Bharathidasan University Tiruchirapalli (1991).
19. John A. Dean, Lange's Hand Book of Chemistry, McGraw-Hill International Edn.., p. 13, (1987).
20. A.E. Martel and M. Galvin, Chemistry of the Metal Chelate Compounds, 3rd Edn., Prentice-Hall, New Jersey (1956).
21. S.K. Saha and A.K. Chaudhuri, *J. Polym. Sci.*, **A(9)**, 1505 (1971).

(*Received*: 2 April 1997; *Accepted*: 2 June 1997) AJC-1290