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SURFACTANT MEDIATED POLYMERIZATION KINETICS OF ACRYLAMIDE USING CR(VI)-CYCLOHEXANONE REDOX SYSTEM

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Key Words: Redox System, Micellar Polymerization, Acrylamide, Surfactant

ABSTRACT

The effect of organized surfactants on the kinetics of acrylamide (AM) polymerization have been studied over a temperature range of 25-45°C using Cr (VI)-cyclohexanone (CH) redox system as initiator. The rate of polymerization, $R_{p(obs)}$, as well as, the percentage of the monomer conversio were found to be increased with increasing the concentration of the anionic surfactant (SDS), above its CMC. But the cationic surfactant (CTAB) reduced the rate considerably at higher concentration, while non-ionic surfactant (TX-100) played no role on the rate. The effect of [Cr(VI)], [CH], [AM], [H+], and ionic strength on the rates have also been examined. The presence of 0.015M SDS decreased the overall activation energy of the polymerization by 6.28 k.Cal/ mole as

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compared to that in the absence of a surfactant. On increasing the SDS concentration, the viscosity average molecular weight was also found to increase. For the polymerization process, a mutable mechanistic scheme has been pro-posed.

INTRODUCTION

The water soluble polymers, i.e., polymers of acrylamide and its derivatives, are widely used for various purposes such as: (a) In agriculture for stabilizing the soils, and as an agent for prevention of water loss in the soil; (b) in industrial uses as flocculating agent for minerals, coals, industrial waste, thickeners and water clarifying agents, flood agent for petroleum recovery, etc., (3) in pharmaceutical and cosmetic purpose for dental fillers, tumor suppressant, and components of hair spray, shaving cream, etc. [1- 4] . Quite a bit of work has been done on the polymerization of acrylamide in the presence of surfactant using various initiators. Friend and Alexander [5] have observed that the different cationic surfactant reduces the rate of acrylamide polymerization initiated by potassium persulphate. They explained it by the assumption that the primary radicals, $S_2O_8{}^{\cdot}_{=}$ are bound strongly to a positively-charged Stern region of cationic micelles as compared to counter ion. Permanganate initiated acrylamide polymerization rate also reduced in the presence of cationic surfactant due to ion-pair binding of MnO_4^- with large cation, RN^+ , which lowers the rate of the formation of primary radicals [6]. Behari *et al.* [7] observed that the anionic surfactant (SDS) enhances the rates, while the cationic surfactant (CTAB) reduces the rates considerably for persulphate initiated acrylamide polymerization in accordance with the result of Hussain *et al*. [8]. A small amount of work has been done on the acrylamide polymerization, in the presence of surfactants using metal ion organic substrate redox system as initiator. Earlier, we have reported the effect of surfactant on the kinetic of acrylamide polymerization using Ce(IV), V(V), and Mn (VII) on initiator in the presence of cyclohexanone [9]. The present piece of work mainly deals with the kinetic of acrylamide polymerization initiated by Cr(VI)-cyclohexanone redox system in the presence of SDS and CTAB, above their CMCs.

EXPERIMENTAL

Materials

Acrylamide (Merck) was recrystallized from methanol twice and dried *in vacuo*. Cyclohexanone (Fluka) was distilled under reduced pressure. Sodium dodecyl sulphate and cetyltrimethylammonium bromide (Sisco Chem.) were purified by standard methods. Chromium trioxide, TX-100, sulfuric acid, and sodium bisulfate were quality chemicals and used as such without further purification.

Methods

The polymerization was carried out in a pyrex tube of 100 ml capacity which was sealed at the bottom and fitted at the top with a cork that had an inlet and outlet with stop-cocks for passing nitrogen gas. The aqueous solutions of acrylamide (AM) cyclohexanone (CH), sulfuric acid, and sodium bisulfate (to maintain the ionic strength) and surfactant (SDS/CTAB/TX-100) in the appropriate concentrations were placed in the reaction tube. Nitrogen gas was passed for half an hour and stopcocks were closed. The solution was then kept in a thermostatic bath to attain the desired temperature, and followed by the addition of standard Cr(VI) solution by means of a hypodermic syringe and the total volume of the reaction mixture was adjusted to 20 ml. After a defined interval of time, 1 ml of the reaction mixture was withdrawn and introduced into a defined amount of an ice cold standard bromination reagent ($KBr0_3$-Br solution) to cease the polymerization reaction. The quenched reaction mixture was then kept in the dark for half an hour with the addition of 1M sulfuric acid and frequent shaking. Once again, the flank was cooled followed by the addition of a known amount of 20 wt% of KI solution. The liberated sodium was then titrated to the starch end point using standard thiosulfate solutions [10]. The percentage of the conversion of monomer to polymer was calculated with the formula suggested by Mishra *et al.* [11].

$$\%\ \text{of conversion} = \frac{N(V_2 - V_1)M}{20W}$$

where N = normality of the thiosulfate solution

V_1 = Volume of thiosulfate consumed at zero time.

V_2 = Volume of thiosulfate consumed at defined time interval.

M = Molecular weight of the monomer (i.e., acrylamide).

W = Weight of the acrylamide in the withdrawn sample.

The rate of polymerization $R_{P(obs)}$ and Cr(VI) consumption-$R_{Cr(obs)}$ were calculated by the methods given in our earlier publication [12].

Molecular Weight Determination

For determination of molecular weight, the polycrylamide was precipitated from methanol. The flow of a very dilute aqueous solution of polycrylamide and that of water were measured by Ubblehode suspended level viscometer at 30°C. The intrinsic viscosity [η] for the solution was computed with the help of Huggins and Kramer's relationship [13] and the viscosity average molecular weight of the polymers, $\overline{M}_v$, were calculated using the following expression given by Suen *et al.* [14].

$$[\eta] = 6.8 \times 10^{-4}\ \overline{M}_v^{\,-0.66}$$

RESULTS AND DISCUSSION

Effect of the Surfactant Concentration

The rate of polymerization $R_{p(obs),}$ as well as the percentage of acrylamide conversion were found to increase on increasing the concentration of anionic surfactant, i.e., SDS (0.0 to 0.03M) in the reaction medium (Figure 1). In an aqueous medium, the surfactant molecules, above their CMC aggregated to form micelles, leading to a biphase system i.e., bulk phase and micellar phase [15]. Due to a highly hydrophilic nature, the solubilization of acrylamide in the micellar core should be minimum [16]. But, in the acidic medium, the protonated species are likely to be present at the Stern layer at the favorable reaction site. The anionic surfactant micelles for electrostatic attraction [17]. Furthermore, the concentration of Cr(VI) increases at the Stern layer of SDS micelle due to electrostatic attraction between then and the solubilization of cyclohexanone in the micellar core is due more to a hydrophobic interaction [18]. As a result, a higher number of free radicals are produced leading to the rate enhancement (Table 1). The reduction in the rate and the percentage of acrylamide conversion in the presence of CTAB is due to electrostatic repulsion of Cr(VI) by the Stern layer of cationic ion. Narain *et al.* had also reported a similar type of trend for acrylamide polymerization using potassium persulphate as an initiator [19], which was also supported by Shukla *et al.* [6]. The rate of Cr(VI) consumption, $-R_{Cr}$, was observed to increase with increasing the SDS concentration and decrease with a CTAB concentration as reported in our earlier work for other redox systems [12].

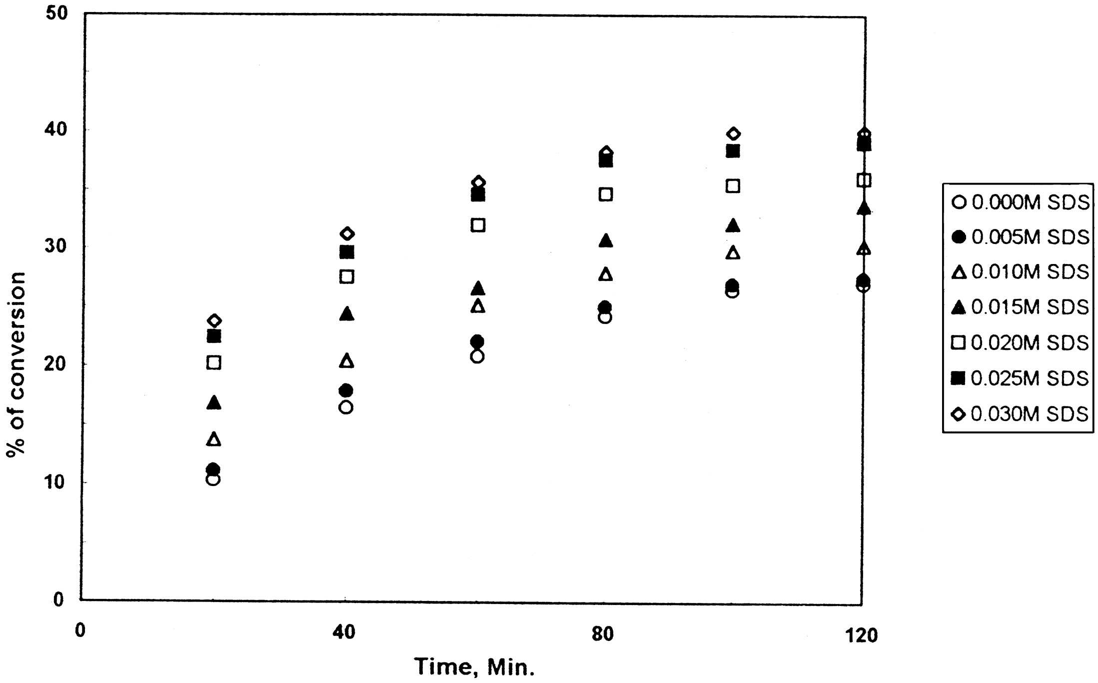

Figure 1. Dependence of percentage of monomer with time. [AM] = 0.512M, [Cr(VI)] = 5.01 × 10^3M, [CH] = 0.108M, [H+] = 0.498M. μ = 0.6M, Temp. = 35°C.

TABLE 1. Effect of Surfactant Concentration on the Rates

[Surfactant]	$R_P \times 10^5$, mol. l^{-1} s^{-1}		$-R_{Cr} \times 10^6$,mol. l^{-1} s^{-1}	
m.mol. l^{-1}	SDS	CTAB	SDS	CTAB
00	4.32	--	1.75	--
05	4.65	2.23	1.87	0.85
10	5.74	1.17	3.98	0.26
15	7.02	1.15	6.32	0.25
20	8.39	1.09	8.61	0.26
25	9.33	1.014	9.48	0.24
30	9.89	1.19	9.60	0.26

[AM] = 0.512 mol.l^{-1}, [Cr(VI)] = 5.08 m. mol.l^{-1},
[CH] = 0.108 mol.l^{-1},[H^+] = 0.498 mol.l^{-1},
μ = 0.6 mol.l^{-1}, Temp. = 35°C

Effect of Acrylamide Concentration

The rate of polymerization, $R_{p(obs)}$, was found to be square dependence on the monomer concentration in the presence of 0.015M SDS, which was confirmed from the bilogarthmic plot of $R_{p(obs)}$ vs. [AM] (Figure 2). The square dependence of the rate on the acrylamide concentration indicates the process is linearly terminated [20]. A similar type of behavior was also reported earlier for a redox system with Cr(VI) [21]. At a high concentration of acrylamide in the reaction mixture, a higher number of acrylamide molecules are available at the reaction site leading to rate enhancement . The rate of Cr (VI) consumption was independent of the monomer concentration.

Effect of Cr(VI)

The $R_{p(obs),}$ as well as the percentage of monomer conversion, were found to be decrease on increasing the Cr(VI) concentration (2.5 to 12.5 mM) at a constant SDS concentration (SDS), in the reaction medium. Cr(VI) can influence both the initiation as well as the termination processes. Perhaps, under our experimental conditions it acts as a better terminator than a initiator at higher concentration. The plots of the reciprocal of $R_{p(obs)}$ vs. [Cr(VI)] is a linear one (Figure 3) , indicating evidence of linear termination [22]. The R_{Cr} also increased with increasing [Cr(VI)] in the presence of 0.015 MSDS. The slopes obtained from a double logarithmic plot of $-R_{Cr}$ vs. [Cr(VI)] (Figure 3), was computed to be 1.12, which confirms first power dependence of $-R_{Cr}$ on the Cr(VI) concentration.

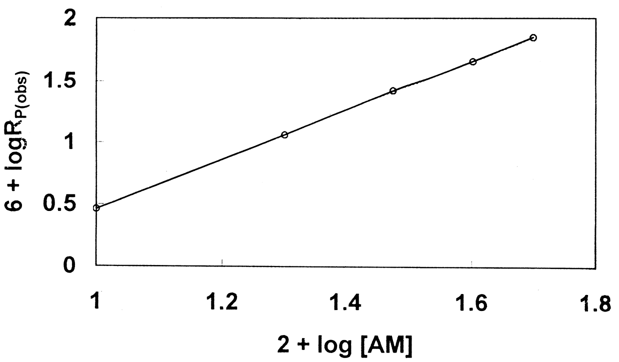

Figure 2. Plot of $\log Rp_{(obs)}$ vs. log[AM]. [SDS] = 0.015M, [Cr(VI)] = 5.01 × 10^3M, [CH] = 0.108M, [H+] = 0.498M. μ = 0.6M, Temp. = 35°C.

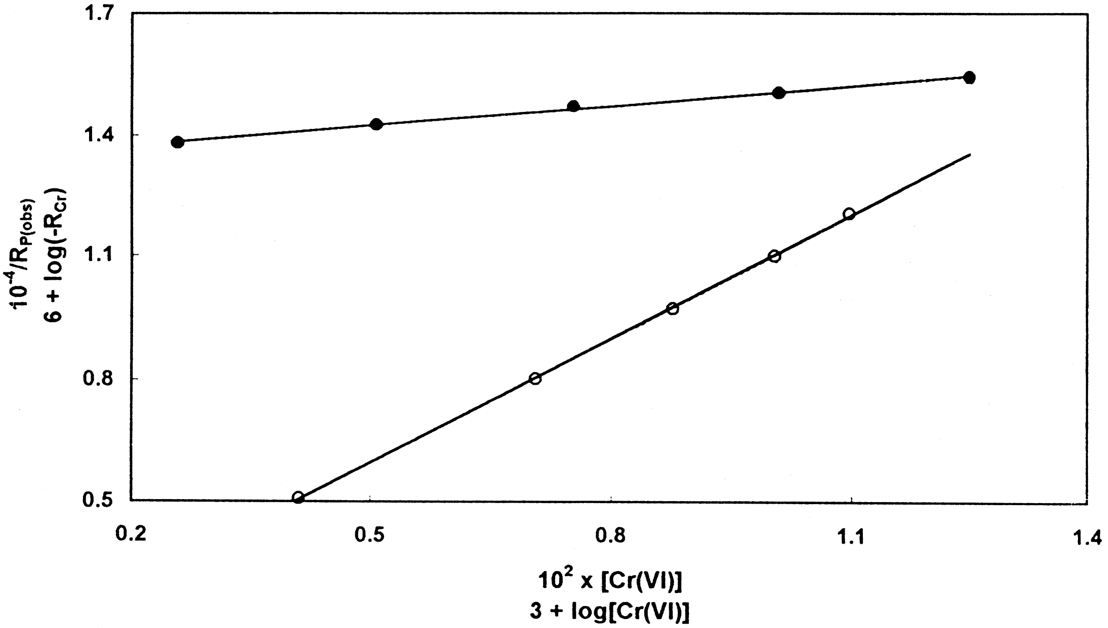

Figure 3. Dependence of Reciprocal of $\log R_{p(obs)}$ with concentration of Cr(VI) (o) and plot of $\log(-R_{Cr})$ vs. log[Cr(VI)] (•). [SDS] = 0.015M, [AM] = 0.5M, [CII] = 0.108M, [H+] = 0.498M. μ = 0.6M, Temp. = 35°C.

Effect of Cyclohexanone Concentration

On increasing the concentration of cyclohexanone (0.05 to 0.25 M) in the reactions mixture, the rate of polymerization as well as the percentage of acrylamide conversion, increased linearly at a constant [SDS] (i.e., 0.015 M). The bilogarthmic plot of $R_{p\,(obs)}$ vs. [CH] (Figure 4) produces a slope having a value of 1.08. At a higher concentration of cyclohexanone, its solubilization into the micellar core is higher, leading to an increase in the number of free radical formation [18]. Hence, a rate enhancement was observed for an increase in the cyclohexanone concentration. Similarly, the rate of Cr(VI) consumption was also linearly dependent on the cyclohexanon concentration which was in conformity with the values of slope (i.e., 1.15) of the bilogarthmic plot of $-R_{Cr}$ vs. [CH] (Figure 4).

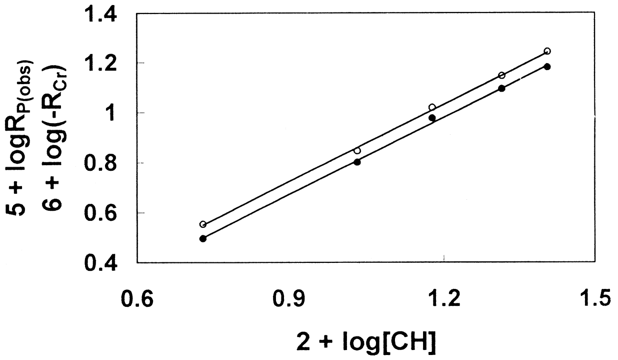

Figure 4. Plot of logRp$_{(obs)}$ (o) and log(-R$_{Cr}$) (•) vs. log[CII]. [SDS] = 0.015M, [AM] = 0.5M, [Cr(VI)] = 5.01 × 10^{3}M, [H+] = 0.498M. μ = 0.6M, Temp. = 35°C.

Effect of [H$^+$] and Ionic Strength

At a constant ionic strength (μ = 0.6 M), the R$_{p(obs)}$ was found to increase with increasing [H$^+$] (Table 2) in a 0.015 M SDS solution. The localization of [H$^+$] at the Stern layer of micelles of SDS, at its higher concentration [19], beyond its CMC, increased the oxidizing power of Cr(VI) leading to a rate enhancement. The rate of Cr(VI) consumption was also observed to increasewith [H$^+$]. An increase in the ionic strength (0.5-0.8) of the reaction medium at con-

TABLE 2. Effect of [H$^+$] and Ionic Strength on the Rates

[H$^+$], mol.l^{-1}	μ , mol.l^{-1}	R$_P$ x 10^5, mol.l^{-1} s^{-1}	-R$_{Cr}$ x 10^6,mol.l^{-1} s^{-1}
0.102	0.6	6.01	5.79
0.191	0.6	6.23	5.91
0.311	0.6	6.57	6.04
0.405	0.6	6.88	6.19
0.498	0.6	7.02	6.32
0.498	0.7	7.15	6.39
0.498	0.8	7.28	6.55

[SDS]= 0.015 mol.l^{-1}, [AM] = 0.512 mol.l^{-1}, [Cr(VI)] = 5.08 m. mol.l^{-1}, [CH] = 0.108 mol.l^{-1}, Temp. = 35°C stant [H^+] (= 0.5M) enhanced the rate of polymerization, Rp(obs), in the presence of 0.015 M SDS, which was in good agreement with the earlier report [23]. The increase in the ionic strength also increased the rate of Cr(VI) consumption.

Effect of Temperature

An enhancement of the polymerization rate has been observed, both in the absence and presence of 0.015 M SDS in the reaction medium, on increasing the temperature from 25-45°C. At the higher temperature, a better solubilization of cyclohexanone in the micellar phase causes the rate enhancement. From the Arrhenius plot (Figure 5) the overall activation energy for the polymerization processes were computed to be 19.11 and 12.83 k.Cal/mol. in the absence and presence of 0.015 M SDS. A decrease of 6.28 k.Cal/mol. in the activation energy supports the positive catalytic role of the surfactant [9, 12, 18, 20].

Reaction Mechanism and Kinetic Scheme

Taking into account all the aforementioned facts, a free radical mechanistic scheme is proposed for the polymerization process as follows:

$$\mathrm{nS} \rightleftharpoons \mathrm{S_n}$$

$$\mathrm{AM + S_n} \rightleftharpoons \mathrm{AMS_n}$$

$$\mathrm{CH + S_n} \rightleftharpoons \mathrm{CHS_n}$$

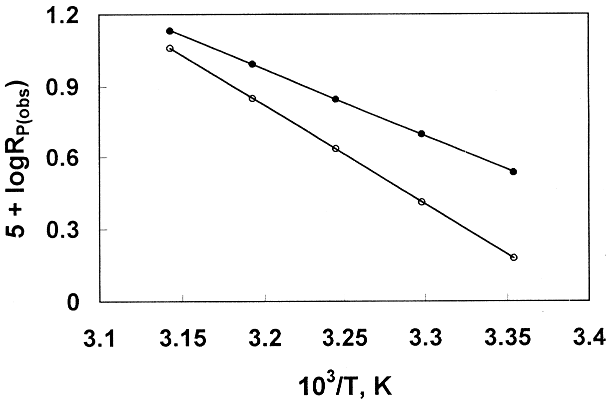

Figure 5. Arrenhius Plot: logRp$_{(obs)}$ vs. Reciprocal of Temperature. [SDS] = 0.015M, (o)/0.000M (•), [AM] = 0.512M, [CH] = 0.108M, [Cr(VI)] = 5.01 × 10^3M, [H^+] = 0.498M, μ = 0.6M.

Reaction of Cr (VI) with Cyclohexanone:

$$\mathrm{Cr\ (VI) + CHS_n \xrightarrow{k_1} Cr(IV) + Product\ -\ 1}$$

Formation of free radical:

$$\mathrm{Cr(IV) + CHS_n \xrightarrow{k_2} \overset{\bullet}{R} + Product\text{-}2}$$

Initiation by Primary radical:

$$\mathrm{\overset{\bullet}{R} + AMS_n \xrightarrow{k_i^m} \overset{\bullet}{R}AMS_n}$$

Initiation by Cr (IV):

$$\mathrm{Cr(IV) + AMS_n \xrightarrow{k_i^m} AMS_n + Cr(III) + H^+}$$

Propagation:

$$\mathrm{AMS_n + RA\overset{\bullet}{M}S_n \xrightarrow{k_p^m} RAM_2S_n}$$

$$\mathrm{AMS_n + RA\overset{\bullet}{M}_2S_n \xrightarrow{k_p^m} RA\overset{\bullet}{M}_3S_n}$$

$$\mathrm{AMS_n + RAM_{(x-1)}S_n \xrightarrow{k_p^m} RA\overset{\bullet}{M}_xS_n}$$

Linear termination:

$$\mathrm{RAM_xS_n + Cr(VI) \xrightarrow{k_t^m} Polymer}$$

Mutual termination:

$$\mathrm{RAM_xS_n} + \mathrm{R\overset{\bullet}{A}M_yS_n} \xrightarrow{k_t^m} \text{Polymer}$$

Reaction of R with Cr (VI):

$$\mathrm{Cr(VI)} + \overset{\bullet}{\mathrm{R}} \xrightarrow{k_o^m} \text{Product - 3}$$

where R = primary radical, S = Surfactant, S_n = Micelles, AM = Acrylamide, k_i^m, k_p^m, k_p^t are respective rate constants, and superscript ‘m’ indicates the micellar phase.

Using a steady state assumption for the free radical, the expression for a rate of polymerization (RPm) and the rate of Cr(VI) consumption (-RmCr) can be derived as follows:

For linear termination:

$$R_p^m = \frac{k_p^m\,[\mathrm{AMS_n}]^2}{k_t^m}\left\{\frac{k'[CHS_n]}{[AMS_n] + \left(k_o^m / k_i^m\right)\,\mathrm{Cr(VI)}} + k_i^m\right\} \qquad (1)$$

$$-R_{Cr}^m = 2[\mathrm{Cr(VI)}]\left\{k'\,[\mathrm{CHS_n}] + k_i^{m'}\,[AMS_n]\right\} \qquad (2)$$

For mutual termination:

$$R_p^m = \frac{k_p^m\,[\mathrm{AMS_n}]^{\frac{3}{2}}\,[\,\mathrm{Cr(VI)}]^{\frac{1}{2}}}{(k_t^m)^{\frac{1}{2}}}\left\{\frac{k'[CHS_n]}{[AMS_n] + \left(k_o^m / k_i^m\right)\,\mathrm{Cr(VI)}} + k_i^{m'}\right\}^{\frac{1}{2}} \qquad (3)$$

$$-R_{Cr}^m = [\mathrm{Cr(VI)}]\left\{k'\,[\mathrm{CHS_n}] + k_i^{m'}\,[AMS_n]\right\} \qquad (4)$$

In the presence of cyclohexanone, it seems likely that its reaction with Cr(IV) is preferred to that between Cr(IV) and the monomer [20]. Hence, the term $k_i^{m'}$, can be ruled out, which is also confirmed from the observation that $-R_{Cr}$ was independent of a acrylamide concentration [24]. The reciprocal of $R_{p(obs)}$ was linearly dependent with the concentration of [Cr(VI)], which indicated the favorable condition for linear termination [22] i.e., the mutual termination was ruled out. As a result, the rate expression can be written as:

$$R_p^m = \frac{k_p^m\,[\mathrm{AMS_n}]^2}{k_t^m} \left\{ \frac{k'[CHS_n]}{[AMS_n] + \left(k_o^m / k_i^m\right)\,\mathrm{Cr(VI)}} \right\} \tag{5}$$

$$-R_{Cr}^m = 2\left\{ \mathrm{k'}\,[\mathrm{Cr(VI)}][\mathrm{CHS_n}\,] \right\} \tag{6}$$

$$\text{or } R_p^m = \frac{k_p^m\,\mathrm{k_1}\,[\mathrm{AM}]^2[\mathrm{S_n}]^2}{k_t^m} \left\{ \frac{k'\,\mathrm{k_2}[CH]S_n}{k_1[AMS_n] + \left(k_o^m / k_i^m\right)\,[\mathrm{Cr(VI)}]} \right\} \tag{7}$$

$$-R_{Cr}^m = 2\left\{ \mathrm{k'k_2}\,[\mathrm{Cr(VI)}][\mathrm{CH}][\mathrm{S_n}\,] \right\} \tag{8}$$

Where $k' = k_1 . k_2$

The overall polymerization rate, $R_{p(obs)}$ can be considered as the sum of the rate of polymerization in the bulk phase R^b_p and that in the micellar phase (R^m_p) i.e., $R_{p(obs)} = R_P^b + R_P^m$. But at higher concentration of SDS above its CMC, $R_{p(obs)}$ can be assumed to be R_P^m . Thus, on rearranging Equation 7,

$$1/R_{p(obs)} = \frac{k_t^m}{k_p^m\ \mathrm{k'\ k_1k_2[AM][CH][S_n]^2}} \left\{ \frac{k_t^m\left(k_o^m / k_i^m\right)\,[\mathrm{Cr(VI)}]}{k_p\ \mathrm{k'\ k_1k_2[AM]^2[CH][S_n]^2}} \right\} \tag{9}$$

Constant Parameter

The constant k^1 in the presence of acrylamide was computed from the plot $-R_{Cr}$ vs{Cr(VI)] and [CH], (figure not given) to be 7.82×10^{-4} and 7.69×10^{-4}, respectively on substituting the value of $K_2 = 9.87 \times 10^4\ \mathrm{mol^{-1}.l}$ and S_n that

TABLE 3. Effect of SDS Concentration on the Viscosity Average Molecular Weight

[SDS], m.mol.l^{-1}	[η], g^{-1}l.	_ $_v$ x 10^{-4}
00	1.11	7.38
05	1.12	7.47
10	1.20	8.30
15	1.34	9.81
20	1.48	11.40
25	1.56	12.35
30	1.60	12.83

[AM] = 0.512 mol.l^{-1}, [Cr(VI)] = 5.08 m. mol.l^{-1},
[CH] = 0.108 mol.l^{-1},$[H^+]$ = 0.498 mol.l^{-1},
μ = 0.6 mol.l^{-1}, Temp. = 35°

determined number 'N' was taken to be 62 [15]. The values of k_o^m/k_i^m and k_p^m/k_t^m were found to be 3.71 and 0.45, respectively, from the plot of $1/R_{P(obs)}$ vs. [Cr(VI)] using the following relationship on modification of Equation 9.

Molecular Weight

In the presence of an anionic surfactant, SDS, the viscosity average molecular weight $\overline{M}_v$ for the polymer were found to increase with increasing SDS concentration in the reaction mixture (Table 3). This may be due to a better environment, which helps in lengthening the polymer chain [9, 12]. Similar types of trends have also been observed by others for acrylamide polymerization using other redox systems [16, 23].

CONCLUSION

The rate enhancement and increase in the viscosity average molecular weight of the obtained polymer in the presence of an anionic surfactant (SDS), are attributed to the favorable hydrophobic and electrostatic interaction of micelle with the monomer and oxidant.

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