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POLYMERIZATION OF ACRYLAMIDE INITIATED BY $KMnO_4$-CYCLOHEXANONE REDOX SYSTEM IN PRESENCE OF SURFACTANT

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Key Words: Acrylamide, Surfactant, Micelle, Polymerization

ABSTRACT

The polymerization kinetics of acrylamide (AM) using $KMnO_4$-Cyclohexanone (CH) redox system as an initiator in the presence of surfactant was studied over a temperature range of 30-50°C in acidic medium. The anionic surfactant, sodium dodecyl sulphate (SDS) above its CMC enhances the rate of polymerization (R_p) as well as the rate of MnO_4^- disappearance ($-R_{Mn}$). However, the presence of a cationic surfactant (CTAB) in the reaction medium, decreases both R_p and $-R_{Mn}$, while a non-ionic surfactant (TX-100) has no effect on the rate. The effects of changes in the con-

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centration of surfactant, monomer, MnO_4^-, cyclohexanone, and acid on the rate of polymerization were also examined. The overall activation energy values were found to be 23.45 and 19.89 Kcal/mole in the absence and in the presence of 0.015M SDS in the reaction medium respectively. The viscosity average molecular weight (M_v) of the obtained polymer has also increased with the concentration of SDS. A suitable mechanistic scheme for the polymerization kinetics involving free radicals has been proposed for the process and rate expressions are derived.

INTRODUCTION

The use of $KMnO_4$ as an oxidant is well known [1]. A lot of work has been done on the kinetics of free radical polymerization of acrylamide and its derivatives in aqueous medium, using $KMnO_4$ as an initiator in the presence of various reductants, i.e., oxalic acid [2, 3], ascorbic acid[4], malic acid[5], thioglycolic acid [6], pyruvic acid [7], thiourea [8], glycine [9], etc. The effect of surfactant on acrylamide polymerization has been studied earlier in different ways such as in micelles [10-13], microemulsions [14] or, inverse emulsion medium [15-18]. The present piece of work deals mainly with the polymerization of acrylamide initiated by $KMnO_4$-Cyclohexanone (CH) redox system in the presence of sodium dodecyl sulphate (SDS), an anionic surfactant.

EXPERIMENTAL

Materials

Acrylamide (Merck) was recrystallized twice from methanol and dried *in vacuo*, cyclohexanone (Fluka) was distilled under reduced pressure. Sodium dodecyl sulphate and cetyltrimthylammonium bromide (Sisco Chemicals) were purified by standard methods. Potassium permanganate, potassium bromide, potassium bromate, and sodium thiosulphate were reagent grade chemicals, and were used as is.

Methods

The polymerization was carried out in a 100 ml capacity pyrex tube, which was sealed at the bottom and fitted at the top with a cork that had an inlet and outlet with stopcocks 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 appropriate concentrations were placed in the reaction tube. Nitrogen gas was passed for half an hour and the stopcocks were closed. The solution was then kept in a thermostatic bath to attain the desired temperature and followed by the addition of standard $KMnO_4$ solution by means of a hypodermic syringe and the total volume of the reaction mixture was adjusted to 20 ml. After a defined time interval, 1 ml of the reaction mixture was withdrawn and introduced into a defined amount of ice cold standard bromination reagent ($KBrO_3$-KBr 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. The percentage of conversion of monomer to polymer was calculated with the formula suggested by Mishra *et al.* [2].

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

where N = normality of the thiosulphate solution; V_1 = volume of thiosulphate solution consumed at zero time; V_2 = volume of thiosulphate solution consumed at a defined time interval; M = molecular weight of the monomer; W = Weight of the monomer in the withdrawn sample.

The rate of polymerization, $R_{P(obs)}$, and rate of permanganate consumption, $-R_{Mn}$, were computed by the method presented in our earlier publications [19].

Molecular Weight Determination

The molecular weight of the polyacrylamide was determined viscometrically using a Ubbelohde suspended level viscometer. The flow time of very dilute aqueous solutions of polyacrylamide and that of water were measured at 30°C. By means of Huggins and Kramer's relationship [20], the intrinsic viscosity, $[\eta]$, for the solutions were computed and the viscosity average molecular weight, M_v, were calculated using the relationship, $[\eta] = 6.8 \times 10^{-4} M_v^{0.66}$, suggested by Suen *et al*. [21].

RESULTS AND DISCUSSION

Effect of Surfactant

On increasing the concentration of the anionic surfactant, sodium dodecyl sulphate (SDS) from 0.00 to 0.03M in the reaction mixture, the observed rate of polymerization, $R_{P(obs)}$, as well as the percentage of conversion of acrylamide were found to be increased (Figure 1). Though acrylamide is neutral and highly hydrophilic in nature [11], the probability of its availability in the Stern layer SDS micelle is mainly due to electrostatic attraction between the protonated acrylamide [22] molecule and the negatively charged Stern layer of anionic micelle. Thus, this factor leads to the observed rate enhancement. But, in the case of the cationic surfactant, CTAB, upon increasing its concentration, the $R_{p(obs)}$ as well as the % of acrylamide conversion decreased considerably as compared to that in the absence of a surfactant. This type of trend for acrylamide polymerization initiated by $KMnO_4$ -ascorbic acid redox system has also been observed by Shukla *et al.* [8]. In persulfate initiated polymerization of acrylamide, the presence of SDS above its CMC, enhances the rate while it is reduced in the presence of CTAB micelles [13]. The rate of MnO_4 consumption

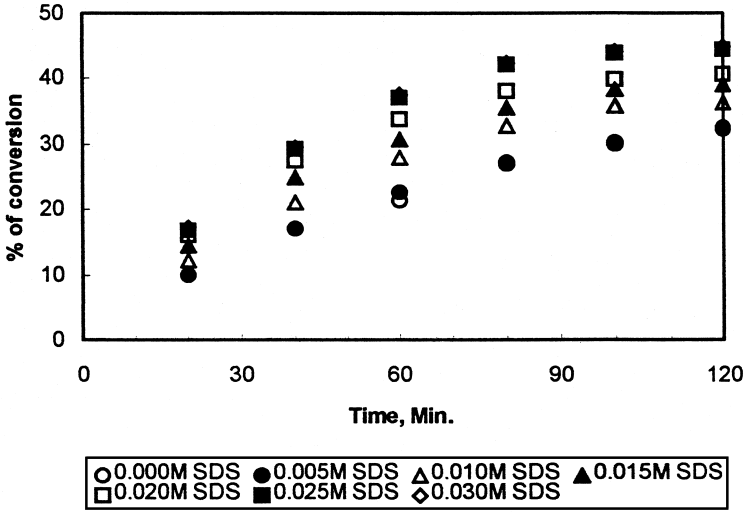

Figure 1. Dependence of percentage of acrylamide conversion with time. [AM] = 0.512 mol.l^{-1}, [MnO_4^-] = 5.08 m. mol.l^{-1}, [CH] = 0.108 mol.l^{-1},[H^+] = 0.498 mol.l^{-1}, μ = 0.6 mol.l^{-1}, Temp. = 35°C.

TABLE 1. Effect of Surfactant Concentration on the Rates

[Surfactant] m.mol. l^{-1}	R_P x 10^5, mol. l^{-1} s^{-1}		$-R_{Mn}$ x10^6,mol. l^{-1} s^{-1}	
	SDS	CTAB	SDS	CTAB
00	4.14	-	1.23	-
05	4.19	1.47	1.28	0.38
10	5.02	0.65	1.45	0.40
15	6.01	0.41	1.73	0.17
20	6.68	0.41	2.01	0.17
25	6.98	0.40	2.22	0.17
30	7.17	0.40	2.31	0.17

$[AM] = 0.512$ mol.l^{-1}, $[Mn(VII)] = 5.08$ m. mol.l^{-1},
$[CH] = 0.108$ mol.l^{-1},$[H^+] = 0.498$ mol.l^{-1},
$\mu = 0.6$ mol.l^{-1}, Temp. = 35°C

($-R_{Mn}$) has also increased with an increasing concentration of SDS and decreased with CTAB concentrations (Table 1).

Effect of the Acrylamide Concentration

The observed rate of polymerization, $R_{p(obs)}$, as well as the percentage of acrylamide conversion were found to increase with an increasing concentration of acrylamide from 0.1 to 0.5M in 0.015M SDS in the reaction mixture at a constant temperature of 35°C. The acrylamide is highly hydrophilic in nature, its solubilization in the micellar core will be minimum [11], but in the acidic medium the protonated acrylamide,

$$CH_2 = CH - CONH_2 \longrightarrow CH_2 = CH - CO - \overset{+}{N}H_3$$

prefers to be present at the micellar interface of anionic micelles (i.e. SDS) due to its electrostatic attraction. Acylamide also acts as a co-surfactant [23], which supports its presence at the micellar interface i.e., at the favorable reaction site. Hence, at a higher concentration of acrylamide, the $R_{p(obs)}$ increased. The slope from the double logarithmic plot (Figure 2) was found to be 2.18, which rules out the mutual termination [24]. The rate of MnO_4 consumption was independent of acrylamide concentration and it conformed with the findings of other workers for such types of redox systems [24-26].

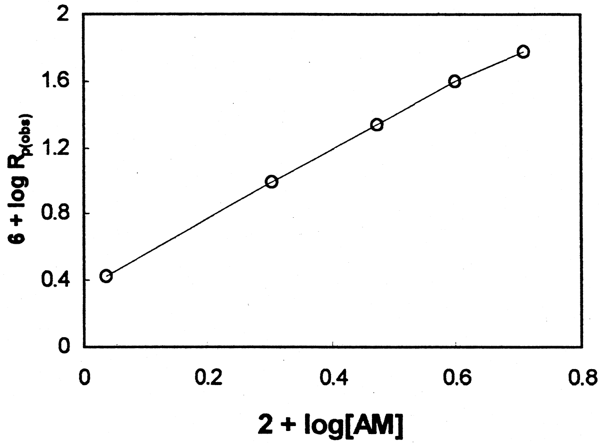

Figure 2. Dependence of log$R_{P(obs)}$ on log[AM]. [SDS] = 0.015 mol.l^{-1}, [MnO_4^-] = 5.08 m. mol.l^{-1}, [CH] = 0.108 mol.l^{-1},[H^+] = 0.498 mol.l^{-1}, μ = 0.6 mol.l^{-1}, Temp. = 35°C.

Effect of MnO_4^- Concentration

Upon increasing the MnO_4^- concentration (5-25m.mol.), the rate of polymerization and percentage of acrylamide conversion were found to decrease. In the permanganate redox system, initially the acrylamide present in the bulk phase reacts with permanganate to produce MnO_2, i.e., Mn(IV), and this in acidic medium dissolves to produce free radical [2-C,9] through complex formation with added organic substrate [27] (i.e., cyclohexanone). The plot of reciprocal of $R_{p(obs)}$ vs. [MnO_4^-] (Figure 3) produces a straight line, supporting the linear termination[24-28]. At a higher concentration of MnO_4, a higher number of Mn(IV) is produced which acts as a better terminator as compared to the initiator resulting in a decrease in the rate of polymerization. The rate of MnO_4 consumption, $-R_{Mn}$, increased linearly with MnO_4^- concentration, which was confirmed from the value of the slope (i.e., 1.12) of the double logarithmic plot $-R_{Mn}$ vs. [MnO_4^-] (Figure 3).

Effect of Cyclohexanone Concentration

The rate of polymerization, as well as the % conversion of acrylamide, were found to increase with increasing the concentration of cyclohexanone (CH) (0.05-0.25 mol.) in the presence of 0.015M SDS. This may be due to a greater

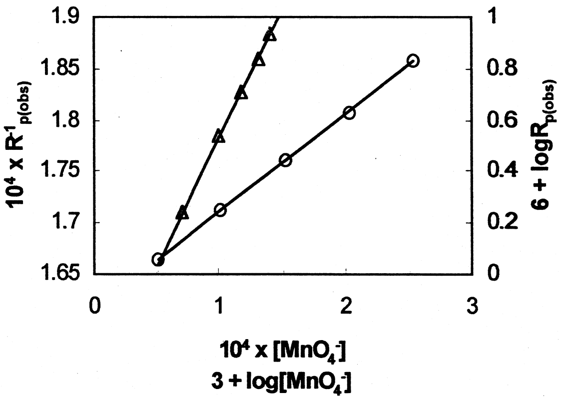

Figure 3. Dependence of reciprocal of $R_{P(obs)}$ on $[MnO_4^-]$ **(o)** and bilogarithmic plot of $-R_{Mn}$ vs. $[MnO_4^-]$ (Δ). [SDS] = 0.015 mol.l^{-1}, [AM] = 0.512 mol.l^{-1}, [CH] = 0.108 mol.l^{-1},[H^+] = 0.498 mol.l^{-1}, μ = 0.6 mol.l^{-1}, Temp. = 35°C.

solubilization of cyclohexanone in the micellar media, leading to the formation of a greater number of free radicals reacting with Mn(IV) at the micellar interface [2-6]. The order with respect to the concentration of cyclohexanone on $R_p(obs)$, was calculated from the slope of the double logarithmic plot $R_{p(obs)}$ vs. [CH] (Figure 4) and it was found to be 1.11, that is the 1st order dependence on the cyclohexanone concentration. Similar results have been reported earlier by Bajpai *et al.* [7, 9]. for permanganate initiated acrylamide polymerization using other organic substrates (i.e., glycine, cystine, serine, etc.). Upon increasing the cyclohexanone concentration, $-R_{Mn}$ also increased linearly. The slope obtained from the double logarithmic plot of $-R_{Mn}$ vs. [CH] (Figure 4) was found to be 1.09, indicating 1st order dependence of $-R_{Mn}$ on the cyclohexanone concentration.

Effect of [H^+] and Ionic Strength

A decrease in the rate of polymerization, as well as the % of acrylamide conversion was observed upon increasing the concentration of H^+ (Table 2). This may be due to the side reaction of Mn(IV) (i.e., MnO_2) with excess of H^+ producing inhibiting oxygen [2-6] as:

$$MnO_2 + 2\,H^+ \rightarrow Mn(II) + H_2O + O$$

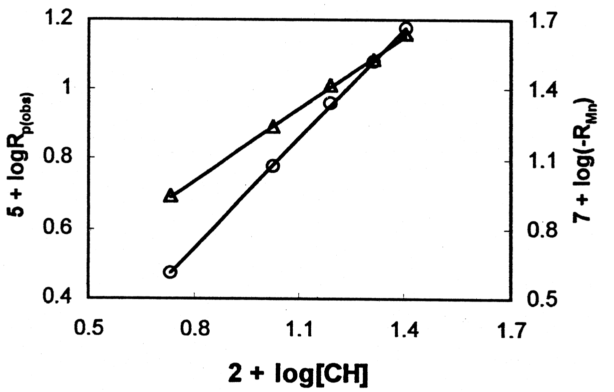

Figure 4. Bilogarithmic plot of $R_{P(obs)}$ and $-R_{Mn}$ vs. [CH]. [SDS] = 0.015 mol.l^{-1}, [MnO_4^-] = 5.08 m. mol.l^{-1}, [AM] = 0.512 mol.l^{-1},[H^+] = 0.498 mol.l^{-1}, μ = 0.6 mol.l^{-1}, Temp. = 35°C

Thus, the formation of free radical was reduced leading to the reduction of the polymerization rate, while $-R_{Mn}$ increased with the [H^+] at a constant ionic strength (μ = 0.6M). Upon increasing the ionic strength at constant [H^+] (= 0.5M) both $R_{p(obs)}$ and $-R_{Mn}$ decreased.

Effect of Temperature

An enhancement of the rate of polymerization, $R_{p(obs)}$, was observed upon increasing the temperature from 25°–45°C, both in the absence and in the pres-

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

[H^+], mol.l^{-1}	μ , mol.l^{-1}	$R_P \times 10^5$, mol.l^{-1} s^{-1}	$-R_{Mn} \times 10^6$,mol.l^{-1} s^{-1}
0.103	0.6	6.49	1.31
0.197	0.6	6.43	1.38
0.293	0.6	6.27	1.44
0.406	0.6	6.11	1.59
0.498	0.6	6.01	1.73
0.498	0.7	5.88	1.64
0.498	0.8	5.63	1.47
0.498	0.9	5.48	1.32

[SDS]= 0.015 mol.l^{-1}, [AM] = 0.512 mol.l^{-1}, [Mn(VII)] = 5.08 m. mol.l^{-1}, [CH] = 0.108 mol.l^{-1}, Temp. = 35°C

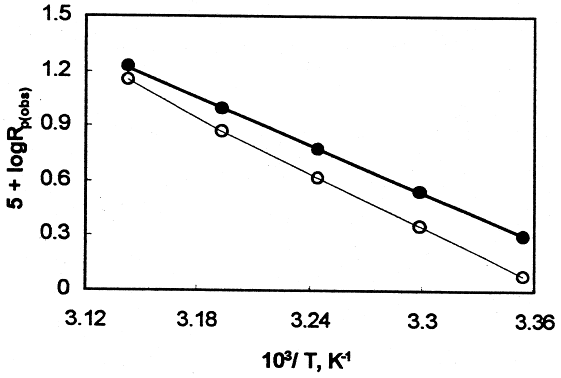

Figure 5. Arrhenius plot: log$R_{P(obs)}$ vs. 1/T. [SDS] = 0.015 mol.l^{-1}(Δ),[SDS] = 0.000 mol.l^{-1}**(o)**, [MnO_4^-] = 5.08 m. mol.l^{-1},[CH] = 0.108 mol.l^{-1}, [AM] = 0.512 mol.l^{-1},[H^+] = 0.498 mol.l^{-1}, μ = 0.6 mol.l^{-1}, μ = 0.6 mol.l^{-1}, Temp. = 35°C.

ence of 0.015M SDS. The reason in this is that at higher temperature, the formation of free radicals at the micellar interface increases due to the increased solubilization of cyclohexanone in the micellar core. The overall activation energy, E_a, for the process, both in the absence and in the presence of 0.015M SDS, was computed from the Arrhenius Plot (Figure 5). A decrease in the activation energy by 5.36 K.Cal/mole was observed in the presence of 0.015M SDS solution (E_a = 18.09 K.Cal/mol) as compared to the absence of the surfactant (Ea= 23.45 K.cal/mol). Such a type of behavior supports the positive catalytic role of the SDS micelles in the polymerization process [19, 29].

Reaction Mechanism and Kinetic Scheme

Considering all the above mentioned facts, it is assumed that the polymerization of acrylamide occurs at the micellar interface in the presence of the anionic surfactant (SDS), above its CMC. In the redox system containing permanganate, initially the permanganate reacts with the acrylamide to produce manganese dioxide, which gets dissolved in acidic medium and acts with the organic substrate (i.e., CH) to produce free radicals which initiate polymerization in the following manner [9]:

$$nS \rightleftharpoons S_n$$

$$AM + S_n \overset{K_1}{\rightleftharpoons} AMS_n$$

$$CH + S_n \overset{K_2}{\rightleftharpoons} CHS_n$$

Formation of Free Radical:

$$\text{Mn(IV)} + \text{CHS}_n \underset{}{\overset{K_3}{\rightleftharpoons}} \text{Complex-1} \xrightarrow{k^m} \dot{\text{R}} + \text{Mn(II)}$$

Initiation by Primary Radical:

$$\text{AMS}_n + \dot{\text{R}} \xrightarrow{k_i^m} \text{R}\dot{\text{A}}\text{MS}_n$$

Initiation by Mn(IV):

$$\text{Mn(IV)} + \text{AMS}_n \xrightarrow{k_i^{m'}} \dot{\text{A}}\text{MS}_n + \text{Mn(II)}$$

Propagation:

$$\text{AMS}_n + \text{R}\dot{\text{A}}\text{MS}_n \xrightarrow{k_p^m} \text{R}\dot{\text{A}}\text{M}_2\text{S}_n$$

$$\text{AMS}_n + \text{R}\dot{\text{A}}\text{M}_2\text{S}_n \xrightarrow{k_p^m} \text{R}\dot{\text{A}}\text{M}_3\text{S}_n$$

$$\text{AMS}_n + \text{R}\dot{\text{A}}\text{M}_{(x-1)}\text{S}_n \xrightarrow{k_p^m} \text{R}\dot{\text{A}}\text{M}_x\text{S}_n$$

Termination by Mn(IV) (Linear):

$$\text{Mn(IV)} + \text{R}\dot{\text{A}}\text{M}_x\text{S}_n \xrightarrow{k_t^m} \text{Polymer}$$

Termination by Combination (Mutual):

$$\text{R}\dot{\text{A}}\text{M}_x\text{S}_n + \text{R}\dot{\text{A}}\text{M}_y\text{S}_n \xrightarrow{k_t^{m'}} \text{Polymer}$$

Reaction of Primary Radical:

$$\text{Mn(IV)} + \dot{\text{R}} \xrightarrow{k_o^m} \text{oxidation product}$$

where M = Monomer (i.e., AM); S = Surfactant (i.e., SDS); S_n = Micelles; k_1 & k_2 = Association constants; $k^m{}_i$, $k^m{}_p$ & $k^m{}_t$ = respective rate constants; Superscript ‘m’ indicates the micellar phase.

Making the usual steady state assumption for free-radical formation, the rate expression for polymerization, R^m_P, and Mn(IV) consumption, $-R^m_{Mn}$ can be given as follows:

For linear termination:

$$R_p^m = \frac{k_p^m [AMS_n]^2}{k_t^m} k' \frac{[CHS_n]}{[AMS_n] + (k_o^m / k_i^m)[Mn(IV)]} + k_i^{m'} \tag{1}$$

$$-R_{Mn} = 2[Mn(IV)] \{ k'[CH_n] + k_i [AMS_n] \} \tag{2}$$

For mutual termination:

$$R_p^m = \frac{k_p^m [AMS_n]^{1.5}[Mn(IV)]^{0.5}}{k_t^{m0.5}} \left\{ k' \frac{[CHS_n]}{[AMS_n] + (k_o^m / k_i^m)[Mn(IV)]} + k_i^{m'} \right\}^{0.5} \tag{3}$$

$$-R_{Mn} = [Mn(IV)] \{ k'[CHS_n] + k_i [AMS_n] \} \tag{4}$$

The possibility of mutual termination is ruled out since the rate of polymerization is square dependent on the acrylamide concentration. Mn(IV) could not initiate the polymerization alone in the absence of the cyclohexanone, thus the term k_i is eliminated. Hence, the rate can be expressed as:

$$R_p^m = \frac{k_p^m [AMS_n]^2}{k_t^m} k' \frac{[CHS_n]}{[AMS_n] + (k_o^m / k_i^m)[Mn(IV)]} \tag{5}$$

$$-R_{Mn} = 2\, k'[Mn(IV)]\, [CHS_n] \tag{6}$$

On proper substitution it can be expressed as:

$$R_p^m = \frac{k_p^m K_1^2 [AM]^2 [S_n]^2}{k_t^m} \times \frac{k' K_2 [CH][S_n]}{K_1 [AM][S_n] + (k_o^m / k_i^m)[Mn(IV)]} \tag{7}$$

$$-R_{Mn} = 2\, k'.K_2[Mn(IV)]\, [CH][S_n] \tag{8}$$

On expressing the [Mn(IV)] in terms of permanganate concentration, the rate can be written as:

$$R_p^m = \frac{k_p^m K_1^2 [\mathrm{AM}]^2 [S_n]^2}{k_t^m} \times \frac{k' K_2 [\mathrm{CH}][S_n]}{K_1 [\mathrm{AM}][S_n] + (k_o^m / k_i^m) k'' [\mathrm{MnO}_4^-]} \tag{9}$$

$$-R_{Mn} = 2\, k'.K_2 k''[\mathrm{MnO}_4]\,[\mathrm{CH}][S_n] \tag{10}$$

$$\text{where, } k' = k^m.\, k_3 \tag{11}$$

The overall polymerization rate, $R_{P(obs)}$, can be considered as the sum of the rate of polymerization in the bulk phase, $R_P{}^b$, and that in the micellar phase, R_P''' i.e., $R_{P(obs)} = R_P{}^b + R_P{}^m$. But at a higher concentration of SDS, above its CMC, it is assumed that polymerization took place mostly in the micellar interface, i.e., ($R_{P(obs)} \approx R_p{}^m$). Hence, on rearranging, Equation 9 can be written as:

$$\frac{1}{R_{p(obs)}} = \frac{k_t^m}{k_p^m k' K_1 K_2 [\mathrm{CH}][\mathrm{AM}][S_n]^2} + \frac{k_t^m (k_0^m / k_i^m) k'' [\mathrm{MnO}_4^-]}{k_p^m k' K_1^2 K_2 [\mathrm{CH}][\mathrm{AM}]^2 [S_n]^3} \tag{12}$$

Constant Parameters

The constant k'.k" (in the presence of acrylamide) was computed from the plot of $-R_{Mn(obs)}$ vs. [Mn(VII)] and [CH] (Figure 6) 1.51×10^{-4} and 1.65×10^{-4}, respectively, on substituting the value of K_2 (9.36×10^4) [19] and S_n, obtained from the relation, $S_n = (C_D - \mathrm{CMC})/N$, where C_D is concentration of the surfactant and the aggregation number (N) was taken to be 62 [30]. The values of $k_o^m k''/k_i^m$ and k_p^m/k_t^m were computed from the plot of reciprocal of $R_{P(obs)}$ vs. [Mn(VII)] (Figure 3) using the following relations derived from Equation 12.

$$\frac{k_0^m k''}{k_i^m} = \frac{\text{slope}}{\text{intercept}} K_1 [\mathrm{AM}][S_n] \tag{13}$$

$$\frac{k_p^m}{k_t^m} = \frac{1}{\text{intercept} \times k' K_1 K_2 [\mathrm{AM}][\mathrm{CH}][S_n]^2} \tag{14}$$

and found to be 3.22 and 0.67, respectively.

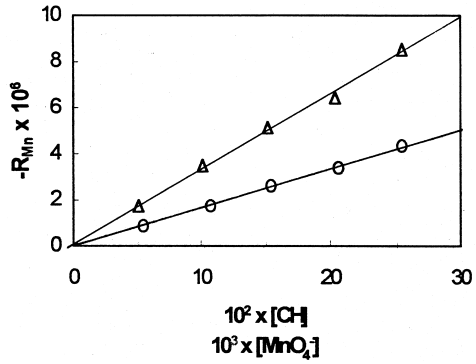

Figure 6. Dependence of $-R_{Mn}$ Vs. $[MnO_4^-]$ **(o)** and [CH] (Δ).

Molecular Weight

Upon increasing the concentration of SDS from 0 to 0.03M in the solution, the viscosity average molecular weight M_v, was observed to be increased (Table 3). This may be attributed to the suitable environment. (i.e., micellar interface) created by SDS micellar, for lengthening the chain of the polymer. Similar type of trends were also observed earlier [14-19].

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

[SDS], m.mol.l^{-1}	[η], g^{-1}l.	$M_v \times 10^{-4}$
00	1.23	8.62
05	1.25	8.83
10	1.33	9.70
15	1.47	11.29
20	1.61	12.96
25	1.68	13.82
30	1.70	14.07

[AM] = 0.512 mol.l^{-1}, [Mn(VII)] = 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

CONCLUSION

The increase in the rate of polymerization, as well as the % of monomer conversion in the presence of SDS, the anionic surfactant, may be due to the hydrophobic interaction and electrostatic attraction of cyclohexanone, acrylamide and Mn (IV) for the SDS micelles.The higher molecular weight polymer was obtained by this method in the presence of SDS due to the presence of more number of monomers at the reaction site.

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