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POLYMERIZATION OF ACRYLAMIDE INITIATED BY V(V)-CYCLOHEXANONE REDOX SYSTEM IN MICELLAR PHASE: A KINETIC STUDY

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Key Words: Acrylamide, Polymerization, Micellar Phase, Free Radical

ABSTRACT

The kinetics of acrylamide (AM) polymerization initiated by V(V)-cyclohexanone(CH) redox system in the presence of anionic surfactant, sodium dodecyl sulphate (SDS), in aqueous sulphuric acid have been studied over a temperature range of 30-50°C. The rate of Polymerization, $R_{P(obs)}$, as well as the rate of V(V) consumption, $-R_V$, were found to increase in the presence of SDS, above its CMC, while decrease with cationic surfactant, cetyl trimethylammonium bromide (CTAB). The non-ionic surfactant, TX-100, has no effects on the rates. Both the rates were also determined at varying concentration of AM, V(V), CH, H^+ and at various ionic strength in the presence of 0.015M SDS in

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the solution. The overall activation energy for the proccesses calculated from the Arrhenious plot, were found to be 19.34 and 26.58 kcal/mol in the presence and absence of 0.015M SDS. The viscosity average molecular weight of the polymer obtained in presence of SDS increases with the concentration of SDS. A suitable free radical mechanistic scheme for the polymerization process is proposed.

INTRODUCTION

The polyacrylamide has a wide range of utility in industries like, flocculent, thickener and structure forming agent, and also to reduce the hydraulic resistance of liquid [1, 2]. Various redox systems metal ion (i.e., Ce(IV), Mn(III), Mn(VII), Tl(III) etc.)-organic substrate, used as initiator for aqueous acrylamide polymerization [3-10], are well known. Little work has been done on the effect of surfactant on the aqueous polymerization of acrylamide. The cationic surfactants (e.g., CTAB, DTAB and TTAB) reduced the rate of polymerization of acrylamide and methacrylamide, as well as the molecular weight of the polymer obtained [11]. According to Kim [12] the rate of acrylamide polymerization and the molecular weight of the polymer so obtained were found to be increased with the increasing concentration of CTAB. Hussain and Gupta [13] have observed that the presence of an anionic surfactant enhances the rate of polymerization of acrylamide initiated by $KMnO_4$-oxalic acid.

EXPERIMENTAL

Materials

Acrylamide (Merck) was recrystallized twice from methanol and dried *in vacuo*. Cyclohexanone (Fluka) was distilled under reduced pressure. Sodium dodecyl sulphate and cetyltrimethylammonium bromide (Sisco Chem) were purified by a standard method. Ammonium meta vanadate (Fluka), sulphuric acid (E. Merck) and sodium bisulphate (BDH) were of analar grade and used as such.

Method

The experimental set up and kinetic procedure are similar to that of our earlier work [14-21].

Molecular Weight Determination

For determination of molecular weight, the polyacrylamide was precipitated from methanol. The flow of a very dilute aqueous solution of polyacrylamide and that of water were measured by a Ubbelohde suspended-level viscometer at 30°C. The intrinsic viscosity, [η], for the solution was computed with the help of Huggin's and Kramer's relationship [22] and viscosity average molecular weights of the polymers, M_V, were calculated using the following expression suggested by Suen *et al.* [23],

$$[\eta] = 6.8 \times 10^{-4} M_V^{+0.66}$$

RESULTS AND DISCUSSION

Effect of Surfactant

On increasing the concentration of SDS (0.0-0.03M) in the reaction mixture, the rate of polymerization, $R_{P(obs)}$ as well as the percentage of acrylamide conversion were found to be increased (Figure 1) The surfactant molecules in

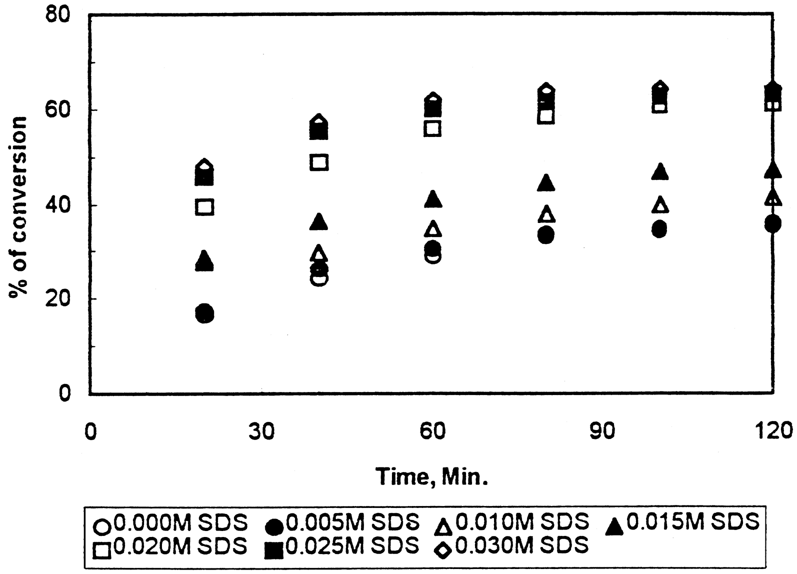

Figure 1. Percentage of monomer conversion with time.

aqueous medium, above their CMC, aggregate to form micelles. Due to the hydrophobic interaction of cyclohexanone for the micelles, it is solubilized in the micelles. And the concentration of V(V) at the micellar interface should be due to its electrostatic attraction with the negatively charged Stern layer of the SDS micelles [19, 20]. As the acrylamide is neutral and highly hydrophilic in nature, its solubilization in the micellar phase is small [12] . However, it is well known that acrylamide acts as co-surfactant [24], which causes it to be present at the micellar interface. For the aforesaid reasons, an initiation of the polymerization is facilitated leading to the rate enhancement (Table 1) and increase in conversion of monomer with its increasing concentration. But, in the presence of cationic surfactant, the rates as well as the percentage of acrylamide conversion decreased considerably as compared to that in absence of surfactant. Behari *et al.* [25, 26] had also observed a similar type of behavior for acrylamide polymerization in the presence of ionic surfactant (i.e., SDS and CTAB). SDS also increased the rate of acrylamide polymerization using peroxodiphosphate as initiator [27]. The non-ionic surfactant played no role on the rates. The rate of consumption of V(V), -R_V was found to increase with the SDS concentration and decrease with an increase of CTAB as observed in our earlier work [19, 20].

TABLE 1. Effect of Surfactant Concentrations on the Rates

[Surfactant]	$R_p \times 10^5$, mol.l^{-1} s^{-1}		$-R_V \times 10^6$, mol.l^{-1} s^{-1}	
mol.l^{-1}	SDS	CTAB	SDS	CTAB
0	32.4	-	2.05	-
5	35.0	18.5	2.25	1.13
10	46.8	7.5	3.13	0.48
15	64.1	6.9	4.47	0.15
20	80.3	6.8	5.81	0.14
25	91.5	7.0	6.92	0.13
30	93.7	6.6	7.08	0.13

[M] = 0.5 mol.l^{-1}, [V(V)] = 0.02 mol.l^{-1} [CH] = 0.108 mol.l^{-1},
[H$^+$] = 3.0 mol.l^{-1}, (μ = 4.0 mol.l^{-1}, Temp. = 40°C

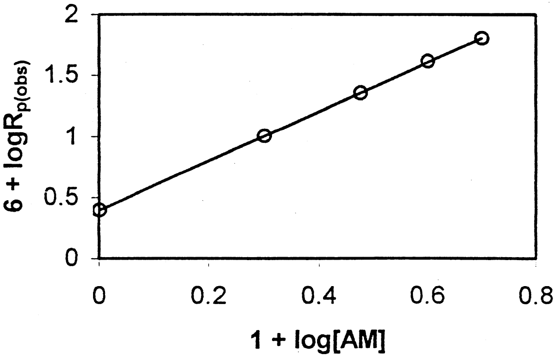

Figure 2. Bi-logarthimic plot of $R_{p(obs)}$ vs. [AM].

Effect of Acrylamide Concentration

On increasing the acrylamide concentration (0.1-0.5M) in the reaction mixture, in the presence of 0.015M SDS, the rate of polymerization, $R_{P(obs)}$ along with the % of acrylamide conversion was found to increase. The availability of the acrylamide at the micellar interfaceis an increase in its concentration, and leads to the rate enhancement. The $R_{P(obs)}$ was found to be square dependent on the acrylamide concentration, confirmed from the value of slope (i.e. 1.985) obtained from bilogarithmic plot of $R_{P(obs)}$ vs. AM (Figure 2). Such types of rate dependence on the monomer concentration in aqueous polymerization have been observed by Santappa *et al.* [26-28] and it is also concluded that the polymerization undergoes linear termination, not a mutual one. The acrylamide concentration plays no role on the V(V) consumption, $-R_V$. The independence of $-R_V$ on monomer concentration was also observed in other redox systems [29, 30].

Dependence of the Rate on V(V) Concentration

A reduction of the rate of polymerization was observed on increasing the [V(V)] (0.02 to 0.06) in the reaction mixture in the presence of 0.015M SDS. V(V) has the capability of influencing both the initiation and the termination processes. Under our experimental conditions, the termination is more effective than the initiation, which leads to a decline in the rate at a higher concentration of V(V) [19, 20]. Plotting of the reciprocal of $R_{P(obs)}$ vs. V(V) resulted in a straight line having an intercept on the co-ordinate (Figure 3). An enhancement of the

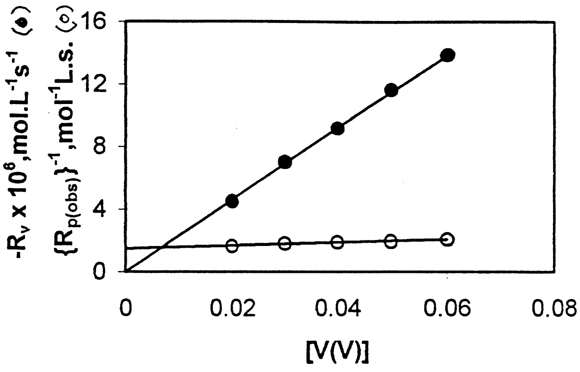

Figure 3. Dependence of reciprocal of $R_{p(obs)}$ and $-R_v$ on [V(V)].

rate of V(V) consumption was seen with increasing [V(V)], which is evident from the plot of $-R_V$ vs. [V(V)] (Figure 3).

Dependence of the Rate on the [CH]

On increasing the cyclohexanone concentration (0.09 to 0.25M), an enhancement of the rate of polymerization was marked, in the presence of 0.015M SDS in the reaction mixture, which was of the first order dependence. This can be explained on the basis of solubilization. At a higher concentration of cyclohexanone, its solubilization in the micellar part will be more, leading to a greater number of free radicals [14-21] which enhances the rate. In the absence of cyclohexanone, no polymerization took place and it rules out the initiation by V(V) alone. The bilogarithmic plot of $R_{P(obs)}$ vs. [CH] (Figure 4) produces a straight line having a slope of value of 0.987, which confirms unit dependence of $R_{P(obs)}$ on the concentration of cyclohexanone. Similarly, the rate of V(V) consumption, also linearly dependent on the concentration of cyclohexanone, as the slope obtained from the double logarithmic plot of $-R_V$ vs. [CH] (Figure 4) was found to be 1.02.

Effect of [H$^+$] on the Rates

The $R_{P(obs)}$ was found to be independent of [H$^+$] (2.6 to 3.2M) at a constant ionic strength ($\mu = 4.0$M), but on decreasing the ionic strength (4.0 to 3.2M), the rate of polymerization was seen to be decreased (Table 2). This can be explained by the following equilibrium,

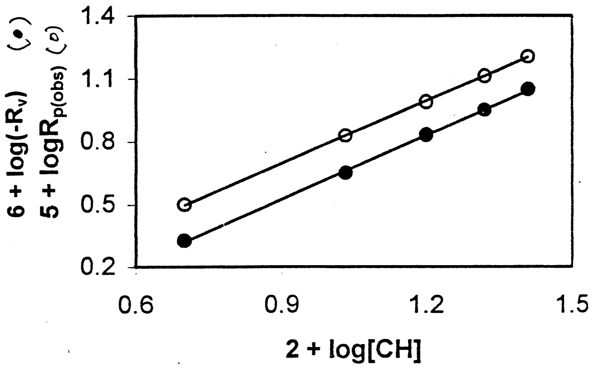

Figure 4. Bi-logarthimic plot of $R_{p(obs)}$ and -R_v vs. [CH].

$$VO_2^+ + HSO_4^- \rightleftharpoons VO_2SO_4^- + H^+$$

which indicates that $VO_2SO_4^-$ species is a more effective initiator than a terminator. The rate of V(V) consumption increased with increasing acid concentration at a constant ionic strength. On increasing the ionic strength, at a constant $[H^+]$, -R_V also increased. Perhaps it has a positive contribution towards the radical formation step.

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

$[H^=]$, $mol.l^{-1}$	μ, $mol.l^{-1}$	$R_P \times 10^5$, $mol.l^{-1}\ s^{-1}$	$-R_V \times 10^6$, $mol.l^{-1}\ s^{-1}$
2.6	4.0	6.48	4.03
2.8	4.0	6.46	4.21
3.0	4.0	6.41	4.47
3.2	4.0	6.48	4.59
3.0	3.2	5.91	3.93
3.0	3.4	6.06	4.04
3.0	3.6	6.15	4.19
3.0	3.8	6.32	4.32

[SDS] = 0.015 $mol.l^{-1}$, [M] = 0.5 $mol.l^{-1}$, [V(V)] = 0.02 $mol.l^{-1}$,
[CH] = 0.108 $mol.l^{-1}$, Temp. = 40°C

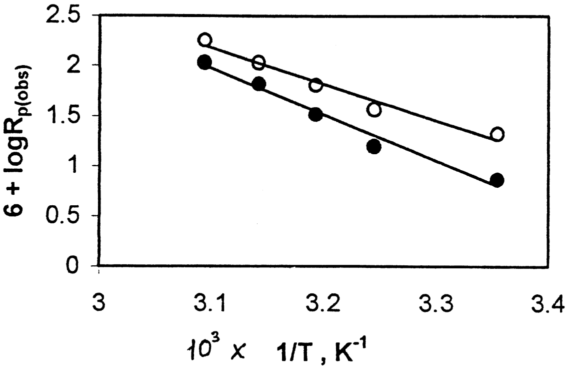

Figure 5. Arrhenius plot: log$R_{p(obs)}$ vs. 1/T.(O) 0.015M SDS, (●) 0.000M SDS.

Effect of Temperature

An increase in the temperature, from 30 to 50°C, ameliorate the polymerization rate, $R_{P(obs)}$, both in the absence and presence of 0.015M SDS (Figure 5). This may be attributed to the formation of an increase in the number of free radicals at the micellar interface due to a greater interaction of V(V) and cyclohexanone with the micellar interface and micellar core at higher temperature, leading to rate enhancement. A remarkable decrease in the E_a values was found in the presence 0.015M SDS (19.39 k cal/mol) as compared to the absence of surfactant (26.58 k cal/mol). This supports the positive catalytic role of the SDS micelle in these polymerization processes [14-21].

Reaction Mechanism and Kinetic Scheme

Taking into account all the above facts, it is assumed that the polymerization of vinyl monomers occurs in the micellar part in the presence of the anionic surfactant (SDS) above its CMC(0.015M). To explain the kinetic results, a free radical mechanistic scheme was proposed in the following manner:

$$nS \rightleftharpoons S_n$$

$$M + S_n \overset{K_1}{\rightleftharpoons} MS_n$$

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

$$VO_2 + H_3O^+ \overset{K_3}{\rightleftharpoons} [V(OH)_3]^{2+}$$

$$[V(OH)_3]^{2+} + HSO_4 \xrightleftharpoons{K_4} [V(OH)_3HSO_4]^{+}$$

Formation of free radical:

$$[V(OH)_3]^{2+} + CHS_n \xrightleftharpoons{K'} \text{Complex-1} \xrightarrow{K^m_{a1}} \overset{\circ}{R} + V(IV)$$

$$[V(OH)_3HSO_4]^{+} + CHS_n \xrightleftharpoons{K''} \text{Complex-2} \xrightarrow{K^m_{a2}} \overset{\circ}{R} + V(IV)$$

Initiation by primary radical:

$$\overset{\circ}{R} + MS_n \xrightarrow{K^m_i} \overset{\circ}{R}MS_n$$

Initiation by V(V):

$$V(V) + MS_n \xrightarrow{K^{m'}_i} \overset{\circ}{M}S_n + V(IV)$$

Propagation:

$$MS_n + \overset{\circ}{R}MS_n \xrightarrow{K^m_p} \overset{\circ}{R}M_2S_n$$

$$MS_n + \overset{\bullet}{R}M_2S_n \xrightarrow{K^m_p} \overset{\circ}{R}M_3S_n$$

$$MS_n + \overset{\circ}{R}M_{(x-1)}S_n \xrightarrow{K^m_p} \overset{\circ}{R}M_xS_n$$

Termination by V(V) (linear):

$$[V(OH)_3]^{2+} + \overset{\circ}{R}M_xS \xrightarrow{K^m_t} \text{Polymer}$$

Termination by combination(mutual):

$$\overset{\circ}{R}M_xS_n + \overset{\circ}{R}M_yS_n \xrightarrow{K^{m'}_t} \text{Polymer}$$

Reaction of Primary Radical with V(V):

$$R + V(V) \xrightarrow{K^m_0} \text{Oxidation Product}$$

Scheme 1.

Where M = Monomer (i.e., AN & AM), R = Primary radical, S = Surfactant (i.e., SDS), and

Sn = 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_p^m, and V(V) consumption, $-R_v^m$, can be derived as follows:

For linear termination,

$$R^m_P = (k^m_p.[MS_n]^2/k^m_t)\{k'[CHS_n]/ ([MS_n] + (k^m_o/k^m_i)[V(V)]) + k^{m'}_i\} \qquad (1)$$

$$-R^m_v = 2[V(V)]\ \ k'[CH_n] + k^{m'}_i\ [MS_n]\} \qquad (2)$$

For mutual termination:

$$R^m_P = (k^m_p.[MS_n]^{1.5}[V(V)]^{0.5}/k^{m'\,0.5}_t)\{k'[CHS_n]/([MS_n] + (k^m_o/k^m_i)[V(V)]) + k^{m'}_i\}^{0.5} \qquad (3)$$

$$-R^m_v = [V(V)]\ \{k'[CHS_n] + k^{m'}_i\ [MS_n]\} \qquad (4)$$

Ruling out the mutual termination (due to the presence of V(V) in the polymer) as also confirmed from square dependence of $R_{P(obs)}$ on monomer concentration, and initiation by V(V) (due to the non-formation of the polymer in absence of organic substrate, i.e. cyclohexanone), the rate can be written as,

$$R^m_p = (k^m_p.[MS_n]^2/k^m_t)\{k'[CHS_n]/ ([MS_n] + (k^m_o/k^m_i)[V(V)])\} \qquad (5)$$

$$= (k^m_p.K_1[M]^2[S_n]^2/k^m_t)\{k'K_2[CH][S_n]/ (K_1[M][S_n] + (k^m_o/k^m_i)[V(V)]\ )\} \qquad (6)$$

$$-R^m_v = 2\ k'[V(V)]\ [CHS_n] \qquad (7)$$

$$= 2\ K_2k'[V(V)]\ [CH][S_n] \qquad (8)$$

where, $k' = k_3K'.k^m_{a1} + K_3.K_4.K''.k^m_{a2}[HSO_4^-]$ (9)

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., $R_{P(obs)} = R^b_P + R^m_P$. But at a higher concentration of SDS, beyond its CMC, $R_{P(obs)}$ can be assumed to be equal to R^m_P, since most of the polymerization took place in the micellar phase. Hence, on rearranging, Equation 6 can be expressed as:

$$1/R_{P(obs)} = k^m_t / \{k^m_p k' K_1 K_2 [CH][M][S_n]^2\} + k^m_t (k^m_o / k^m_i)[V(V)] / \{k^m_p k' K_1 K_2 [CH][M]^2 [S_n]^3\} \quad (10)$$

Constant Parameter

The constant k' (in the presence of acrylamide) was computed from the plots of $-R_{V(obs)}$ vs. [CH] and [V(V)] (Figure not given), to be 1.03×10^{-4} and 0.99×10^{-4}, respectively, on substituting the value of $K_2(9.87 \times 10^4 \text{ mol}^{-1}\text{L})$[21] and S_n, that was obtained from the relation $S_n = (C_D - CMC)/N$, where the aggregation number (N) was taken to be 62 [33]. From the plots of reciprocal $R_{p(obs)}$ Vs... [V(V)], using the following relationship on modification of Equation 10,

$$k^m_o/k^m_i = (\text{slope/ intercept}) \times K_1[M][S_n] \quad (11)$$

$$k^m_p/k^m_t = 1/(\text{intercept}) \times k'.K_1.K_2.[M][CH][S_n]^2 \quad (12)$$

the value of k^m_o/k^m_I and k^m_p/k^m_t were found to be 1.31 and 5.13, respectively.

Molecular Weight

Increasing the concentration of SDS (0-0.3M) in the reaction mixture, the viscosity average molecular weight, M_V, was found to be increased (Table 3). Such types of behavior were also marked by other workers [12, 16-21, 34] . This may be due to a suitable environment, which is created by SDS micelles, for lengthening the chain of the polymer.

Cosolvent Effect

The cosolvent plays a major role in micellisation and affects:

(i) The CMC of the surfactant [35] .
(ii) Shape and size of the micelle [36].
(iii) The aggregation number (i.e., surface charge density) [37].

TABLE 3. Effect of Surfactant Concentration on the Molecular Weight

[Surf.]x10^{a}	[η], g^{-1}l	M$_{v}$ x 10^{-4}
00	3.34	5.98
05	3.43	6.11
10	4.81	6.68
15	7.13	7.31
20	8.88	9.15
25	10.13	10.26
30	11.12	11.06

[M] = 0.5 mol.l^{-1}, [V(V)] = 0.02 mol.l^{-1}, [CH] = 0.108 mol.l^{-1},
[H^{+}] = 3.0 mol.l^{-1}, (μ = 4.0 mol.l^{-1}, Temp. = 40°C

Thus, the presence of co-solvent can change the rate of polymerization. The retardation constant(l) of the different organic co-solvents have been calculated (Table 4) using the intercept method suggested by Bajpai *et al.* [38, 39] . The relation between [monomer] and retardation constant (I) is as follows,

$$[M] = l[Z_o]/\{(x-x')/x'\} - l.K.t/\{(x-x')/x'\} \qquad (13)$$

TABLE 4. Effect of 5% (V/V) Cosolvent on R^{P} and Retardation Constant(1)

Cosolvent	R$_{P}$ x 10^{5} , mol.l^{-1} s^{-1}	Retardation Constant(I)
Control	6.41	-
Benzene	5.13	0.1878
Methanol	5.96	0.0313
Ethanol	5.81	0.0439
Acetone	6.66	- 0.0979
Hexane	4.91	0.4081
DMF	5.59	0.1616

[SDS] = 0.015 mol.l^{-1}, [M] = 0.5 mol.l^{-1}, [V(V)] 0.02 mol.l^{-1}, [CH] = 0.108 mol.l^{-1},
[H^{+}] = 3.0 mol.l^{-1}, (μ = 4.0 mol.l^{-1}, Temp. = 40°C

where l is the retardation constant, [M] is the monomer concentration at a particular time, t, x' is the rate of polymerization under retarded conditions, x is the rate of polymerization under unretarded conditions, K is a constant and $[Z_0]$ is the initial retardor concentration .

It has been observed in this study that the addition of 5% (V/V) organic solvent (except acetone) has inhibited the rate of polymerization. It may be due to changes in CMC of the surfactant by addition of organic cosolvent, which decreases the solubilization of monomer and organic substrate. The formation of sluggish radical with the organic additive may not be equally effective for initiation of polymerization. The peculiar behavior of acetone may be due to its role as an organic substrate, since acetone itself is oxidized by V(V) [40] as:

$$\mathrm{V(V)} + \mathrm{CH_3\ COCH_3} + 3\mathrm{H_2O} \longrightarrow \mathrm{CH_3COOH} + \mathrm{V(IV)} + 6\mathrm{H^+}$$

The free radical intermediate formed in this oxidation may also initiate polymerization [41], causing a rate enhancement.

CONCLUSION

The enhancements of polymerization rate and increase in average molecular weight of polymer are due to the favorable electrostatic and hydrophobic interaction among anionic micelles, oxidant, and monomer (acrylamide).

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