Polymerization of Methyl Acrylate Initiated by V(V)-Cyclohexanone Redox System in Micellar Phase

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ABSTRACT: The kinetics of methyl acrylate (MA) polymerization initiated by a V(V)-Cyclohexanone redox system, in the presence of surfactant, over a temperature range of 30–50°C in acidic medium are analyzed. The anionic surfactant (SDS) enhances the rate of polymerization (R_p) as well as the rate of V(V) consumption ($-R_v$). The cationic surfactant, cetyl trimethylammonium bromide (CTAB), decreases both the rates. The effect of variation of the concentration of surfactant, monomer, substrate, and acid have been examined. A suitable free radical mechanistic scheme has been proposed for the above process. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2081–2088, 1997

Key words: kinetics; methyl acrylate; micellar; polymerization; critical micelle concentration

INTRODUCTION

The important role of surfactant on the polymerization process has been studied since the early 1940s.[1–7] Many workers have used surfactant to study the vinyl polymerization in different forms, such as emulsions,[8–12] microemulsions,[13–23] micelles,[24–34] inverse micelle,[35–38] and adsolubilization.[39] Lot of work has been done on the kinetic studies of vinyl polymerization using V(V)–organic substrates as redox systems.[40–44] The present piece of work deals mainly with polymerization of methyl acrylate (MA) initiated by a V(V)-cyclohexanone (CH) redox system in the presence of sodium dodecyl sulphate (SDS), an anionic surfactant.

EXPERIMENTAL

Materials

Methyl acrylate (Koch Light Lab., London) and cyclohexanone (Fluka, Switzerland) were dis-

tilled in an atmosphere of nitrogen under reduced pressure, respectively, before use. Sodium dodecyl sulphate and cetyltrimethylammonium bromide (Merck, India) were purified by standard methods. Ammonium meta vanadate (Fluka, Switzerland), sulphuric acid, and sodium bisulphite were of reagent grade and used as such.

Method

The experimental setup and kinetic procedure are similar to that of our earlier work published elsewhere.[25–30]

Test for the Presence of V(V) in the Polymer

A little of polymer was dissolved in the concentrated of HNO_3. An equal volume of amyl alcohol was added to it, followed by 1 mL of H_2O_2. A brownish red precipitate was obtained, indicating presence of V(V).

RESULT AND DISCUSSION

Effect of Surfactant

The observed rate of polymerization, $R_{p(\text{obs})}$, as well as the percentage of conversion of methyl acrylate, were found to increase on increasing the concentration of anionic surfactant (i.e., SDS) in the reaction mixture (Fig. 1). In aqueous solution, surfactant molecules, above their critical micelle concentration (CMC), get aggregated to form micelles,[45] leading to a biphase system, namely, bulkphase and micellar phase. Due to hydrophobic interaction, methyl acrylate and the organic substrate (cyclohexanone) are solubilized in micelles. From the electronic spectral study, the solubility of methyl acrylate was found to be 4.86 and 16.23% in the absence and the presence, respectively, of $0.015M$ SDS. And for electrostate attraction, the [V(V)] will increase at the Stren layer of the anionic micelles. These two types of interaction facilitate the free radical formation and are responsible for increasing $R_{p(\text{obs})}$ as well as the percentage of conversion and the decrease of $-R_v$ (Table I); but in presence of the cationic surfactant (CTAB), the $R_{p(\text{obs})}$ decreased considerably on increasing its concentration up to $0.20M$ and then attained a constant value. This may be attributed to the electrostatic repulsion between V(V) and cationic CTAB micelles. As a result, the approach of V(V) towards the micellar solubilized cyclohexanone hindered leads to a decrease in the formation of initiating free radicals. Hence, the
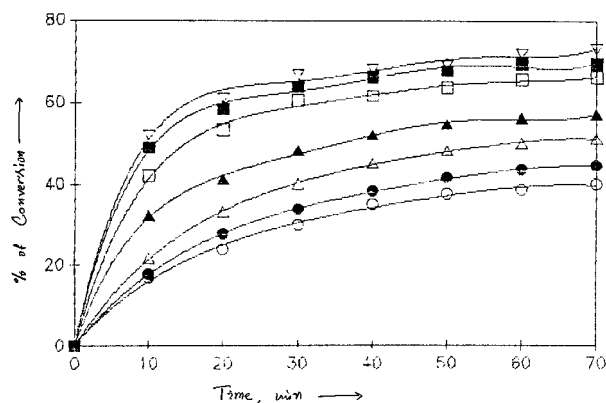
Figure 1 Percentage of conversion versus time: [MA] = $0.5052M$, [V(V)] = $0.02M$, [CH] = $0.108M$, [H$^+$] = $3.03M$, μ = $4.0M$, temperature = 40°C, (○) 0.000 SDS, (●) 0.005 SDS, (△) 0.010 SDS, (▲) 0.015 SDS, (□) 0.020 SDS, (■) 0.025 SDS, and (▽) 0.030 SDS.

Table I   Effect of Surfactant on $R_{p(\text{obs})}$ and $-R_{v(\text{obs})}$

Surfactant (mol L^{-1})	$R_{o(\text{obs})} \times 10^4$ (mol L^{-1} s^{-1})		$-R_{v(\text{obs})} \times 10^6$ (mol L^{-1} s^{-1})	
	SDS	CTAB	SDS	CTAB
0.000	1.42	1.42	1.58	1.58
0.005	1.49	0.92	1.75	1.01
0.010	1.82	0.40	2.25	0.58
0.015	2.71	0.12	4.12	0.12
0.020	3.54	0.09	6.08	0.09
0.025	4.12	0.08	6.83	0.09
0.030	4.38	0.08	7.08	0.09

[MA] = $0.5052M$, [CH] = $0.108M$, [V(V)] = $0.02M$, temperature = 40°, [H$^+$] = $3.03M$, μ = $4.0M$.

rate of polymerization and consumption of V(V) have decreased. The constant values of these rates observed at higher CTAB are perhaps due to small fraction of monomer and substrate present in the aqueous bulk phase (Table I). The nonionic surfactant, Triton-X-100, plays no role on these rates. A similar type of effect of surfactant on the rate is also observed by other workers.[46-49]

Effect of Variation of Methyl Acrylate

On increasing the methyl acrylate concentration (0.2 to 0.5M), the rate of polymerization was found to increase. The reason of rate enhancement is for the greater solubilization of methyl acrylate in the micelles, which is a better environment.[25-32] The plot of log $R_{p(\text{obs})}$ versus log [MA] shows a slope having value of 2.056, which indicates that $R_{p(\text{obs})}$ is the square dependence on the [MA] (Fig. 2), and it rules out mutual termination.[29,43] The concentration of methyl acrylate plays no role on the consumption of V(V), also reported by others.[40-43]

Effect of V(V)

A reduction of rate of polymerization was observed on increasing [V(V)] (0.02 to 0.06M). V(V) has the capability of influencing both the initiation and the termination process. Under our experimental condition, the termination is more effective than the initiation, which leads to a declination in the rate at a higher concentration of V(V).[25-30,40-43] Plotting the reciprocal of $R_{p(\text{obs})}$
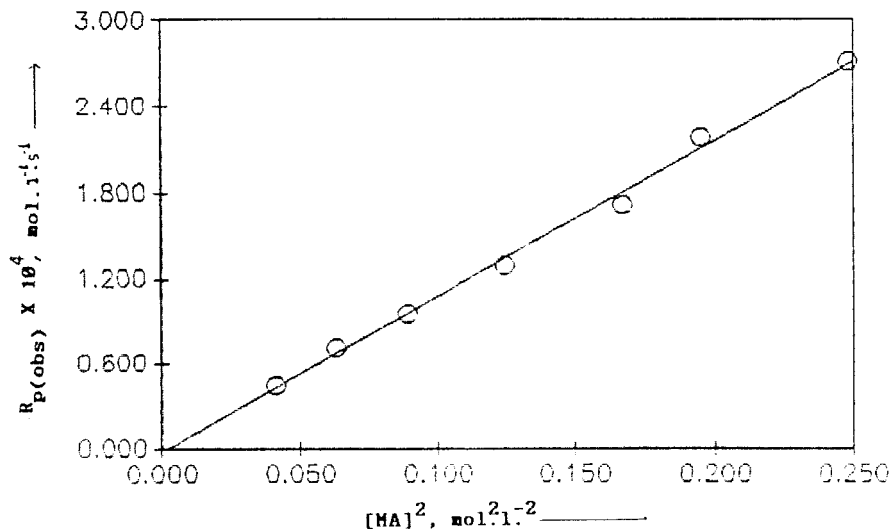
Figure 2 Rate dependence on monomer concentration: $[SDS] = 0.015M$, $[V(V)] = 0.02M$, $[CH] = 0.108M$, $[H^+] = 3.03M$, $\mu = 4.0M$, and temperature = 40°C.

against $[V(V)]$, a straight line has been produced, having an intercept on the ordinate (Fig. 3). An enhancement of rate of V(V) consumption was seen with increasing V(V) concentration, which is evident from the plot of $-R_v$ versus $[V(V)]$ (Fig. 3).
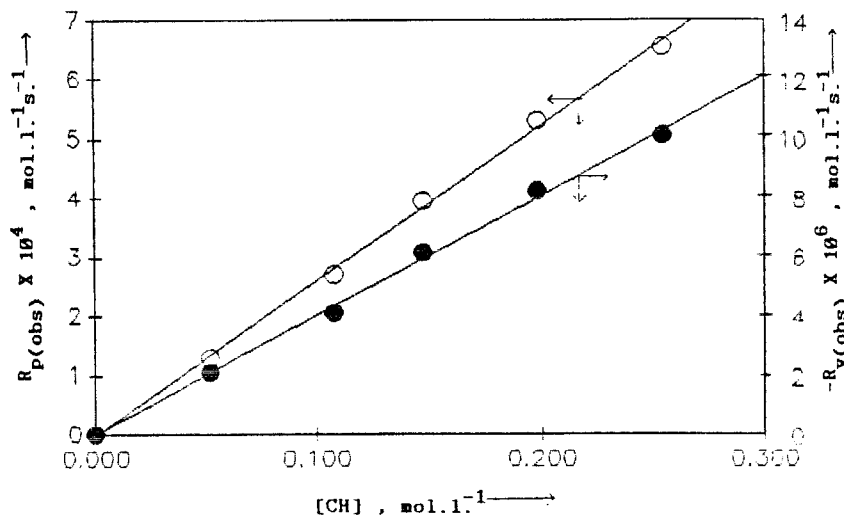
Effect of Cyclohexanone

An enhancement of observed rate of polymerization was found on increasing the [cyclohexanone]

(Fig. 4), which has a first-order dependence on it, since the slope of log–log plot of $R_{p(obs)}$ versus $[CH]$ was found to be unity. This can be attributed to the greater solubilization of cyclohexanone in the micellar phase, leading to the formation of more free radicals; as a result, enhancement of the rate was observed. A similar type of observation is also seen by us[25–30] and by other workers[31–32,40–43] previously. In the absence of cyclohexanone (i.e., $[CH] = 0.0M$), no polymerization took place. The rate of V(V) consumption also increases with the
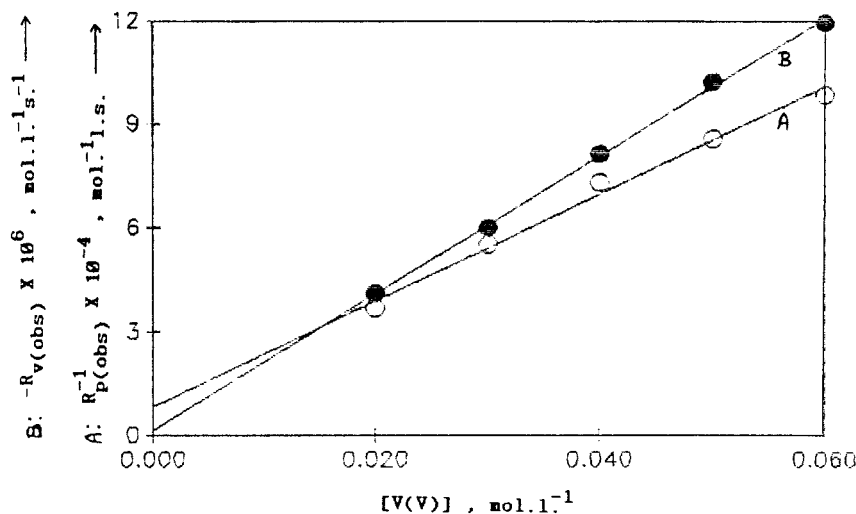
Figure 3 Dependence of the reciprocal of $R_{p(obs)}$ and $-R_{v(obs)}$ on $[V(V)]$: $[SDS] = 0.015M$, $[MA] = 0.5052M$, $[CH] = 0.108M$, $[H^+] = 3.03M$, $\mu = 4.0M$, and temperature = 40°C.

Figure 4 Effect of cyclohexanone on the rates: $[SDS] = 0.015M$, $[MA] = 0.5052M$, $[V(V)] = 0.02M$, $[H^+] = 3.03M$, $\mu = 4.0M$, and temperature = 40°C.

increasing concentration of cyclohexanoen (Fig. 4), with first-order dependence.

Effect of $[H^+]$

The rate of polymerization, $R_{p(obs)}$, was independent of $[H^+]$ (2.6 to 3.2M) at a constant ionic strength ($\mu = 4.0M$); but on increasing the ionic strength (3.4 to 4.0M), the rate of polymerization was found to increase (Table II). This may be attributed to the following equilibrium:

$$VO_2^+ + HSO_4^- \rightleftharpoons VO_2SO_4^- + H^+$$
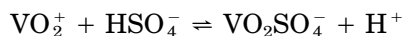
which indicates that the $VO_2SO_4^-$ species is more effective as an initiator than as a terminator.[40,41] The rate of V(V) disappearance increased with increasing acid concentration at a constant ionic

strength. $-R_v$ also increases with increasing ionic strength at constant $[H^+]$; perhaps it has positive contribution towards the radical formation step.

Effect of Temperature

An increase in temperature from 30 to 50°C ameliorates the polymerization rate, $R_{p(obs)}$, both in the absence and presence of 0.015M SDS. This may be due to formation of more free radicals in the micellar surface since the solubilization of methyl acrylate and cyclohexanone increases on increasing the temperature. The overall activation energy of the above polymerization process was calculated to be 26.95 and 22.54 kcal/mol in the absence and presence of 0.015M SDS, respectively (Fig. 5). The decrease in 4.41 kcal/mol in overall activation energy shows that SDS micelles

Table II   Effect of $[H^+]$ and μ on the Rates

$[H^+]$ (mol L^{-1})	μ (mol L^{-1})	$R_{p(obs)} \times 10^4$ (mol L^{-1} s^{-1})	$-R_{v(obs)} \times 10^6$ (mol L^{-1} s^{-1})
2.62	4.0	2.68	3.25
2.81	4.0	2.64	3.58
3.03	4.0	2.71	4.12
3.23	4.0	2.69	4.51
3.03	3.4	2.37	3.42
3.03	3.6	2.50	3.67
3.03	3.8	2.61	4.00

$[MA] = 0.5052M$, $[CH] = 0.108M$, $[V(V)] = 0.02M$, temperature = 40°C, $[SDS] = 0.015M$.
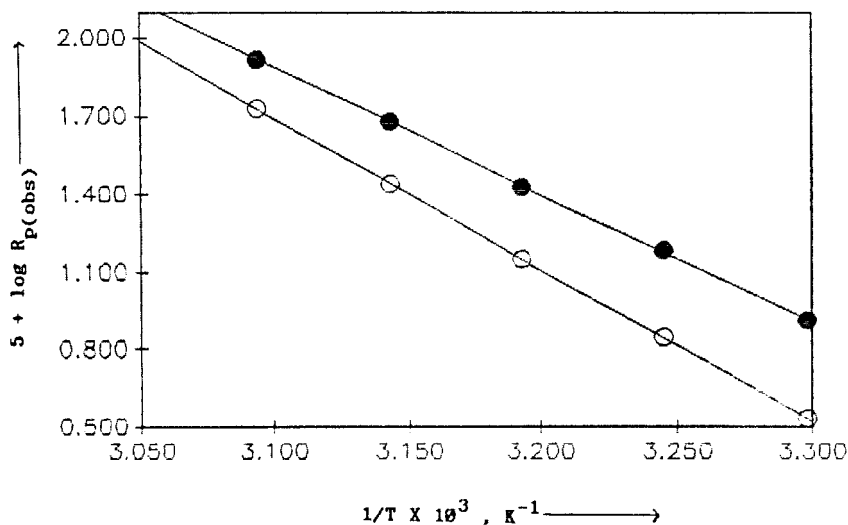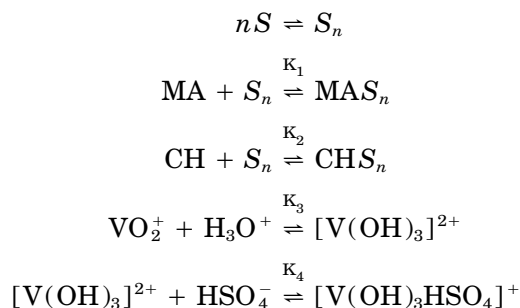
Figure 5 Arrhenius plot: $[SDS] = 0.015M$, $[MA] = 0.5052M$, $[CH] = 0.108M$, $[V(V)]$ $= 0.02M$, $[H^+] = 3.03M$, and $\mu = 4.0M$.
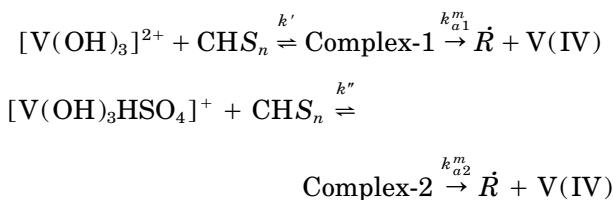
play a positive catalysis role. Such a type of observation was also reported earlier.[25-32,49]
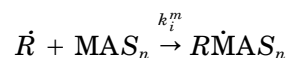
Reaction Mechanisms and Kinetic Scheme

Based on the aforementioned facts, it is assumed that the polymerization process occurs mostly in the micellar phase in presence of anionic surfactant (SDS), above its CMC. In order to explain the kinetic results, the following free radical mechanistic scheme has been proposed.
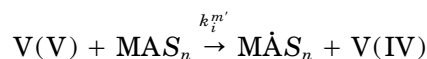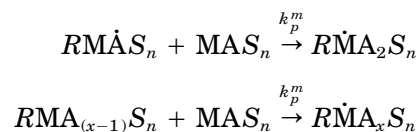
$$nS \rightleftharpoons S_n$$

$$MA + S_n \overset{K_1}{\rightleftharpoons} MAS_n$$

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

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

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

Formation of free radical:

$$[V(OH)_3]^{2+} + CHS_n \overset{k'}{\rightleftharpoons} Complex\text{-}1 \overset{k_{a1}^m}{\rightarrow} \dot{R} + V(IV)$$

$$[V(OH)_3HSO_4]^+ + CHS_n \overset{k''}{\rightleftharpoons}$$

$$Complex\text{-}2 \overset{k_{a2}^m}{\rightarrow} \dot{R} + V(IV)$$

Initiation by primary radical:

$$\dot{R} + MAS_n \overset{k_i^m}{\rightarrow} R\dot{M}AS_n$$

Initiation by V(V):

$$V(V) + MAS_n \overset{k_i^{m'}}{\rightarrow} M\dot{A}S_n + V(IV)$$

Propagation:

$$R\dot{M}AS_n + MAS_n \overset{k_p^m}{\rightarrow} R\dot{M}A_2S_n$$

$$RMA_{(x-1)}S_n + MAS_n \overset{k_p^m}{\rightarrow} R\dot{M}A_xS_n$$

Linear termination:

$$[V(OH)_3]^{2+} + RMA_xS_n \overset{k_t^m}{\rightarrow} polymer$$

Mutual termination:

$$R\dot{M}A_xS_n + RMA_yS_n \overset{k_t^{m'}}{\rightarrow} polymer$$
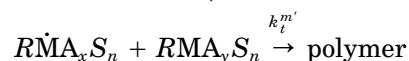
Reaction of primary radical with V(V):

$$[V(OH)_3]^{2+} + \dot{R} \overset{k_0^m}{\rightarrow} product$$
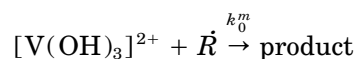
Making the usual steady-state assumption for the free radical formation, the rate expression for polymerization (R_p^m) and V(V) disappearance ($-R_v^m$) can be derived as follows. For mutual termination,

$$R_p^m = \frac{k_p^m[\text{MAS}_n]^{3/2}[\text{V(V)}]}{k_t^m}$$

$$\times \left(\frac{k'[CHS_n]}{[\text{MAS}_n] + (k_0^m/k_i^m)[\text{V(V)}]} + k_i^{m'}\right)^{1/2} \quad (1)$$

$$-R_v^m = [\text{V(V)}](k'[CHS_n] + k_i^{m'}[\text{MAS}_n]) \quad (2)$$

For linear termination,

$$R_p^m = \frac{k_p^m[\text{MAS}_n]^2}{k_t^m}$$

$$\times \left(\frac{k'[CHS_n]}{[\text{MAS}_n] + (k_0^m/k_i^m)[\text{V(V)}]} + k_i^{m'}\right) \quad (3)$$

$$-R_v^m = 2[\text{V(V)}](k'[CHS_n] + k_i^{m'}[\text{MAS}_n]) \quad (4)$$

In the absence of cyclohexanone, the polymerization did not take place at all; i.e., V(V) itself cannot initiate it in the absence of organic substrate. Hence the $k_i^{m'}$ term can be ignored; and, also, the mutual termination can be ruled out since V(V) was found to be present in the polymer obtained. Taking these facts into account, the rate equation can be expressed as

$$R_p^m = \frac{k_p^m[\text{MAS}_n]^2}{k_t^m}$$

$$\times \left(\frac{k'[CHS_n]}{[\text{MAS}_n] + (k_0^m/k_i^m)[\text{V(V)}]}\right) \quad (5)$$

$$-R_v^m = 2k'[\text{V(V)}][CHS_n] \quad (6)$$

or,

$$R_p^m = \frac{k_p^m K_1^2[\text{MA}]^2[S_n]^2}{k_t^m}$$

$$\times \left(\frac{k'K_2[\text{CH}][S_n]}{K_1[\text{MA}][S_n] + (k_0^m/k_i^m)[\text{V(V)}]}\right) \quad (7)$$

$$-R_p^m = 2k'K_2[\text{V(V)}][\text{CH}][S_n] \quad (8)$$

where,

$$k' = K_3K'K_{a1}^m + K_3K_4K''k_{a2}^m[\text{HSO}_4^-] \quad (9)$$

The observed rate of polymerization, $R_{p(\text{obs})}$, can be taken as the sum of the rate of polymerization in the micellar phase (R_p^m) and that in bulk aqueous phase (R_p); i.e., $R_{p(\text{obs})} = R_p^m + R_p$. But at a higher concentration, $R_{p(\text{obs})}$ will be almost equal to R_p^m, due to high solubilization of methyl acrylate and cyclohexanone in the micelles.

Constant Parameters

From the plot of $-R_v^m$ versus [CH] (Fig. 4) and $-R_v^m$ versus [V(V)] (Fig. 3), k' was calculated to be 1.72×10^{-4} and 1.693×10^{-4}, respectively, on substituting the value of $[S_n]$ that obtained from relation $[S_n] = (C_D - \text{CMC})/N$, where the aggregation number (N) has taken to be 62,[45] and the K_2 value was taken from our earlier work[27] ($K_2 = 9.87 \times 10^4 \text{ mol}^{-1}\text{ L}$).

On rearranging eq. (7),

$$\frac{1}{R_p^m} = \frac{k_t^m}{k_p^m k'K_1K_2[\text{CH}][\text{MA}][S_n]^2}$$

$$+ \frac{k_t^m(k_0^m/k_i^m)[\text{V(V)}]}{k_p^m k'K_1^2K_2[\text{CH}][\text{MA}]^2[S_n]^3} \quad (10)$$

The values of (k_0^m/k_t^m) can be calculated from the plot of $\frac{1}{R_{p(\text{obs})}}$ versus [V(V)] (Fig. 3) using the above relationship; i.e.,

$$(k_0^m/k_i^m) = (\text{slope/intercept})K_1[\text{AN}][S_n] \quad (11)$$

$$(k_p^m/k_t^m) = ((\text{intercept})Xk'$$
$$\times K_1K_2[\text{MA}][\text{CH}][S_n]^2)^{-1} \quad (12)$$

and were found to be 8.74 and 4.96, respectively.

Cosolvent Effect

The cosolvent plays a major role in micellization. It effects the CMC,[50] shape and size,[51] and aggregation number[52] of the micelles. Thus presence of cosolvent can change the rate of polymerization. The retardation constants of the different organic cosolvents have been calculated using the intercept method suggested by Bajpai et al.[53–54] and

Table III Retardation Constant for 5% Cosolvent

Cosolvent	$R_{p(obs)} \times 10^4$ (mol L^{-1} s^{-1})	Retardation Constant (I)
Control	2.71	—
Benzene	2.12	0.1933
Methanol	2.52	0.0193
Ethanol	2.45	0.04
Acetone	2.21	0.1574
Hexane	2.07	0.1774
DMF	2.35	0.1075

[MA] = 0.5052M, [SDS] = 0.015M, [V(V)] = 0.02M, [CH] = 0.108M, [H$^+$] = 3.03M, μ = 4.0M, temperature = 40°C.

are given in Table III. The relationship between the [monomer] and the retardor constant (I) is as follows,

$$[M] = \frac{I[Z_0]}{(x - x')/x'} - \frac{IK}{(x - x')/x'} t \quad (13)$$

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

It has been observed in this study that addition of 5% (V/V) organic solvent has inhibited the rate of polymerization. It may be due to the increase of CMC of the surfactant by the organic additions, which decreases the solubilization of the monomer and substrate. The formation of sluggish radical with the organic additive may not be equally effective for initiation of polymerization. The increasing order of retardation by different classes of solvent used is protic < dipolar aprotic < nonpolar.

CONCLUSION

The hydrophobic interaction of micelles for methyl acrylate and cyclohexanone and electrostatic attraction of negatively charged Stern layer for V(V) are responsible for the enhancement of rate of polymerization as well as for the percentage of monomer conversion in the presence of anionic surfactant, sodium dodecyl sulphate, above its CMC.

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