Effect of Organized Anionic Surfactant System on the Kinetics of V(V)-Organic Substrate-Initiated Polymerization of Acrylonitrile

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ABSTRACT: The kinetics of polymerization of acrylonitrile (AN) initiated by a V(V)-cyclohexanone redox system in the presence of a surfactant was studied over a temperature range of 30–50°C in acidic medium. The anionic surfactant sodium dodecyl sulfate (SDS) enhances the rate of polymerization (R_p) as well as rate of V(V) consumption ($-R_v$). The cationic surfactant, cetyltrimethylammonium bromide (CTAB), decreases both R_p and $-R_v$, while the nonionic surfactant, Triton-X-100, has no effect on the rate. The change of concentration of the surfactant, monomer, acid, and cosolvent on the rate of polymerization were examined. Both R_p and $-R_v$ are computed in the presence of different organic substrates, i.e., cyclohexanone, cyclopentanone, glycerol, and citric acid. The viscosity-average molecular weight ($\bar{M}_v$) of the polycrylonitrile, obtained at different [SDS], was determined using the Mark–Howink relationship. A suitable mechanistic scheme was proposed for the process. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1825–1833, 1997

INTRODUCTION

Reviews of the literature indicate that an appreciable amount of work has been carried out on the kinetics of aqueous vinyl polymerization by V(V) with an organic substrate by various workers.[1–4] The effect of a surfactant on such polymerization using a different redox system was studied in the micellar phase,[5–11] in microemulsion,[12–14] in emulsion,[15–18] and in phase-transfer catalysis.[19–21] The present piece of work deals mainly with the effect of micellar aggregates of sodium dodecyl sulfate (SDS) on the kinetics of polymerization of acrylonitrile initiated by the V(V)-cyclohexanone redox system.

EXPERIMENTAL

Materials

Acrylonitrile (Sisco Chem.) was washed with 5% NaOH and 3% o-phosphoric acid and, finally, with water followed by drying over $CaCl_2$. It was further purified by distillation in a nitrogen atmosphere. Sodium dodecyl sulfate (BDH) was recrystallized from absolute alcohol and methanol.[22] Cyclohexanone and cyclopentanone (Fluka-AG) were distilled under a reduced pressure. Ammonium *meta*-vanadate obtained from Fluka-AG was used as such. Glycerol, citric acid, and sulfuric acid were analar-grade chemicals and used without further purification. All the solutions for this study were prepared using triply distilled water free from oxygen. The nitrogen gas used for deaeration was made free from oxygen, by passing through several columns of Fieser's solution, a column of saturated solution of lead acetate, and,

finally, a bottle containing triply distilled water. The acidity of the stock V(V) solution was determined by titrating it with a standard NaOH solution using bromocresol green as an indicator.[23]

Method of Polymerization

The polymerization was carried out in a Pyrex tube (150 mL capacity) fitted with a standard joint stopper having inlet and outlet tubes for passing nitrogen gas and a microburette fitted vertically to the stopper. An aqueous solution of acrylonitrile, sodium dodecyl sulfate, cyclohexanone, sulfuric acid, and sodium bisulfate (which serves to maintain the ionic strength) were placed in the reaction tube. A bottle containing an aqueous solution of acrylonitrile of the same concentration as in the reaction tube was interposed between the nitrogen train and the reaction vessel, to avoid the loss of the monomer during deaeration. The nitrogen gas, free from oxygen, was bubbled through the reaction mixture for about 0.5 h and the stopcock was closed to maintain an inert atmosphere. It was thermostated to attain the desired temperature followed by the addition of the V(V) solution in $2M$ H_2SO_4 from the microburette and the total volume of the reaction mixture was adjusted to 20 mL. After a definite interval of time, the reaction was arrested by addition of a known volume of excess standard ferrous ammonium sulfate solution. The polyacrylonitrile was filtered off through a G_4 crucible and kept at 50–60°C until a constant weight was obtained. The filtrate obtained was analyzed for residual V(V) by vanadometry titration[24] using a Knop indicator and followed by the addition of 5% o-phosphoric acid for the violet end point. The R_p was computed from the initial slopes of the plot of the percentage conversion of the monomer vs. time and $-R_v$ from V(V) consumption vs. time curve in a similar manner.

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

A small amount of the polymer was dissolved in concentrated 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 the presence of V(V).

Determination of Molecular Weight of the Polymer

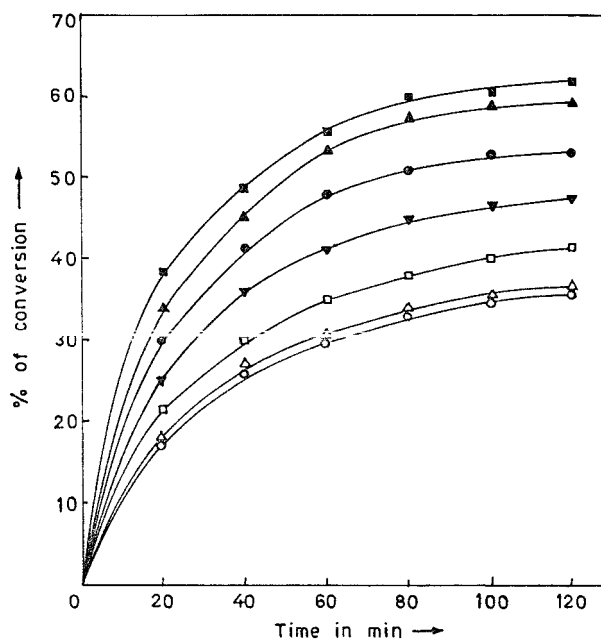The viscosity-average molecular weight, $\bar{M}_v$, of the polyacrylonitrile sample was determined

Figure 1   Percentage of conversion vs. time. [AN] = $0.498M$; [V(V)] = $0.05M$; [CH] = $0.108M$; [H$^+$] = $3.0M$; [μ] = $4.0M$; temp = 40°C. (○) $0.000M$ SDS; (△) $0.0015M$ SDS; (□) $0.010M$ SDS; (▼) $0.015M$ SDS; (●) $0.020M$ SDS; (▲) $0.025M$ SDS; (■) $0.030M$ SDS.

viscometrically. A solution of the polymer (0.1%) in DMF was placed in an Ubbelohde suspended level viscometer. The flow time of the solution as well as of the solvent were measured at 25°C. Intrinsic viscosities for the solutions were obtained using Huggin and Kramer's relationship[25] and the M_v were evaluated using the Mark–Houwink equation given by Stockmeyer and Cleveland[26]:

$$[\eta] = 2.43 \times 10^{-4}(\bar{M}_v)^{0.75}$$

Solubility Measurement

An equal volume of solvent ($0.015M$ SDS/pure water) and acrylonitrile were shaken for 24 h and then left undisturbed for 48 h. The concentration of acrylonitrile in the aqueous parts was determined spectrophotometrically.

RESULTS AND DISCUSSION

Effect of Surfactant

On increasing the concentration of sodium dodecyl sulfate ($0.00–0.03M$) in the reaction mixture, the observed rate of polymerization, $R_{p(obs)}$, as well as the percentage of conversion of acrylonitrile increased (Fig. 1). In the aqueous medium,

surfactant molecules, above its CMC, become aggregated to form micelles,[27] resulting in a biphase system, i.e., a bulk phase and a micellar phase. The monomer (acrylonitrile) and the organic substrate (cyclohexanone) are solubilized in the micelles, due to hydrophobic interaction. From the solubility measurement of acrylonitrile by the spectrophotometric method, it was observed that in the 0.015M SDS solution (beyond its CMC) and in pure water, the percentage of solubility were 32.82 and 7.95, respectively, at 33°C. In other words, in the SDS solution above its CMC, the solubility of acrylonitrile is about four times more in comparison to that in pure water. The concentration of V(V) increased at the Stern layer of anionic SDS micelles due to the electrostatic attraction between them, as a result of which the $R_{p\,(\mathrm{obs})}$ and the percentage of conversion of the monomer in the presence of the anionic surfactant (SDS) increased. But the cationic surfactant (CTAB), above its CMC, suppressed the rate as well as the percentage of conversion drastically as compared to that in the absence of the surfactant. It can be explained by the electrostatic repulsion between V(V) and the Stern layer of CTAB micelles. As a result, formation of a free radical at the interface becomes almost negligible, which is essential for polymerization. The nonionic surfactant, Triton-X-100, plays no role in the rate of polymerization. While studying the polymerization of acrylamide initiated by the permanganate–oxalic acid redox system, Hussain and Gupta[28] observed an enhancement of the rate in the presence of an anionic surfactant. Litt and Stannett[29] observed that in the presence of SDS up to a certain concentration $R_{p\,(\mathrm{obs})}$ increases considerably as compared to that in the absence of

Table I Effect of [Surfactant] on R_p and $-R_v$[a]

[Surfactant] (mol L^{-1})	$R_{p(\mathrm{obs})} \times 10^5$ (mol L^{-1} s^{-1})		$-R_{v(\mathrm{obs})} \times 10^6$ (mol L^{-1} s^{-1})	
	SDS	CTAB	SDS	CTAB
0.000	8.15	—	2.08	—
0.005	8.28	3.98	2.14	1.01
0.010	10.34	1.12	2.95	0.34
0.015	12.12	0.82	3.92	0.12
0.020	17.83	0.81	5.40	0.12
0.025	20.44	0.82	6.29	0.12
0.030	21.22	0.79	6.53	0.12

[a] [AN] = 0.498M; [V(V)] = 0.05M; [CH] = 0.108M; [H$^+$] = 3.0M; μ = 4.0M; temp = 40°C.
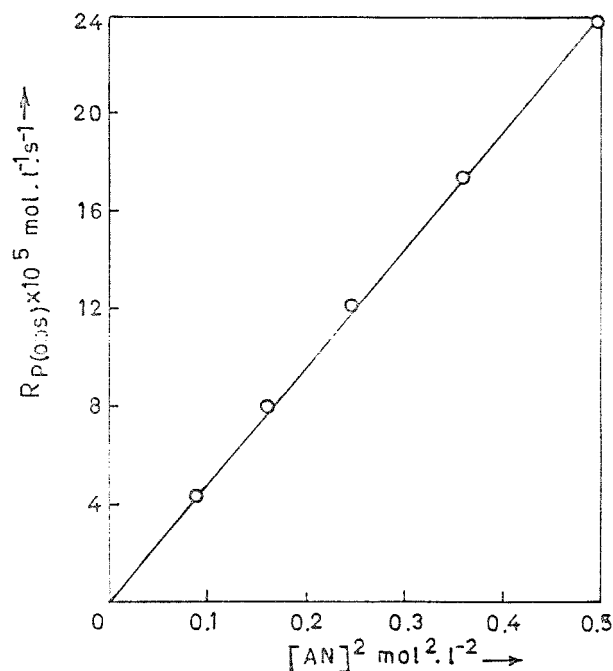

Figure 2 Rate dependence on monomer concentration. [SDS] = 0.015M; [V(V)] = 0.05M; [CH] = 0.108M; [H$^+$] = 3.0M; [μ] = 4.0M; temp = 40°C.

the surfactant. Then, on further increase of SDS, a constant rate was attained. A similar type of observation was also remarked on by other workers.[5,6,8] The rate of V(V) decomposition, $-R_v$, also increased with [SDS], while it decreased in the presence of CTAB (Table I).

Effect of Acrylonitrile Concentration

The rate of polymerization was found to increase with increase in the concentration of acrylonitrile (0.3–0.8M). A straight line was obtained, which passes through the origin, on plotting $R_{p\,(\mathrm{obs})}$ vs. [AN]^2 (Fig. 2). This type of rate enhancement may be due to the greater solubilization of acrylonitrile in the micellar pseudophase, which leads to a better environment.[5,6] The concentration of acrylonitrile had no effect on the rate of V(V) consumption. Some workers have also observed such a type of behavior.[2,3]

Effect of [V(V)]

A declination of the rate of polymerization was observed on increasing the concentration of V(V) (0.02–0.06M). V(V) can play a good role in both initiation as well as in the termination process. At our experimental condition, termination is more

effective than is initiation, which leads to a decrease in the rate at a higher concentration of V(V).[2,3] The plot of $[R_{p\,(\mathrm{obs})}]^{-1}$ vs. [V(V)] produces a straight line having an intercept on the ordinate (Fig. 3). The rate of V(V) consumption also increased on increasing the [V(V)]. The $-R_v$ was of first-order dependence on the [V(V)] (Fig. 4).

Effect of Organic Substrate

On increasing the cyclohexanone concentration ($0.05-0.25M$), an enhancement of the rate was observed, which was of first-order dependence (Table II). This can be explained by the greater solubilization of cyclohexanone in the micellar phase, leading to formation of a greater number of free radicals at the micellar surface, as a result of the increase in the rate. A similar rate enhancement was seen in the presence of cyclopentanone, glycerol, and citric acid. The rate of polymerization with respect to the organic substrate was found to be in the following order: cyclopentanone (CP) > cyclohexanone (CH) > glycerol (G) > citric acid (CA). The rate of V(V) consumption also increased with increase in the concentration of cyclohexanone (Fig. 5), with first-order dependence.

Effect of [H$^+$]

At a constant ionic strength ($\mu = 4.0M$), the $R_{p\,(\mathrm{obs})}$ was independent of [H$^+$] ($2.6-3.4M$), but
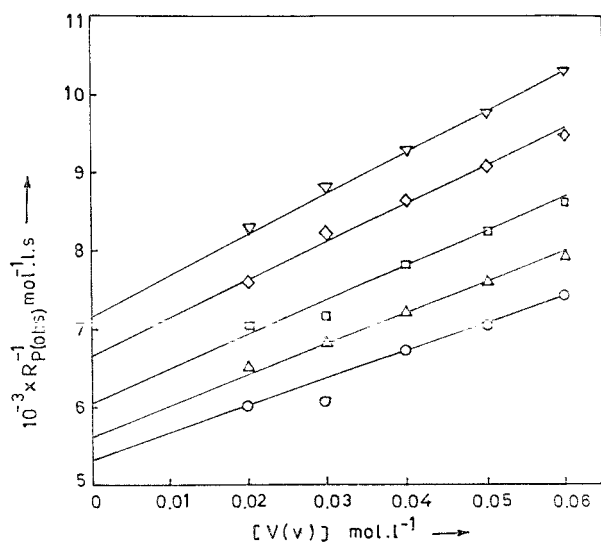

Figure 3 $R_{p\,(\mathrm{obs})}^{-1}$ vs. [V(V)]. [AN] = 0.498M; [SDS] = 0.015M; [CH] = 0.108M; [H$^+$] = 3.0M; [μ] = 4.0M; ($\triangledown$) 30°C; ($\diamondsuit$) 35°C; ($\square$) 40°C; ($\triangle$) 45°C; ($\bigcirc$) 50°C.
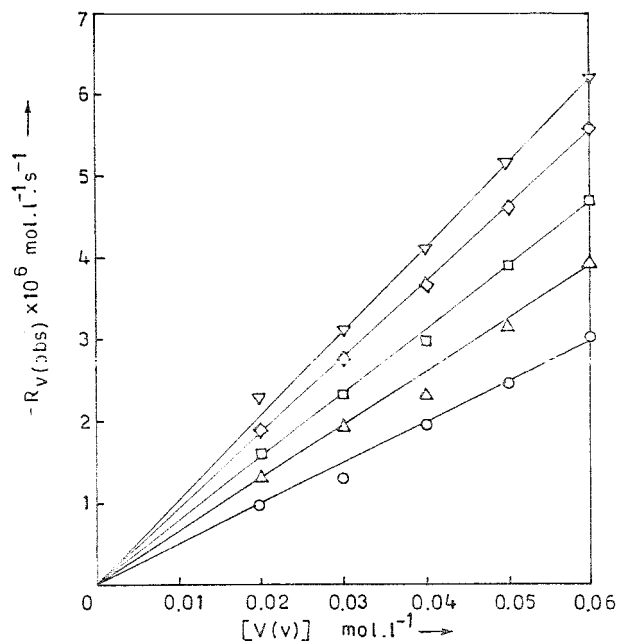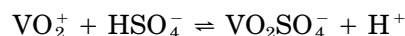

Figure 4 Effect of [V(V)] on $-R_v$. [AN] = 0.498M; [SDS] = 0.015M; [CH] = 0.108M; [H$^+$] = 3.0M; [μ] = 4.0M; ($\bigcirc$) 30°C; ($\triangle$) 35°C; ($\square$) 40°C; ($\diamondsuit$) 45°C; ($\triangledown$) 50°C.

on increasing the ionic strength ($3.2-4.0M$), the rate of polymerization was found to increase (Table III). This may be due to following equilibrium:

$$\mathrm{VO_2^+ + HSO_4^- \rightleftharpoons VO_2SO_4^- + H^+}$$

which indicates that the $\mathrm{VO_2SO_4^-}$ species were a more effective initiator than a terminator.[2] The rate of V(V) consumption increased with increasing acid concentration at a constant ionic strength. On increasing the ionic strength, at constant [H$^+$], $-R_v$ also increased. Perhaps it has a positive contribution toward a radical formation step.

Temperature Effect

An enhancement of the rate of polymerization, $R_{p\,(\mathrm{obs})}$, was observed on increasing the temperature for 30–50°C in the presence and absence of SDS. The solubilization of acrylonitrile and cyclohexanone increases on increasing the temperature, resulting in the formation of a greater number of free radicals, which causes rate acceleration. From the Arrhenius plot (Fig. 6), the overall activation energy of the polymerization process was computed to be 3.92 and 3.07 kcal/mol, in

Table II   Effect of Organic Substrate on R_p[a]

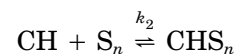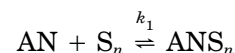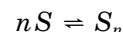| [Organic Substrate] (mol L^{-1})	$R_p \times 10^5$ (mol L^{-1} s^{-1})							
	CH					CP	G	CA
	30°C	35°C	40°C	45°C	50°C	40°C	40°C	40°C
0.05	5.08	5.61	6.14	6.83	7.49	7.12	3.28	3.01
0.10	10.04	11.01	12.12	13.12	14.32	13.93	6.42	6.23
0.15	15.24	16.43	18.23	19.94	22.38	21.42	9.19	8.89
0.20	20.12	22.12	24.37	24.79	30.33	28.09	12.33	12.13
0.25	25.03	27.69	26.89	33.21	36.25	32.47	14.98	14.77

[a] [AN] = 0.498M; [V(V)] = 0.05M; [SDS] = 0.015M; [H$^+$] = 3.0M; μ = 4.0M.

the absence and presence of 0.015M SDS. The decrease of 0.85 kcal/mol in the overall activation energy indicates that SDS micelles play a positive catalytic role. Similar observations have been reported by others.[5,30]
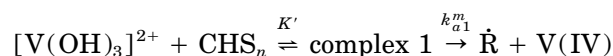
Reaction Mechanism and Kinetic Scheme

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

$$nS \rightleftharpoons S_n$$

$$AN + S_n \overset{k_1}{\rightleftharpoons} ANS_n$$

$$CH + S_n \overset{k_2}{\rightleftharpoons} CHS_n$$

$$VO_2^+ + H_3O^+ \overset{k_3}{\rightleftharpoons} [V(OH)_3]^{2+}$$

$$[V(OH)_3]^{2+} + HSO_4^- \overset{k_4}{\rightleftharpoons} [V(OH)_3HSO_4]^+$$
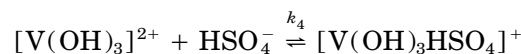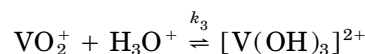
Formation of free radical:

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

Figure 5   Effect of organic substrate on $-R_v$. [AN] = 0.498M; [SDS] = 0.015M; [V(V)] = 0.05M; [H$^+$] = 3.0M; [μ] = 4.0M; ($\bigcirc$) 30°C; ($\triangle$) 35°C; ($\square$) 40°C; ($\diamondsuit$) 45°C; ($\triangledown$) 50°C.

Table III   Effect of [H$^+$] and Ionic Strength on R_p and $-R_v$[a]

[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})
2.62	4.0	12.14	3.29
2.81	4.0	12.23	3.63
3.02	4.0	12.12	3.92
3.22	4.0	12.16	4.33
3.02	3.2	8.22	3.21
3.02	3.4	9.15	3.42
3.02	3.6	9.90	3.63
3.02	3.8	10.61	3.75

[a] [AN] = 0.498M; [V(V)] = 0.05M; [CH] = 0.108M; [SDS] = 0.015M; temp = 40°C.
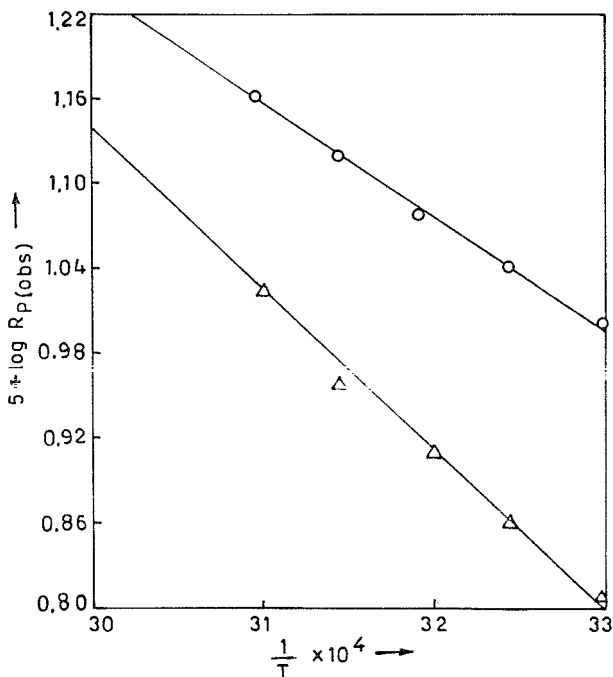
Figure 6 Arrhenius plot: ($\bigcirc$) $0.015M$ SDS; ($\triangle$) $0.000M$ SDS.

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

$$\text{complex } 2 \overset{k_{a2}^m}{\rightarrow} \dot{R} + V(IV)$$
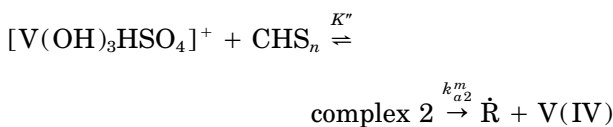
Initiation by primary radical:

$$\dot{R} + ANS_n \overset{k_i^m}{\rightarrow} RA\dot{N}S_n$$

Initiation by V(V):

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

Propagation:

$$ANS_n + RA\dot{N}S_n \overset{k_p^m}{\rightarrow} RA\dot{N}_2S_n$$
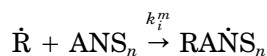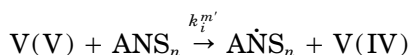
$$ANS_n + RA\dot{N}_{x-1}S_n \overset{k_p^m}{\rightarrow} RA\dot{N}_xS_n$$
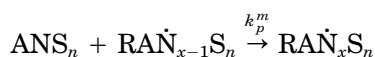
Termination by V(V) (linear):

$$[V(OH)_3]^{2+} + RA\dot{N}_xS_n \overset{k_t^m}{\rightarrow} \text{polymer}$$

Termination by combination (mutual):

$$RA\dot{N}_xS_n + RA\dot{N}_yS_n \overset{k_t^{m'}}{\rightarrow} \text{polymer}$$

Reaction of primary radical with V(V):

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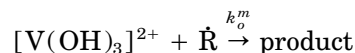
Making the usual steady-state assumption for free-radical formation, the rate expression for polymerization (R_p) and V(V) consumption ($-R_v$) can be derived as follows:

For linear termination:

$$R_p^m = \frac{k_p^m[ANS_n]^2}{k_t^m}$$
$$\times \left\{ \frac{k'[CHS_n]}{[ANS_n] + (k_o^m/k_i^m)[V(V)]} + k_i^{m'} \right\} \quad (1)$$

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

For mutual termination:

$$R_p^m = \frac{k_p^m[ANS_n]^{3/2}[V(V)]}{k_t^{m'}}$$
$$\times \left\{ \frac{k'[CHS_n]}{[ANS_n] + (k_o^m/k_i^m)[V(V)]} + k_i^{m'} \right\}^{1/2} \quad (3)$$

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

Ruling out mutual termination (due to the presence of V(V) in the polymer) and initiation by V(V) (due to the nonformation of the polymer in the absence of the organic substrate), the rate equation can be written as

$$R_p^m = \frac{k_p^m[ANS_n]^2}{k_t^m}$$
$$\times \left\{ \frac{k'[CHS_n]}{[ANS_n] + (k_o^m/k_i^m)[V(V)]} \right\} \quad (5)$$

$$= \frac{k_p^m}{k_t^m} K_1^2[AN]^2[S_n]^2$$

$$\times \left\{ \frac{k'K_2[CH][S_n]}{K_1[AN][S_n] + (k_o^m/k_i^m)[V(V)]} \right\} \quad (6)$$

$$-R_v^m = 2k'[V(V)][CHS_n] \quad (7)$$

$$= 2k'K_2[V(V)][CH][S_n] \quad (8)$$

where

Table IV   Constant k' and Its Thermodynamic Parameters[a]

Temp (°C)	$k' \times 10^4$	ΔE_1 (kcal mol^{-1})	ΔH_1 (kcal mol^{-1})	ΔG_1 (kcal mol^{-1})	$-\Delta S_1$ (kcal mol^{-1})	$K_2 \times 10^{-4}$ (mol^{-1} L)
30	2.76	5.47	4.87	22.68	58.73	9.11
35	3.28		4.86	22.96	58.74	9.36
40	3.89		4.85	23.34	59.00	9.87
45	4.31		4.84	23.55	58.80	10.13
50	5.01		4.83	23.84	58.83	10.67

[a] [AN] = 0.498M; [V(V)] = 0.05M; [SDS] = 0.015M; [H$^+$] = 3.0M; μ = 4.0M; temp = 40°C.

$$k' = K_3 K' k_{a1}^m + K_3 K_4 K'' k_{a2}^m [\text{HSO}_4^-] \quad (9)$$

The overall polymerization rate, $R_{p\,(\text{obs})}$, can be considered as the sum of the rate of polymerization in the bulk phase (R_p) and that in the micellar phase (R_p^m), i.e., $R_{p\,(\text{obs})} = R_p + R_p^m$, but at a higher concentration of SDS, beyond its CMC, $R_{p\,(\text{obs})}$ can be assumed equal to R_p^m for higher solubilization of the monomer in the micellar phase.

Evaluation of Constants and Their Thermodynamic Parameters

The constant k' (in the presence of acrylonitrile) was computed from the plot of $-R_v$ vs. [CH] (Fig. 5). K_2 was calculated from eq. (8) by substituting the value of k' and S_n, that obtained from the relation $S_n = (C_D - \text{CMC})/N$, where the aggregation number (N) was taken to be 62.[27] It was observed that the value of k' and K_2 were increased with increase in temperature. The ΔE_1 value computed from k' is 5.47 kcal mol^{-1}. Among other thermodynamic parameters (Table IV), only an appreciable change in the activation free energy had taken place gradually with increase in temperature. The negative values of the entropy changes indicate that the system is less mobile.

On rearranging, eq. (6) can be written as

$$\frac{1}{R_p^m} = \frac{k_t^m}{k_p^m k' K_1 K_2 [\text{CH}][\text{AN}][\text{S}_n]^2}$$

$$+ \frac{k_t^m (k_o^m/k_i^m)[\text{V(V)}]}{k_p^m k' K_1^2 K_2 [\text{AN}]^2 [\text{CH}][\text{S}_n]^3} \quad (10)$$

Using the above relation, the values of (k_o^m/k_i^m) and (k_p^m/k_t^m) were calculated from the plots of $1/R_{p\,(\text{obs})}$ vs. [V(V)]:

$$(k_o^m/k_i^m)$$
$$= (\text{slope/intercept}) \times K_1 [\text{AN}][\text{S}_n] \quad (11)$$

$$(k_p^m/k_t^m)$$
$$= (\text{intercept} \times k' K_1 K_2 [\text{AN}][\text{S}_n]^2 [\text{CH}])^{-1} \quad (12)$$

The thermodynamic quantities involved in various steps of this polymerization process are computed and furnished in Table V.

Molecular Weight

The viscosity-average molecular weight ($\bar{M}_v$) of polyacrylonitrile was found to increase on in-

Table V k_o^m/k_i^m and k_p^m/k_t^m and Their Thermodynamic Parameters[a]

Temp (°C)	k_o^m/k_i^m	ΔE_2	$-\Delta H_2$ (kcal/mol)	ΔG_2 (kcal/mol)	$-\Delta S_2$ (cal/mol K)	k_p^m/k_t^m	ΔE_3	$-\Delta H_3$ (kcal/mol)	ΔG_3 (kcal/mol)	$-\Delta S_3$ (cal/mol K)
30	2.45	1.64	2.24	17.24	64.12	1.35	4.57	5.17	17.56	74.97
35	2.34		2.25	17.72	64.81	1.16		5.18	17.96	75.09
40	2.25		2.26	17.82	64.16	1.03		5.19	18.33	75.11
45	2.17		2.27	18.16	64.18	0.97		5.20	18.67	75.03
50	2.06		2.28	18.49	64.27	0.85		5.21	19.06	75.10

[a] [AN] = 0.498M; [SDS] = 0.015M; [CH] = 0.108M; [H$^+$] = 3.0M; μ = 4.0M.

creasing the SDS concentration (Table VI). Such type of behavior was reported by Kim[8] and Badran et al.[31]

Cosolvent Effect

The presence of the cosolvent in the micellar solution affects the following:

(i) The CMC of the surfactant.[32]
(ii) Shape and size of the micelle.[33]
(iii) The aggregation number (i.e., surface charge density).[34]

Changes in these factors affect the micelles, which play an important role in the rate of polymerization. Depending upon the nature of the cosolvent, R_p may increase or decrease. Benzene, DMF, hexane, methanol, and ethanol decrease the rate while acetone enhances the rate. The peculiar behavior of acetone may be due to its role as an organic substrate, since acetone itself is oxidized by V(V)[35] as follows:

$$V(V) + CH_3COCH_3 + 3H_2O \rightarrow$$
$$CH_3COOH + V(IV) + 6H^+$$
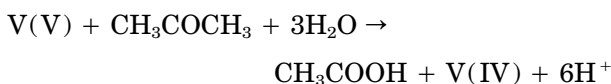
The free-radical intermediate formed in the oxidation may also initiate polymerization,[36] causing an enhancement of the rate.

The retardation constant of these organic solvents was computed (Table VII) using the "intercept method" suggested by Bajpai et al.[37]:

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

where I = the retarder constant, $[Z_0]$ = initial concentration of the retarder, x' = rate of change

Table VI   Effect of Surfactant on Intrinsic Viscosity and Molecular Weight

[SDS] (mol L^{-1})	[η] (g^{-1} L^{-1})	($M_v \times 10^4$)
0.000	0.60	3.34
0.005	0.61	3.41
0.010	0.79	4.81
0.015	1.06	7.13
0.020	1.25	8.88
0.025	1.38	10.13
0.030	1.48	11.12

Table VII   Retardation Constants in Presence of 5% Cosolvents

Cosolvent	$R_p \times 10^6$ (mol L^{-1} s^{-1})	Retardation Constant (I)
Control	12.12	—
Benzene	9.45	0.2165
Acetone	14.34	-0.1135
DMF	10.52	0.1165
Hexane	9.29	0.3992
Methanol	11.27	0.0305
Ethanol	10.94	0.0611

of the monomer concentration under the retarded condition, x = rate of change of the monomer concentration under the unretarded condition, K = a constant, t = the time, and $[M]$ = the monomer concentration.

CONCLUSION

Due to the hydrophobic interaction of micelles for the vinyl monomer and organic substrate and the electrostatic attraction of a negatively charged Stern layer for V(V), the rate of polymerization as well as the percentage of monomer conversion increased in the presence of an anionic surfactant (SDS) above its CMC. Similarly, the molecular weight ($\bar{M}_v$) of the polyacrylonitrile obtained in the presence of SDS is found to be higher than in the absence of SDS.

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