

Micellar Effect on the Kinetics of Ceric Ion-Initiated Polymerization of Acrylonitrile in the Presence of Organic Substrate

C. M. PATRA and B. C. SINGH*

P. G. Department of Chemistry, Utkal University, Bhubaneswar-751004, Orissa, India

SYNOPSIS

The micellar effect on the kinetics of ceric ion-initiated polymerization of acrylonitrile (AN) in the presence of *N*-acetylglycine has been studied in the temperature range 30–50°C. The neutral emulsifier (Triton X-100) has no effect on the R_p , whereas both anionic (NaLS) and cationic (NCTAB) emulsifiers accelerate the rate of polymerization appreciably. Comparison of the effect of different organic substrates on the rate of polymerization has been made. Various effects such as the concentration of metal ion, surfactant, monomer, sulfuric acid, organic solvents, and inorganic salts on R_p have also been investigated. The most remarkable feature of the investigation involves the enhancement of R_p in the presence of micelles. A suitable mechanism for the derivation of the rate expression for the above system is proposed along with the calculation of activation energy and prediction of optimum conditions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A considerable amount of work has been done on the kinetics of the polymerization of vinyl monomers using various redox systems and different monomers. Santappa et al.^{1–3} studied the vinyl polymerization using Ce(IV) as the initiator. However, the study of the micellar effect on polymerization of acrylonitrile (AN) is still insufficient and needs further investigation.

The rates of many chemical reactions are affected by incorporating the reactants into their micellar pseudophase.⁴ Jayakrishnan and Shah^{5,6} investigated the effect of surfactants on the emulsion and microemulsion polymerization of some vinyl monomers. A few years back, Chatterjee et al.⁷ studied the potassium persulfate-initiated emulsion polymerization of styrene. The effect of an emulsifier on the composition of a copolymer prepared from a monomer sparingly soluble in water with water-insoluble monomer was reported by Cepak et al.,⁸ Uchida and Nagao,^{9,10} and Antonova et al.¹¹ Barton

et al.^{4,12} showed that the anionic emulsifier (sodium dodecyl phenoxybenzene disulfonate) affects the relative molecular mass of polyacrylamide (water-soluble monomer), but that it showed no effect on the polymerization rate. According to Shukla and Mishra,¹³ the rate of polymerization of AN in water with KMnO_4 /ascorbic acid as the initiator in the presence of an anionic emulsifier is not affected below a critical micellar concentration (CMC) of the surfactant, but the rate is increased at a concentration higher than the CMC. The nonionic emulsifiers α -hydro-w-(-4-isooctyl phenoxy)poly(oxyethylene) and Triton X-100 did not affect the rate, whereas cation-active emulsifier *N*-cetyl trimethylammonium bromide (NCTAB) and cetylpyridinium bromide decreased the polymerization rate.¹³ A redox system as the initiator for AN polymerization in presence of the surfactant NCTAB was used by Baxendale et al.,¹⁴ and Lind et al.¹⁵ used potassium lauryl sulfate as an emulsifier with potassium persulfate as the initiator. There are many similar reports, including emulsion polymerization of isoprene using $\text{K}_2\text{S}_2\text{O}_8$, of Harkins¹⁶ and classic investigations of Smith and Ewart.^{17,18} The present article reports the influence of surfactant on Ce(IV)–*N*-acetylglycine-initiated polymerization of AN.

* To whom correspondence should be addressed.

EXPERIMENTAL

Acrylonitrile (AN) (BDH) was purified by washing with 5% NaOH and 3% orthophosphoric acid, followed by repeated washing with conductivity water and drying over fused CaCl_2 . Then, it was distilled in an atmosphere of nitrogen and finally stored in the refrigerator for use. Reagents like ceric ammonium sulfate, *N*-acetylglycine, ferrous ammonium sulfate, sulfuric acid, and glacial acetic acid are all of AnalaR grade and were used as such. *N*-cetyltrimethylammonium bromide (NCTAB) was purified according to the method of Dynstee and Grunwald.¹⁹ Conductivity water was prepared by redistilling distilled water over alkaline KMnO_4 in an all-glass Pyrex unit. The polymerization was studied under atmospheric pressure.

Requisite quantities of monomer, *N*-acetylglycine, surfactant, and sulfuric acid were mixed in the reaction vessel (vessel fitted with a $\text{B}_{24/29}$ socket, carrying a $\text{B}_{24/29}$ cone with inlet and outlet tubes) and thermostated at the desired temperature with an accuracy of $\pm 0.1^\circ\text{C}$. The required amount of ceric ammonium sulfate solution (in 1M H_2SO_4) was added and the time was noted. After the specified time interval, the polymerization was arrested by adding an excess of Mohr's salt solution. The polymer formed was filtered off, washed repeatedly with conductivity water, and dried to constant weight. The rate of polymerization, R_p , and percentage conversion were calculated by using the following formula:

$$\text{Rate of polymerization } R_p = \frac{100 \times W}{V \times t \times M}$$

where W is the weight of the polymer; V , the volume of reaction mixture in milliliters (20 mL here); t , the time in seconds; and M , the molecular mass of monomer (for AN, $M = 53.06$);

$$\% \text{ Conversion} = \frac{\text{weight of polymer}}{\text{weight of monomer}} \times 100$$

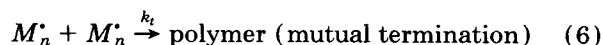
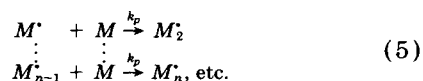
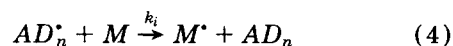
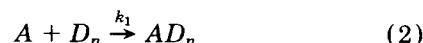
RESULTS AND DISCUSSION

Conversion vs. time curves for the polymerization of AN in the absence and presence of two emulsifiers, cationic (NCTAB) and anionic (NaLS), at the temperature range $30\text{--}50^\circ\text{C}$ using Ce(IV) as the initiator are shown in Figure 1(A) and (B), re-

spectively. The overall R_p and the percentage conversion were higher in the presence of micelles. The percentage yield was also higher in the cationic surfactant (NCTAB) than in the anionic counterpart. However, in the presence of NCTAB, a limiting conversion was attained within 60 min. The limiting conversion is attributed to the creation of a biphasic system, namely, bulk phase and micellar pseudophase of the surfactants beyond their CMC in aqueous medium, since they form aggregates that affect the R_p . Free radicals present in the system undergo more frequent collisions with micelles than with other single molecules. This fact is in close agreement with the findings of Konar et al.⁷ and Sinha et al.²⁰ But in case of NaLS, the % conversion keeps increasing without a maximum in the range of study. The difference in R_p in case of cationic and anionic micelles may be due to the difference in surface potential of the micelles above the CMC.

Reaction Mechanism and Kinetic Scheme

Based on these facts, it is proposed that the polymerization process occurs in the micellar phase in the presence of surfactants. Hence, to explain the kinetic results satisfactorily, a free-radical mechanism can be proposed in the present case:



where D is a detergent; D_n , a micelle; A , an organic substrate (*N*-acetylglycine [NAG]); and M , a monomer, AN.

Taking into account the above reaction scheme and making the usual assumption for the steady-state concentration of AD_n^* and M^* , the rate expression for R_p can be derived. Here, the radical reactivity is independent of radical size:

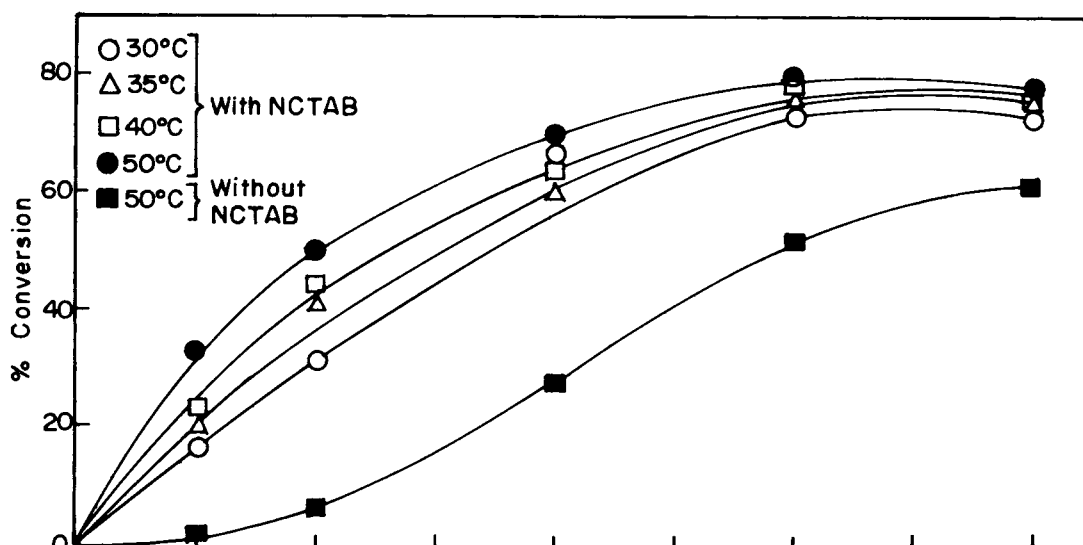


Fig.1A

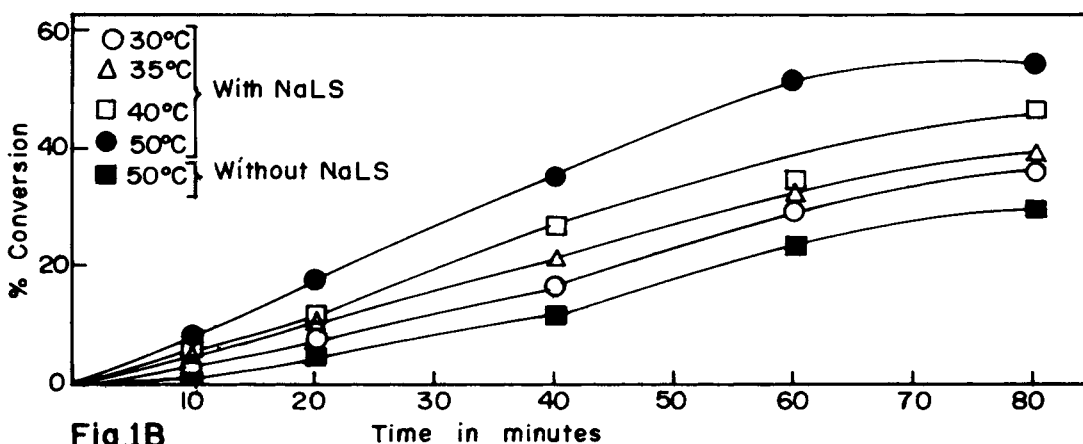


Fig.1B

Figure 1 (A) Time conversion curves: $[AN]$ 0.759 mol L⁻¹; $[Ce(IV)]$ 0.035 mol L⁻¹; $[NAG]$ 0.025 mol L⁻¹; $[NCTAB]$ 0.01 mol L⁻¹; $[H_2SO_4]$ 0.256 mol L⁻¹. (B) Time conversion curves: $[AN]$ 0.759 mol L⁻¹; $[Ce(IV)]$ 0.035 mol L⁻¹; $[NAG]$ 0.025 mol L⁻¹; $[NaLS]$ 0.01 mol L⁻¹; $[H_2SO_4]$ 0.256 mol L⁻¹.

$$\frac{d[AD_n^*]}{dt} = k_1 k_r [A][D_n][Ce(IV)] - k_i [M][AD_n^*] - k_0 [AD_n^*][Ce(IV)] = 0 \quad (8)$$

$$R_p = k_p [M^*][M] = k_p \left\{ \frac{k_1 k_i k_r [A][D_n][Ce(IV)][M]}{k_i k_i [M] + k_0 k_t [Ce(IV)]} \right\}^{1/2} \times [M] \quad (9)$$

or

$$R_p^2 = \frac{k_p^2 k_1 k_i k_r [A][D_n][Ce(IV)]}{k_i k_i [M] + k_0 k_t [Ce(IV)]} \times [M]^3 \quad (10)$$

or

$$\frac{1}{R_p^2} = \frac{k_0 k_t}{k_p^2 k_1 k_i k_r [A][D_n]} + \frac{k_i k_t [M]}{k_p^2 k_1 k_i k_r [A][D_n][Ce(IV)]} \times \frac{1}{[M]^3} \quad (11)$$

where $Ce(IV)$, R_p , k_1 , k_r , k_i , k_t , and k_0 are the ceric ion, rate of polymerization, and different rate constants, respectively. All our kinetic results are explained by the above rate expression.

The rate of polymerization has been studied within the concentration range 0.001 to 0.01 mL⁻¹ of an emulsifier at 30, 40, and 50°C and without an

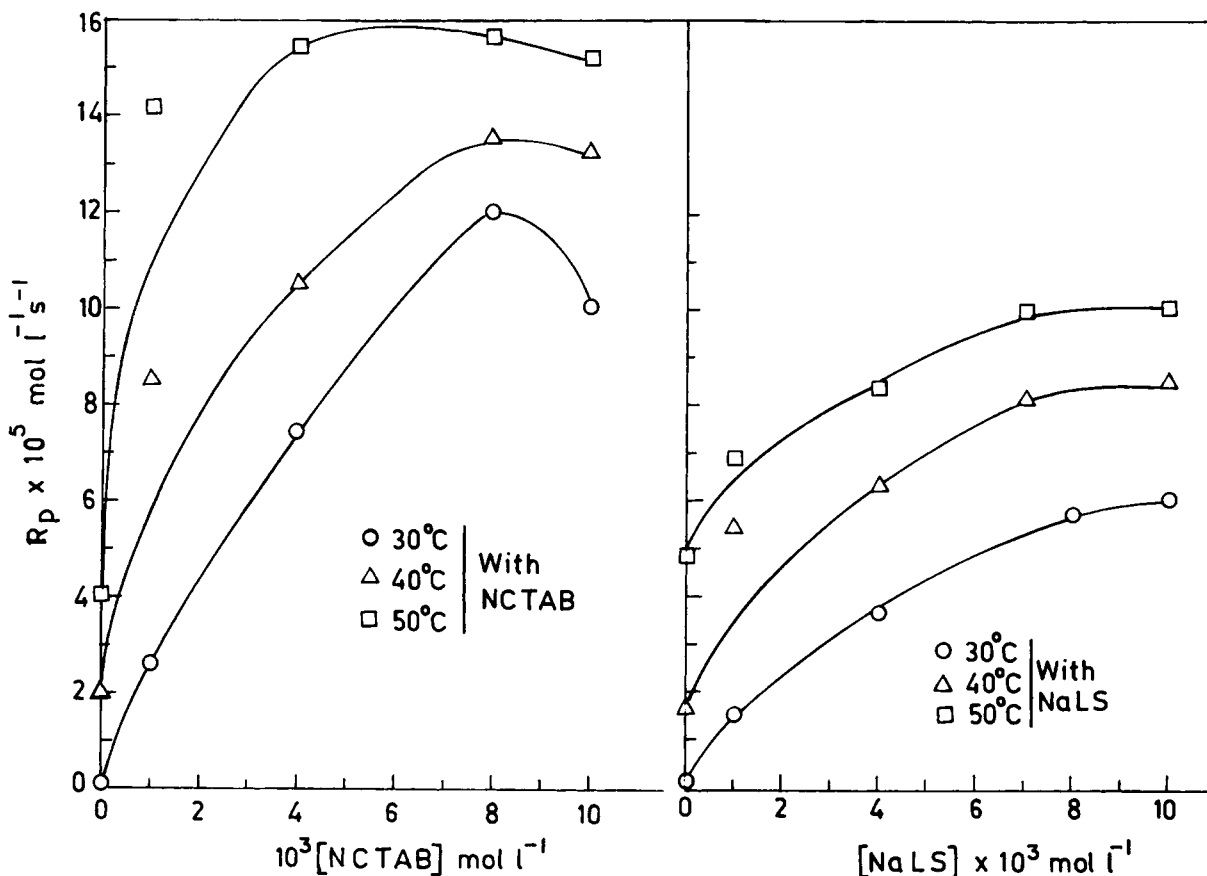


Figure 2 (A) R_p vs. [NCTAB] plots. [AN] 0.759 mol L^{-1} ; [Ce(IV)] 0.025 mol L^{-1} ; [NAG] 0.025 mol L^{-1} ; [H_2SO_4] 0.256 mol L^{-1} ; time 1 h. (B) R_p vs. [NaLS] plots. [AN] 0.759 mol L^{-1} ; [Ce(IV)] 0.025 mol L^{-1} ; [NAG] 0.025 mol L^{-1} ; [H_2SO_4] 0.256 mol L^{-1} ; time 1 h.

emulsifier at 50°C . The R_p keeps increasing up to 0.008 mL^{-1} in the case of NCTAB and then it decreases above that value, whereas it keeps increasing in the case of NaLS up to 0.01 mL^{-1} [Fig. 2(A) and 2(B)]. At a critical micellar concentration (CMC), the surfactant molecules aggregate to form micelles, thereby creating a biphasic system. This system affects the rate of polymerization. But with further increase in the concentration, the rate decreases in the case of NCTAB. As reported by Baxendale et al.,¹⁴ this may be due to the fast rate of mutual termination by the growing molecules initiated in the interior of soap micelles at higher emulsifier concentration.

The effect of NAG on R_p , studied at three different temperatures, 30, 40, and 50°C , is shown in Figure 3. The rate keeps increasing in the range 0.0025 – 0.01 mL^{-1} , and after this, it decreases. The increase in rate of polymerization is probably due to the greater solubilization of NAG molecules in the micellar pseudophase, due to hydrophobic interaction

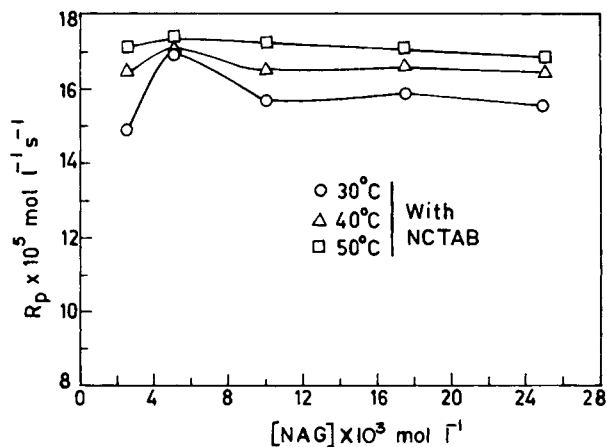


Figure 3 R_p vs. [NAG] plots. [AN] 0.759 mol L^{-1} ; [Ce(IV)] 0.04 mol L^{-1} ; [H_2SO_4] 0.512 mol L^{-1} ; [NCTAB] 0.008 mol L^{-1} ; time 1 h.

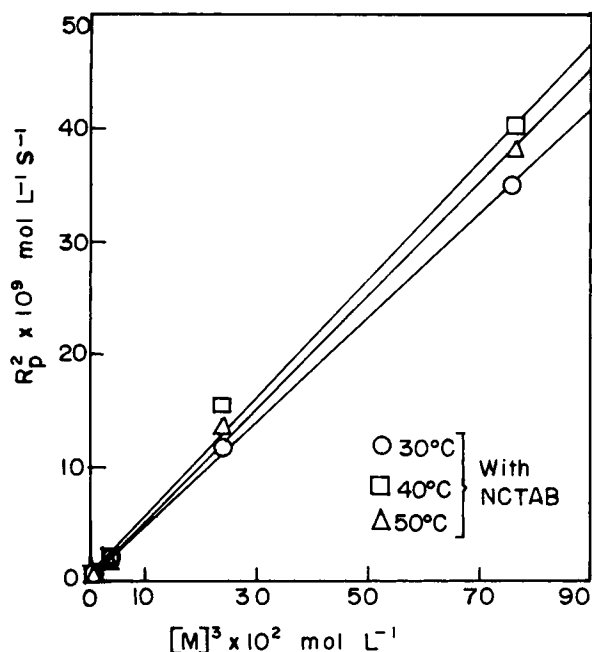


Figure 4 R_p^2 vs. $[M]^3$ plots. $[\text{Ce(IV)}]$ 0.025 mol L^{-1} ; $[\text{NAG}]$ 0.005 mol L^{-1} ; $[\text{H}_2\text{SO}_4]$ 0.512 mol L^{-1} ; $[\text{NCTAB}]$ 0.008 mol L^{-1} ; time 1 h.

producing a greater number of free radicals (AD_n^*). As the concentration of NAG goes beyond 0.01 mL^{-1} , the primary radical $[AD_n^*]$ termination probably becomes prevalent, which decreases the

rate. A similar observation was reported by Konar et al.⁷ and Sinha et al.^{20,21}

In the case of both emulsifiers, the R_p keeps increasing with increase in the concentration of the metal ion from 0.005 to 0.04 mL^{-1} and then it decreases. Similar observations have been reported by Panda et al.²¹ and Smith¹⁸ for variable initiator concentrations. This may be due to the formation of an increasing number of free radicals in the reaction mixture at low concentration. The plot of R_p^2 vs. $[M]^3$ (Fig. 4), a straight line passing through the origin, supports the view that termination by $[\text{Ce(IV)}]$ at its low value can be ruled out.²⁰ In Figure 5, $\frac{1}{R_p^2}$ vs. $1/[\text{Ce(IV)}]$, a straight line with an intercept, explains the rate expression, [eq. (11)] satisfactorily. The effect of sulfuric acid concentration on the rate of polymerization is depicted in Table I. The rate increases steadily with increase in the concentration of the acid. This may be due to the formation of more effective Ce(IV) species with increasing concentration of the acid.

It is observed that R_p as well as the % conversion increases steadily with monomer concentration. Monomer as well as NAG are dissolved in the micellar pseudophase by the process of solubilization and thus increases the thickness of the micelle.^{16,22} The higher rate of polymerization is attributed to the presence of a greater number of polymer-mono-

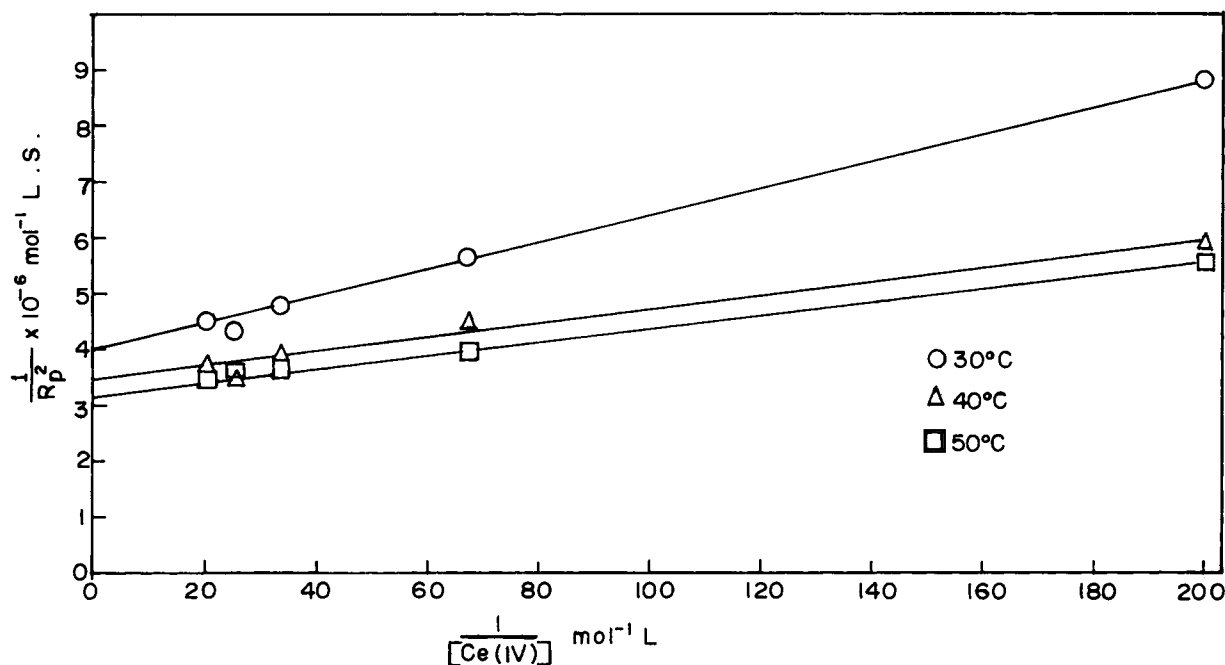


Figure 5 $[\text{AN}]$ 0.759 mol L^{-1} ; $[\text{NAG}]$ 0.025 mol L^{-1} ; $[\text{H}_2\text{SO}_4]$ 0.512 mol L^{-1} ; $[\text{NCTAB}]$ 0.008 mol L^{-1} ; time 1 h.

Table I Effect of Sulfuric Acid Concentration, $[\text{H}_2\text{SO}_4]$, on Rate: $[\text{AN}] 0.759 \text{ mol L}^{-1}$; $[\text{NAG}] 0.005 \text{ mol L}^{-1}$; $[\text{Ce(IV)}] 0.015 \text{ mol L}^{-1}$; $[\text{NCTAB}] 0.008 \text{ mol L}^{-1}$ Time 1 h

$[\text{H}_2\text{SO}_4]$ (mol L^{-1})	Temp 30°C		Temp 40°C		Temp 50°C	
	% Conversion	$R_p \times 10^5$ ($\text{mol L}^{-1} \text{ s}^{-1}$)	% Conversion	$R_p \times 10^5$ ($\text{mol L}^{-1} \text{ s}^{-1}$)	% Conversion	$R_p \times 10^5$ ($\text{mol L}^{-1} \text{ s}^{-1}$)
0.15	37.30	7.86	56.42	11.89	57.96	12.21
0.25	53.54	11.28	66.68	14.05	68.50	14.43
0.35	59.40	12.52	70.93	14.95	68.67	14.47
0.45	61.58	12.98	74.68	15.74	75.80	15.97
0.6	70.15	14.78	77.54	16.34	78.81	16.61

mer particles in the micellar system as per Smith and Ewart's¹⁷ equation $R_p = k_p (N/2) [M]$, where N is the number of polymer particles in a cc of the aqueous phase. The R_p (observed) was found to be proportional to $[M]^{3/2}$, as is evident from the plot of R_p^2 vs. $[M]^3$ (Fig. 4). The plot is a straight line passing through the origin.

The effect of different categories of cosolvents depending upon their nature is reflected in Table II.

Acetone enhances the R_p considerably, whereas benzene and, to some extent, DMF retard it. For the NCTAB-H₂O—CH₃OH system, the diffusion coefficient of the micellar aggregate is probably higher than for NCTAB-H₂O alone. This fact is in agreement with that reported by Ionescu et al.²³ Therefore, an enhanced R_p is observed in case of acetone. But in the case of DMF, which forms stoichiometric hydrates with H₂O as DMF·2H₂O, the presence of hydrogen bonding is there. The highly ordered array of the hydrate probably restricts the

motion of the surfactant molecule and essentially eliminates hydrophobic interaction. So, it has an inhibitory effect on micellization and, hence, R_p is decreased. In case of benzene, it is the solubility and dielectric properties that affect the rate. The inhibitory effect of acetone to micellization at low concentration is negligible and is less than that of dioxane. This is due to the formation of hydrogen bonds between cosolvent and water.

The effect of a few salts when added in low concentration on the R_p is depicted in Table III.

The apparent CMC decreases as a function of added salts. For a low value of NaCl and KCl concentration (0.01 mL^{-1}), the diffusion coefficient $[D]$ ²⁸ for the solution of NCTAB—NaCl—H₂O increases as a function of NCTAB and so the size of the micelle increases,²² allowing more and more radicals to be formed in the micellar phase. Ionescu et al.²³ reported that the increase in diffusion coefficient (D) is in close agreement with this. But in case of CuSO₄, MnSO₄, etc., the maximum depres-

Table II Effect of Organic Solvent Concentration on Rate: $[\text{AN}] 0.759 \text{ mol L}^{-1}$; $[\text{Ce(IV)}] 0.025 \text{ mol L}^{-1}$; $[\text{NAG}] 0.005 \text{ mol L}^{-1}$; $[\text{H}_2\text{SO}_4] 0.512 \text{ mol L}^{-1}$; $[\text{NCTAB}] 0.008 \text{ mol L}^{-1}$; Time 1 h

Solvent 5% (v/v)	Temp 40°C	
	% Conversion	$R_p \times 10^5$ ($\text{mol L}^{-1} \text{ s}^{-1}$)
Control	79.13	16.67
DMF	68.67	14.47
Benzene	46.68	9.84
Dioxane	74.83	15.77
Acetone	93.64	19.73
Methanol	71.57	15.08

Table III Effect of Inorganic Salt Concentration on Rate: $[\text{AN}] 0.759 \text{ mol L}^{-1}$; $[\text{Ce(IV)}] 0.025 \text{ mol L}^{-1}$; $[\text{NAG}] 0.005 \text{ mol L}^{-1}$; $[\text{H}_2\text{SO}_4] 0.512 \text{ mol L}^{-1}$; $[\text{NCTAB}] 0.008 \text{ mol L}^{-1}$; Time 1 h

Salt (0.01 mol L^{-1})	Temp 40°C	
	% Conversion	$R_p \times 10^5$ ($\text{mol L}^{-1} \text{ s}^{-1}$)
Control	79.13	16.67
CuSO ₄ ·5H ₂	9.57	2.02
MnCO ₃	24.35	5.13
NaCl	77.33	16.29
KCl	79.32	16.71
MnSO ₄ ·4H ₂ O	11.99	2.53

Table IV Comparative Effects of Micelle Concentration on Rate: [AN] 0.759 mol L⁻¹; [NAG] 0.005 mol L⁻¹; [Ce(IV)] 0.025 mol L⁻¹; [H₂SO₄] 0.5 mol L⁻¹; Time 1 h; Temp 40°C

[Micelles] (0.01 mol L ⁻¹)	Nature	% Conversion	R _p × 10 ⁵ (mol L ⁻¹ s ⁻¹)
Control	—	6.42	1.35
Triton X-100	Neutral	Nil	Nil
NaLS	Anionic	36.42	7.68
NCTAB	Cationic	79.13	16.67

sion of R_p may probably be due to the dissociation of added salt that catalyzes decomposition, resulting in premature termination of the growing polymer chain.

The presence of cationic emulsifier enhances the R_p appreciably, as shown in Table IV. But the neutral surfactant has no effect on R_p. This may be due to the micellar size and value of CMC, since the surfactant that forms larger micelles at low CMC can help to generate more free radicals due to more solubilization of monomer in the Stern layer.²² Triton-X 100 cannot produce charged micelle and so has no effect on R_p.

The present polymerization process was studied at three different temperatures, 30, 40, and 50°C. The overall energy or activation of AN polymerization in the presence of 0.004 mL⁻¹ NCTAB was 6.86 kcal mol⁻¹, as is calculated from the slope of the Arrhenius plot (Fig. 6). The rate of polymerization increases with increase in temperature.²¹

CONCLUDING REMARKS

In conclusion, it should be noted that our results are sufficient to establish the rate expression of the polymerization reaction. The enhanced rate of polymerization in the presence of NCTAB and NaLS is probably due to greater solubilization of monomer molecules and NAG in the micellar pseudophase due to hydrophobic interaction. Second, due to Coulombic interaction, the initiation by Ce(IV) will be more favorable as concentration of Ce(IV) increases in the Stern layer of the cationic and anionic micelles. Taking into consideration the % yield at different temperatures, Ce(IV)-NAG is found to be an effective redox system. The optimum conditions for the homopolymerization reaction has been worked out as follows:

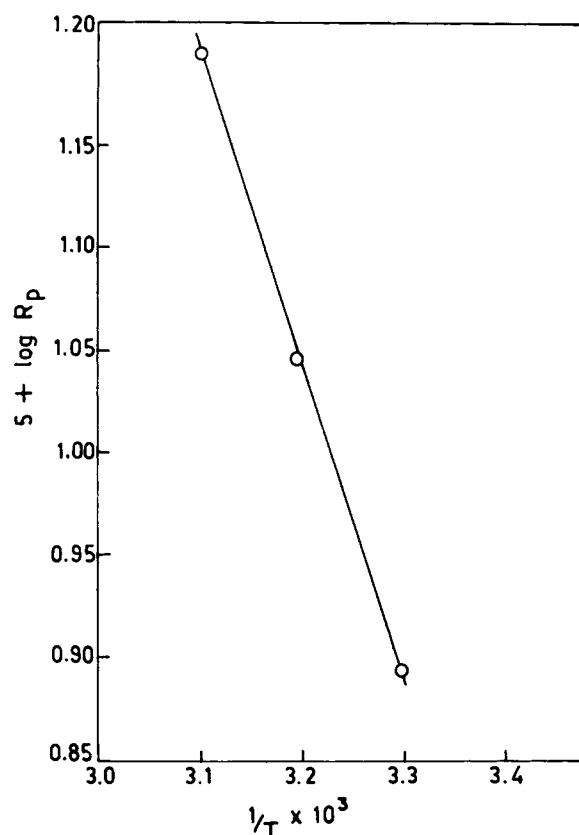


Figure 6 Arrhenius plot: [AN] 0.759 mol L⁻¹; [Ce(IV)] 0.015 mol L⁻¹; [NAG] 0.025 mol L⁻¹; [H₂SO₄] 0.512 mol L⁻¹; [NCTAB] 0.008 mol L⁻¹; time 1 h. Temp 30, 40, and 50°C.

[Ce(IV)] 0.04 mL⁻¹; [NCTAB] 0.008 mL⁻¹;
[NaLS] 0.01 mL⁻¹; [NAG] 0.01 mL⁻¹;
[H₂SO₄] 0.6 mL⁻¹; Time 1 h (NCTAB)

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Received April 28, 1993

Accepted September 27, 1993