

Acrylonitrile Polymerization Initiated by Ce(IV)–Cyclohexanone Redox System in Presence of Surfactant

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Received 17 July 2002; accepted 12 February 2003

ABSTRACT: The rate of polymerization of acrylonitrile, using the Ce(IV)–cyclohexanone redox system as an initiator, was studied kinetically, in the presence of 0.015M sodium dodecyl sulfate (SDS), over a temperature range of 25–45°C. The rate of polymerization (R_p), percentage of monomer conversion, and rate of Ce(IV) consumption ($-R_{Ce}$) were found to increase with the concentration of SDS, above its CMC. The effect of [AN], [Ce(IV)], [H⁺], and

the ionic strength were also studied. The overall activation energies for the polymerization processes were computed to be 23.14 and 17.64 kcal/mol in the absence and presence of 0.015M SDS. A suitable kinetic mechanistic scheme for the free-radical mechanism was proposed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2066–2072, 2003

Key words: surfactants; micelles; kinetics (polym.)

INTRODUCTION

A review of the literature reveals that surfactants have been used in vinyl polymerization initiated by various redox systems in different forms, for example, emulsions,^{1–9} microemulsions,^{10–15} micelles,^{16–18} and adsolubilization.¹⁹ Some work has been done on the effect of a surfactant on polymerization processes using Ce(IV) as an initiator.²⁰ The mechanism and kinetics of the polymerization of vinyl monomers, that is, acrylonitrile, acrylamide, methyl acrylate, methyl methacrylate, etc., involving Ce(IV) alone and with a reducing substrate, such as alcohol,^{21–23} diols,^{24,25} and polyols,²⁶ in an aqueous medium have been reported. It is generally known that both Ce(IV) and the primary free radicals, that is, obtained from the decomposition of the complex of Ce(IV) and a reducing agent, can participate in the initiation processes, while the termination occurs exclusively by the interaction of growing chain radicals with themselves or with Ce(IV).²² The present work deals with the effect of an anionic surfactant, sodium dodecyl sulfate, on Ce(IV)-initiated polymerization kinetics of acrylonitrile in the presence of cyclohexanone.

EXPERIMENTAL

Materials

Acrylonitrile (AN: SISCO Chemical) was purified by washing with 5% NaOH, 3% orthophosphoric acid, and, finally, triply distilled water. Finally, it was distilled under reduced pressure. Sodium dodecyl sulfate (SDS; British Drug House sample) was recrystallized from absolute alcohol and methanol sequentially. Cyclohexanone (Merck) was distilled under reduced pressure twice and kept in a refrigerator. Other chemicals like ceric ammonium sulfate (SISCO Chemical), sulfuric acid (SISCO Chemical), sodium bisulfate (Glaxo), etc., were of reagent grade and were used as such without further purification. All solutions for the study were prepared with triply distilled water free from oxygen. Nitrogen gas, used for deaeration, was made free from oxygen and other impurities by passing through several columns of Fieser's solution, a column of a saturated solution of lead acetate, and, finally, through a bottle containing triply distilled water.

Methods

The polymerization was carried out in a Pyrex tube of 150-mL capacity, which was sealed at the bottom and the top was fitted with a standard joint stopper having inlet and outlet tubes for the passing of nitrogen. A microburette was fitted vertically on the stopper. The aqueous solutions of AN, cyclohexanone (CH), sulfuric acid, sodium bisulfate (to maintain proper ionic strength), and SDS in appropriate concentrations were taken in the reaction tube. Nitrogen gas was bubbled

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Contract grant sponsors: UGC, New Delhi (DRS-SAP); DST, India (FIST).

TABLE I
Effect of Surfactant Concentration on the Rates

[SDS] (mol L ⁻¹)	10 ⁴ × R _p (mol L ⁻¹ s ⁻¹)				10 ⁷ × (-R _{Ce}) (mol L ⁻¹ s ⁻¹)			
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
0.000	1.08	1.60	2.11	2.63	3.16	5.18	8.22	9.77
0.005	1.16	1.71	2.13	2.69	3.34	5.39	8.31	9.88
0.010	1.30	1.86	2.42	3.16	3.76	5.92	9.02	10.65
0.015	1.47	2.01	2.72	3.56	4.26	6.58	9.96	11.70
0.020	1.62	2.23	3.01	4.09	5.73	7.17	10.68	12.63
0.025	1.70	2.34	3.23	4.46	6.08	7.59	11.16	13.11
0.030	1.72	2.40	3.35	4.69	6.19	7.74	11.35	13.33

[AN] = 0.5 mol L⁻¹; [Ce(IV)] = 5.08 mmol L⁻¹; [CH] = 01.08 mol L⁻¹; [H⁺] = 0.5 mol L⁻¹; [μ] = 0.6 mol L⁻¹,

for about 0.5 h and the stopcocks were closed. The solution was thermostated to attain the desired temperature, followed by the addition of the Ce(IV) solution from the microburette, and then mixed by shaking. The volume of the reaction mixture was adjusted to 20 mL. The polymerization started immediately after the addition of the Ce(IV) solution. After a definite interval of time, the reaction was quenched by the addition of the excess of a standard ferrous ammonium sulfate solution. The polymer formed was filtered off through a G₄ crucible and kept at 50–60°C until a constant weight was attained. The filtrate, along with washings after separation of the polymer, was estimated for residual Ce(IV) by cerimetry using ferroin as an indicator. The rate of polymerization and the rate of Ce(IV) consumption were calculated from the initial slope of the curve of the percentage of monomer conversion versus time and Ce(IV) consumption versus the time curve, respectively.^{16,17,20}

RESULTS AND DISCUSSION

Effect of surfactant

The most interesting features observed in these polymerization processes, in the presence of the anionic surfactant, are

- An enhancement of the rate of polymerization, $R_{P(\text{obs})}$, with an increase in the SDS concentration (Table I).
- An enhancement of the percentage of the monomer conversion with an increase in the SDS concentration (Fig. 1).

In an aqueous medium, the surfactant molecules, beyond the critical micelle concentration (CMC), self-aggregate to form micelles, resulting in a biphasic system, namely, bulk and micellar phases. AN and CH become solubilized in the micellar phase due to a hydrophobic interaction. From the spectroscopic study, it was found that the percentage of the solubility of AN in pure water was 7.95, whereas that in a 0.015M SDS solution was 32.82.²⁰ In other words, the

solubility of the monomer increased about four times in the 0.015M SDS solution as compared to that in pure water. Similarly, due to the electrostatic attraction of Ce(IV) for the negatively charged Stern layer of SDS micelles, the concentration of Ce(IV) is high at the micellar surface. As a result, $R_{P(\text{obs})}$ and $-R_{Ce}$ were increased with an increasing SDS concentration, above its CMC. A similar type of observation was noted by Behari et al.²⁷ and Sinha et al.³⁰

Effect of monomer concentration

For AN polymerization, $R_{P(\text{obs})}$ was found to be proportional to a 1.5 power concentration of the monomer, which supports that termination is mutual¹⁶ (Table II). The slope of the bilogarithmic plot of $R_{P(\text{obs})}$ versus [AN] was found to be 1.5. These values are in good agreement with the results published by Santappa et al.²⁸ The rate of Ce(IV) consumption, $-R_{Ce}$, was also linearly dependent on the monomer concentration, since the slope obtained from the log-log plot of $-R_{Ce}$ versus [AN] was approximately one. This may be due to greater number of monomers available

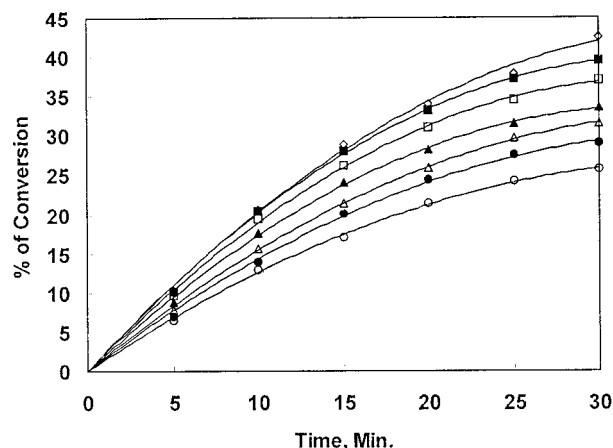


Figure 1 Percentage of conversion of AN with time in the presence of SDS at 25°C: (○) 0.000M SDS; (●) 0.005M SDS; (△) 0.010M SDS; (▲) 0.015M SDS; (□) 0.020M SDS; (■) 0.025M SDS; (◇) 0.030M SDS.

TABLE II
Effect of Acrylonitrile Concentration on the Rates

[AN] (mol L ⁻¹)	10 ⁴ × R _p (mol L ⁻¹ s ⁻¹)				10 ⁷ × (-R _{Ce}) (mol L ⁻¹ s ⁻¹)			
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
0.4	0.98	1.46	1.97	2.58	6.81	10.53	16.12	18.77
0.5	1.47	2.01	2.72	3.55	8.48	13.17	19.99	23.45
0.6	1.78	2.64	3.56	4.66	10.17	15.84	24.11	28.15
0.7	2.26	3.33	4.49	5.83	11.22	18.45	28.07	32.83
0.8	2.71	4.04	5.46	7.15	13.57	21.03	32.01	37.55

[SDS] = 0.015 mol L⁻¹; [Ce(IV)] = 5.08 mmol L⁻¹; [CH] = 01.08 mol L⁻¹; [H⁺] = 0.5 mol L⁻¹; [μ] = 0.6 mol L⁻¹.

in a favorable reaction site, that is, a micellar core or micellar interface.

Effect of [ce(IV)]

On increasing the concentration of [Ce(IV)] (2.5–12.5 × 10⁻² M), it was found that R_{P(obs)} (Table III) as well as the percent of the monomer conversion increased. The order of R_{P(obs)} with respect to [Ce(IV)] is half, which was confirmed by the value of the slope (0.5) of the bilogarithmic plot of R_{P(obs)} versus [Ce(IV)]. Due to the electrostatic attraction of Ce(IV) for the Stern layer of SDS micelles, a greater number of Ce(IV) species were available at the micellar surface on increasing the concentration in the reaction mixture, which ameliorated the free-radical formation, resulting higher values of R_{P(obs)}. The square-root dependence of R_{P(obs)} on the Ce(IV) concentration was also reported by other workers earlier.^{27,28} The rate of Ce(IV) consumption, -R_{Ce}, has a linear dependence on the Ce(IV) concentration. Such Ce(IV) dependence in the polymerization process was reported earlier.²⁹ This also was confirmed by the slope of the bilogarithmic plot (Table III).

Effect of CH concentration

On increasing the concentration of CH (0.05–0.25M), the R_{P(obs)} also increased (Table IV). The bilogarithmic plot of R_{P(obs)} versus [CH] produces straight lines having slopes of 0.50 for all the temperatures. With

increase of the concentration of CH in the reaction medium, its solubilization increases in the micellar phase, resulting in a better environment for rapid polymerization.^{16,20} In the absence of CH, no polymerization took place in the case of AN. -R_{Ce} is linearly dependent on [CH] and the order was unity obtained from the log-log plot of -R_{Ce} versus [CH].

Effect of [H⁺]

At a constant ionic strength (0.5M), increasing the acid concentration leads to an increase in R_{P(obs)} (Table V) in 0.015M SDS. The localization [H⁺] at the Stern layer of the micelles of SDS, at its higher concentration,³⁰ led to the enhancement of the rates. When the ionic strength was not maintained, R_{P(obs)} was found to be independent of [H⁺].

Effect of temperature

An enhancement of the rate of polymerization was observed, both in the absence and the presence of 0.015M SDS in the reaction medium, on increasing the temperature from 25–45°C. Perhaps it is the increased propagation rate constant and -R_{Ce} with the temperature that promotes the rate of polymerization. From the Arrhenius plot (Fig. 2), the overall activation energy for the polymerization processes were computed to be 23.14 and 17.64 kcal/mol in the absence and presence of 0.015 M SDS. A decrease of 5.5 kcal/mol in

TABLE III
Effect of Ce(IV) Concentration on the Rates

[Ce(IV)] (mol L ⁻¹)	10 ⁴ × R _p (mol L ⁻¹ s ⁻¹)				10 ⁷ × (-R _{Ce}) (mol L ⁻¹ s ⁻¹)			
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
5.03	1.47	2.01	2.72	3.56	4.26	6.58	9.96	11.70
10.08	1.94	2.85	3.86	5.06	8.48	13.17	19.99	23.45
15.09	2.37	3.51	4.73	6.19	12.75	19.73	30.21	34.98
20.03	2.73	4.03	5.45	7.14	16.98	26.35	39.89	46.66
25.05	3.04	4.49	6.06	7.95	21.21	32.91	49.88	58.51

[SDS] = 0.015 mol L⁻¹; [AN] = 0.5 mol L⁻¹; [CH] = 01.08 mol L⁻¹; [H⁺] = 0.5 mol L⁻¹; [μ] = 0.6 mol L⁻¹.

TABLE IV
Effect of Cyclohexanone Concentration on the Rates

[CH] (mol L ⁻¹)	10 ⁴ × R _p (mol L ⁻¹ s ⁻¹)				10 ⁷ × (-R _{Ce}) (mol L ⁻¹ s ⁻¹)			
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
0.054	0.96	1.41	1.91	2.50	2.15	3.29	4.45	5.82
0.108	1.47	2.01	2.72	3.56	4.26	6.58	9.96	11.70
0.152	1.66	2.43	3.28	4.29	6.47	9.91	15.12	17.41
0.206	1.91	2.84	3.84	5.03	8.63	13.18	20.23	23.29
0.262	2.15	3.16	4.27	5.59	10.74	16.48	24.89	29.11

[SDS] = 0.015 mol L⁻¹; [AN] = 0.5 mol L⁻¹; [Ce(IV)] = 5.08 mmol L⁻¹; [H⁺] = 0.5 mol L⁻¹; [μ] = 0.6 mol L⁻¹.

the activation energy supports the positive catalytic role of the surfactant.^{16,17,20}

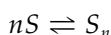
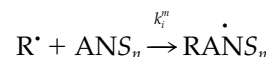
Formation of free radical:



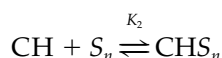
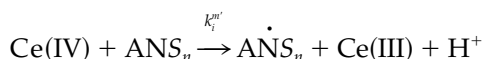
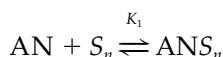
Reaction mechanism and kinetic scheme

Taking into account all the aforementioned facts, it is concluded that the polymerization process occurs mostly in the micellar phase of the anionic surfactant, SDS. To explain this, a free-radical mechanistic scheme was proposed for redox polymerization, which is as follows:

Initiation by Primary radical:



Initiation by Ce (IV):



Propagation:



Reaction of Ce(IV) with Cyclohexanone:

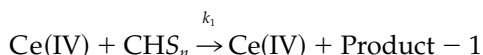


TABLE V
Effect of [H⁺] and Ionic Strength on the Rates

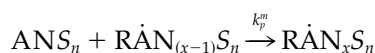
[H ⁺] (mol L ⁻¹)	μ (mol L ⁻¹)	10 ⁴ × R _{p1} (mol L ⁻¹ s ⁻¹)				10 ⁷ × (-R _{Ce}) ₁ (mol L ⁻¹ s ⁻¹)			
		25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
0.1	0.5	0.67	0.92	1.33	1.79	2.12	3.83	4.99	7.12
0.2	0.5	0.81	1.22	1.71	2.22	3.29	5.44	9.88	10.32
0.3	0.5	1.09	1.54	2.02	2.72	4.39	8.19	12.52	14.89
0.4	0.5	1.32	1.76	2.39	3.01	6.11	10.77	16.31	18.33
0.5	0.5	1.47	2.01	2.72	3.55	8.48	13.17	19.99	23.45
0.2	0.2	1.49	1.99	2.72	3.57	8.46	13.19	19.98	23.48
0.3	0.3	1.48	2.02	2.69	3.56	8.47	13.16	20.01	23.43
0.4	0.4	1.47	2.00	2.69	3.56	8.46	13.15	19.97	23.44

[SDS] = 0.015 mol L⁻¹; [AN] = 0.5 mol L⁻¹; [Ce(IV)] = 5.08 mmol L⁻¹; [CH] = 0.108 mol L⁻¹.

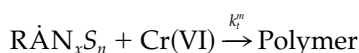
TABLE VI
Rate Parameters for Polymerization of Acrylonitrile
in Presence of Cyclohexanone by Ce(IV)

Temperature	$(k_0^m/k_t^m) \times 10^3$		$k_p^m/k_t^{m0.5}$	
	1	2	1	2
25	2.41	2.43	1.86	1.81
30	1.81	1.78	2.41	2.40
35	1.66	1.62	3.12	3.19
40	1.44	1.48	3.98	4.10

1, From $\{[AN]/R_{p(\text{obs})}\}^2$ versus $1/[AN]$.
2, From $\{[AN]/R_{p(\text{obs})}\}^2$ versus $1/[Ce(IV)]$.



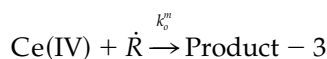
Linear termination:



Mutual termination:



Reaction of \dot{R} with Ce(VI):



where R is the primary radical; S , the surfactant; S_n , micelles; AN, acrylonitrile; and k_i^m , k_p^m , and k_t^m , the respective rate constants. The superscript m indicates the micellar phase.

Using a steady-state assumption for the free radical, the expression for the rate of polymerization (R_p^m) and the rate of Ce(VI) consumption ($-R_{Ce}^m$) can be derived as follows:

For linear termination,

$$R_p^m = \frac{k_p^m [ANS_n]^2}{k_t^m} \left\{ \frac{k' [CHS_n]}{[ANS_n] + \left(\frac{k_0^m}{k_t^m}\right) [Ce(IV)]} + k_i^{m'} \right\} \quad (1)$$

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

For mutual termination,

$$R_p^m = \frac{k_p^m [ANS_n]^{1.5} [Ce(IV)]^{0.5}}{(k_t^m)^{0.5}} \times \left\{ \frac{k' [CHS_n]}{[ANS_n] + \left(\frac{k_0^m}{k_t^m}\right) [Ce(IV)]} + k_i^{m'} \right\}^{0.5} \quad (3)$$

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

It was observed that no polymerization took place in the absence of an organic substrate, that is, Ce(IV) alone could not initiate polymerization, leading to the elimination of the term k_0^m . Since the polymer obtained was found not to contain Ce(IV), the linear termination was also not considered. Hence, the rate expression be given as

$$R_p^m = \frac{k_p^m [ANS_n]^{1.5} [Ce(IV)]^{0.5}}{(k_t^m)^{0.5}} \left\{ \frac{k' [CHS_n]}{[ANS_n] + \left(\frac{k_0^m}{k_t^m}\right) [Ce(IV)]} \right\}^{0.5} \quad (5)$$

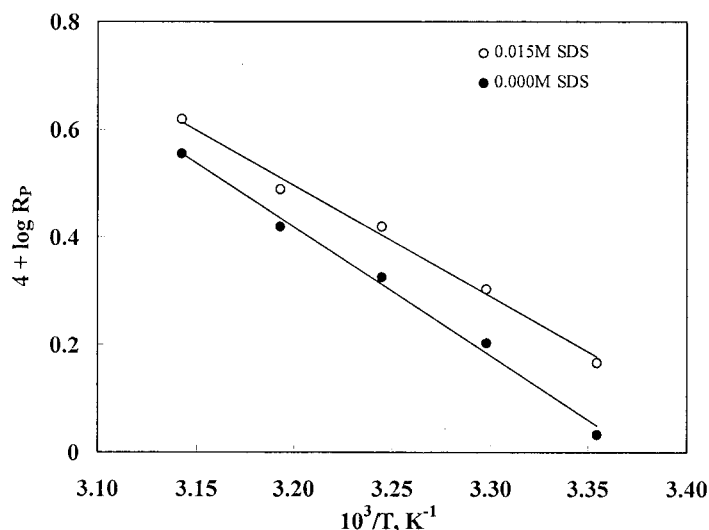


Figure 2 Arrhenius plot: $\log R_{p(\text{obs})}$ versus $1/T$.

$$-R_{Ce}^m = [Ce(IV)]\{k'[CHS_n] + k_i^m[ANS_n]\} \quad (6)$$

$$-R_{Ce}^m = k'K_2[Ce(IV)][CH][S_n] \quad (7)$$

The observed rate of polymerization, $R_{P(obs)}$, can be taken as the sum of the polymerization in the bulk phase, R_p^b , and that in the micellar phase, R_p^m , that is, $R_{P(obs)} = R_p^b + R_p^m$. Since at a higher concentration of the surfactant, above its CMC, the rate of the observed polymerization is almost equal to the rate of polymerization in the micellar phase, due to the high solubilization of AN and CH,¹⁷ that is, $R_{P(obs)} \approx R_p^m$. Then, eq. (5) can be rearranged after squaring and with proper substitution as follows:

$$\frac{[AN]^2}{R_{P(obs)}^2} = \frac{k_t^i}{K_1^2 K_2 k_p^m k' k_i^m [AN][CH][S_n]^3} + \frac{k_0^m k_t^m}{K_1^3 K_2 k_p^m k' k_i^m [AN][CH][S_n]^4} \quad (8)$$

Rate parameters

The values of k_0^m/k_i^m and $k_p^m/k_t^{m0.5}$ for AN at various concentrations were calculated from the plot of $\{[AN]/R_{P(obs)}\}^2$ versus $1/[AN]$ (Fig. 3) and $\{[AN]/R_{P(obs)}\}^2$ versus $1/[Ce(IV)]$ (Fig. 4) on substituting the value of $[S_n]$ obtained from the relationship $[S_n] = (C_D - CMC)/N$, where C_D is the concentration of the surfactant, and N , the aggregation number, which was taken as 62 (ref. 31), and the values of K_1 and K_2 , (i.e., $7.92 \times 10^2 \text{ mol L}^{-1}$ and $9.11 \times 10^4 \text{ mol L}^{-1}$) were obtained previously^{16,20} and are furnished in Table III, using following relationship:

From plot $\{[AN]/R_{P(obs)}\}^2$ versus $1/[AN]$

$$\frac{k_0^m}{k_i^m} = \frac{\text{slope}}{\text{intercept}} \frac{K_1[S_n]}{[Ce(IV)]} \quad (9)$$

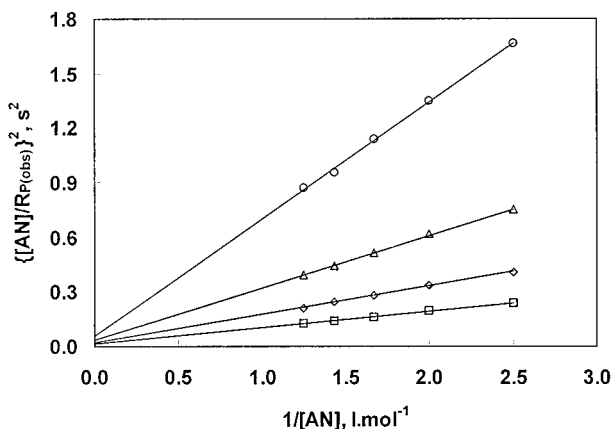


Figure 3 Plot of $\{[AN]/R_{P(obs)}\}^2$ versus $1/[AN]$: (○) 25°C; (△) 30°C; (◇) 35°C; (□) 40°C.

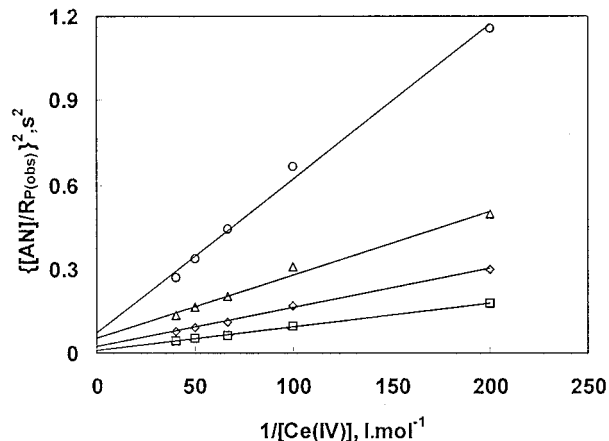


Figure 4 Plot of $\{[AN]/R_{P(obs)}\}^2$ versus $1/[Ce(IV)]$: (○) 25°C; (△) 30°C; (◇) 35°C; (□) 40°C.

$$\frac{k_p^m}{k_i^{m0.5}} = \frac{k_0^m/k_i^m}{\{\text{intercept} \cdot K_1^2 K_2 k' [Ce(IV)][CH][S_n]^3\}} \quad (10)$$

From plot $\{[AN]/R_{P(obs)}\}^2$ versus $1/[Ce(IV)]$

$$\frac{k_0^m}{k_i^m} = \frac{\text{slope}}{\text{intercept}} \frac{1}{K_1[AN][S_n]} \quad (11)$$

$$\frac{k_p^m}{k_i^{m0.5}} = \frac{k_0^m/k_i^m}{\{\text{intercept} \cdot K_1^3 K_2 k' [AN][CH][S_n]^4\}} \quad (12)$$

CONCLUSIONS

The increase in $R_{P(obs)}$ as well as the percent of the conversion of AN in the presence of SDS is probably due to the hydrophobic interaction of the monomer and organic substrate for the micellar core as well as the electrostatic interaction of the Ce(IV) species for the negatively charged Stern region of the SDS micelles.

The authors are thankful to UGC, New Delhi (DRS-SAP), and DST, India (FIST), and one of the authors (M. P.) to CSIR, New Delhi for the RA position.

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