

# Effect of Toluene on the Polymerization of AN Initiated by Ce(IV)–Sucrose Redox System in the Presence of Surfactants

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## SYNOPSIS

The effects of toluene on the kinetics of polymerization of acrylonitrile (AN) initiated by the Ce(IV)/sucrose redox system were studied in the presence of an emulsifier, *N*-cetyltrimethylammonium bromide (NCTAB) in the temperature range 35–45°C. The effects of concentration of metal ion, monomer, sulfuric acid, substrate (sucrose), emulsifier, toluene, some inorganic salt, and organic solvent on  $R_p$  have also been investigated. The remarkable features of the investigation involve the derivation of the rate expression for the above system with the calculation of activation energy. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Surfactants serve the purpose of lowering the surface tension at the monomer water interface and facilitate emulsification of the monomer in water. They stabilize the emulsion of the monomer and the polymer monomer particle by forming a monolayer of soap around each. At low concentration, surfactants become fully dissolved or molecularly dispersed. Beyond a particular concentration, i.e., critical micelle concentration (CMC), the excess amount forms molecular aggregates known as micelles and an equilibrium exists between the dissolved surfactant and the aggregated ones. With relatively insoluble monomers, nearly all of the polymer particle nuclei are initiated in the monomer solubilized in the interior of the soap micelles.

The rates of many chemical reactions are affected by incorporating the reactants into their micellar pseudophase.<sup>1</sup> Barton et al.<sup>2,3</sup> showed that the anion-active emulsifier affects the relative molecular mass of polyacrylamide and polymethacrylamide (water-soluble monomer), but that it showed no effect on the polymerization rate. In this type of polymerization, potassium peroxy disulfate in water and 2,2'-azoisobutyronitrile (AIBN) in a water/ethanol

mixture were used as initiator and sodium dodecyl phenoxybenzene disulfonate was used as emulsifier. Kim<sup>4</sup> observed an increase of the rate of polymerization of acrylamide initiated by sodium hydrogen trioxosulfate at concentrations of the emulsifier higher than its critical micellar concentration. Shukla and Misra<sup>5</sup> found that the rate of polymerization of acrylamide in water initiated by the potassium permanganate/ascorbic acid system increases only at concentrations higher than the CMC of the applied anion-active emulsifier, but was not affected below the CMC value. However, the cation-active emulsifier cetyltrimethylammonium bromide and cetylpyridinium bromide decrease the rate of polymerization. Capek, et al.,<sup>6</sup> Uchida and Nagao,<sup>7,8</sup> and Antonova et al.<sup>9</sup> reported the effect of an emulsifier on the composition of a copolymer prepared from a monomer sparingly soluble in water with a water-insoluble monomer. Baxendale et al.<sup>10</sup> used a redox system as the initiator for polymerization of acrylonitrile with cetyltrimethylammonium bromide as the emulsifier and Corrin et al.<sup>11</sup> used potassium lauryl sulfate as the emulsifier with potassium persulfate as the initiator. In both these cases, a large increase in the rate was noticed, but in the case of redox systems, the rate enhancement was remarkable. The present paper deals with the influence of toluene on Ce(IV)–sucrose-initiated polymerization of acrylonitrile in presence of a cation-active emulsifier.

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## EXPERIMENTAL

### Materials

Acrylonitrile (AN) was washed with 5% NaOH, 3% *ortho*-phosphoric acid followed by repeated washing with conductivity water, dried over calcium chloride, and, finally, stored in a refrigerator for use. Reagents like ceric ammonium sulfate, sucrose, ferrous ammonium sulfate, toluene, *N*-cetyltrimethylammonium bromide (emulsifier), sulfuric acid (18*M*), and glacial acetic acid were all of AnalaR grade and were used as such. Conductivity water was prepared by redistilling distilled water over alkaline  $\text{KMnO}_4$  in an all-glass Pyrex unit. The polymerization was studied under atmospheric conditions.

### Polymerization

Appropriate quantities of monomer, sucrose, toluene, emulsifier (NCTAB), sulfuric acid, and glacial acetic acid were mixed in the reaction vessel (Pyrex 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  $\pm 0.1^\circ\text{C}$ . A required amount of ceric ammonium sulfate solution (in 1*M*  $\text{H}_2\text{SO}_4$ ) was added and the time was noted. After the specified time interval, the polymerization was arrested by adding an excess of ferrous ammonium sulfate solution. The polymer formed was filtered off, washed repeatedly with conductivity water, and dried to constant weight. The rate of polymerization ( $R_p$ ) and the percentage conversion were calculated by using the following formula:

$$\text{Rate of polymerization } (R_p) = \frac{1000 \times W}{V \times t \times M}$$

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

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

## RESULTS AND DISCUSSION

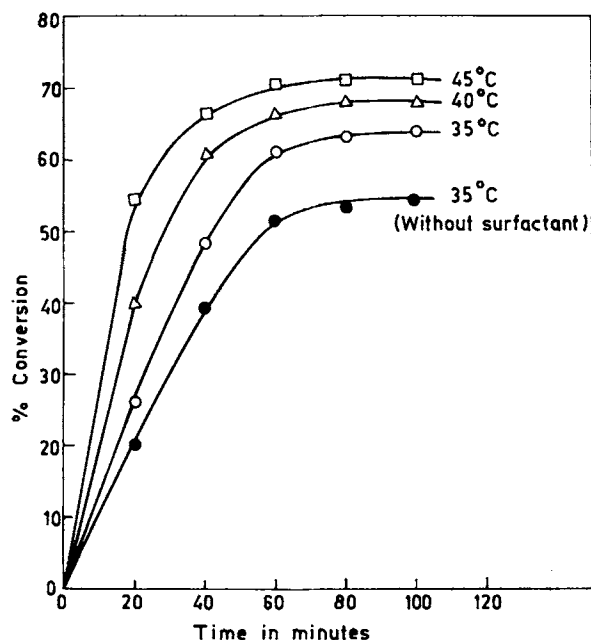
### Effect of Time on Percentage Conversion

Effect of time on percentage conversion was studied both in the presence of the emulsifier and in the absence of the emulsifier at different temperatures

from 35 to 45°C, as shown in Figure 1. The percentage conversion was higher for systems having an emulsifier and a limiting conversion was attained within 60 min, which can be attributed to the presence of micelles. At higher temperature, the monomer dissolves in the middle of the micelles by a process known as solubilization,<sup>12</sup> forming a small number of polymer molecules. These polymer molecules capture other monomer molecules, thus forming polymer particle nuclei that enhance the rate of polymerization. The slow rate of polymerization in soap-free water as compared with that in micellar solutions is explained as due to the much smaller number of polymer monomer particles present at any time in the soap-free system.

### Reaction Mechanism and Kinetic Scheme

A free-radical mechanism is assumed in the present system as reported by Harkins<sup>13</sup> for emulsion polymerization. Here, Ce(IV)–sucrose serves as the redox initiator system. The micelle formed from the emulsifier (NCTAB) is designated as CH. As reported by Barton et al.,<sup>3</sup> the concentration of emulsifier can be used for the transfer reaction of the growing macro free radical with the emulsifier. Thus,

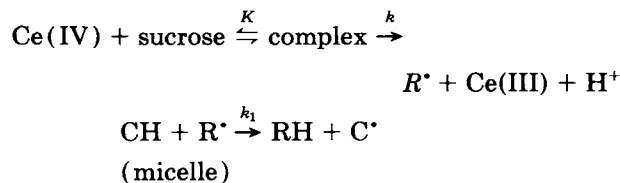


**Figure 1** Time-conversion curve:  $[\text{AN}] = 0.759 \text{ mL}^{-1}$ ,  $[\text{H}_2\text{SO}_4] = 0.3 \text{ mL}^{-1}$ ,  $[\text{toluene}] = 0.2 \text{ mL}^{-1}$ ,  $[\text{gl. HOAc}] = 2.61 \text{ mL}^{-1}$ ,  $[\text{sucrose}] = 0.04 \text{ mL}^{-1}$ ,  $[\text{Ce(IV)}] = 0.02 \text{ mL}^{-1}$ ,  $[\text{NCTAB}] = 0.006 \text{ mL}^{-1}$ . (●) Without surfactant at 35°C; (○) with surfactant at 35°C; (△) with surfactant at 40°C; (□) with surfactant at 45°C.

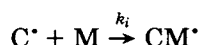
it leads to the formation of a free radical of the emulsifier taken.

However, the following mechanism is proposed to explain the kinetic results satisfactorily:

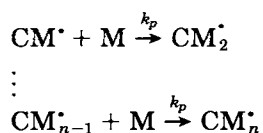
Radical formation:



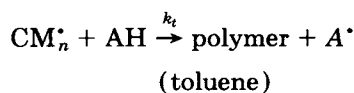
Initiation:



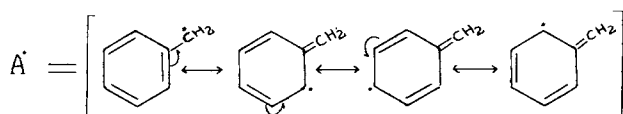
Propagation:



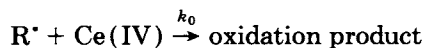
Termination:



where A<sup>•</sup> is the resonance stabilized radical:



Oxidation:



Applying the steady-state principle for the concentration of the free radicals, we have

$$\frac{d[\text{R}^{\bullet}]}{dt} = Kk[\text{R}][\text{Ce(IV)}] - k_1[\text{CH}][\text{R}^{\bullet}] - k_0[\text{R}^{\bullet}][\text{Ce(IV)}] = 0$$

$$[\text{R}^{\bullet}] = \frac{Kk[\text{R}][\text{Ce(IV)}]}{k_1[\text{CH}] + k_0[\text{Ce(IV)}]}$$

$$\frac{d[\text{C}^{\bullet}]}{dt} = k_1[\text{CH}][\text{R}^{\bullet}] - k_i[\text{C}^{\bullet}][\text{M}] = 0$$

$$[\text{C}^{\bullet}] = \frac{k_1[\text{CH}][\text{R}^{\bullet}]}{k_i[\text{M}]}$$

Putting the value of [R<sup>•</sup>]

$$= \frac{Kk k_1 [\text{R}][\text{Ce(IV)}][\text{CH}]}{k_1 k_1 [\text{CH}][\text{M}] + k_0 k_i [\text{M}][\text{Ce(IV)}]}$$

$$\frac{d[\text{CM}_n^{\bullet}]}{dt} = k_i[\text{C}^{\bullet}][\text{M}] - k_t[\text{CM}_n^{\bullet}][\text{AH}] = 0$$

$$[\text{CM}_n^{\bullet}] = \frac{k_i[\text{C}^{\bullet}][\text{M}]}{k_t[\text{AH}]}$$

Putting the value of [C<sup>•</sup>]

$$[\text{CM}_n^{\bullet}] = \frac{Kk k_1 k_i [\text{R}][\text{Ce(IV)}][\text{CH}][\text{M}]}{k_i k_1 k_t [\text{CM}][\text{M}][\text{AH}] + k_0 k_i k_t [\text{M}][\text{Ce(IV)}][\text{AH}]}$$

The rate of polymerization  $R_p$  is given by

$$R_p = k_p[\text{CM}_n^{\bullet}][\text{M}]$$

$$= \frac{Kk k_1 k_i k_p [\text{R}][\text{Ce(IV)}][\text{CH}][\text{M}]^2}{k_i k_1 k_t [\text{CH}][\text{M}][\text{AH}] + k_0 k_i k_t [\text{M}][\text{Ce(IV)}][\text{AH}]}$$

$$= \frac{Kk k_1 k_i k_p [\text{R}][\text{Ce(IV)}][\text{CH}][\text{M}]}{k_i k_t [\text{AH}] k_1 [\text{CH}] + k_0 [\text{Ce(IV)}]}$$

$$= \frac{Kk k_1 k_0 [\text{R}][\text{Ce(IV)}][\text{CH}][\text{M}]}{k_t [\text{AH}] k_i [\text{CH}] + k_0 [\text{Ce(IV)}]}$$

$$\frac{1}{R_p} = \frac{k_t [\text{AH}] k_1 [\text{CH}]}{Kk k_1 k_p [\text{R}][\text{Ce(IV)}][\text{CH}][\text{M}]}$$

$$+ \frac{k_t [\text{AH}] k_0 [\text{Ce(IV)}]}{Kk k_1 k_p [\text{R}][\text{Ce(IV)}][\text{CH}][\text{M}]}$$

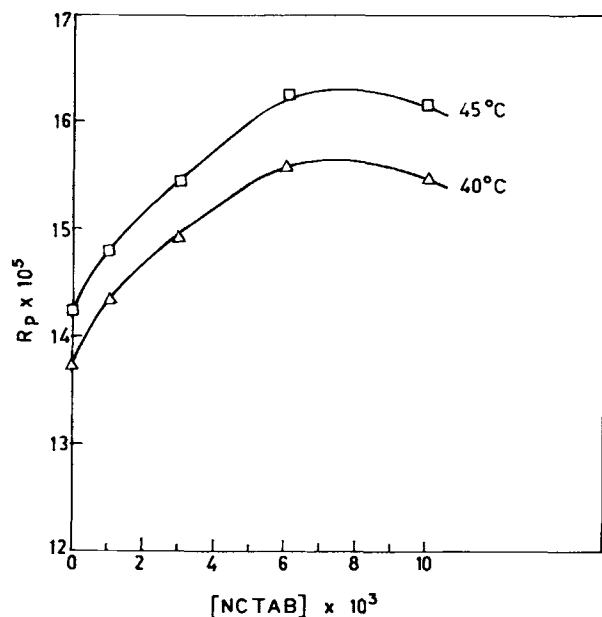
$$= \frac{k_t [\text{AH}]}{Kk k_p [\text{R}][\text{Ce(IV)}][\text{M}]}$$

$$+ \frac{k_t [\text{AH}] k_0}{Kk k_1 k_p [\text{R}][\text{CH}][\text{M}]}$$

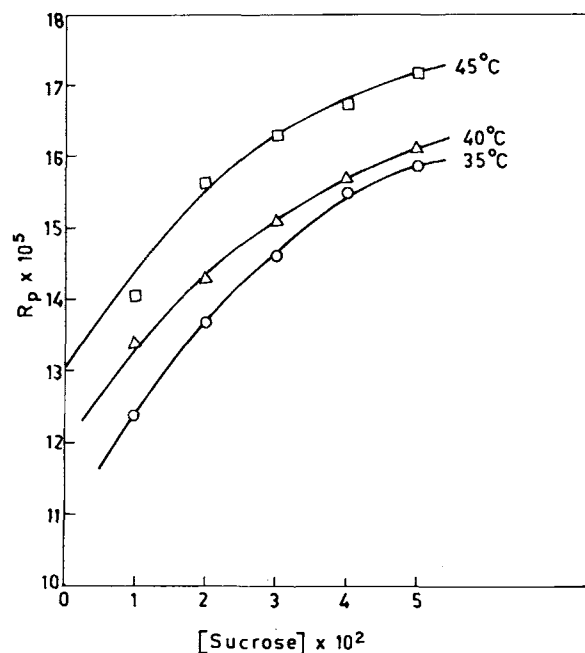
$$= \frac{k_t [\text{AH}]}{Kk k_p [\text{R}][\text{M}]} \left[ \frac{1}{[\text{Ce(IV)}]} + \frac{k_0}{k_1 [\text{CH}]} \right]$$

### Dependence of Rate on Emulsifier Concentration

By increasing the concentration of the cationic emulsifier, the rate of polymerization ( $R_p$ ) increases to a certain extent and then decreases. Plots of  $R_p$  vs. [NCTAB] are shown in Figure 2. It was found that the  $R_p$  value was low at zero concentration of [NCTAB] and it increases steadily from 0.001 mL<sup>-1</sup> until the concentration of [NCTAB] attains 0.006 mL<sup>-1</sup> and thereafter falls. The higher concentration



**Figure 2**  $R_p$  vs. [NCTAB] plots. [AN] = 0.759 mL<sup>-1</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 0.3 mL<sup>-1</sup>, [toluene] = 0.2 mL<sup>-1</sup>, [gl. HOAc] = 261 mL<sup>-1</sup>, [sucrose] = 0.04 mL<sup>-1</sup>, [Ce(IV)] = 0.02 mL<sup>-1</sup>, time = 1 h.



**Figure 3**  $R_p$  vs. [sucrose] plots. [AN] = 0.759 mL<sup>-1</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 0.3 mL<sup>-1</sup>, [Ce(IV)] = 0.02 mL<sup>-1</sup>, [toluene] = 0.2 mL<sup>-1</sup>, [gl. HOAc] = 1.74 mL<sup>-1</sup>, [NCTAB] = 0.006 mL<sup>-1</sup>, Time = 1 h.

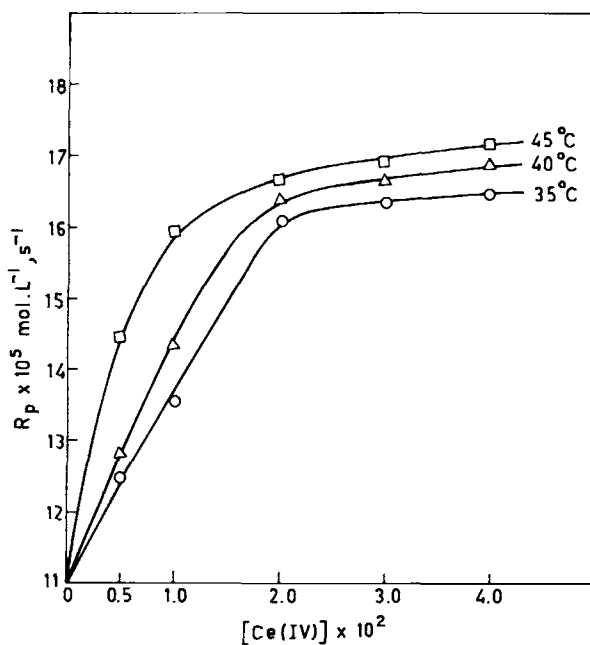
of emulsifier at which the  $R_p$  is maximum represents the CMC. The increasing trend of  $R_p$  with soap concentration is due to the emulsifying effect of soap on monomer-polymer particles, i.e., soap prevents their aggregation and thus keeps their number high. The decrease in the  $R_p$  value as reported by Baxendale et al.<sup>10</sup> may be due to the fast rate of mutual termination by the growing macroradicals initiated in the interior of soap micelle at higher emulsifier concentration.

#### Effect of Sucrose on Rate

The effect of variation of sucrose concentration on rate of polymerization is shown in Figure 3. The rate of polymerization increases with increasing concentration of sucrose within the range of 0.01–0.05 mL<sup>-1</sup> at all temperatures. The sucrose constituting a part of the redox system of Ce(IV)–sucrose appears more efficient in initiating a large growth of free radicals in the monomer inside the micelle, forming a huge number of latex particles.

#### Effect of Metal Ion Ce(IV) on Rate

Figure 4 represents the effect of variation of Ce(IV) concentration at three different temperatures (35, 40, and 45°C) on the rate of polymerization. The



**Figure 4**  $R_p$  vs. [Ce(IV)] plots. [AN] = 0.759 mL<sup>-1</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 0.4 mL<sup>-1</sup>, [toluene] = 0.2 mL<sup>-1</sup>, [gl. HOAc] = 2.61 mL<sup>-1</sup>, [sucrose] = 0.04 mL<sup>-1</sup>, [NCTAB] = 0.006 mL<sup>-1</sup>, time = 1 h.

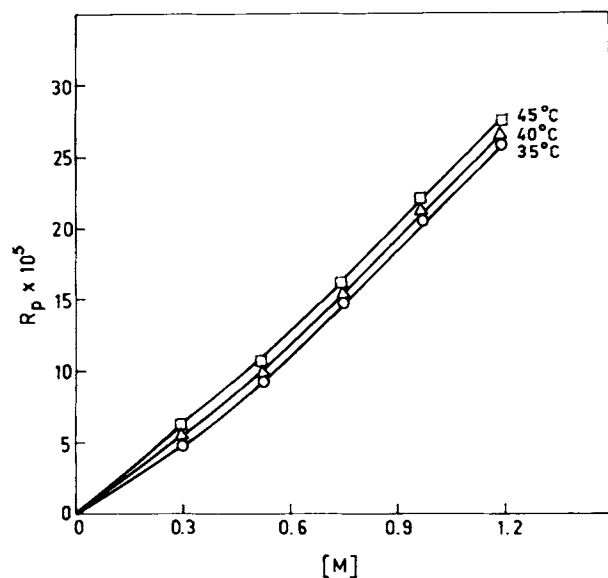
rate of polymerization increases by increasing the concentration of Ce(IV) from 0.005–0.02 mL<sup>-1</sup> and then levels off. This may be due to the formation of increasing number of free radicals within the reaction mixture.

### Effect of Monomer on Rate

The effect of variation monomer (AN) concentration on the rate of polymerization ( $R_p$ ) has been shown in Figure 5. It is observed that the rate of polymerization as well as the percent conversion increases steadily with increase in monomer concentration. The increasing trend of polymerization at higher concentrations of monomer is due to the diffusion of a number of free radicals of the monomer to the core of micelle where it starts the growth of a polymer free radical, which under usual conditions grows large. This absorbs more monomers and starts the growth of polymer–monomer particle that culminates in the formation of polymers.

### Effect of Acid Concentration on Rate

The effect of sulfuric acid concentration on the rate of polymerization is presented in Table I. The rate of polymerization increases slowly with increasing the acid concentration within the range of 0.2–0.5 mL<sup>-1</sup>. This may be accounted for by the formation



**Figure 5**  $R_p$  vs.  $[M]$  plots.  $[Ce(IV)] = 0.02 \text{ mL}^{-1}$ ,  $[H_2SO_4] = 0.3 \text{ mL}^{-1}$ ,  $[toluene] = 0.2 \text{ mL}^{-1}$ ,  $[sucrose] = 0.04 \text{ mL}^{-1}$ ,  $[NCTAB] = 0.006 \text{ mL}^{-1}$ , time = 1 h,  $[gl. HOAc] = 1.74 \text{ mL}^{-1}$ .

**Table I** Effect of  $H_2SO_4$

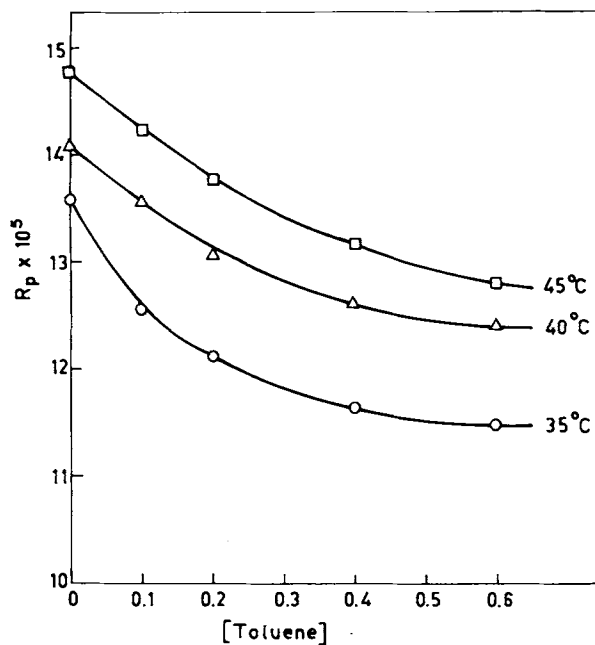
$[H_2SO_4]$ $\text{mL}^{-1}$	$R_p \times 10^5$		
	35°C	40°C	45°C
0.20	14.690	14.847	15.554
0.25	15.109	15.528	16.078
0.30	15.397	15.606	16.261
0.40	15.528	15.714	16.444
0.50	15.737	15.816	16.496

$[AN] = 0.759 \text{ mL}^{-1}$ ,  $[Ce(IV)] = 0.02 \text{ mL}^{-1}$ ,  $[toluene] = 0.2 \text{ mL}^{-1}$ ,  $[sucrose] = 0.04 \text{ mL}^{-1}$ ,  $[NCTAB] = 0.006 \text{ mL}^{-1}$ , time = 1 h,  $[gl. HOAc] = 1.74 \text{ mL}^{-1}$ .

of more effective species at a higher concentration of acid.

### Effect of Toluene on Rate

The rate of polymerization and percentage conversion decrease consistently with increase in concentration of toluene as shown in Figure 6 at three different temperatures: 35, 40, and 45°C. The rate is high at zero concentration of toluene and it falls sharply until the concentration of toluene attains 0.2 mL<sup>-1</sup> and thereafter the decrease is slow. The propagating polymer chain undergoes termination



**Figure 6**  $R_p$  vs.  $[toluene]$  plots.  $[AN] = 0.759 \text{ mL}^{-1}$ ,  $[H_2SO_4] = 0.3 \text{ mL}^{-1}$ ,  $[Ce(IV)] = 0.02 \text{ mL}^{-1}$ ,  $[sucrose] = 0.04 \text{ mL}^{-1}$ ,  $[gl. HOAc] = 5.22 \text{ mL}^{-1}$ ,  $[NCTAB] = 0.006 \text{ mL}^{-1}$ , time = 1 h.

by the retarder, toluene, by hydrogen abstraction, which leads to the formation of polymer and a resonance-stabilized free radical ( $A^*$ ).

### Effect of Salt and Solvent

The effect of various inorganic salts and organic solvents is demonstrated in Table II. All the salts depress the  $R_p$  and  $\text{CuSO}_4$  depresses it considerably. If a salt is added, the effect of the charge of the ionic micelle is to attract more of the ions of opposite charge than that which corresponds to electrical neutrality into the ionic atmosphere, thus giving a screening effect that reduces the repulsion between the ionic ends of the soap and resulting ions of approach.<sup>14</sup> This increases the size of the micelle and reduces the CMC. Thus, the concentration of [NCTAB] lies above the CMC value, for which  $R_p$  decreases on addition of salts. The maximum depression in case of  $\text{CuSO}_4$  may be due to the dissociation of the added salt that interferes with the normal polymerization process, resulting in premature termination of the growing polymer chain.

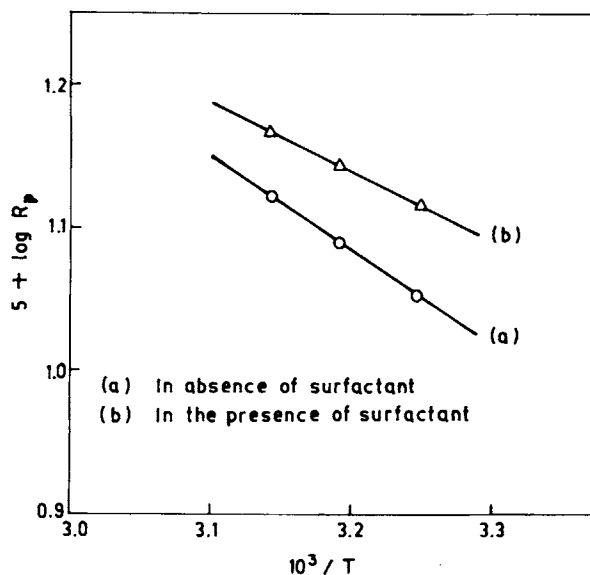
The effect of organic solvents when added in equal proportions (5% v/v) was found to be in the following order: control > methanol > acetone > DMF > dioxane.

This can be explained in terms of solubilization of the solvent molecule inside the micelle. The presence of an —OH group in methanol involves solvophobic interaction, and this is the case of micellization. For the NCTAB– $\text{H}_2\text{O}$ – $\text{CH}_3\text{OH}$  system, the diffusion coefficient of micellar aggregate is probably higher than that of NCTAB– $\text{H}_2\text{O}$  alone. This fact is in agreement with that reported by Ionescu et al.<sup>15</sup> Therefore, the  $R_p$  value of the increase of methanol does not change appreciably. Similar

**Table II** Effect of Solvent and Salt at 45°C

Name of Solvent 5% (v/v)	$R_p \times 10^5$	Name of Salt (0.01 mL <sup>-1</sup> )	$R_p \times 10^5$
Control	16.392	Control	16.901
Methanol	15.816	$\text{CuSO}_4$	8.222
Acetone	15.213	$\text{MnCO}_3$	8.798
DMF	15.135	NaCl	16.339
Dioxane	2.932	$\text{K}_2\text{SO}_4$	16.615

[AN] = 0.759 mL<sup>-1</sup>, [ $\text{H}_2\text{SO}_4$ ] = 0.3 mL<sup>-1</sup>, [toluene] = 0.2 mL<sup>-1</sup>, [sucrose] = 0.04 mL<sup>-1</sup>, [Ce(IV)] = 0.02 mL<sup>-1</sup>, [NCTAB] = 0.006 mL<sup>-1</sup>, time = 1 h, [gl. HOAc] = 1.74 mL<sup>-1</sup>.



**Figure 7** Arrhenius plots: (a) in absence of surfactant; (b) in the presence of surfactant. [AN] = 0.759 mL<sup>-1</sup>, [ $\text{H}_2\text{SO}_4$ ] = 0.3 mL<sup>-1</sup>, [toluene] = 0.2 mL<sup>-1</sup>, [gl. HOAc] = 2.61 mL<sup>-1</sup>, [sucrose] = 0.04 mL<sup>-1</sup>, [Ce(IV)] = 0.02 mL<sup>-1</sup>, [surfactant] = 0.006 mL<sup>-1</sup>, time = 1 h.

observations have been made in the case of acetone and DMF. The inhibiting effect of acetone methyl alcohol and DMF to micellization at low concentrations is negligible and is less than that of dioxane. This is due to the formation of hydrogen bonds between dioxane and water.

### Effect of Temperature

The emulsion polymerization of AN was studied in the temperature range 35–45°C. The rate of polymerization as well as the % conversion increases on increasing the temperature. The effect of temperature is demonstrated in Figures 1–6. The overall activation energy of AN polymerization in the absence and presence of 0.006 mL<sup>-1</sup> [NCTAB] was found to be  $3.140 \times 10^3$  and  $2.355 \times 10^3$  cal/mol. In the presence of the surfactant, the activation energy is low in comparison to that without surfactant, but the difference is not too large because Ce(IV)–sucrose is a good redox initiator for the polymerization of AN (Fig. 7).

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## REFERENCES

1. J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Molecular Systems*, Academic Press, New York, 1975.
2. J. Barton, V. Juranicova, and V. Vaskova, *Makromol. Chem.*, **186**, 1943–1949 (1985).
3. J. Barton, V. Juranicova, and V. Vaskova, *Makromol. Chem.*, **186**, 1935–1941 (1985).
4. O. K. Kim, in *Micellization, Solubilization and Microemulsions*, Vol. 2, K. L. Mittal, Ed., Plenum Press, New York, 1977, p. 627.
5. J. S. Shukla and D. C. Misra, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 751 (1973).
6. I. Capek, J. Barton, and E. Orotinova, *Acta Polymer.*, **36**, 187 (1985).
7. M. Uchida and H. Nagao, *Bull. Chem. Soc. Jpn.*, **30**, 311 (1957).
8. M. Uchida and H. Nagao, *Bull. Chem. Soc. Jpn.*, **30**, 314 (1957).
9. L. F. Antonova, G. V. Lepljanin, E. E. Zaer, and S. R. Ralikov, *Vysokomol. Soedin, Ser. A*, **20**, 687 (1978).
10. J. H. Baxendale, M. G. Evans, and J. K. Kilham, *Trans. Faraday Soc.*, **42**, 674 (1946).
11. M. L. Corrin, S. C. Lind, and W. D. Harkins, University of Chicago, unpublished.
12. R. S. Stearns, H. Oppenheimer, E. Simon, and W. D. Harkins, *J. Chem. Phys.*, **15**, 496–507 (1947).
13. W. D. Harkins, Three private communications to the Office of Rubber Reserve.
14. W. D. Harkins, *J. Polym. Sci.*, **5**(2), 217 (1949).
15. L. G. Ionescu, L. Stalein Romanesco, and F. Nome, *Surfactants in Solution*, K. L. Mittal and B. Lindmann, Eds., 1982, Vol. II, p. 789.

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