

Some Observations in the Aqueous and Emulsion Polymerizations of Common Vinyl Monomers Initiated by Sodium Metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) at 50°C

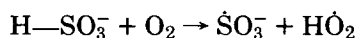
TARUN K. PAUL, UMASHANKAR SATHPATHY, and RANAJIT S. KONAR,* *Chemistry Department, Regional Engineering College, Durgapur-713209, West Bengal, India*

Synopsis

Analytical grade sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) has been found to initiate the polymerizations of methyl methacrylate (MMA) and ethyl methacrylate (EMA) in the aqueous media in the presence and absence of detergents, and of styrene in the presence of detergents only, but it fails to initiate the polymerization of methylacrylate (MA) at low concentrations of the initiator and of acrylonitrile (AN) in the absence of cationic detergent micelles. If a mixture of AN (2.0%, v/v) and metabisulfite (1.60%, w/v) is kept for 16 h at 50°C in the presence of nitrogen, no polymerization occurs, but if a little ferric chloride (0.001%, w/v) is added to this mixture in nitrogen atmosphere, the initiation of AN polymerization is found to occur. MA can be polymerized partly by adding metabisulfite to an aqueous solution of MA and a cationic detergent (above CMC) in the presence and absence of air. Very little polymer is found under similar conditions with AN. No polymerizations were found to occur with any of the above-mentioned monomers if hydroquinone was present in the system. In the $\text{Na}_2\text{S}_2\text{O}_5$ —MMA and $\text{Na}_2\text{S}_2\text{O}_5$ —EMA systems, the average rates of the aqueous polymerizations were found to decrease with the increase of the initiator concentrations (from 1.316×10^{-3} to 2.63×10^{-1} m/L) at 50°C in the presence of nitrogen, and to be approximately inversely proportional to the square root of the initiator concentrations. It is suggested that the bisulfite (produced by the reaction of $\text{S}_2\text{O}_5^{2-}$ ions with water) adds to vinyl monomers as well as initiating polymerization reactions by the reduction activation of the monomers in the presence of nitrogen. The presence of bulky groups such as methyl, phenyl, etc., at the β -position of the ethylenic double bond of the monomer, probably prevents or slows down the bisulfite addition reactions due to the steric hindrance, and so the polymerization reactions will predominate in the system of MMA, EMA, and styrene-like monomers. The complex species formed due to the interactions of the cetyltrimethyl ammonium bromide (CTAB) micelles and free CTAB cations with HSO_3^- and $\text{S}_2\text{O}_5^{2-}$ ions initiate the polymerizations of MA and of AN in the presence of nitrogen or air. Cationic detergent micelles protect the monomers from the direct attack of the $\text{HSO}_3^-/\text{S}_2\text{O}_5^{2-}$ ions.

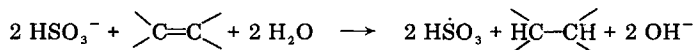
INTRODUCTION

It has been reported by Morton and Landfield¹ that bisulfites add quantitatively to the double bond of a vinyl monomer, viz., methyl methacrylate (MMA), methyl acrylate (MA), acrylonitrile (AN), or methacrylonitrile (MAN), and the addition reactions are found to be very sensitive to the pH of the media. They did not observe any polymerization reaction. Konar and Palit² reported that potassium or sodium bisulfite (HSO_3^-) could initiate the aqueous polymerization of MMA at a pH of about 4–5 (due to the bisulfite alone) in the presence of nitrogen. They suggested that trace of air in the media might have generated the initiating free radicals by the known redox reaction³



* Senior author and to whom correspondence should be addressed.

Mukherjee et al.⁴ later on reported that NaHSO₃ alone could initiate the aqueous and emulsion polymerizations of MMA, EMA, styrene, etc., but failed to initiate the polymerizations of AN, MA, acrylic acid, and vinyl acetate in the presence of nitrogen. They postulated an overall reaction for the initiating radical:



Kim et al.⁵⁻⁸ reported recently that NaHSO₃ could initiate the aqueous polymerization of MMA and acrylamide easily, but the emulsion polymerizations of MA and AN could take place only in the presence of a cationic detergent micelles and in the presence of oxygen only. Later on, Kim⁷ reported that the emulsion polymerization of MA in the presence of CTAB micelles and NaHSO₃ also took place in the nitrogen atmosphere to a negligible extent.

Mukherjee et al.⁴ did not study the kinetics of the polymerization reactions thoroughly. They were interested primarily in the detection and estimation of the end groups of polymers and in the initiator exponent. They determined the initial rate by drawing tangents at the origin of the yield vs. time curves (Hinschelwood's method), which is unreliable. Kim⁸ measured time average rate and assumed it as initial rate. Such assumptions may not be valid, and he did not show the nature of yield-time curves of his systems. He estimated⁶ the rate of bisulfite oxidation from the initial slope in the plot of the oxygen uptake vs. time. Determination of initial rates by this method is now obsolete and unreliable. Besides, none of the authors⁴⁻⁸ have noted the effect of impurities present in the initiator. In view of these uncertainties, we decided to reinvestigate the bisulfite initiated aqueous and emulsion polymerizations of common vinyl monomers. As we did not get a very good quality bisulfite, we used E. Merck (Germany) GR-grade sodium metabisulfite (Na₂S₂O₅) as an initiator of polymerization,⁴ and some experimental observations are reported here.

EXPERIMENTAL

The reagents used were all analytical grade (AR/GR). The detergents CTAB and sodium lauryl sulfate (NaLS), were further purified by recrystallization/precipitation from organic solvents.^{6,9} GR-grade Na₂S₂O₅ of E. Merck (Germany) was stated to contain the following impurities (upper limit): chloride 0.005%, lead 0.001%, copper 0.001%, iron 0.0005%, zinc 0.001%, and arsenic 0.0005%. It was used as such. The monomers were purified and fractionated by vacuum distillation described elsewhere.¹⁰ The purified and dehydrated monomers were also distilled in air/nitrogen atmosphere at atmospheric pressure and collected at their respective boiling points¹¹ just before use. AR/GR grade (of BDH/E. Merck) salts such as NaCl, KCl, KBr, etc. were recrystallized three times from the double distilled water. Analytical grade NaHSO₄, Na₂HPO₄, NaH₂PO₄, and NaHCO₃ (of BDH/E. Merck/Glaxo Lab./Sarabai Merck, India) were used as such for pH measurements.

Polymerizations were carried out in 250-mL pyrex/Corning conical flasks fitted with glass stopper and nitrogen passing arrangement. Total volume of the reactants and the solvent (water) was made 100 mL. The calculated amount of water in the conical flask was saturated with pure nitrogen at 50°C in a water thermostat ($t \pm 0.10$)°C for half an hour with continuous shaking. Then the

monomer was added in the presence of nitrogen, and finally the metabisulfite solution (freshly prepared in N₂ atmosphere) was added quickly in the presence of nitrogen to the reaction flask. The flask was then stoppered properly, the nitrogen supply was cut off, and the mixture was shaken vigorously. The sudden appearance of a haze or turbidity indicated the end of the induction period and the onset of polymerization. Once the polymerization started in the detergent-free system, the stirring was stopped. After a definite time period, the reaction flask was opened and 10 mL of 1.0% hydroquinone solution was added. The mixture was shaken vigorously in air, and filtered through a tared gooch crucible (No. 4) immediately. The polymer was washed thoroughly with hot distilled water, and dried at 60°C in vacuum to a constant weight.

When detergents were used, then either the monomer was added to an aqueous solution of the detergent and metabisulfite or the metabisulfite was added to the aqueous solution of the detergent and the monomer.

Molecular weights of the polymers were determined by the conventional viscometric method. pH of the solutions was measured with a pH meter and a glass electrode (of M/S. Systronics Ltd., Calcutta), which was calibrated against a series of buffer solutions.¹²

RESULTS

Results of this investigation have been summarized in the following tables. MMA can be polymerized easily in the presence and absence of air, and the polymer separated as a precipitate during the reaction, and in the colloidal state if detergents were added to the system initially. No polymerization was found to occur in the presence of hydroquinone. The results of MMA polymerizations have been displayed in Table I. The average rate of polymerization was found to decrease with the increase of metabisulfite concentrations in the range 1.316×10^{-3} (m/L) to 2.63×10^{-1} (m/L). Similar results were obtained from the metabisulfite—EMA system (Table II). Results of styrene polymerization are shown in Table III. It should be noted that the average rate of polymerization

TABLE I
Polymerization of Methyl Methacrylate (MMA) by Metabisulfite at 50°C. Recipe: MMA (1.0%, v/v) Initiator (Na₂S₂O₅) Varies

Initiator (<i>I</i>) (w/v %)	Induction period (min)	Time of polymerization (min)	Conver- sion (%)	Nature of polymer phase	(η) (dL/g)	$\bar{M}_v \times$ 10^{-4}
0.025	2.50	30.0	34.80	Precipitate	2.85	0.372
0.05	2.00	30.0	19.20	Precipitate	2.55	0.322
0.10	2.00	30.0	16.20	Precipitate	2.48	0.309
0.50	1.50	30.0	11.80	Precipitate	1.82	0.207
0.10 + CTAB (0.50%)	0.50	180.0	23.50	Stable colloid	0.52	0.039
0.025 ^a	12.0	30.0	12.00	Precipitate	—	—
0.05 ^a	8.0	30.0	21.90	Precipitate	—	—

^a Polymerization carried out in the presence of air. (η) was measured in benzene at 20°C. (\bar{M}_v) was measured from the equation¹⁸ (η) = $5.50 \times 10^{-3} (\bar{M}_v)^{0.76}$. It should be noted that the molecular weight of the polymers is relatively higher when the separating phase is a precipitate, probably due to the slower rate of termination as the polymeric radicals are likely to be buried in the polymer coils of the precipitated polymers.^{19,20}

TABLE II
 Polymerization of Ethyl Methacrylate by $\text{Na}_2\text{S}_2\text{O}_5$ at 50°C. Recipe: Monomer (1.0%, v/v),
 Initiator (*I*) Varies

(<i>I</i>) (w/v %)	Induction period (min)	Time of polymerization (min)	Conversion (%)	Nature of polymer	(η) ^a (dL/g)	$\overline{M}_v \times 10^{-4}$
0.025	2.50	30.0	74.30	Precipitate	3.19	0.416
0.05	2.00	30.0	49.51	Precipitate	—	—
0.10	2.00	30.0	40.40	Precipitate	1.93	0.205
0.50	2.00	30.0	11.08	Precipitate	1.66	0.165
0.10 + CTAB (1.0%)	1.00	30.0	50.40	Stable colloid	0.757	0.057
5.00	2.00	30.0	2.63	Precipitate	—	—

^a (η) was measured in ethyl acetate at 35°C, and (η) = $8.60 \times 10^{-3} (\overline{M}_v)^{0.71,18}$

of EMA is much higher than that of MMA under identical experimental conditions. The inhibitory effect of the metabisulfite in the styrene–sodium lauryl sulfate system is also pronounced when the initiator concentrations were relatively higher.

AN could not be polymerized either in air or nitrogen, if it were added to a freshly prepared metabisulfite solution. AN did not polymerise even when 5.0% (w/v) metabisulfite was added to the system. This indicates that the iron salt impurity (stated to be 0.0005% maximum in the GR-grade reagent) present in the initiator had no effect on the aqueous polymerization of AN. This monomer can, however, be easily polymerized at 20°C if the metabisulfite were added to an aqueous solution of FeCl_3 (0.001%, w/v), and AN (2.0%, w/v) in the presence of nitrogen, although the conversion is low (Table IV). If AN was added to an aqueous solution of the cationic detergent and metabisulfite, or if the metabisulfite were added to an aqueous solution of AN and the cationic detergent, then no significant amount of polymer was obtained in the presence and absence of air (Table IV).

The behavior of methyl acrylate (MA) was rather different. It was found that if the initiator was in higher concentrations (about 1.0%, w/v), then the initiation of polymerization of MA in the detergent-free system was found to occur in the nitrogen atmosphere, but the conversion was not high (Table V). MA could, however, be easily polymerized if it were added to an aqueous solution of a cationic detergent, CTAB, above CMC and metabisulfite (system A), or if the metabisulfite were added to an aqueous solution of MA and CTAB (system B) in

TABLE III
 Aqueous Polymerization of Styrene Initiated by $\text{Na}_2\text{S}_2\text{O}_5$ at 50°C. Recipe: Monomer, 2.0% (v/v); Sodium Lauryl Sulfate (NaLS), 0.60% (w/v), Time of Polymerization after Induction Period (IP) = 30.0 min.

Initiator (<i>I</i>) (w/v %)	IP (min)	Conversion (%)	Nature of polymer	(η) (dL/g)	$\overline{M}_v \times 10^{-6}$
0.05	1.50	39.48	stable colloid	5.65	2.78
0.10	1.50	67.03	stable colloid	7.99	4.092
0.50	1.00	51.81	stable colloid	5.30	2.26

(η) was determined in toluene at 30°C, and \overline{M}_v was estimated from the equation¹⁸ (η) = $1.60 \times 10^{-4} (\overline{M}_v)^{0.69}$.

TABLE IV
Aqueous Polymerization of AN Initiated by Na₂S₂O₅ at 50°C. Recipe: Monomer, 2.0% (v/v),
Initiator (*I*) Varies

<i>I</i> (w/v %)	Time of polymerization, Conversion			Remarks
	IP (min)	(min)	(%)	
1.0	—	600	nil	No polymerization
5.0	—	300	nil	No polymerization
1.61 + 0.01% FeCl ₃	4.0	60	10.0	
1.61 + 0.01% FeCl ₃	8.0	60	1.5	FeCl ₃ added 16 h after addition of Na ₂ S ₂ O ₅
1.61 + 0.001% FeCl ₃	—	120.0	0.013	FeCl ₃ added after 20 h of the addition of <i>I</i> ; polymer isolated from the solution by adding dilute H ₂ SO ₄
0.076 + CTAB (0.3%)	—	180.0	2.29	In N ₂ atmosphere. AN added to an aqueous solution of (<i>I</i>) and CTAB
0.076 + CTAB (0.3%)	—	180.0	0.45	In N ₂ atmosphere, (<i>I</i>) added to an aqueous solution of AN and CTAB.
0.076 + CTAB (0.3%)	—	180.0	0.48	In air, AN added to aqueous solution of (<i>I</i>) and CTAB
0.076 + CTAB (0.30%)	—	180.0	0.39	(<i>I</i>) added to aqueous solution of AN and CTAB in air

the presence and absence of air. It was found that the yield of polymer in the system A was always higher than that of B for a given residence time (Table V). It was also observed that the aqueous polymerization of MA initiated by the metabisulfites was strongly influenced by the Fe³⁺ ions. If the concentration of FeCl₃ in the reaction flask were 0.00012% (w/v), the average rate of polymerization was found to increase by a factor of about 1.5 (Table V).

It had been noted that the pH of the metabisulfite solutions always decreased if a detergent (cationic or anionic) or a salt such as NaCl, KCl, KBr, etc. were added to the system (Table VI). It was also observed that the pH of KHSO₄, NaHCO₃, or NaH₂PO₄ solutions decreased when CTAB was added to the system (Table VII).

DISCUSSION

It is well known¹³ that when Na₂S₂O₅ is added to water at low concentrations (below 10⁻³ m/L), it is instantaneously converted into bisulfite. Since the polymerization rate decreases with the increase of metabisulfite concentrations (Tables I and II), it appears that the reactive species which are responsible for the initiation of polymerizations, are the bisulfite ions (HSO₃⁻) and not S₂O₅²⁻ ions. Further, it has been shown¹⁴ that if the initial concentration of metabisulfite is 10⁻³ (m/L) or less at 20°C, the equilibrium concentration of S₂O₅²⁻ ions will be almost zero in the aqueous solution due to the reaction:

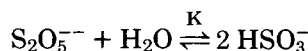


TABLE V
Aqueous Polymerization of Methyl Acrylate (MA) by $\text{Na}_2\text{S}_2\text{O}_5$ at 50°C . Recipe: Monomer 1.0% (v/v), Initiator (I) Varies

(I) (w/v %)	IP (min)	Time of polymerization (min)	Conversion (%)	Nature of polymer phase	(η) (dL/g)	(\bar{M}_v) $\times 10^{-5}$
0.025	—	300	nil	—	—	—
0.05	40.0	120	2.84	Stable colloid	1.14,	3.38
0.50	30.0	120	5.05	Stable colloid	1.10,	3.23
1.00	10.0	60	5.68	Stable colloid	—	—
5.00	6.0	60	Not in measurable quantity	Stable colloid	—	—
1.00 + FeCl_3 (0.012%)	0.50	30	50.31	Stable colloid	0.381	0.936
1.00 + FeCl_3 (0.00012%)	5.00	45	8.00	Stable colloid	1.27	3.93

Recipe: Monomer 2.0 (v/v), (I) = 0.076% (w/v), Time 2 h, CTAB = 0.30% (w/v)

Conversion (%)	(η) (dL/g)	(\bar{M}_v) $\times 10^{-4}$	Remarks
42.80	0.20	2.0	Initiator (I) added to aqueous solution of MA and CTAB in air
28.40	0.35	3.50	(I) added to mixture of MA and CTAB in presence of N_2
61.50	0.15	1.37	MA added to aqueous solution of (I) and CTAB in air
53.15	0.18	1.75	MA added to aqueous solution of (I) and CTAB in presence of N_2

(η) was measured in benzene at 30°C . (\bar{M}_v) was estimated from the equation of Sen et al.,²¹ (η) = $1.282 \times 10^{-4} (\bar{M}_v)^{0.7143}$. No polymerization of MA was found to occur in the presence and absence of air, when CTAB was replaced by NaLS. It is interesting to note that polymerization of styrene occurs in the presence of NaLS (Table III). This supports the idea that the emulsion polymerization of styrene in the styrene—NaLS— $\text{Na}_2\text{S}_2\text{O}_5$ system starts in the aqueous phase and not in the monomer swollen detergent micelles.²²

where $K = 14.0$ (m/L) at 20°C . Since the bisulfite ions exist in two tautomeric forms¹³⁻¹⁵

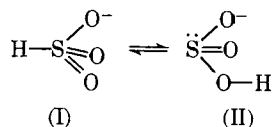


TABLE VI
Effect of Salts on pH of Aqueous Solution of $\text{Na}_2\text{S}_2\text{O}_5$ at Room Temperature, (29°C)

Composition of solution	pH	ΔpH
(1) 0.005(M) $\text{Na}_2\text{S}_2\text{O}_5$	4.25 (in air) 4.30 (in N_2)	
(2) 0.005(M) $\text{Na}_2\text{S}_2\text{O}_5$ + 0.017(M) NaCl	4.09 (in air)	-0.16
(3) 0.005(M) $\text{Na}_2\text{S}_2\text{O}_5$ + 0.170(M) NaCl	3.83 (in air)	-0.42
(4) 0.005(M) $\text{Na}_2\text{S}_2\text{O}_5$ + 0.084(M) KBr	3.89 (in air)	-0.36
(5) 0.005(M) $\text{Na}_2\text{S}_2\text{O}_5$ + 0.130(M) KCl	3.79 (in air)	-0.46
(6) 0.005(M) $\text{Na}_2\text{S}_2\text{O}_5$ + 0.008(M) CTAB	3.19 (in air) 3.29 (in N_2)	-1.06 (in air) -1.01 (in N_2)
(7) 0.005(M) $\text{Na}_2\text{S}_2\text{O}_5$ + 0.008(M) NaLS	3.71 (in air)	-0.54

timate the initial rate of adduct formation for MMA at 50°C and at $(\text{Na}_2\text{S}_2\text{O}_5) = 1.31 \times 10^{-3}$ (m/L) and $(\text{MMA}) = 0.094$ (m/L), and k (rate constant) = 0.837×10^{-2} (L/m/s) as

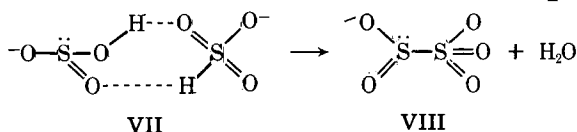
$$\text{initial rate of adduct formation} = k (\text{MMA}) (\text{HSO}_3^-)$$

i.e.,

$$\begin{aligned} \text{rate of adduct formation} &= 0.837 \times 10^{-2} \times 2 \times 1.31 \times 10^{-3} \times 0.094 \\ &= 2.06 \times 10^{-6} \text{ (m/L/s)} \end{aligned}$$

whereas the average rate of polymerformation (i.e., yield of polymer in 30 min/30 min) = 1.82×10^{-5} (m/L/s) under identical experimental conditions. In the case of methyl acrylate, the initial rate of adduct formation is 8.80×10^{-4} (m/L/s) when the $(\text{MA}) = 0.1105$ (m/L), and $(\text{Na}_2\text{S}_2\text{O}_5) = 2.63 \times 10^{-3}$ (m/L), whereas the average rate of polymerization (= yield of polymer in 120 min/120 min) is 4.36×10^{-7} (m/L/s). Thus very little polymerization will occur in the case of MA.

The decrease in the average rate of polymerizations with the increase of the metabisulfite concentrations (Tables I and II) is probably associated with the chain termination reactions by $\text{S}_2\text{O}_5^{2-}$ ions. Golding¹⁴ has shown that an aqueous solution of bisulfite contains four species, viz., I, II, VII, and VIII, the concentrations of which depend on the concentration of bisulfite:



From the data of Golding, we estimate that the equilibrium concentration of metabisulfite ions ($\text{S}_2\text{O}_5^{2-}$) will be appreciable if the initial concentration of metabisulfite added to the system is 10^{-2} (m/L), under our experimental conditions. Kim also noted the fall in the rate of polymerization at higher bisulfite concentrations,⁵⁻⁸ although Mukherjee et al.⁴ did not observe such effects at 35°C when the concentration of NaHSO_3 was as high as 0.20 (m/l). Statistical treatment of the average rate data indicates that the average rate of polymerization is approximately inversely proportional to the 0.62 ± 0.06 power of the metabisulfite concentrations.

The function of the detergents in the bisulfite/metabisulfite systems appears to be twofold: (i) to provide micelles for the solubilization of the monomer and to protect it from the bisulfite addition reactions since HSO_3^- ions cannot enter the micelles (positively or negatively charged) and (ii) to initiate polymerization inside the monomer swollen detergent micelles by the detergent-bisulfite/metabisulfite complex.⁵⁻⁸ Initiation probably takes place on the surface of the monomer-loaded detergent micelles by the process of micellar catalysis. Detergents also stabilize the emulsions and the latex particles during the reaction as suggested by Harkins.

It has been observed in the system of CTAB— $\text{S}_2\text{O}_5^{2-}$ —MA, the yield of polymer is always higher if MA is added to the aqueous solution of CTAB and $\text{S}_2\text{O}_5^{2-}$ (2:1 molar ratio) than that when $\text{S}_2\text{O}_5^{2-}$ is added to the aqueous solution of CTAB and MA. This is probably due to the fact that the added MA distrib-

utes itself between the micellar phase and the aqueous phase, and polymerizations in both the phases take place by the complex of CTAB and $\text{HSO}_3^-/\text{S}_2\text{O}_5^{--}$ ions in the presence of air or nitrogen. The addition reaction of bisulfite with MA will be prevented as there will be very little free bisulfite ions in the aqueous phase under the experimental conditions. On the other hand, if metabisulfite is added to the aqueous solutions of CTAB and MA, then the MA inside the micelles will undergo polymerization due to micellar catalysis, whereas the monomer in the aqueous phase will compete with the detergent micelles for the HSO_3^- ions. This will produce some addition products of bisulfite with the monomer, and so the total yield of polymer will be less in this case for a given residence time. This hypothesis has been tested by adding CTAB to the system of MA and $\text{S}_2\text{O}_5^{--}$ in water at 50°C for 1 h, when very little polymer was obtained. It has also been found that MA polymerization did not take place in the system of NaLS—MA— $\text{S}_2\text{O}_5^{--}$. This observation supports the idea that the micellar complex of CTAB and $\text{HSO}_3^-/\text{S}_2\text{O}_5^{--}$ is responsible for polymerization of methyl acrylate. In the presence of air, oxidation of the complex probably enhances the rate of generation of primary radicals for the polymerization reactions, and so the rate of reaction will be higher.⁶

The yield of polymer in the CTAB— $\text{S}_2\text{O}_5^{--}$ —AN system is very small. This is probably due to the fact that acrylonitrile, being hydrophilic, will remain mainly in the aqueous phase and very little in the micellar phase. Polymerization by the micellar catalysis will be negligible, and so the conversion will be low. This observation differs significantly from that of Kim et al.,⁵⁻⁷ who found identical behavior of AN and MA in the CTAB— HSO_3^- —monomer systems.

It has been observed that the pH of an aqueous metabisulfite solution decreased, when the CTAB was added to it (Fig. 1 and Table VI). It is suggested that the decrease of pH is due to the formation of various types of complexes when additional quantities of H^+ ions are released in the media. The nature of the complexes has been discussed by Kim.⁵⁻⁸ When all the bisulfite and metabisulfite ions will be complexed by the gradual addition of CTAB, the pH of the media will then be independent of the CTAB concentration, as has actually been found in Figure 1. The effect of ionic strength on pH at comparable molar concentrations of CTAB has been checked by adding neutral salts (Table VI). The pH of 0.005(M) Na₂S₂O₅ aqueous solution at 29°C is 4.25 in air, that of

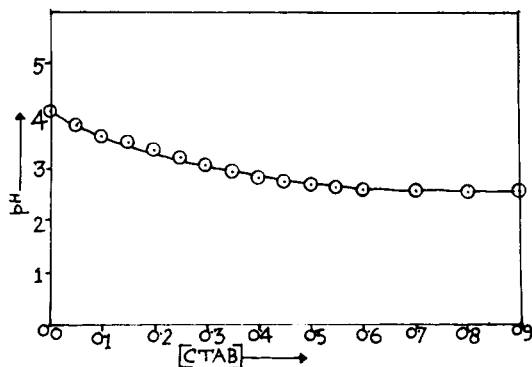


Fig. 1. Plot of pH vs. Cetyl trimethyl ammonium bromide (CTAB) concentrations. CTAB (solid) was added to 0.005 (M) sodium metabisulfite solution (100 mL), and its concentration was expressed as percent (w/v). pH was measured at 29°C (room temperature).

0.005(*M*) $\text{Na}_2\text{S}_2\text{O}_5$ + 0.024(*M*) KBr is 4.05. This shows that the pH change is significant when CTAB is added to the aqueous solution of metabisulfite. In the presence of nitrogen, the pH of the metabisulfite—CTAB mixture is slightly higher, indicating that air oxidizes the micellar complex of metabisulfite/bisulfite ions and CTAB cations, when additional H^+ ions will be released. This is supported by the fact that the pH of the HSO_4^- —CTAB complex in aqueous solution measured in nitrogen atmosphere did not alter in the presence of air. HSO_4^- acid is relatively strong, and its dissociation into H^+ + SO_4^{2-} ions will be almost complete at 25°C (the dissociation constant is 10^{-2} at 25°C). Very few H^+ ions will therefore be released when the micellar complex of CTAB and $\text{HSO}_4^-/\text{SO}_4^{2-}$ will be oxidized in air. CTAB also lowers the pH of NaH_2PO_4 and of NaHCO_3 solutions (Table VII). All these facts suggest that the micelles of the cationic detergent form complexes with the anions of the salts and thereby release additional H^+ ions in the media. Some of the CTAB— HSO_3^- complexes have been identified by Kim⁵⁻⁷ spectrophotometrically and our observations confirm his findings.

Since the pH of a solution is related to the activity of H^+ ions (a_{H^+}), i.e.,

$$\text{pH} = -\log_{10} (a_{\text{H}^+}) = -\log_{10} (c_{\text{H}^+} \times f_{\text{H}^+})$$

and the activity coefficient (f) changes with the ionic strength of the media, it is evident that pH will change when neutral salts are added to the media. It has been found that the pH decreases when neutral salts are added (Tables VI and VII), but the pH of NaHCO_3 solution increased when KBr was added to it. The reason is not clear to us. The change of pH in NaH_2PO_4 solution due to KBr addition is very small possibly because of the buffering action of H_2PO_4^- and HPO_4^{2-} ions,^{12(a)} the HPO_4^{2-} ions being produced by the dissociation of H_2PO_4^- ions.

The effect of impurities (metal ions) present in the initiator is remarkable and is very specific for a monomer in the polymerization reactions. 0.00012% FeCl_3 accelerates the polymerization of MA, while it has no effect on the polymerization of AN initiated by the metabisulfite (Tables IV and V).

In conclusion, it may be said that $\text{Na}_2\text{S}_2\text{O}_5$ differs significantly from NaHSO_3 as an initiator of polymerizations:

- (a) $\text{S}_2\text{O}_5^{2-}$ ions do not initiate polymerization, but act as a retarder;
- (b) the average rate of polymerization decreases at higher initiator concentrations in the range 1.136×10^{-3} to 10^{-1} (m/L);
- (c) AN can hardly be polymerized either in the AN— $\text{S}_2\text{O}_5^{2-}$ or AN—CTAB— $\text{S}_2\text{O}_5^{2-}$ systems in the presence or absence of air;
- (d) MA can be polymerized alone by $\text{Na}_2\text{S}_2\text{O}_5$ to a very limited extent if the concentration of the initiator is relatively higher;
- (e) MA can be polymerized in the system, MA—CTAB— $\text{S}_2\text{O}_5^{2-}$ in the presence and absence of air; the yield of polymer is always higher in the presence of air;
- (f) ferric salts at very low concentrations (ca. 10^{-4} %, w/v in the reaction flask) have a remarkable effect in the aqueous polymerization of MA.

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