

## NOTE

**Permanganate-Oxalic acid Reaction: Autocatalytic Suppression in Surfactant Media**

R. VENKATARAMAN and P.S. RAGHAVAN\*

*Department of Chemistry, Madras Christian College, Tambaram, Chennai-600 059, India*

The permanganate-oxalic acid reaction is a well known autocatalytic redox reaction, due to the catalytic effect of the  $Mn^{2+}$  ion formed during the course of the reaction. In the present paper, it has been shown that this autocatalysis can be suppressed in micellar media.

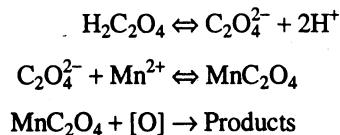
The title reaction is well known for its two important characteristics, viz., (i) the reaction is usually carried out only at high temperature, at about 70°C and (ii) it is autocatalytic. We have already reported<sup>1</sup> a simple titrimetric procedure that is operative at room temperature (30°C) itself, involving surfactant media. In continuation of this work, we undertook a study on the kinetics of this reaction in surfactant media.

The kinetics of this reaction was carried out at 30°C by keeping the relative concentrations of the reactants  $\geq 10$ , in sodium laurylsulphate (NaLS) media in the presence and absence of sulphuric acid. The aliquots (5 mL) were withdrawn from the reaction mixture consisting of oxalic acid ( $10^{-2}$  M),  $KMnO_4$  ( $10^{-3}$  M) and NaLS ( $10^{-4}$ – $10^{-3}$  M) at different time intervals and titrated against standard ferrous ammonium sulphate solution. The first order rate constants were evaluated from the titre values.

As expected from the autocatalytic nature of the reaction, there was an upward drag in the rate constants with increasing percentage of the reaction. Assuming that the first rate constant ( $k$ ) which is usually obtained at the initial stages of the reaction (< 5% completion) is independent of any autocatalytic influence, the ratio  $k'/k$ , where  $k'$  is the rate constant at any higher percentage of completion of the reaction, has been taken to be an estimate of the magnitude of the auto-catalysis. This ratio (say,  $k_{ac} = k'/k$ ) has been evaluated at different percentage completion of the reaction in NaLS media in the presence and absence of 0.1 N  $H_2SO_4$ . For an increase in [NaLS] in the absence of acid, the values of  $k_{ac}$  were found to decrease at least threefold (Table-1), while in presence of acid  $k_{ac}$  is not significantly affected. The reduction of  $k_{ac}$  values by 3 times indicates that the autocatalysis is suppressed to that extent by the surfactant media.

The autocatalysis has been attributed to the  $Mn^{2+}$  ion produced in the reaction.

which would form manganous oxalate which undergoes oxidation more easily than oxalic acid itself.



The autocatalytic suppression by the addition of NaLS could be due to any one or both of the following: (i)  $\text{Mn}^{2+}$  ions getting exchanged for the counter ions on the anionic surfactant micelles, and (ii) addition of the surfactant would reduce the polarity of the medium and hence favours the undissociated oxalic acid then the formation of the oxalate ion thereby reducing the concentration of the more active manganese oxalate.

TABLE-1  
THE RELATIVE MAGNITUDE OF  $\text{Mn}^{2+}$  AUTOCATALYSIS  
IN THE ABSENCE OF ACID

[NaLS]M $\times 10^4$	k'/k values at the completion of		
	15%	50%	65%
3.0	1.40	2.84	3.29
4.0	1.19	2.61	2.98
5.0	0.74	1.35	1.77
8.0	0.43	0.96	1.42

### REFERENCES

1. D. Suresh Ponraj, R. Venkataraman and P.S. Raghavan, *J. Chem. Educ.*, **67**, 621 (1990).

(Received: 11 January 2001; Accepted: 5 May 2001)

AJC-2349