Reply to the Comments by L'. Adamčiková, Z. Farbulová and P. Ševčik on "Belousov−Zhabotinsky Oscillations in Bromate−Oxalic Acid−$MnSO_4$−H_2SO_4−Acetone System in Nonionic Surfactant Medium. A Calorimetric Study".

Sudeshna Biswas,[†] Kallol Mukherjee,[‡] Dulal Chandra Mukherjee,[§] and Satya Priya Moulik*,[†]

Centre for Surface Science, Department of Chemistry, Jadavpur University, Calcutta- 32, India, A.P.C. College, New Barrackpur, 24 Pgs. (North), West Bengal, India, and Department of Chemistry, University of Calcutta, Calcutta-9, India

Received: April 9, 2002

It is known that in the bromate−oxalic acid−$MnSO_4$−H_2SO_4−acetone reaction, acetone scavenges the Br_2 formed during the process and the reaction oscillates. In the absence of the scavenger acetone, the oscillation is not observed. In the study of the reaction, we have observed that nonionic surfactants TritonX-100, Tweens, and Brijs can inhibit the reaction, and at low concentration of $\sim 10^{-5}-10^{-4}$ mol dm^{-3} they can totally inhibit the process. The results have been published in *J. Phys. Chem. A*, **2001**, *105*, 8857.

Adamčiková et al. have commented that in the presence of nonionic surfactant, the reaction becomes complex and bromate can oxidize the nonionic surfactant to produce Br_2. In the presence of the nonionic surfactant, an extra amount of Br_2 is formed, which may be the reason for the inhibition of the otherwise oscillatory process. Adamčiková et al. have also shown from spectrophotometric method the extent of Br_2 formed by reacting with bromate at the concentration of TX-100 that causes complete inhibition of the process. They have even reported the kinetics of the Br_2 decay after its formation.

To us it is a good observation. Oxidation of nonionic surfactants having hydroxyl groups in the molecule is a possibility, which we did not consider. We were of the understanding that the formation of Br_2 by the oxidation of oxalic acid would be much more compared to that with the nonionic surfactants at very low concentrations such as $10^{-8}-10^{-4}$ mol dm^{-3} used in the study.

We have now performed the Br_2 evolution experiment in a Shimadzu (Japan) UV−Vis spectrophotometer (using 1 cm silica cuvettes) in the absence and presence of oxalic acid with surfactant solutions of TX-100, Tween 20, Tween 60, and Brij 56. In the experiment with bromate/H_2SO_4/TX-100 (TX 100 = 2×10^{-4} mol dm^{-3}), we have observed minor and weakly increasing evolution of Br_2. We have not observed any growth and decay of the halogen as observed by Adamčiková et al. In the experiment with bromate/oxalic acid/H_2SO_4/acetone/TX-100 or Tween 20 or Tween 60 or Brij 56, we have observed comparable evolution of Br_2 with and without the nonionic surfactants. In fact, even a lower rate of evolution of Br_2 has been observed for Tween 60 having one order less concentration than Tween 20 required to completely inhibit the oscillatory reaction. Thus, the length of the hydrophobic tail has some influence on the inhibitory effect of the surfactant, which we have reported in our paper.

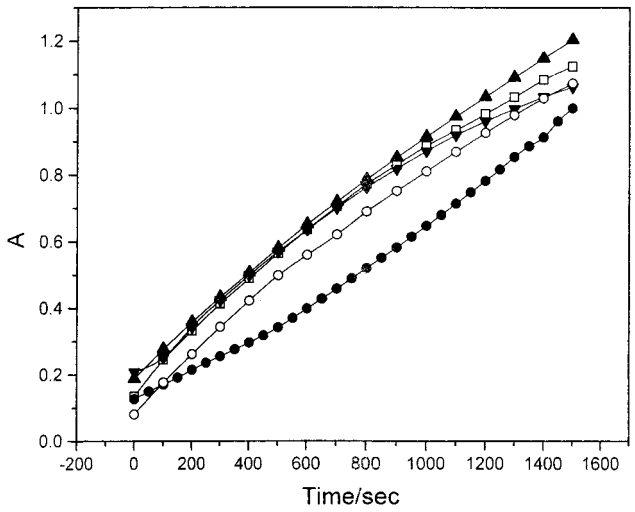

Figure 1. Absorbance (A) of evolved Br_2 at 400 nm in the oxalic acid (0.0625 mol dm^{-3})−bromate (0.14 mol dm^{-3})−H_2SO_4 (1.25 equiv dm^{-3})−acetone (1 mol dm^{-3}) system in the presence and absence of nonionic surfactants at 298 K. □, no surfactant; ●, TX-100-(4×10^{-4} mol dm^{-3}); ▲, Bj-56 (4×10^{-4} mol dm^{-3}); ▼, Tw-20 (4×10^{-4} mol dm^{-3}); ○, Tw-60 (2×10^{-5} mol dm^{-3}).

Our results are depicted in Figure 1. It can be seen that the production of Br_2 goes on increasing with a leveling effect in the cases of Tweens and Brij. The trend is different with TX-100; it tends upward with a shallow upward curvature. It may be mentioned that although the total time for observation in the present experiments was 1500 s, in the reported calorimetric studies, the elapsed time was within 600 s.

We thus make the following conclusions. (1) The evolution of Br_2 in the oscillatory mixture with and without the nonionic surfactants follows similar trends without showing a fall in concentration. (2) The evolution of Br_2 in the main reaction is guided by [oxalic acid]. (3) The trend of formation of Br_2 in the presence of TX-100 differs from the trends of Tweens and Brij. (4) In our opinion, some species other than Br_2 formed during the reaction is responsible for inhibiting the reaction. These species may be the products of oxidation of surfactants. Alternatively, some vital products of the main reaction are removed from the reaction sphere by the nonionics and/or their oxidative products to inhibit the oscillatory process. There, thus remains further scope for study of the present oscillatory system using different kinds of nonionic and ionic surfactants.

Acknowledgment. We thank Mr. Arindam Chatterjee for performing the spectrophotometric measurements.

* Corresponding author.
[†] Jadavpur University.
[‡] A.P.C. College.
[§] University of Calcutta.

10.1021/jp0209345 CCC: $22.00
Published on Web 07/03/2002