Effects of sodium dodecyl sulphate concentration on the autooxidation of 3,5-di-*tert*-butylcatechol in solutions of hydrated transition metal ions

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Abstract

The rates of the autooxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) in transition metal ions (Cu^{2+}, Co^{2+}, Mn^{2+}) in the presence of sodium dodecyl sulphate were investigated at 25°C in the acidic pH region. The results show that the maximum rate enhancement occurs at the cmc region.

Keywords: Autooxidation ; 3,5-di-*tert*-Butylcatechol; Transition metal ions; SDS

Recently, we have published a report on the rate enhancing effects of some hydrated transition metal ions on the autooxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) in the presence of sodium dodecyl sulphate (SDS) [1]. In the paper, rates based on a fixed concentration of SDS only were measured and therefore the conclusions drawn may not be general. Subsequent to its publication, it was found that the rate constant reported for the Cu^{2+} ion system is in error [2]. Since then, we have therefore carried out more work in this area, yielding some interesting findings, which rectify the errors reported in the earlier paper.

The experimental procedures, which include spectrophotometric method of monitoring the oxidized product, 3,5-di-*tert*-butyl-*o*-benzoquinone and data treatment are similar to those reported

earlier [1]. The observed first order rate constants were obtained under the following conditions: Same starting pH, same initial oxygen (air saturated), 3,5-DTBC (4.48×10^{-5} M) and metal ion concentrations (1.8 mM). The metal ions chosen for study are Cu^{2+}, Co^{2+} and Mn^{2+}. Due to the extreme slowness of the observed rate in the cases of Co^{2+} and Mn^{2+} at pH = 5.0, these two systems were investigated at pH = 6.0. Data were collected over a period of 2000 to 3000 s depending on the magnitude of the rate constant.

The K_{obs} vs. [SDS] plots for the three metal ions are shown in Fig. 1. In all of the cases, the observed rate constant increases initially with the concentration SDS, reaching a maximum at around 2 mM concentration and falling off above that concentration.

At the beginning, the increase in rate can be ascribed to the concentration of the metal ions and the substrate, 3,5-DTBC, in the micellar region.
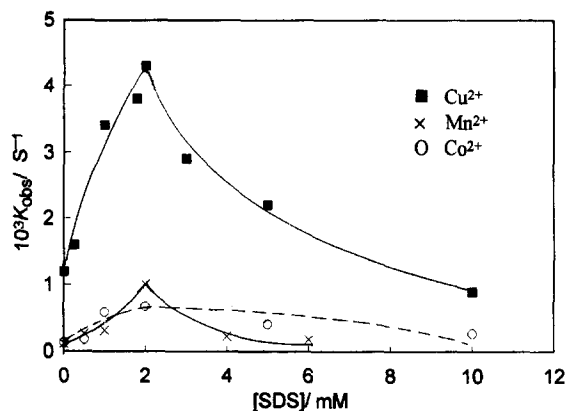
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Fig. 1. Effects of SDS concentrations on the rate constants for the autooxidation of 3,5-DTBC (0.0448 mM) in 1.8 mM aqueous metal ion solutions at 25°C and pH = 5.0 (Cu^{2+}) and pH = 6.0 (Co^{2+}, Mn^{2+}).

The maximum rate at around 2 mM is consistent with the cmc values of SDS in the presence of 1.8 mM metal ions. In fact, for the sample of SDS used in this work (Fluka; > 99% purity), the cmc values as determined by the surface-tensiometric method are in the region 1.5–2.0 mM in the presence of 1.8 mM metal ions. It is interesting to note that micellization causes the rate to increase in spite of the expected lowering of pH in the interface region of the sulphate headgroup [3], which would lead to a rate inhibition effect [4].

The decrease of the rate constants above the cmc may be due to the dilution of the metal ions and the substrate molecules in the micellar medium as the concentration of the micelles increase with increasing surfactant concentration. In the extreme, the combined effects of the pH and dilution can even decrease the rate to that lower than that of the pure metal ion alone (see the plot for the Cu^{2+} ion).

In conclusion, this short note serves to correct the erroneous results reported earlier. The study shows that the occurrence of rate enhancement or retardation would depend on the concentration of the anionic surfactant and the maximum rate enhancement occurs at the cmc region.

Acknowledgements

References

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