

Autocatalysis in Surfactant Systems

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Autocatalysis in Surfactant Systems: Kinetics & Model of Tertiary Amine Oxidation in Water

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With increasing concerns regarding global warming, the chemical industry has been moving towards more sustainable processes. A main focus has been the reduction of solvents in chemical reactions. Eliminating solvents from processes can lead to great improvements in sustainability and process economy [1,2].

One such reaction which is traditionally produced in the industry using solvents is the oxidation of fatty tertiary amines to amine oxides with hydrogen peroxide; in a batch process [3]. If solvents are eliminated, this reaction begins as a biphasic mixture due to the presence of an organic (tertiary amine) and aqueous (hydrogen peroxide) phase. As the tertiary amine oxides are formed, the reactants are solubilized by the zwitterionic, surface active amine oxides. This solubilization effect greatly increases the reaction rates compared to the initial biphasic mixture. Thus, tertiary amine oxidations show typical autocatalytic reaction behavior. This inherent characteristic can therefore be used to develop a more sustainable process with reaction rates comparable to solvent systems.

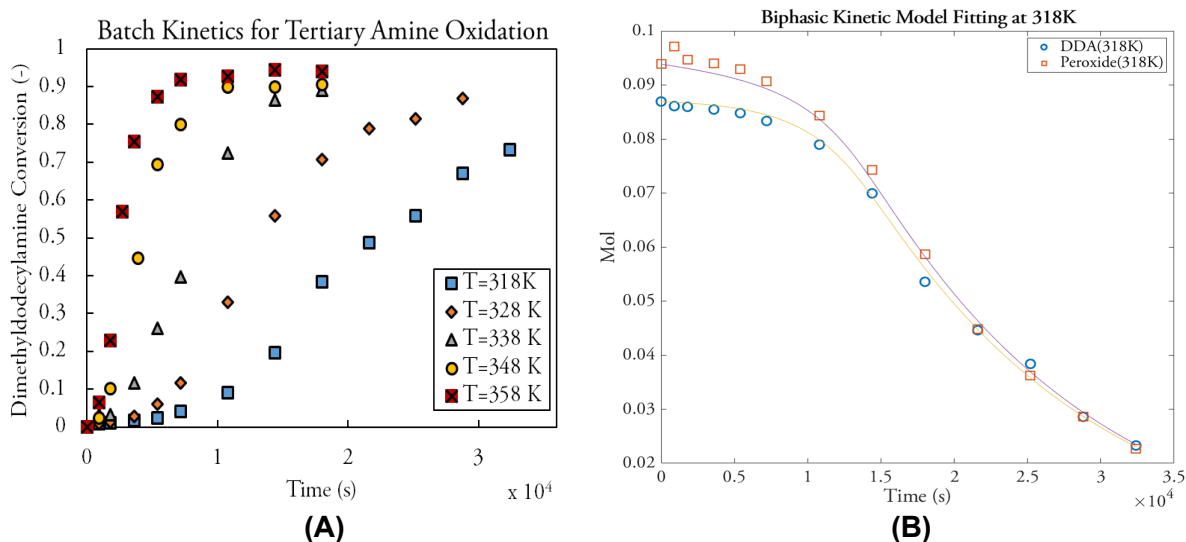


Figure 1: A) Kinetic data obtained for tertiary amine oxidation. B) An example of the fitting obtained for the modified phase transfer model.

The results obtained with batch experiments at 318-358K (Fig 1A) confirm that the reaction is kinetically limited and illustrates autocatalytic behavior. There is however, an upper limit on the temperature as degradation of the amine oxides occurs at higher values [4].

The reaction can be described by a phase transfer model as suggested in literature [5]. In this model, initially, there is only surface reaction at the interface of the organic and aqueous phases which forms amine oxides. At the critical micellar concentration (cmc) of the amine oxides, micellar structures form which solubilizes the organic phase. This leads to reactions at the micellar interface. Here, reaction rates increase drastically due to the increase in the surface area. While there is good agreement between this model and the data, we have observed that

the acceleration of the reaction occurs at concentrations of amine oxide much higher than the cmc. Therefore, we have also investigated an alternative model for micellar autocatalysis based on interfacial tension and energy dissipation rates.

The Arrhenius analysis (Fig 2A) illustrates that the activation energy of the pseudophase/micellar reaction is almost half of the surface reaction activation energy (41 kJ/mol vs 83 kJ/mol). Consequently, a simple method which can be used to accelerate the reaction times is initially seeding the reaction mixture with amine oxides^[6] (Fig 2B). This method already illustrates how solvents can be eliminated from this reaction while making reaction times/reactor volumes more viable for sustainable processes.

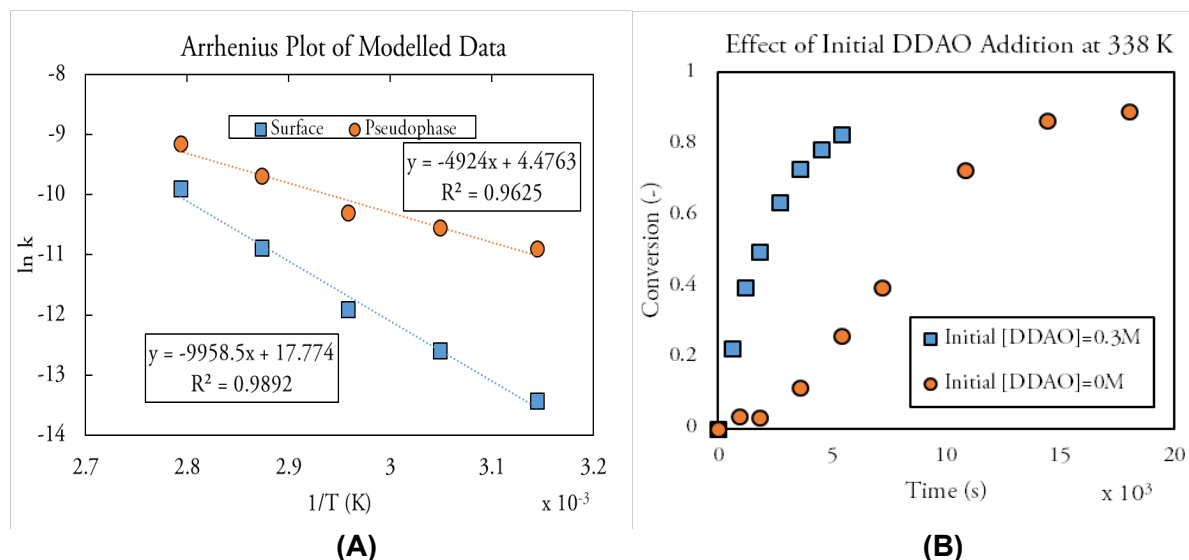


Figure 2: A) Arrhenius analysis of the surface reaction vs the pseudophase reaction B) Results illustrating the acceleration obtained in batch by initially seeding with amine oxide.

The results presented in this abstract illustrate how we are better able to design sustainable and/or continuous processes which uses the micellar autocatalytic properties inherently existing in the reaction to eliminate the use of solvents. The understanding of the intrinsic reaction kinetics and mechanism therefore aids in making existing industrial processes more sustainable. We will further discuss other methods, such as catalysis which can further aid to bridge the gap between the reactions times observed with solvent and the neat system.

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