

INFLUENCE OF SUPERCRITICAL CO₂ IN THE REACTIVITY OF A REACTIVE DYE WITH A MODEL ALCOHOL IN A TUBULAR REACTOR

M.V. Fernandez Cid*^a, M. van der Kraan^a, W.J.T. Veugelers^b, G.F. Woerlee^b, G.J. Witkamp^a

^aDelft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

^bFeyeCon D&I B.V. Rijnkade 17A, 1382 GS Weesp, The Netherlands

M.V.Fernandez@wbmt.tudelft.nl

Fax: +31 (0)15 2786975

A novel design tubular reactor has been constructed to study the influence of concentration of supercritical CO₂, as well as the temperature, in the reaction of a dichlorotriazinyl reactive dye and a model alcohol. Reactions were carried out at different pressures (200, 250 and 300 bar), temperatures (100, 120 and 140°C) and concentrations of CO₂. The rate constants and the activation energy were calculated. It has been found that rate constant k_1 increases with the temperature but strongly decreases when the concentration of supercritical CO₂ increases. Unexpectedly k_2 is not affected for the increase of temperature as well as concentration of supercritical CO₂.

INTRODUCTION

During the last decade research has been carried out on the dyeing of textiles in supercritical CO₂ as a substitute for the conventional aqueous (batchwise) dyeing process, which uses large amounts of water. Supercritical dyeing is a new approach in the dyeing industry, where a supercritical fluid is used as a dye solvent. Supercritical carbon dioxide is used because of environmental, economic, and chemical reasons. In this project, reactive dyes have been chosen because they are the only textile dyes designed to form a covalent bond between the dye and the textile. In addition, reactive dyes with two reactive sites present higher fixation on textiles than the corresponding dyes with one reactive site. Therefore, bifunctional reactive dyes tend to exhibit high colour yields whilst offering high wash-fastness properties.

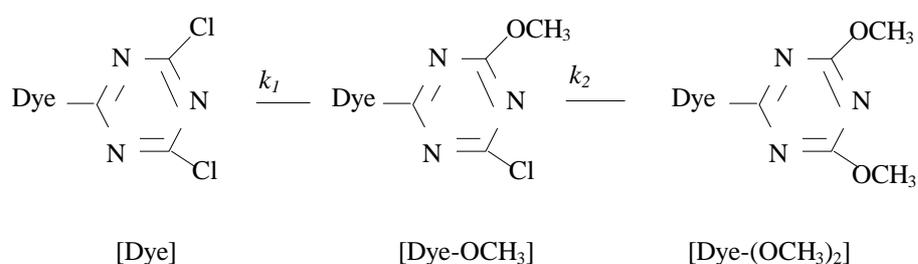
The kinetics of the reactive dyeing of cellulose has been studied by different authors [1, 2], as an essential step in the development of the dyeing process. In order to study the kinetics of the fixation process more readily, the heterogeneous reactive dye-textile system has been replaced by the homogeneous reactive dye-alcohol system. Different alcohols have been proposed as models for cellulose. It has been demonstrated that methanol is a satisfactory and convenient model for cotton [3]. The kinetics of the methanolysis of reactive dyes in supercritical carbon dioxide as a solvent medium has not previously been studied. Recent data from Schmidt [4] shows a low fixation of dichlorotriazinyl reactive dyes on cotton in supercritical carbon dioxide. Consequently, a study of the methanolysis reaction of reactive dyes in supercritical carbon dioxide has been carried out to investigate the efficacy of the substitution reaction under homogeneous conditions.

The methanolysis reaction of a dichlorotriazinyl reactive dye has been previously studied in a batch reactor [5]. Nevertheless more systematic study was required to find out the influence of the pressure, temperature and concentration of supercritical CO₂ on the reaction rate of the methanolysis reaction. Therefore, a continuous tubular reactor was constructed and tested.

THEORY

Bifunctional reactive dyes react with the methanol by a nucleophilic bimolecular substitution mechanism [1]. When the dichlorotriazinyl reactive dye is dissolved in a solution of pure methanol a consecutive methanolysis reaction occurs both in pure methanol and supercritical CO₂.

First order reactions are common and are often observed in solution, particularly if the solvent is one of the reactants and is present in large excess, in which case the reaction may be considered as a pseudo-first order reaction. The concentrations of dye and methanol were therefore chosen to conform to such reaction kinetics, assuming the reaction to be irreversible. The reaction can be written as follows:



The decrease in the concentration of dye can be expressed by the differential equation:

$$\frac{d[\text{Dye}]}{dt} = -k_1 [\text{Dye}] \quad (1)$$

Where [Dye] is the concentration of the bifunctional reactive dye at reaction time t and k_1 is the pseudo-first order rate constant for the formation of monomethoxy-dye, Dye-OCH₃. The peak areas of the components calculated from the HPLC chromatograms are linearly related to their amounts. Equation (1) is integrated and the concentration of reactive dye is replaced by its relative peak areas.

Equation (2.1) is obtained:

$$[\text{Dye}]_t = [\text{Dye}]_0 \exp(-k_1 t) \quad (2.1)$$

Or:

$$\ln[\text{Dye}]_t = \ln[\text{Dye}]_0 - k_1 t \quad (2.2)$$

In order to calculate k_1 and k_2 , a model to predict the concentrations of the three forms

of dye was used. The concentration of the different forms can be calculated using equation (2.1) and the two following equations (3) and (4) [6].

$$[Dye - OCH_3]_t = [Dye - OCH_3]_0 \exp(-k_2 t) + \frac{k_1 [Dye]_0}{k_2 - k_1} \times (\exp(-k_1 t) - \exp(-k_2 t)) \quad (3)$$

$$[Dye - (OCH_3)_2]_t = [Dye]_0 - [Dye - OCH_3]_t - [Dye]_t \quad (4)$$

The best values of the model parameters are then obtained by minimizing the weighed sum of the squares of the difference between the experimental data and the theoretical model.

MATERIALS AND METHODS

I. Materials

The reactive dichlorotriazinyl dye was synthesized by a well known dye manufacturer. The carbon dioxide from Hoek Loos exhibited a purity of 99.97%. The methanol and acetonitrile used were HPLC grade from Rathburn and Acros respectively.

II. Experimental set-up

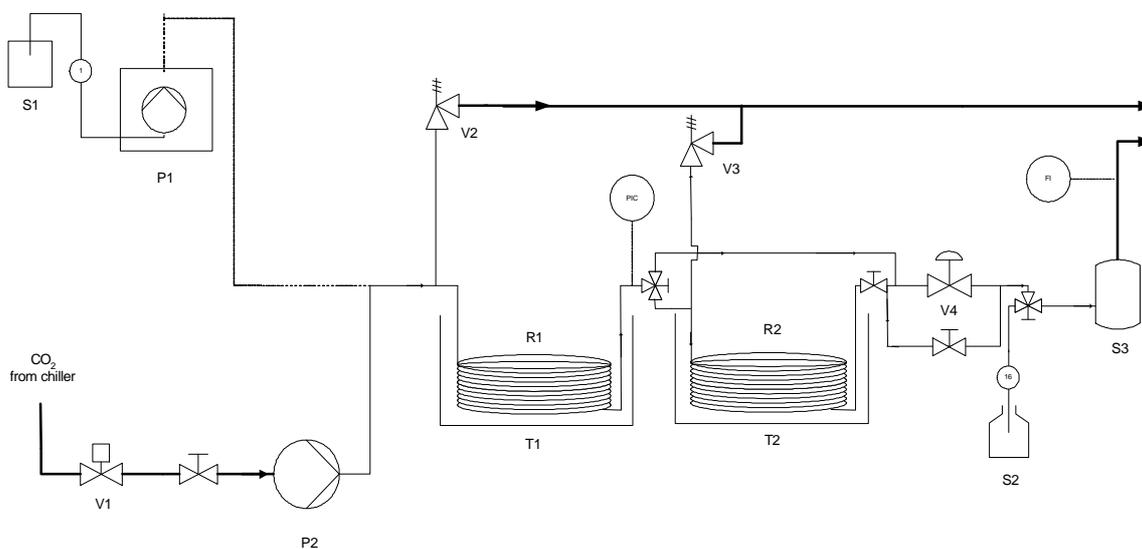


Figure 1: Schematic drawing of the tubular reactor used for the experiments. *S1*, alcohol-dye solution; *P1*, HPLC pump; *P2*, diaphragm CO₂ pump; *R1*, *R2*, tubular reactors; *T1*, *T2*, thermostatic baths; *S2*, sample vessel; *S3*, expansion vessel; *V1*, 3-way valve connected to the reactors; *V2*, back pressure regulator valve.

The reactions were carried out in the tubular reactor (fig 1). A solution of 2ppm of reactive dye in methanol was made and placed in an ultrasonic bath for 5 min to complete the dissolution of the dye. This solution is pumped via a HPLC Gilson 305 pump (P1) and the CO₂ via a Lewa diaphragm (P2). The flows were changed in order that the total flow was always 10ml/min. Both streams were mixed and fed into the reactor (R1), which is placed in

thermostatic bath (T1). The reactor has been design so that the volume can be 290ml (R1) or 670ml (R1+R2) by a 3-way valve (V1). The pressure was kept constant in the system by a back pressure regulator valve (V2) and the CO₂ flow was controlled at the vent with a flowmeter. Study temperatures were 100, 120 and 140 °C and pressures 200, 250 and 300 bar. Samples were collected in the sample vessel (S2) and immediately analyzed by HPLC.

III. HPLC Analysis

The chromatographic analyses were performed with a Chrompack liquid chromatograph with an (250×4.6mm) Intersil 5 ODS-2 column and using 85 % acetonitrile and 15% water as mobile phase. Samples (20µl) were injected with a Marathon autosampler and the chromatographic column was maintained at 22°C. The dye samples were detected at their maximum wavelength (513nm) with a Varian ProStart 310 UV/VIS Detector.

RESULTS AND DISCUSSION

The rate constants k_1 and k_2 were calculated for different concentrations of CO₂ in the methanol-dye-CO₂ mixture. All these experiments were carried out at the same conditions of pressure at 300 bar and temperature 120°C. The results are shown in graphic 1.

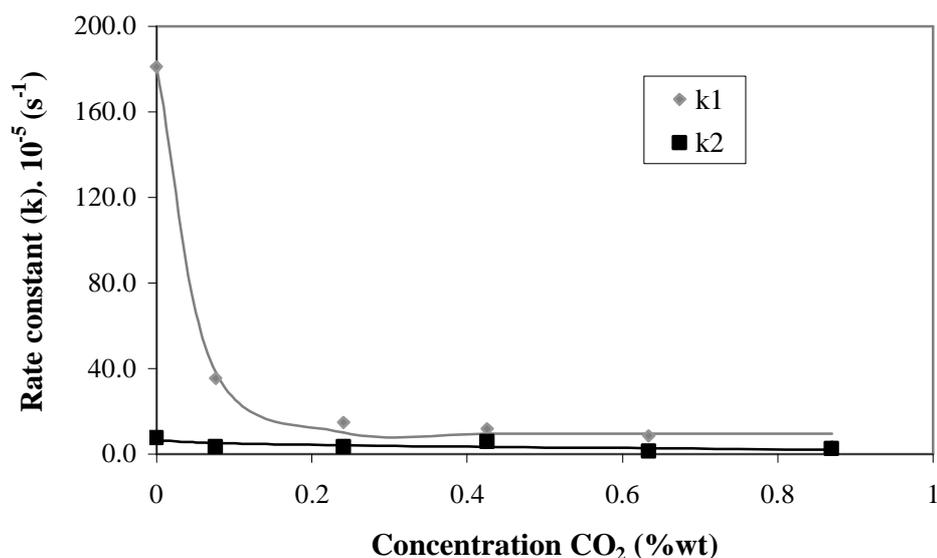


Figure 2: Influence of the concentration of CO₂ (% wt) at the rate constants k_1 and k_2 of the methanolysis reaction at 120°C and 300 bar.

As it can be observed in figure 2 the value of k_1 exponentially decreases with the concentration of supercritical CO₂. Conversely, the value of k_2 is almost constant over the whole concentration range.

In figure 3 it is showed the fitting between the experimental data and the data predicted for the model represented for the equations (2.2, 3 and 4) described in the theory.

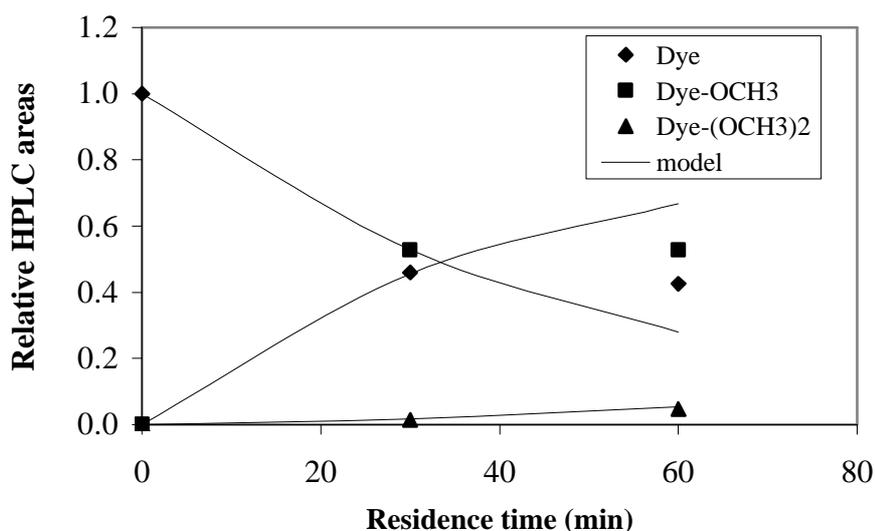


Figure 3: Fitting model-experimental data at 300 bar 120C and 0.08% wt CO₂.

It is observed in figure 3 that the model slightly diverts from the experimental data. This behavior can be owed to the few experimental data at different residence time, and maybe to the influence of the concentration of CO₂ that is not considered in the model, as it was found in the experiments.

The influence of the temperature and pressure were also studied in the tubular reactor. The experiments were carried out at 100, 120 and 140 °C at 200 and 250bar. As it was expected, the rate constant k_1 increases with the temperature, however the rate constant k_2 tends to be unaffected by the temperature. This is clearly an unexpected phenomenon. In figure 4 the results are shown for the values of k_1 and k_2 .

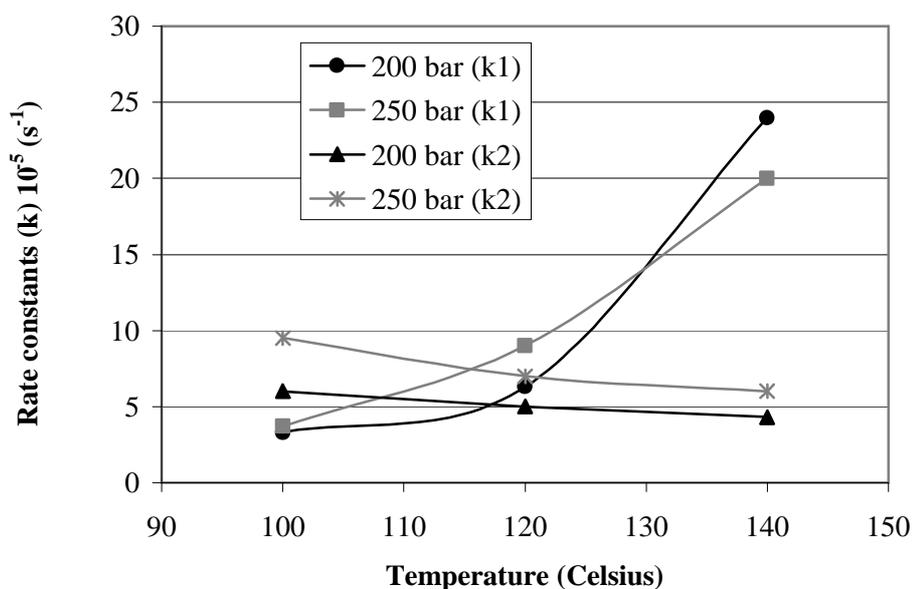


Figure 4: Influence of the temperature in the rate constant k_1 and k_2 at 200 and 250bar

The activation energies for the rate constants k_1 were calculated and are shown in table1.

Table 1: Activation energies, E_a (KJ mol^{-1}) for k_1 at 200 and 250 bar at the range temperature (100-140°C), and the absolute standard deviation (SD (Abs.))

	E_a (KJ mol^{-1})	SD (Abs.)
200 bar	65	1.0
250bar	52	0.8

CONCLUSIONS

A new continuous tubular reactor has been designed and constructed in order to carry out a more systematic study of the kinetics of a dichlorotriazinyl reactive dye.

The rate constant k_1 of the methanolysis reaction of dichlorotriazinyl decreases exponentially with increasing CO_2 concentration. The values of rate constant k_2 are, however, not affected.

As expected, k_1 increases with the temperature but the values of k_2 are almost constant for the whole temperature range. The activation energies for k_1 at 200 bar were 65 KJmol^{-1} , and 52 KJmol^{-1} at 250 bar.

As a result of the decrease of k_1 in the presence of supercritical CO_2 , and the unexpected behavior of k_2 with temperature, more research is required to optimized the experimental conditions in the continuous tubular reactor.

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