Kinetics of Anthraquinone Reduction with Sodium Dithionite in Alkaline Medium

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Currently, the use of redox catalyst additives in wood alkaline pulping is considered to be one of the most important improvements. In 1977 Holton and Chapman experimented several quinone compounds in soda and kraft cookings. Among them, 9,10-anthraquinone (AQ) was the best, evaluated on the basis of pulp yields and the degree of delignification. Later, similar results were obtained by many other authors (Blain, 1979; Lachenal et al., 1979a, b; McDonough and Van Drunen, 1980; Fossum et al., 1980a, b; Bhandari et al., 1982; Wandelt and Surewicz, 1983; El-Saied et al., 1984).

The AQ reduction mechanism in the cooking shows that its reduced form in alkaline medium—the dianion of 9,10-dihydroxyanthracene (AQ^{2-})—is the active phase in the delignification process. Subsequently, the direct use of alkaline salts of AQ^{2-} instead of AQ was proposed by Fullerton (1978, 1979). The main advantage of this substitution is derived from the introduction of the additive in solution, improving its contact with the solid phase and consequently in reducing the catalyst induction time.

The aim of this work is to study the heterogeneous solid-liquid reaction kinetics between AQ and sodium dithionite in an alkaline medium. The dithionite was chosen because of its high reduction power at low temperatures. Runs with different size particles of AQ and sodium dithionite/hydroxide mixtures of several strengths were carried out in a stirred batch reactor under atmospheric pressure and temperatures ranging from 303 to 323 K. Kinetic data were fitted according to the shrinking-core model (SCM) with the surface chemical reaction as the controlling step of the overall process. Rate constants were experimentally determined for the above temperature range. The activation energy was obtained from the Arrhenius law and was found to be 45.0 kJ · mol^{-1}. The application of the SCM to solid-liquid systems was an interesting fact since limited information is available from the literature.

Theory

Thermodynamic equilibrium

The reaction between sodium dithionite and AQ in an alkaline medium can be represented by the equation:

$$Na_2S_2O_4(l) + AQ(s) + 4NaOH \rightleftharpoons 2Na_2SO_3(l) + Na_2AQ(l) + 2H_2O \quad (1)$$

This is a redox process where the following is involved.

$$S_2O_4^{2-} + 4OH^- \rightleftharpoons 2SO_3^{2-} + 2H_2O + 2e^- \quad (2)$$

$$AQ + 2e^- \rightleftharpoons AQ^{2-} \quad (3)$$

Taking into account the standard reduction potentials and the Nernst equation, the equilibrium constant can be calculated as:

$$\ln K = \frac{nF}{RT}(E_{o_{AQ/AQ^{2-}}} - E_{o_{SO_3^{2-}/S_2O_4^{2-}}}) \quad (4)$$

There are no data available for $E_{o_{AQ/AQ^{2-}}}$ derived from the literature, although the existence of AQ^{2-} in a strong alkaline medium has been proved elsewhere (Landucci, 1980). Therefore it is not possible to calculate the equilibrium constant according to Eq. 4. For its estimation the following reactions have been considered (Ksenzhek et al., 1977; Bard, 1975):

$$AQ + H^+ + 2e^- \rightleftharpoons AQH^- \quad E_o = -0.177V \quad (5)$$

$$S_2O_4^{2-} + 2H_2O \rightleftharpoons 2SO_3^{2-} + 4H^+ + 2e^- \quad E_o = -0.416V \quad (6)$$

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where the protonated form of AQH$^-$ appears. Hence

$$\ln K = \frac{nF}{RT}(E_{o_{AQ/AQH^-}} - E_{o_{SO_3^{2-}/S_2O_4^{2-}}}) \tag{7}$$

At 298 K the value obtained for the equilibrium constant is 8.97×10^{-21}. This indicates that AQ reduction cannot be carried out in an acid medium. Taking into account the AQ/AQH$^-$ and $SO_3^{2-}/S_2O_4^{2-}$ systems' conditional potentials, the conditional equilibrium constant is given by

$$\ln K_c = \frac{nF}{RT}(E_{o_{AQ/AQH^-}} - E_{o_{SO_3^{2-}/S_2O_4^{2-}}}) + 6.91\text{pH} \tag{8}$$

With $T = 298$ K and pH $= 14$, hence $K_c = 9.12 \times 10^{21}$. Under these conditions the reaction is practically displaced toward the AQH$^-$ formation and backward reaction is neglected. Due to hard alkaline pH in experimental conditions, the estimation of the equilibrium constant of reaction 1 using Eq. 8 can be worked out reasonably and thus the reaction can be assumed to be irreversible.

Description of kinetic model

Since the solubility of AQ in aqueous media is extremely low, the associated solid diffusion phenomena in the liquid film can be rejected. Obviously, chemical reaction either in the liquid film or in the bulk never takes place. The system studied in this paper deals with a solid-liquid heterogeneous noncatalytic process. The solid phase was nonporous and the liquid phase was a dithionite-sodium hydroxide solution. In an alkaline medium the reaction products are all in solution, so the ash layer formation does not take place during a run.

The kinetic data treatment was carried out by using the isothermal SCM for solid-fluid reaction with changing particle size (Levenspiel, 1962). The following reaction scheme has been considered:

$$A(\text{fluid}) + bB(\text{solid}) \rightarrow \text{Products (fluid)} \tag{9}$$

In the development of the model, overall process rate control by surface chemical reaction was assumed. Taking into account the pseudosteady-state approximation and integrating the mass flow balance equations for spherical solid particles, the reaction time was obtained as a function of the solid fractional conversion, X_B

$$\frac{t}{\tau_S} = 1 - (1 - X_B)^{1/3} \tag{10}$$

where the complete conversion time of the particle, τ_S, is given by

$$\tau_S = \frac{\rho_B R_o}{b k_s C_A} \tag{11}$$

When diffusion is the controlling step, the reaction time, as a function of X_B, is:

$$\frac{t}{\tau_D} = 1 - (1 - X_B)^{2/3} \tag{12}$$

where τ_D is the complete conversion time.

A check of the proposed model was carried out by determining if the influence of the different kinetic variables on the required complete conversion time was in agreement with the model-predicted influence.

Experimental Method

A cylindrical, thermostated, mechanically-agitated glass contactor (500 cm^3 capacity) with four vertical glass baffles mounted against the vessel wall at 90° intervals was used. A 3 cm dia. four-blade stainless-steel turbine impeller was used to ensure good dispersion. At the top, the vessel was provided with standard glass joints for temperature measurement, reactants addition, mechanical agitation, reflux condensation, and sampling draw. The temperature never varied more than ±0.5 K during any of the experiments performed. Nitrogen was used in order to ensure the absence of oxygen, keeping an inert atmosphere in the reactor.

The AQ fractional conversion was calculated from the disodic salt of 9,10-dihydroxyanthracene (Na_2AQ) analysis. The direct measurement of this reaction product is difficult due to its easy oxidation in the presence of air (Armentrout, 1981). To deal with this difficulty, the equivalent AQ was computed by quantitative oxidation with dilute hydrogen peroxide. A filtered sample of known volume is withdrawn from the reactor and oxidized to AQ, which is separated by vacuum filtration, dried, and resolved in cyclohexanone. Afterward, the samples were analyzed by liquid chromatography (HPLC) with the conditions summarized in Table 1.

The variables studied and their application ranges were:

- Temperature: 303–323 K
- $Na_2S_2O_4$ initial concentration: 1.0×10^{-4}–3.8×10^{-4} mol · cm^{-3}
- AQ particle initial average radius: 2.20×10^{-3}–1.15×10^{-2} cm
- NaOH concentration: 1.0×10^{-3}–3.0×10^{-3} mol · cm^{-3}

In a preliminary run carried out with stoichiometric amounts of reactants for reaction 1, 9,10-dihydroxyanthracene deposition was detected due to a medium pH diminution below 9.7. This value corresponds to the pK of the AQH$_2$/AQH$^-$ system. Consequently, a 1.0×10^{-3} mol · cm^{-3} sodium hydroxide concentration limit was chosen as minimum. This value exceeds the stoichiometric amount.

The fractional conversion function, $f(X_B) = 1 - (1 - X_B)^{1/3}$, was obtained and plotted vs. reaction time. From this representation, the complete conversion time of the solid was derived.

Results and Discussion

When applying the shrinking-core model (SCM) for particles of changing size with chemical reaction as the rate-controlling step, film diffusion must be eliminated; in addition, the constancy of fluid reactants concentration has to be satisfied. In

Table 1. Analysis of AQ by HPLC

Sample	9,10-anthraquinone
Column	Perkin-Elmer HC ODS-SilX, 25 × 0.26 cm id Particle size of packing, 10 μm
Mobile phase	Water/methanol, 38/62
Flow	1.5 cm^3 · min^{-1}
Loading	5 μL
Wavelength	254 nm
Temperature	323 K

order to verify whether these conditions are attained in the operating ranges of the variables studied, two sets of runs described below were carried out.

Agitation rate effect on solid fractional conversion

When diffusion control predominates, a rise in the agitation rate leads to a solid-liquid mass transfer coefficient increase and consequently a higher fractional conversion is attained. From Figure 1 it can be clearly seen that AQ fractional conversion is unaffected by varying the agitation speed. This fact shows that the surface chemical reaction controls the overall process in the agitation speed range studied. In accordance with these results, a stirrer speed of 1,200 rev · min^{-1} was chosen for all the experiments.

Dispersed phase fraction effect on solid fractional conversion

During a run, dithionite concentration constancy has to be supported. This condition is obtained when operating with sufficiently high $S_2O_4^{2-}/AQ$ initial concentration ratios. A set of runs with several AQ amounts for the minimum dithionite concentration chosen was carried out.

Figure 2 shows that AQ fractional conversion is unaffected by the solid dispersed phase fraction in the tested range. A minimum AQ concentration value of 2.4×10^{-5} was selected for every experiment. This concentration assure an excess amount of dithionite with respect to the solid sufficient to consider $C_{Na_2S_2O_4}$ invariant throughout a test.

Effect of variables

In order to verify the model validity, the influence of variables on the complete conversion time was studied. Afterward the kinetic constant as a temperature function was calculated.

The kinetic coefficient k_s is an exponential function related to temperature. Therefore, a plot of ln τ_s vs. $1/T$ should yield a straight line. Any variation in the slope of this line obeys either a kinetic equation change or an overall resistance control step change. Figure 3 shows a linear relationship betwen ln τ_S and $1/T$, confirming the validity of the proposed model in the selected temperature range.

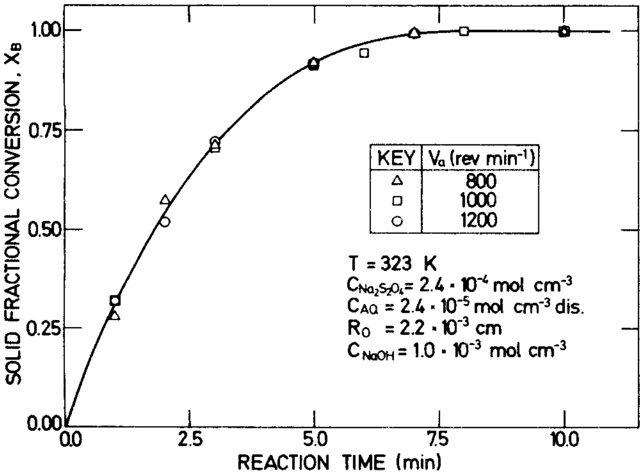

Figure 1. Agitation rate effect on AQ fractional conversion.

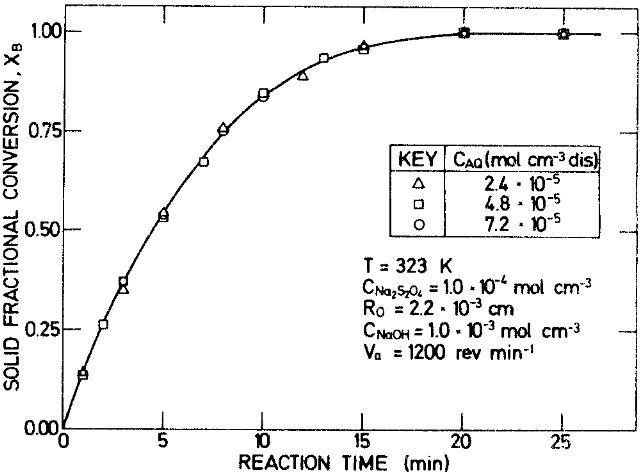

Figure 2. Dispersed phase fraction effect on AQ fractional conversion.

The SCM with chemical reaction as control step predicts an inverse relation between sodium dithionite concentration and complete conversion time, as Eq. 11 indicates. Complete conversion times are plotted in Figure 4 as a function of sodium dithionite concentration for both 303 and 323 K. Straight lines passing through the origin are obtained, confirming that the model fits the data satisfactorily with respect to the fluid reactant concentration.

According to Eq. 11, complete conversion time is a linear function of the initial average solid particle radius. In Figure 5, τ_S vs. average particle radius at 303 and 323 K is represented. It can be seen that for average particle radius smaller than approximately 50 μm and for both temperatures, system behavior agrees well with the spherical geometry model chosen. But for initial particle radius greater than 50 μm, the proposed model is inappropriate.

Reaction model selection was made taking into account that alkali strength affects only the equilibrium, displacing it to the AQ reduction. Therefore, when chemical reaction is the controlling step, the complete conversion time should be independent of

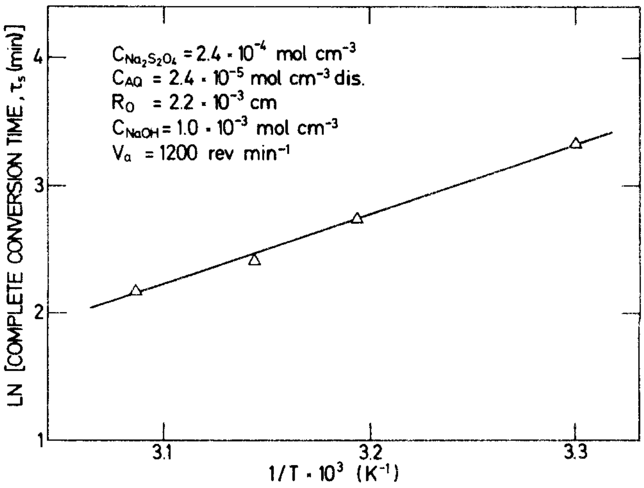

Figure 3. Temperature effect on complete conversion time.

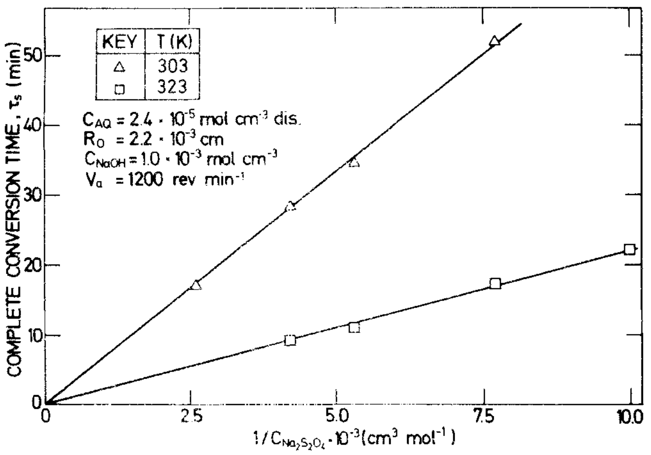

Figure 4. Sodium dithionite concentration effect on complete conversion time.

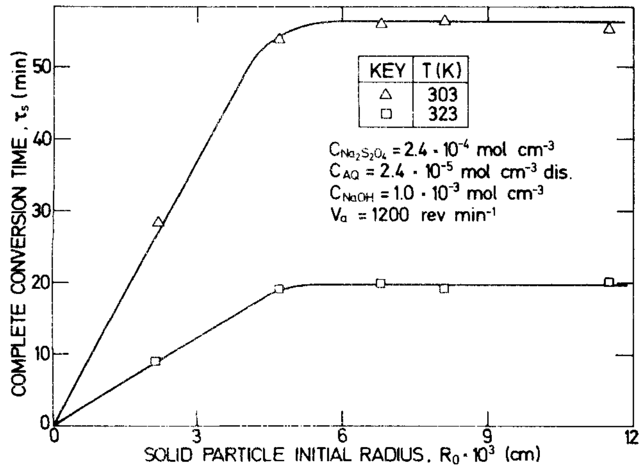

Figure 5. Average solid particle radius effect on complete conversion time.

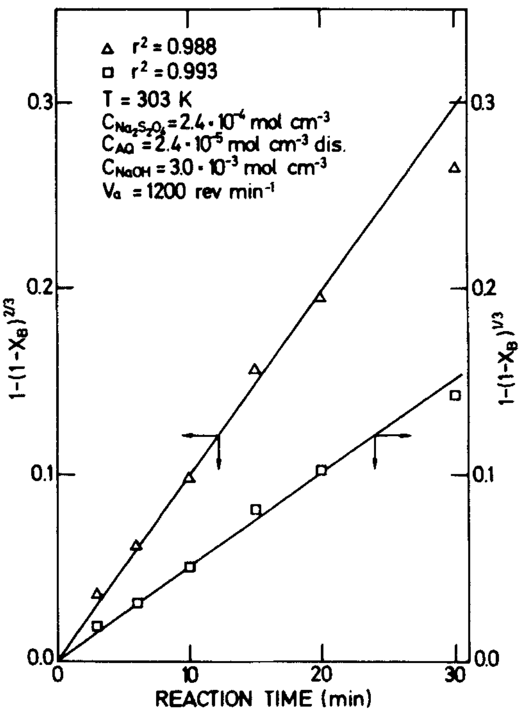

Figure 6. Diffusion and chemical reaction control functions vs. reaction time.

sodium hydroxide concentration. For the sodium hydroxide concentrations of 1.0 × 10^{-3} and 1.5 × 10^{-3} mol · cm^{-3} complete conversion time values of 27.5 and 28.3 min., respectively, were obtained. No appreciable variation of τ_S is detected and thus the overall rate is unaffected. However, for 3.0 × 10^{-3} mol · cm^{-3} concentration a decrease of the solid fractional conversion was observed and the calculated complete conversion time was 200 min., which is in disagreement with the model predictions. This particular behavior can be explained by taking into account that when the sodium hydroxide concentration increases a remarkable increase of solution viscosity, at low temperature, is produced. Because of that, a decrease of $S_2O_4^{2-}$ diffusivity takes place and this in turn causes a decay of solid-liquid mass transfer coefficient (Reid et al., 1977). This decrease can be so sharp that the solid-liquid mass transfer coefficient can reach a value equal to or even lower than that of the chemical reaction rate constant. Consequently, a transition regime from chemical reaction control to diffusional control takes place. In these conditions the solid fractional conversion obtained is less than the conversion attained when chemical reaction controls the overall process rate. In Figure 6 the fractional conversion function for both cases in which diffusion and chemical reaction control exists has been plotted against the reaction time. It can be seen that there is no clear definition of the controlling step because the data fit both the diffusional control function and the chemical reaction control function. Therefore the two mentioned steps can presumably contribute to the overall rate. Hence, the model agrees well with the experimental results only when sodium hydroxide concentration is below 1.5 × 10^{-3} mol · cm^{-3}.

Kinetic parameters estimation

The rate constant k_s can be worked out by substituting the complete conversion time, τ_S (s), and the corresponding experimental kinetic variables in Eq. 11. As described above, runs carried out with initial average solid particle radius greater than 50 μm and/or 3.0 × 10^{-3} mol · cm^{-3} sodium hydroxide concentration do not satisfy the conditions imposed by the model. In consequence, its practical application is restricted to the range where the data are in concurrence with the kinetic model. Hence these values were rejected when both the rate constants and the activation energy were calculated. The stoichiometric coefficient takes a value of 1 and the solid molar density when the reaction starts is 6.907 × 10^{-3} mol · cm^{-3}. Once the different k_s were calculated, the average values for the several temperatures were determined; they are summarized in Table 2. The activa-

Table 2. Temperature Effect on Reaction Rate Constant

Temp. K	Rate Constant k_s cm · s^{-1}
303	3.90 × 10^{-5}
313	6.86 × 10^{-5}
318	9.42 × 10^{-5}
323	11.70 × 10^{-5}

tion energy in the investigated temperature range was found to be 45.0 kJ · mol^{-1}.

Conclusions

The analysis of the results was made according to an isothermal SCM for spherical particles with no ash layer formation. It was shown that the influence of sodium dithionite concentration over the process rate agreed well with that predicted by the proposed model in the range studied. The average solid particle size effect is in agreement with the model only in the 22–50 μm particle radius interval. In the 1.0×10^{-3}–1.5×10^{-3} mol · cm^{-3} range, the process kinetics is unaffected by the sodium hydroxide concentration. Rate constants were worked out for temperatures from 303 to 323 K and their values varied from 3.90×10^{-5} to 11.7×10^{-5} cm · s^{-1}, the activation energy being 45.0 kJ · mol^{-1}.

From the results it can be concluded that in AQ reduction with sodium dithionite in an alkaline medium, high ratio conversions are reached at relative short times and low temperatures. Furthermore, the SCM is applicable to solid-liquid systems, with the operating conditions of the pseudosteady-state approximation. Bischoff (1963) and Wen (1968) have found restriction limits in applying the pseudosteady-state assumption to this kind of system. For gases and very dilute solutions $C_A/\rho_B < 0.001$ is satisfied. In the present work this relation is in the 0.01–0.06 range; nevertheless, a good agreement between complete conversion times obtained and those predicted by the model was attained. This agreement supports the pseudosteady-state approximation used, and is in concurrence with the Lindman and Simonsson (1979) work in applying the SCM to solid-liquid systems.

Notation

b = stoichiometric coefficient
C_A = liquid phase concentration, mol · cm^{-3}
C_{AQ} = dispersed phase fraction, mol · cm^{-3} dissolution
C_{NaOH} = sodium hydroxide concentration, mol · cm^{-3}
$C_{Na_2S_2O_4}$ = sodium dithionite concentration, mol · cm^{-3}
E_a = activation energy, kJ · mol^{-1}
E_o = reduction standard potential, V
F = Faraday's constant
K = thermodynamic equilibrium constant
K_c = conditional thermodynamic equilibrium constant
k_s = surface chemical reaction rate constant, cm · s^{-1}
n = number of electrons
R = gas constant
R_o = solid particle initial radius, cm
r = correlation coefficient
t = reaction time, min
T = temperature, K
V_a = stirrer speed, rev · min^{-1}
X_B = solid fractional conversion

Greek letters

ρ_B = solid molar density, mol · cm^{-3}
τ_D = complete conversion time with diffusion control, min
τ_S = complete conversion time with chemical reaction control, min

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