

Kinetics of Polyester Fiber Alkaline Hydrolysis: Effect of Temperature and Cationic Surfactants

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SYNOPSIS

The surface kinetic model was applied to the interpretation of the dissolution of poly(ethylene terephthalate) fibers in alkaline medium. The model assumes first-order kinetics with respect to surface area and concentration of OH⁻ ions. The dependency of the rate constant of dissolution on temperature was treated by the Arrhenius equation. The addition of a cationic surfactant resulted in an increase in both activation energy and preexponential factor. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

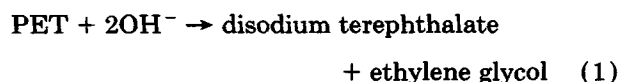
One of the methods of artificial silk production is alkaline hydrolysis of synthetic poly(ethylene terephthalate) (PET) fabric at elevated temperature.¹⁻³ The kinetics of this dissolution process attracted appreciable attention, but it was treated by semiempirical approaches. Some authors assumed linear time dependence of the weight loss,^{2,4} whereas others found an exponential function to better fit the experimental data.^{5,6} Recently, the kinetics of PET dissolution in alkaline medium was treated⁷ theoretically by a physicochemical model assuming the surface reaction rate to depend on both surface area and concentration of OH⁻ ions.^{8,9} Such an approach enables the complete characterization of the reaction system with respect to its kinetic behavior and, thus, the optimization of the technology of the artificial silk production. The quality of the final products depends on numerous parameters, such as fabric-to-solution mass ratio, sodium hydroxide concentration, additives (surfactants), temperature, and the duration of the treatment.

The previous article⁷ described, and experimentally confirmed, the proposed kinetic model. The aim of this work was to further test the model by taking into account temperature dependence of the rate

constant through the activation energy. In addition, the effect of surfactant was examined and interpreted in terms of the proposed model.^{3,10-13}

THEORETICAL

The dissolution of PET can be represented by



where PET denotes a poly(ethylene terephthalate) repeat unit (C₁₀O₄H₈).

According to the model,⁷ the rate of PET dissolution is given by

$$\frac{dn}{dt} = -kAc \quad (2)$$

where n denotes amount (in moles) of undissolved PET units; t , time; A , the reactive surface area; c , the concentration of OH⁻ ions (sodium hydroxide), and k , the rate constant of the process.

The fabric was approximated by a system of independent infinite fibers of circular cross section. As the reaction proceeds, their surface area A reduces as well as does the concentration of OH⁻ ions. Accordingly, the rate of the dissolution decreases

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with time and is of the first order with respect to both reactants (PET surface and OH^-).

By taking into account decreases in A and c , the following relationship was obtained:

$$F = -\frac{kV_m\sqrt{n_0}}{r_0} \cdot t + F_0 \quad (3)$$

n_0 and r_0 are the initial amount of PET and the initial radius of fibers, respectively, and V_m , the molar volume of PET, whereas function F and F_0 (at time t and at the initial state) are defined as follows:

For the initial excess of the base, $Vc_0 > 2n_0$ (V is volume of liquid medium):

$$F = \left(\frac{V}{2c_0 - 4n_0/V}\right)^{1/2} \times \arctan\left(\frac{2n}{c_0V - 2n_0}\right)^{1/2} \quad (4)$$

For the initial excess of PET, $2n_0 > Vc_0$:

$$F = -\frac{1}{2} \left(\frac{V}{4n_0/V - 2c_0}\right)^{1/2} \times \ln\left(\frac{\sqrt{n} - \sqrt{n_0 - c_0V/2}}{\sqrt{n} + \sqrt{n_0 - c_0V/2}}\right) \quad (5)$$

The interpretation of the kinetic data involves plotting of function F vs. time. The function [eq. (3)] is linear and the rate constant can be evaluated from the slope.

Once the value for the rate constant is known, one can calculate the amount (or mass) of undissolved PET by the following relationships:

Excess of base:

$$n = (c_0V/2 - n_0) \left(\frac{1 - f_t\sqrt{c_0V/2n_0 - 1}}{f_t + \sqrt{c_0V/2n_0 - 1}}\right)^2 \quad (6)$$

where

$$f_t = \tan\left[\frac{kV_m}{r_0} \sqrt{n_0} \left(\frac{2c_0 - 4n_0/V}{V}\right)^{1/2} t\right] \quad (7)$$

Excess of PET:

$$n = (n_0 - c_0V/2) \left(\frac{1 - f_t\sqrt{1 - c_0V/2n_0}}{f_t - \sqrt{1 - c_0V/2n_0}}\right)^2 \quad (8)$$

In this case,

$$f_t = \tanh\left(\frac{kV_mt}{Vr_0} \sqrt{4n_0^2 - 2c_0n_0V}\right) \quad (9)$$

The temperature dependence of the rate constant can be accounted for by introducing the activation energy E_a :

$$k = B \exp(-E_a/RT) \quad (10)$$

where B is the preexponential factor; R , the gas constant; and T , the thermodynamic temperature.

EXPERIMENTAL

The PET fabric was a Belira (Incel, Banja Luka, Bosnia and Hercegovina) product, woven from texturized filament yarn, consisting of delustered fibers with a circular cross section (50 dtex, 16f) previously heat set. The average initial radius of fibers was found to be $r_0 = 9 \mu\text{m}$. The molar mass of the PET repeat unit is $M = 192 \text{ g/mol}$ and the density equals 1.38 g/cm^3 , so that $V_m = 139 \text{ cm}^3/\text{mol}$. Sodium hydroxide was the laboratory-grade reagent and the cationic surfactant (fatty acid amino amide) used in the study was Lyogen BPN, a commercial product of Sandoz (Basel). In all experiments, NaOH was kept in excess over PET.

Experiments were performed using stainless-steel bowls (Linitest Original, Hanau) that were rotated in a closed reactor containing diethylene glycol at the desired temperature. The fabric was cut to the desired weight and immersed in sodium hydroxide (and surfactant) solution in bowls. Following the kinetics of dissolution, several samples (equal in composition) were treated for different durations (up to 4 days). After the predetermined durations, the samples were removed from the bath and washed with hot and cold water. Residual alkali in the fabric was removed by immersion in 1% aqueous hydrochloric acid for 5 min. Distilled water was used for the final rinsing of the fabric. The samples were dried overnight at 102°C and cooled in a dessicator. Weight loss was determined by a balance with an accuracy of $5 \mu\text{g}$. The results were expressed as relative weight loss (in %) as a function of the treatment time.

RESULTS

Figures 1 and 2 present typical results of the kinetic measurements performed at two different temperatures in the absence as well as in the presence of surfactant (Lyogen BPN). The lines in these figures are results of model calculations and show the agreement of experiments with the proposed model.

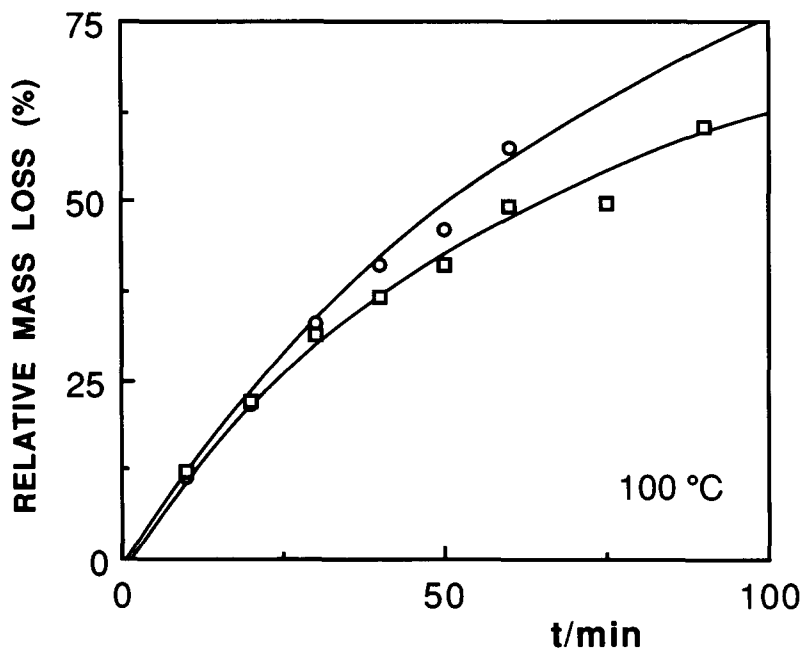


Figure 1 Dissolution of PET in aqueous sodium hydroxide solution (3.75 mol dm^{-3}) at 100°C in (○) the absence and (□) in the presence of Lyogen BPN (0.66 g of dry substance per liter).

It is evident that the process was faster at higher temperature and that the surfactant reduced the rate of the dissolution. All the results were interpreted by use of eqs. (3) and (4). The values of F were

calculated [eq. (4)] from each data point and plotted vs. time. Figure 3 represents the interpretation of the data from Figure 1, whereas Figure 4 corresponds to the data displayed in Figure 2. In all cases, sat-

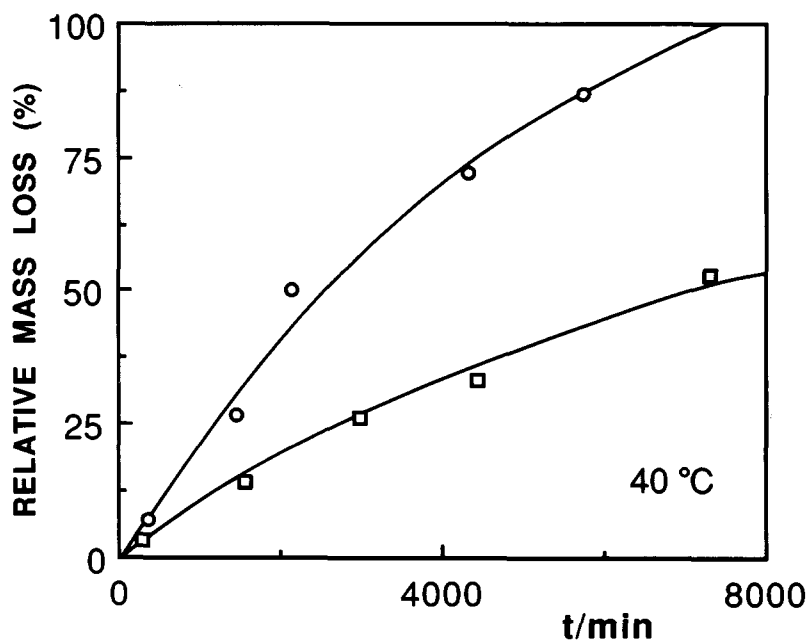


Figure 2 Dissolution of PET in aqueous sodium hydroxide solution (3.75 mol dm^{-3}) at 40°C in (○) the absence and (□) in the presence of Lyogen BPN (0.66 g of dry substance per liter).

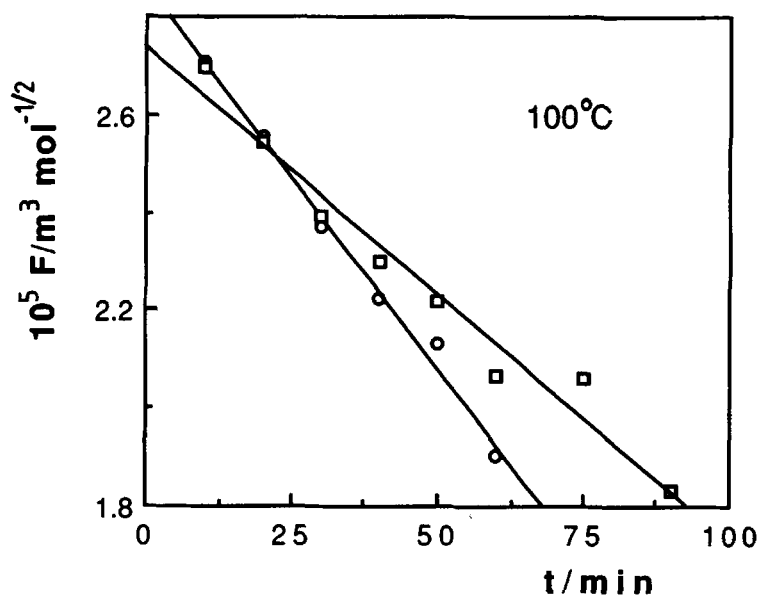


Figure 3 Interpretation of the kinetic data at 100°C presented in Figure 1 by use of eqs. (3) and (4). Results of linear regression are (○) 3.75 mol dm⁻³ NaOH and absence of surfactant, $k = 1.6 \cdot 10^{-9} \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$; (□) 3.75 mol dm⁻³ NaOH and 0.66 g dm⁻³ Lyogen BPN, $k = 1.1 \cdot 10^{-9} \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$.

isfactory linearity was obtained, and the slopes enabled calculation of the rate constants [eq. (3)].

The rate constants of PET dissolution in the absence of surfactant Lyogen BPN for two NaOH concentrations are presented as a function of tem-

perature, according to the Arrhenius eq. (10) in Figure 5.

The solid lines as obtained from linear regression are drawn through these data points and yielded the activation energy of $E_a = 66 \text{ kJ mol}^{-1}$ for both NaOH

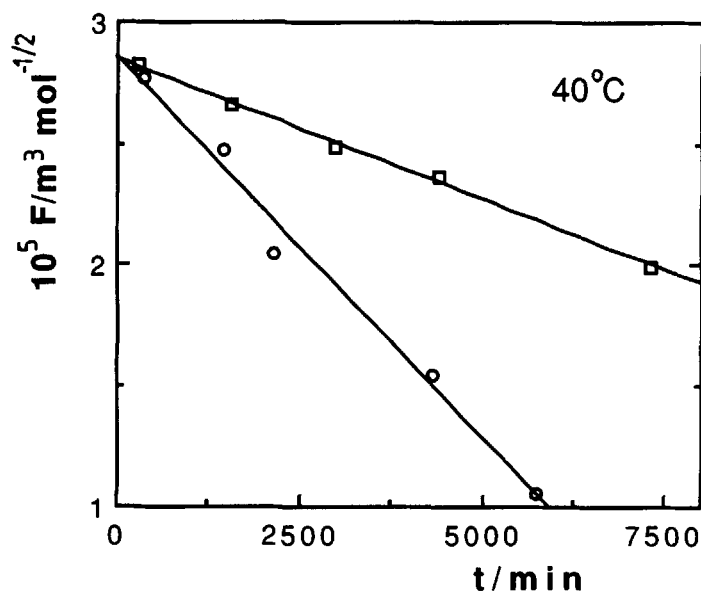


Figure 4 Interpretation of the kinetic data at 40°C presented in Figure 2 by use of eqs. (3) and (4). Results of linear regression are (○) 3.75 mol dm⁻³ NaOH and absence of surfactant, $k = 3.3 \cdot 10^{-11} \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$; (□) 3.75 mol dm⁻³ NaOH and 0.66 g dm⁻³ Lyogen BPN, $k = 1.2 \cdot 10^{-11} \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$.

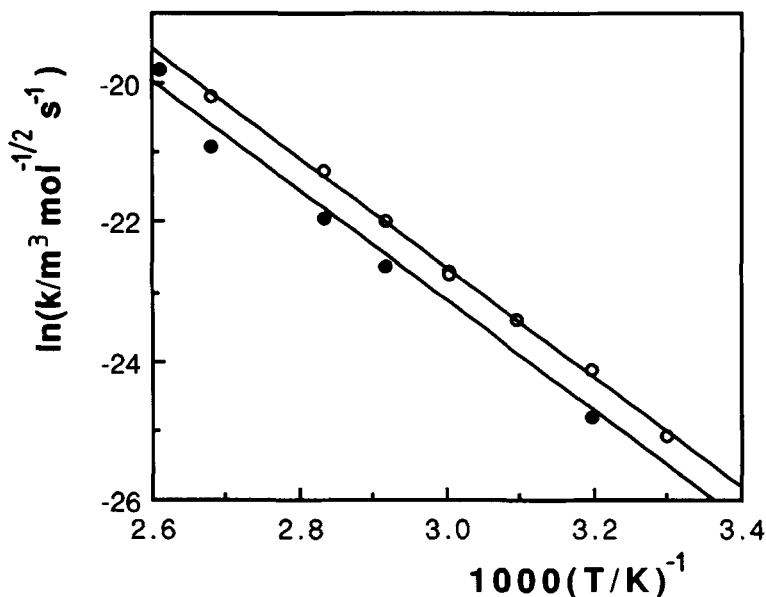


Figure 5 The Arrhenius plot, according to eq. (10) for experiments in the absence of surfactant performed with (O) 3.75 mol dm^{-3} and (●) 1.5 mol dm^{-3} NaOH. Results of the linear regression are (O) $E_a = 66 \text{ kJ mol}^{-1}$ and $B = 2.9 \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$ and (●) $E_a = 66 \text{ kJ mol}^{-1}$ and $B = 1.8 \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$.

concentrations. However, the preexponential factors were found to be somewhat different for two different concentrations of base.

The presence of Lyogen BPN caused changes to the values of E_a and B (Fig. 6). For the system containing 0.66 g dm^{-3} of Lyogen BPN at 1.5 mol

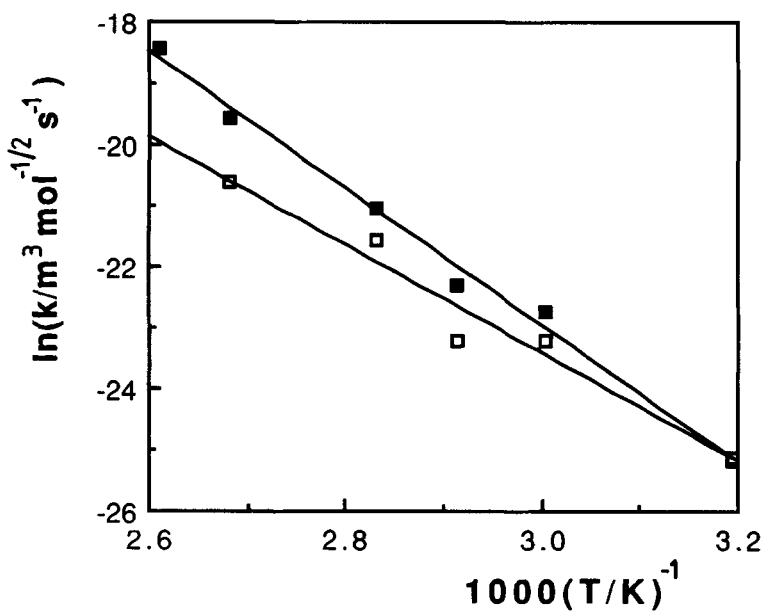


Figure 6 The Arrhenius plot, according to eq. (10), for experiments in the presence of surfactant Lyogen BPN performed at two different NaOH concentrations. Results of the linear regressions are (□) 3.75 mol dm^{-3} NaOH and 0.66 g dm^{-3} Lyogen BPN, $E_a = 74 \text{ kJ mol}^{-1}$ and $B = 23 \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$; (■) 1.5 mol dm^{-3} NaOH and 0.66 g dm^{-3} Lyogen BPN, $E_a = 94 \text{ kJ mol}^{-1}$ and $B = 4500 \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$.

dm^{-3} NaOH, $E_a = 94 \text{ kJ mol}^{-1}$ and $B = 4500 \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$, whereas the same content of Lyogen at 3.75 mol dm^{-3} NaOH yields $E_a = 74 \text{ kJ mol}^{-1}$ and $B = 23 \text{ m}^3 \text{ mol}^{-1/2} \text{ s}^{-1}$. It is obvious that the presence of surfactant causes changes in both the "collision frequency" and the activation energy.

DISCUSSION

The experimental results obtained in this work supported the applicability of the surface reaction model as proposed previously.⁷ This study additionally supported the model since the temperature effect can be satisfactorily interpreted on basis of the Arrhenius equation and the parameters obtained, activation energy and preexponential factor, do not depend on NaOH concentration, as required.

These findings enable the use of E_a and B values in the optimization of the technology of artificial silk production. One can simply set the desired mass loss and calculate the content of the reaction system (fabric-to-solution mass ratio, concentration of NaOH), temperature, and duration of the treatment. These parameters are mutually interrelated so that one may choose, e.g., a convenient duration and temperature and also account for the quality of the product. In contrast to our findings, Betschewa and Wangelov⁶ obtained somewhat higher activation

energy for the polyester dissolution ($97\text{--}125 \text{ kJ mol}^{-1}$), which may be also due to their empirical treatment of the reaction kinetics.

The dissolution in the presence of cationic surfactant (Lyogen BPN) is characterized by higher activation energy, which reduces the rate (especially at lower temperatures), but also with higher values of B generally leading to a more rapid process. The fact that E_a and B values for the reaction systems in the presence of surfactant depend on NaOH concentration is not surprising. The adsorption of surfactant molecules should depend on the OH^- concentration because the latter ions determine the surface charge and, thus, the adsorption of charged surfactant chains. Therefore, the conditions at the surface depend on the concentration of both solutes, so that kinetic behavior is changed. The adsorption of positively charged quaternary ammonium ions shield the negatively charged groups at the polyester surface and thus facilitate attack by hydroxyl ions and promote the dissolution.¹⁴

Optimization of the process with respect to the surfactant addition is not as simple as in the pure PET–NaOH–water reaction system. Figure 7 displays the dependence of the rate constant on temperature for different conditions, as calculated from the values of E_a and B obtained in this study. It can be concluded that the rate constant is generally lower when the surfactant is added to the systems of high

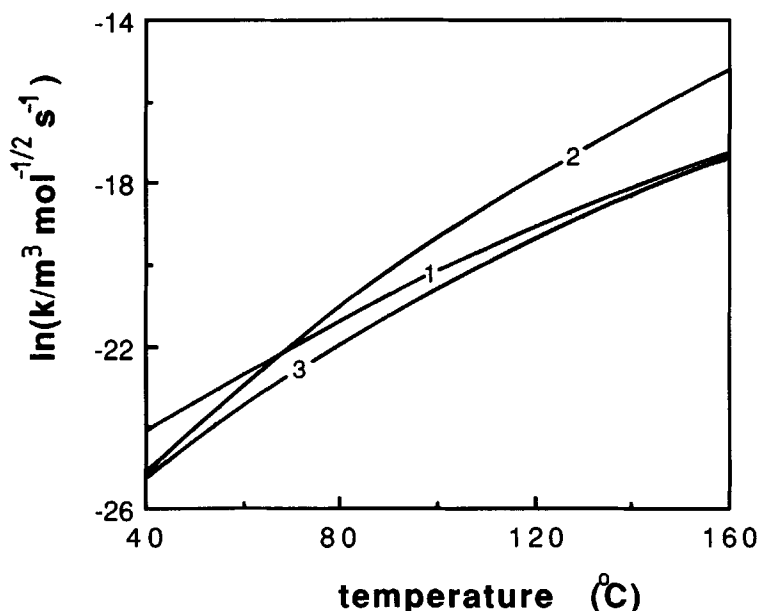


Figure 7 The rate constant of PET dissolution as a function of temperature (1) in the absence of surfactant, and in the presence of Lyogen (0.66 g dm^{-3}) for NaOH concentrations of (2) 1.5 mol dm^{-3} and (3) 3.75 mol dm^{-3} . The curves were calculated by using the E_a and B values as obtained in this study.

NaOH concentration, but significantly increases for lower base constant. However, one should also keep in mind that the rate of the process depends on both the rate constant and the NaOH concentration.

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