Bleaching Kinetics of Sunflowerseed Oil

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ABSTRACT: The bleaching process for sunflowerseed oil follows a rate formula, $\log (A/A_0) = -k\sqrt{t}$, according to absorbance measurements. The dark color of crude oil converts to a light color as the absorbance value decreases. The activation energy E_a was calculated from the Arrhenius equation as 3 kJ, and other activation thermodynamic parameters were determined as $\Delta S^{\neq} = -4.4$ J K^{-1}, $\Delta H^{\neq} = -31.2$ J mol^{-1}, and $\Delta G^{\neq} = 1.6$ kJ mol^{-1}. The study showed that the bleaching process was exothermic, presented a decrease of entropy, and was a nonspontaneous process during activation.

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KEY WORDS: Activation energy, bleaching, enthalpy, entropy, free energy, kinetics, sunflowerseed oil.

Bleaching of vegetable oils with bleaching clays in industry has been reviewed by Norris (1) and Kaufmann and Mukherjee (2). Bleaching is a complex process, but its rate-determining step is fairly simple. The pigment has the state of a stable colloid in the oil. The primary function of the bleaching clay is to separate the pigment from the oil by breaking the stability of the colloid. Bleaching of oils by adsorption involves the removal of pigments that are either dissolved in the oil or present in the form of colloidally dispersed particles (3).

Mezei *et al.* (4) studied the bleaching of sunflowerseed oil to monitor changes in the oxidation degree and percentage of colored matter removed by measuring the absorbances of oil samples. Boki *et al.* (5) investigated the bleaching of rapeseed and soybean oils with synthetic adsorbents and attapulgites.

There are a few papers on the kinetics of the bleaching process (6–8). Results with rapeseed oil have been published by Brimberg (9). Rate formulas were derived from the experimental data. The experiments with rapeseed oil showed that the bleaching process follows the rate formula (10),

$$\ln \frac{c}{c_0} = -k\sqrt{t} \qquad [1]$$

where t is the time from addition of the clay, c is the pigment concentration at time t, c_0 is the concentration at $t = 0$, and k is the rate constant. This equation pertains to destabilization of a colloid by removal of the stabilizer, in this case by adsorption onto the bleaching clay. Thus, chlorophyll and carotene are particulate substances in stable dispersion in the oil. The stabilizer is the surface-active lipid among the components of the oil. When enough stabilizer with attached pigments has been removed, the pigment particles aggregate among themselves and settle out until an equilibrium is reached.

According to the Beer-Lambert law (11), because absorbance is proportional to the concentration, Equation 1 can be rearranged as follows:

$$\ln \frac{A}{A_0} = -k\sqrt{t} \qquad [2]$$

where A is the absorbance of pigment at time t, and A_0 is the absorbance at $t = 0$.

The purposes of this study are to elucidate the kinetics of bleaching of sunflowerseed oil and to determine the activation thermodynamic parameters for this process.

EXPERIMENTAL PROCEDURES

Sunflowerseed oil. Crude sunflowerseed oil was supplied by Trakya Birlik Co. (Edirne, Turkey).

TABLE 1
Typical Characteristics of Bentonit EY-09[a]

Characteristics	Amount
Density	2.5 g cm^{-3}
Surface area (BET)[b]	200–220 m^2 g^{-1}
Moisture (2 h at 100°C)	max. 10%
pH (10% suspension)	4 ± 0.5
Oil retention (wt%)	max. 35%
Particle size analysis	
150 micron	max. 1%
150–106 micron	max. 4%
106–63 micron	61%
Chemical composition	
SiO_2	70 ± 2.0%
Al_2O_3	14 ± 1.0%
Fe_2O_3	1.8 ± 0.2%
CaO	0.7 ± 0.2%
MgO	1.7 ± 0.2%
K_2O	1.8 ± 0.2%
Na_2O	0.4 ± 0.2%

[a]Bensan Co. Ltd. [Edirne (Enez), Turkey].
[b]Determined by means of Brunauer-Emmett-Teller adsorption isotherm.

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Bleaching clay. Bentonit EY-09 was supplied by Bensan Co. Ltd. [Edirne (Enez), Turkey]. Its typical characteristics are given in Table 1. All other chemicals were reagent grade.

Methods. The bleaching vessel was a 500-mL Pyrex glass flask with a magnetic stirrer. The vessel was immersed in a thermostated glycerol bath. Crude sunflowerseed oil (200 g) was heated to the desired temperature before adding the bleaching clay. The mixture was then heated with stirring for 2 h at the desired temperature. A vacuum of 700 mm Hg was maintained throughout all experiments. The hot oil and clay mixture was filtered by taking samples at regular intervals (15 min).

Absorbance of the bleached oil was measured by ultraviolet spectrophotometry (Model Octagon 200 UV-160 A; Shimadzu Co., Tokyo, Japan) at 269 nm. During the measurement of the absorbance, the filtered oil was diluted to a concentration of 1.25% (wt/vol) by addition of hexane. The concentration of bleaching clay was 1% by weight. All kinetic experiments were carried out at temperatures of 60, 70, 80, and 90°C.

RESULTS AND DISCUSSION

The absorbance values determined are tabulated in Table 2. Decreasing absorbance values show that the color bodies and impurities in crude sunflowerseed oil are absorbed by bleaching clay, and crude oil is becoming lighter in color in the course of the experiment. Bleaching clay performs not only color removal but also removes trace metals, adsorbs phospholipids and soaps, and decomposes oxidation products, such as peroxides (12).

If ln A vs. $\sqrt{t}$ is plotted according to Equation 2, the slope gives the k. Figure 1 shows that the plot of ln A vs. $\sqrt{t}$ is linear for bleaching of sunflowerseed oil. Thus, the values of the rate constant k in the formula $\ln (A/A_0) = -k\sqrt{t}$ for bleaching of sunflowerseed oil with 1% of clay (Bentonit EY-09) by weight are calculated as follows [t(°C), k(min^{-2})]: 60°, 0.0199; 70°, 0.0205; 80°, 0.0211; and 90°, 0.0217.

TABLE 2
Absorbance Values at 269 nm with 1% of Clay (Bentonit EY-09) by Weight for Bleaching of Sunflowerseed Oil at Different Temperatures[a]

	Absorbance (°C)			
t (min)	60	70	80	90
0	2.383	2.383	2.383	2.383
15	2.207	2.201	2.196	2.191
30	2.137	2.130	2.123	2.116
45	2.086	2.077	2.068	2.060
60	2.043	2.033	2.024	2.014
75	2.007	1.996	1.985	1.975
90	1.974	1.962	1.951	1.939
105	1.944	1.932	1.919	1.908
120	1.917	1.904	1.891	1.879

[a]See Table 1 for company source.

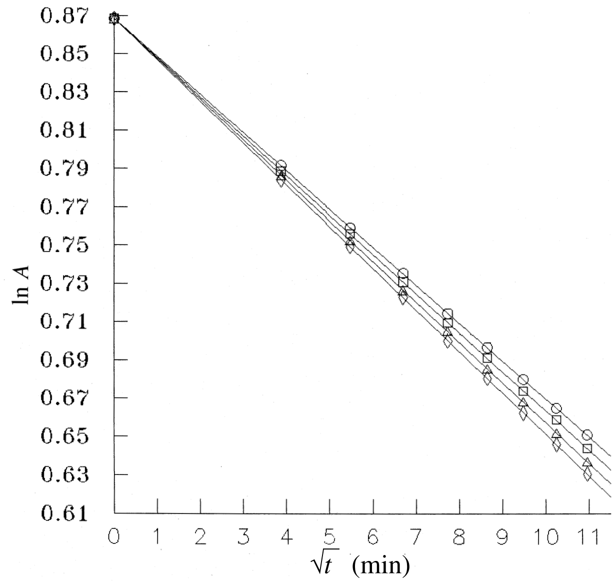

FIG. 1. The plot of ln A vs. $\sqrt{t}$ for bleaching of sunflowerseed oil with 1% of clay [Bentonit EY-09, Bensan Co. Ltd., Edirne (Enez), Turkey] by weight at various temperatures: ○: 60°C, □: 70°C, △: 80°C, and ◇: 90°C. A = absorbance.

The activation energy can be determined by the Arrhenius equation (13):

$$k = Ae^{-E_a/RT} \quad [3]$$

where k is the rate constant, A is the frequency factor or the Arrhenius constant, E_a is the activation energy, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), and T is the absolute temperature. When ln k is plotted against the reciprocal of the temperature (1/T), $-E_a/R$ represents the slope, and the intercept gives ln A (Fig. 2). The values of E_a and A for bleaching of sunflowerseed oil have been calculated as 3 kJ and 0.0584 min^{-1} = 0.00097 s^{-1}, respectively.

According to transition state theory, thermodynamic parameters are assigned to the activated complex as follows (14):

$$A = \frac{RT}{Nh} e^{\Delta S^{\neq}/R} \quad [4]$$

$$\Delta H^{\neq} = E_a - RT \quad [5]$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S \quad [6]$$

where N is the Avogadro constant (6.022 × 10^{23} mol^{-1}, h is the Planck constant (6.626 × 10^{-34} J s), $\Delta S^{\neq}$ is the activation entropy, $\Delta H^{\neq}$ is the activation enthalpy, and $\Delta G^{\neq}$ is the activation free energy or the Gibbs energy of activation.

Thermodynamic parameters for bleaching of sunflowerseed oil at 90°C have been calculated by means of Equations 4, 5, and 6 as $\Delta S^{\neq} = -4.4$ J K^{-1} mol^{-1}, $\Delta H^{\neq} = -31.2$ J mol^{-1}, and $\Delta G^{\neq} = 1.6$ kJ mol^{-1}.

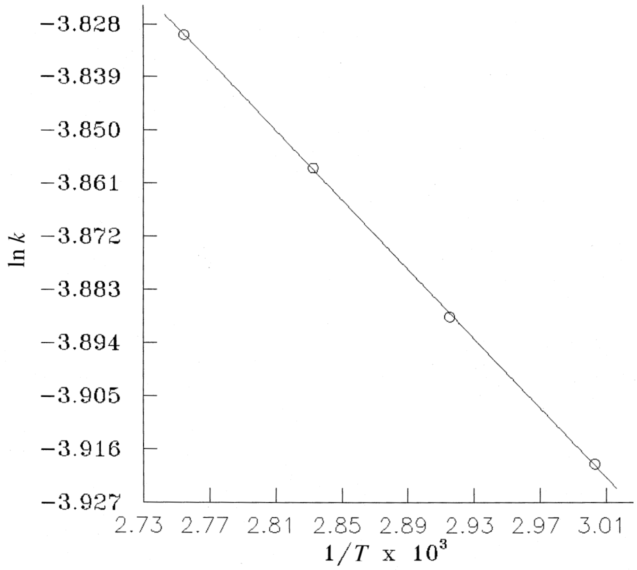

FIG. 2. The plot of ln *k* vs. 1/*T* for bleaching of sunflowerseed oil with 1% of clay (Bentonit EY-09) by weight. See Figure 1 for company source.

The negative value of $\Delta H^{\neq}$ shows that a certain amount of energy is released during activation of the bleaching reaction of sunflowerseed oil.

The negative value of $\Delta S^{\neq}$ indicates that there are impurities in crude oil before bleaching, and these are decreased or removed by the bleaching clay. Thus, it seems that entropy is high in the presence of impurities and low in the absence of them.

The positive value of $\Delta G^{\neq}$ means that the bleaching process is a nonspontaneous process from a physicochemical respect.

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