

Synthesis of a New Cationic Surfactant for the Alkaline Hydrolysis of Solvent-Pretreated Polyester Fabrics

S. M. GAWISH, S. MOSLEH, A. M. RAMADAN

National Research Centre, Textile Division, Tahrir Street, Dokki, Cairo, Egypt

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ABSTRACT: The synthesis of a cationic surfactant was based on diethanolamine and alkyl halides such as cetyl bromide with epichlorohydrin as a quaternizing agent. It was characterized by the elemental microanalysis of nitrogen and chloride and infrared spectroscopy. Polyester (PET) crepe fabric was pretreated with a series of solvents, including tetrachloroethane and tetrachloroethylene, at 25, 50, and 100°C. Untreated and solvent-pretreated PET fabric was hydrolyzed with 8 g/L NaOH at 100°C in the absence and presence of a cationic surfactant as a catalyst, and the weight loss was determined. The effects of solvent pretreatment on alkaline hydrolysis and PET dyeing were also examined. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1652–1660, 2002

Key words: cationic surfactant catalyst; alkaline hydrolysis; solvents; pretreated polyesters

INTRODUCTION

A literature review of the alkaline hydrolysis of polyester (PET) revealed that Teli and Purkayastha¹ studied the effects of pretreated solvents and solvent treatments on weight-reduced fabrics. They used cationic and dyeable PET and a series of solvents, including dimethylformamide, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and dichloromethane. The heat setting of yarns was carried out for 1 min at 180°C and resulted in an increase in the amorphous volume, and a more open structure was formed that was easily penetrated by the dye molecules. It was concluded that the various solvents had different extents of swelling, leading to increases in the dye uptakes of weight-reduced fibers. 1,1,2,2-Tetrachloroethane had the highest swelling action, and 1,1,1-trichloroethane had the lowest.

Teli and Purkayastha² followed up the alkaline hydrolysis of cationic and dyeable PET, heat-set or unset, in the presence and absence of the activator cetyl trimethyl ammonium bromide (0.1%) at 100 and 120°C with 12.5 and 3% NaOH, respectively. With an increase in the temperature and reaction time, the weight reduction of PET increased almost linearly. The weight-reduced samples were then analyzed for moisture regain, dyeability, critical dissolution time, and tenacity.

The alkaline hydrolysis of heat-set poly(ethylene terephthalate) fibers was compared in the presence and absence of dodecyl benzyl dimethyl ammonium chloride.³ The fibers set at lower temperatures were increased in weight loss with respect to those set at higher temperatures by the alkaline hydrolysis in the presence of the catalyst.

The alkaline hydrolysis of PET fabric with 0.3M NaOH in the presence of organic solvents such as dimethylformamide, dimethyl sulfoxide, and dimethylacetamide was investigated⁴ at 80°C for 40 min. A fabric treated with a solution of NaOH containing solvents had a vertical wicking height and an increase in dye uptake with respect to a fabric

Correspondence to: S. M. Gawish (mgawish@yahoo.com).

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treated with the NaOH solution only. Also, the former fabric had a lower breaking strength and elongation retention than the latter at the same weight loss. The fabric treated with the NaOH solution containing solvents was more pitted than that treated with the NaOH solution only.

The effect of PET yarns being pretreated and textured with tetrachloroethylene and a carrier on dyeability was studied by Turcu et al.⁵ The dye sorption capacity was increased by 18 and 16% by the carrier and tetrachloroethylene, respectively.

The alkaline hydrolysis of PET fabrics with NaOH in the presence of Katamin AB as an accelerant was carried out.⁶

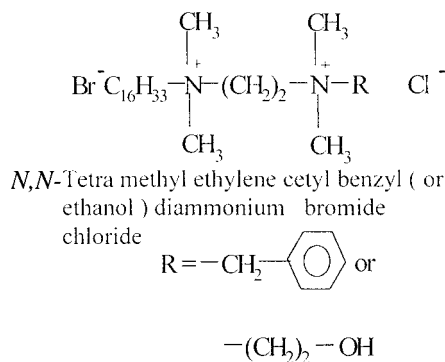
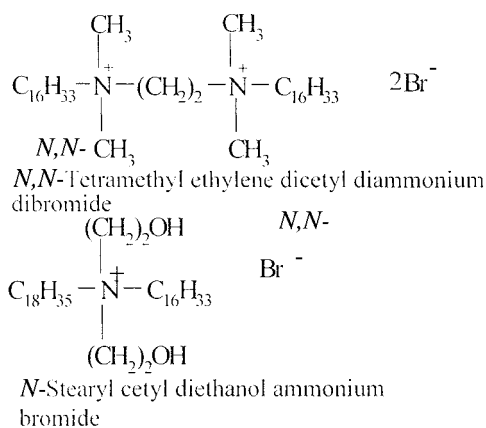
The use of polymeric cationic catalysts^{7,8} was compared with that of the usual catalysts, such as amines or quaternary ammonium compounds, during the alkaline deweighting of PET fabrics with 10–20 g/L NaOH at 90–130°C to an extent of 10–25%. The hygienic properties, handling, and

dyeability of the fabrics were improved, and static electrification was reduced.

The hydrolysis of PET fabrics in NaOH solutions was measured by ultraviolet and fluorescence spectroscopy, turbidimetry, electrokinetic potential, and sorption properties. Cationic polymers⁸ were shown to have greater catalytic effectiveness than ammonium salts. The stages of PET hydrolysis catalyzed by polyelectrolytes were given.

The kinetics of the alkaline hydrolysis of PET fibers were examined as a function of temperature.⁹ The addition of a cationic surfactant increased the activation energy.

Gawish et al.^{10,11} reported on the synthesis of a series of cationic surfactants used as accelerators for the alkaline saponification of PET, starting with tetramethyl ethylene diamine or stearyl diethanol amine and quaternizing the tertiary amino groups with cetyl bromide, benzyl chloride, or 2-chloroethanol as follows:



In this investigation, we proceeded to supplement our previous work^{10–17} on the synthesis of quaternary ammonium salt surfactants or polymers as catalysts for the alkaline hydrolysis of PET fabrics to produce silky-like handling with a new cationic surfactant synthesized by the alkylation of diethanolamine with cetyl bromide and the quaternization of the product with epichlorohydrin.

The effects of PET pretreatment with some solvents on the alkaline hydrolysis and the dyeing process were studied.

EXPERIMENTAL

Materials

PET crepe fabric (118 g/m²) was supplied by Ciba-Geigy Co (Basel, Switzerland). The pretreatment

solvents were tetrachloroethane and tetrachloroethylene. A new cationic surfactant containing a quaternary ammonium group was synthesized for this purpose. The disperse dye was terasil red (reddish-yellow C.I.23 from Ciba-Geigy).

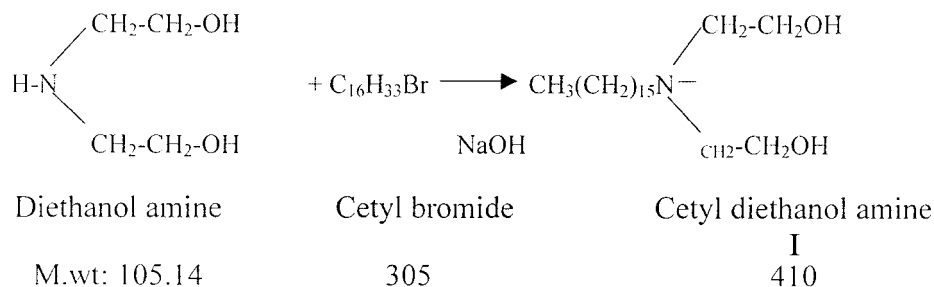
Methods

Synthesis of the Cationic Quaternary Ammonium Salt Surfactant

The cationic surfactant was synthesized by the alkylation of diethanolamine (0.1 mol, 10.5 g) with cetyl bromide (0.1 mol, 30.5 g) in 50 mL of isopropanol for 3 h at the solvent reflux temperature. The produced tertiary amino salt was stirred with 10% alcoholic NaOH at room temperature and was filtered. Then, the solvent was

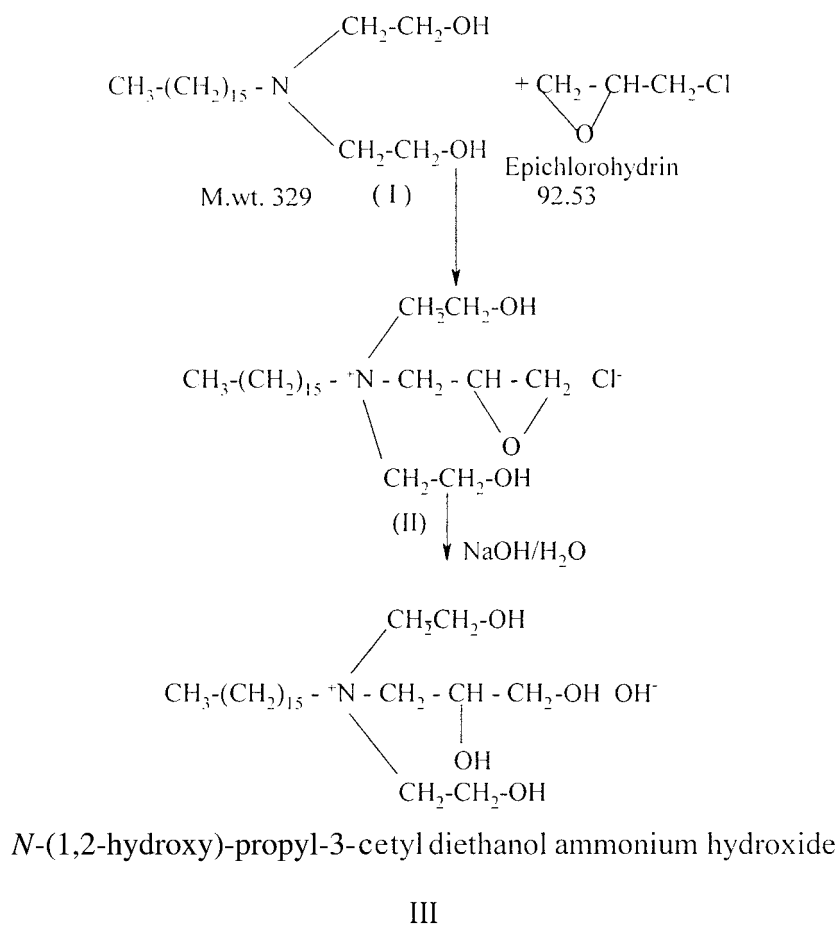
evaporated in a rotary evaporator until dryness was obtained. The product was crystallized with petroleum ether (40–60°C); it was insoluble, and the unreacted cetyl bromide was soluble. It was

centrifuged, and the solid product was vacuum-dried in a desiccator over phosphorous pentoxide. The reaction was performed according to the following equation:



The tertiary amino surfactant (35 g) was quaternized with an excess of epichlorohydrin (three times the theoretical amount, 30 g) in 50 mL of isopropanol for 1 h at the reflux temperature. The

solvent was evaporated to yield a viscous liquid that was recrystallized from acetone to yield a white powder and finally dried over phosphorous pentoxide. The reaction was performed as follows:



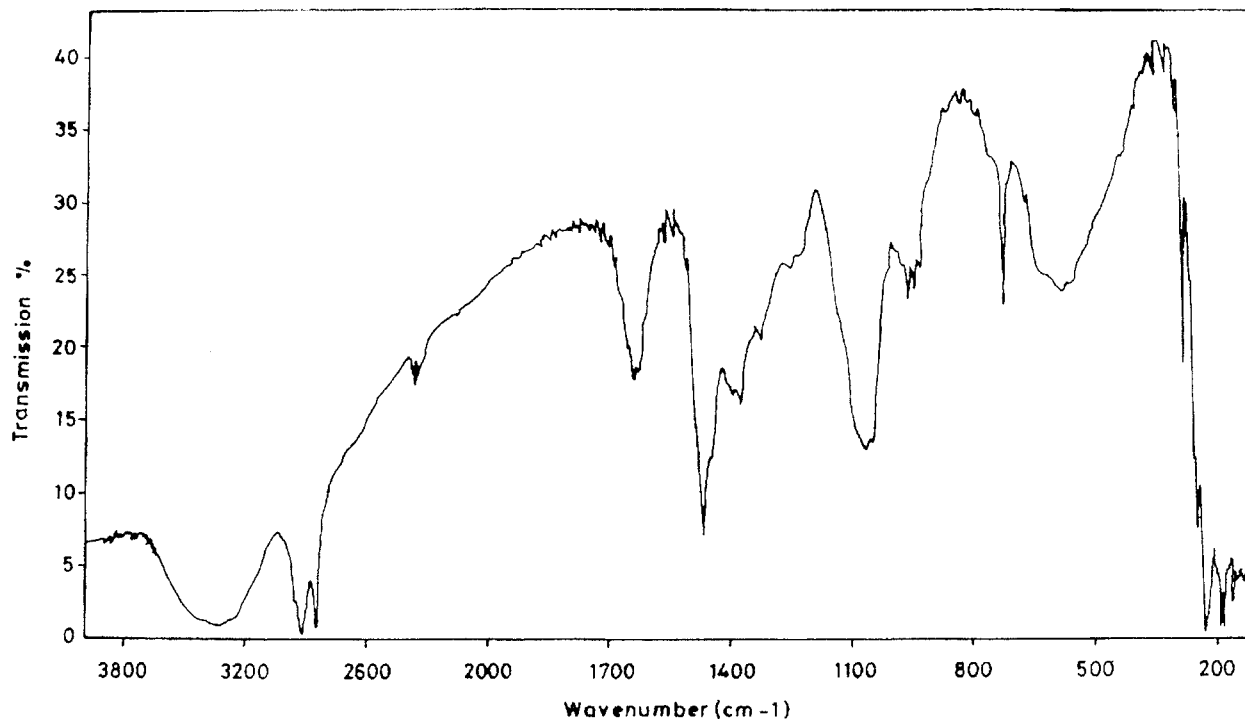


Figure 1 Infrared spectra of compound II.

Infrared Spectroscopy

An infrared analysis was carried out with a Fourier transform infrared spectrophotometer (300E Jasco Co., Japan). Compound II was measured as KBr disks and revealed the following absorption bands (Fig. 1): 3200–3600 cm^{-1} for OH stretching, 2920–2800 cm^{-1} for the stretching of methyl and methylene groups of the long hydrocarbon chain that confirm the reaction between diethanol amine and cetyl bromide, 1640 cm^{-1} for C—N stretching, 1460 cm^{-1} for CH_2 stretching on nitrogen, 1250 cm^{-1} for epoxide, 1050 cm^{-1} for C—O stretching, and 1390 cm^{-1} for CH_3 deformation.

Solvent Pretreatment and Alkaline Hydrolysis of PET Fabric

PET fabric samples (1 g, 12.3 cm \times 6.7 cm) were pretreated with the solvent tetrachloroethane or tetrachloroethylene at a liquor ratio of 1/30 at 25, 50, and 100°C for 1.5 h, were thoroughly washed with hot water and then acetone, and were air-dried.

The alkaline hydrolysis of the solvent-pretreated and untreated samples was effected with

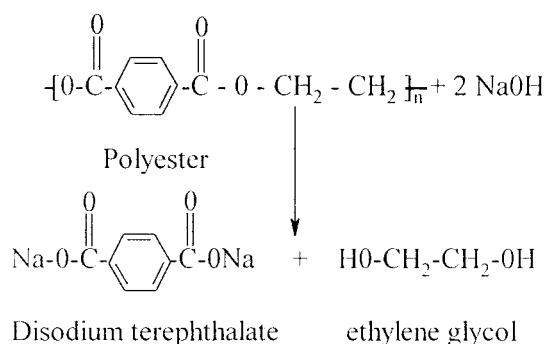
8 g/L NaOH at 100°C in the presence or absence of 1 g/L of the prepared cationic surfactant as a catalyst for different time periods. The samples were washed with warm distilled water and then with 6 g/L acetic acid for the removal of excess NaOH and were rinsed with water and dried until a constant weight was obtained. The weight loss was determined gravimetrically.

RESULTS AND DISCUSSION

A new cationic surfactant was synthesized and characterized with elemental microanalysis (see Table I) and infrared spectroscopy (see Fig. 1). The saponification of PET fabric to produce silky handling must be performed to reduce the weight loss to an extent of 15–25%. The saponification reaction of PET fabric is the nucleophilic attack of alkali hydroxyl ions on ester carbonyl atoms, giving rise to the hydrolyzed products disodium terephthalate and ethylene glycol in the reaction bath and a silky-like PET fabric product as follows:

Table I Characterization of the Cationic Surfactants by Elemental Microanalysis

Compound	Molecular Formula	Molecular Weight	Analysis				
			Nitrogen Calcd	Observed	Chloride Calcd	Observed	Yield (%)
I	C ₂₀ H ₄₃ O ₂ N	329	4.25	4.4	—	—	60
II	C ₂₃ H ₄₈ O ₃ NCl	421.5	3.32	3.12	8.4	9.2	90



Therefore, for every mole of PET, 2 mol of NaOH are required to complete the saponification reaction.

Theoretical Weight Loss

The weight loss is $192/80 \times 100$ NaOH (OWF), where OWF is the on-weight of the fabric. There-

fore, for 10 and 20% NaOH, the weight loss would be 24 and 58% respectively. The saponification of PET in the presence of 8 g/L NaOH at 100°C was very slow and did not exceed a 1% weight loss after 90 min (as shown in Figs. 2–6). The incorporation of a low-concentration cationic surfactant in an alkaline caustic soda bath greatly accelerated the saponification reaction rate. Therefore, the presence of a 1 g/L cationic surfactant increased the maximum weight loss to 13%, leading to a 12% increase in weight loss with respect to the sample treated with NaOH under the same conditions for 90 min (Fig. 2). The saponification of PET fabric in the presence of 8 g/L NaOH only and pretreated with the solvent tetrachloroethane or tetrachloroethylene slightly increased the weight loss to 2% (Figs. 1 and 2) for PET pretreated with tetrachloroethane at 25 and 50°C and to 4% at 100°C (Fig. 2).

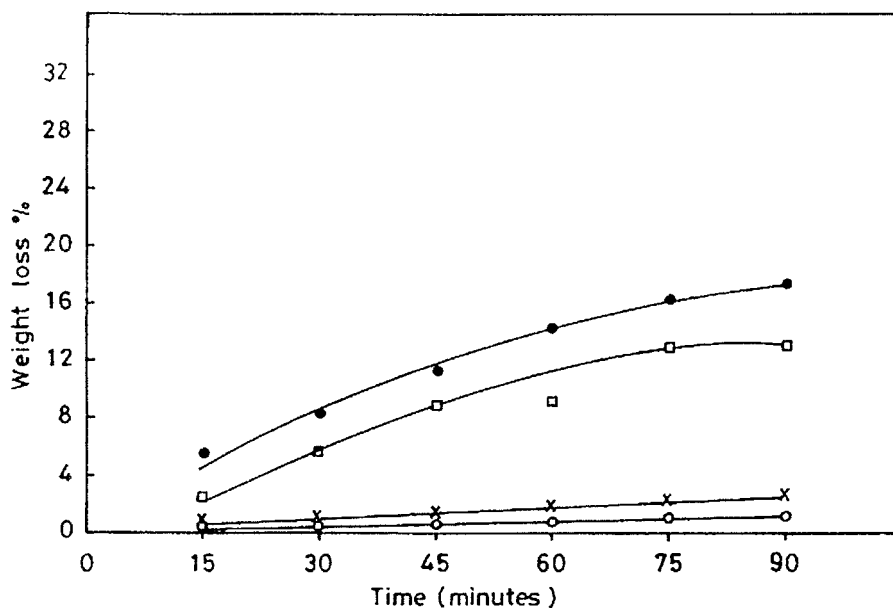


Figure 2 Rate of the alkaline hydrolysis of PET crepe fabric with 8 g/L NaOH at 100°C: (○) samples treated only with NaOH, (×) samples pretreated with tetrachloroethane (1.3 h at 25°C) followed by NaOH, (□) samples treated with NaOH in the presence of a 0.1% cationic surfactant, and (●) samples pretreated with tetrachloroethane followed by NaOH in the presence of a 0.1% cationic surfactant.

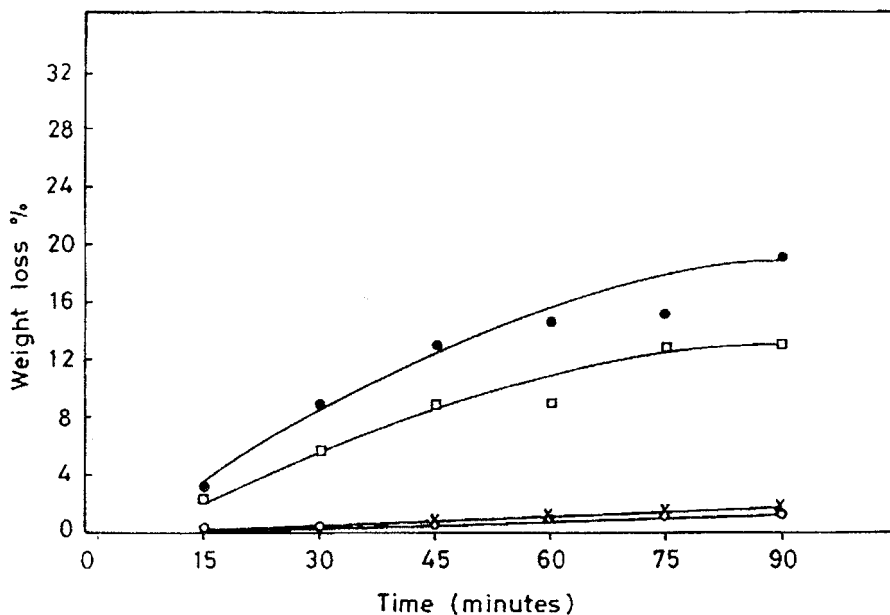


Figure 3 Rate of the alkaline hydrolysis of PET crepe fabric with 8 g/L NaOH at 100°C: (○) samples treated only with NaOH, (□) samples treated with NaOH in the presence of a 0.1% cationic surfactant, (×) samples pretreated with tetrachloroethane (1.3 h at 50°C) followed by NaOH, and (●) samples pretreated with tetrachloroethane followed by NaOH in the presence of a 0.1% cationic surfactant.

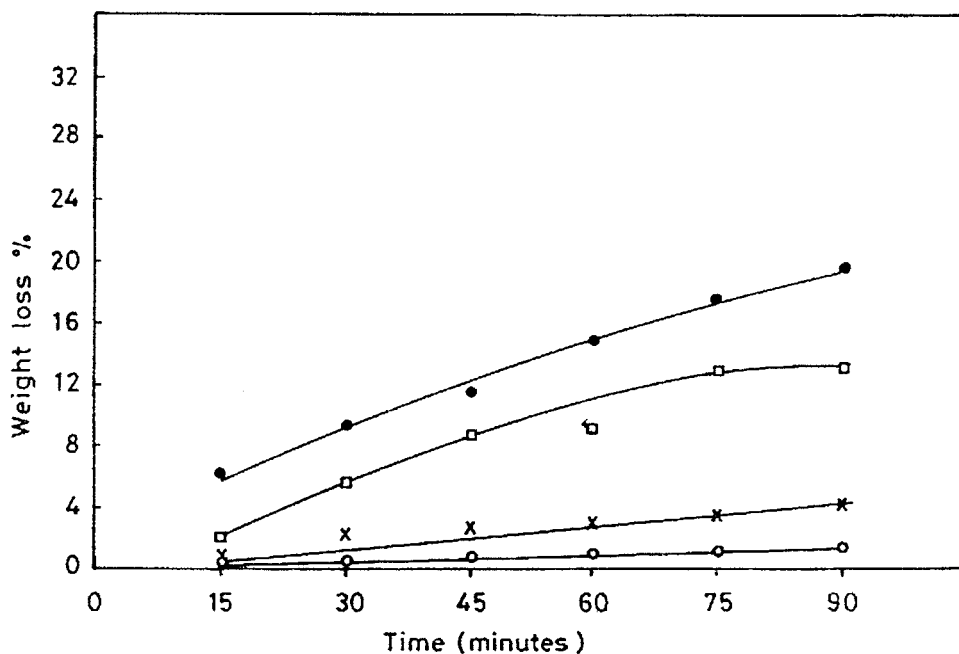


Figure 4 Rate of the alkaline hydrolysis of PET crepe fabric with 8 g/L NaOH at 100°C: (○) samples treated only with NaOH, (□) samples treated with NaOH in the presence of a 0.1% cationic surfactant, (×) samples pretreated with tetrachloroethane (1.3 h at 100°C) followed by NaOH, and (●) samples pretreated with tetrachloroethane followed by NaOH in the presence of a 0.1% cationic surfactant.

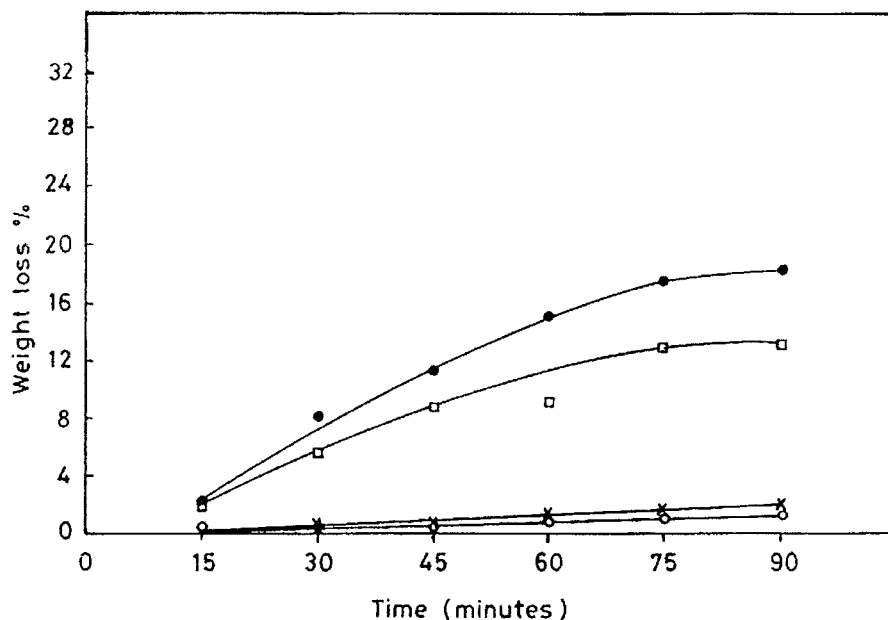


Figure 5 Rate of the alkaline hydrolysis of PET crepe fabric with 8 g/L NaOH at 100°C: (○) samples treated only with NaOH, (×) samples pretreated with tetrachloroethylene (1.3 h at 50°C) followed by NaOH, (□) samples treated with NaOH in the presence of a 0.1% cationic surfactant, and (●) samples pretreated with tetrachloroethylene followed by NaOH in the presence of a 0.1% cationic surfactant.

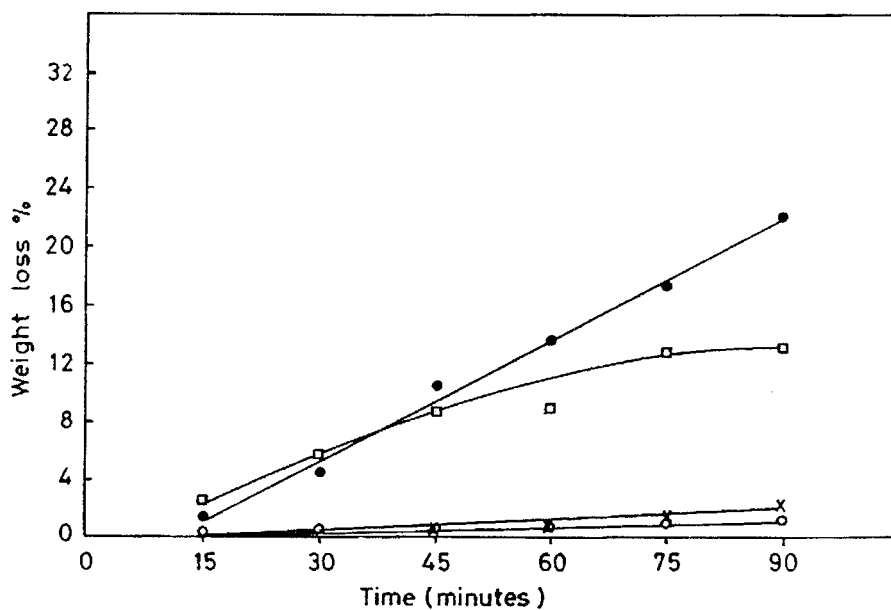


Figure 6 Rate of the alkaline hydrolysis of PET crepe fabric with 8 g/L NaOH at 100°C: (○) samples treated only with NaOH, (×) samples pretreated with tetrachloroethylene (1.3 h at 100°C) followed by NaOH, (□) samples treated with NaOH in the presence of a 0.1% cationic surfactant, and (●) samples pretreated with tetrachloroethylene followed by NaOH in the presence of a 0.1% cationic surfactant.

Table II Relation of the Color Strength (Measured at 494.5 nm of PET Dyed with 1% Disperse Dye) and Weight-Loss Percentage of Alkali-Saponified PET at 100°C in the Presence of a Cationic Surfactant

Sample	Weight Loss (%)	Color Strength
Blank	—	6.61
Sample only alkali-treated	1.2	6.61
Sample alkali-treated in the presence of a 1% cationic surfactant	13.2	6.61
Sample pretreated with tetrachloroethylene (50°C) and saponified in the presence of 1% cationic surfactant	18.37	6.82
Sample pretreated with tetrachloroethylene (100°C) and saponified in the presence of a 1% cationic surfactant	22.06	7.8
Sample pretreated with tetrachloroethane (50°C) and saponified in the presence of a 1% cationic surfactant	19.32	7.23
Sample pretreated with tetrachloroethane (100°C) and saponified in the presence of 1% cationic surfactant	19.68	9.27

For tetrachloroethylene, the weight loss was 2% (Figs. 4 and 5) for the pretreatment at 50 and 100°C, respectively. The saponification of solvent-pretreated PET in the presence of a 1 g/L cationic surfactant increased with tetrachloroethane at 25, 50, and 100°C, respectively (Figs. 2–4), with respect to a 13% weight loss for PET fabric untreated with solvents. The PET saponification in the presence of a 1% cationic surfactant and pretreated with tetrachloroethane or tetrachloroethylene at 50°C (Figs. 3 and 5) was the same; that is, the two solvents had the same effect on the saponification reaction for pretreatment at 50°C, and the maximum weight loss attained was 18% after 90 min. The PET saponification pretreated with tetrachloroethane at 100°C in the presence of a 1% cationic surfactant increased with respect to tetrachloroethylene by a 4.8% weight loss until 30 min; then, the two curves intersected at 75 min, giving rise to the same weight loss of 17%. That is, tetrachloroethane was a better pretreatment solvent at 100°C than tetrachloroethylene.

Dyeing

The color strength was constant and had a value of 6.61 for the blank, alkali-saponified PET in the presence or absence of the cationic surfactant that was untreated with solvents (Table II). This indicated that the saponification reaction had no effect on the dyeing.

The color strength increased with the increasing weight-loss percentage of samples saponified in the presence of the cationic surfactant and solvent-pretreated before the saponification reaction. Both solvents used in the pretreatment of

PET fabric, tetrachloroethane and tetrachloroethylene, enhanced fiber swelling, led to better dye diffusion, and increased the color strength because of the change in the fine structure of the fabric. The samples solvent-pretreated at higher temperatures gave higher color strengths than those treated at a lower temperature with an appropriate solvent and a fixed weight loss. Therefore, increasing the pretreatment temperature of PET from 50 to 100°C increased the color strength from 6.82 to 7.8 for tetrachloroethylene and from 7.23 to 9.27 for tetrachloroethane (Table II). This clearly indicates that the swelling of fibers at 100°C gave PET a more open structure than that swollen at 50°C; although the weight loss was fixed at 19%, the color strength increased from 7.23 to 9.27 for samples pretreated with tetrachloroethane at 50 and 100°C, respectively. It is concluded that tetrachloroethane is more efficient than tetrachloroethylene as a pretreatment solvent, giving rise to better color strength on the alkali-saponified PET.

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