Reactive Black Dyes containing Acetoxyethyl sulfone moiety

Kim Tae kyung, Oh Sea Wha, Shin Seung Rim
Korea Research Institute of Chemical Technology

Abstract : This thesis related to a reactive black dyes containing acetoxyethyl sulfone moiety which is characterized by lessening the loss of dyes in filtering process owing to the low solubility by introducing the aminophenyl-β-acetoxyethyl sulfone moiety, saving the cost for waste water treatment by using a small amount of salt in salting-out process and furthermore obtaining bright color with high dyeing yield and substantivity.

1. Introduction

Conventionally, salting-out method has been adapted in order to isolate dyes from reation mixture after synthesizing the reactive dyes. However, if aminophenyl-β sulfatoethyl sulfone is used as an intermediate in the course of manufacturing vinylsulfone-based reactive dyes, spray-dry method is adapted or large amount of salts is used because high water solubility of dyes hinder the salting out. The isolation of dyes by spray-drying or by using large amount of salts may cause environmental pollution with waste water containing a good deal of dyes and salts and eventually require much expenses on sewage treatment.

Recently, in some developed countries such as European countries and U.S.A., there is restriction on salt concentration in dye water waste, thus continuous studies have been conducted in order to obtain low-salt dye and succeeded in marketing. In addition, the liquid dyes are used more favorably because they can be exactly measured and from which the automatization of dyeing process and the promotion of worker's health can be achieved. Therefore, the highly concentrated dyes by removal of salts are required for the manufacture of the stable liquid dyes.

Therefore, in comparison with dyes synthesized with aminophenyl-β sulfatoethyl sulfone group, salting-out is generally easier in the dyes synthesized with aminophenyl-β-acetoxyethylsulfone group, which has relatively low water solubility.

In synthesizing process of dyes with using aminophenyl-β-acetoxyethylsulfone group, it is possible to lower the concentration of salt in water waste because only a

small amount of salt is used in salting-out process than the conventional dyes. Also it is cost-effective in sewage treatment because only a small amount of dyes is lost during the filtering owing to low solubility of dyes. Furthermore, thus prepared dyes has a high purity containing a small amount of salt and be able to lower the concentration of salt and make it easier desalting process in manufacturing liquid dyes.

2. Experiment

2.1 Preparation of 4-aminophenyl-β-acetoxyethylsulfone

After attaching condenser with rubber balloon to reaction vessel of 100ml, 60g (1mol) of acetic acid and 1.8g (0.1mol) of water are put into it. With maintaining the reaction solution at 15°C, 5.5g (0.15mol) of hydrogen chloride gas is added slowly for 1.5 to 2 hours. After adding 24.3g (0.1mol) of 4-acetaminophenyl-β-hydroxyethylsulfone, the solution, whose temperature is slowly raised to 70-75°C is stirred for 9 hours.

Then the solution is cooled down to room temperature with slow stirring, filtered and rinsed twice with acetic acid (5ml), After drying the filtered solid at 60°C in vacuum and dispersing it at 10g of ice and 25ml of water, this solution is neutralized with 10% of sodium carbonate solution and filtered the crystals. With rinsing with water (5ml) there times and drying, white pure 20.6g of 4-aminophenyl-β acetoxyethylsulfone (yield 84.8%, purity 97.5%) in solid type is obtained.

melting point : 92-93°C

2.2 Manufacturing of dyes

Dye 1

3N $NaNO_2$(40ml, 0.12mol) is added to the dispersed solution of 26.76g(0.11mol) 4-aminophenyl-β-acetoxyethylesulfone and 200ml of water with maintaining the temperature at 0-5°C and 90g of ice is added; this is followed by the addition of 24ml (0.276mol) of 35% HCl and diazotization. The diazotization is completed and excess nitrous acid is then destroyed by means of sulfamic acid.

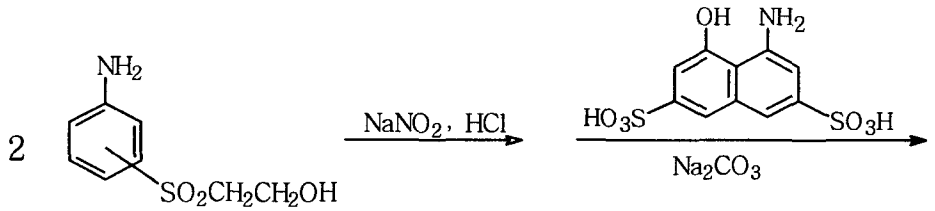
15.97g (0.05mol) of 1-napththol-8-amino-3,6-disulfonic acid is dissolved in 200 ml of water, neutralized with 2.0g (0.05mol) of NaOH and is cooled down to 0-5°C. The diazotized solution is added at once to neutralized 1-naphthol-8-amino-3,6-disulfonic acid solution and then it is reacted with maintaining pH below 7 by means of slow addition of NaOH solution. In the middle of reaction, 30g of ice is added three times in

order to prevent the raise of temperature. The reaction is ended after 4 hours of stirring and then reactive dyes is obtained by spray-drying.

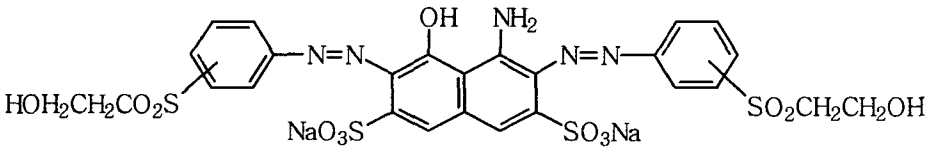
^{1}H-NMR(300MHz, DMSO-d_6): δ 1.75(3H, s), 1.77(3H, s), 3.73(2H, t), 3.79(2H, t), 4.28(4H, q), 7.42(1H, s), 7.48(1H, s), 7.92(2H, d), 8.00(2H, d), 8.03(2H, d), 8.26(2H, d), 10.41(1H, s), 10.61(1H, s), 15.36(1H, s)

Dye 2

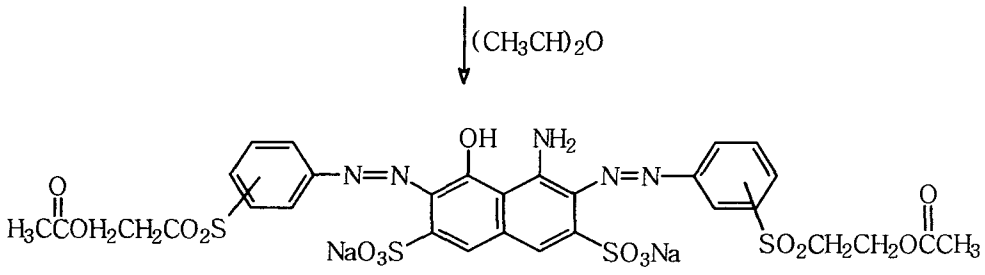
An intermediate is prepared by coupling reaction in the same manner of Example 1 except using 4.06g of 4-aminophenyl-β-acetoxyethylsulfone. After adding 20ml acetic anhydride to 1g of dried intermediate, it is reacted for 8 hours at 80-90℃ and resulted in reactive black dyes. (scheme 1)



(5)



(6)



(1)

scheme 1

2.3 Dyeing

The reactive black dye prepared by the above methods is used for exhaust-dyeing the fabrics such as cotton, wool and silk. and is compared with those dyed with Reactive Black 5. (Dyeing levelness, fixation value, light fastness properties etc.)

3. Result and Discussion

1. The reactive black dye with aminophenyl-β-acetoxyethylsulfone as reaction group instead of conventionally used aminophenyl-β-sulfatoethylsulfone which can lessen the wastes in manufacturing.

2. Dye 2 shows red shade due to the red by-product produced during its synthesizing and its fixation value is 3% low than above Dye 1 and its light fastness is also low.

3. When applied to cotton, wool, silk fabric, the reactive black dye with aminophenyl-β-acetoxyethylsulfone shows excellent dyeing levelness and reproducibility and superior light fastness properties. In particular, when applied to wool fabric, Dye 1 shows superior color yield in comparison with Reactive Black 5.