

ABSTRACT

NATTAYA PUNRATTANASIN. Synthesis and Application of Azo Dyes in Supercritical Carbon Dioxide. (Under the direction of David Hinks).

This dissertation is concerned with the utilization of supercritical carbon dioxide (SC-CO₂) for the synthesis of azo dyes and their application to textile substrates. One of the major benefits to diazotization and coupling in SC-CO₂ and small amounts of water includes elimination of mineral acid as a proton source for the diazotization reaction, thereby negating the requirement of neutralization and effluent treatment of highly colored and electrolyte-concentrated effluent.

The work was divided into five main parts. In the first part, ten common arylamines were selected to study the effect of type and placement of substituents on the product yield of a series of simple azo dyes using a SC-CO₂-water medium to act as both solvent and proton source. Azo dyes from arylamines containing nitro- and vinylsulfonyl- substituents in the *para*-position relative to the diazotizable amino group were easily synthesized in SC-CO₂ in reasonable yield. The synthesis of azo dyes in SC-CO₂ was dependent on a combination of basicity, solubility and steric hindrance around the amino group to be diazotized.

The second part involved optimization of the reaction yield of a vinylsulfonyl-based disperse reactive dye via a statistical design of experiment. For the reaction system employed, the primary influences on product yield were, by far, water, followed by pressure and time. Temperature had little effect on

product yield. The optimized synthetic procedure afforded near complete conversion to the target dye.

Part three demonstrated a new SC-CO₂ azoic dyeing method, in which the diazotization and coupling of a simple arylamine, aniline, to form a dye inside cotton fibers was optimized using a statistical design of experiments. It was found that H₂O, pressure and dyeing time had a significant effect on shade depth, levelness and fastness properties. Under optimized conditions, the dyed fabrics produced uniform dyeings with high color strength and fastness properties that were comparable to those from conventional aqueous azoic dyeing. Furthermore, the potential wide scope of azoic dyeings using SC-CO₂ was demonstrated, with cellulose acetate, viscose, wool and silk all being dyed successfully. However, the coupling component had to be applied to the substrate using a conventional pad-dry procedure.

Part four was an investigation of the effects of temperature and pressure on dyeing nylon 6,6 and wool in SC-CO₂ using the vinylsulfonyl fiber-reactive disperse dye under various reaction conditions. In addition, equivalent dyeings were performed using a nonreactive disperse dye analog in order to determine the effects of the reactive group on dye fixation. Nylon 6,6 and wool were effectively and efficiently dyed with a high degree of color strength and fixation. Color strength increased with increasing temperature and pressure for both substrates, with greater than 96% apparent fixation achieved. In a model experiment, the fiber reactive dye was successfully reacted with butylamine in SC-CO₂ under the conditions used for dyeing, demonstrating that covalent bond

formation between the dye and an aliphatic amine (similar to the nucleophilic groups present on nylon 6,6 and wool) was achieved using this dyeing system. The alkylamine derivative of the dye was characterized by FAB-MS and ^1H -NMR.

The final part of this work involved the attempted synthesis of the most important fiber-reactive dye, C.I. Reactive Black 5, in SC-CO₂ in the absence of mineral acid by two-step method. It was found that coupling in SC-CO₂ was only successful at the 7-position of H acid, and not at the position *ortho* to the amino group of that coupling component, possibly due to steric hindrance and reduced reactivity at that position.

Synthesis and Application of Azo Dyes in Supercritical Carbon Dioxide

by

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TABLE OF CONTENTS

	PAGE
LIST OF TABLES	xi
LIST OF FIGURES	xiii
 1. Introduction	 1
1.1 Supercritical Fluids	1
1.1.1 Supercritical Carbon Dioxide	3
1.2 Classification of Dyes According to Application Method	4
1.2.1 Fiber-Reactive Dyes	5
1.2.1.1 Constitutional Characteristic of Reactive Dyes.....	5
1.2.1.2 Chemical Reactions between Reactive Dyes and Fibers	13
1.2.2 Acid Dyes.....	17
1.2.3 Basic Dyes	18
1.2.4 Direct Dyes	19
1.2.5 Azoic Dyes.....	20
1.2.5.1 Coupling Components.....	21
1.2.5.2 Diazo Components.....	23
1.2.6 Disperse Dyes	26
1.2.7 Vat Dyes	28
1.2.8 Sulfur Dyes	30
1.3. Azo Dyes.....	30
1.3.1 Synthesis of Azo Dyes	31

	PAGE
1.3.1.1 Diazotization of Aromatic Amines.....	31
1.3.1.2 Coupling Reaction.....	33
1.4 Applications of SC-CO ₂ in Textiles.....	35
1.4.1 Solubility of Disperse Dyes in SC-CO ₂	35
1.4.2 Dyeing of Synthetic Fibers in SC-CO ₂	37
1.4.2.1 Mechanism of Dyeing Synthetic Fiber in SC-CO ₂	39
1.4.2.2 Modeling Sorption/fluid Flow in SCF Dyeing	40
1.4.3 Dyeing of Natural Fiber in SC-CO ₂	40
1.4.3.1 Impregnation of Swelling and Crosslink agents.....	41
1.4.3.2 Fiber Modification Technology	41
1.4.3.3 Use of Polar Co-solvents	44
1.4.3.4 Use of Fiber-Reactive Disperse Dyes	45
1.4.3.5 Use of a Nonionic Surfactant.....	48
1.5 Use of SC-CO ₂ in Dye Synthesis	50
1.6 Damage of Natural and Synthetic Fibers Treated in SC-CO ₂	51
1.7 Proposal.....	52
1.7.1 Diazotization and Coupling in SC-CO ₂	52
1.7.2 Azoic Dyeing in SC-CO ₂	57
1.7.3 Dye-Fiber Formation of Fiber-Reactive Dyes and Polyamide Fibers ..	58
2. Synthesis of Azo Dyes via <i>in Situ</i> Diazotization and Coupling	
in Supercritical Carbon Dioxide.....	60

	PAGE
2.1 Introduction	60
2.2 Experimental	62
2.2.1 Materials	62
2.2.2 Equipment.....	62
2.2.3 Visible Absorption Spectra.....	63
2.2.4 Synthesis Method	64
2.2.4.1 Preparation of <i>p</i> -Aminophenylvinylsulfone	64
2.2.4.2 Dye Synthesis using SC-CO ₂	64
2.2.4.3 Analysis of Dyes Synthesized in SC-CO ₂	65
2.2.4.4 Synthesis by Conventional Diazotization and Coupling	67
2.3 Results and Discussion	71
2.3.1 Effect of Basicity, Hydrophobicity and Position of Auxochromes on Product Yield	72
2.3.2 Comparison of Absorption Spectra of Dyes: Conventional versus SC- CO ₂ Synthesis	80
2.3.3 Side Reactions.....	81
2.4 Conclusions.....	87
 3. Synthesis of 4-(4-vinylsulfonylphenylazo)-<i>N,N</i>-diethylaniline in Supercritical Carbon Dioxide.....	 89
3.1 Introduction	89
3.2 Experimental	90

	PAGE
3.2.1 Statistical Design of Experiments	90
3.2.2 Synthesis of Dye (76) in SC-CO ₂	91
3.2.3. Absorption Spectra and Calculation of Spectroscopic Yield	92
3.3 Results and Discussion	92
3.3.1 Statistical Analysis	93
3.3.2 Optimization of the Process	100
3.4 Conclusions.....	101
4. Azoic Dyeing in Supercritical Carbon Dioxide	102
4.2 Experimental	103
4.2.1 Materials	103
4.2.2 Equipment.....	103
4.3 Methods	104
4.3.1 Pretreatment of Fabrics with Sodium Naphtholate.....	104
4.3.2 Azoic Dyeing in SC-CO ₂	104
4.3.3 Azoic Dyeing by Conventional Aqueous Method	105
4.3.4 Colorimetric Measurement.....	106
4.3.5 Fastness Assessment.....	106
4.3.5.1 Wash Fastness	106
4.3.5.2 Light Fastness.....	107
4.3.5.3 Crock Fastness	107
4.3.6 Statistical Design of Experiment	107
4.4 Results and Discussion	108

	PAGE
4.4.1 Statistical Analysis	109
4.4.2 Fastness Properties	119
4.4.3 Predicted Optimization	122
4.4.4 Colorimetric Data	122
4.4.5 Cross-sectional Analysis	124
4.4.6 Possible Fibers that can Be Dyed via SC-CO ₂ Azoic Dyeing	125
4.5 Conclusions.....	128
 5. Fiber-Reactive Dyeing of Nylon 6,6 and Wool in Supercritical	
Carbon Dioxide	130
5.1 Introduction	130
5.2 Experimental	131
5.2.1 Materials	131
5.2.2 Dyeing.....	132
5.2.3 Colorimetric Assessment	133
5.3 Results and Discussion	134
5.3.1 Effect of Temperature on Dye Uptake and Fixation using the VS	
Reactive Dye	134
5.3.2 Effect of Temperature on Dye Uptake and Fixation using the ES	
Nonreactive Dye	136
5.3.3 Effect of Pressure on Dye Uptake and Fixation using the VS Reactive	
Dye	137

	PAGE
5.4 Dye-fiber Covalent Bond Formation	140
5.5 Conclusions.....	146
5.6 Acknowledgements	147
 6. Investigation into the Synthesis of C.I. Reactive Black 5 in Supercritical Carbon Dioxide.....	 148
6.1 Introduction	148
6.2 Experimental	150
6.2.1 Materials	150
6.2.2 Equipment.....	150
6.3 Methods	150
6.3.1 Conventional Diazotization of 4-Aminophenylvinylsulfone and Coupling	150
6.3.1.1 Acid Coupling	150
6.3.1.2 Alkali Coupling	151
6.3.2 Diazotization of 4-Aminophenylvinylsulfone and Coupling in SC-CO ₂	152
6.3.2.1 Coupling to Monoazo Dye (81) in SC-CO ₂	152
6.3.2.2 Coupling to Monoazo Dye (82) in SC-CO ₂	153
6.3.3 Visible Absorption Spectra	153
6.3.4 Dyeing of Cotton Fabric	153
6.3.5 Colorimetric Measurement.....	154

	PAGE
6.4 Results and Discussion	154
6.4.1 Colorimetric Data	156
6. Conclusions.....	157
7. Summary and Future Work.....	158
8. References.....	161
Appendix A. ¹H-NMR SPECTRA.....	170
Appendix B. MASS SPECTRA	191

LIST OF TABLES

	PAGE
Table 1. Physical properties of gas, liquid and supercritical fluid.	3
Table 2. Major reactive systems used for commercial reactive dyes for exhaust dyeing.	7
Table 3. List of chromophors found in organic dyes.....	10
Table 4. List of commercially important bridging groups for reactive dyes.....	12
Table 5. Important coupling components of azoic coloration.	22
Table 6. Influence of the reactive group on color strength and fastness properties after dyeing in SC-CO ₂	45
Table 7. Structures of targeted azo dyes synthesized in SC-CO ₂	55
Table 8. Summary of data pertinent to the synthesis of azo dyes (70) to (79).	74
Table 9. Summary of $\lambda_{\max}$ values of dyes synthesized conventionally and in SC-CO ₂	81
Table 10. Coded and actual levels of the design factors.....	91
Table 11. Central composite design of dye (76) synthesized in SC-CO ₂	94
Table 12. ANOVA for response surface using a reduced 2FI model ($R^2 = 0.9983$) after exclusion of insignificant terms.	95
Table 13. Predicted optimization of synthesis of dye (76) in SC-CO ₂	101
Table 14. Coded and actual levels of the design factors.....	108
Table 15. Central composite design data for azoic dyeing in SC-CO ₂	111
Table 16. ANOVA data for the quadratic model ($R^2 = 0.9160$) after exclusion of insignificant terms.	112

PAGE

Table 17. Fastness properties of azoic dyeing cotton fabric in SC-CO ₂	120
Table 18. Fastness of cotton fabric via conventional azoic dyeing.....	121
Table 19. Predicted optimization of azoic dyeing in SC-CO ₂	122
Table 20. L* a* b* and K/S values of dyed naphtholated cotton fabrics.	123
Table 21. Colorimetric data of dyed multifiber fabrics in SC-CO ₂	126
Table 22. The $\lambda_{\max}$ of reactive dyes (81) to (84) and C.I. Reactive Black 5.....	156
Table 23. L* a* b* values and color strength (K/S) of dyed fabrics.....	157

LIST OF FIGURES

	PAGE
Figure 1. Schematic phase diagram showing the supercritical state.....	2
Figure 2. Structures of some fiber-reactive groups in commercial reactive dyes. .	6
Figure 3. Reaction of a monochlorotriazine dye with cellulose and water.	14
Figure 4. Reaction of a MCT dye with wool.	14
Figure 5. Nucleophilic addition reaction of a vinylsulfone dye.	16
Figure 6. Reaction of the α -bromoacrylamido reactive dye and wool.	16
Figure 7. Formation of an azoic dye by diazotization and coupling reactions.	25
Figure 8. Partial chemical structures of sulfur dyes.....	30
Figure 9. Mechanism of diazotization of aromatic amines.	32
Figure 10. Mechanism of diazotization process of a weakly basic amine.	33
Figure 11. Azo coupling reaction between a diazonium ion and arylamine.....	34
Figure 12. Azo coupling reaction between diazonium ion and phenolate ion.....	35
Figure 13. Modified cotton with 2,4,6-trichloro-1,3,5-triazine.	43
Figure 14. Thermal degradation of sulphonylazide dyes.....	46
Figure 15. Reaction of polyamide fiber and VS disperse reactive dye.....	48
Figure 16. Reverse micelle system.	49
Figure 17. Formation and dissociation reaction of carbonic acid.	53
Figure 18. General reaction for preparation of the diazonium ion.	54
Figure 19. A typical reaction scheme for azo coupling.....	54
Figure 20. General azoic coupling reaction in SC-CO ₂	58
Figure 21. Dyes synthesized in SC-CO ₂	61

Figure 22. Schematic diagram of the high-pressure reactor used for all experiments.	63
Figure 23. Graph of pK_a of substituted aniline versus % dye yield.	78
Figure 24. Graph of Log P of substituted aniline versus % dye yield.	79
Figure 25. Graph of Log P of substituted aniline versus % dye yield after excluding <i>ortho</i> substituents.	79
Figure 26. Comparison of absorption spectra for selected dyes prepared in conventional and SC-CO ₂ reaction conditions.	80
Figure 27. Reaction scheme showing possible nitrosation of <i>N,N</i> -dithylaniline in SC-CO ₂	82
Figure 28. Reaction scheme showing possible azo dye formation via a condensation reaction in SC-CO ₂	83
Figure 29. ¹ H-NMR spectrum of compound (87).	85
Figure 30. Diazotization and coupling of coupler-coupler in SC-CO ₂	86
Figure 31. The effect of pressure and temperature on spectroscopic yield (%). .	96
Figure 32. The effects of water and temperature on spectroscopic yield (%).	97
Figure 33. The effect of water and pressure on spectroscopic yield (%).	98
Figure 34. The effect of time and pressure on spectroscopic yield (%).	99
Figure 35. The effect of time and water on spectroscopic yield (%).	100
Figure 36. Formation of azoic dye in SC-CO ₂	109
Figure 37. The effect of pressure and temperature on color strength (K/S).	114
Figure 38. The effect of temperature and water on color strength (K/S).	115

PAGE

Figure 39. The effect of water and pressure on color strength (K/S).....	116
Figure 40. The effect of dyeing time and water on color strength (K/S).	117
Figure 41. The effect dyeing time and temperature on color strength (K/S).....	118
Figure 42. The effect dyeing time and pressure on color strength (K/S).	119
Figure 43. Graph of K/S as a function of λ for the optimized dyeing in SC-CO ₂ and the conventional azoic dyeing method.	123
Figure 44. Photomicrograph of azoic dyeing of cotton in the weft direction.	124
Figure 45. Photomicrograph of azoic dyeing of cotton in the warp direction.	125
Figure 46. Photograph of dyed multifiber fabric dyed using the optimized SC-CO ₂ azoic dyeing method.	127
Figure 47. Effect of temperature on dye uptake and fixation with VS reactive dye on nylon 6,6 fabric.....	135
Figure 48. Effect of temperature on dye uptake and fixation with VS reactive dye on wool fabric.....	135
Figure 49. Effect of temperature on dye uptake and fixation for the ES non- reactive dye on nylon 6,6.	136
Figure 50. Effect of temperature on dye uptake and fixation for the ES non- reactive dye on wool.	137
Figure 51. Effect of pressure on dye uptake and fixation for the VS reactive dye on nylon 6,6 fabric at 125°C.....	138
Figure 52. Effect of pressure on dye uptake and fixation for the VS reactive dye on wool fabric at 125°C.....	138

PAGE

Figure 53. Effect of pressure on dye uptake and fixation for the VS reactive Dye on nylon fabric at 140°C.....	139
Figure 54. Effect of pressure on dye uptake and fixation for the VS reactive dye on wool fiber at 140°C.....	139
Figure 55. ¹ H-NMR spectrum of the reaction product from the VS dye and butylamine reaction in ethanol.	142
Figure 56. ¹ H-NMR spectrum of the reaction product from the VS dye and butylamine reaction in SC-CO ₂	143
Figure 57. Positive ion FAB mass spectrum of the reaction product from the VS dye and butylamine reaction in ethanol.....	144
Figure 58. Positive ion FAB mass spectrum of the reaction product from the VS dye and butylamine reaction in SC-CO ₂	145
Figure 59. Michael addition reaction of VS dye and butylamine in SC-CO ₂	146
Figure 60. Reaction sequence for the synthesis of C.I. Reactive Black 5.	148

1. Introduction

1.1 Supercritical Fluids

A substance is in a supercritical state when temperature (T) and pressure (P) are both above the critical point of the substance. The temperature and pressure at the critical point are called critical temperature (T_c) and critical pressure (P_c), respectively. Hence, a supercritical fluid (SCF) can be characterized using a simple phase diagram, as shown in Figure 1. Under these conditions, the fluid exhibits unique properties that are characteristic of both gases (e.g., extremely low viscosity and high diffusivity) and liquids (e.g., reasonable solvation properties of certain solutes) [1,2]. The physical properties of SCFs, such as the diffusion coefficient, viscosity, and dissolving power, are determined by the pressure and temperature of the system. Some typical physical properties of a gas, liquid, and a SCF are compared in Table 1. A simple way to predict the solvent characteristics of a low-boiling substance in its supercritical state is to compare the normal boiling point (T_b) and the critical temperature (T_c) using Guldberg's rule [1] (equation 1).

$$T_b = 2/3 T_c \text{ (K)} \quad \text{(equation 1)}$$

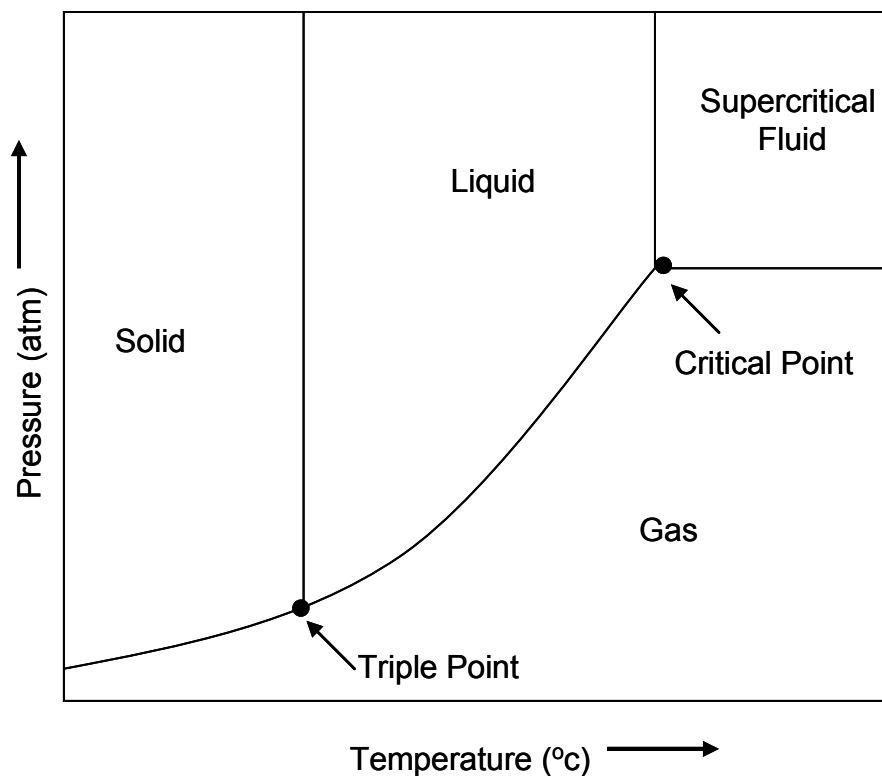


Figure 1. Schematic phase diagram showing the supercritical state.

SCFs have the ability to dissolve nonpolar solids which makes them useful in various applications ranging from classical extraction to sophisticated industrial processes, for instance in the area of polymer processing involving impregnation of pharmaceutical products into polymer matrix [3]. Also, over the last decade, research has focused on the development of SCF technology for various textile applications, including extraction of impurities (scouring), bleaching and dyeing (see section 4).

Table 1. Physical properties of gas, liquid and supercritical fluid.

	Density (g/cm ³)	Diffusivity (cm ² /sec)	Viscosity (g/cm.sec)
Gas	10 ⁻³	10 ⁻¹	10 ⁻⁴
Liquid	1	5x10 ⁻⁶	10 ⁻²
SCF	0.3-0.8	10 ⁻³	10 ⁻⁴

1.1.1 Supercritical Carbon Dioxide

Although several substances are useful as SCFs, CO₂ has been the most widely used in SCF textile research and development, primarily due to its attractive environmental and technical properties. In particular, the critical temperature of CO₂ is 31.3°C, and the critical pressure is 72.9 atm (73.8 bar) [4]. Therefore, supercritical carbon dioxide (SC-CO₂) can be produced at relatively low pressure and temperature compared to water, for example, which enters the supercritical state at 374.4°C and 226.8 atm (229.8 bar). The low T_c and P_c for SC-CO₂ make its use economically feasible. In the case of coloration of textile fibers, a number of benefits can be realized when using SC-CO₂, including:

- (1) Complete elimination of water (aqueous effluent).
- (2) Vastly reduced energy costs due to elimination of a drying step.
- (3) Elimination of auxiliary agents (e.g., surfactants, salts).
- (4) Rapid diffusion and potential for high degree of dye exhaustions.
- (5) No after treatment is required.
- (6) Mild critical properties (31.3°C and 72.9 atm).

- (7) Non-toxic at low concentration.
- (8) Non-flammable.
- (9) Inexpensive, abundant and easily recycled.

Furthermore, since SCF technology is being used successfully in commercial processing (e.g., extraction of caffeine), further development and transfer of the technology to textile finishing industry appears feasible [5]. However, there are a number of potential barriers to the widespread use of SCF technology, particularly the high capital cost of high-pressure equipment for very low viscosity fluids, the limited range of solutes that will dissolve in SC-CO₂, and slow rate of transfer of certain solutes from the solid phase to dissolution (see section 4). In the case of dyeing fibers using SC-CO₂, it is critical to ascertain the types and range of dyes that may be used in this medium.

1.2 Classification of Dyes According to Application Method

There are several ways by which coloring materials can be classified, including classification according to end uses, method of application and chemical constitution. The classification of dyes by the application methods to the textile fibers is perhaps the most common one, and will be used here.

1.2.1 Fiber-Reactive Dyes

Fiber-reactive dyes are colored organic compounds that contain reactive functional groups that can react to form covalent bond with nucleophilic groups present on polymer chains of certain fibers [6,7]. The first commercial fiber-reactive dyes for cotton were developed by ICI and Ciba and were commercialized in 1956. A key advantage of fiber-reactive dyes is their ability to dye cotton with bright shades and high washfastness property due to the strength of the covalent bond formation between dye and the fiber [7,8].

1.2.1.1 Constitutional Characteristic of Reactive Dyes

The characteristic features of typical reactive dyes can be categorized into four areas: reactive group, chromophoric group, bridging group and solubilizing group

Reactive Groups

In the 50 years since fiber-reactive dyes were developed, a large number of reactive functional groups have been developed and commercialized. Figure 2 shows a summary of the major groups. Dyes may be monofunctional, bifunctional or in some cases, multifunctional. Adding more reactive groups to the dye molecule increases the probability of dye-fiber reaction but usually decreases the color per unit weight of dyes [9]. This shortcoming can be

overcome somewhat by bridging two monofunctional reactive dyes with a suitable low molecular weight diamine.

The most important monofunctional and bifunctional reactive systems are displayed in Table 2. These groups are reactive toward the hydroxyl anion present on cellulosic fibers (in the presence of alkali) and primary or secondary amino groups present in wool, nylon and silk.

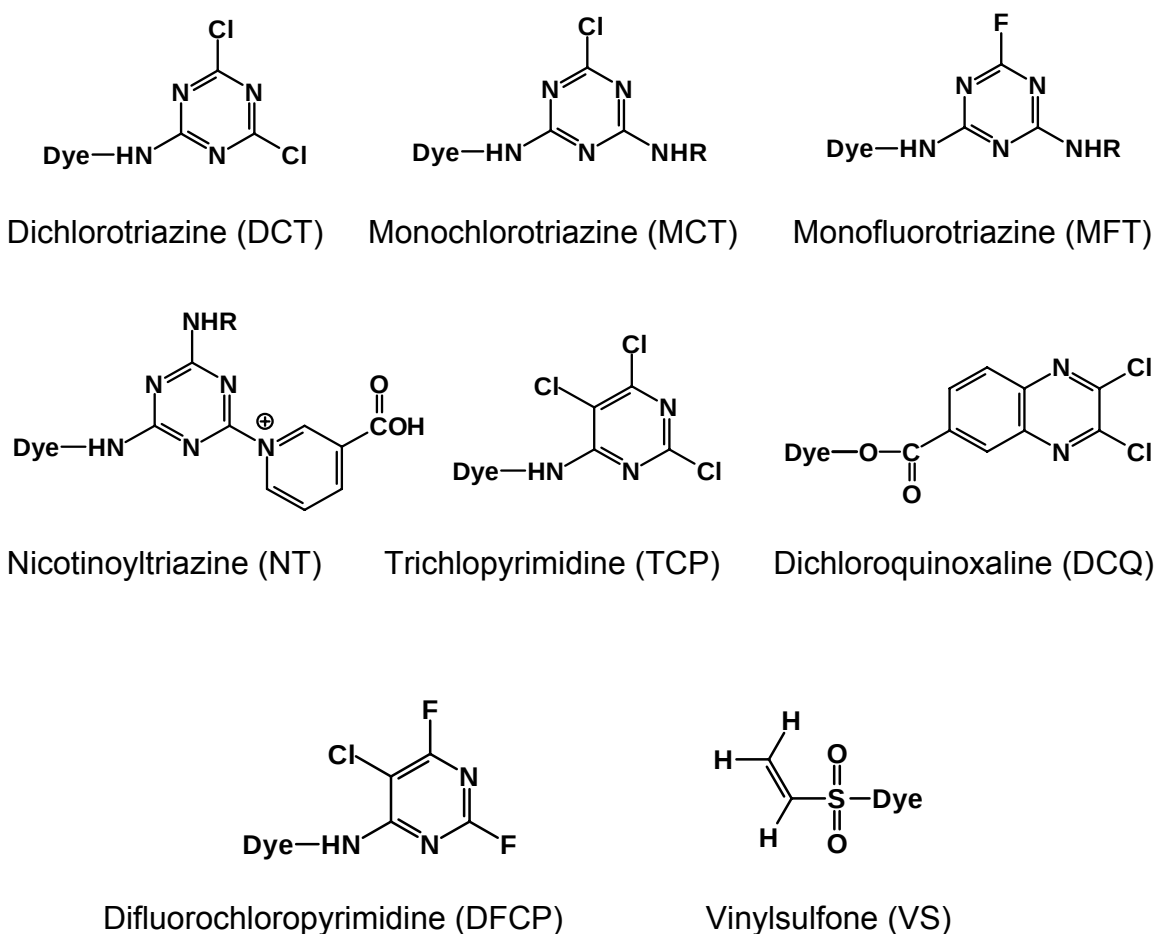


Figure 2. Structures of some fiber-reactive groups in commercial reactive dyes.

("Dye" represents chromogen).

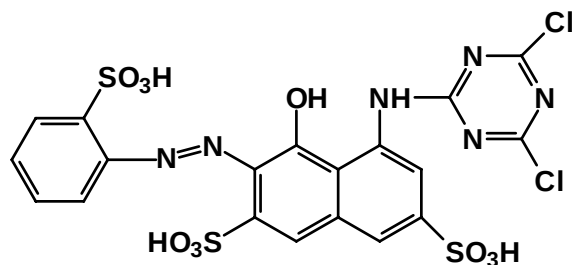
Table 2. Major reactive systems used for commercial reactive dyes for exhaust dyeing.

System	Commercial name
Monofunctional Systems	
Dichlorotriazine	Procion MX (ICI)
Monochlorotriazine	Procion H (ICI)
Monofluorotriazine	Cibacron F (Ciba)
Trichloropyrimidine	Drimarene X (Sandoz)
Chlorodifluoropyrimidine	Drimarene K (Sandoz)
Dichloroquinoxaline	Levafix E (Bayer)
Sulfatoethylsulfone	Ramazol (Hoechst)
Sulfatoethylsulfonamide	Ramazol D (Hoechst)
Bifunctional Systems	
Bis(monochlorotriazine)	Procion HE (ICI)
Bis(mononicotinoyltriazine)	Kayacelon React (Nippon Kayaku)
Monochlorotriazine-sulfatoethylsulfone	Sumifix Supra (Sumitomo)
Monofluorotriazine-sulfatoethylsulfone	Cibracron (Ciba)

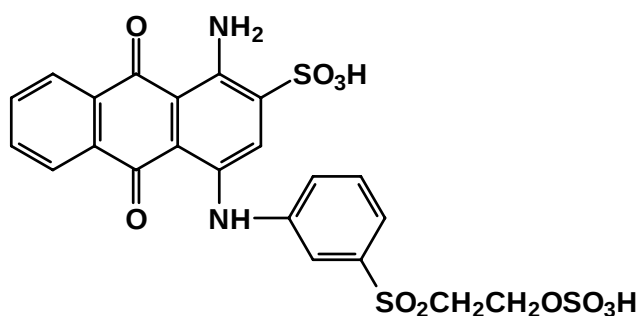
Monofunctional Reactive System

Monofunctional dyes can react only once with nucleophilic groups in the fiber via nucleophilic addition or substitution. Halotriazine (e.g., C.I. Reactive

Red 1, (1)) and vinylsulfone-containing (e.g., C.I. Reactive Blue 19 (2)) dyes are examples of monofunctional reactive systems.



(1)

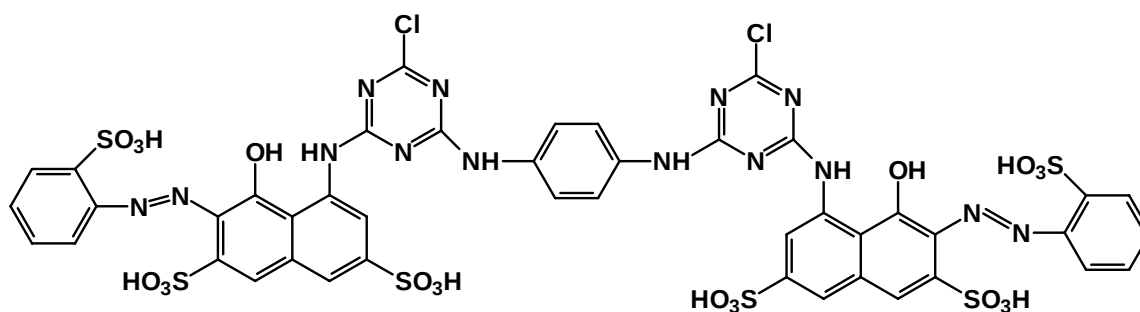


(2)

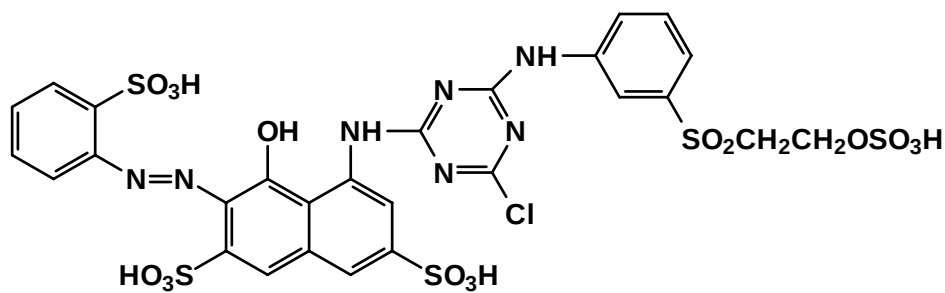
Bifunctional and Polyfunctional Reactive Systems

The major weakness of fiber-reactive dyes in all dyeing processes is the inherent hydrolysis reaction that may take place with hydroxide ions present in water, particularly under alkaline conditions. To improve fixation between the dye and the fiber, dyes with more than one fiber reactive group in the molecule have been developed, as this increases the probability of achieving a covalent bond forming with the fiber. For instance, even if one reactive group hydrolyzes (thereby rendering the group unreactive towards nucleophilic groups present on the fiber), the second reactive group may still react if it has not yet hydrolyzed.

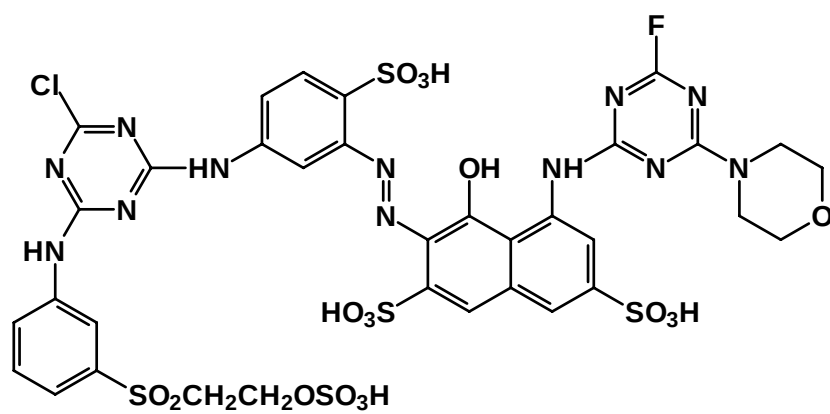
Examples of bifunctional reactive dyes are C.I. Reactive Red 120 (3), and C.I. Reactive Red 194 (4). An example of a polyfunctional reactive dye is (5).



(3)



(4)



(5)

Chromophoric Groups

The chromophoric group is the part of the molecule that is essential to provide absorption of visible light, and contributes significantly to key fastness properties such as photostability. The most important chromophoric groups used for the preparation of reactive dyes are azo (yellow, orange, and red shades), anthraquinone (blue shades), phthalocyanine (turquoise shades), formazan and dioxazine (violet and blue shades) chemical classes [8,10-12]. The basic structural component of these chromophores are given in Table 3.

Table 3. List of chromophors found in organic dyes.

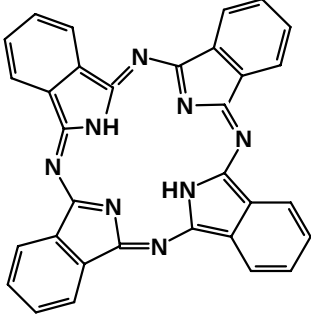
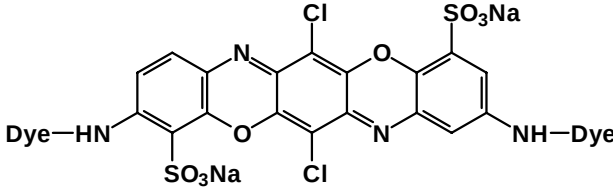
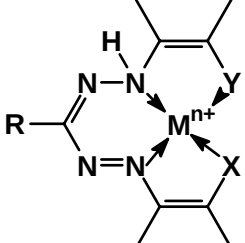
Chromophoric groups	Chemical Structures
Azo	—N=N—
Carbonyl	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$
Nitroso	—N=O
Nitro	—NO_2
Phthalocyanine	

Table 3. (Continued)

Chromophoric groups	Chemical Structures
Dioxazine	
Formazan	

Bridging Group

The term bridging group is used to identify the group of atoms which link the chromogen moiety to the fiber-reactive group [13,14]. There are many commercially important bridging groups, the samples of which are shown in Table 4. These groups are necessary for ease of synthesis and they can significantly influence both reactivity and degree of fixation.

Table 4. List of commercially important bridging groups for reactive dyes.

Bridging groups	Chemical Structures
Imino group	—NH—
Ether	—O—
Mercapto	—S—
Carbonyl	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$
Carboxamido	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—NH—} \end{array}$
Sulfonamido	$\begin{array}{c} \text{—HN—} \langle \text{benzene ring} \rangle \text{—C(=O)—NH—} \\ \text{—S(=O)}_2\text{—NH—} \end{array}$

Solubilizing Groups

All commercially important fiber-reactive dyes today are applied from an aqueous environment. Hence, water solubilizing groups are incorporated into the chromogen. The dominant solubilizing group is the sodium sulfonate substituent. Solubilizing groups are important as they influence substantivity, migration and the relative ease with which hydrolyzed and unreacted dye is removed from the fiber [15,16]. In order for fiber-reactive dyes to display superior wash fastness, all unreacted dye must be removed. Also, from an economic and environmental stand-point, it is important that unreacted dye is washed off with minimal number

of washes to reduce the volume of waste water that must later be treated. Therefore fiber-reactive dyes generally should have very low affinity. However, the low affinity fiber-reactive dyes require high amounts of electrolyte during applications which contributes negatively to the environmental impact of the dye class.

1.2.1.2 Chemical Reactions between Reactive Dyes and Fibers

Nucleophilic Substitution

The first important reaction of fiber-reactive dyes involves heteroaromatic nucleophilic substitution. A leaving group in the reactive dye is displaced as a result of an interaction with a nucleophilic group on the polymer chain. Figure 3 shows the reaction of a MCT reactive dye with a cellulosate anion under alkaline conditions, while Figure 4 illustrates the reaction of a MCT reactive dye with an amino group in wool or keratin fibers. As mentioned previously, all reactive dye systems undergo a competing hydrolysis reaction, which leads to a degree of fixation less than 100%. In some cases, as little as 60-70% of dye is fixed on the fibers. Reactive dye hydrolysis is an undesirable feature because it must be washed out of the fiber after dyeing to ensure optimum washfastness. Furthermore, it means that significant quantities of synthesized reactive dyes never reach the intended target and instead must be treated as effluent.

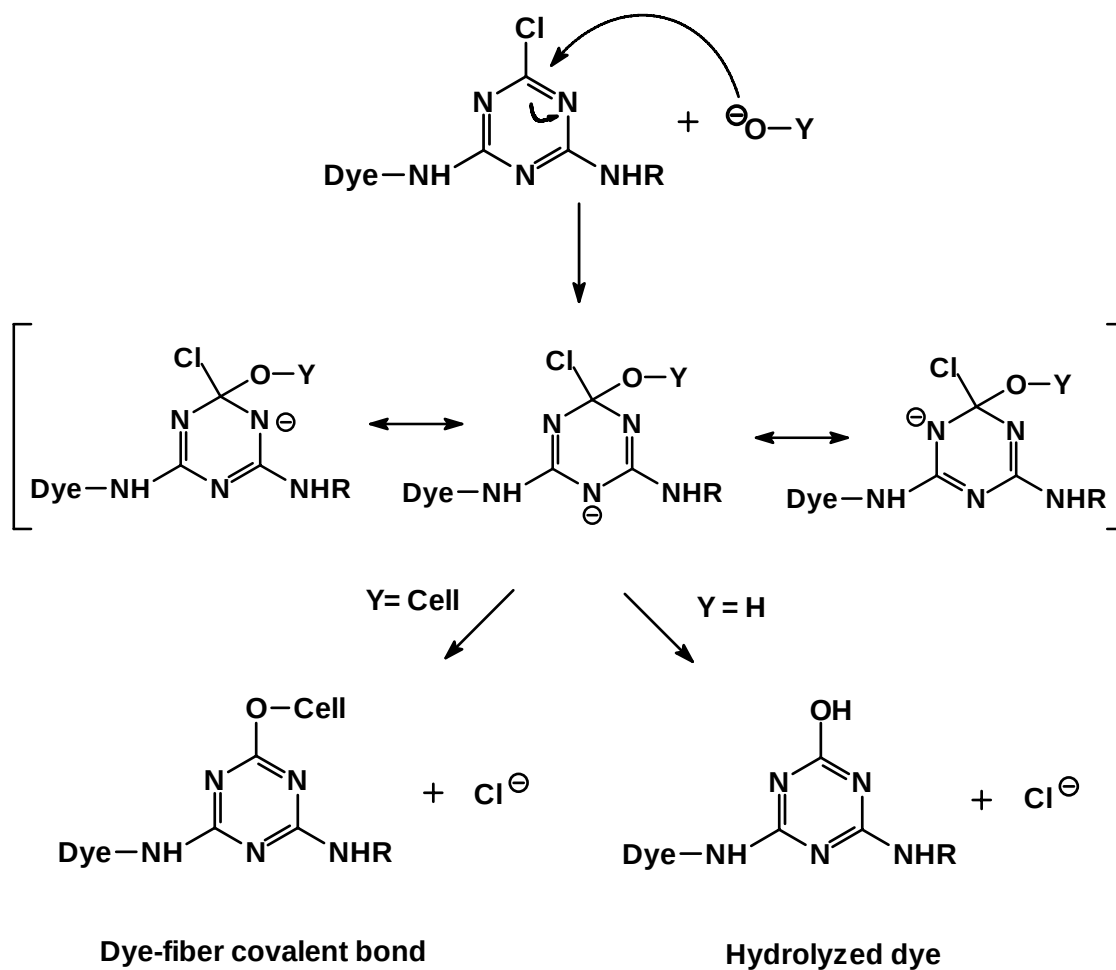


Figure 3. Reaction of a monochlorotriazine dye with cellulose and water.

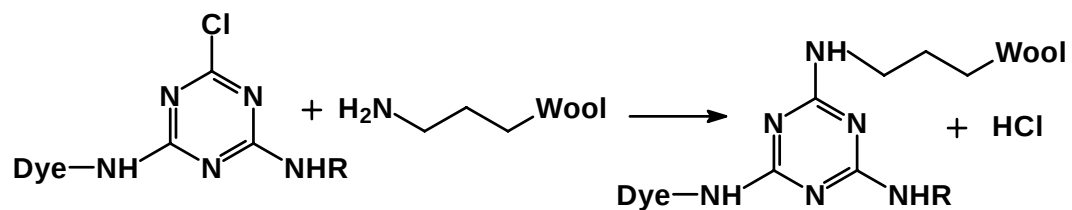


Figure 4. Reaction of a MCT dye with wool.

Nucleophilic Addition

The second important dye-fiber reaction involves nucleophilic addition to an activated double bond. Nucleophilic addition reaction of alkenes is alternatively referred to as either conjugate addition or Michael addition.

The most important reactive group is based on vinylsulfone (VS) which is the preferred reactive group for both cellulosic and protein fibers. Vinylsulfonyl fiber-reactive dyes are usually supplied as the β -sulfatoethylsulfone derivative, which is a stable precursor; the sulfato group is readily β -eliminated under mild alkaline conditions to produce the reactive VS group. The reaction mechanism for fiber fixation is illustrated in Figure 5. The attack by cellulosate anion on the vinylsulfone initially leads to an anion intermediate which is stabilized by resonance of electronegative oxygen atoms of the sulfone group. The addition reaction is completed by proton transfer. As with nucleophilic substitution reactions of MCT dyes, hydrolysis also takes place in competition with the dye-fiber reaction leading to hydrolyzed dye.

There are relatively few other reactive groups which react by nucleophilic addition that have achieved significant commercial success. One system is the α -bromoacrylamido group found in Lanazol dyes (Ciba). These are the most widely used reactive dyes for wool. The chemistry involved in the reaction of dyes with the amino groups present on the wool fibers is shown Figure 6. Not only the nucleophilic addition reaction can take place but also nucleophilic substitution reaction can occur leading to cross-linking of the fibers.

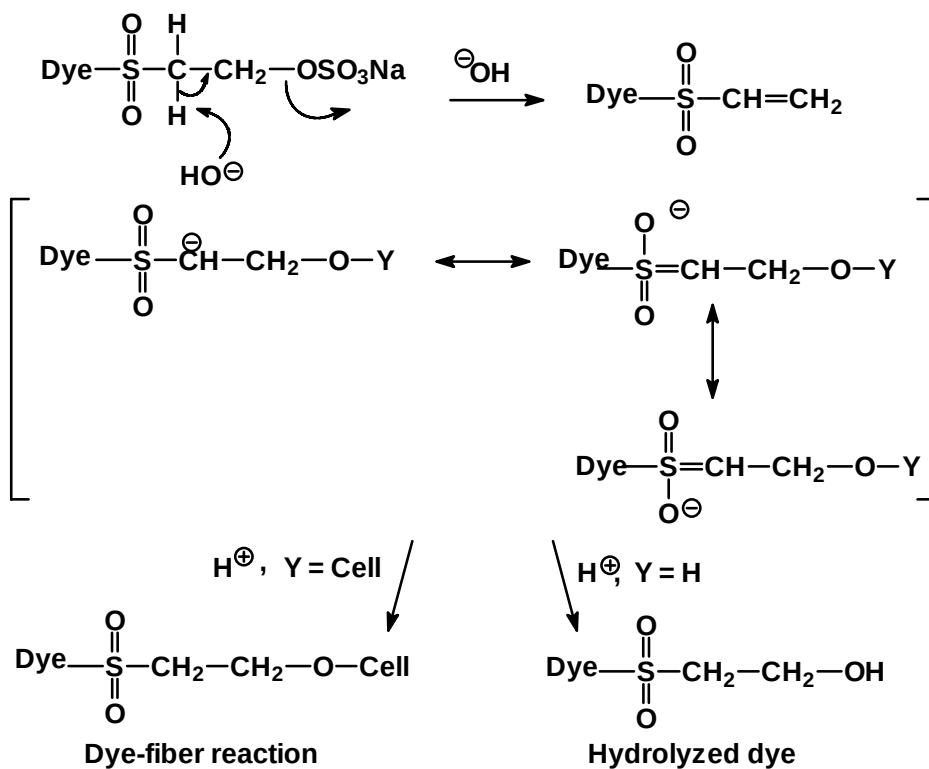


Figure 5. Nucleophilic addition reaction of a vinylsulfone dye.

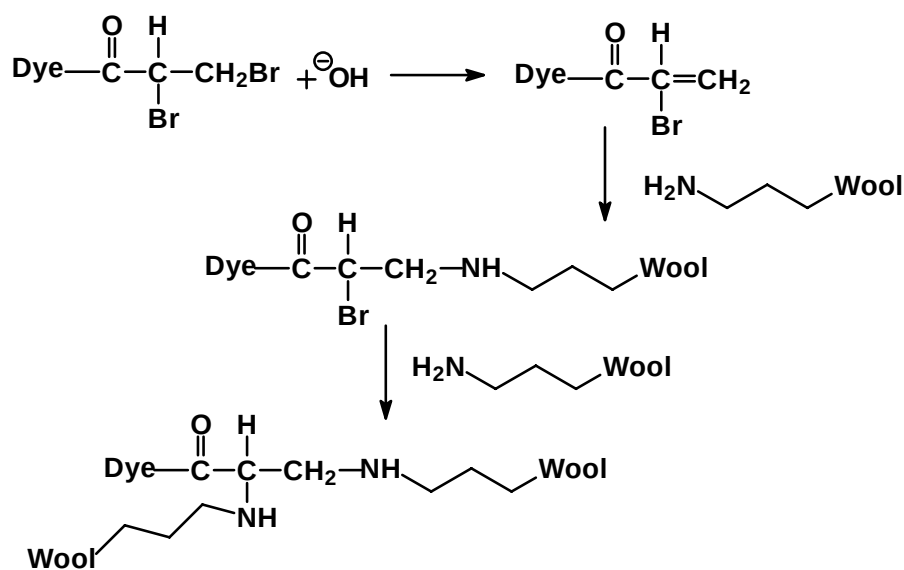
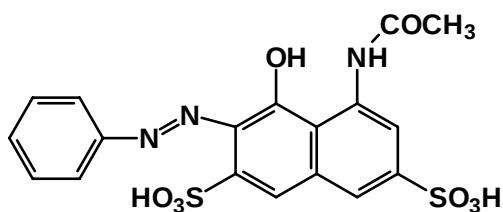


Figure 6. Reaction of the α -bromoacrylamido reactive dye and wool.

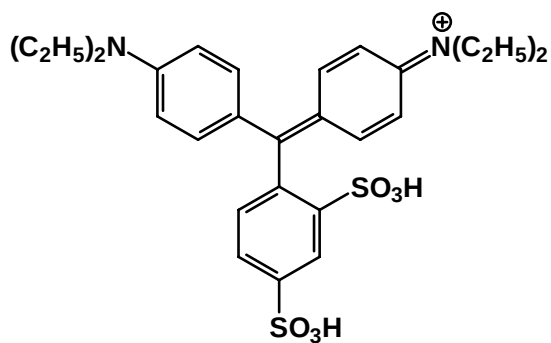
1.2.2 Acid Dyes

Acid dyes are used to dye protein and polyamide. A characteristic feature of acid dyes is the presence of one or more anionic groups ($-\text{SO}_3^-$, $-\text{COO}^-$, or O^-). These groups provide aqueous solubility and produce a negative charge that facilitates ionic attraction with cationic groups on polyamide and protein fibers under acid conditions. Additional dye-fiber affinity occurs between other parts of the dye molecule and the fiber via van der Waals forces and hydrogen bonding [8].

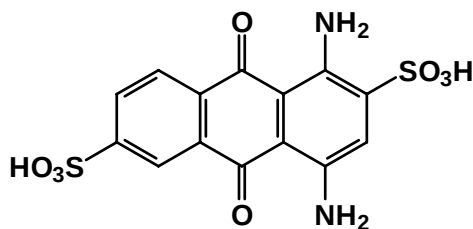
Most acid dyes, especially yellows, oranges, and reds, belong to the azo chemical class, while blues and greens are often provided by carbonyl dyes, especially anthraquinone, and to a lesser extent by arylcarbonium ion based dye (triphenylmethane). Examples of acid dyes are C.I. Acid Red 1 (6), C.I. Acid Blue 1 (7) and C.I. Acid Blue 56 (8).



(6)



(7)



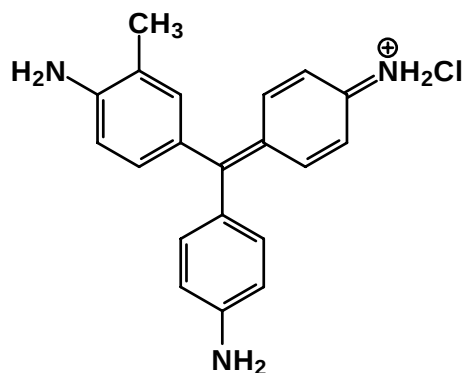
(8)

1.2.3 Basic Dyes

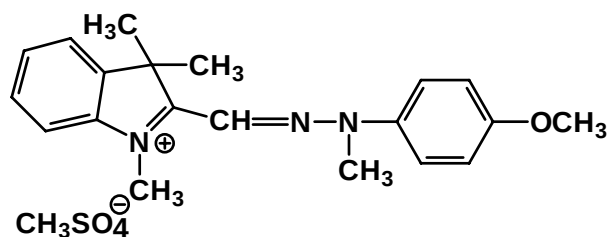
This is the most important class of dyes used on acrylic fibers. The dye-fiber bonding is essentially the same as acid dyes on polyamide fibers, except the charges are reversed. Polyacrylonitrile (PAN) or acrylic fibers are produced from polymers which contain 85% or more of acrylonitrile as the principle monomer. The other monomers are methacrylic acid, methyl methacrylate, or vinyl acetate.

Commercial PAN is polymerized by using catalysts such as potassium persulfate and sodium bisulfite which leave terminal negatively charged sulfonate groups on the fibers [17]. The sulfonate groups are attracted to the cationic groups present in all basic dyes. Other comonomers containing sulfonic acid groups may be introduced to interrupt the chain regularity and to increase the negative sites to the fibers.

In general, basic dyes produce brilliant hues with excellent wash fastness and very high tinctorial strength [7,17]. Examples of basic dyes are C.I. Basic Violet 14 (9) and C.I. Basic Yellow 28 (10).



(9)



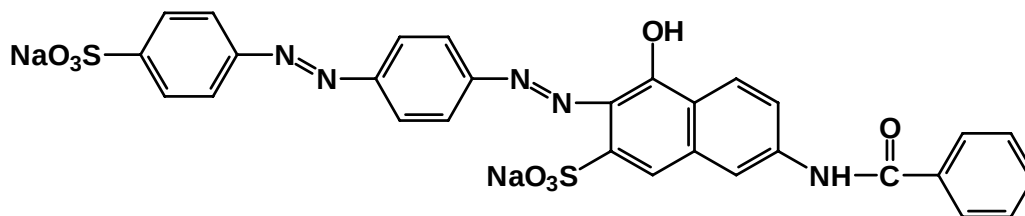
(10)

1.2.4 Direct Dyes

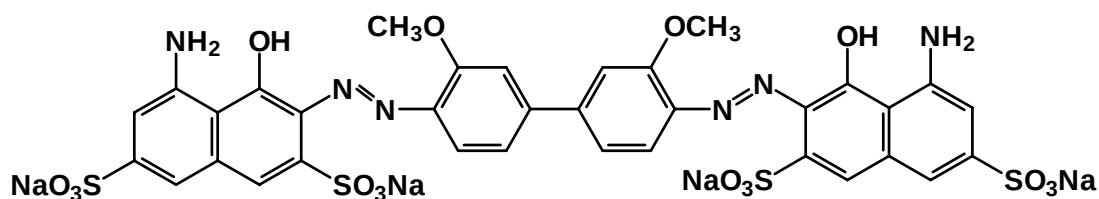
Direct dyes are long, planar anionic dyes and have substantivity to cellulosic materials without any requirement of a pre-treatment of the fibers with mordants [18]. The application of direct dyes is simple since the only dyeing assistant usually used is a strong electrolyte such as sodium chloride or sodium sulfate to neutralize the zeta potential of the cellulosic fibers in an aqueous environment, thereby assisting exhaustion.

The main disadvantage of direct dyes is poor washfastness properties since direct dyes are attached to cellulosic fibers through relatively weak van der Waals and hydrogen bonding. Although several attempts have been developed to improve washfastness properties, it still does not meet the fastness requirements of many high performance garments.

The majority of direct dyes are diazo and trisazo derivatives. Examples of azo direct dyes are C.I. Direct Red 81 (**11**) and C.I. Direct Blue 218 (**12**).



(11)



(12)

1.2.5 Azoic Dyes

Azoic dyes can be considered a special class of water-insoluble azo compounds in which the azo chromophore is produced inside the textile fiber (usually cotton) by separate application of a coupling component and a diazo component [17]. Hence, the fabric is treated with the two components used to synthesize the dye within the fiber structure. Most azoic dyes produce monoazo compounds, but a few produce disazo dyes.

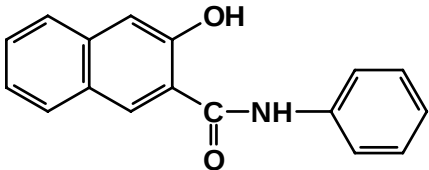
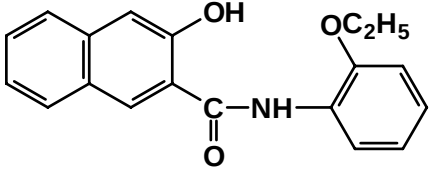
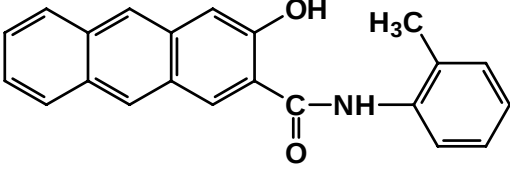
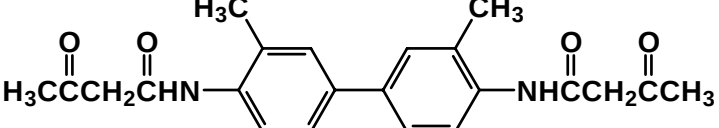
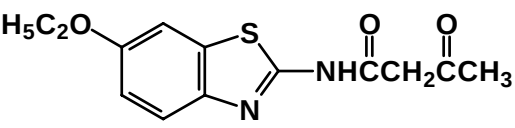
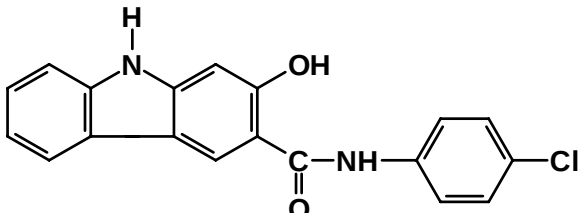
Both the coupling component and the diazo component are relatively small molecules that easily diffuse into the pores and spaces between the cellulosic fibers. When the two components come into close proximity to each

other they react to form the insoluble dye, which is trapped inside the fibers because of the larger size of the resultant dye molecule.

1.2.5.1 Coupling Components

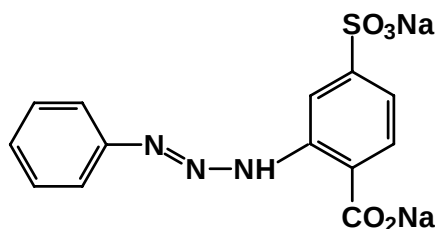
The most important of coupling components are known as naphthols. The majority are anilides of 2,3-hydroxynaphthoic acid. The substantivity of these compounds toward cotton is due to the anilide group. The high mobility of the relatively small molecular size of coupling components leads to rapid diffusion into cellulosic fibers. The water-insoluble coupling components are rendered soluble by conversion into sodium salts by reacting with sodium hydroxide prior to application to the substrate. Naphtholates in solutions are unstable, and therefore should be used immediately after preparation [17]. The naphthol may be applied by an exhaust method, or by a padding process. The most important coupling components are given in Table 5 [19].

Table 5. Important coupling components of azoic coloration.

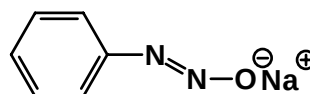
Coupling components	Structures
Naphthol AS	
Naphthol AS-PH	
Naphthol AS-GR	
Naphthol AS-G	
Naphthol AS-L4G	
Naphthol AS-LB	

1.2.5.2 Diazo Components

A wide range of diazotizable aromatic primary amines are produced in the form of a so-called free base (Fast Color Bases), or as an amine salt (Fast Color Salts). Owing to the instability of many diazo compounds, including Fast Color Bases, a variety of stabilized diazonium components have been developed. Fast Color Salts are complexes between a diazo group and zinc chloride (ZnCl_4), borofluoride (BF_4) or aryl sulfonate. Diazonium ions also can be stabilized by conversion into a diazoamino compound acid (**13**) with an amino or into trans-diazotate ions (**14**).



(13)



(14)

The formation of both diazoamino and diazotate derivatives (Rapid Fast Colors) is reversible in acidic condition to regenerate the diazonium ion. These stabilized diazonium compounds overcome the poor storage stability of the stock solutions of diazotized amines, and are readily soluble in water. However, they are much more expensive.

Azoic dyes are principally used for dyeing and printing cellulosic fibers. They are ideal for printing applications, in which any unreacted coupler is simply

washed off. It is important to remove mechanically held naphtholate components prior to development; otherwise the azoic colorant is deposited on the fiber surface leading to poor fastness properties. A common problem associated with azoic dyes is poor crockfastness, as some dye formation occurs on the surface rather than inside the fibers. A summary of chemical reactions involved in the application of azoic dyes is shown in Figure 7 [17].

Azoic dyes provide a wide range of bright hues, with the exception of greens and bright blues. The actual hue produced with these colorants is determined by the particular combination of diazo and coupling components used.

The introduction of alkoxy, phenoxy, halogen or sulfone substituents into the diazo component imparts enhanced light fastness, compared to when these auxochromes are not present on the resultant dye.

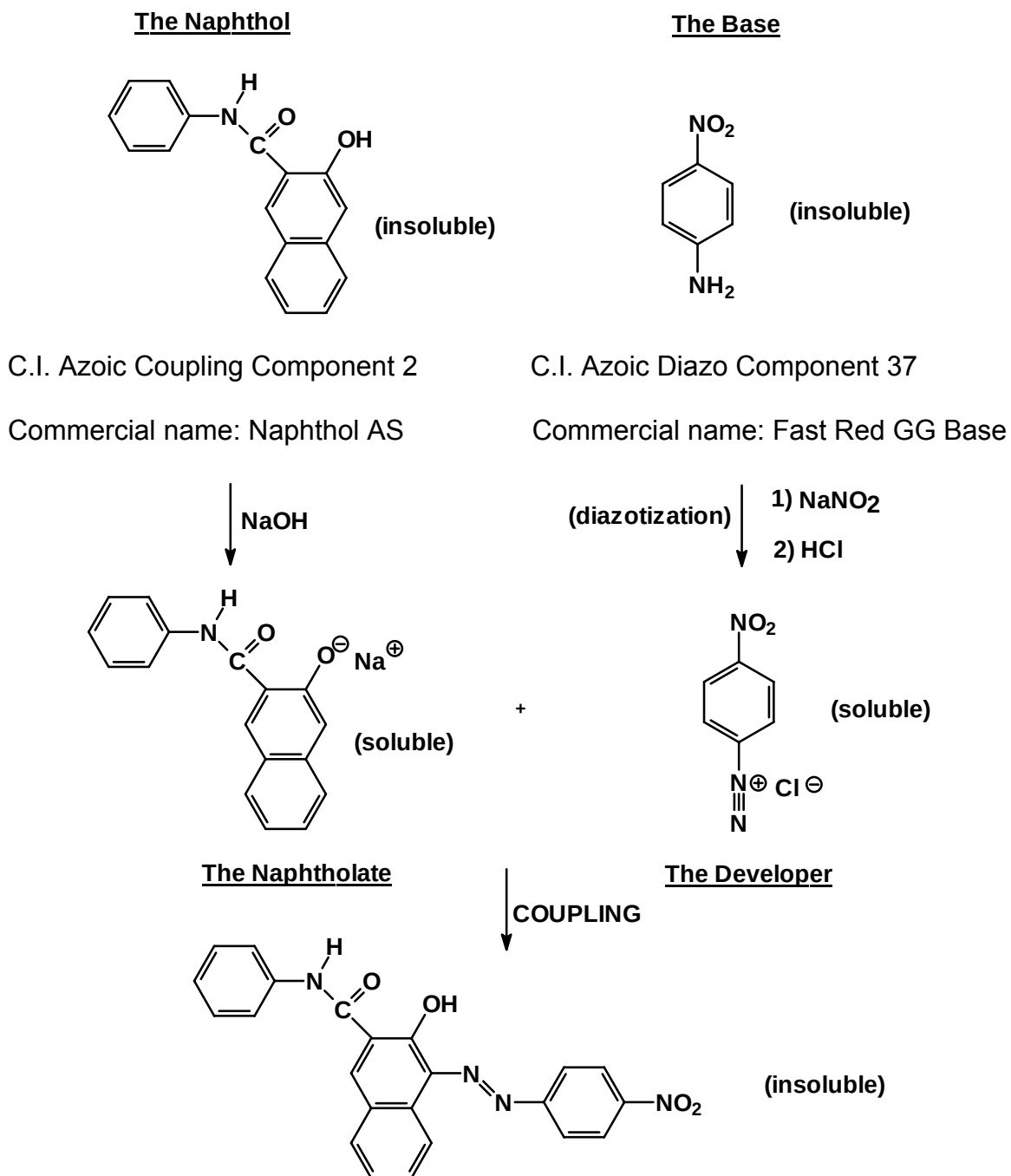


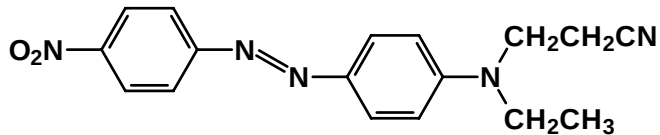
Figure 7. Formation of an azoic dye by diazotization and coupling reactions.

1.2.6 Disperse Dyes

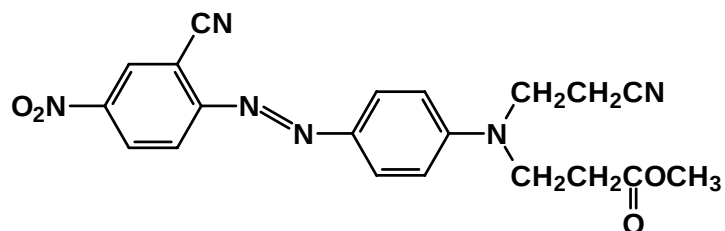
Disperse dyes are an application class of dyes with relatively low molecular weight, nonionic structures with low water solubility. Disperse dyes are used to dye polyester, cellulose acetate and triacetate fibers. In order for the dyes to exhibit substantivity and distribution through the fiber, relatively small, hydrophobic dyes were developed. The dyes are usually applied under pressure at 130°C when polymer chain mobility is relatively high. At this stage, the polymer structures allow rapid diffusion of dye into the fiber to form a solid solution. Once surface dye is removed (e.g. through reduction clear, which destroys the chromophore of dye on the surface), dyeings of satisfactory wash fastness can be achieved.

Disperse dyes generally possess polar groups, including the nitro, cyano, hydroxyl, amino, ester, amide and sulfone groups. These polar groups contribute to the application properties of dyes such as providing the appropriate level of water solubility as well as enhanced fiber affinity.

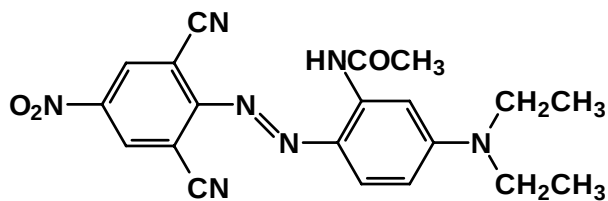
Azo dyes are the most important class of disperse dyes because of the numerous substitution patterns possible in the diverse diazonium ion and coupling components. Azo disperse dyes provide important color in the orange, red, violet and blue sectors. Examples include C.I. Disperse Orange 25 (**15**), C.I. Disperse Red 90 (**16**) and C.I. Disperse Blue 165 (**17**).



(15)

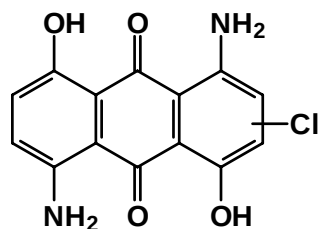


(16)

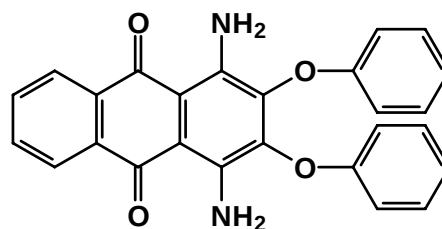


(17)

Antraquinone disperse dyes are next in importance to azo dyes and are predominantly used for red, violet, blue and blue-green hues [20]. Examples include C.I. Disperse Blue 56 (**18**) and C.I. Disperse Violet 26 (**19**).



(18)



(19)

1.2.7 Vat Dyes

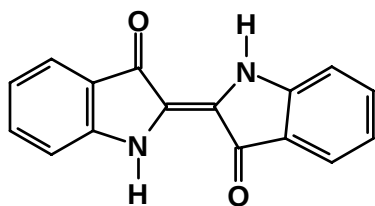
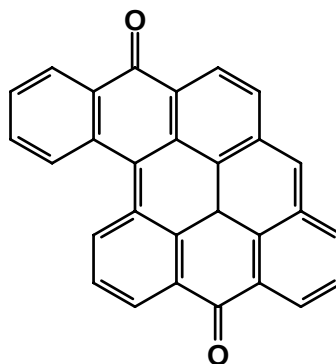
Vat dyes are water insoluble aromatic compounds and in this respect they are like pigments. However, technically these compounds are still classified as dyes because they are converted into soluble (leuco) forms during application to fibers. Vat dyes can be converted to the soluble leuco form by means of alkaline reduction with NaOH and $\text{Na}_2\text{S}_2\text{O}_4$. In this soluble form, the leuco dyes may or may not exhibit substantivity for cellulosic fiber in the presence of electrolyte. Following application to cotton, the leuco dyes are oxidized and converted back to their original insoluble form. Washfastness is very high for vat dyes following removal of surface dyes by hot washing in the presence of surfactant.

The German Interessen Gemeinschaft fur Farbenindustrie (IG) classified quinone vat dyes based on leuco compound substantivity and dyeing conditions into three main groups:

- (1) the IN (indantrene normal) groups require the application of concentrated NaOH, high vatting (60°C) and dyeing temperature (60°C). No salt is added to dyebath because of the high substantivity of leuco dyes.

- (2) the IW (indantrene warm) groups require moderate amounts of NaOH, lower vatting (50°C) and dyeing temperature (50°C). Addition of salt is needed during dyeing to promote dye exhaustion due to moderate substantivity of the vat dyes.
- (3) the IK (indantrene cold) groups require a low concentration of NaOH, low vatting (40°C) and dyeing temperature (40°C). Since these dyes have low substantivity for cotton, they required high salt concentration to ensure good dyebath exhaustion.

There are two important types of vat dyes: anthraquinone derivatives and indigoid derivatives. Examples of the two types are C.I. Vat Blue 1 (**20**) and C.I. Vat Orange 9 (**21**). C.I. Vat Blue 1 is by far the most important dye for the denim industry.

**(20)****(21)**

1.2.8 Sulfur Dyes

Sulfur dyes are a type of dye used for dyeing cellulosic fibers with very good washfastness and moderate light fastness properties at a low cost. The chemistry of sulfur dyes is very complex involving difficult to analyze mixtures. In general, they are polymeric structures having sulfur containing aromatic heterocyclic unit such as thiazines and thiazoles linked by di- or polysulfide bonds [9] (Figure 8).

Sulfur dyes are converted to leuco compounds (soluble form) by reduction with a mild reducing agent, such as sodium sulfide and subsequently oxidized back into an insoluble forms following application to cotton. Sulfur dyes have the duldest shade of colors of all dye classes. Hence, color limitation in bright shade is the main disadvantages of sulfur dyes.

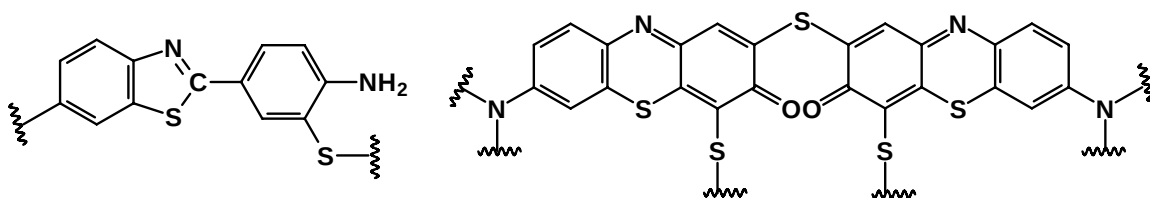


Figure 8. Partial chemical structures of sulfur dyes.

1.3. Azo Dyes

Section 1.2 was concerned with a discussion of dyes classified by their application method. A cursory review of the literature shows clearly that azo

dyes constitute the most important chemical class of dyes for many application classes. In fact, azo dyes account for over 50% of all commercial dyes. Consequently, it is fitting to review the chemistry of azo dyes as a separate section. Moreover, azo dyes are the principle compounds involved in this research.

1.3.1 Synthesis of Azo Dyes

Azo dyes are compounds that contain at least one azo group attached to sp^2 -hybridized carbon atoms. The azo groups are usually bound to substituted phenyl, naphthyl, or aromatic heterocyclic groups. The most stable structural isomer is the *trans* form with a the bond angle *ca.* 120° [21]. The first stage of azo dye synthesis is diazotization of an aromatic amine to produce a diazonium ion.

1.3.1.1 Diazotization of Aromatic Amines

Azo dyes are produced by diazotization of an aromatic or a heteroaromatic primary amine followed by coupling the resultant diazonium ion to an electron-rich nucleophile. The diazotization reaction is effected by treating the primary aromatic amine with nitrous acid (HNO_2) at $0\text{-}5^\circ\text{C}$ (Figure 9) [22]. Nitrous acid is generally obtained by combining an aqueous mineral acid such as hydrochloric acid with sodium nitrite (NaNO_2). The nitrous acid reacts with aromatic amines to form an N-nitroso intermediate and later tautomerizes to a

diazo hydroxide. Protonation of the hydroxyl group followed by elimination of water generates the diazonium ion.

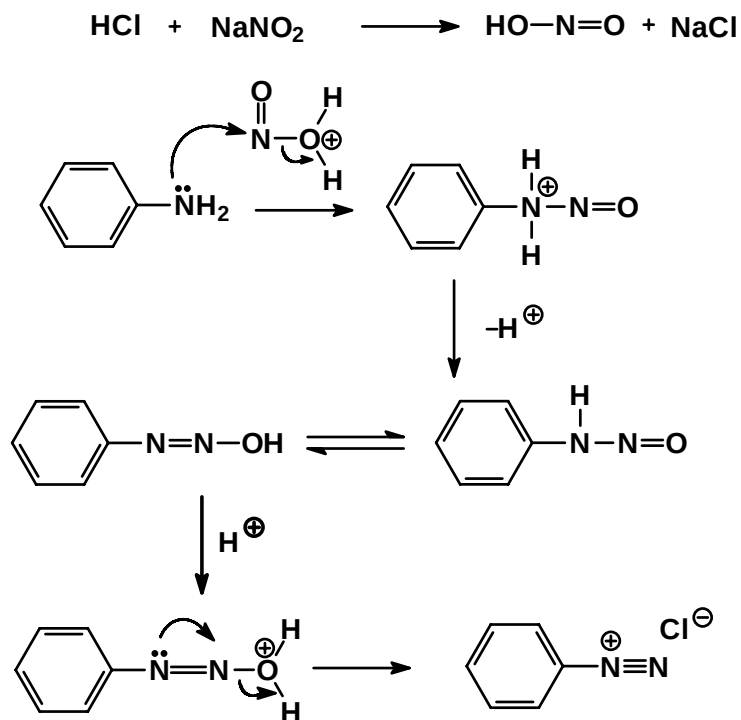


Figure 9. Mechanism of diazotization of aromatic amines.

For weakly basic amines containing several electron withdrawing groups, nitrosyl sulfuric acid ($\text{NO}^+\text{HSO}_4^-$) is utilized as the nitrosating agent and the temperature may be reduced to -5°C to reduce decomposition of the diazo group (Figure 10) [21,22].

Nitrous acid can be readily detected with starch iodine paper (instantaneous bluing) and can be destroyed with urea or sulfamic acid.

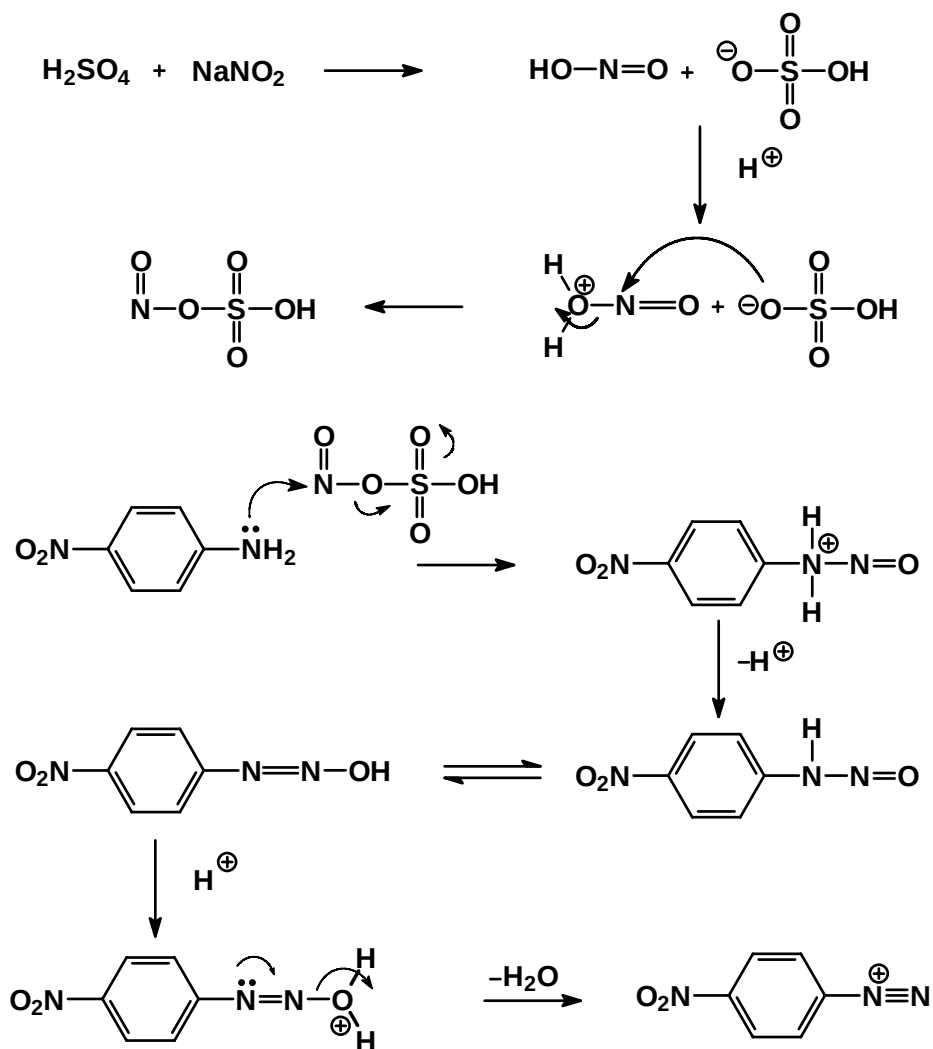


Figure 10. Mechanism of diazotization process of a weakly basic amine.

1.3.1.2 Coupling Reaction

The diazonium ion is a relatively weak electrophile and therefore only reacts with highly activated aromatic systems containing strong electron releasing groups such as hydroxyl and/or amino groups by electrophilic substitution. Hence, coupling components are commonly either phenols or

aromatic amines (primary, secondary or tertiary). The pH is one of the most important factors in azo coupling reactions and is principally dependent on the particular coupling component used. Coupling with amines (Figure 11) under slightly acidic conditions provides stability for the diazonium salt without deactivating the amino group. Phenols or naphthols (Figure 12) are coupled under alkaline conditions. Phenol is converted predominantly into the phenolate anion (alkaline pH) which is a more powerful electron donating group and hence much more strongly activates the system.

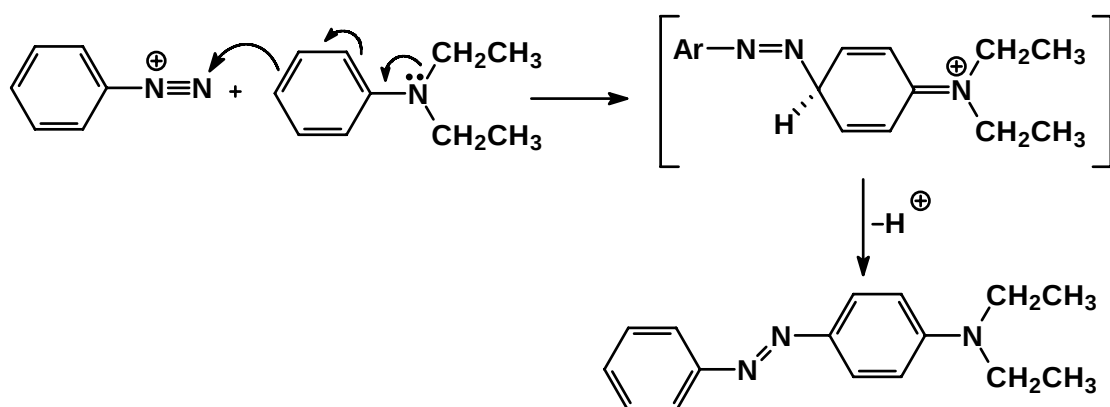


Figure 11. Azo coupling reaction between a diazonium ion and arylamine [12].

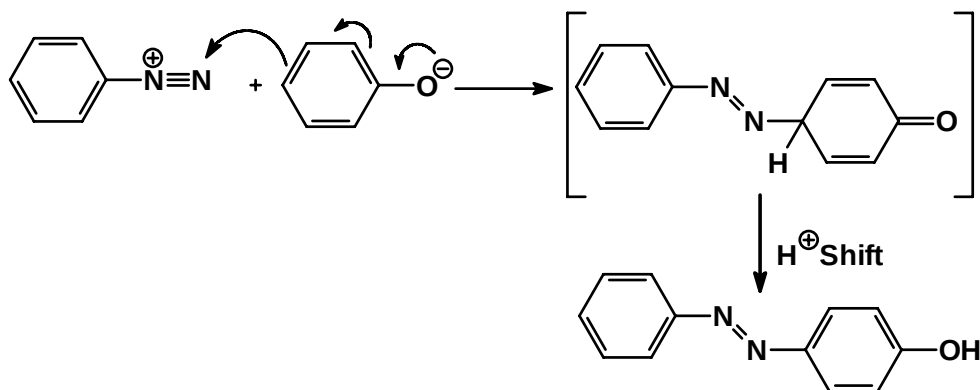


Figure 12. Azo coupling reaction between diazonium ion and phenolate ion [12].

1.4 Applications of SC- CO_2 in Textiles

The vast majority of dyes developed for commercial applications were developed for applications using water, either via complete dissolution of the dye, or through dispersion. The concept of applying dyes to fibers using supercritical fluid carbon dioxide offers several interesting benefits as described previously. However, a key factor in the utility of this medium is that the dyes exhibit adequate solubility in the SCF. This is the main topic of this section.

1.4.1 Solubility of Disperse Dyes in SC- CO_2

Carbon dioxide has a linear molecular structure with two symmetrical polar bonds [23]. Although it has no dipole moment, its quadrupole is sufficiently strong to affect its thermodynamic properties significantly [24]. These properties are different from those of other nonpolar molecules of similar size and molecular

weight. Without strong quadrupoles, it was found that there were no significant differences in polarity between liquid and supercritical phase of CO₂ [24].

Since most dyes have been developed specifically for water-based applications, they will likely exhibit very limited solubility in SC-CO₂. The only obvious dye class with potential to be used in this medium is disperse dyes. Hence, knowledge of the solubility of disperse dyes in SC-CO₂ is of interest both for thermodynamic considerations and for new dyeing techniques.

Dye solubility data is essential for the process design and optimization of SC-CO₂ dyeing process. A significant amount of data exist for azo [25-43] anthraquinone [26,28,30,31,34,36,40,43-48], mordant [40], and benzothiazoleazo disperse dyes [39,40]. The solubility, or at least the rate of dissolution, can increase after extensive grinding of the dyes due to increasing of the surface area, which increases the accessibility of the solid dye molecules to the SCF medium. It has been reported that during dyeing in a static dyeing machine, agglomeration, crystallization and melting of the dyes can take place leading to lower solubility in carbon dioxide [49].

It has been observed that solubility increases as a function of density and the effect is generally more pronounced at high temperature [26]. Dyes that contain -OH, -COOH, and -NH₂ groups, which enable intermolecular hydrogen bonding, were reported to exhibit relatively low solubilities in SC-CO₂ [26,34]. The -COOH group shows the largest decrease in solubility while, interestingly, halogen and nitro groups generally have a positive effect on the solubility [34]. Nevertheless, dye solubility in SC-CO₂ is low and often a co-solvent is required to

enhance the solubility to a practically appropriate value. The prediction of dye solubilities from the molecular mass, polarity and polarizability has been attempted with limited success [25,50].

1.4.2 Dyeing of Synthetic Fibers in SC-CO₂

It is well-known that the dyeing of polyester fibers with disperse dyes in an aqueous medium often requires high temperature (120-140°C) and addition of surfactants and dispersing agents attain sufficient dye solubility [17]. Moreover, due to increasing legislation limiting the concentrations and types of pollutants that can be released into rivers and lakes, the cost of using water and treating waste in the textile dyeing industry is confidently expected to increase. Hence, the concept of dyeing fibers in a nonaqueous environment such as SC-CO₂ is desirable from an environmental perspective.

Extensive research during the last decade using supercritical fluid dyeing (SFD) has shown that a variety of mainly hydrophobic fibers can be dyed with this technique [3,49,51-56]. Polyester fibers have been found to be most suitable for SFD technology due to the compatibility of hydrophobic dyes, hydrophobic solvent and the hydrophobic nature of the fiber.

In 1993 Schlenker *et al.* [57] described a process for dyeing a hydrophobic textile substrate with disperse azo dyes having a variety of chemical structures. In the same year, Saus *et al.* [58] developed and patented a SC-CO₂ dyeing method. This process described a technique for dyeing hydrophobic textile materials with disperse dyes by heating the textile material and the disperse dye

in SC-CO₂ under a pressure of 73 to 400 bar to a temperature in the range from 80 to 300°C, and subsequently lowering the pressure and the temperature to below the P_c and the T_c of CO₂ in a step-wise manner. Surprisingly, substantially deeper dyeings were reported. Undesirable agglomeration of disperse dyes does not occur in this process which sometimes takes place in aqueous-dyeing method, leading to reduction in shade and surface dyeing.

In 1999, Eggers *et al.* [59,60] described inventive methods for dyeing of polyester yarns with disperse dyes. The dyeing results according to this method exhibited a high color fastness to rubbing, washing and sweat.

In 2000, Hendrix *et al.* [61] invented a process for introducing dyes and other chemicals into a process for processing hydrophobic materials in a SCF. The process includes the steps of a preparation vessel, loading a textile treatment material, dissolving or suspending the textile treatment material in near-critical liquid CO₂ or SC-CO₂ and introducing the solution or suspension of textile treatment material into the dyeing system. The textile treatment material can be a brightening agent, a whitening agent and a dye.

In 2004, Smith *et al.* [62] patented a process for the dyeing and treatment (preparation and finishing) of textile substrates (hydrophilic, hydrophobic fibers, or blends) in SC-CO₂ in the presence of small amounts of water as a transport medium. A variety of dye classes (acid, basic, azo, carbonyl, sulfur, methine, triaryl carbonium, mordant, direct reactive and cationic dyes) and finishing chemicals (bleach, optical brightener, softener, anti-static agent and lubricant, etc.) were claimed in this process. Prior to SC-CO₂ processing, the textile

substrates were prewetted. Deep shades with good color fastness properties were obtained in the case of dyeing, and textile substrates were successfully treated with claimed auxiliaries in the case of finishing application.

Drews *et al.* [49] investigated the effect of SC-CO₂ on properties of polyester fiber and found that CO₂ can penetrate into the fiber faster than water, but heat and tension are the major parameters for changing fiber properties. The dyeing temperature could be considerably reduced [49,54] when dyeing is carried out in SC-CO₂ medium because CO₂ acts like a plasticizer and may cause a structural change of the polymer molecular arrays, allowing migration of dye molecules through the fiber in very short time periods.

1.4.2.1 Mechanism of Dyeing Synthetic Fiber in SC-CO₂

In some ways, dyeing of hydrophobic fibers in SC-CO₂ is similar to dyeing using in organic solvents [54,63]. There are four steps explaining dyeing mechanism. (1) dissolution of dyes, (2) transfer to the fiber, (3) adsorption of dye molecules on the fiber surface, (4) dye diffusion into the fiber.

Due to the low viscosity of SC-CO₂, dissolved dyes will readily penetrate into pores and capillaries of fibers. The diffusion coefficients of dye molecules in SC-CO₂ are greater than those of liquids which allows faster mass transport and therefore, significant higher dyeing rates which resulting in a short dyeing time.

1.4.2.2 Modeling Sorption/fluid Flow in SCF Dyeing

Since SFD process of synthetic is an emerging technology, study of flow models in SC-CO₂ will allow a better understanding of the effects of substrate and fluid properties on dynamic flow behavior of dyeing process. In 1999, Shannon [64] developed a Darcy flow model of polyester yarn packages in SC-CO₂. This model predicted the pressure drop across a package of yarn and allowed for the identification and correction of levelness problems in processing yarn packages in SC-CO₂. Sicardi *et al.* [65] used a radial flow approach to determine the permeability of polyester yarn packages in SC-CO₂ and reported that air can simulate SC-CO₂ flow through a yarn package.

1.4.3 Dyeing of Natural Fiber in SC-CO₂

While hydrophobic fibers can be dyed in SC-CO₂ with high color strength using commercial disperse dyes, hydrophilic fibers or natural fibers (cotton, viscose, wool, and silk) are difficult to dye using this medium with high fastness properties and high color depth. The problem of dyeing natural fibers under SC-CO₂ arises from the inability of carbon dioxide to sufficiently break massive intermolecular hydrogen bonding that exists throughout the fibers (particularly cotton) [66]. High hydrogen bonding in natural fibers hinders the diffusion of disperse dyes into the polymer chains resulting in unacceptable, low fastness properties. Many approaches have been developed to overcome the limitations of the SC-CO₂ dyeing process of natural fibers due to importance of cotton in the

global market with an approximate market share of 37% [66]. Several techniques have been reported to overcome the limitation of dyeing natural fiber in SC-CO₂.

1.4.3.1 Impregnation of Swelling and Crosslink agents

One approach to dyeing hydrophilic natural fibers under SC-CO₂ involves pretreatment of the fiber with swelling or plasticizing agents, such as a low molecular weight hydrogen bond-breaking substances (diethanolamine) [67], a high molecular weight polyether derivative [67], and polyethylene or polypropylene glycol [68,69] to overcome this limitation. The auxiliary agents must be applied to the fiber at concentrations of 8-20% owf. The high concentration of these substances swell cotton fiber, thereby breaking hydrogen bonding between polymer chains, which increases the accessibility of dyes into the pores of cellulosic chains. However, washfastness of the resultant dyeings using this approach was found to be very low. The main disadvantage of this process is that the impregnation and the removal of the substances have to be conducted under aqueous processes, which involves two drying steps.

1.4.3.2 Fiber Modification Technology

An alternative method to increase dye uptake of cellulosic fiber using SC-CO₂ is to make the substrate hydrophobic by derivatizing the fiber via introduction of certain functional groups. In 1996, Schrell *et al.* [70,71] patented a process for dyeing cellulosic fibers or cellulose/polyester fiber blend by reacting

with compounds containing primary amino group. The aminated fiber was then dyed with fiber-reactive disperse dyes in SC-CO₂. The reactive groups of fiber-reactive disperse dyes can react and form covalent bonds with amino groups present in these modified fibers. It was found that level and deep dyeing with very good fastness properties were obtained without use of any alkaline agents.

In 1998, Ozcan *et al.* studied cotton modified by benzoyl chloride and sodium benzoylthioglycollate (BTG) [72]. In the case benzoylated cotton, the reported color yields and wash fastness were good. However, a high degree of modification (22% weight gain) was considered necessary, while dyeing of BTG modified cotton with disperse dyes resulted in low color strength and poor fastness due to the lower degree of arylation than the former benzoylation method.

In 2003, Veugelers *et al.* [73] reported a method for dyeing textile materials (silk, wool, cellulose, or blend with synthetic fibers) with fiber-reactive dyes by modified with aminating agents. Very good fixation and color fastness properties were achieved. In this work, the fiber was derivatized using aliphatic polyamine (Sandene).

In 2004, dyeing cotton after modification with colorless fiber reactive groups such as 2,4,6-trichloro-1,3,5-triazine (Figure 13) were reported [74]. Dyeing was conducted in SC-CO₂ with dyes containing hydroxyl or amino groups. Acceptable depths of shade but poor wash fastness were obtained. Rubbing and light fastness were between moderate. As expected, significant

fiber damage occurred due to the generation of highly corrosive hydrochloric acid during fiber modification and the fiber reactive dyeing.

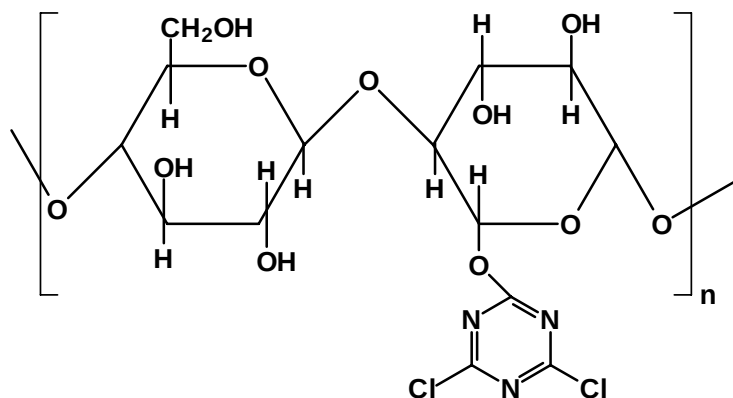


Figure 13. Modified cotton with 2,4,6-trichloro-1,3,5-triazine.

For dyeing wool and silk with disperse dyes in SC-CO₂, a special pre-treatment of the substrate with a mordant was attempted [75]. The fiber was first pre-treated with a metal and was then reacted with a ligand (complexing agent) dissolved in SC-CO₂. The reaction between a ligand and the exchanged metal formed an immobilized metal-chelate complex on the surface of fiber. Depending on the metals and the ligands, different colors were obtained. This approach eliminated the problem of wastewater treatment since both metal ion and metal complex are not soluble in depressurized CO₂. In addition, it was reported that unreacted ligand could be recovered and reused.

1.4.3.3 Use of Polar Co-solvents

The uptake of dye molecules with polar functional groups increases when slightly polar co-solvents are applied with SC-CO₂. A co-solvent not only improves the dye solubility but also increases the polymeric chain mobility, resulting in faster penetration to the polymeric matrix. To increase the polarity and the solvating power of SC-CO₂, water, alcohols or a mixture of both may be employed as co-solvents. The co-solvent added will alter the CO₂-dye fiber distribution. In this way, traditional reactive, cationic, anionic, and direct dyes can be applied to natural protein and cellulosic fibers using SC-CO₂.

In 2001, Sicardi and Frigerio [76] patented a process for dyeing natural textile using water-soluble polar dyes by incorporation of a polar co-solvent into a SC-CO₂ medium. The dye samples showed very good color intensity, and good colorfastness properties. At the end of dyeing the co-solvent must be removed from the fiber, which requires an additional drying step. In cases where flammable solvents are used as co-solvents the processing cost dramatically increases since the dyeing plant has to be explosion-safe. Also, the co-solvent must be separated from the carbon dioxide after dyeing [66].

In 2004, Smith *et al.* [62] not only patented a process for dyeing hydrophobic textile materials, but also hydrophilic natural fibers (cotton, wool and silk) using small amount of water to wet out the textile substrate. Any dyes classes for natural fiber can be used as long as they are soluble in transport medium and capable of dyeing textile substrate, e.g., use of direct dyes to dye cotton substrate.

1.4.3.4 Use of Fiber-Reactive Disperse Dyes

Most of the methods described above require fiber pre-treatments. To overcome this disadvantage, an alternative approach is to design fiber-reactive dyes that are soluble in SC-CO₂ and can react with fiber with no or limited presence of protic solvent to form covalent bonds with the fiber. The important reactive groups that have been investigated in SC-CO₂ and their qualitative degree of fixation and color strength on cellulose and protein fibers are summarized in Table 6 [66].

Table 6. Influence of the reactive group on color strength and fastness properties after dyeing in SC-CO₂.

Reactive Group	Substrate	Color Strength
Sulphonylazide (-SO ₂ N ₃)	Cotton	Low
Dichlorotriazine	Cotton	Low
	Protein fibers	No fixation
SO ₂ X (X = Cl, Br or I)	Protein fibers	Mid-high
2-Bromoacrylic acid ester or amide	Cotton	Mid-high
	Protein fibers	Mid-high
Vinylsulfone	Cotton	Mid-high
	Protein fibers	Mid-high

Dyes Containing a Sulphonyl Azide Group

Modified cotton was dyed with sulphonyl azide dyes. The $-\text{SO}_2\text{N}_3$ group form highly reactive nitrenes [77,78] upon heating, which can then form covalent bonds, as shown in Figure 14. Sulphonylazide dyes are capable of reacting with all fibers containing C-H bonds [66]. Disperse reactive dyes containing sulphonyl azide groups were developed from alizarin, quinizarin, indigo, and coumarin based dyes via both sulfonation and chlorosulfonation processes.

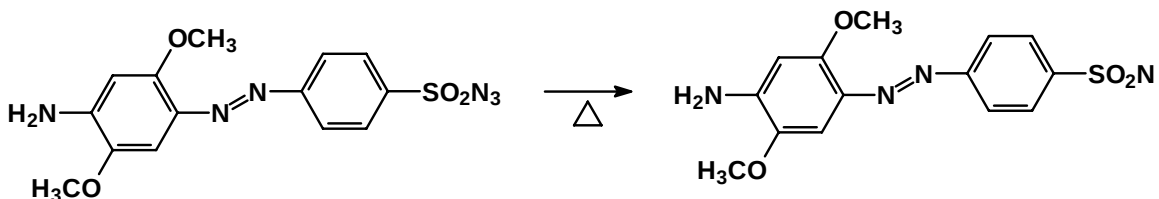
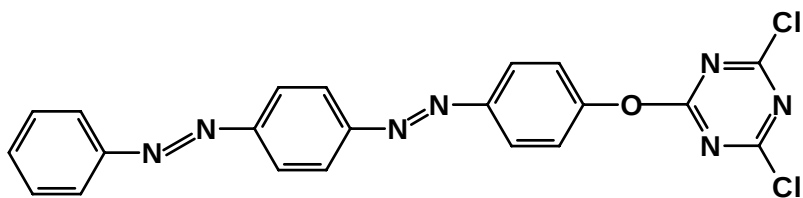


Figure 14. Thermal degradation of sulphonylazide dyes.

Dyes Containing a Dichlorotriazine Group

Another fiber-reactive group for dyeing cotton in SC-CO_2 is based on dichlorotriazine (DCT). DCT-modified disperse dyes (**22**) on cotton [79] have been shown to produce a low degree fixation in SC-CO_2 . Significantly low color yield and poor fastness properties were obtained due to the generating of HCl during the substitution reaction between hydroxyl groups of the fiber and dye molecule. Under acidic conditions hydrolysis by protonation of the oxygen of the dye-cellulose bond may take place.



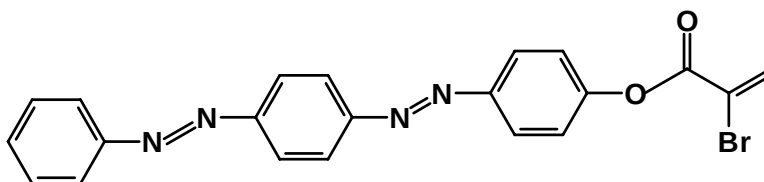
(22)

Dyes Containing a SO₂X Group

Another reactive group that has been used to produce disperse reactive dyes for use in SC-CO₂ is SO₂X (X = Cl, Br or I) [66]. Like DCT dyes, there is a release of HCl, HBr and HI during the reaction, which can attack the fiber leading to fiber degradation, and can produce pitting in the stainless steel of the dyeing machine [66].

Dyes Containing a 2-Bromoacrylic Acid Ester or Amide Group

This reactive group is well known in the dyeing of wool and other protein fibers. An example of this type of dye is (23). After dyeing, it was found that protein fibers can be dyed in higher color yields [79] than cotton probably because amino- and thiol-groups are significantly more reactive than undissociated hydroxyl groups. Man-made fibers such as polyamide and polyester/cotton blends could also be dyed with this type of dye in SC-CO₂.



(23)

Dyes Containing a Vinylsulfone Group

The vinylsulfonyl (VS) group has been used for dyeing polyamide and cotton fibers under SC-CO₂. The wash fastness and the color strength are very promising with apparent high degrees of fixation on wool and polyamide. To date, vinylsulfone-containing disperse dyes appear to be highly suitable dyes for dyeing fibers containing amino groups (e.g. Figure 15 [2]) in SC-CO₂ at moderate temperature without fiber damage. However, optimization of the reaction conditions and confirmation of dye-fiber covalent bond via SC-CO₂ has not been studied in detail.

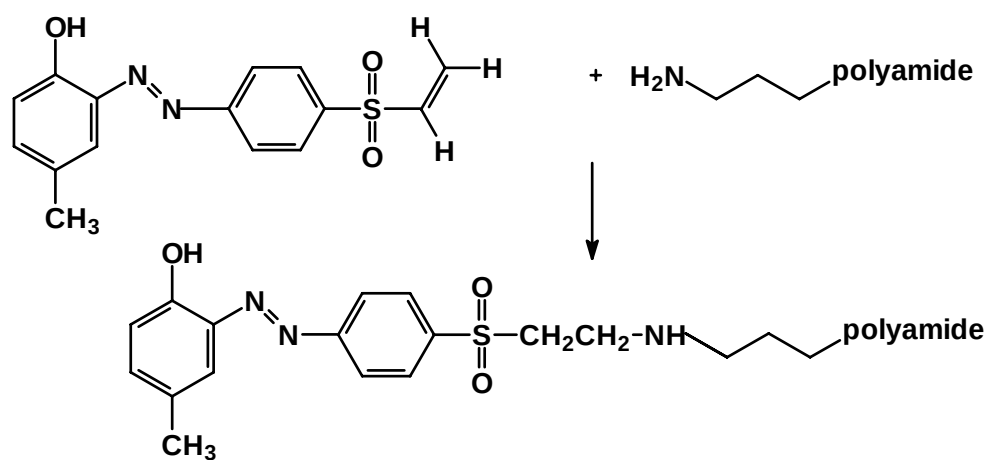


Figure 15. Reaction of polyamide fiber and VS disperse reactive dye [2].

1.4.3.5 Use of a Nonionic Surfactant

Surfactant-modified SCFs have also been used in the dyeing of fibers. The main reason for using these solvent systems is to enhance the solubility of polar dyes in SC-CO₂. In 2000, DeYoung *et al.* [80] patented methods for dyeing substrates in the presence of surfactants in SC-CO₂. Firstly, a surface treatment

of substrates was conducted to lower the surface tension by using perfluoropolymers. A surfactant or co-surfactant was also employed to solubilize or emulsify the dye to enhance the efficacy of the surface treatment component.

While DeYoung *et al.*'s technique required a surface modification prior dyeing. A reverse micellar dyeing system in SC-CO₂ was reported in 2002 by Sawada *et.al* [81] without any pretreatment. In this study, the investigation of dyeing unmodified natural fibers in SC-CO₂ using conventional water-soluble dyes was conducted. The surfactants used were pentaethylene glycol n-octyl ether (C₈E₅) [81] and perfluoro polyether [82,83]. Water-soluble dyes can be solubilized in a microenvironment (water pool) in a non-aqueous medium as shown in Figure 16. With this method, unmodified silk and wool fabrics were successfully dyed with conventional acid dyes while cotton fabrics dyed with conventional acid dye did not produce deep shades, presumably due to high electrostatic repulsion between the dye and cellulosic fiber. However, a significant improvement in dyeability was obtained when the cotton was chemically pretreated with a cationic agent.

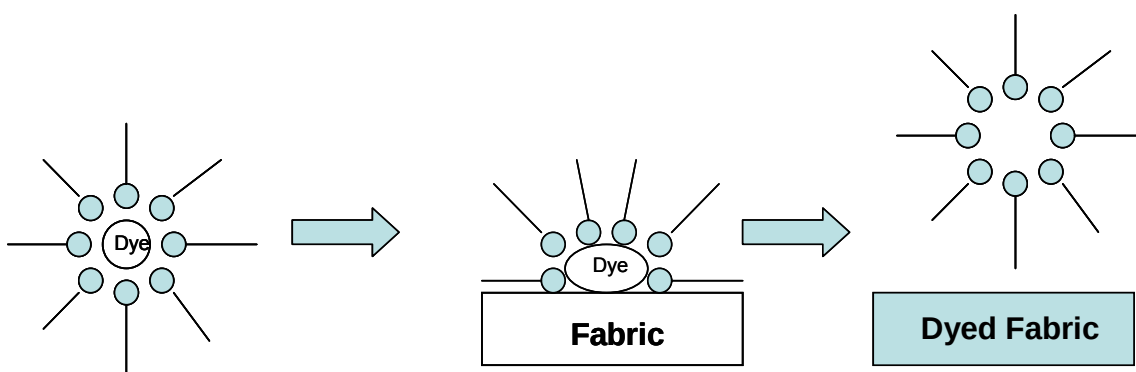


Figure 16. Reverse micelle system.

In 2004, Lewin-Kretzschmar and Harting [84] studied the solubilities of different polar dyes in SC-CO₂ and SC-C₂H₆, both modified and unmodified with various surfactants. In addition, dyeing experiments using wool and cotton were conducted in order to characterize the impact of the modifiers on the dyeing procedure and coloring properties. The experiments showed the potential and limitations of using common commercial surfactants as modifiers for increasing the solubility of highly polar dyes in supercritical fluids by the formation of reverse-micellar structures. It was reported that in many cases acceptable dye solubilities were achieved that resulted in acceptable dyeing depths. However, levelness and fastness properties were not satisfactory.

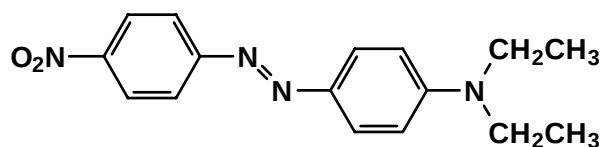
1.5 Use of SC-CO₂ in Dye Synthesis

In recent years, significant research has focused on reducing the environmental impact associated with dye synthesis, with particular emphasis being directed toward decreasing or eliminating color, salts and toxic metals from industrial wastewater effluent. Interestingly, SC-CO₂ can be used as both solvent and as a reactant during diazotization and coupling reactions.

The concept of azo dye synthesis in SC-CO₂ was first demonstrated by Raue *et al.* [85-87]. The main concept is the generation of carbonic acid when carbon dioxide is mixed with water, which can be used as the acid source *in lieu* of mineral acids in the diazotization of aromatic amines. Hence, it is feasible that relatively environmentally-benign diazotization and coupling reactions can be undertaken using water and CO₂ in the presence of a suitable nitrite. Elimination

of mineral acids means that no neutralization of the reaction mixture is required, and therefore high electrolyte concentrations in effluent are avoided.

Hooker *et al.* [88] used this concept to synthesize the first azo dye of *N,N*-diethyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}amine (**73**) via *in situ* diazotization and coupling in SC-CO₂ without using a mineral acid. It was found that the product yield increased significantly with temperature, with 91% theoretical yield afforded at 80°C, while the pressure of the system had little effect on product yield.



(73)

1.6 Damage of Natural and Synthetic Fibers Treated in SC-CO₂

One of the potential problems for using SC-CO₂ for processing fibers is fiber damage via thermal degradation and/or acid attack of the polymer. In certain cases, polymer chains can be cleaved by heat, the fiber can melt or crystallinity can be increased [49]. Fiber damage can also be caused by acid. In the carbon dioxide environment, carbonic acid is formed in the presence of water, resulting from the moisture content in the fibers. In man-made fibers, carbonic acid can cleave the chemical bonds between monomer units of polyamide, while polyester is resistant to saponification by weak acids. Cellulosic fibers can be oxidized by oxygen from the air or water [89] and they

can depolymerize under acidic conditions. Natural protein fibers (silk and wool) can denature in an acid medium at high temperatures in the presence of water [90].

1.7 Proposal

The primary goals of this research are to investigate the utilization of SC-CO₂ for the synthesis and application of azo dyes for coloration of textile fibers.

1.7.1 Diazotization and Coupling in SC-CO₂

Conventional diazotization of aromatic or heterocyclic amines in aqueous media requires relatively high levels of mineral acid to form the diazotizing agent (nitrous acid or nitrosonium ion). Therefore, significant levels of inorganic salt are generated upon neutralization of the reaction mixture, which leads to an environmental problem in dyestuff manufacture and wastewater treatment. To prepare stable dyestuff solutions, these inorganic salts have to be removed by an expensive process, such as pressure permeation or reverse osmosis.

The diazotization reaction is commonly very sensitive to temperature due to instability of the diazo salt formed with potential degradation and loss of N₂. Hence, reactions are usually undertaken at temperatures less than 5°C. Furthermore, in some cases relatively low yields are obtained owing to the instability of the diazo group in an aqueous environment. The preparation process in SC-CO₂ has potential to avoid these disadvantages.

In SC-CO₂, as shown in Figure 17, carbonic acid can be generated and dissociated forming a bicarbonate (HCO₃⁻) and hydrogen ion (H⁺). Subsequently, the bicarbonate dissociates into carbonate (CO₃²⁻) and hydrogen ion (H⁺) until chemical equilibrium is reached [91].

The secondary dissociation involves forming a weaker acid and will be used *in lieu* of a mineral acid in conventional diazotization and coupling reactions in SC-CO₂. Bicarbonate is present in a greater amount than carbonate as pH drops. Hence, the carbonic acid reaction can be exploited to produce the diazotizing species in the presence of nitrite, thus facilitating diazotization of primary aromatic amine compounds, as shown in Figure 18.

Examples of suitable nitrites are sodium nitrite (NaNO₂), potassium nitrite (KNO₂), methyl nitrite (CH₃NO₂), isopropyl nitrite (C₃H₇NO₂), amyl nitrite (C₅H₁₁NO₂) and glycol nitrite [85,86]. Azo dye formation can be achieved by coupling to suitable coupling components, as shown in Figure 19.

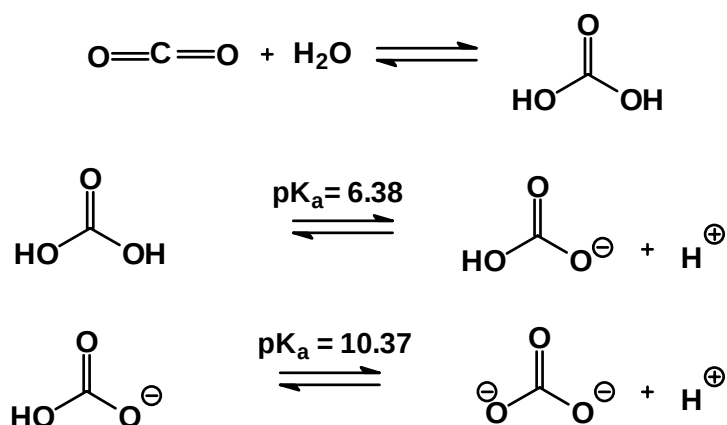


Figure 17. Formation and dissociation reaction of carbonic acid.

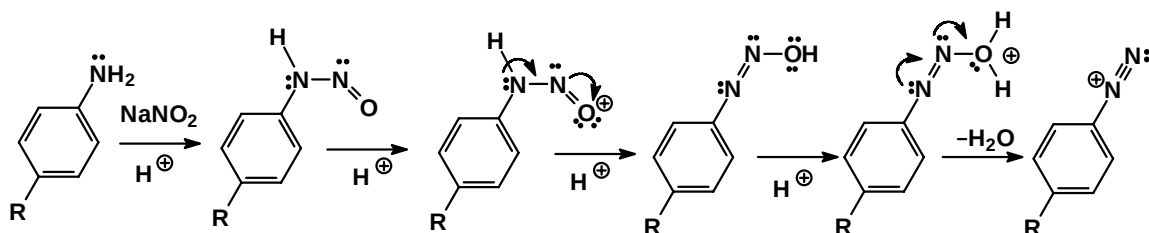


Figure 18. General reaction for preparation of the diazonium ion.

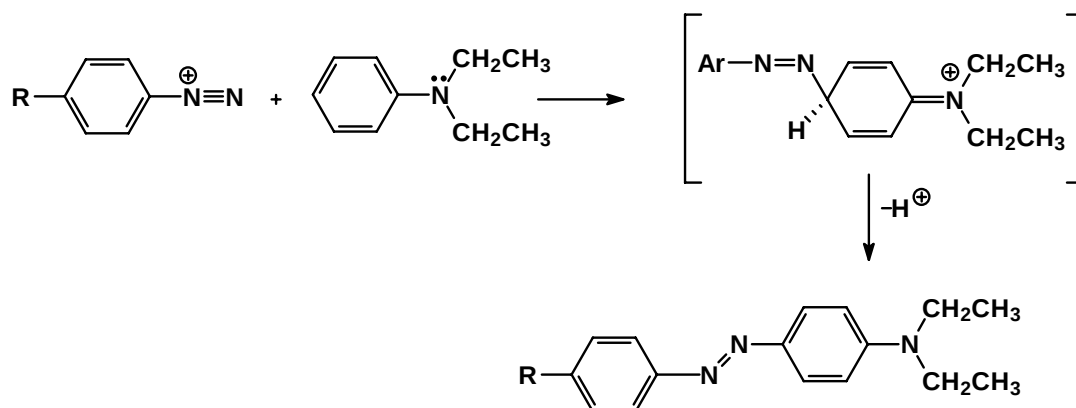


Figure 19. A typical reaction scheme for azo coupling.

In order to investigate the key variables related to azo dye synthesis in SC-CO₂, azo dyes (**70**) to (**79**) will be synthesized from various types of arylamine with differing pK_a (basicity) and coupling with *N,N*-diethylaniline, as shown in Table 7. In order to test product yield as a function of solubility, small amounts of polar co-solvents, such as methanol, will be incorporated into the reaction mixture. In addition, all dyes will be synthesized, purified, and characterized by a conventional aqueous method for comparison with the SC-CO₂ synthesis methods.

Table 7. Structures of targeted azo dyes synthesized in SC-CO₂.

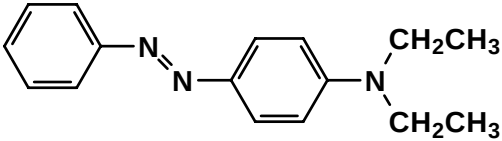
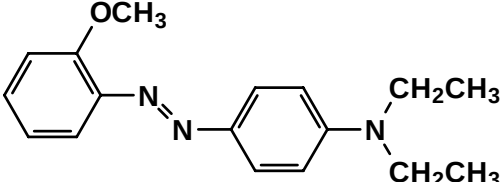
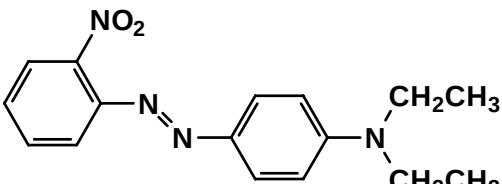
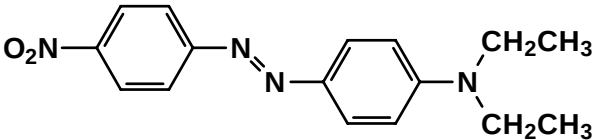
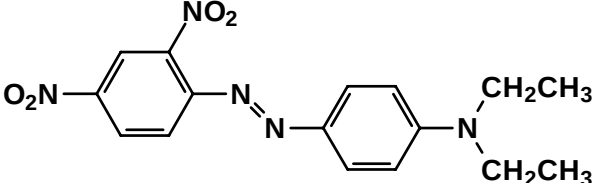
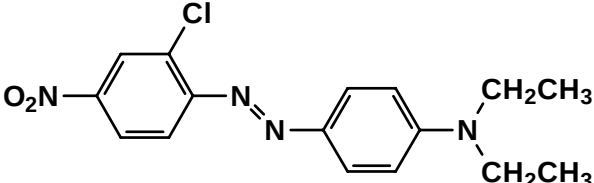
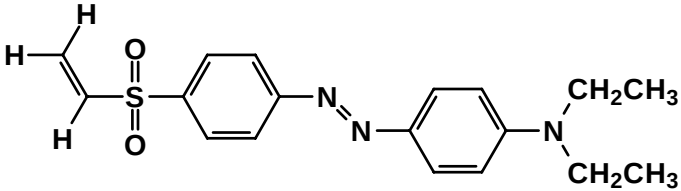
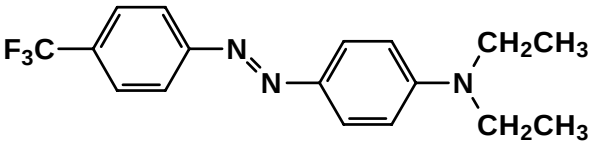
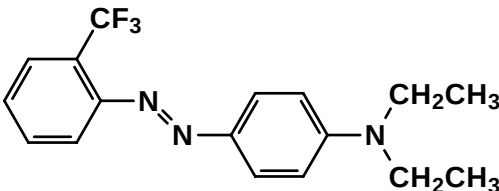
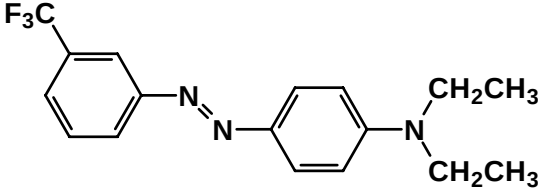
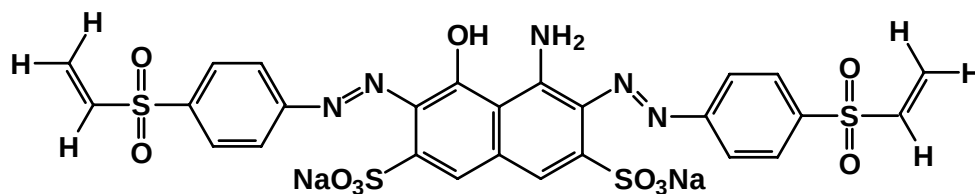
Dyes	Structures
(70)	
(71)	
(72)	
(73)	
(74)	
(75)	

Table 7. (Continued)

Dyes	Structures
(76)	
(77)	
(78)	
(79)	

In addition to the synthesis of disperse dyes and disperse reactive dyes in SC-CO₂, an investigation will be conducted into the potential to synthesize water-soluble reactive dyes using liquid or SC-CO₂ as the primary solvent. One focus will be toward the SC-CO₂ synthesis of C.I. Reactive Black 5 (**83**).



(83)

1.7.2 Azoic Dyeing in SC-CO₂

The traditional approach to the synthesis of an insoluble azo dye within a fiber is called azoic dyeing. However, the prior art literature shows no evidence of research toward azo dye formation within fibrous materials using SC-CO₂ as the primary solvent/transport medium. Research in this regard will focus on a proof of concept and approaches to optimization of the conditions of diazotization and coupling within cotton fibers.

For the initial proof of concept, initial work will utilize cotton pre-treated with a common β -naphthol-based coupling component in order to demonstrate that diazotization and coupling reaction can be achieved. The second component, the diazonium salt, will be prepared in SC-CO₂ by reacting a substituted aromatic amine in the presence of sodium nitrite, water and CO₂. The reaction sequence is shown in Figure 20. The effect of key variables on color strength will be assessed, including temperature, pressure and reaction time. Furthermore, the application of the coupling component in SC-CO₂ will be investigated in order to provide a complete SC-CO₂ azoic dyeing application.

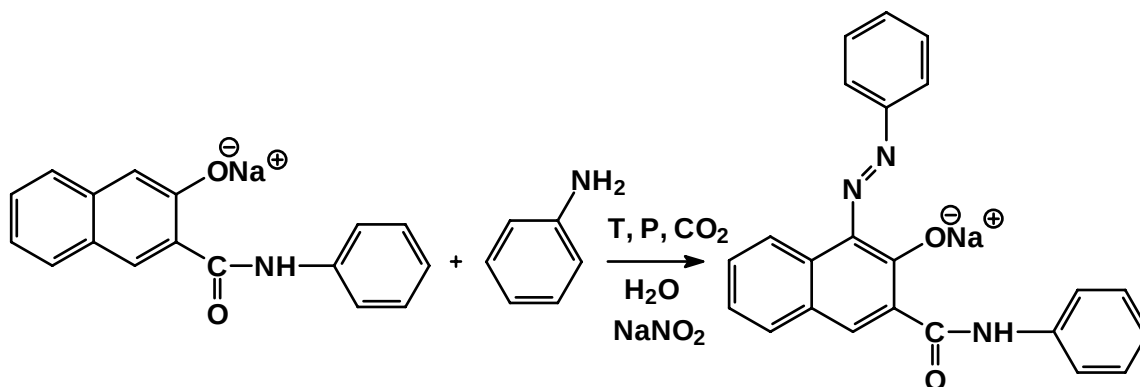


Figure 20. General azoic coupling reaction in SC-CO₂.

1.7.3 Dye-Fiber Formation of Fiber-Reactive Dyes and Polyamide Fibers

A hydrophobic vinylsulfone disperse-reactive dye will be synthesized and used to investigate fiber-reactive dye application to wool and nylon fabrics since these dyes have the potential for Michael addition reactions between the vinylsulfone group and a suitable nucleophile (e.g., amino groups in wool and polyamide fibers) in a dense gas fluid [78,92].

Although some preliminary studies by other research groups have been conducted involving the coloration of polyamide fiber with vinylsulfone-containing disperse-reactive dyes in SC-CO₂ [78,92], no conclusive evidence has been reported to prove the formation of dye-fiber covalent bonds when using SC-CO₂ in the absence of significant levels of protic solvents. This should be demonstrated in order to determine the value, if any, of research into fiber-reactive dye applications using highly hydrophobic nonaqueous solvents such as SC-CO₂. In this study, compounds possessing primary amino functional groups

(e.g., butylamine) will be used as a model for primary amino groups present in nylon and wool. The reaction will be carried out in SC-CO₂ under conditions typical of dyestuff applications, and the reaction product(s) will be characterized by ¹H-NMR, elemental analysis, and mass spectrometry.

2. Synthesis of Azo Dyes via *in Situ* Diazotization and Coupling in Supercritical Carbon Dioxide

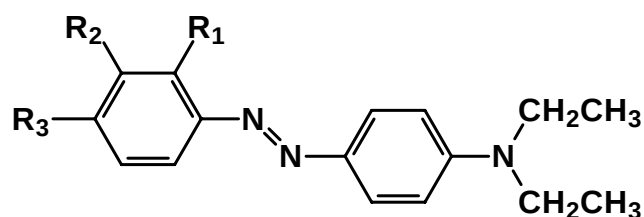
2.1 Introduction

Approaches to the design of new dyes with varying hue, color strength and photostability involve incorporation of various electron-donating/withdrawing substituents (auxochromes) in the chromogen. Today, computational methods for dye design can be used effectively to predict key properties, and the remaining task is to select the best candidates for synthesis and then determine (in the case of azo dyes) the most appropriate diazotization and coupling method.

In conventional aqueous diazotization and coupling, a number of well-known methods are used to prepare azo dyes in satisfactory yield, with dyes prepared from, for example, arylamines of low basicity being diazotized in concentrated nitrosating media (such as nitrosyl sulfuric acid), while diazotization of amines with high solubility and basicity can be achieved easily in dilute aqueous mineral acids [18].

However, the limited prior art literature pertaining to the synthesis of azo dyes using supercritical or liquid CO₂ does not include significant data on reaction efficiency as a function of the auxochromes incorporated on the aryl compounds used in the reaction. Of particular interest is determination of the scope and limitations of the CO₂-based reaction with regard to selection of diazotizing amine. With this endeavor in mind, reported here are results from the

attempted synthesis of ten azo dyes in SC-CO₂ in the absence of mineral acid. The arylamine used in each case contained one or more electron-donating or withdrawing groups, as shown in Figure 21, except for aniline which was used to synthesize dye (70).



	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>
(70)	H	H	H
(71)	OCH ₃	H	H
(72)	NO ₂	H	H
(73)	H	H	NO ₂
(74)	NO ₂	H	NO ₂
(75)	Cl	H	NO ₂
(76)	H	H	SO ₂ CH=CH ₂
(77)	H	H	CF ₃
(78)	CF ₃	H	H
(79)	H	CF ₃	H

Figure 21. Dyes synthesized in SC-CO₂.

2.2 Experimental

2.2.1 Materials

Reagent grade sodium nitrite, *N,N*-diethylaniline, aniline, *o*-anisidine, *p*-nitroaniline, *o*-nitroaniline, 2,4-dinitroaniline, 2-chloro-4-nitroaniline, 2-(trifluoromethyl)aniline, 3-(trifluoromethyl)aniline, and 4-(trifluoromethyl)aniline were obtained from Aldrich Chemical (Milwaukee, WI, USA). 4-Aminophenyl- β -sulfatoethylsulfone was obtained from Hoechst Chemical. Reagent grade ethyl acetate, methanol, spectrophotometric grade acetone and Whatman Thin Layer Chromatography (TLC) plates (60A^o silica gel plates with fluorescent indicator, size 20x20 cm, layer thickness: 1000 μ m) were purchased from Fisher Scientific (Pittsburg, PA, USA). “Bone dry” and 99.0% pure CO₂ was purchased from National Specialty Gases (Durham, NC, USA).

2.2.2 Equipment

Reactions were performed using a jacketed 300 mL high-pressure reactor from Autoclave Engineers (Erie, PA, USA) equipped with a high speed stirrer, cooling/heating coil and a high-pressure pump as shown in Figure 22. Proton Nuclear Magnetic Resonance (¹H-NMR) spectra were obtained using a Bruker AVANCE 400 Hz spectrometer.

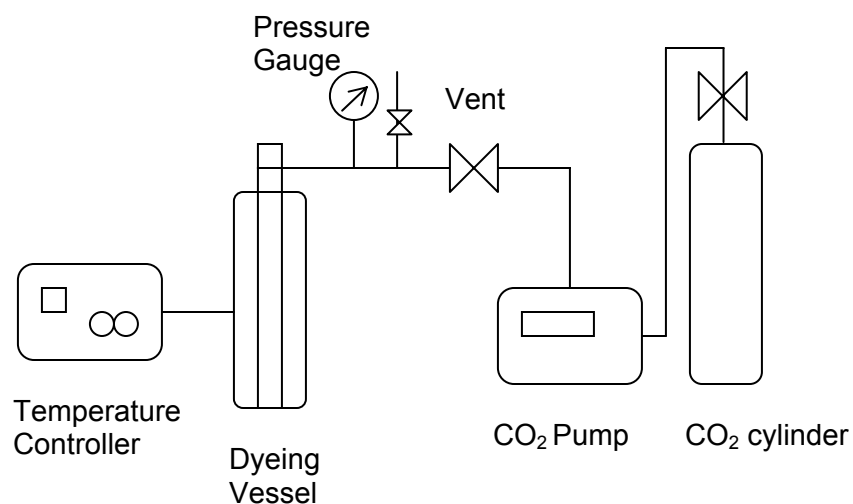


Figure 22. Schematic diagram of the high-pressure reactor used for all experiments.

2.2.3 Visible Absorption Spectra

Solutions of pure dye sample (5×10^{-5} mol) were prepared by dissolving them in acetone (50.0 mL) and diluting 1.0 mL with acetone (24.0 mL) to give a final concentration of 4×10^{-5} mol/L. Visible spectra were recorded by using a Varian Cary 3E UV-visible spectrophotometer. From the resultant absorption spectra, $\epsilon_{\max}$ values were calculated from equation 2.

$$A = \epsilon \cdot b \cdot c \quad (\text{equation 2})$$

Where

- A = absorption at $\lambda_{\max}$ (nm)
- b = path length of the sample (cm)
- c = concentration of dyes (mol/L)
- ϵ = molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)

2.2.4 Synthesis Method

2.2.4.1 Preparation of *p*-Aminophenylvinylsulfone

4-Aminophenyl- β -sulfatoethylsulfone (20.0 g, 0.071 mol) was dispersed by stirring in water (100 mL) at 20°C and pH of the mixture was raised to 11 by the addition of 2 M NaOH solution. After stirring for 30 min the pale brown precipitate was filtered, washed with cold H₂O and dried.

2.2.4.2 Dye Synthesis using SC-CO₂

Diazotization and coupling reactions were performed in a one-pot process at 80°C and 207 bar (3000 psi). In each case, deionized H₂O (4.0 mL, 0.22 mol), sodium nitrite (0.465 g, 6.9 mmol), *N,N*-diethylaniline (1.10 mL, 6.9 mmol) and primary arylamine (X g, 0.67 mmol) were loaded in a 300 mL high-pressure reactor. In some cases, MeOH was added (1.0 mL, 0.025 mol). The reactor was then sealed and pressurized to 60 bar (860 psi). The reaction mixture was stirred at 800 rpm and heated to 80°C. CO₂ was isothermally compressed to 207 bar (3000 psi) under a constant stirring speed of 800 rpm. The pressure and temperature were maintained for 3 h after which CO₂ was released slowly.

Upon completion of the reaction, stirring was terminated and CO₂ was slowly released from the vessel. The reaction mixture was extracted from the reactor with ethyl acetate (200 mL). The extract was washed several times with H₂O (100 mL) and 1.0% HCl (w/v, 0.5 mL) to remove unreacted *N,N*-

diethylaniline. The organic solvent was removed via rotary evaporation and the crude product was collected and dried.

Samples of dyes (**70**), and (**77**) to (**79**) were purified via preparatory thin layer chromatography (TLC) using toluene as eluent. Silica containing the target component of the mixture was removed from the plate and dye was extracted using acetone. Crude products of dyes (**72**), (**73**) and (**76**) were recrystallized from methanol and the structures of all dyes made were confirmed by $^1\text{H-NMR}$ and FAB-MS (positive ion).

2.2.4.3 Analysis of Dyes Synthesized in SC-CO₂.

Dye (**70**)

$^1\text{H-NMR}$ (CDCl₃): δ = 6.5-8.0 (m, 9H, aromatic protons), 3.46 (q, 4H), 1.24 (t, 6H) (see Appendix A, Figure A2). FAB-MS (positive ion) m/z (rel. int.): 254 (M+H, 72), 253 (M+, 100) (see Appendix B, Figure B1).

Dye (**72**)

TLC: R_f = 0.44 (toluene). $^1\text{H-NMR}$ (CDCl₃): δ = 6.5-8.0 (m, 8H, aromatic protons), 3.47 (q, 4H), 1.24 (t, 6H) (see Appendix A, Figure A5). FAB-MS (positive ion) m/z (rel. int.): 299 (M+H, 95), 298 (M+, 100) (see Appendix B, Figure B2).

Dye (73)

TLC: R_f = 0.47 (toluene). $^1\text{H-NMR}$ (CDCl_3): δ = 6.5-8.5 (m, 8H, aromatic protons), 3.50 (q, 4H), 1.27 (t, 6H) (see Appendix A, Figure A7). FAB-MS (positive ion) m/z (rel. int.): 299 (M+H, 92), 298 (M+, 100) (see Appendix B, Figure B3).

Dye (76)

TLC: R_f = 0.77 (EtOAc). $^1\text{H-NMR}$ (CDCl_3): δ = 8.0 -7.7 (m, 6H, aromatic protons), 6.8-6.7 (m, 2H, aromatic protons), 6.67 (d, ethylene H), 6.47 (d, cis H), 6.05 (d, trans H), 3.46 (q, 4H), 1.24 (t, 6H) (see Appendix A, Figure A11). FAB-MS (positive ion) m/z (rel. int.): 344 (M+H, 100), 343 (M+, 93) (see Appendix B, Figure B4).

Dye (77)

TLC: R_f = 0.75 (toluene). $^1\text{H-NMR}$ (CDCl_3): δ = 6.7-8.0 (m, 8H, aromatic protons), 3.48(q, 4H), 1.26 (t, 6H) (see Appendix A, Figure A13). FAB-MS (positive ion) m/z (rel. int.): 322 (M+H, 66), 321 (M+, 100) (see Appendix B, Figure B5).

Dye (78)

TLC: R_f = 0.75 (toluene). $^1\text{H-NMR}$ (CDCl_3): δ = 6.7-8.0 (m, 8H, aromatic protons), 3.48(q, 4H), 1.26 (t, 6H) (see Appendix A, Figure A15). FAB-MS (positive ion) m/z (rel. int.): 322 (M+H, 65), 321 (M+, 100) (see Appendix B, Figure B6).

Dye (79)

TLC: R_f = 0.75 (toluene). $^1\text{H-NMR}$ (CDCl_3): δ = 6.7-8.0 (m, 8H, aromatic protons), 3.48(q, 4H), 1.26 (t, 6H) (see Appendix A, Figure A17). FAB-MS (positive ion) m/z (rel. int.): 322 (M+H, 68), 321 (M+, 100) (see Appendix B, Figure B7).

2.2.4.4 Synthesis by Conventional Diazotization and Coupling

All dyes synthesized in SC-CO_2 were also synthesized by conventional diazotization and coupling. The structure of each pure dye was confirmed by $^1\text{H-NMR}$. The purpose of this synthesis was to facilitate identification of the products made in SC-CO_2 and to compare the yield obtained in each method.

Dye (70)

Aniline (0.93 g, 0.01 mol) was suspended in 2 M HCl (15.0 mL). The mixture was cooled to 0-5°C using an ice bath and NaNO_2 (0.76 g, 0.011 mol) dissolved in water (3.0 mL) was slowly added. The solution was stirred for 45 min, at which time excess HNO_2 was destroyed by addition of sulfamic acid (0.3 g). Activated carbon was added and the mixture was stirred and filtered to give a clear yellow solution.

The diazonium solution was added dropwise to *N,N*-diethylaniline (1.53 g, 0.102 mol) dissolved in methanol (25.0 mL) at 0-5°C. The pH of the coupling reaction was maintained near pH 5 by the additional of solid $\text{NaOAc} \cdot 3\text{H}_2\text{O}$. The coupling step was continued for 1 h and the mixture produced was stirred overnight. The precipitate was collected by filtration, washed with H_2O and dried

to give dye (**70**) (2.38g, 94%). TLC: R_f = 0.55 (toluene). $^1\text{H-NMR}$ (CDCl_3): δ = 6.5-8.0 (m, 9H, aromatic protons), 3.46 (q, 4H), 1.24 (t, 6H) (see Appendix A, Figure A1)

Dye (**71**)

The procedure described above for the synthesis of dye (**70**) was employed, with *o*-anisidine (1.23 g, 0.01 mol) used as the starting material to give dye (**71**) (2.46 g, 87%) and TLC: R_f = 0.57 (toluene:EtOAc/3:1). $^1\text{H-NMR}$ (CDCl_3): δ = 6.5-8.0 (m, 8H, aromatic protons), 4.03 (s, 3H), 3.46 (q, 4H), 1.24 (t, 6H) (see Appendix A, Figure A3).

Dye (**72**)

O-Nitroaniline (1.38 g, 0.01 mol) was dissolved in hot concentrated HCl (10.0 mL). The solution was stirred and cooled to 30°C with addition of ice (10.0 g). NaNO_2 (0.76 g, 0.011 mol) dissolved in H_2O (3.0 mL) was added with vigorous stirring. Stirring was continued and the mixture was kept cold until nearly complete dissolution was achieved. Excess HNO_2 was destroyed by adding sulfamic acid. Activated carbon was added and the mixture was stirred and filtered to give a clear yellow solution.

The diazonium solution was added dropwise to *N,N*-diethylaniline (1.53 g, 0.102 mol) dissolved in HOAc (25 mL) at 0-5°C. The pH of the coupling reaction was maintained near pH 5 by the addition of solid $\text{NaOAc} \cdot 3\text{H}_2\text{O}$. The mixture was stirred overnight. The precipitate was collected by filtration, washed with H_2O ,

and dried to give dye (**72**) (2.68 g, 90%). TLC: R_f = 0.44 (toluene). $^1\text{H-NMR}$ (CDCl_3): δ = 6.5-8.0 (m, 8H, aromatic protons), 3.47 (q, 4H), 1.24 (t, 6H) (see Appendix A, Figure A4)

Dye (**73**)

The procedure described above for the synthesis of dye (**72**) was employed, with *p*-nitroaniline (1.38 g, 0.01 mol) used as the starting material to give dye (**73**) (2.83 g, 95%). TLC: R_f = 0.47 (toluene). $^1\text{H-NMR}$ (CDCl_3): δ = 6.5-8.5 (m, 8H, aromatic protons), 3.50 (q, 4H), 1.27 (t, 6H) (see Appendix A, Figure A6).

Dye (**74**)

The procedure described above for the synthesis of dye (**72**) was employed, with 2,4-dinitroaniline (1.83 g, 0.01 mol) used as the starting material to give dye (**74**) (3.29 g, 96%). TLC: R_f = 0.47 (toluene). $^1\text{H-NMR}$ (CDCl_3): δ = 6.5-8.8 (m, 7H, aromatic protons), 3.52 (q, 4H), 1.29 (t, 6H) (see Appendix A, Figure A8).

Dye (**75**)

The procedure described above for the synthesis of dye (**72**) was employed, with 2-chloro-4-nitroaniline (1.72 g, 0.01 mol) used as the starting material to give dye (**75**) (3.15 g, 95%). TLC: R_f = 0.64 (toluene). $^1\text{H-NMR}$

(CDCl₃): δ = 6.7-8.0 (m, 7H, aromatic protons), 3.48(q, 4H), 1.26 (t, 6H) (see Appendix A, Figure A9).

Dye (76)

The procedure described above for the synthesis of dye (70) was employed, with 4-aminophenylvinylsulfone (1.83 g, 0.01 mol) used as the starting material to give dye (76) (3.12 g, 91%). TLC: R_f = 0.65 (toluene:EtOAc/3:1). ¹H-NMR (CDCl₃): δ = 8.0-7.7 (m, 6H, aromatic protons), 6.8-6.7 (m, 2H, aromatic protons), 6.67 (d, ethylene H), 6.47 (d, cis H), 6.05 (d, trans H), 3.46 (q, 4H), 1.24 (t, 6H) (see Appendix A, Figure A10).

Dye (77)

The procedure described above for the synthesis of dye (72) was employed, with 4-(trifluoromethyl)-aniline (1.61 g, 0.01 mol) used as the starting material to give dye (77) (2.89 g, 90%). TLC: R_f = 0.75 (toluene). ¹H-NMR (CDCl₃): δ = 6.7-8.0 (m, 8H, aromatic protons), 3.48(q, 4H), 1.26 (t, 6H) (see Appendix A, Figure A12).

Dye (78)

The procedure described above for the synthesis of dye (72) was employed, with 2-(trifluoromethyl)-aniline (1.61 g, 0.01 mol) used as the starting material to give dye (78) (2.63 g, 82%). TLC: R_f = 0.75 (toluene). ¹H-NMR

(CDCl₃): δ = 6.7-8.0 (m, 8H, aromatic protons), 3.48(q, 4H), 1.26 (t, 6H) (see Appendix A, Figure A14).

Dye (79)

The procedure described above for the synthesis of dye (72) was employed, with 3-(trifluoromethyl)-aniline (1.61 g, 0.01 mol) used as the starting material to give dye (79) (2.73 g, 85%). TLC: R_f = 0.75 (toluene). ¹H-NMR (CDCl₃): δ = 6.7-8.0 (m, 8H, aromatic protons), 3.48(q, 4H), 1.26 (t, 6H) (see Appendix A, Figure A16).

2.3 Results and Discussion

Ten common arylamines were selected to gain insight into the role of basicity of the amine in determining the efficiency of conversion to dye using SC-CO₂ in the absence of mineral acid. Amine basicity is likely to be particularly critical to diazotization reactions in which CO₂/H₂O is used as the proton source (see Figure 17, page 54) due to the relatively high pK_a of carbonic acid, as described in section 1.7.1 [91]. The first step to diazotization is protonation of amine, and so very weak bases usually require reaction systems with very low pH to even commence the diazotization reaction. In addition, amine solubility in the reaction medium will also contribute to the reaction efficiency. It is well-known, for instance, that dye solubility is commonly a rate-limiting step in achieving level dyeings with high exhaustion efficiency of fibers using SC-CO₂ [34,66]. Hence, amines that exhibit very low solubility in the SC-CO₂ medium will

likely fail to diazotize efficiently. For this reason, the potential for increased product yield using a small amount of polar co-solvent was investigated.

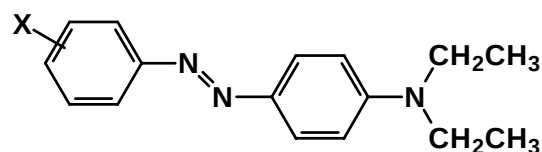
An operating temperature of 80°C and 207 bar was selected for all reactions, as previous research in our laboratories showed these conditions produced *N,N*-diethyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}amine (**73**) in high yield [88]. The mole amount of each reactant/solvent was also kept constant to facilitate direct comparison of the effect of substituents on the diazotizing amine on product yield. The amounts of reactants charged was kept small to avoid the possibility of crystallizing significant amounts of highly reactive, unstable diazo salts in the reactor.

2.3.1 Effect of Basicity, Hydrophobicity and Position of Auxochromes on Product Yield

Table 8 shows a summary of yield and other pertinent data for dyes (**70**) to (**79**). A limitation of the scope of diazotization and coupling using SC-CO₂ and water as the proton source is demonstrated by the results obtained using very weakly basic amines. The attempted diazotization and coupling of arylamines, 2,4-dinitroaniline and 2-chloro-4-nitroaniline, to obtain dyes (**74**) and (**75**) produced no measurable colored product.

These amines are weakly basic and require diazotization in concentrated acids in conventional aqueous reactions. Moreover, the presence of both nitro and chloro substituents on aromatic compounds has been shown to increase CO₂ solubility [34], indicating that the reaction failure for these disubstituted

anilines is mainly due to the low basicity of the amine and the relatively high pK_a of carbonic acid compared to the mineral acids used in conventional syntheses of these arylamines. However, CO_2 solubility has been shown to diminish if more than one NO_2 or Cl group is present on an aryl ring [93]. Incorporation of polar co-solvent to the reaction mixture produced further evidence that the reaction failure was due to incompatibility between the basicity of the amine and the pK_a of the carbonic acid. The addition of MeOH produced no improvement in the SC- CO_2 reactions.

Table 8. Summary of data pertinent to the synthesis of azo dyes (70) to (79).

X	Dye	M _w	E _{max} (L mol ⁻¹ cm ⁻¹)	Yield (%)			PK _a ⁽⁴⁾	Log P ⁽⁵⁾
				(1)	(2)	(3)		
H	(70)	253	17,243	94.0	16.0	15.0	4.61	0.936±0.19
2-OMe	(71)	283	22,917	87.0	0	0	4.54	1.092±0.22
2-NO ₂	(72)	298	30,596	90.0	24.0	25.0	-0.23	1.830±0.26
4-NO ₂	(73)	298	19,875	95.0	50.0	50.0	1.01	1.390±0.23
2,4-(NO ₂) ₂	(74)	343	36,707	96.0	0	0	-4.26	2.222±0.29
2-Cl,4-NO ₂	(75)	332	26,025	95.0	0	0	1.05	2.458±0.26
4-VS	(76)	343	28,245	91.0	60.0	62.0	1.14	0.218±0.27
4-CF ₃	(77)	321	18,183	90.0	12.0	15.0	2.77	1.950±0.26
2-CF ₃	(78)	321	37,193	82.0	2.0	3.0	1.10	2.410±0.49
3-CF ₃	(79)	321	23,094	85.0	7.0	9.0	3.37	2.390±0.28

⁽¹⁾ conventional aqueous method.

⁽²⁾ SC-CO₂ method without co-solvent.

⁽³⁾ SC-CO₂ method with co-solvent (methanol).

⁽⁴⁾ pK_a for the arylamine used in the diazotization reaction [94].

⁽⁵⁾ log P for the arylamine used in the diazotization reaction [94].

It is clear from Table 8 that yields obtained using conventional aqueous-based diazotization and coupling reactions produced high yields in all cases, whereas yields of equivalent dyes prepared using SC-CO₂ are much lower (or negligible) yields. However, it should be noted that the conditions used in all cases might not produce optimum product yields. The goal of the work was to gain insight into the contribution of substituents on the diazotizing arylamine rather than determine the best yields obtainable for each dye.

Although results from many studies suggest that the solubility of certain solutes (e.g., disperse dyes [25-43]) in SC-CO₂ is increased sharply by adding small amounts of a polar co-solvent. However, the presence of MeOH in the set of dyes studied here did not significantly increase the product yields (compared to when no co-solvent was used) of any of the attempted syntheses. Furthermore, the use of co-solvents such as EtOH and iso-propyl alcohol did not improve the reaction yield, suggesting that enhancement of solubility is not a primary factor in reaction efficiency in the present case.

However, relatively little is known regarding the mechanisms for solvent enhanced solubility in CO₂. Alsten and coworkers [95] found that coupling between dipolar species exists in the condensed phase, which could lead to aggregation between polar solutes and polar solvents, thus producing an overall decrease in polar solute solubility in the system.

An additional factor to consider in diazotization and coupling in SC-CO₂ is the position of substituents on the aryl ring. For the dyes studied, the presence of bulky substituents *ortho* to the amino group reduced the efficiency of the

reaction, as evidenced by the zero yield obtained when *ortho*-anisidine was used in the attempted synthesis of dye (**71**). The failure of this dye formation was particularly surprising because the starting primary amine has a high pK_a value and could be expected to diazotize easily. However, solubility may also be an issue in the case of dye (**71**). While limited experimental data have been reported for the solubility of aniline analogs in SC-CO₂, the CO₂ solubilities of aniline and *ortho*-anisidine have been measured; the former was shown to be approximately 3% (at P= 955 psi, T= 25°C) while *ortho*-anisidine was < 2% under the same condition [93].

Additional evidence of the problem of incorporating *ortho* substituents in the arylamine to be diazotized can be seen by comparison of dye yield for the two isomeric dyes (**72**) and (**73**) prepared using *ortho*- and *para*-nitroaniline, respectively. The yield of the *para* isomer was approximately twice that of the *ortho* isomer while conventional synthesis produced each dye in high yield. However, the pK_a of the *ortho* compound is lower than the *para*; hence the yield differences between (**72**) and (**73**) are likely due to a combination of steric hindrance, solubility and basicity.

Aniline analogs containing a trifluoromethyl substituted group were also studied, since dyes incorporating these auxochromes often show desirable physical properties in some applications, including solubility and photostability. Furthermore, it is well-known that fluorocarbons generally exhibit good solubility in SC-CO₂ [34,81]. Hence, *ortho* (**78**), *meta* (**79**) and *para* (**77**) isomers of trifluoromethylaniline were used as diazotizing amines. Interestingly, despite

relatively high pK_a values, the product yields obtained in each case where CF_3 was incorporated were low for the reaction conditions used. The lowest yield obtained was from *ortho*- CF_3 substituted aniline, showing further evidence of problems in the CO_2 synthesis of azo dyes in which bulky *ortho*-substituted groups are incorporated into the diazotizing arylamine, presumably due to steric hindrance at the *ortho* position.

Summarized in Table 14 are data showing the reported pK_a (acidity/basicity) and calculated log P values for octanol:water partition -a measure of solute hydrophobicity- of substituted anilines on final product yield. The pK_a and log P values were calculated using Advanced Chemistry Development (ACD/Labs) Software V 8.14 for Solaris. Interestingly, as shown in Figure 23, no correlation was found between dye yield and arylamine pK_a ($R^2 = 0.251$ for a polynomial fit line), further indicating that factors such as solubility and steric hindrance must also be considered in determining reaction efficiency. However, a weak correlation was found between yield level and calculated log P values as shown in Figure 24 ($R^2 = 0.483$ for a linear fit line). The correlation improves ($R^2 = 0.687$ for a linear fit line) if the data for compounds with *ortho* substituents (i.e., dyes **(71)**, **(72)** and **(78)** are excluded (Figure 25), thereby reducing the contribution of steric effects. The log P data indicate that reducing hydrophobicity enhances reaction efficiency, providing the basicity of the amine is not very low and bulky substituents are not located in the position *ortho* to the diazotizing amine.

While this work has focused on the synthesis of non-ionic (disperse) dyes, Figure 31 indicates that further work is warranted for the synthesis of dyes with much lower log P values, for instance, azo dyes in which the diazo component (or coupling component or both) possesses auxochromes that are ionic (e.g., sodium sulfonate or sodium carboxylate groups). This endeavor could lead to the synthesis of acid dyes and water-soluble fiber-reactive dyes using a SC-CO₂-water medium.

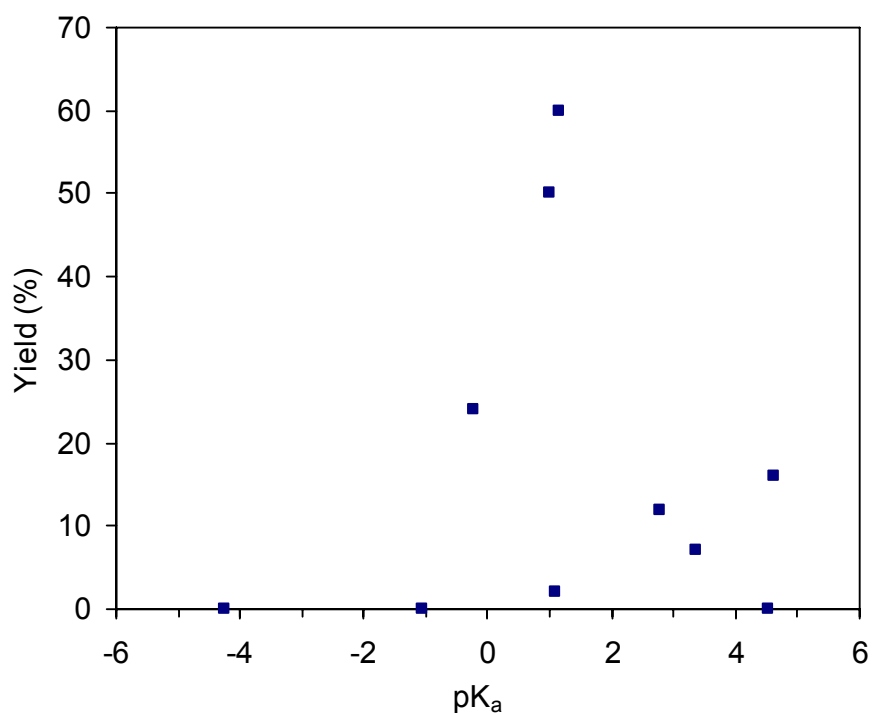


Figure 23. Graph of pK_a of substituted aniline versus % dye yield.

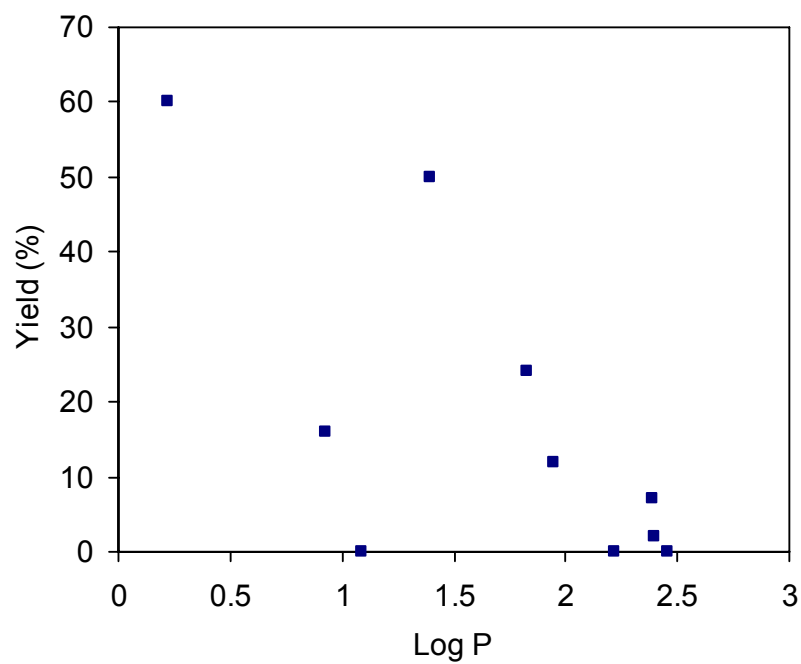


Figure 24. Graph of Log P of substituted aniline versus % dye yield.

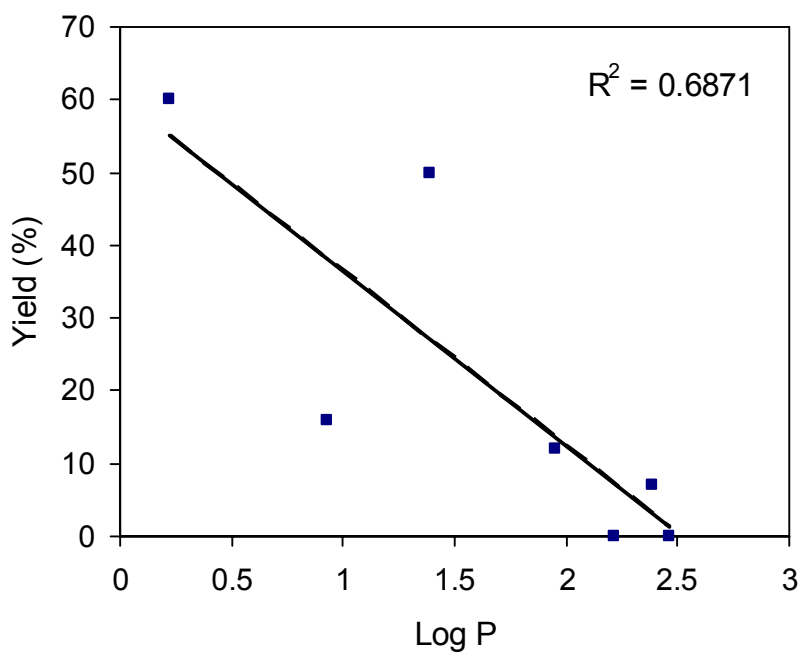


Figure 25. Graph of Log P of substituted aniline versus % dye yield after excluding *ortho* substituents.

2.3.2 Comparison of Absorption Spectra of Dyes: Conventional versus SC-CO₂ Synthesis

Figure 26 shows a comparison of absorption spectra for the dyes (**73**) and (**76**) prepared in SC-CO₂, as well as the same dyes prepared using conventional methods. Also, Table 9 shows a summary of λ_{max} for dyes prepared conventionally and under SC-CO₂ conditions. The absorption spectra are similar in shape regardless of synthesis method for a particular dye, which is reflected in the λ_{max} values.

Hence, while the SC-CO₂ yields are low, the correct dye is being formed. Nevertheless, competing side reactions are commonly encountered during diazotization and coupling, which can lead to undesirable impurities.

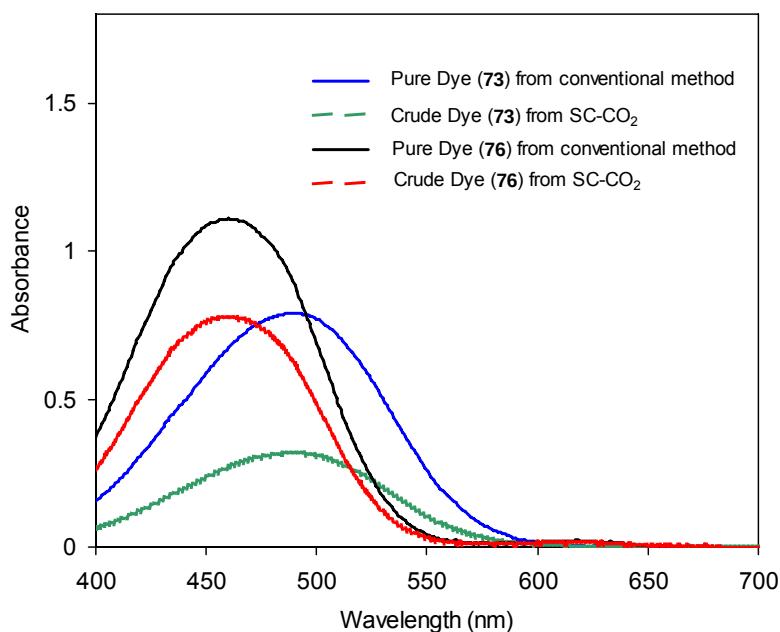
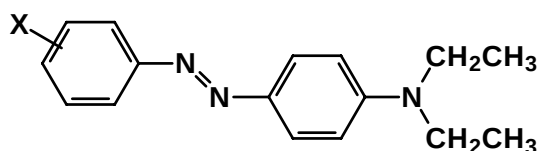


Figure 26. Comparison of absorption spectra for selected dyes prepared in conventional and SC-CO₂ reaction conditions.

Table 9. Summary of $\lambda_{\max}$ values of dyes synthesized conventionally and in SC-CO₂.



X	Dye	$\lambda_{\max}$ (nm)	
		Conventional method	SC-CO ₂
H	(70)	420	420
2-OMe	(71)	422	-
2-NO ₂	(72)	457	458
4-NO ₂	(73)	489	488
2,4-(NO ₂) ₂	(74)	529	-
2-Cl,4-NO ₂	(75)	475	-
4-VS	(76)	460	460
4-CF ₃	(77)	441	440
2-CF ₃	(78)	439	439
3-CF ₃	(79)	434	434

2.3.3 Side Reactions

In conventional diazotization and coupling reactions, a number of undesirable side reactions are commonly encountered, including hydrolysis of the diazo group to liberate N₂, self-coupling between the diazo group and undiazotized primary amine, and N-coupling. Each side reaction can contribute significantly to reduced product yield and changes in color and other physical properties resulting in the requirement for extensive purification. The potential for

such side reactions in SC-CO₂ is not known. However, it is a reasonable assumption that the level and type of side reactions could be significantly different from conventional azo dye synthesis. The fact that much higher reaction temperatures can be used successfully in the former case make it reasonable to expect a very different reaction mechanism to occur when SC-CO₂-water is used in lieu of an aqueous-mineral acid system. In fact, the reaction mechanism for azo dye formation using SC-CO₂ may not even be based on diazotization. A possible reaction is nitrosation of the coupling component (Figure 27) followed by *in situ* condensation with the primary amino group of the arylamine intended for diazotization, as shown in Figure 28. Nitrosation of the coupler is an interesting possibility considering the relatively high solubility of the coupler in SC-CO₂ (17% at T= 25°C, P= 955 psi [94]).

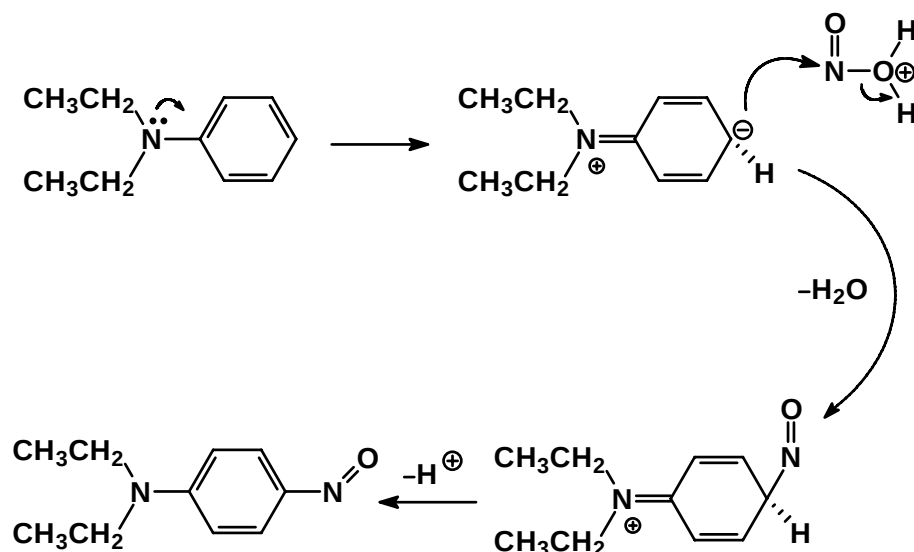


Figure 27. Reaction scheme showing possible nitrosation of *N,N*-diethylaniline in SC-CO₂.

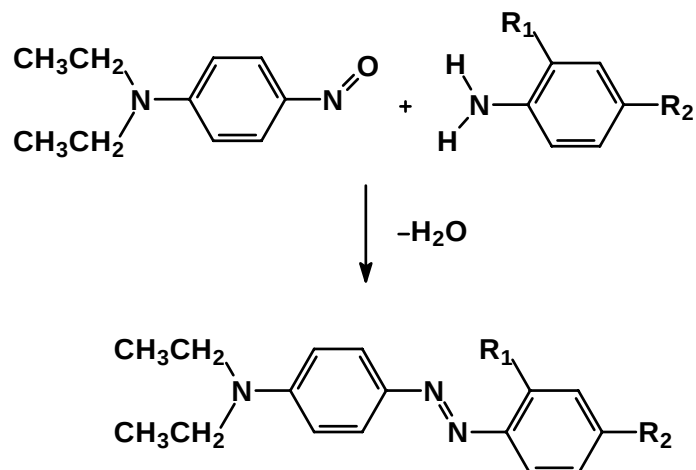
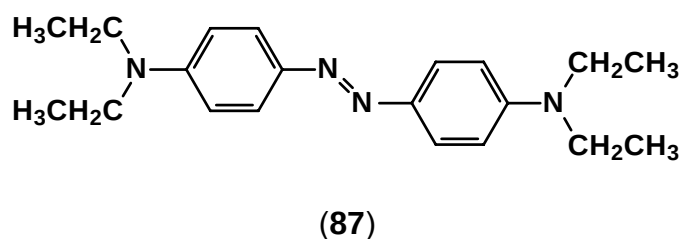


Figure 28. Reaction scheme showing possible azo dye formation via a condensation reaction in SC-CO₂.

In addition to the reaction shown in Figure 27, a possible side reaction is self-coupling between two nitrosated coupling components to produce the pale yellow compound (**87**).



Compound, (**87**) was actually isolated in very small amount from several of the SC-CO₂ reaction and, following purification by prep TLC, the structure was confirmed by ¹H-NMR (CDCl₃): δ = 6.45-6.65 (m, 4H, aromatic protons), 8.15-8.25 (m, 4H, aromatic protons), 3.48 (q, 8H), 1.26 (t, 12H); TLC: R_f = 0.46

(toluene) as shown in Figure 29. This impurity was found in the synthesis of dyes (70), (71), (75) to (79) conducted in SC-CO₂ and was less pronounced in the synthesis of dye (72). TLC analysis of crude product mixtures showed weakly colored yellow impurities in all the above cases, while TLC analysis of dyes (73) and (76) showed no such impurities. Significantly, no evidence of compound (87) was found in conventional synthesis of any of the dyes using an aqueous mineral acid system.

Mechanisms for producing compound (87) have been reported, but all require reduction of the nitroso derivative via catalysis such as Lawesson's reagent [96], MeOK [97], or a silylamine [97]. The mechanism was reported to occur via formation of an azoxy intermediate followed by reduction to the final azo product. Denonne *et. al* [97] reported that homo-coupling between two nitroso compounds was not possible in the absence of silylamine. However, such homo coupling clearly occurred in the SC-CO₂ reactions as shown in Figure 30 to produce compound (87). The formation of compound (87) in SC-CO₂ has not been reported elsewhere. A possible reaction mechanism is shown in Figure 29.

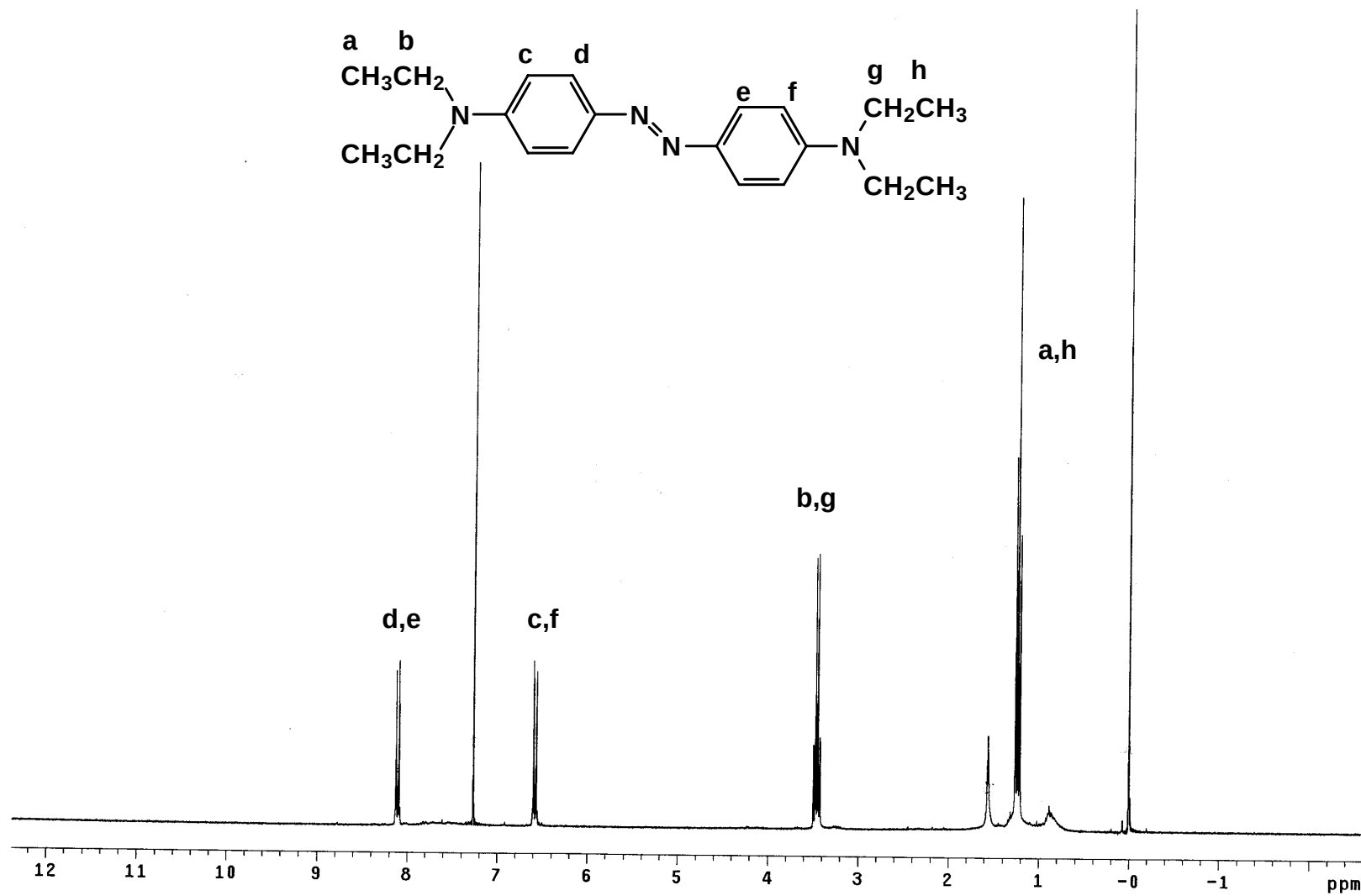


Figure 29. ^1H -NMR spectrum of compound (87).

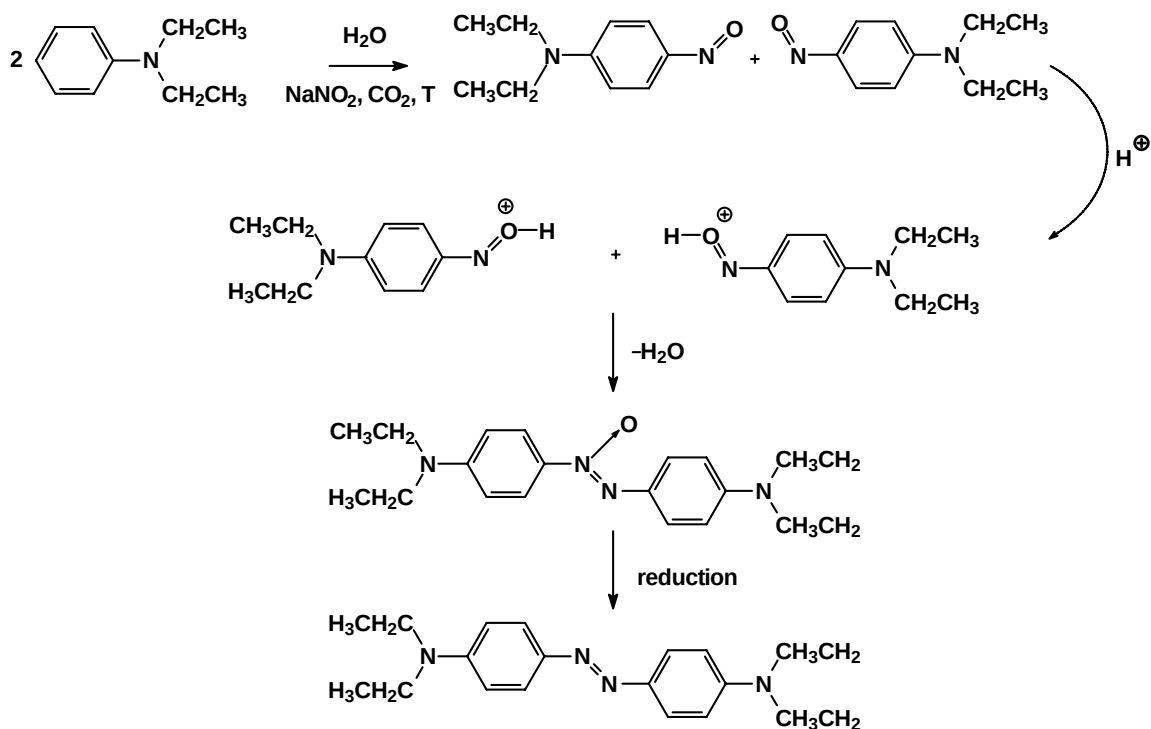


Figure 30. Diazotization and coupling of coupler-coupler in SC-CO₂.

2.4 Conclusions

The primary objective of this work was to determine the effects of type and placement of substituents on the product yield of a series of simple azo dyes using a SC-CO₂-water medium to act as solvent and proton source.

The synthesis of azo dyes in SC-CO₂ appears to be dependent on a combination of basicity, solubility and the absence of steric hindrance around the amino group to be diazotized. Compounds with substituents *ortho* to the diazotizing arylamine did not form azo dyes in significant yield. In addition, disubstituted arylamines with two ring deactivating groups (e.g., dinitroaniline) failed to produce any colored product. However, dyes from arylamines containing nitro- and vinylsulfonyl- substituents in the *para*-position relative to the primary amine could be easily synthesized in SC-CO₂ in modest yields. High yields for the synthesis of these dyes may be possible following a statistical design of experiments to optimize the yield.

Interestingly, the use of small amounts of MeOH as co-solvent did not improve the reaction of any dyes studied, and pK_a value of the diazo component did not correlate with product yield. However, a correlation did exist for calculated log P (octanol:water) of the arylamines and product yield, with the correlation improving if *ortho*-substituted amines were excluded from the calculation.

A major benefit of a mineral-free diazotization reaction would be elimination of a neutralization step and the need to remove large quantities of electrolyte from crude azo dye reaction mixtures. Also, with reasonable product

yields, isolation of pure dye by selective dissolution and precipitation using SC-CO₂ is feasible. However, more work is required to understand the key factors that drive the reaction, including: the effect of substituents on the reactivity of coupling components, use of alternatives to sodium nitrite (e.g. isoamyl nitrite) to completely remove Na⁺ from the reaction, optimization of reaction conditions for commercially important dyes, expansion of the role of log P to include highly water soluble diazotizing arylamines, such as sulfanilic acid and related compounds. Importantly, the potential hazards to synthesizing azo dyes in SC-CO₂ in scaled up reactions must be assessed, and the reaction mechanism determined.

3. Synthesis of 4-(4-vinylsulfonylphenylazo)-*N,N*-diethylaniline in Supercritical Carbon Dioxide

3.1 Introduction

Results in the previous chapter showed that the type and position of substituents present on the diazotizable arylamine have very significant effects on azo dye yield when using SC-CO₂ as a medium. It was demonstrated that the diazotization and coupling of certain arylamines will not occur using SC-CO₂-water as the reaction medium and protonation source. However, it was also evident that some arylamines have the potential to be synthesized in good yield.

While Raue *et al.* patented a SC-CO₂ azo dye synthesis method [85-87], no published data exist showing approaches to yield optimization or the key variables in the reaction. Data presented in this chapter show a statistical approach to the optimization of dye yield for one novel disperse reactive dye (dye **(76)**) using SC-CO₂, and to provide insight into the key variables for this reaction. This dye is of particular interest in SC-CO₂ research as it has potential for use as a SC-CO₂ soluble fiber-reactive dye that can react with fibers possessing nucleophilic groups, such as primary and secondary amino groups. Much of the prior art pertaining to supercritical fluid dyeing has employed conventional disperse dye structures originally designed for application to hydrophobic fibers from an aqueous medium. Hence, there exists the potential for development of new dye structures specifically optimized for SC-CO₂ applications. The basic

structure of dye (**76**) is a point of departure for structure optimization for fiber-reactive dye application studies.

3.2 Experimental

All materials, equipment and the preparation of 4-aminophenylvinylsulfone were the same as described in 2.2.4.1 (page 64).

3.2.1 Statistical Design of Experiments

Thirty diazotization and coupling experiments to produce dye (**76**) were conducted based on a central composite design (CCD). The experimental design and statistical analysis were performed using the statistical software package, Design-Expert (v 6.0.8) by Stat-Ease, Inc. (Minneapolis, MN, USA). Four factors were evaluated: temperature, pressure, water, and reaction time, with % product yield the output variable to be optimized. The CCD contained three levels for each factor. The coded levels and actual values used are given in Table 10.

Table 10. Coded and actual levels of the design factors.

Factor Symbol	Factor	-1	0	+1
A	Temperature (°C)	30	55	80
B	Pressure (psi)	1500	2250	3000
C	Water (mL)	0.5	4.5	8
D	Time (min)	30	105	180

3.2.2 Synthesis of Dye (76) in SC-CO₂

Deionized H₂O (x mL) was mixed with sodium nitrite (0.083 g, 1.2 mmol), 4-aminophenylvinylsulfone (0.183g, 1.0 mmol) and *N,N*-diethylaniline (0.19 mL, 1.2 mmol) in a 300 mL high-pressure reaction cylinder. A schematic diagram of the reactor system is shown in Figure 22. The reactor was then sealed and pressurized to 60 bar (860 psi). The reaction mixture was stirred using a high-speed mixer and heated to the working temperature, and CO₂ was isothermally compressed to the chosen working pressure under constant stirring speed of 800 rpm. Pressure was maintained for the required time after which CO₂ was released slowly. The reaction mixture was collected via dissolution in acetone and solvent was removed by rotary evaporation and dried.

For comparison purposes, dye (76) was synthesized by conventional diazotization and coupling, purified and characterized, as described in section 2.2.4.4 (page 67). The λ_{max} of dye (76) = 460 nm, and $\epsilon_{\text{max}} = 2.82 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

3.2.3. Absorption Spectra and Calculation of Spectroscopic Yield

Visible absorption data of dye (**76**) synthesized both conventionally and in SC-CO₂ were recorded in order to obtain the spectroscopic yield of each reaction using a Varian Cary 3E UV-visible spectrophotometer.

A sample of pure dye as well as a sample of the crude product of each reaction was dissolved separately in 100 mL acetone and the solution diluted to a concentration of 1.0×10^{-2} mg/L. The absorption spectrum was measured and the absorption coefficient calculated from the Beer-Lambert equation (equation 2). The % spectroscopic yield was calculated using the absorption coefficient of the pure dye (in $\text{g}^{-1} \text{L}^{-1} \text{cm}^{-1}$), via equation 3.

$$\text{Spectroscopic yield} = \frac{a_{\text{exp}}}{a_{\text{pure}}} * 100 \quad (\text{equation 3})$$

3.3 Results and Discussion

An efficient way to optimize a multi-component process with multiple variables is to develop a statistical design of experiments (DOE). Not only does a DOE enable the development of the minimum number of reactions to develop significant response surfaces, it also affords the development of a model to predict optimum conditions gain insight into the most significant variables affecting the process.

In the current DOE, 30 reactions involving the synthesis of azo disperse reactive dye (**76**) were performed in SC-CO₂ via a simultaneous diazotization and

coupling process. The amount of reactants was deliberately kept low in order to avoid potential crystallization of significant amounts of the unstable diazo amine.

3.3.1 Statistical Analysis

The CCD contained three levels for each factor. Within these levels, the design generates sufficient data to fit a two-factor interaction model (2FI). Table 11 shows the pattern of the level of the four factors along with spectroscopic yield (%) values from each individual trial. After Analysis of Variance (ANOVA) for this model including all terms, the terms having probability values (p-values) greater than 0.05 were eliminated as these were statistically insignificant at the 95% confidence level.

The ANOVA data for the significant model terms are listed in Table 12. The model p-value of < 0.0001 implies that the model is significant. The first term is the intercept, a constant. The next four terms (A-D) are the main effects and the corresponding values demonstrate the level of contribution for each of the main factors [98]. Hence, pressure, amount of H_2O charged to the system, and reaction time have significant effects on percentage yield (each had a p-value < 0.0001), with amount of water exhibiting by far the most significant effect. Interestingly, the model showed that temperature changes did not have a significant effect on product yield, which is interesting considering the often extreme temperature sensitivity of conventional diazotization reactions

Table 11. Central composite design of dye (**76**) synthesized in SC-CO₂.

NO.	Temperature (°C) A	Pressure (psi) B	Water (mL) C	Time (min) D	% Yield Y
1	30	3000	8.0	180	77
2	80	3000	8.0	180	91
3	30	3000	0.5	30	56
4	80	3000	0.5	30	58
5	30	1500	8.0	30	99
6	80	1500	8.0	30	99
7	30	3000	8.0	30	69
8	80	3000	8.0	30	85
9	30	1500	0.5	180	51
10	80	1500	0.5	180	38
11	30	3000	0.5	180	55
12	80	3000	0.5	180	56
13	30	1500	8.0	180	93
14	80	1500	8.0	180	92
15	30	3000	8.0	180	77
16	80	3000	8.0	180	91
17	30	2250	4.25	105	70
18	80	2250	4.25	105	70
19	55	1500	4.25	105	74
20	55	3000	4.25	105	69
21	55	2500	0.5	105	53
22	55	2500	8.0	105	89
23	55	2500	4.25	30	72
24	55	2500	4.25	180	70
25	55	2500	4.25	105	71
26	55	2500	4.25	105	72

Table 11. (continued)

NO.	Temperature (°C) A	Pressure (psi) B	Water (mL) C	Time (min) D	% Yield Y
27	55	2250	4.25	105	71
28	55	2250	4.25	105	71
29	55	2250	4.25	105	71
30	55	2250	4.25	105	71

Table 12. ANOVA for response surface using a reduced 2FI model ($R^2 = 0.9983$) after exclusion of insignificant terms.

Model terms	Estimated coefficient	Standard error	P-value
Model	-	-	< 0.0001
Intercept	70.80	-	-
A	0.33	0.14	0.0775
B	-2.28	0.18	< 0.0001
C	17.56	0.18	< 0.0001
D	-1.44	0.18	< 0.0001
AB	3.75	0.19	< 0.0001
AC	3.25	0.19	< 0.0001
BC	-5.38	0.19	< 0.0001
BD	2.88	0.19	< 0.0001
CD	1.62	0.19	< 0.0001

The lack-of-fit statistic was used to test the adequacy of the model obtained and the p-value after the exclusion of the statistically insignificant terms was 0.0581, which exceeds the threshold value of 0.05. Hence, the lack of fit

was not significant and the model is valid for prediction of spectroscopic yield (%) using the particular reactor system and conditions. The model shown in equation 7 was used to predict the response (spectroscopic yield) throughout the experiments. A summary of the effects of each factor on spectroscopic yield (%) of dye (76) are illustrated in Figures 31-35.

$$Y = 88.26 - 0.58A - 0.01B + 6.47C - 0.1591D + 2.00 \times 10^{-4}AB + 0.035AC - 1.915 \times 10^3 BC + 5.115 \times 10^{-5}BD + 5.778 \times 10^{-3}CD \quad (\text{equation 4})$$

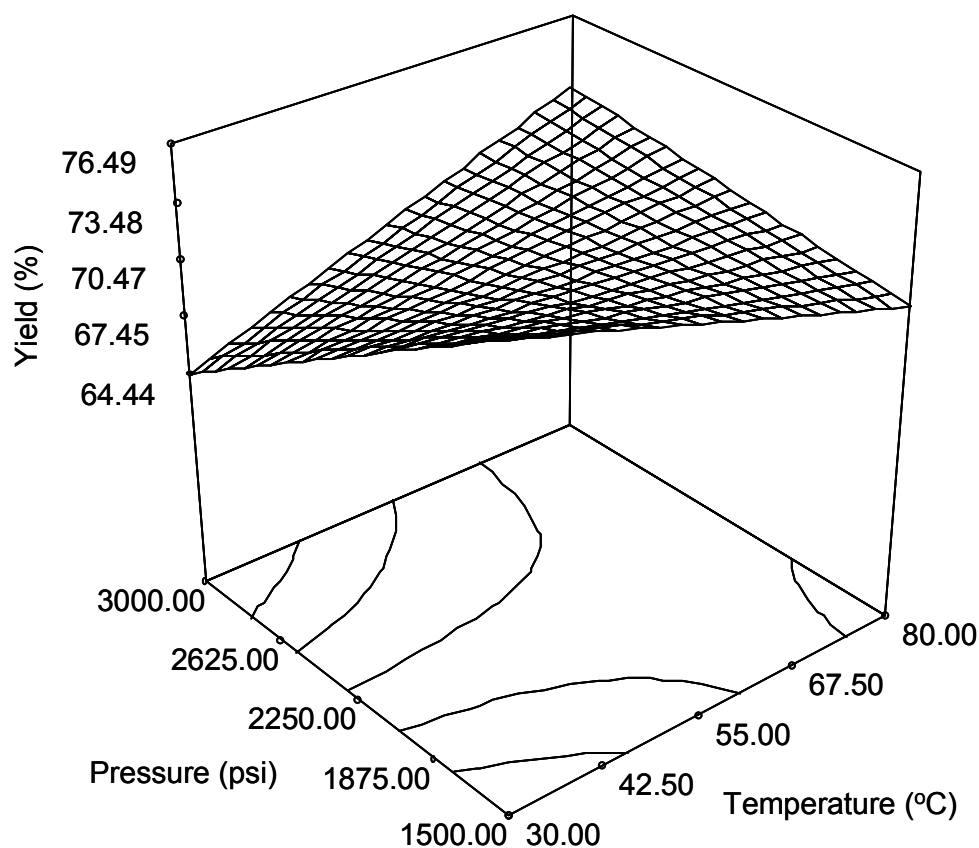


Figure 31. The effect of pressure and temperature on spectroscopic yield (%).

(H₂O = 4.25 mL, t = 145 min)

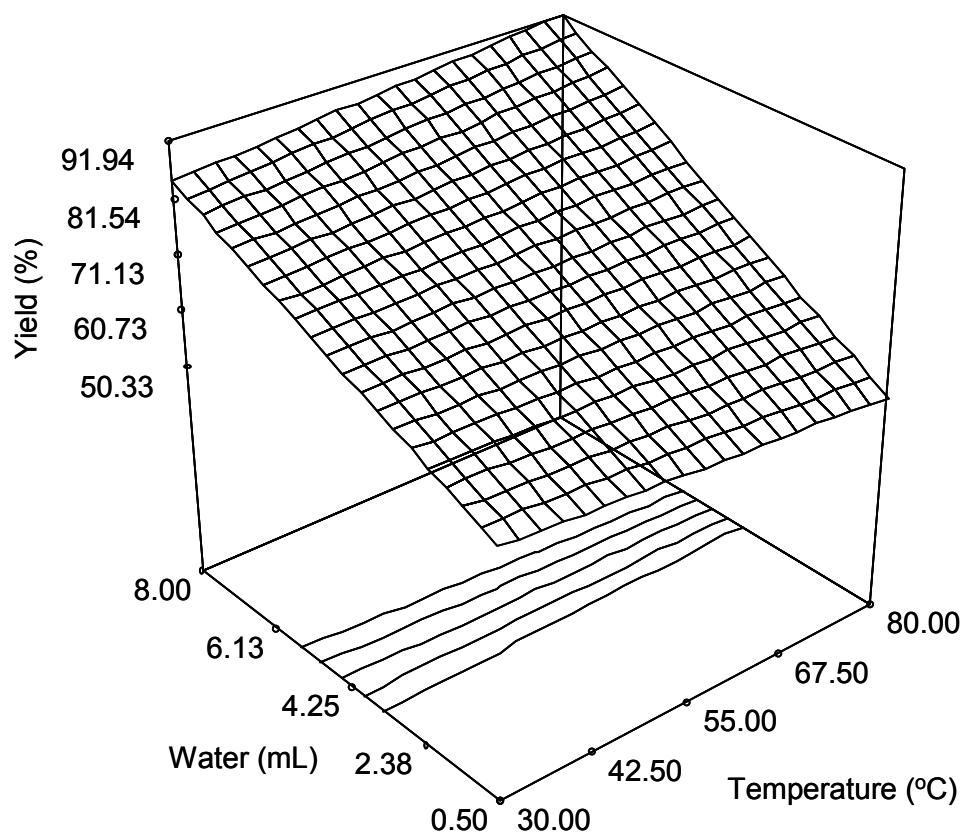


Figure 32. The effects of water and temperature on spectroscopic yield (%).

(P = 2250 psi (155 bar), t = 145 min)

Figure 31 shows the effect of pressure and temperature on spectroscopic yield. The suitable synthesis condition of dye (**76**) is at lower pressure and temperature. The amount of H₂O has a significant effect on dye productivity, while temperature and pressure does not show much influence to the yield percentage, as indicate in the Figures 32-33.

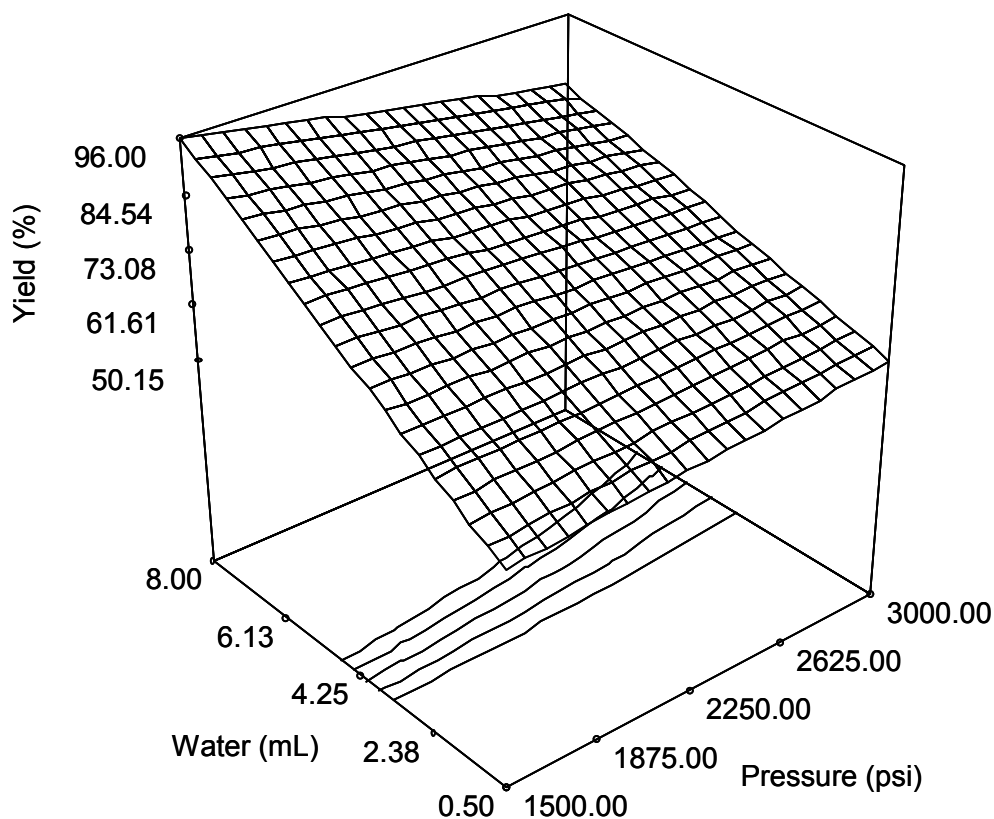


Figure 33. The effect of water and pressure on spectroscopic yield (%).

(T = 55°C, t = 145 min)

As the amount H₂O charged to the system increases, the yield is remarkably increased, presumably due to increased solubility of the diazo compound formed prior to coupling. The yield increases from below 50% to above 95% as the amount of H₂O in the system increases from 4.5-8.0 mL. The synthesis of dye (**76**) in SC-CO₂ is a relatively rapid process as illustrate in Figures 32-33, with little increase % yield for reactions longer than 30 min.

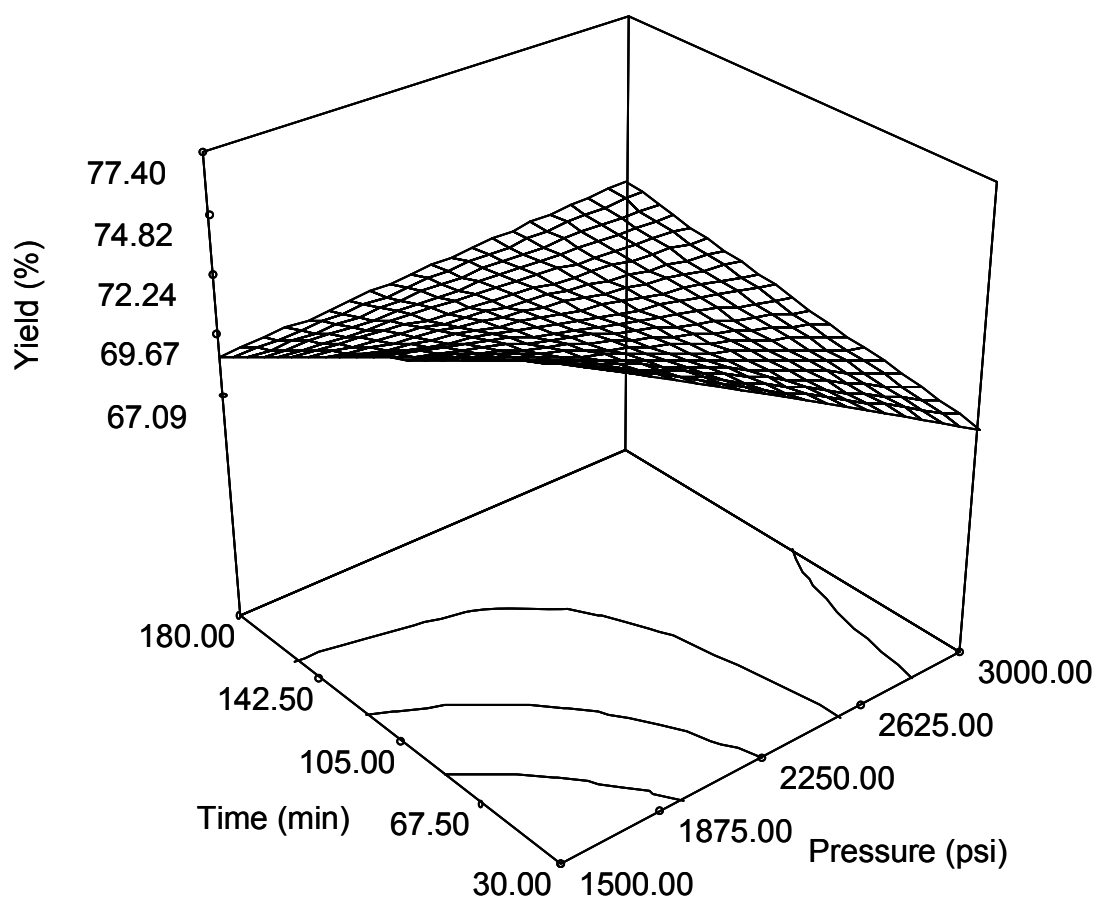


Figure 34. The effect of time and pressure on spectroscopic yield (%).

($T = 55^{\circ}\text{C}$, $\text{H}_2\text{O} = 4.25 \text{ mL}$)

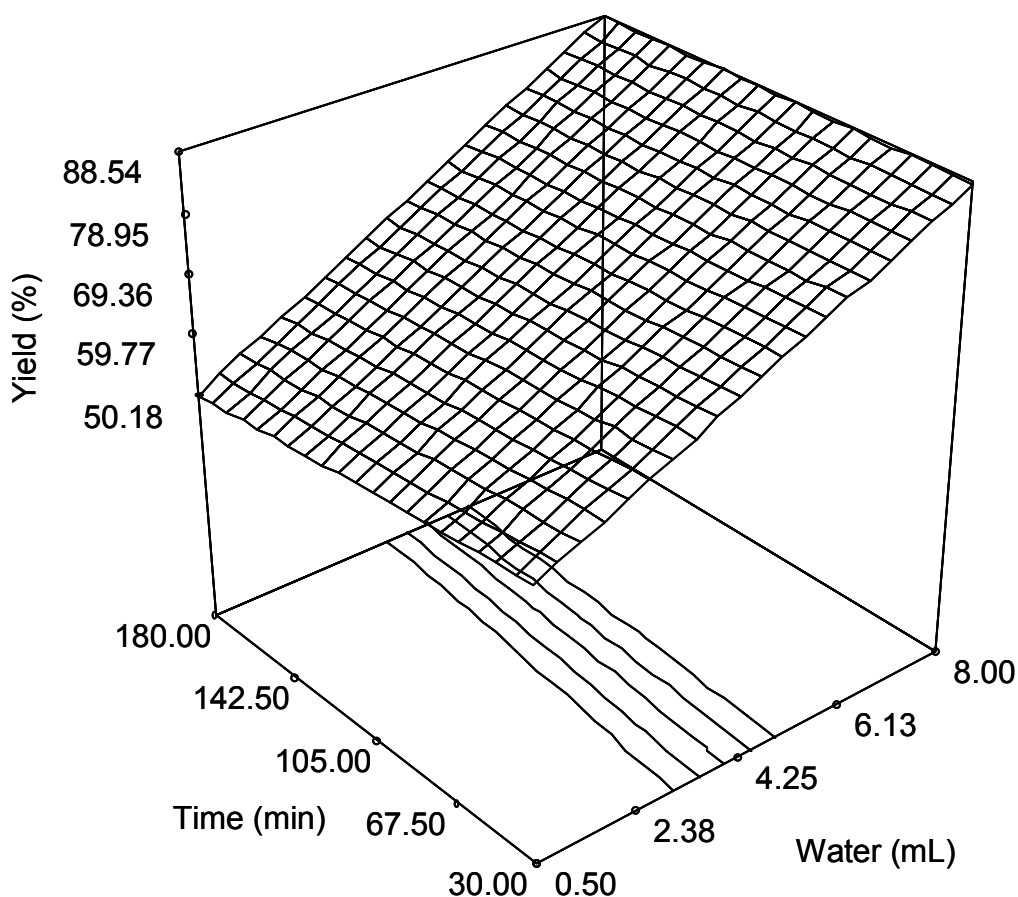


Figure 35. The effect of time and water on spectroscopic yield (%).

($T = 55^{\circ}\text{C}$, $P = 2250 \text{ psi}$ (155 bar))

3.3.2 Optimization of the Process

The model was used to predict an optimal % yield for dye (**76**) in SC- CO_2 , as a function of time, pressure, and temperature. The predicted optimized procedure is given in Table 13, along with some comparative predicted yields when varying temperature ± 5 to 7°C , and pressure $\pm 300\text{psi}$ (20 bar). Near

complete conversion of the reactants is predicted, and this was validated experimentally with a maximum yield of 99%, which is clearly as good as, or better than an optimized conventional diazotization and coupling process. The optimum temperature and pressure are 55°C and 1500 psi (103 bar), respectively, while the amount of H₂O required was 8.0 mL.

Table 13. Predicted optimization of synthesis of dye (**76**) in SC-CO₂.

% Yield	Temperature (°C)	Pressure (psi)	Water (mL)	Time (min)
99.0	48.0	1000	8.00	100
95.0	48.0	1800	8.00	60
99.0	55.0	1500	8.00	30
95.0	58.0	1800	8.00	50
99.0	60.0	1000	8.00	70

3.4 Conclusions

A statistically designed experiment was used to optimize the reaction conditions for the synthesis of dye (**76**). For the reaction system employed, the primary influences on product yield were, by far, water, followed by pressure and time. Temperature had little effect on product yield. A predicted optimized procedure was validated and showed near complete conversion to product (99%) at 55 °C, 1500psi and 30 min reaction time.

4. Azoic Dyeing in Supercritical Carbon Dioxide

4.1 Introduction

Azoic dyeing is an old dyeing process that can produce high washfast dyeings on cotton (and some other natural and synthetic fibers), owing to the generation of an insoluble dye inside the polymer matrix of the fiber. It is a unique two-step process in which an azo dye is synthesized during the textile application process via a two-stage method involving: a) pre-treatment of cotton fabric with a coupling component (commonly a sodium naphtholate derivative) in an aqueous medium, and, following drying, b) application of an aqueous diazotized arylamine solution. Typically, the application of the diazo solution is by padding or printing.

While azoic dyeing is a mature technology, no prior art exists in which an azo dye has been synthesized within a polymer matrix using a SC-CO₂ and H₂O mixture to act as both solvent and protonation source for the diazotization reaction. Such an approach is potentially valuable, not only as a novel dyeing method; it also may provide new avenues for derivatization of, and synthesis within, porous polymeric materials.

Reported here are data demonstrating a new SC-CO₂ azoic dyeing method, in which the diazotization and coupling of a simple arylamine, aniline, to form a dye inside the fiber has been optimized using a statistical design of experiment. The data are also compared to a conventional aqueous azoic dyeing method using HCl as the proton source for diazotization. The potential

scope of the method for application to multiple substrates was also investigated using a standard multifiber 'strip'.

4.2 Experimental

4.2.1 Materials

Bleached, desized and mercerized cotton print cloth and multifiber fabric (No. 43, 13 fiber fabric) were purchased from Testfabrics, Inc. (West Pittston, PA, USA). Reagent grade sodium nitrite and aniline were obtained from Sigma-Aldrich Chemical. "Bone dry" and 99.0% pure CO₂ was purchased from National Specialty Gases. All other chemicals were reagent grade obtained from Fisher Scientific (Pittsburg, PA, USA).

4.2.2 Equipment

All reactions were performed using a jacketed 300 mL high-pressure reactor from Autoclave Engineers (Erie, PA, USA) equipped with a high speed stirrer, cooling/heating coil and a high-pressure pump, as shown in Figure 22.

4.3 Methods

4.3.1 Pretreatment of Fabrics with Sodium Naphtholate

Sulfonated castor oil (20.0 mL) and C.I. Naphthol Coupling Component 2 (Naphthol AS) (15.0 g) were rapidly stirred in hot water (50.0 mL). Sodium hydroxide (26.0 mL of 45% (w/v)) and hot water (500 mL) were added to the mixture and stirred until complete dissolution was achieved. Then, sodium nitrite solution (75.0 mL of 30% (w/w)) diluted to 1 L was added. The solution was placed in a padder and applied to cotton or multiber fabric at 85% wet pick-up (WPU) and then dried at 110°C.

4.3.2 Azoic Dyeing in SC-CO₂

Azoic dyeing reactions in SC-CO₂ were carried out using equipment shown in Figure 20. A statistical design of experiment was used to optimize the reaction conditions. Four factors affecting dyeing performance were evaluated: temperature, pressure, water, and dyeing time. In each case 3% owf aniline was used. Deionized H₂O (X mL) was mixed with sodium nitrite (9×10^{-5} mol, 0.0062 g) and aniline (8×10^{-5} mol, 0.0076 g) in the 300 mL high-pressure reactor. The naphtholated fabric (15x5 cm, 1.0 g) was loosely fixed to the cooling coils surrounding the mechanical stirrer inside the reaction vessel. The reactor was then sealed and pressurized to 60 bar (860 psi). The reaction mixture was stirred at 800 rpm. The system was maintained at 60 bar for a period of 30 min, at which time the system was heated to the working temperature, then CO₂ was

isothermally compressed to the required working pressure under constant stirring speed. The pressure and temperature were maintained for the required dyeing period after which CO_2 was released slowly. The dyed fabric was removed, soaped in warm water using AATCC detergent (2.0 g/L) at 160°F for 5 min. The fabrics were rinsed again in warm water and dried.

The SC- CO_2 azoic dyeing procedure described above was also used to dye pre-naphtholated multifiber fabrics at $T = 50^\circ\text{C}$, $P = 2250$ psi (155 bar), $\text{H}_2\text{O} = 4.5$ mL, and $t = 40$ min.

4.3.3 Azoic Dyeing by Conventional Aqueous Method

The diazonium salt was prepared by dissolving aniline (0.014 g, 0.15 mmol, 3% owf) in H_2O (50.0 mL), and conc. HCl (1.0 mL). The reaction mixture was cooled to 0-5°C using an ice bath and then NaNO_2 (0.014 g, 0.2 mmol) dissolved in H_2O (2.0 mL) was slowly added. The solution was stirred for 30 min. and then sulfamic acid was added to destroy excess HNO_2 . Sodium acetate was added to maintain the pH 4-5 (suitable for coupling). In order to prevent the naphtholate from being washed from the fiber and to increase % exhaustion, NaCl (1.25 g, 25 g/L) was added to the diazonium salt solution. The naphtholated cotton fabric (1.86 g, 5X5 cm) was immersed in the diazonium salt solution. The solution was stirred for 30 min to ensure complete coupling. The dyed fabric was removed, soaped in warm water using AATCC detergent (2.0 g/L) at 160°F for 5 min. The fabrics were rinsed again in warm water and dried.

4.3.4 Colorimetric Measurement

Colorimetric assessment was conducted using a Datacolor International SF300 Spectroflash Spectrophotometer with the following settings: illuminant D₆₅, 10 degree standard observer, specular included, UV included. Samples were measured three times with 90° rotation between each measurement, and the data were averaged. In the case of calculation of color strength, K/S values at $\lambda_{\max}$ were calculated using the Kubelka-Munk equation.

4.3.5 Fastness Assessment

4.3.5.1 Wash Fastness

The wash fastness properties of dyed fabrics were assessed using AATCC Test Method 61-2001, test No. 2A. The conditions used are listed below.

Temperature:	49°C
Bath Volume:	150 mL
% Detergent:	0.15%
No. of steel balls:	50
Time:	45 min

Multifiber test fabric from Test Fabrics, Inc., was attached to each fabric sample to assess the degree of staining. The resultant fabrics were evaluated colorimetrically for color change and staining using AATCC Evaluation Procedure 7 [99]. The rating system used was 1 (poor) to 5 (excellent).

4.3.5.2 Light Fastness

The light fastness of dyed fabrics was measured using AATCC test method 16-1998, option E [100] using the conditions listed below.

Light source:	Xenon (6500 watts)
Black panel temperature:	$63\pm 1^{\circ}\text{C}$
Dry Bulb temperature:	$43\pm 2^{\circ}\text{C}$
% Relative humidity:	$30\pm 5\%$
Test Duration:	20 h

The resultant fabrics were assessed for color change, per the standard method, using a Datacolor International SF300 Spectroflash Spectrophotometer and the rating system used was 1 (poor) to 5 (excellent).

4.3.5.3 Crock Fastness

Crock fastness testing was employed using AATCC test method 8-2001 [99]. The dyed fabrics were evaluated in both dry and wet tests. Color transfer to a white test square was measured colorimetrically, per the standard method, and the rating system used was 1 (poor) to 5 (excellent).

4.3.6 Statistical Design of Experiment

The azoic diazotization and coupling experiments of pretreated (naphtholated) cotton to form an azo dye within the fiber using SC-CO₂ were

conducted based on a central composite design (CCD). The experimental design and statistical analysis were performed using the statistical software, Design-Expert (v. 6.0.8) by Stat-Ease, Inc. (Minneapolis, MN, USA). The CCD contained three levels for each factor. The coded levels and actual values are given in Table 14. The optimization parameter was color strength (K/S) of the dyed fabric.

Table 14. Coded and actual levels of the design factors.

Factor Symbol	Factor	-1	0	+1
A	Temperature (°C)	30	50	70
B	Pressure (psi)	1500	2250	3000
C	Water (mL)	2	4.5	7
D	Time (min)	20	40	60

4.4 Results and Discussion

The primary goal of the experiment was to test the diazotization and coupling reaction within fibers using carbonic acid in lieu of conventional mineral acids. To limit the number of variables to be optimized, the method for the first stage of azoic dyeing, the application of coupler, was kept constant and was done using a conventional application. The same dry, pre-naphtholated cotton fabric was used in a statistical design of experiment. To a 300 mL high-pressure reactor was added aniline (3% owf), NaNO_2 , fabric and a small amount of water. The variables investigated were water, temperature, pressure and dyeing time.

Dyeing trials on cotton were carried out in SC-CO₂ to predict the optimum method for diazotization and coupling. Azoic dyeing is a two step method involving pre-treatment of cotton fabric with Na⁺ naphtholate in an aqueous medium, while the second step was developed in SC-CO₂ by diazotization of a diazo component (aniline) and finally, dye (**80**) was produced inside fibers with bright orange shade (Figure 36).

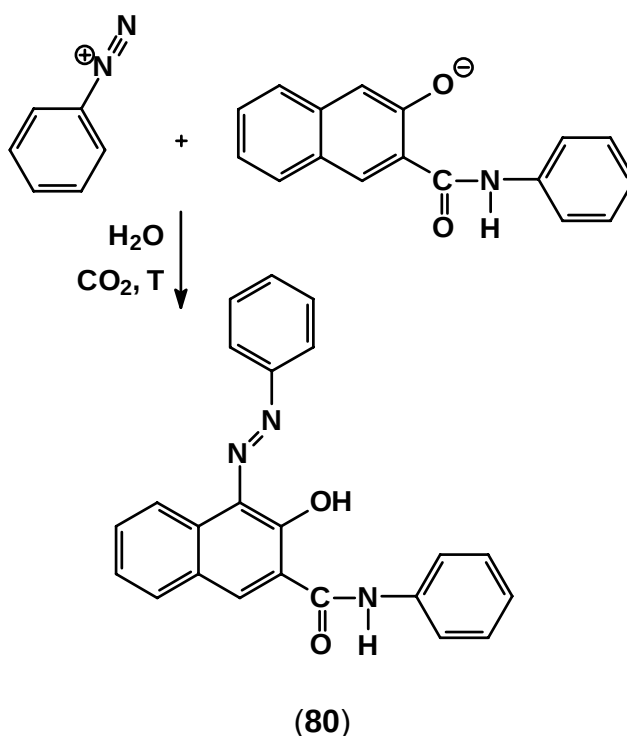


Figure 36. Formation of azoic dye in SC-CO₂.

4.4.1 Statistical Analysis

30 reactions were undertaken, including 16 trials at the factorial point, 8 trials at star points, and 6 replications at the center point. The specific details of

the central composite design are summarized in Table 15, along with the resulting color strength values from each individual trial. The CCD contained three levels for each factor. With these levels, the design generated sufficient data to fit a quadratic model. After Analysis of Variance (ANOVA) for the quadratic model, including all model terms, the terms having probability values (p-values) greater than 0.05 were eliminated due to statistical insignificance at the 95% confidence level.

The ANOVA data for the significant model terms are summarized in Table 16. The model p-value of < 0.0001 demonstrates that the model is significant. The first term, a constant, is the intercept. The next four terms (A-D) are the main effects and the values demonstrate the level of contribution for each factor [98]. Hence, the largest effect on K/S, with a confidence level over 99.9%, is water followed by pressure and dyeing time. In fact, it was found that if the amount of H_2O added in the reactions was less than 4.0 mL in a 300 mL reactor, uneven dyeing occurred. The levelness value was estimated using a levelness measurement method [101] rating from 1 (poor) to 5 (excellent). The results of levelness are shown in Table 17.

Table 15. Central composite design data for azoic dyeing in SC-CO₂.

Dyeing #	Temperature (°C) A	Pressure (psi) B	Water (mL) C	Time (min) D	Color strength Y
1	30	1500	2.0	60.0	4.48
2	30	3000	2.0	20.0	9.00
3	70	1500	7.0	60.0	6.33
4	50	2250	4.5	40.0	11.81
5	50	2250	4.5	40.0	11.03
6	70	3000	2.0	60.0	3.14
7	70	3000	7.0	20.0	9.27
8	30	1500	7.0	20.0	9.09
9	30	3000	7.0	60.0	9.30
10	70	1500	2.0	20.0	3.07
11	70	1500	7.0	20.0	8.22
12	70	1500	2.0	60.0	2.04
13	70	3000	2.0	20.0	3.00
14	70	3000	7.0	60.0	8.53
15	30	3000	2.0	60.0	4.90
16	50	2250	4.5	40.0	11.39
17	30	1500	2.0	20.0	4.00
18	50	2250	4.5	40.0	10.16
19	30	3000	7.0	20.0	7.69
20	30	1500	7.0	60.0	3.01
21	50	2250	4.5	40.0	9.40
22	50	2250	4.5	20.0	9.40
23	50	1500	4.5	40.0	8.24
24	70	2250	4.5	40.0	7.55
25	50	2250	7.0	40.0	7.89
26	50	2250	4.5	60.0	6.98
27	50	2250	4.5	40.0	11.31
28	30	2250	4.5	40.0	8.50
29	50	2250	2.0	40.0	4.50
30	50	3000	4.5	40.0	8.29

Table 16. ANOVA data for the quadratic model ($R^2 = 0.9160$) after exclusion of insignificant terms.

Model terms	Estimated coefficient	Standard error	P-value
Model	-	-	< 0.0001
Intercept	9.95	0.50	-
B	0.81	0.36	0.0331
C	1.73	0.36	< 0.0001
D	-0.78	0.36	0.0403
C^2	-4.28	0.78	< 0.0001

The lack-of-fit statistic was used to test the adequacy of the model obtained; the p-value after the exclusion of the statistically insignificant terms was 0.232. The lack of fit value did not exceed the threshold value of 0.05. Therefore, the model generated is valid. The quadratic model used to predict color strength in terms of actual values at different factor levels within the scope of the experiment is shown in Equation 4. This model was used for prediction of the color strength.

$$\text{Color strength} = -7.90 + 1.09 \times 10^{-3}B + 6.85C - 0.04D - 0.68C^2 \quad (\text{Equation 4})$$

The interactive effects of the selected azoic dyeing parameters on color strength of the dyed cotton fabric are illustrated graphically in Figures 37-42. As pressure increases from 1500-3000 psi (103-207 bar) the color strength values also increase. For this experimental design, the optimum temperatures used for SC-CO₂ dyeing were in the range 35-55°C, highlighting the unusually high

temperature needed (and also a wide range of temperatures possible) for diazotization and coupling in the system. To achieve uniform dyeing, the amount of H_2O used should not be less than 4.0 mL. The minimum amount of H_2O required for SC-CO_2 dyeing will likely be a function of substrate mass, reactor dimensions and target depth of shade. If the amount of H_2O used is insufficient to facilitate the intimate substrate contact, dyeings will be unlevel. It is clear that SC-CO_2 azoic dyeing on pre-naphtholated cotton fabrics can be accomplished in a reasonable time (40-60 min). However, it was surprising that K/S dropped significantly for dyeing times less than 40 min, whereas conventional azoic dyeing is commonly achieved in a short time period (typically 15-20 min for exhaust dyeing [17]). This indicates that the diffusion kinetics are slower in the SC-CO_2 system than conventional aqueous azoic dyeing, and/or the reaction rate of coupling is lower for SC-CO_2 for the reaction studied.

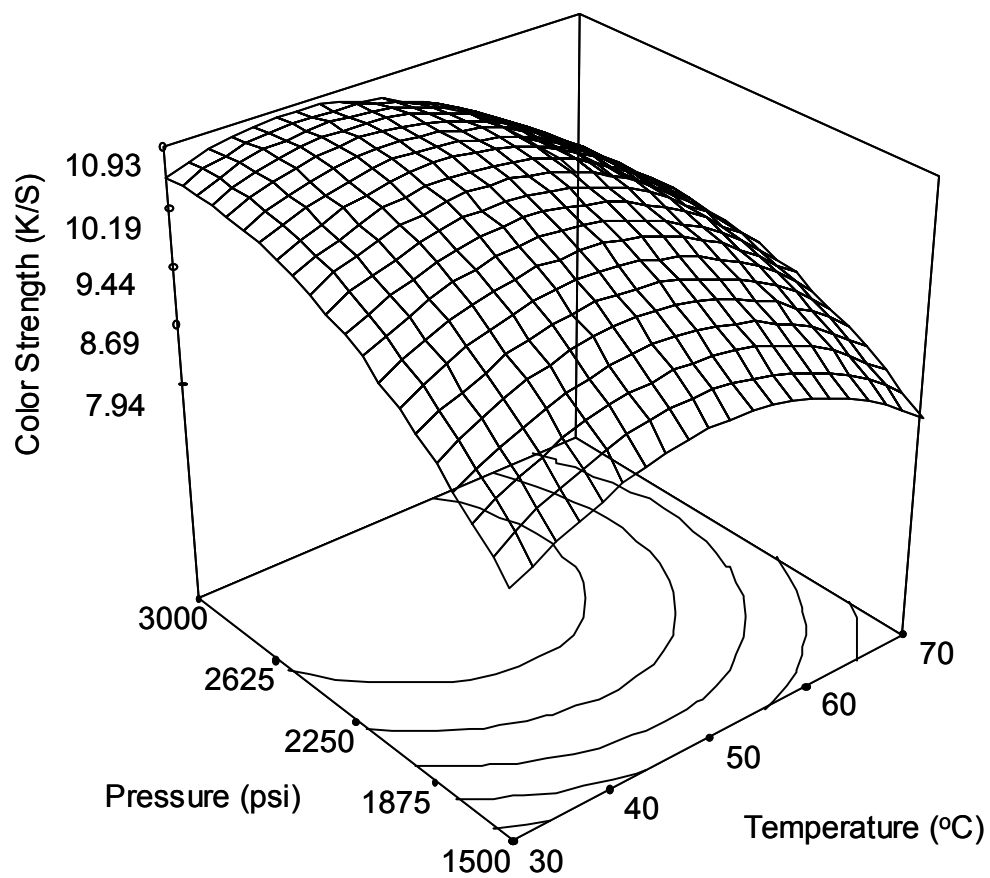


Figure 37. The effect of pressure and temperature on color strength (K/S).

(H₂O = 4.50 mL, t = 40 min)

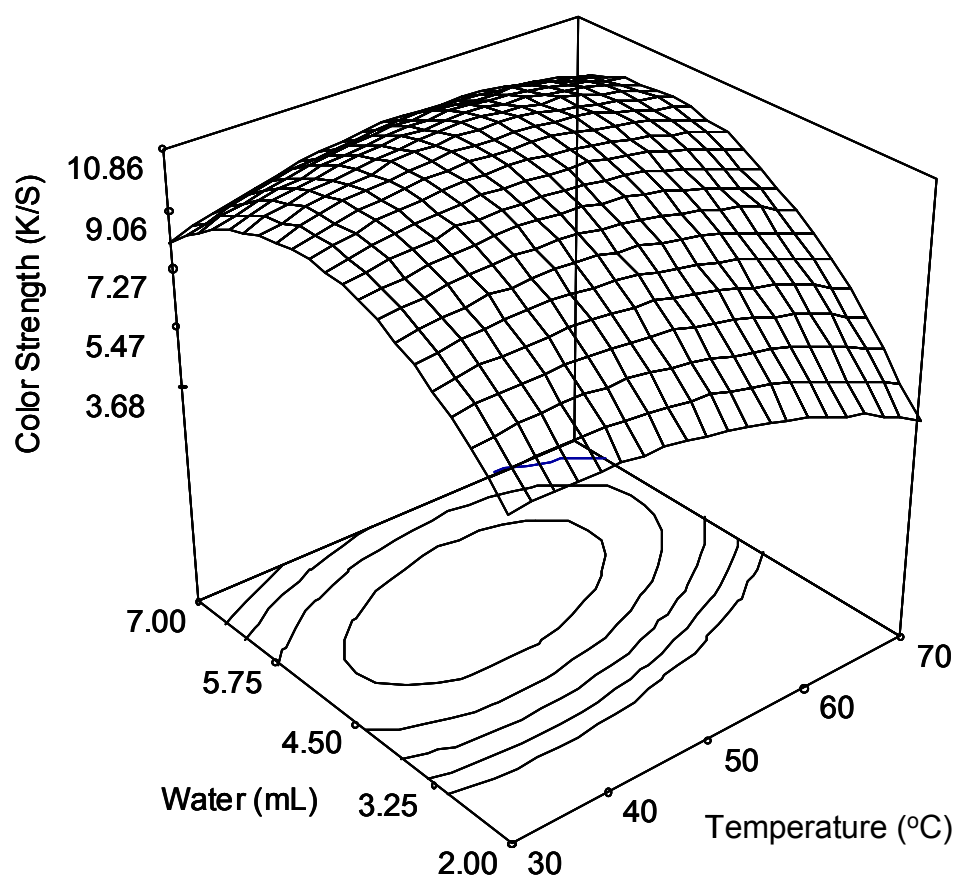


Figure 38. The effect of temperature and water on color strength (K/S).

(H₂O = 4.50 mL, t = 40 min)

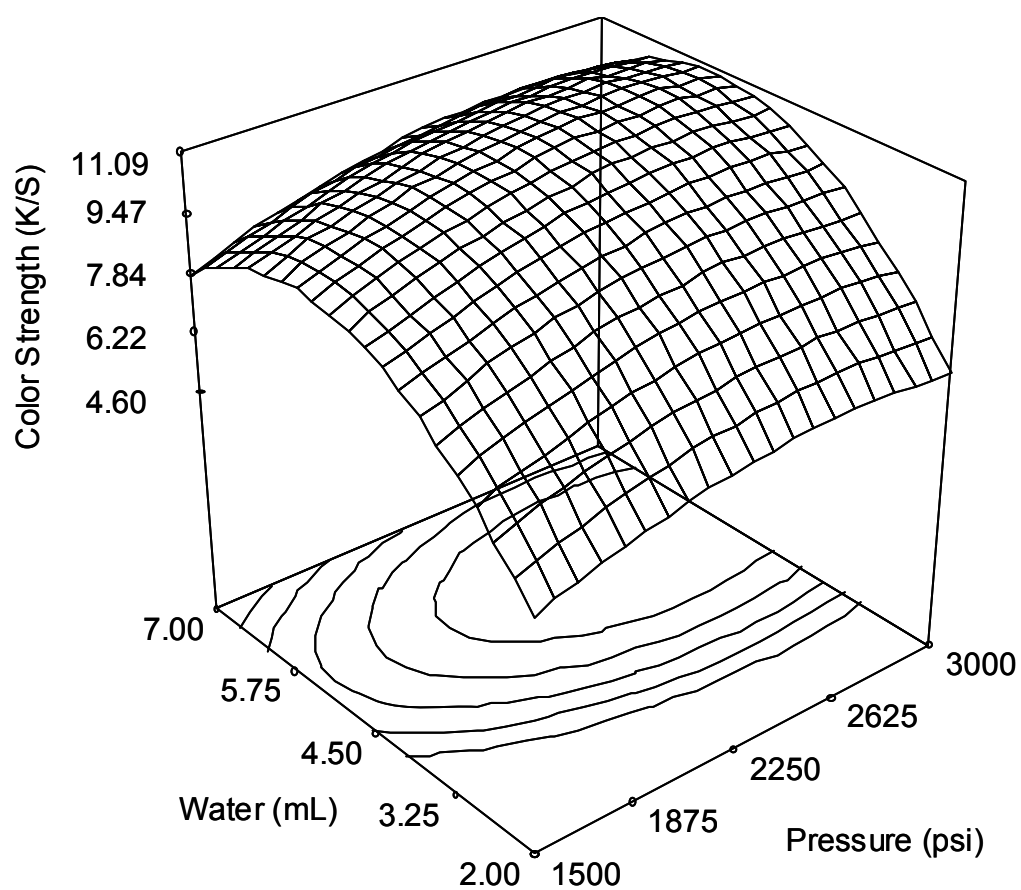


Figure 39. The effect of water and pressure on color strength (K/S).

(pressure = 2250 psi (115 bar), $t = 40$ min)

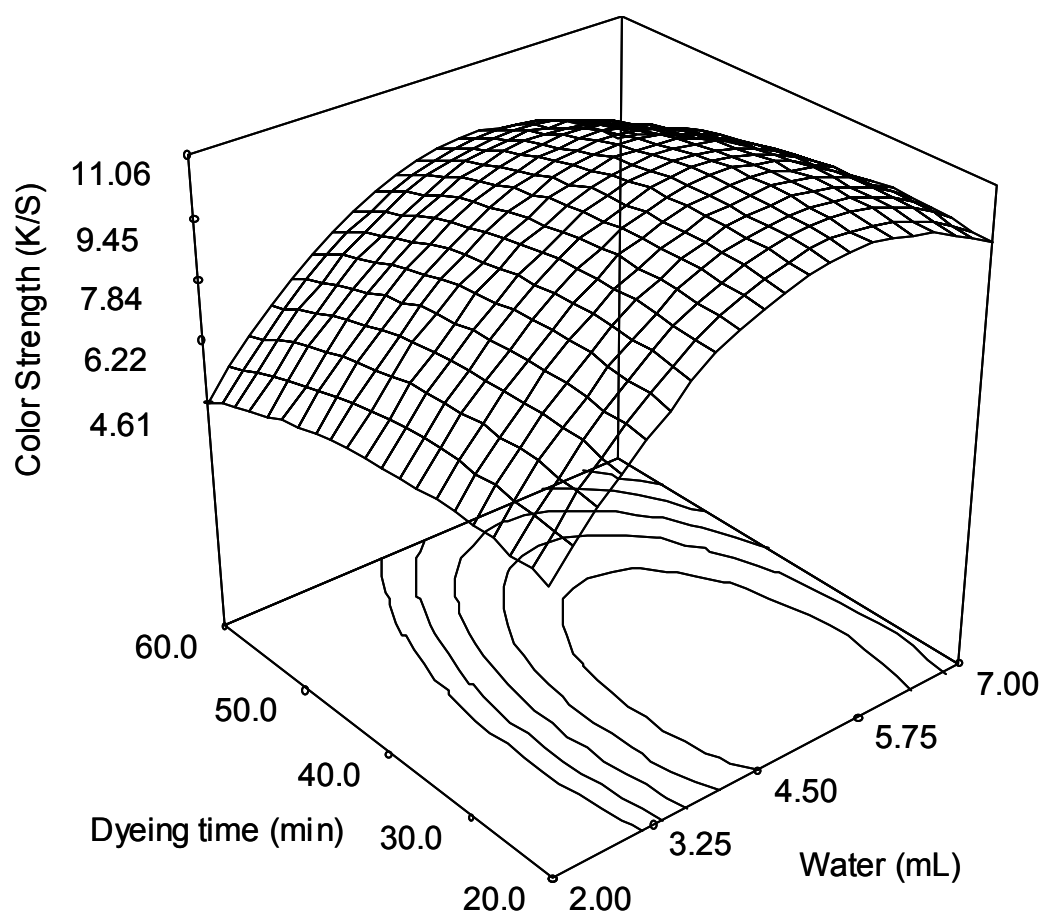


Figure 40. The effect of dyeing time and water on color strength (K/S).

(P = 2250 psi (115 bar), H₂O = 4.50 mL)

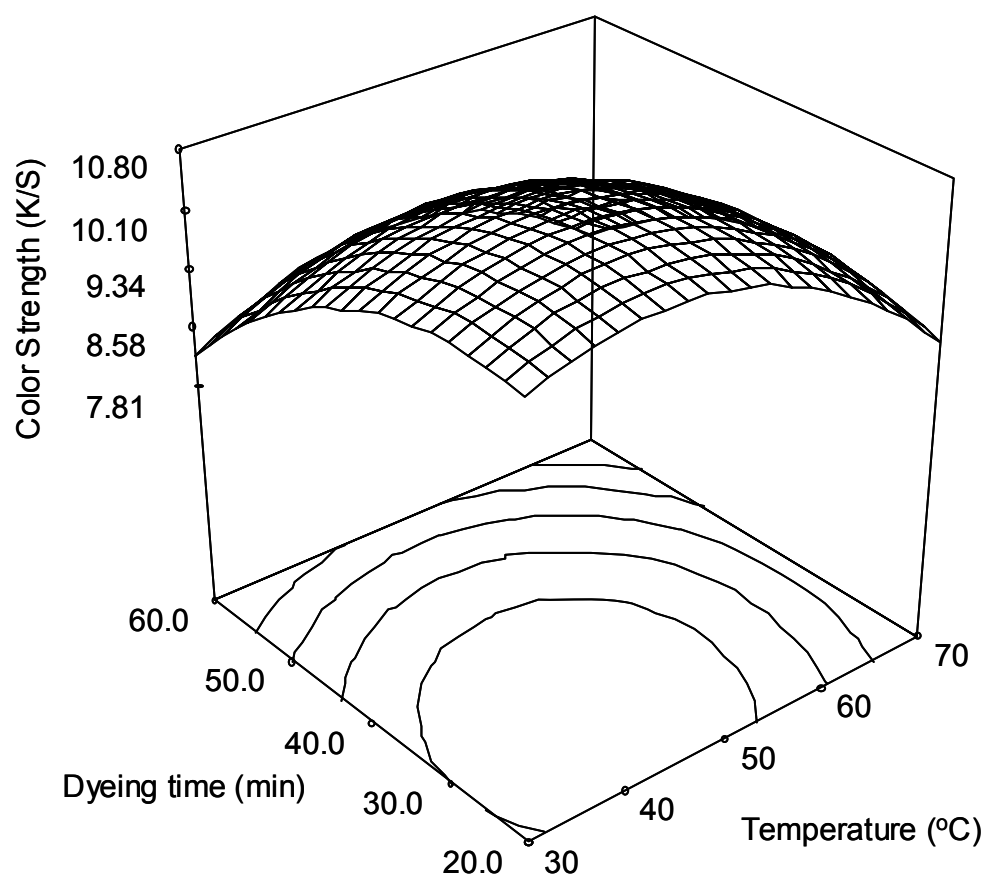


Figure 41. The effect dyeing time and temperature on color strength (K/S).

(P = 2250 psi, (155 bar), H₂O = 4.50 mL)

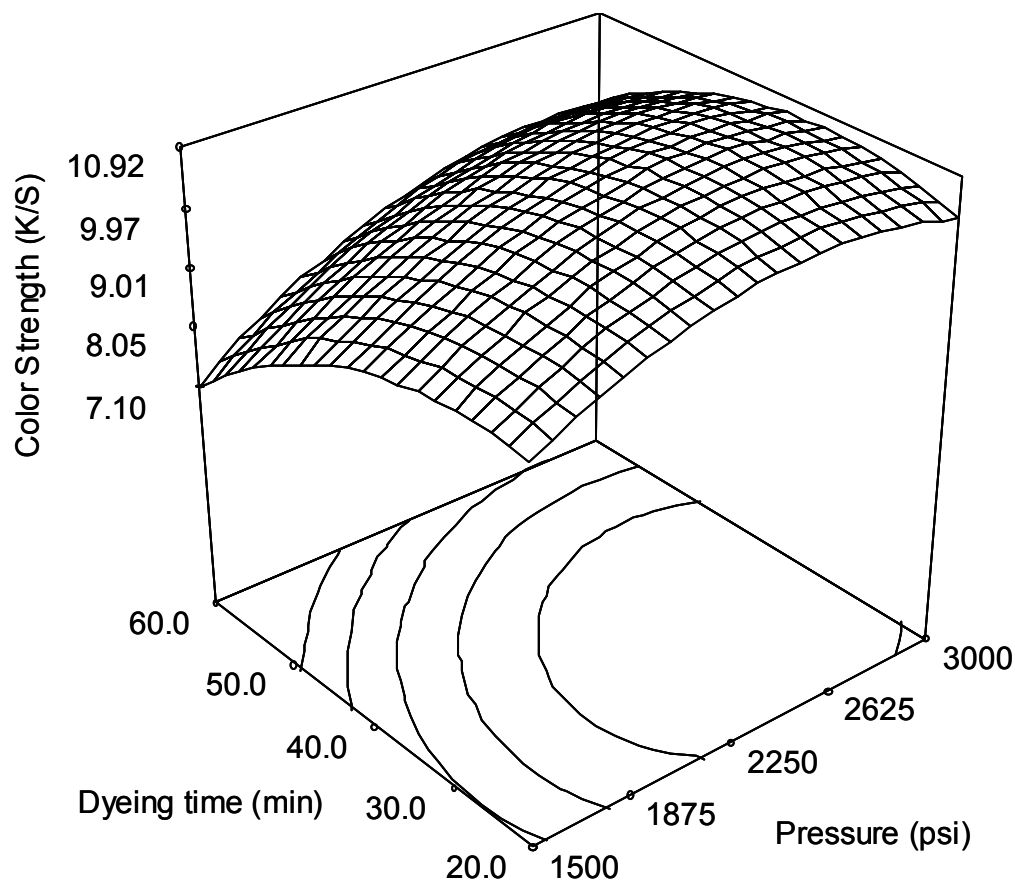


Figure 42. The effect dyeing time and pressure on color strength (K/S).

($T = 50^{\circ}\text{C}$, $t = 40 \text{ min}$)

4.4.2 Fastness Properties

Table 17 summarizes the fastness properties of the SC CO_2 dyed fabrics. In general, acceptable fastness, apart from light fastness, was obtained, providing sufficient H_2O was charged to the reactor. Also, in general the dyed fabrics exhibited good dry crock fastness, indicating the dyeings were not on the fiber surface, although wet crock fastness was moderate. For the fabric size used

and the final dyeing concentration, at least 4 mL of H₂O was necessary to obtain a uniform dyeing.

Table 17. Fastness properties of azoic dyeing cotton fabric in SC-CO₂.

Dyeing #	K/S	Crock Fastness		Levelness	Light Fastness	Wash fastness		
		Dry	Wet			Color change	Stain on cotton	Stain on wool
1	4.48	4.5	3.5	2.6	2	1.5	3.5	3
2	9.00	4.5	3	3.8	2.5	3	4	3
3	6.33	4.5	2.5	4.7	2	3.5	3	3
4	11.81	4.5	2.5	4.3	2.5	3.5	3.5	3
5	11.03	4	3.5	4.3	2.5	3	3.5	3
6	3.14	4	2.5	3.8	2	3.5	3.5	3
7	9.27	4	2.5	4.6	1.5	3.5	4	3
8	9.09	4.5	3.5	4.4	2	3.5	3	3
9	9.30	4.5	3	4.4	1.5	3.5	4	3
10	3.07	4	3.5	3.9	2.5	3.5	3.5	3
11	8.22	4	3	4.7	2	3.5	4	3
12	2.00	3.5	2.5	3.3	2	2.5	4	3
13	3.00	4	3	2.9	1.5	3.5	3.5	3
14	8.53	4	2.5	4.5	3	3.5	4.5	3
15	4.90	4.5	3	2.9	3	2	3.5	3
16	11.39	4	3.5	4.3	2	3	3	3
17	4.00	4.5	3	3.9	2.5	2.5	3	3
18	10.16	4	3	4.2	2	3	4	3
19	7.69	4.5	3.5	4.7	1.5	2.5	3.5	3
20	3.01	4	3	4.3	2	2	4	3
21	9.40	4	3	4.1	1.5	2.5	4	3
22	9.40	4.5	3.5	4.6	2.5	3	4	3
23	8.24	4.5	3.5	4.5	2	3	4	3
24	7.55	4	3	4.7	2.5	2.5	4	3
25	7.89	4	3	4.2	2.5	3	4	3

Table 17. (Continued)

Dyeing #	K/S	Crock Fastness		Levelness	Light Fastness	Wash fastness		
		Dry	Wet			Color change	Stain on cotton	Stain on wool
26	6.98	4.5	3.5	4.4	2.5	3	4	3
27	11.31	4	3	4.3	2.5	3	4	3
28	8.50	4	3	4.3	2.5	3	4	3
29	4.50	4	3	3.8	2	2.5	3	3
30	8.29	4	3	4.4	2.5	3	4	3

It is likely that, in addition to the diazotization reaction requiring H₂O to generate carbonic acid, sufficient H₂O is needed to enable penetration of reactants into the hydrophilic cotton fibers, via substantial breaking and reforming of intermolecular H bonding. It has been established that CO₂ dyeing of cotton is not feasible using SC-CO₂ alone [66]. Light fastness properties were poor while wash fastness values were acceptable. The low light fastness was not surprising considering the azo chromophore produced. However, the wash and dry fastness properties of dyed fabrics by SC-CO₂ are comparable to cotton fabric dyed using a conventional mineral acid/aqueous-based azoic method, as shown in Table 18.

Table 18. Fastness of cotton fabric via conventional azoic dyeing.

Color Strength (K/S)	Crock fastness		Levelness	Light fastness	Wash fastness		
	Dry	Wet			Color Change	Staining on cotton	Staining on wool
11.50	4.5	4	4.9	3.5	3.5	3.5	3.5

4.4.3 Predicted Optimization

A method for maximizing color strength for the diazotization and coupling step in SC-CO₂ was predicted using the experimental design data. The predicted optimization recipe is shown in Table 19, along with similar predicted color strengths for several formulae. To yield high color strength, significant flexibility exists in the operating conditions for this azoic dyeing, unlike many conventional diazotization reactions. Temperatures and pressures in the range 40-55°C and 2500-3000 psi (172-207 bar), respectively, are predicted to produce high K/S. The optimum amount of H₂O and dyeing time are between 5-6 mL and 25-40 min, respectively.

Table 19. Predicted optimization of azoic dyeing in SC-CO₂.

Color strength	Temperature (°C)	Pressure (psi)	Water (mL)	Time (min)
11.1	49.0	2590	5.7	25
11.2	49.0	2485	5.6	28
11.2	49.0	2735	5.6	30
11.1	47.0	2675	5.67	23
11.2	42.0	2825	5.23	29
11.1	38.0	2750	4.53	32
11.1	47.0	3000	4.94	39

4.4.4 Colorimetric Data

The colorimetric data for the dyed fabrics for both conventional and optimized SC-CO₂ azoic dyeing methods are shown in Table 20. The optimized

SC-CO₂ azoic dyeing method produced color strength and L* a* b* values comparable to the conventional azoic dyeing method. In addition, the predicted optimized K/S value (Table 20) is in agreement with the experimental K/S value. Figure 43 shows K/S absorption spectra in the visible region for the optimized SC CO₂ method and the azoic dyeing via the conventional aqueous method.

Table 20. L* a* b* and K/S values of dyed naphtholated cotton fabrics.

Fiber Types	L*	a*	b*	K/S
Conventional dyeing	43.73	49.03	32.52	11.50
SC-CO ₂ dyeing ⁺	44.17	50.61	35.53	11.39

⁺ T = 50°C, P = 2250 psi (155 bar), H₂O = 4.5 mL, time = 40 min

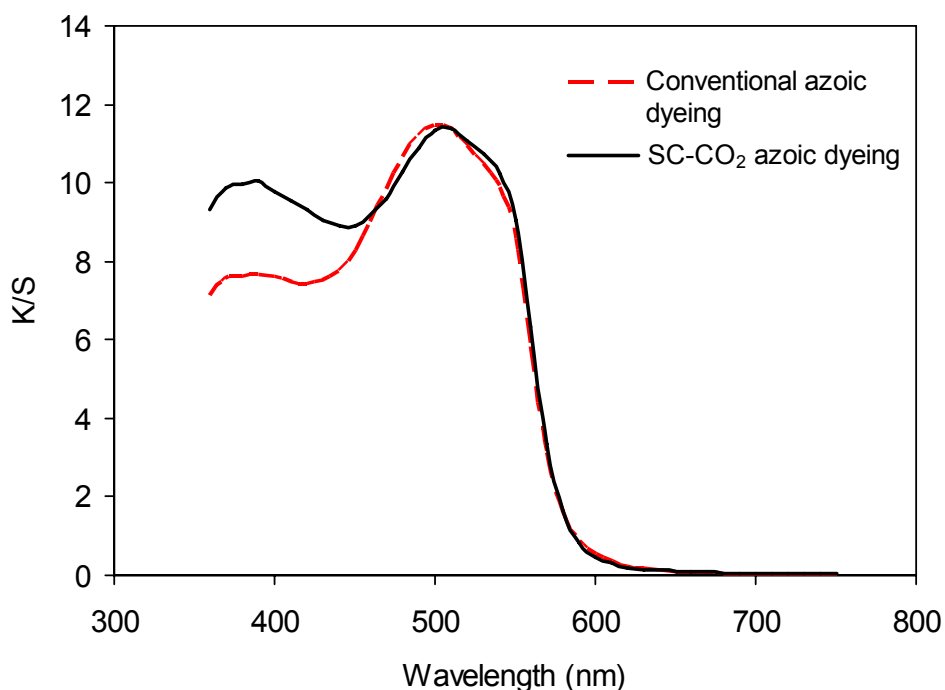


Figure 43. Graph of K/S as a function of λ for the optimized dyeing in SC-CO₂ and the conventional azoic dyeing method.

4.4.5 Cross-sectional Analysis

Fiber cross-sections of SC CO₂ azoic dyed cotton fabric were prepared showing that dye distribution through the fiber in the weft yarns is more homogeneous (Figure 44) than in warp yarns (Figure 45). Inhomogeneous penetration in the warp direction possibly results from higher tension in warp yarns during weaving, or possibly incomplete desizing during scouring.

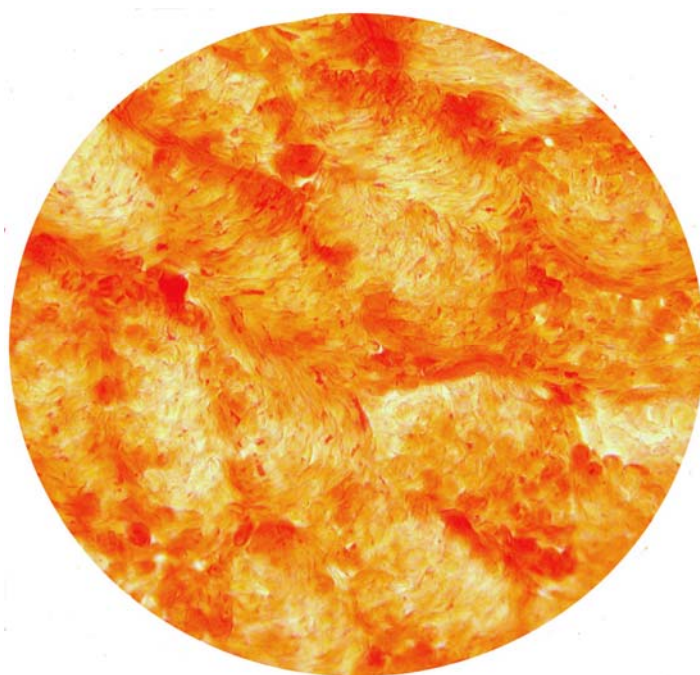


Figure 44. Photomicrograph of azoic dyeing of cotton in the weft direction.



Figure 45. Photomicrograph of azoic dyeing of cotton in the warp direction.

4.4.6 Possible Fibers that can Be Dyed via SC-CO₂ Azoic Dyeing

The majority of azoic dyeing is used for dyeing cotton. However, one of the longer-term goals of this research is the ability to conduct reactions in SC CO₂ within the polymer chains of a wide range of fibers and materials. Hence, to test the possible scope of successful diazotization and coupling in SC CO₂ using different substrates, the optimized azoic dyeing method described above was applied to a standard multifiber test fabric comprising 13 different fibers types pretreated with naphthol AS coupler.

Table 21 shows colorimetric data for the dyed multifiber fabrics via SC-CO₂ azoic dyeing methods at optimized condition (T = 50°C, P = 2250 psi (155 bar), H₂O = 4.5 mL, time = 40 min). Different fabric types gave different depths of shade, as shown in Figure 46. In addition to cotton, both hydrophilic and hydrophobic fibers, including acetate, polyamide, silk, viscose and wool fabrics were successfully dyed with a high depth of shade (K/S > 9), while other fibers, e.g., polyester 54 (disperse dyeable), polyester 64 (cationic dyeable), acrylic (modacrylic; 36-85% of acrylonitrile monomer), Creslan 61 (90% of acrylonitrile monomer) and polypropylene were stained a relatively light orange hue (K/S < 5). The degree of color strength of the fabrics from highest to lowest was viscose > cotton > wool > silk > acetate > Arnel (triacetate) > polyamide > polyester 54 (disperse dyeable) > creslan 61 > polyester 64 (cationic dyeable) > modacrylic > polyacrylic > polypropylene.

Table 21. Colorimetric data of dyed multifiber fabrics in SC-CO₂.

Fiber Types	L*	A*	b*	K/S
Filament acetate (Dull)	49.93	53.69	45.27	11.91
Modacrylic	57.38	44.25	33.46	4.31
Bright filament (Arnel)	53.81	51.69	44.73	10.41
Bleached cotton	43.67	51.13	41.11	16.26
Creslan 61	57.02	45.41	35.54	4.75
Polyester 54	55.58	46.48	35.44	5.06
Polyester 64	56.77	45.11	34.86	4.5

Table 21. (Continued)

Fiber Types	L*	A*	b*	K/S
Polyamide	49.18	51.33	39.8	9.66
Polyacrylic	57.55	43.44	31.93	3.83
Silk	40.28	46.04	33.07	14.54
Polypropylene	58.77	37.26	28.5	3.17
Viscose	42.84	50.91	41.71	18.02
Wool	40.66	49.25	35.55	15.85

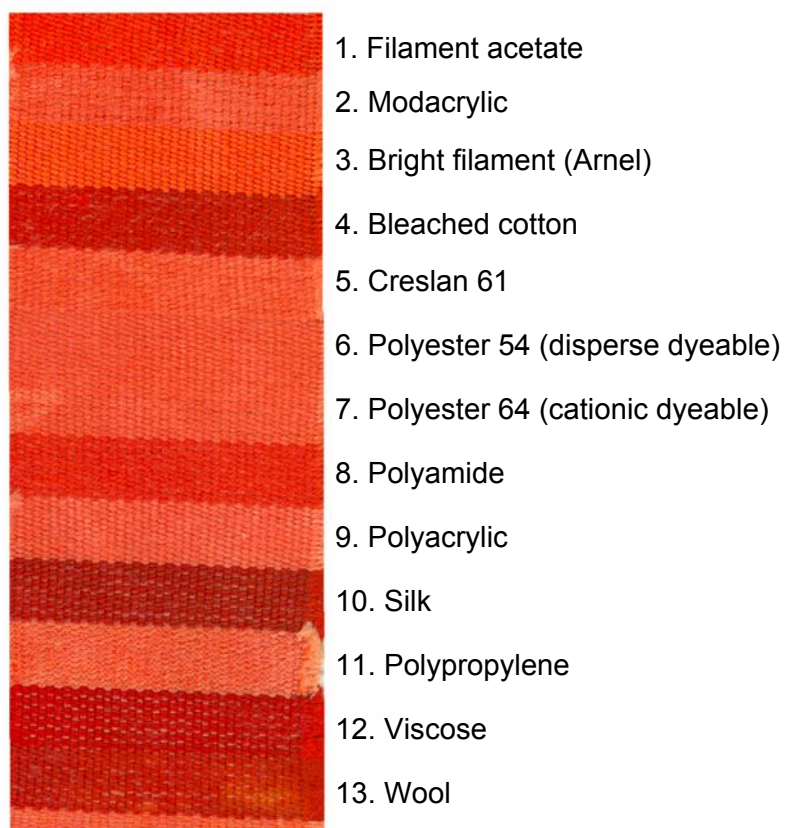


Figure 46. Photograph of dyed multifiber fabric dyed using the optimized SC-CO₂ azoic dyeing method.

4.5 Conclusions

The concept of synthesizing an azo dye inside cotton fibers using SC-CO₂ and water as the solvent and proton source for the diazotization reaction has been successfully demonstrated. Using sodium nitrite, the diazo component (aniline) was diazotized in the presence of pressurized CO₂, NaNO₂ and H₂O. The relatively small molecules of diazo components combined with electrostatic and other attraction forces makes feasible diffusion into cellulosic fibers and subsequent coupling with the coupling component, Naphthol AS, to form an insoluble azoic dye. The presence of H₂O is critical not only for facilitating diazotization, but also to enable diffusion into hydrophilic substrates, and promotes level dyeing.

Acceptable crock fastness indicates that reasonable penetration was achieved as also evidenced by cross-sectional analysis, particularly in the weft direction. It was found that H₂O, pressure and dyeing time have a significant effect on the depth of shade, levelness and fastness properties of the resultant dyed fabrics. Under optimum conditions, the dyed fabrics exhibited uniform dyeing with high color strength and favorable fastness properties, equivalent to those from conventional aqueous azoic dyeing.

While the concept of chromophore formation using an aqueous SC-CO₂ system has been demonstrated, it is clear that future work is required to apply the coupling component via SC CO₂ instead of conventional aqueous alkali pretreatment. However, it is also clear that the reaction can be applied to a number of hydrophilic and hydrophobic natural and synthetic polymer systems in

addition to cotton, in particular cellulose acetate, polyamide fibers, wool, regenerated cellulosic fibers, and silk. Also, the fact that diazotization and coupling within a polymer matrix is possible leaves open the potential to use SC-CO₂ as a medium to perform various novel reactions within polymer matrices or even diazotizing suitable pendant reactive aromatic amines present on novel polymer chains themselves.

5. Fiber-Reactive Dyeing of Nylon 6,6 and Wool in Supercritical Carbon Dioxide

5.1 Introduction

Supercritical fluid carbon dioxide as a medium for dyeing fibers has been studied extensively over the last two decades. An excellent recent review by Schollmeyer *et al.* summarizes the prior art for SFD [66]. Polyester fibers have been found to be very suitable for SFD technology due to the compatibility of hydrophobic dyes, hydrophobic solvent and the hydrophobic nature of the fiber. While hydrophobic fibers can be dyed successfully in SC-CO₂ with high color strength using commercial disperse dyes, hydrophilic fibers such as cotton, viscose, wool, and silk appear to produce unsatisfactory dyeings in pure SC-CO₂, presumably due to the failure of the solvent to penetrate and break the myriad intermolecular H-bonding present throughout the polymer matrix of these materials. Many attempts have been made to overcome the limitation of the SC-CO₂ dyeing of natural fibers, primarily due to the importance of cotton in the global market with an approximate market share of 37% [66]. Interestingly, incorporation of relatively small amounts of co-solvents, such as incorporation of water by wetting out the fiber prior to SC-CO₂ treatment, have shown significant promise in producing level dyeings for a wide range of natural and synthetic fibers [62]. The use of novel surfactants to produce micelles in SC-CO₂ also looks to be an interesting approach to dyeing hydrophilic fibers [81,102,103].

However, the study of dyeing in this medium using fiber-reactive dyes has received relatively little attention, and a paucity of convincing data exist confirming dye-fiber covalent bond formation following fiber-reactive dyeings in SC-CO₂. The following data were generated to provide evidence of the scope of fiber reactive dyeing of two major fibers that have some significant hydrophobicity, nylon 6,6 and wool, and can therefore accept a disperse reactive dye. Also, focus was placed on providing significant evidence of dye-fiber covalent bond formation.

Evidence of dye-fiber bond formation between a vinylsulfonyl group and primary amines present on the fibers was obtained using two dyes, one reactive and the other a nonreactive analog in which ethylsulfone was used *in lieu* of the vinylsulfonyl group. Also, reactions were undertaken using the disperse-reactive dye and butylamine in SC-CO₂; the amine was employed as a model reactive group that is present on both polyamide and wool fibers.

5.2 Experimental

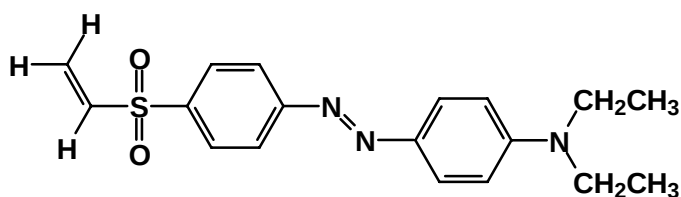
5.2.1 Materials

Wool and nylon fabric were purchased from Testfabrics, Inc. (West Pittston, PA, USA). All chemicals were reagent grade purchased from Aldrich Chemical (Milwaukee, WI, USA). Two azo dyes previously synthesized via conventional diazotization and coupling, [104,105] were purified and characterized, and these were used for all dyeings: a vinyl sulfonyl-based dye

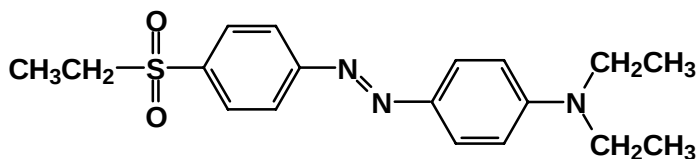
(VS) (**76**) and ethyl sulfonyl-based dye (ES) (**86**). Following purification, the pure dyes were characterized.

The VS dye was obtained as a bright yellow powder, mp 143-144°C. ^1H -NMR (CDCl_3): 1.25 (t, $J = 7.2$ Hz, 6H), 3.48 (q, $J = 7.2$ Hz, 4H), 6.04 (d, $J = 10$ Hz, 1 H), 6.47 (d, $J = 16.8$ Hz, 1H), 6.83 (t, $J = 10$ Hz, 1H), 6.75 (d, $J = 8.8$ Hz, 4H), 7.87-7.90 (m, $J = 8.8$ Hz, 4H). TLC: $R_f = 0.68$ (toluene: EtOAc/4:1).

The ES dye obtained as a bright yellow powder, mp 124-125°C, ^1H -NMR (CDCl_3): 1.23-1.31 (m, 9H), 3.15 (q, $J = 7.2$, 2 H), 3.48 (Q, $J = 7.2$, 4H), 6.74 (d, $J = 7.26$, 2 H), 7.88-7.99 (m, 6H) (Figure 15). TLC: $R_f = 0.70$ (toluene: EtOAc/4:1).



(**76**)



(**86**)

5.2.2 Dyeing

All dyeings were carried out in a jacketed high-pressure reactor from Autoclave Engineers (Erie, PA, USA) equipped with a high speed stirrer, cooling/heating coil and a high-pressure pump as shown in section 2.2.2, except

the reactor volume was 1000 mL instead of 300 mL. The fabric (5.0 g) was loosely fixed to the cooling coils surrounding the mechanical stirrer inside the reaction vessel and 1% owf of the dye was loaded in the bottom of the reactor. The reactor was then sealed and pressurized to 860 psi (60 bar). The reaction mixture was stirred at 800 rpm. The system was heated to the working temperature and then CO₂ was isothermally compressed to the required working pressure under constant stirring speed. The pressure and temperature were maintained for the required dyeing period of 2 h after which CO₂ was released slowly.

After depressurization, the dry sample was removed and washed with acetone to remove surface dye. A portion of each sample was then placed in a cotton thimble and placed in a soxhlet extractor for a period of 6 hr until no further color was removed by ethyl acetat. The % dye remaining on the fabric was spectroscopically determined by measuring K/S (at λ_{max}) before and after extraction.

5.2.3 Colorimetric Assessment

The dyed fabric was measured via reflectance spectrophotometry, as described in section 4.3.4.

5.3 Results and Discussion

5.3.1 Effect of Temperature on Dye Uptake and Fixation using the VS

Reactive Dye

Color strength values for nylon 6,6 and wool fibers dyed with the VS reactive dye at varying temperatures are shown in Figures 47 and 48. The pressure was maintained at 3500 psi (241 bar) with 1% owf dye for 2h. In the case of nylon 6,6, the color strength of the dyed fabric increased with increasing dyeing temperature up to 140°C, at which condition a maximum K/S value was reached. Higher temperatures reduced the K/S value slightly. In the case of wool fiber, as the temperature increased color strength also increased. However, for both substrates, temperatures higher than 140°C produced a dulling effect of the dyed fabrics, possibly due to decomposition of the dye.

Fixation of the VS dye was near complete (96% for nylon and 94% for wool) at 140°C. These reactions are ideal from the stand-point of competing hydrolysis reactions, since very little H₂O, if any, is present in the system, thereby eliminating the potential for significant hydrolysis. The only H₂O present would be due to moisture already contained within the fiber structure. The water content for wool is relatively high, but low for nylon 6,6, which may be the reason for a slight difference in fixation for these two fibers under identical processing conditions.

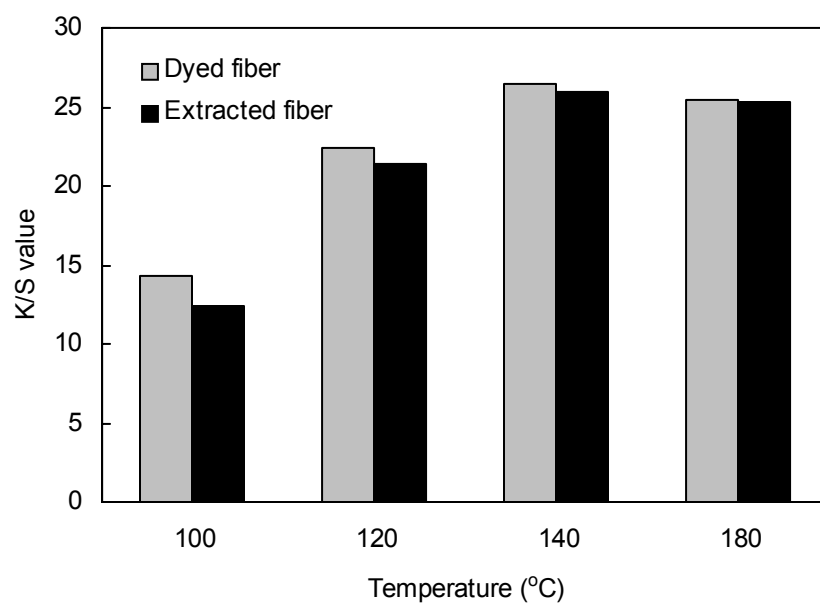


Figure 47. Effect of temperature on dye uptake and fixation with VS reactive dye on nylon 6,6 fabric.

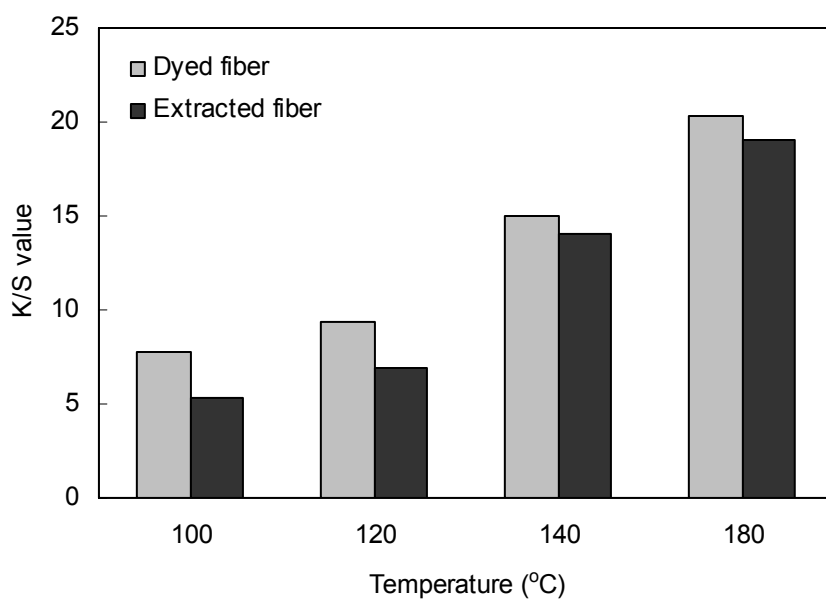


Figure 48. Effect of temperature on dye uptake and fixation with VS reactive dye on wool fabric.

5.3.2 Effect of Temperature on Dye Uptake and Fixation using the ES

Nonreactive Dye

Unlike the VS dye, as dyeing temperature increased, the color strength of the ES dyed fabric decreased slightly from 120°C to 140°C, although a maximum K/S value was achieved at 180°C for both nylon and wool, as shown in Figures 49 and 50. However, after extraction with ethyl acetate, the color strength of the fibers were much lower when compared to those of VS dye fibers, demonstrating the positive effect of the reactive group on fixation. However, interestingly, despite repeated extraction, a significant level of ES dye remained on the nylon 6,6 fiber, while almost all the ES dye was extracted from wool.

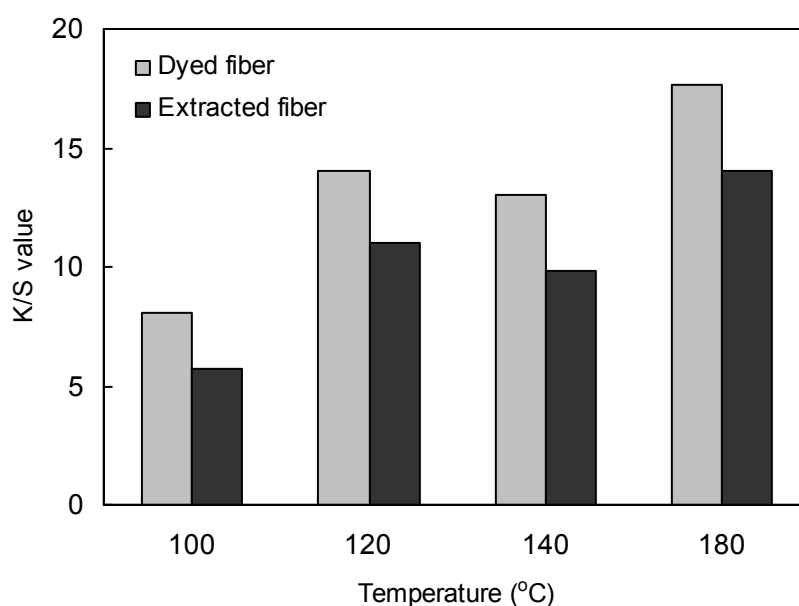


Figure 49. Effect of temperature on dye uptake and fixation for the ES non-reactive dye on nylon 6,6.

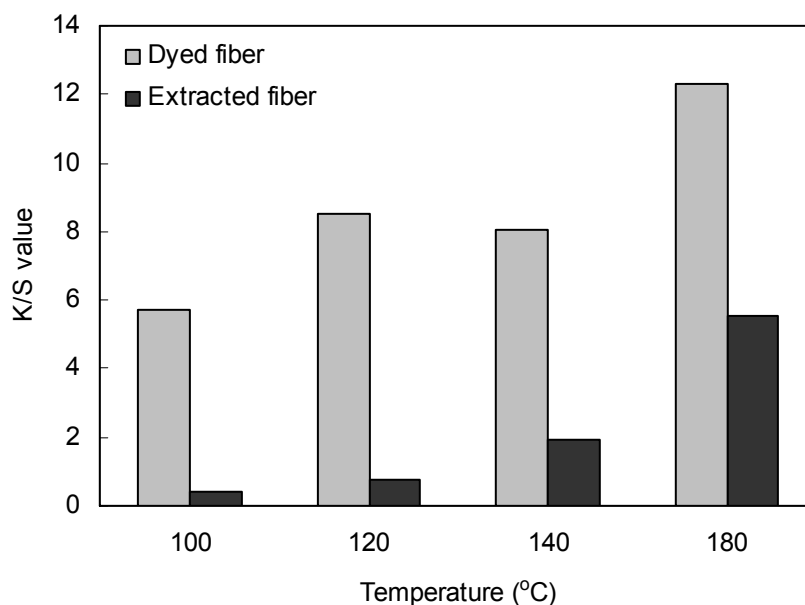


Figure 50. Effect of temperature on dye uptake and fixation for the ES non-reactive dye on wool.

5.3.3 Effect of Pressure on Dye Uptake and Fixation using the VS Reactive Dye

Color strength values for nylon 6,6 and wool fiber dyed with the VS dye at varying operating dyeing pressure are shown in Figures 51-54. Increasing pressure (thereby increased CO₂ density) increased the K/S values for nylon 6,6, while a maximum K/S value was observed at 3000 psi (207 bar) and both 125°C and 140°C for wool.

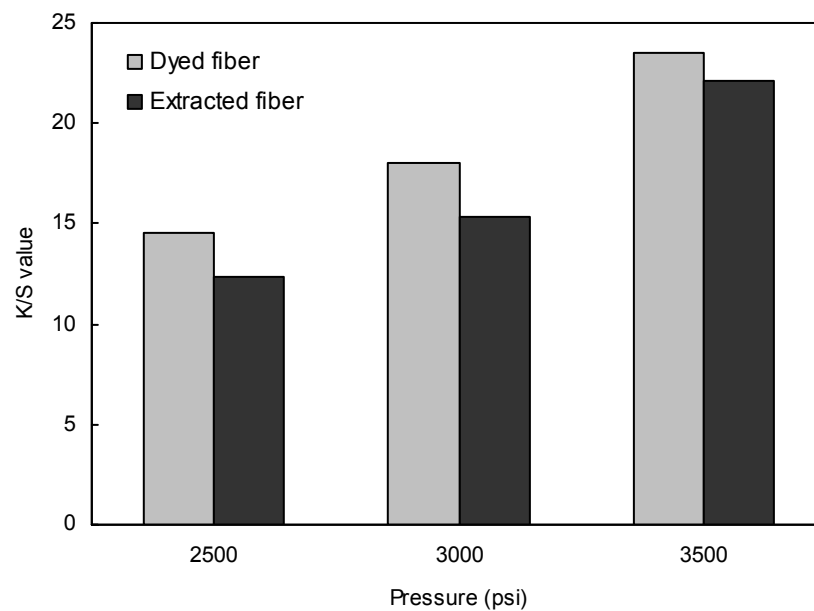


Figure 51. Effect of pressure on dye uptake and fixation for the VS reactive dye on nylon 6,6 fabric at 125°C.

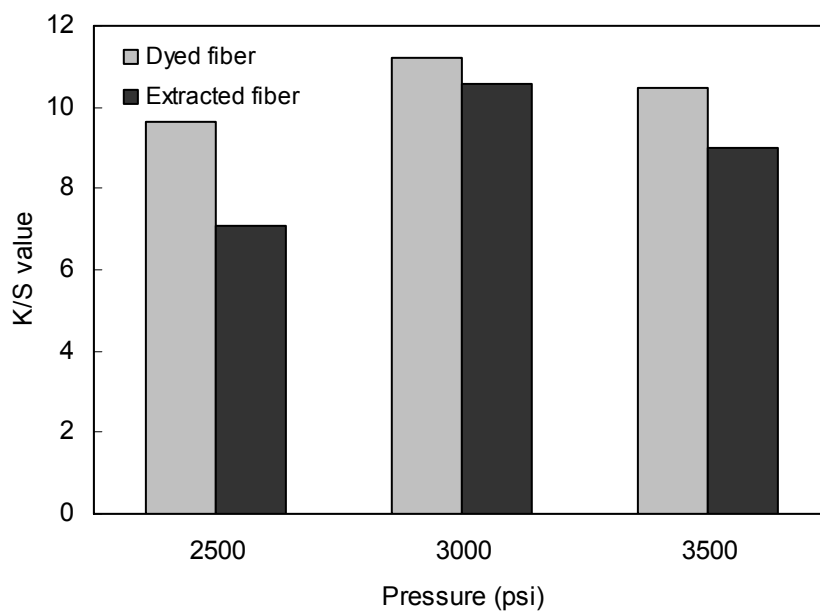


Figure 52. Effect of pressure on dye uptake and fixation for the VS reactive dye on wool fabric at 125°C.

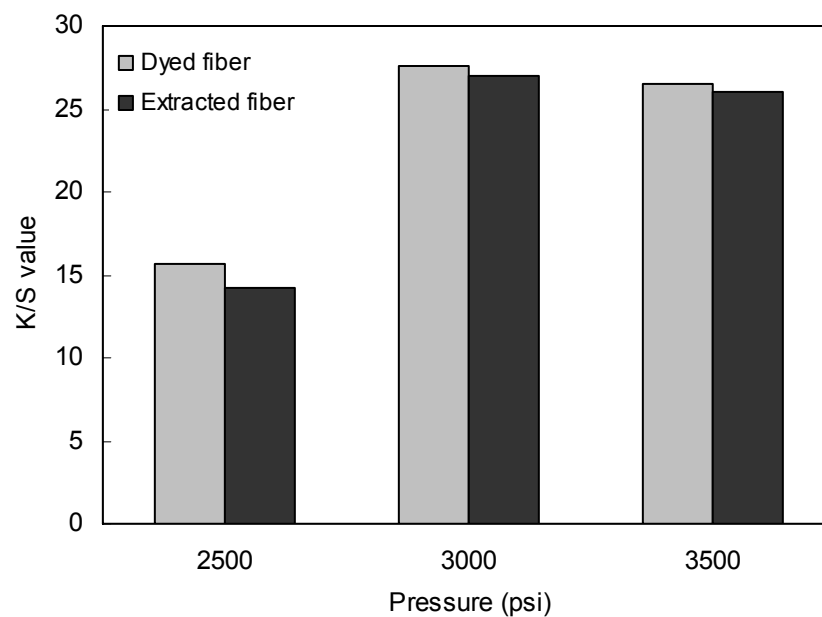


Figure 53. Effect of pressure on dye uptake and fixation for the VS reactive Dye on nylon fabric at 140°C.

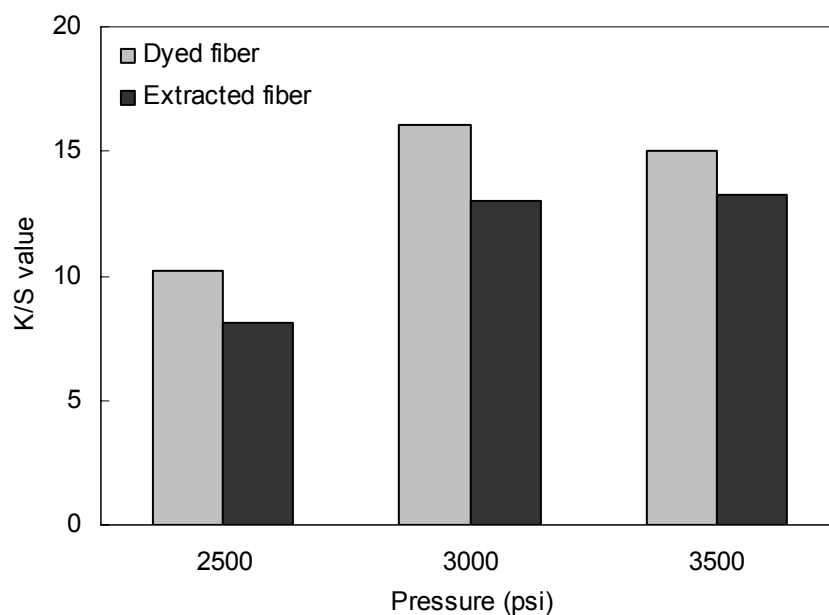


Figure 54. Effect of pressure on dye uptake and fixation for the VS reactive dye on wool fiber at 140°C.

5.4 Dye-fiber Covalent Bond Formation

While obtaining direct quantifiable data that confirms covalent bond formation between a dye and fiber can be very difficult. Results presented in Figures 47-54 are consistent with covalent bonding between the VS dye and both wool and nylon 6,6. In order to gain indisputable evidence that such a bond is possible between a vinylsulfonyl-based dye and aliphatic amino groups present in both fibers, butylamine was used as a reactant model nucleophile. Hence, SC-CO₂ conditions were established similar to the dyeing conditions described above, except only the VS dye and butylamine were added in a 1:1 mol ratio. The reaction was also duplicated using ethanol as solvent with conventional reflux, as described below.

A mixture of the VS dye (0.034 g, 0.1 mmol) and butylamine (7.31×10^{-3} , 0.1 mmol) in ethanol (50 mL) was refluxed for 2 h and then the solvent was removed by rotary evaporation. The residue was purified by preparatory TLC (60A° silica gel plates with fluorescent indicator, size 20x20 cm, layer thickness: 250 μ m); R_f = 0.39 (toluene: EtOAc/1:4) affording an orange viscous oil, which gave a clean ¹H-NMR spectrum as shown, in Figure 55. Elemental analysis calculated for C₂₂H₃₂N₄O₂S: C, 63.43; H, 7.74; N, 13.45; S, 7.70. Found: C, 62.24; H, 7.58; N, 12.18; S, 7.07. ¹H-NMR (300 MHz, CDCl₃): δ 8.00-7.93 (m, 4H), 7.88 (d, 2H), 6.73 (d, 2H), 3.48 (q, 4H), 3.34 (t, 2H), 3.06 (t, 2H), 2.59 (t, 2H), 1.82 (s, 1H), 1.43 (Qt, 2H), 1.35-1.29 (m, 2H), 1.25 (t, 6H), 0.90 (t, 3H). FAB-MS (positive ion) m/z (rel. int.): 417 (M+H, 100), 416 (M+, 19) as shown in Figure 57.

The reaction was repeated using CO₂ at 80°C and 3000 psi for 2 h. After isolation of the crude product and purification via preparatory TLC (60°A silica gel plates with fluorescent indicator, size 20x20 cm, layer thickness: 250 μm), the orange viscous product gave an identical product to the ethanol-based reaction described above, as evidenced by ¹H-NMR (Figure 56) and FAB-MS (positive ion) analysis (Figure 58), with the latter showing a parent ion at M_w = 415.76. Elemental analysis calculated for C₂₂H₃₂N₄O₂S: C, 63.43; H, 7.74; N, 13.45; S, 7.70. Found: C, 62.73; H, 7.84; N, 12.04; S, 6.89. ¹H-NMR (300 MHz, CDCl₃): δ 8.00-7.94 (m, 4H), 7.89 (d, 2H), 6.73 (d, 2H), 3.48 (q, 4H), 3.36 (t, 2H), 3.08 (t, 2H), 2.61 (t, 2H), 1.69 (s, 1H), 1.46 (q, 2H), 1.37-1.29 (m, 2H), 1.25 (t, 6H), 0.90 (t, 3 H). FAB-MS (positive ion) m/z (rel. int.): 417 (M+H, 100), 416 (M+, 19). In addition, R_f values by TLC were identical for the two reactions.

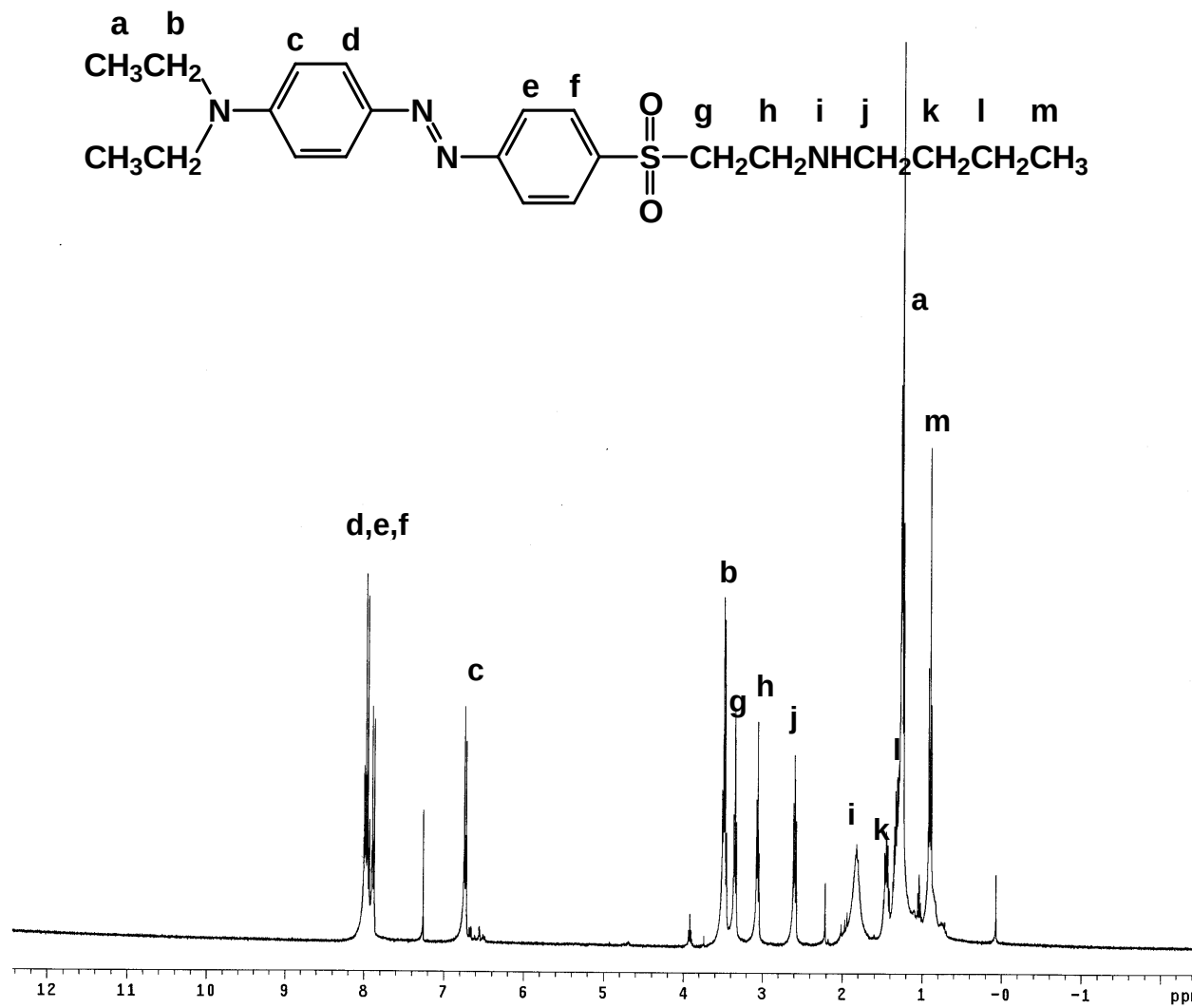


Figure 55. ^1H -NMR spectrum of the reaction product from the VS dye and butylamine reaction in ethanol.

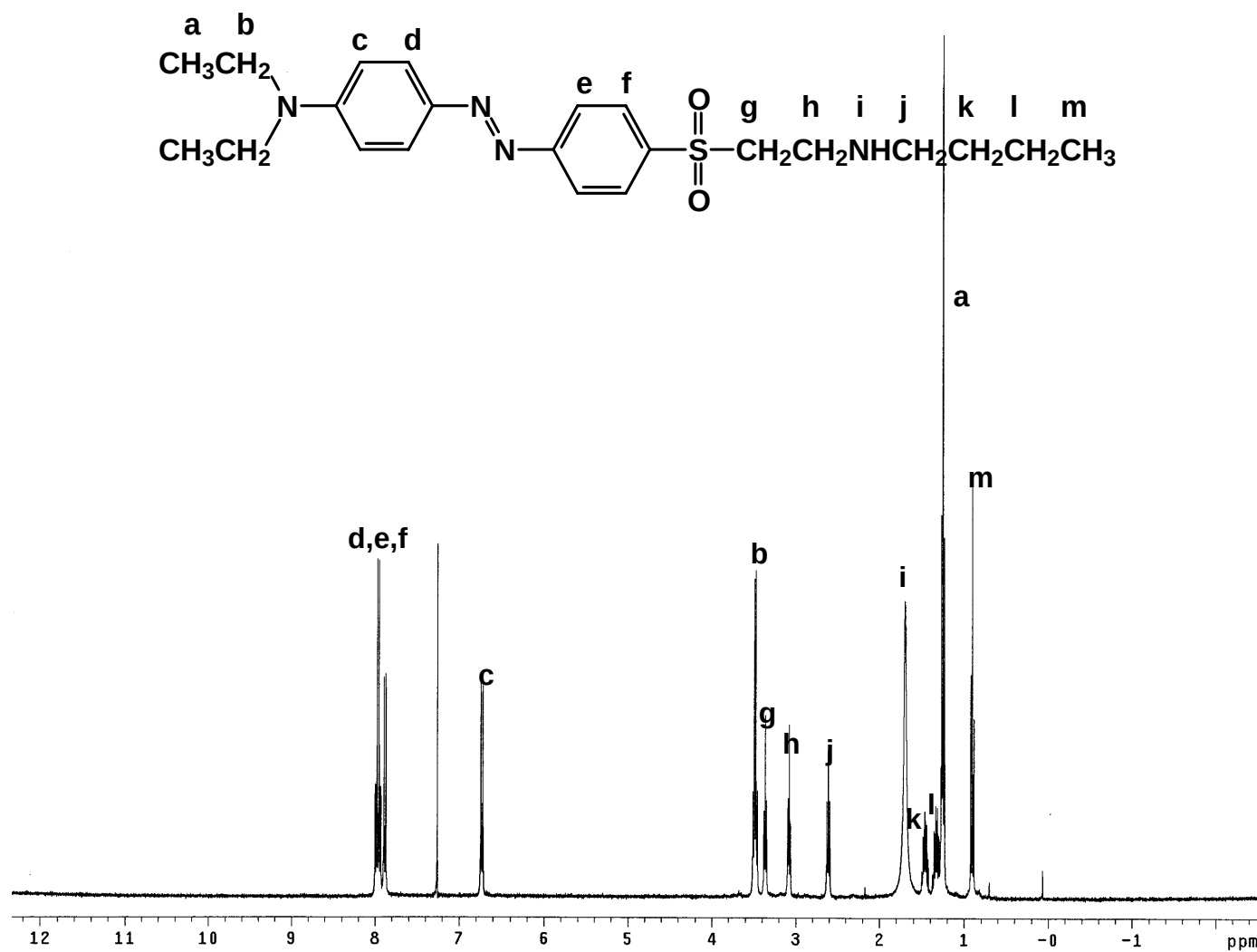


Figure 56. ^1H -NMR spectrum of the reaction product from the VS dye and butylamine reaction in SC-CO_2 .

[Mass Spectrum]
Data : Punrattanasin002 Date : 29-Mar-2006 16:05
Sample: FAB(+) CPD2, C22H32N4O2S, NM=416, NBR/Acetone
Note : 1000R, MF, 0-2000, 20s, cycle=14s, 200-900amu, gain=1100
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.47 min Scan# : (2,4)
BP : m/z 417.2197 Int. : 46.49
Output m/z range : 200.0000 to 900.0000 Cut Level : 0.00 %

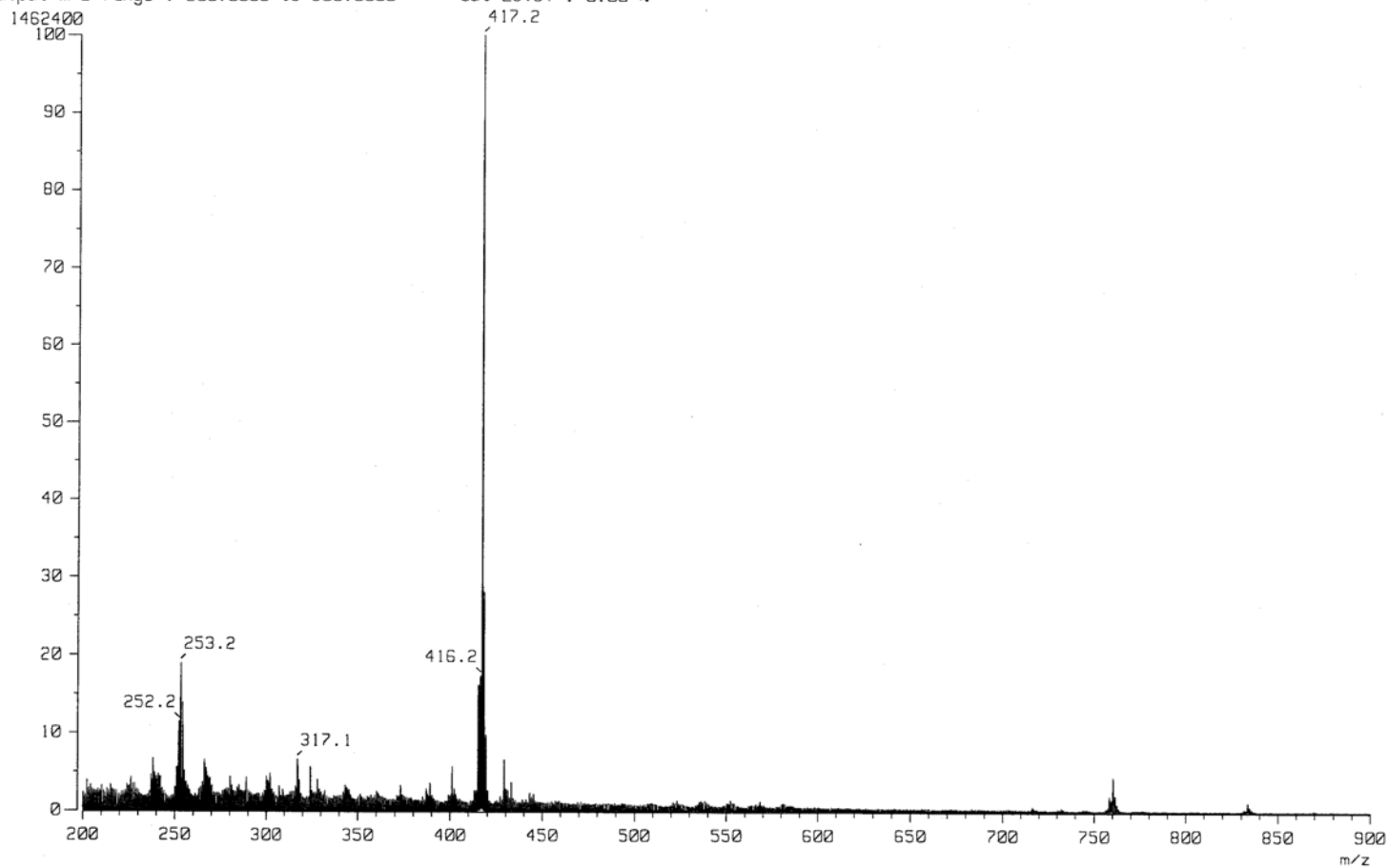


Figure 57. Positive ion FAB mass spectrum of the reaction product from the VS dye and butylamine reaction in ethanol.

[Mass Spectrum]
Data : Punrattanasin001 Date : 29-Mar-2006 16:01
Sample: FAB(+) CPD1, C₂₂H₃₂N₄O₂S, MW=416, NBA/Acetone
Note : 1000R, MF, 0-2000, 20s, cycle=14s, 200-900amu, gain=1100
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.47 min Scan# : (2,4)
BP : m/z 417.3412 Int. : 263.03
Output m/z range : 200.0000 to 900.0000 Cut Level : 0.00 %

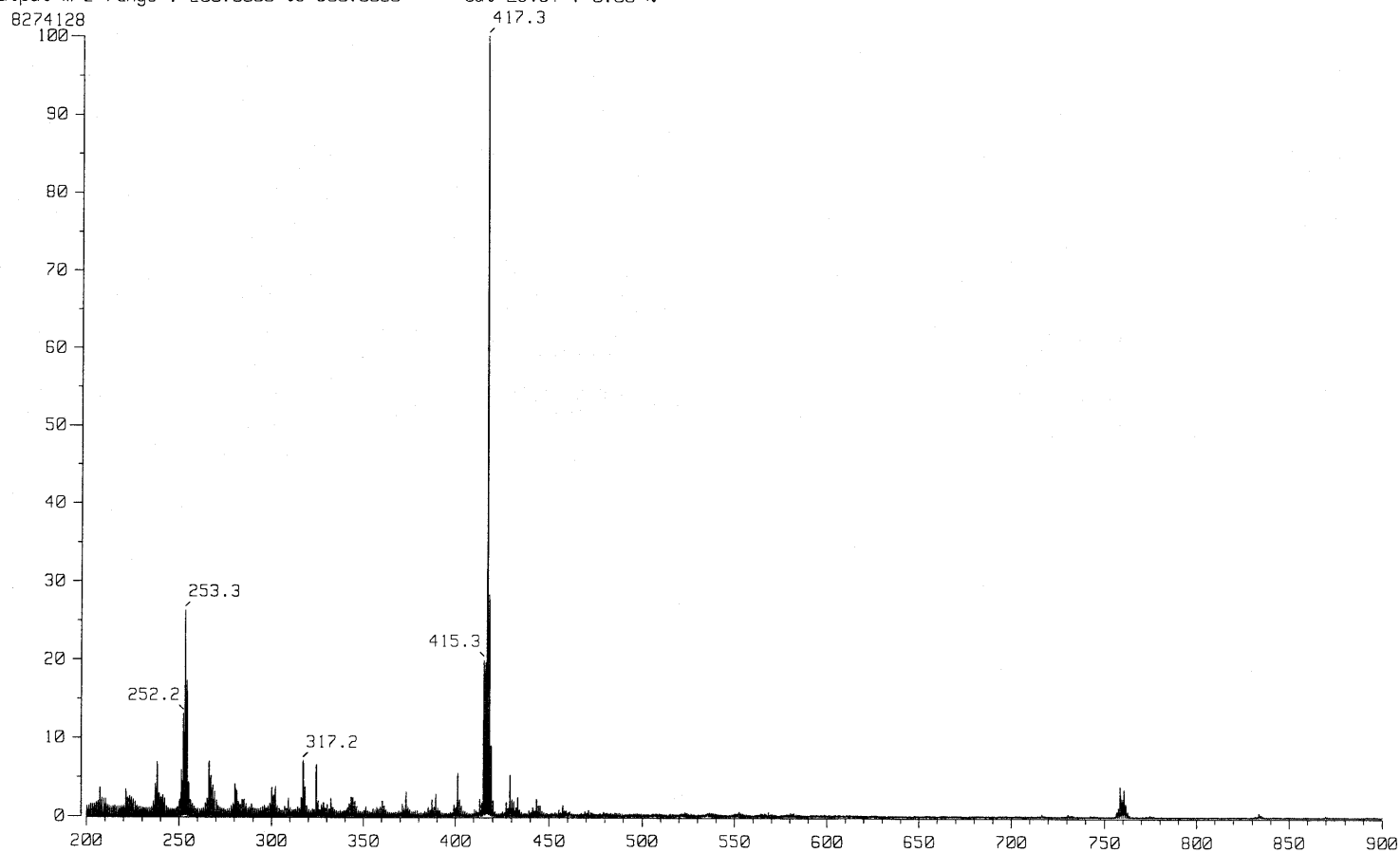


Figure 58. Positive ion FAB mass spectrum of the reaction product from the VS dye and butylamine reaction in SC-CO₂.

The resultant products from both reactions demonstrate that a Michael addition-type reaction was afforded in SC-CO₂, as shown in Figure 59, which strongly indicates the same reaction is feasible between a dye and suitable fibers with aliphatic primary amino groups, such as nylon 6,6 and wool.

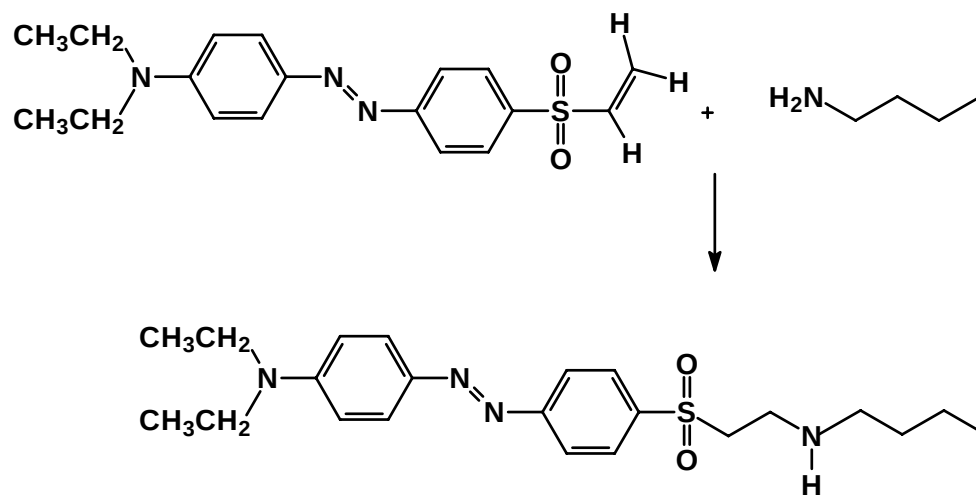


Figure 59. Michael addition reaction of VS dye and butylamine in SC-CO₂.

5.5 Conclusions

Nylon 6,6 and wool were effectively and efficiently dyed using a disperse-reactive dye in SC-CO₂ with a high degree of color strength and fixation. The dyeings were at least as effective as conventional dyeings using the same dye in water. In general K/S values increased with increasing temperature and pressure for both substrates, with greater than 94% apparent fixation achieved. Also, temperatures in the range 120-140°C and pressure from 2000-2500 psi (138-172 bar) gave good results. At temperatures higher than these ranges,

some dulling of shade was observed, particularly for wool dyeings, while little improvement in fixation or color strength was observed.

In addition, for the first time, a comparison of dyeings using a nonreactive ethylsulfonyl-based dye and an equivalent reactive vinylsulfonyl dye showed significant increase in fixation for the reactive versus the nonreactive dye. Moreover, reaction between butylamine (employed as a model primary amino reactive group for both wool and nylon) and the disperse reactive dye using typical SC-CO₂ dyeing conditions produced the alkylamine derivative of the dye, confirmed by ¹H-NMR and FAB-MS (positive ion), in good yield. This demonstrates the capability of covalent bond formation between a vinylsulfonyl group and an aliphatic primary amine in SC-CO₂, and, together with the comparative dyeing behavior for the VS and ES-based dyes, provides strong evidence for true dye-fiber reaction for the VS dye in the absence of water.

5.6 Acknowledgements

The author would like to express her gratitude to Mr. Qinglin Che for providing samples of the synthesized ES dye (**86**), and Mr. Ben Mead and Ms. Nneka Ubeka-Adams for conducting the dyeings shown in Figures 47-54.

6. Investigation into the Synthesis of C.I. Reactive Black 5 in Supercritical Carbon Dioxide

6.1 Introduction

C.I. Reactive Black 5 (**83**) is the most commercially important fiber-reactive dye for textile applications. This disazo dye is synthesized globally on a very large scale. The conventional reaction sequence used is shown in Figure 60.

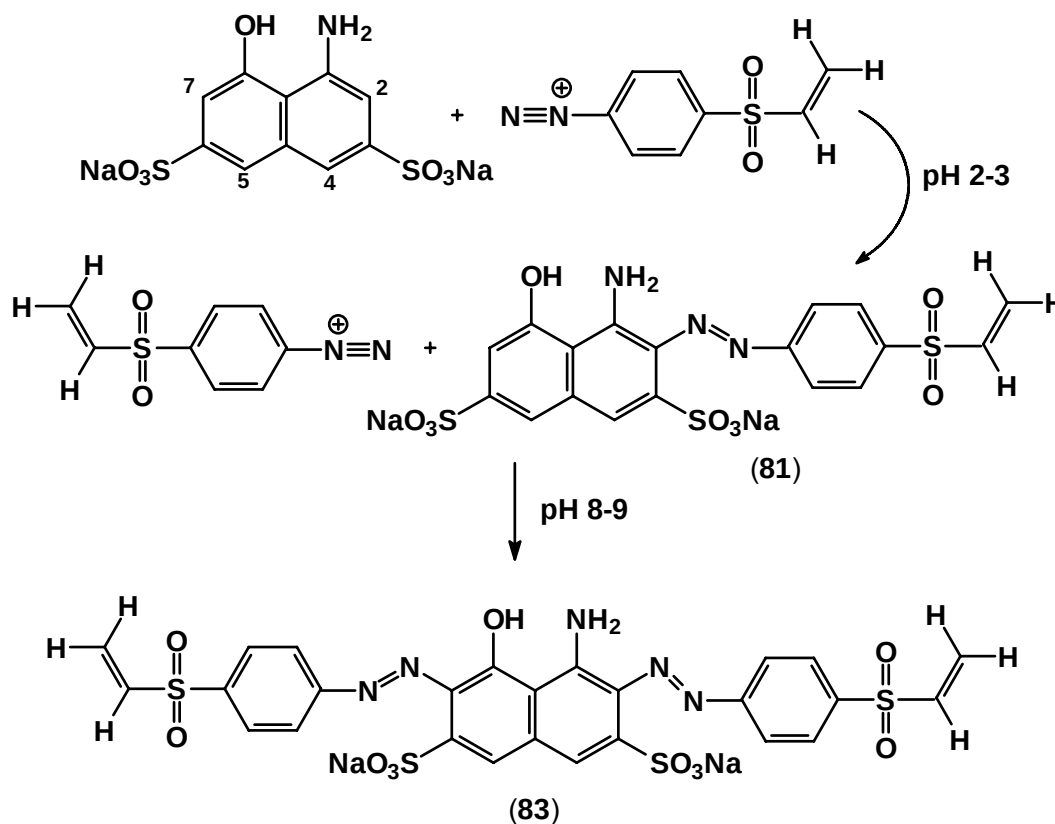


Figure 60. Reaction sequence for the synthesis of C.I. Reactive Black 5.

While the synthesis of this dye requires careful control of reaction conditions, especially due to the coupler having two coupling sites with differential sensitivity to the diazo coupling reaction, the dye is not considered to be particularly difficult to manufacture. However, the use of large amounts of mineral acid for the diazotization reaction, followed by required neutralization and salting out to precipitate the dye, means that significant amounts of electrolyte are generated. Depending on the prevailing environmental legislation and purification practices of the dyestuff manufacturer, these salts are either discharged to waste streams or the waste water is treated to remove the salt. Furthermore, significant levels of other impurities (e.g. unreacted coupler and side products following decomposition of the diazotized amine) and unprecipitated dye are also discharged as effluent, requiring further environmental treatment prior to release. Hence, a new, efficient synthesis method that reduces the environmental impact of the synthesis of this important dye is highly desirable.

The data shown in Chapters 2 and 3 showed that 4-aminophenylvinylsulfone (**76**) is a very good candidate for diazotization and coupling reactions in SC-CO₂, and this is the starting arylamine used in the diazotization reaction for the preparation of (**83**), C.I. Reactive Black 5. Hence, the data presented here summarize an extensive investigation into attempts to synthesize C.I. Reactive Black 5 in SC-CO₂ in the absence of mineral acid, thereby avoiding the requirement for neutralization and salting out.

6.2 Experimental

6.2.1 Materials

Reagent grade sodium nitrite and H-acid were obtained from Aldrich Chemical (Milwaukee, WI, USA). 4-aminophenyl- β -sulfatoethylsulfone was obtained from Hoechst, and a commercial sample of C.I. Reactive Black 5 was purchased from Rite Industries Inc. (Highpoint, N.C., USA). “Bone dry” 99.0% pure CO₂ was purchased from National Specialty Gases. Spectrophotometric grade acetone was purchased from Fisher Scientific (Pittsburgh, PA, USA).

6.2.2 Equipment

Reactions were performed using a jacketed 300 mL high-pressure reactor from Autoclave Engineers (Erie, PA, USA) equipped with a high speed stirrer, cooling/heating coil and a high-pressure pump, as shown in Figure 22.

6.3 Methods

6.3.1 Conventional Diazotization of 4-Aminophenylvinylsulfone and Coupling

6.3.1.1 Acid Coupling

4-Aminophenylvinylsulfone (1.83 g, 0.01 mol) was suspended in water and conc. HCl (2.5 mL). The mixture was cooled to 0-5°C using an ice bath and NaNO₂ (0.76 g, 0.011 mol) dissolved in H₂O (3.0 mL) was added dropwise. The

solution was stirred for 45 min. Excess HNO_2 was destroyed by addition of sulfamic acid. Activated carbon was added and the mixture was stirred and filtered to give a clear yellow solution.

H-acid (80%, 5.0 g, 0.012 mol) was suspended in water (30.0 mL) and the pH was adjusted to 7-8 using 10 % (w/v) NaOH to give a clear brown solution. H-acid solution was added dropwise into the prepared diazonium salt. HCl was added to maintain pH 2-3. The mixture was stirred overnight. The red precipitate was filtered and dried under vacuum. This gave dye **81** (6.16 g, 80 %).

^1H -NMR (300 MHz, DMSO, 70°C): δ 10.46 (1H, br), 7.89 (4 H, m), 7.54 (1H, s), 7.39 (2H, s), 7.13-7.10 (ethylene H, dd), 6.35-6.30 (cis H, d), 6.20-6.16 (trans H, d), 3.83 (2H, br), as shown in Figure A18, Appendix A.

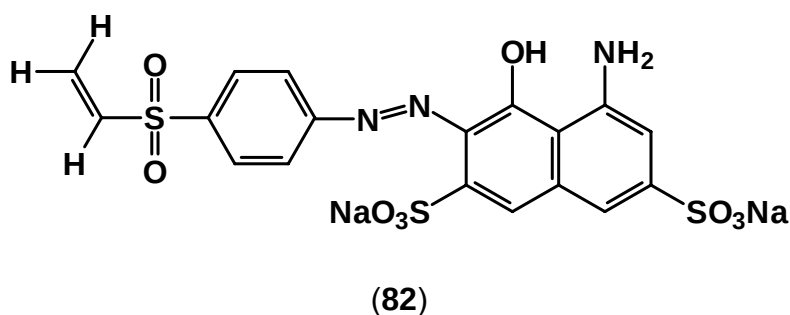
6.3.1.2 Alkali Coupling

H-acid (80%, 5.0 g, 0.012 mol) was suspended in H_2O (30 mL) and the pH was adjusted to 8-9 by using 10 % (w/v) NaOH to give a clear brown solution. 4-Aminophenylvinylsulfone (1.83 g, 0.01 mol) was suspended in water and conc. HCl (2.5 mL). The mixture was cooled to 0-5°C using the ice bath and NaNO_2 (0.76 g, 0.011 mol) dissolved in water (3.0 mL) was added dropwise. The solution was stirred for 45 min, and excess HNO_2 was destroyed by addition of sulfamic acid. Activated carbon was added and the mixture was stirred and filtered to give a clear yellow solution.

The diazonium salt was slowly added into H-acid solution. 10 % (w/v) NaOH was added to maintain the pH 8-9. The mixture was stirred overnight. The

dye was precipitated by addition of solid NaCl and the mixture was adjusted to pH 6-7 using 6% (w/v) HCl. The mixture was stirred for 2 h, and the product was collected by filtration. Salt was removed by DMF extraction. The resulting powder was dried under vacuum at 40°C, producing dye (**82**) (6.55g, 85 %).

¹H-NMR (300 MHz, DMSO, 70°C): δ 7.96-7.82 (7H, m), 7.35 (ethylene H, s), 7.11(cis H, s), 6.89 (trans H, s), 3.32 (2H, br), as shown in Figure A19, Appendix A.



6.3.2 Diazotization of 4-Aminophenylvinylsulfone and Coupling in SC-CO₂

6.3.2.1 Coupling to Monoazo Dye (**81**) in SC-CO₂

4-Aminophenylvinylsulfone (0.095 g, 0.52 mmol), NaNO₂ (0.036 g, 0.52 mmol), pure dye (**81**) (0.27 g, 0.50 mmol) and H₂O (4 mL) were added into a 300 mL high-pressure reactor. The reactor was then sealed and pressurized to 60 bar (860 psi) using CO₂. The reaction mixture was stirred using a high-speed mixer, and was heated to 80°C. CO₂ was isothermally compressed to 137 bar (2000 psi) under constant stirring at 800 rpm. Pressure was maintained for 3 h after which the CO₂ was depressurized slowly. The resultant dark blue product was collected, washed with water and later evaporated. The crude product was stirred

in acetone (50.0 mL) to remove unreacted 4-aminophenylvinylsulfone and later evaporated to give 0.32 g of crude dye (**83**). Without further purification, the structure of dye (**83**) was confirmed by $^1\text{H-NMR}$, as shown in Figure A20, Appendix A.

6.3.2.2 Coupling to Monoazo Dye (**82**) in SC-CO_2

The procedure described above for the synthesis of dye (**83**) was employed, with dye (**82**) (0.27 g, 0.50 mmol) used as the starting material to give 0.25 g of crude dye (**84**).

6.3.3 Visible Absorption Spectra

Solutions (5×10^{-5} mol) of dyes (**81**) to (**84**) were made by dissolving the prepared dyes in water (50.0 mL) and diluting 1.0 mL with H_2O (24.0 mL) to give the final concentration 4×10^{-5} mol/L. The visible absorption spectra were recorded using a Varian Cary 3E UV-visible spectrophotometer. From the resultant absorption spectra λ_{max} was recorded and ϵ_{max} calculated.

6.3.4 Dyeing of Cotton Fabric

Cotton fabric samples (2.0 g) were dyed by exhaustion dyeing method in a Roaches Pyrotec dyeing machine in the presence of sodium carbonate (20.0 g/L), and 5.0 % owf. of dye (**83**) synthesized dye, together with a commercial sample of C.I. Reactive Black 5. The liquor ratio was 20:1. Fabric was entered

into the dyebath at 40°C in the presence of dye and sodium sulfate (50g/L). The dyebath temperature was raised to 60°C during 20 min at which time sodium carbonate was added (20 g/L) was added, and the dyeing continued for 2 h. After completion of the dyeing cycle, the fabrics were rinsed in warm water and scoured with AATCC detergent (2.0 g/L) at 160°F for 5 min. The dyed fabric was then rinsed again in warm water and dried.

6.3.5 Colorimetric Measurement

Reflectance measurement and calculation of colorimetric data were performed using the method described in section 4.3.4.

6.4 Results and Discussion

The synthesis of C.I Reactive Black 5 is a two-stage reaction, as shown in Figure 60. In conventional aqueous synthesis, the first stage involves diazotization and coupling under acidic conditions to produce dye (**81**), which is usually not isolated. The second stage involves an identical diazotization procedure, but in this case, coupling is conducted under alkaline conditions to ionize the hydroxyl group of H acid and force coupling onto the remaining and less reactive 7 position of the naphthyl ring. Hence, synthesis of this dye in SC-CO₂ requires two coupling reactions. Initial experiments using SC-CO₂ focused on a one-pot *in situ* diazotization and coupling process in which coupling to the two open positions in H acid would occur simultaneously. However, TLC

analysis showed the reaction did not form any disazo product, despite multiple attempts to synthesize the target reactive dye by varying T, P, water, and time. Rather, a monoazo dye (**82**) was formed.

Consequently, the two separate diazotization and coupling reactions were investigated separately, and compared to the conventional aqueous synthesis method for producing C.I. Reactive Black 5. The target dye (**83**) was characterized successfully via $^1\text{H-NMR}$ after coupling the diazotizing amine to the monoazo intermediate (**81**). Hence, coupling to the position *ortho* to the OH group in H acid is demonstrated. However, unfortunately coupling the diazotized 4-aminophenylvinylsulfone to monoazo dye (**82**) in SC-CO₂ was unsuccessful; the reason for the absence of coupling to this position is unclear, although it is possibly due to the presence of the bulky amino group in the *ortho* position inhibiting the reaction. Interestingly coupling to this position in conventional methods is conducted under mild acidic conditions, which are similar to the carbonic acid medium found in the SC-CO₂-H₂O system. It is clear, therefore, that an alternative approach to synthesizing C.I. Reactive Black 5 in SC-CO₂ is required.

The λ_{max} of dye (**81**) to (**83**) and a sample of C.I. Reactive Black 5, synthesized via a conventional method, are shown in Table 19. Dye (**83**) (prepared in SC-CO₂ described in section 6.3.2.1 above) exhibited a slight hypsochromic shift and lower molar extinction coefficient compared to the commercial dye. The hypsochromic shift is possibly due to a small amount of colored impurity and the reduced ϵ is potentially due to electrolyte still present in

(**83**) acting as a diluent. Nevertheless, the second coupling reaction of dye (**81**) in SC-CO₂ is feasible. However, the success of this reaction is important as it opens the door to synthesis of water soluble dyes in SC-CO₂.

Table 22. The $\lambda_{\max}$ of reactive dyes (**81**) to (**84**) and C.I. Reactive Black 5.

Dye	$\epsilon_{\max}$	$\lambda_{\max}$ (nm)
(81)	24,990	539
(82)	12,480	526
(83)	24,300	589
(84)	12,480	524
C.I. Reactive Black 5	27,090	595

6.4.1 Colorimetric Data

The colorimetric data for the dyed fabrics are shown in Table 22. Dyed cotton fabrics using the dyes synthesized in SC-CO₂ exhibited color strength and L* a* b* values that were lower than equivalent dyeings of cotton fabric using C.I. Reactive Black 5 synthesized via a conventional method. Also, although both dyed fabrics exhibited the same $\lambda_{\max}$ value (590 nm), the color of the fabric dyed with C.I. Reactive Black 5 exhibited higher color strength, and was slightly redder and bluer than the SC-CO₂ prepared dye, (**83**), indicating significant impurities are present in the SC-CO₂ synthesized dye.

Table 23. L* a* b* values and color strength (K/S) of dyed fabrics.

Dyed fabric with	L*	a*	b*	K/S	$\lambda_{\max}$ (nm)
(83) (using SC-CO ₂)	22.79	-1.72	-13.36	19.93	590
C.I. Reactive Black 5 (conventional)	16.93	-0.41	-8.25	27.42	590

6. Conclusions

The method used to diazotize 4-aminophenylvinylsulfone and couple to H acid was unsuccessful in producing C.I. Reactive Black 5, due to the failure of the coupling reaction at the 2-position (*ortho* to the amino group in H acid). However, coupling was possible at the 7-position (*ortho* to the OH group in H acid) using a simple SC-CO₂-H₂O system as both solvent and protonation source.

7. Summary and Future Work

A major benefit of a mineral acid-free diazotization reaction would be elimination of a neutralization step and the need to remove large quantities of electrolyte from crude azo dye reaction mixtures. Also, with reasonable product yields, isolation of pure dye by selective dissolution and precipitation using SC-CO₂ is feasible. In fact, a continuous synthetic process with continuous feeding of reactants into a SC-CO₂-H₂O system may be possible. However, more work is required to understand the key factors that drive the reaction, including:

- the effect of substituents on the coupling component,
- the use of alternatives to sodium nitrite (e.g. isoamyl nitrite) to completely remove Na⁺ from the reaction,
- optimization of reaction conditions for commercially important dyes,
- expansion of the role of log P to include highly water soluble diazotizing arylamines, such as sulfanilic acid and related compounds,
- development of a statistically valid structure activity relationship model for the synthesis of azo dyes in SC-CO₂, and especially,
 - a full elucidation of the reaction mechanism
 - scale-up of optimized reactions
 - investigation into potential for a continuous synthesis process using SC-CO₂-water systems

In regard to the issue of reaction mechanism, it is clear that the reaction in SC-CO₂ proceeds differently from that of conventional diazotization and coupling, particularly in regard to the temperature required. Also the homocoupling reaction to form a symmetrical dye from two *N,N*-diethylaniline molecules is evidence that the reaction may in fact proceed via nitrosation of the coupling component rather than diazotization of the primary arylamine. Hence, a fundamental study to determine the reaction mechanism is warranted.

In addition, a study to determine the scope of azo dye formation in SC-CO₂ reaction for water-soluble dyes, such as acid and fiber-reactive dyes, could provide significant evidence as to which commercially important azo dyes can be synthesized in this medium.

In regard to fiber-reactive dyeing, the approach of using a vinylsulfonyl-based disperse reactive dye for dyeing nylon 6.6 and wool can provide level dyeings with high color strength and a high degree of fixation, compared to when dyed with an analogous dye without the ability to react with the fiber. A very interesting and new approach would be to use a disperse reactive dye in combination with water soluble fiber-reactive dyes in SC-CO₂ in the presence of relatively small amounts of water to dye polyester/cotton blends, as well as other blends such as wool/cotton and silk/nylon. The application method could follow the same procedure patented recently by Smith *et al.* in 2004. Another potential high impact area for further study is to incorporate disperse fiber-reactive dyes into SC-CO₂ dyeings using novel surfactants to produce reverse micelles in the

dyeing of combinations of hydrophilic and hydrophobic fibers such as polyester/cotton blends.

The dyeing of cotton fabric in SC-CO₂ via an azoic dyeing method was demonstrated for the first time in the presence of an arylamine, a small amount of water and NaNO₂. Level dyeings with reasonable dye penetration, high color strength and high fixation were achieved under optimized synthetic conditions. However, the coupling component was applied to the substrate prior to SC-CO₂ azoic reaction. Further work is needed to devise a method for application of the coupling component using a SC-CO₂ medium. Also, a study is required to determine the effect of varying substituents on both the arylamine to be diazotized and the coupling component.

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Appendix A.
 ^1H -NMR SPECTRA

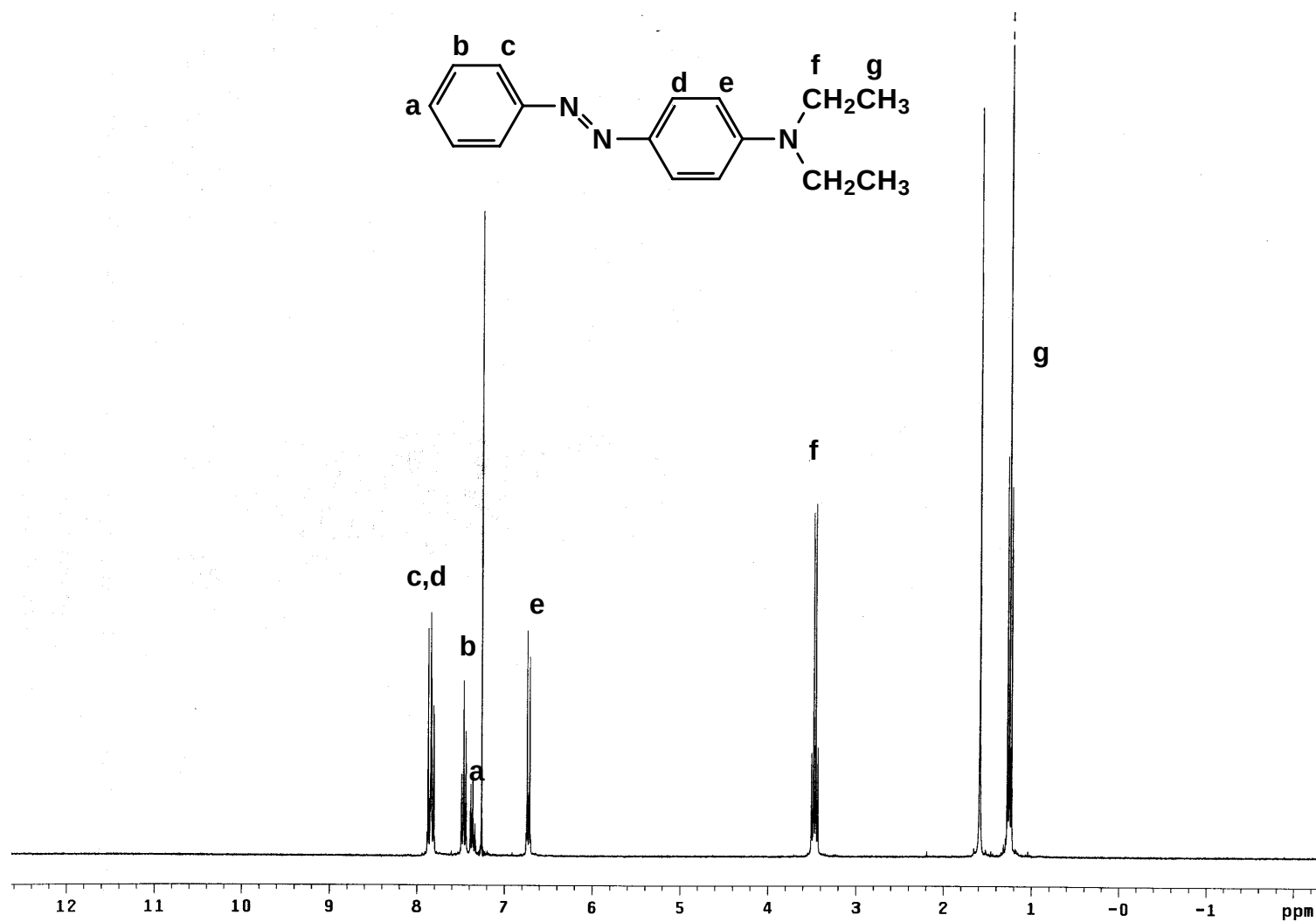


Figure A1. ^1H -NMR spectrum of dye (70) synthesized by conventional method.

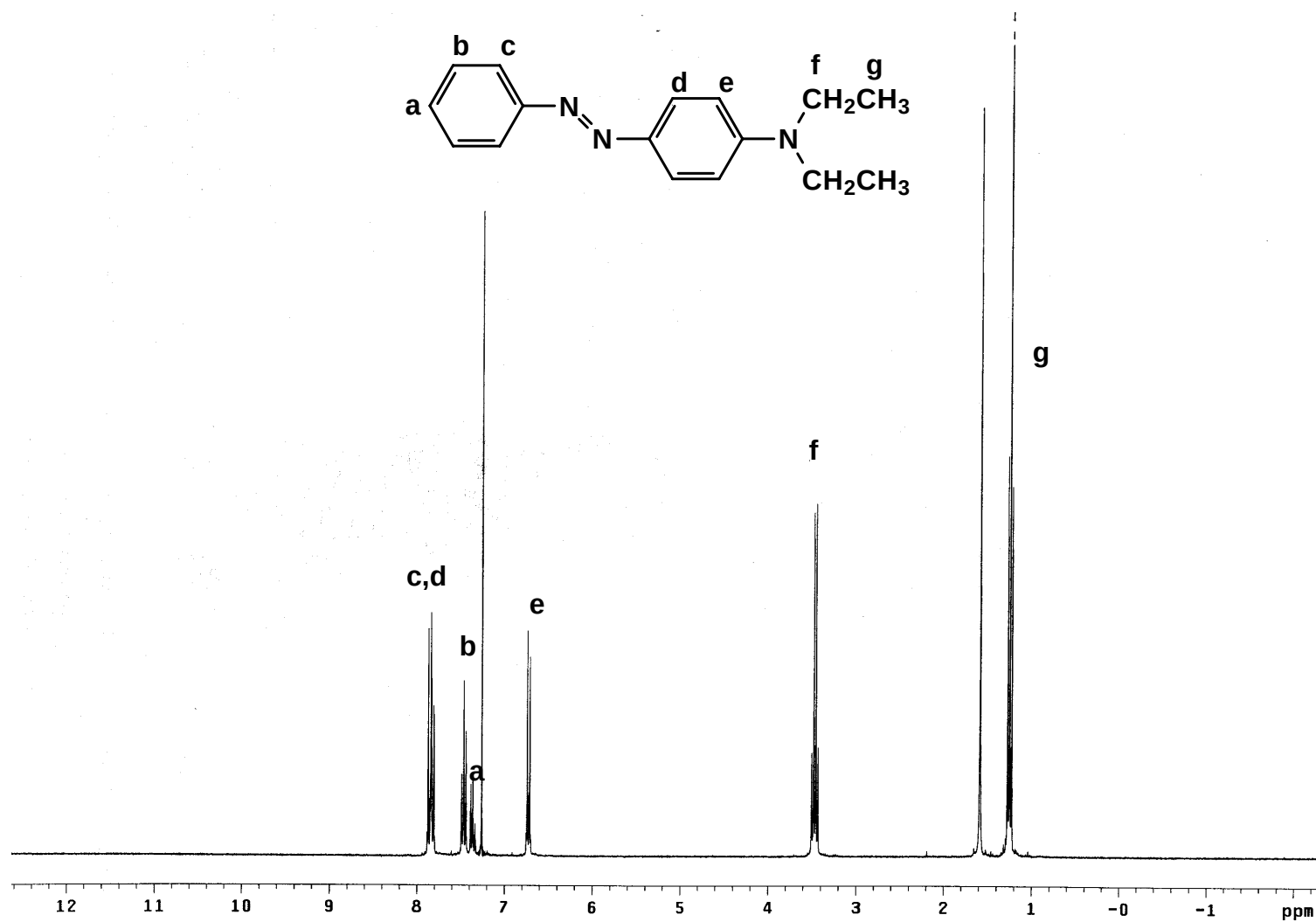


Figure A2. ^1H -NMR spectrum of dye (70) synthesized by SC- CO_2 .

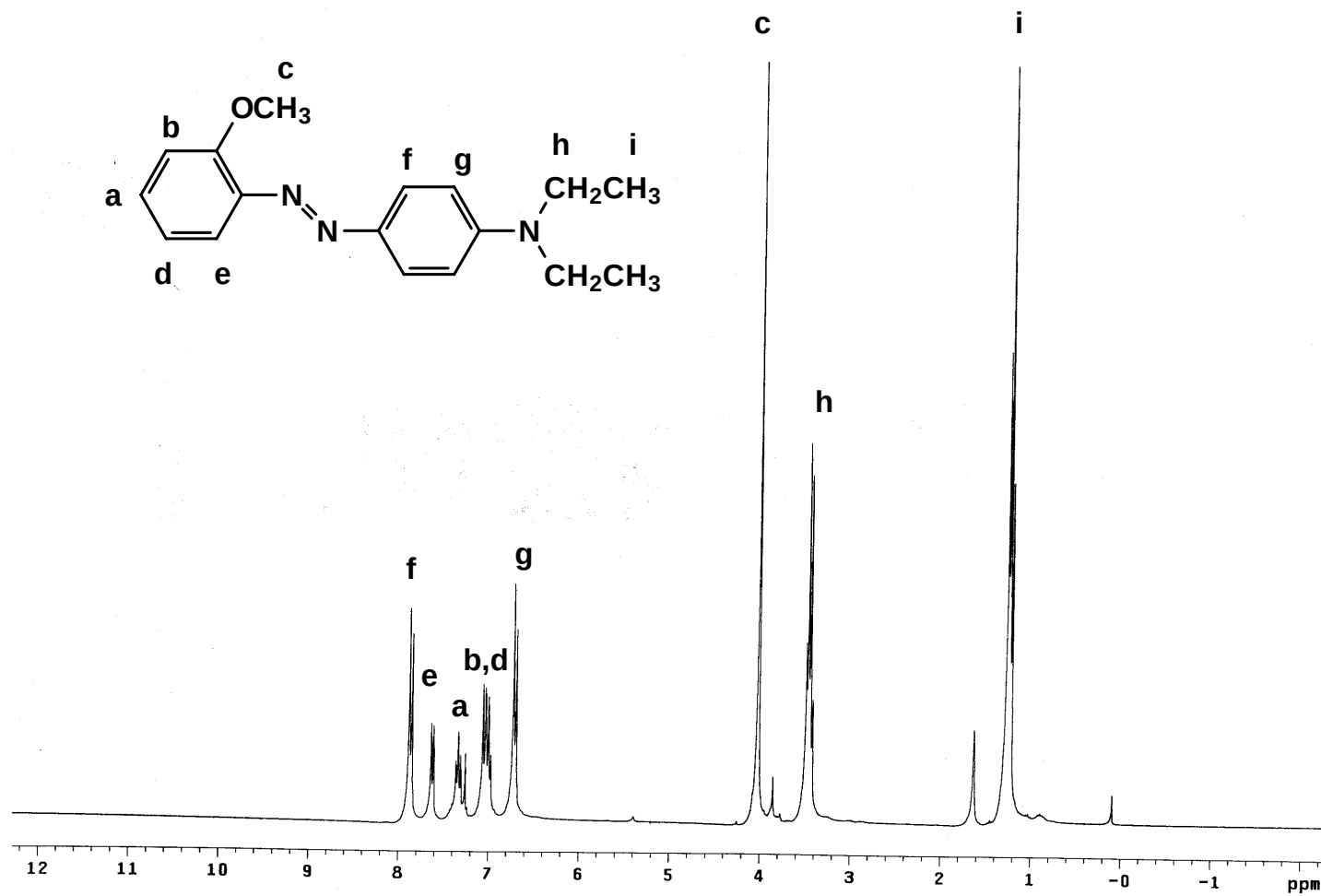


Figure A3. ^1H -NMR spectrum of dye (71) synthesized by conventional method.

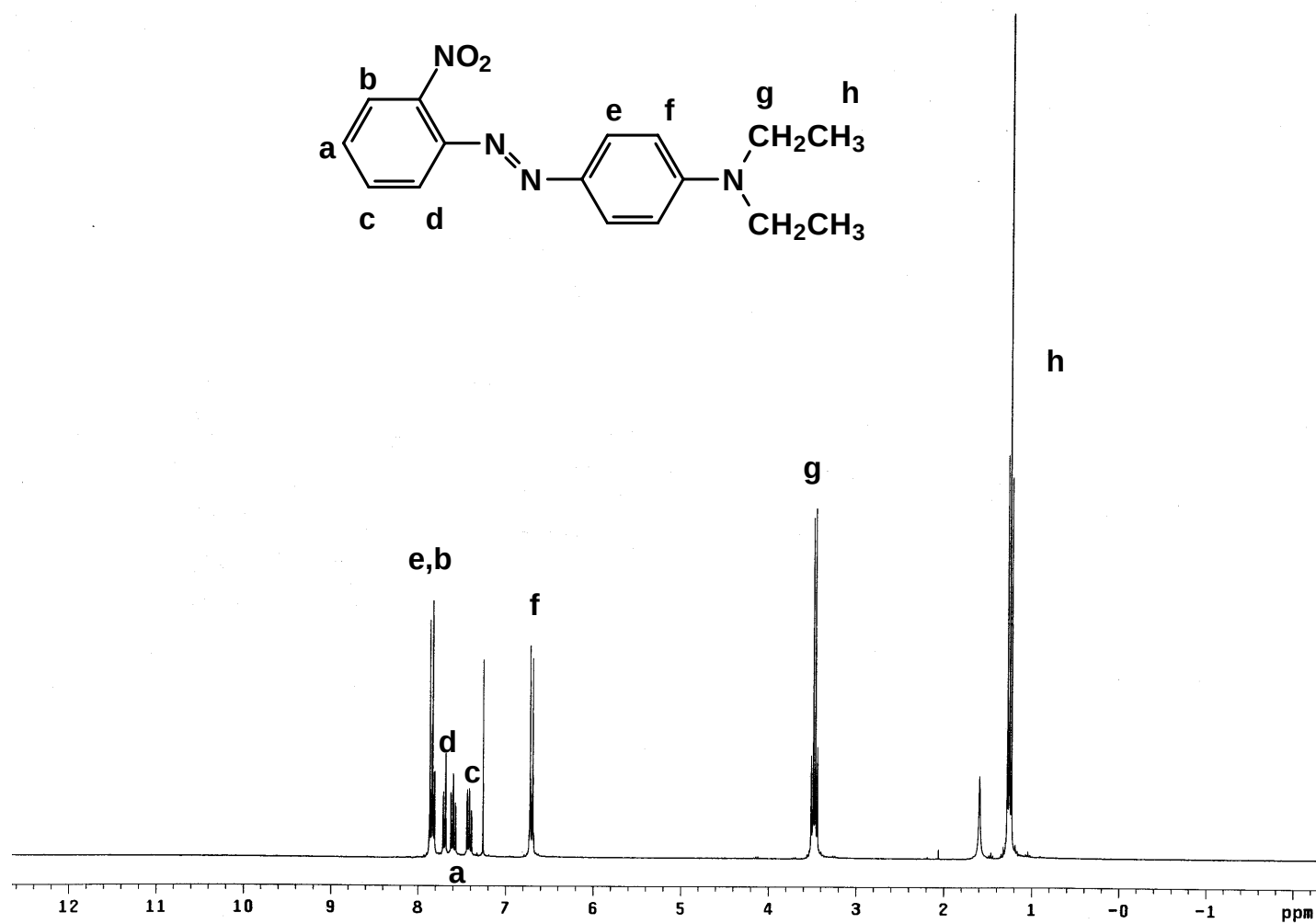


Figure A4. ^1H -NMR spectrum of dye (72) synthesized by conventional method.

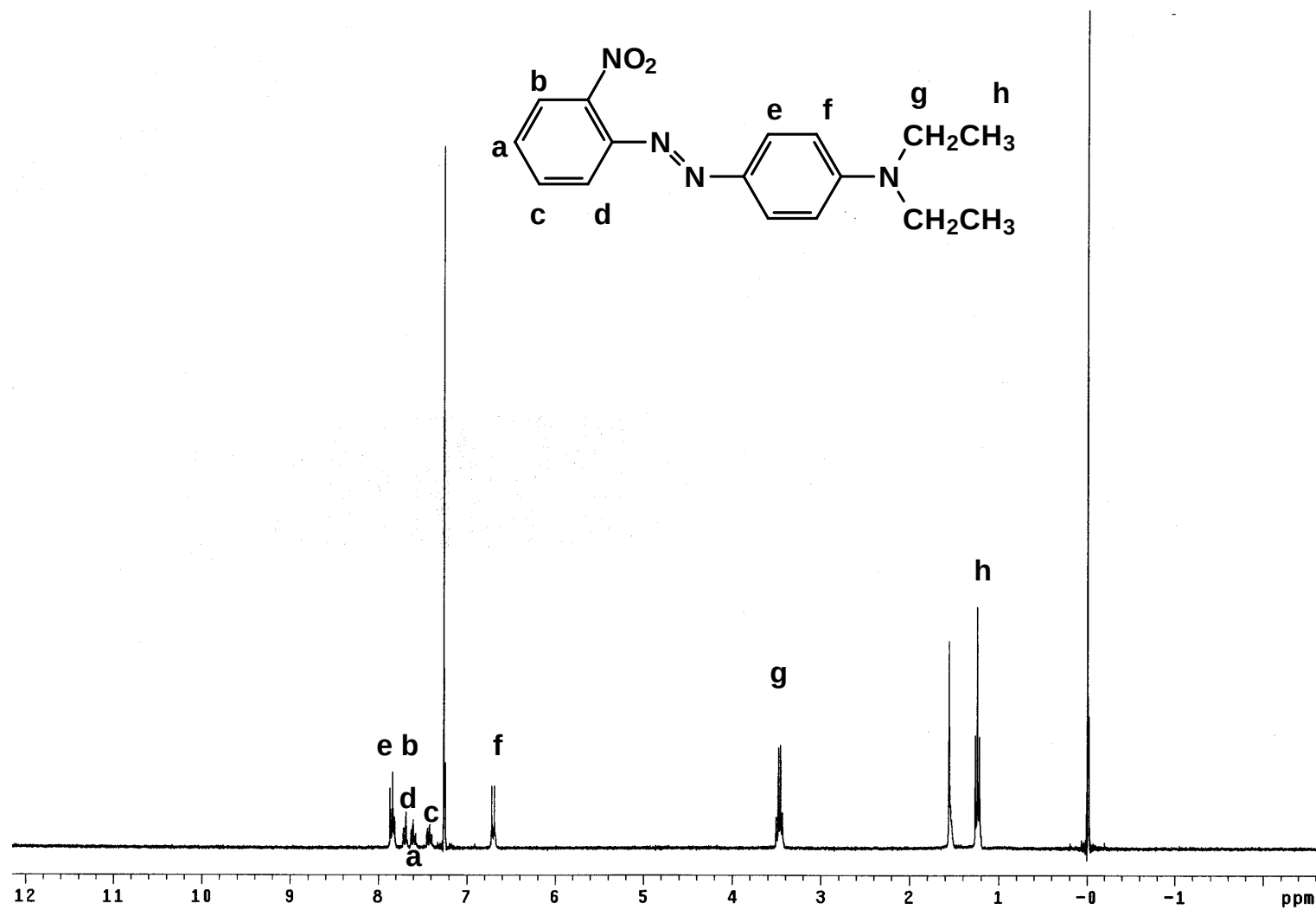


Figure A5. ^1H -NMR spectrum of dye (72) synthesized by SC-CO₂.

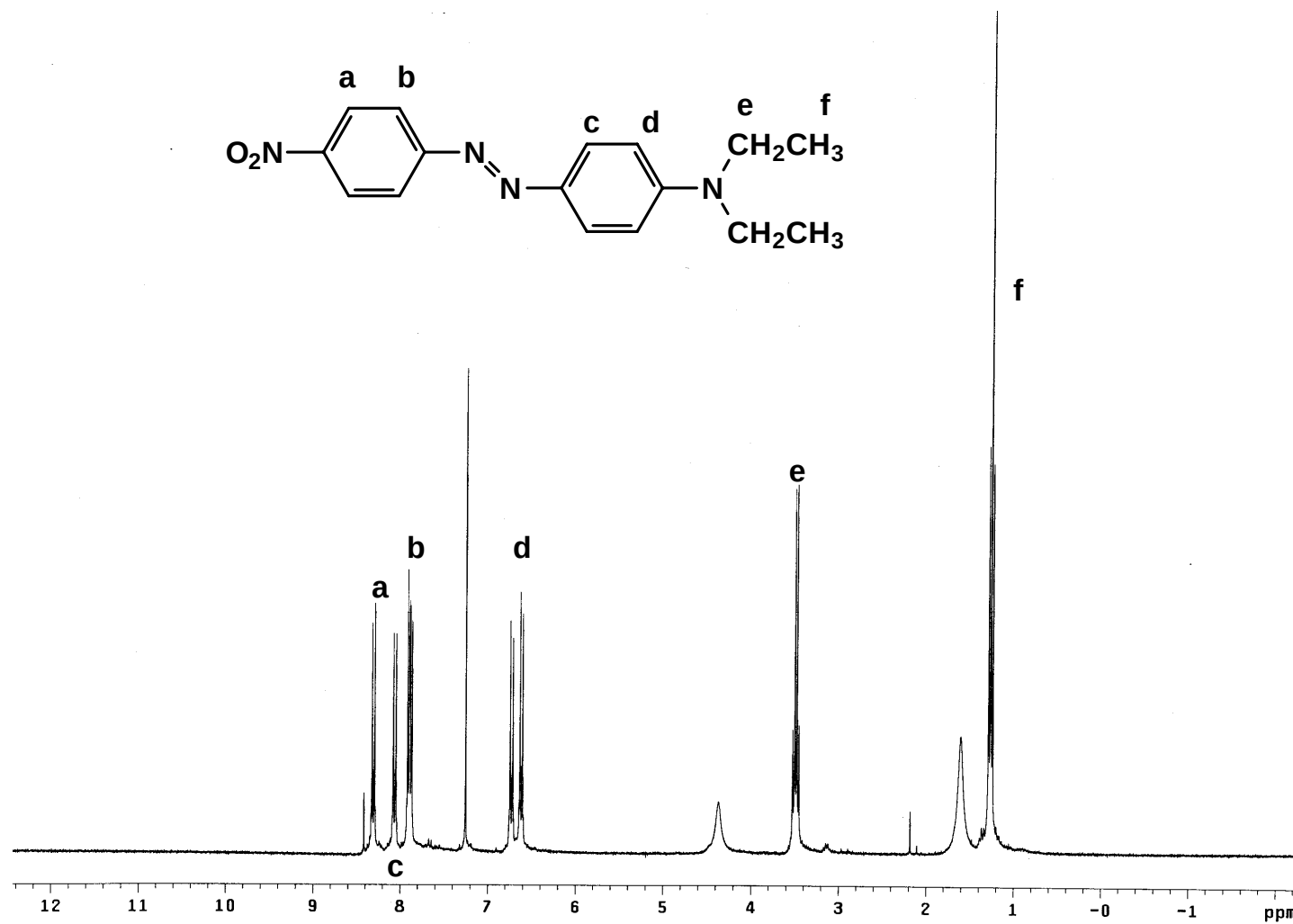


Figure A6. ^1H -NMR spectrum of dye (73) synthesized by conventional method.

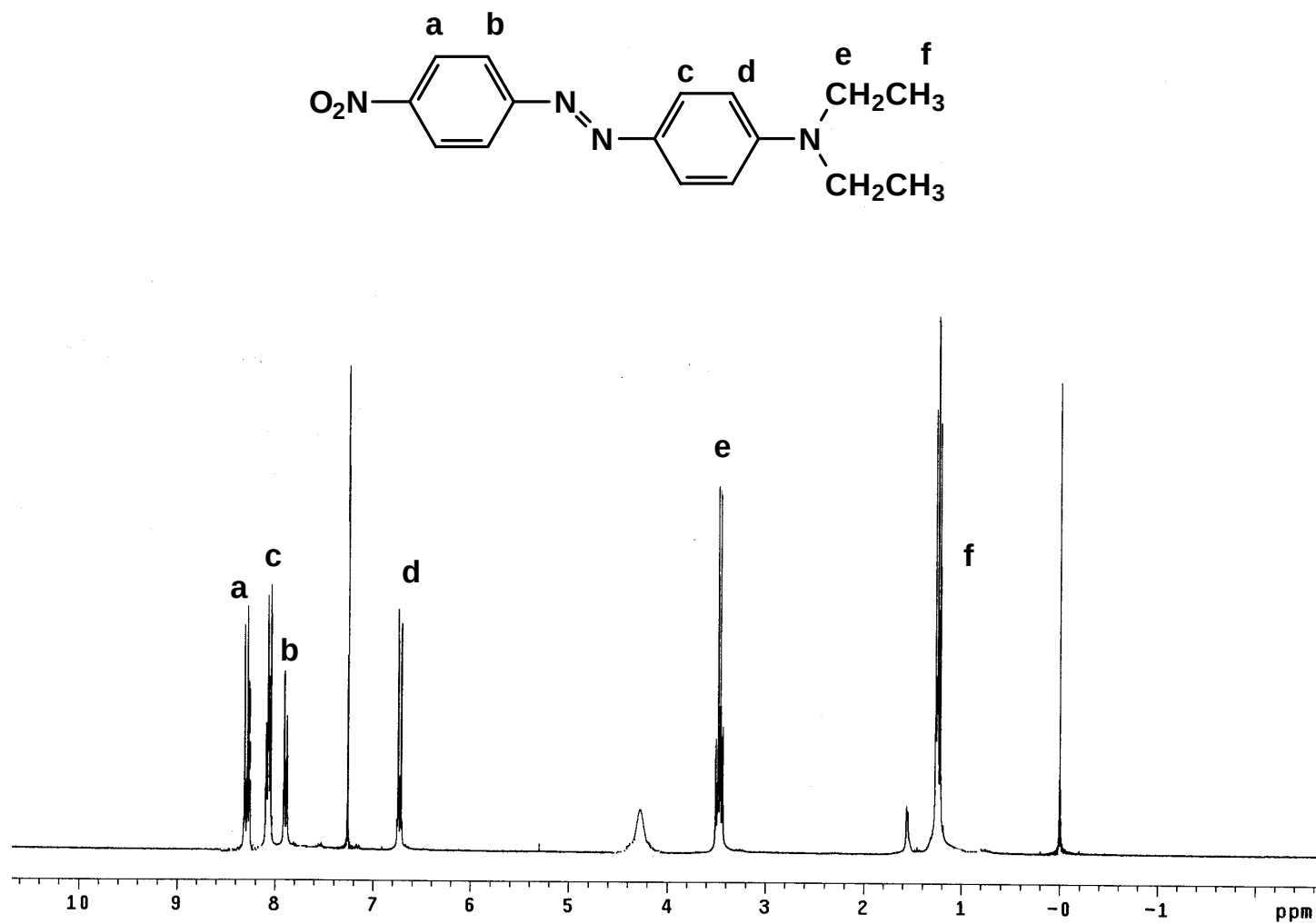


Figure A7. ^1H -NMR spectrum of dye (73) synthesized by SC- CO_2 .

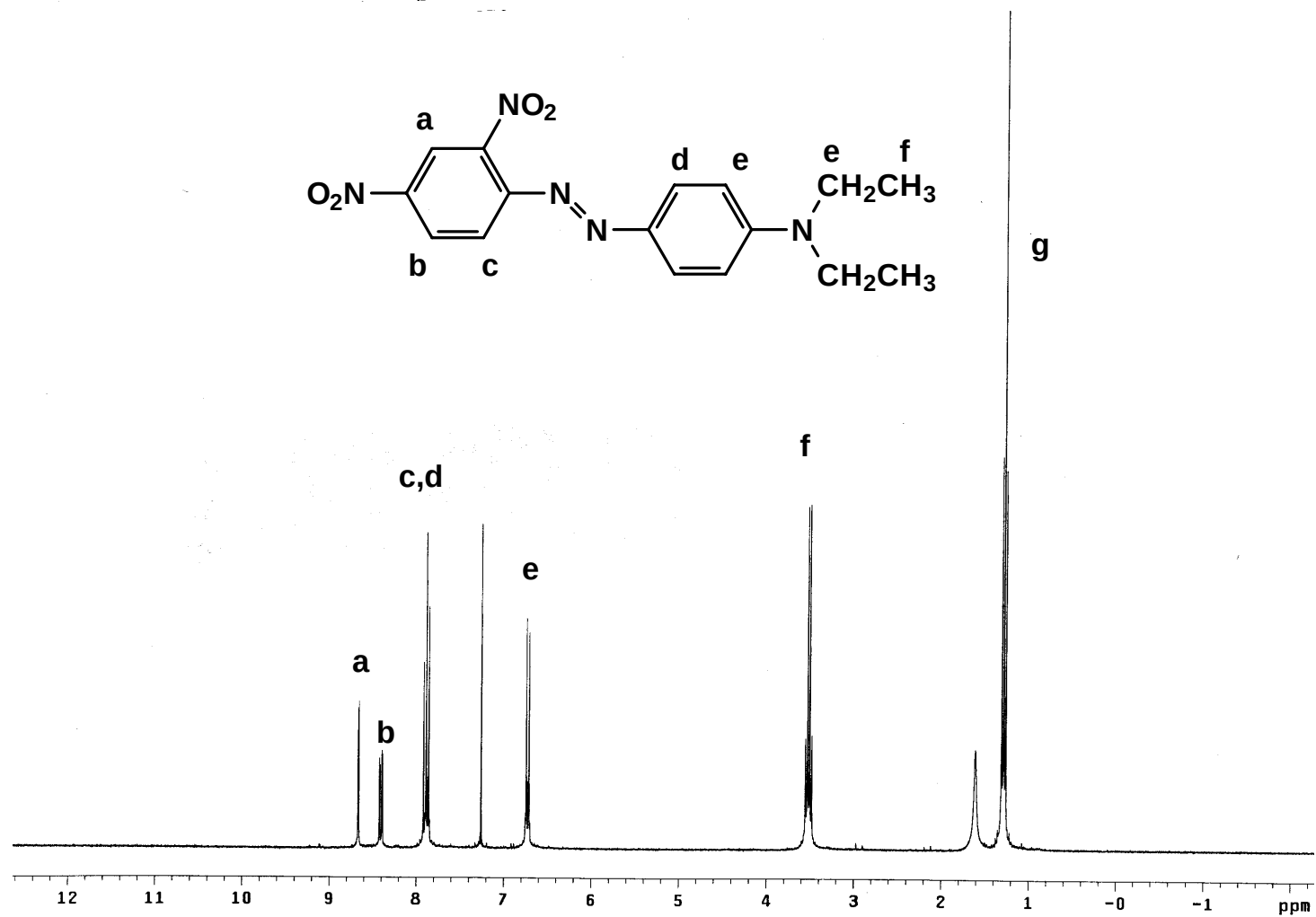


Figure A8. ^1H -NMR spectrum of dye (74) synthesized by conventional method.

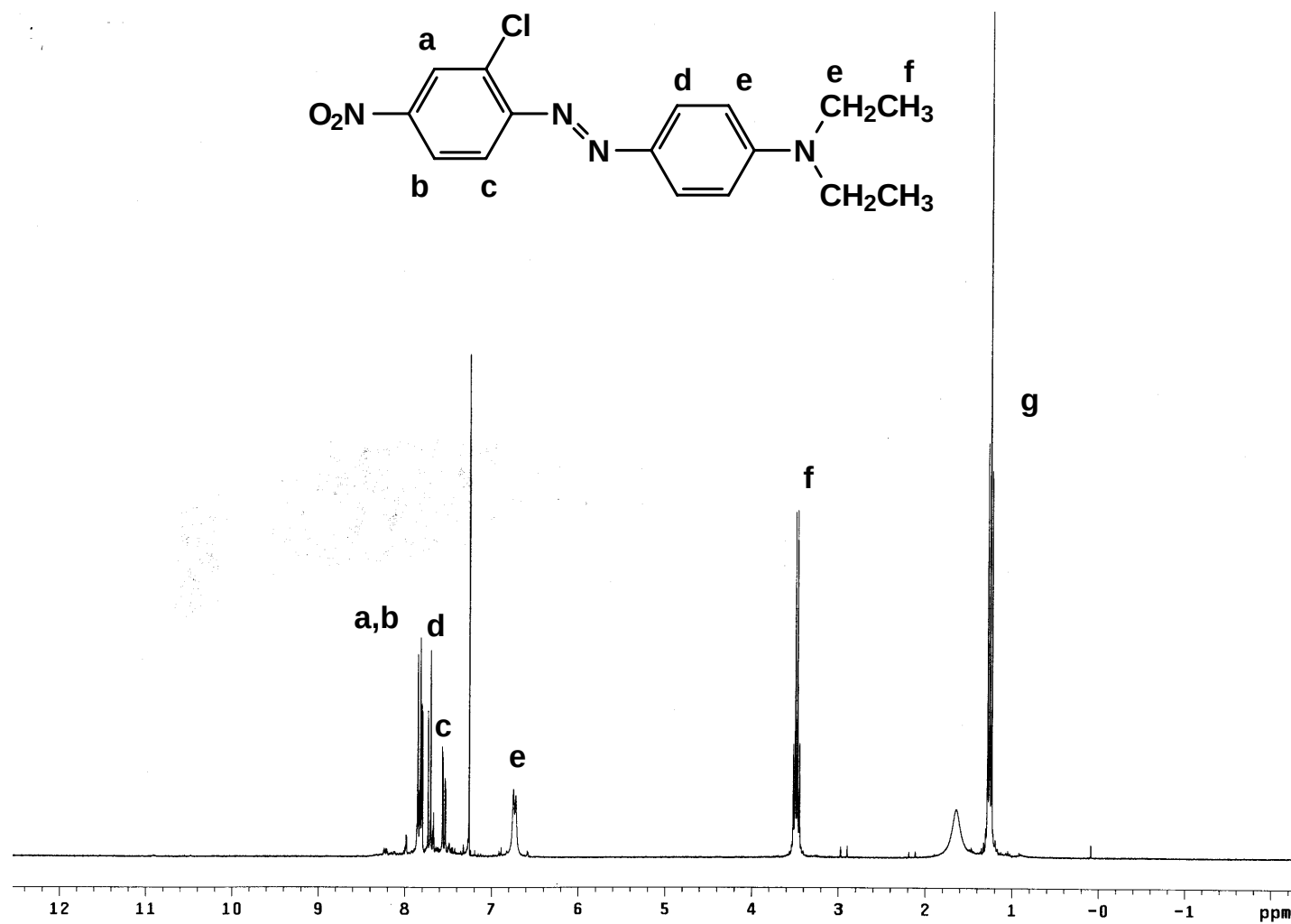


Figure A9. ^1H -NMR spectrum of dye (75) synthesized by conventional method.

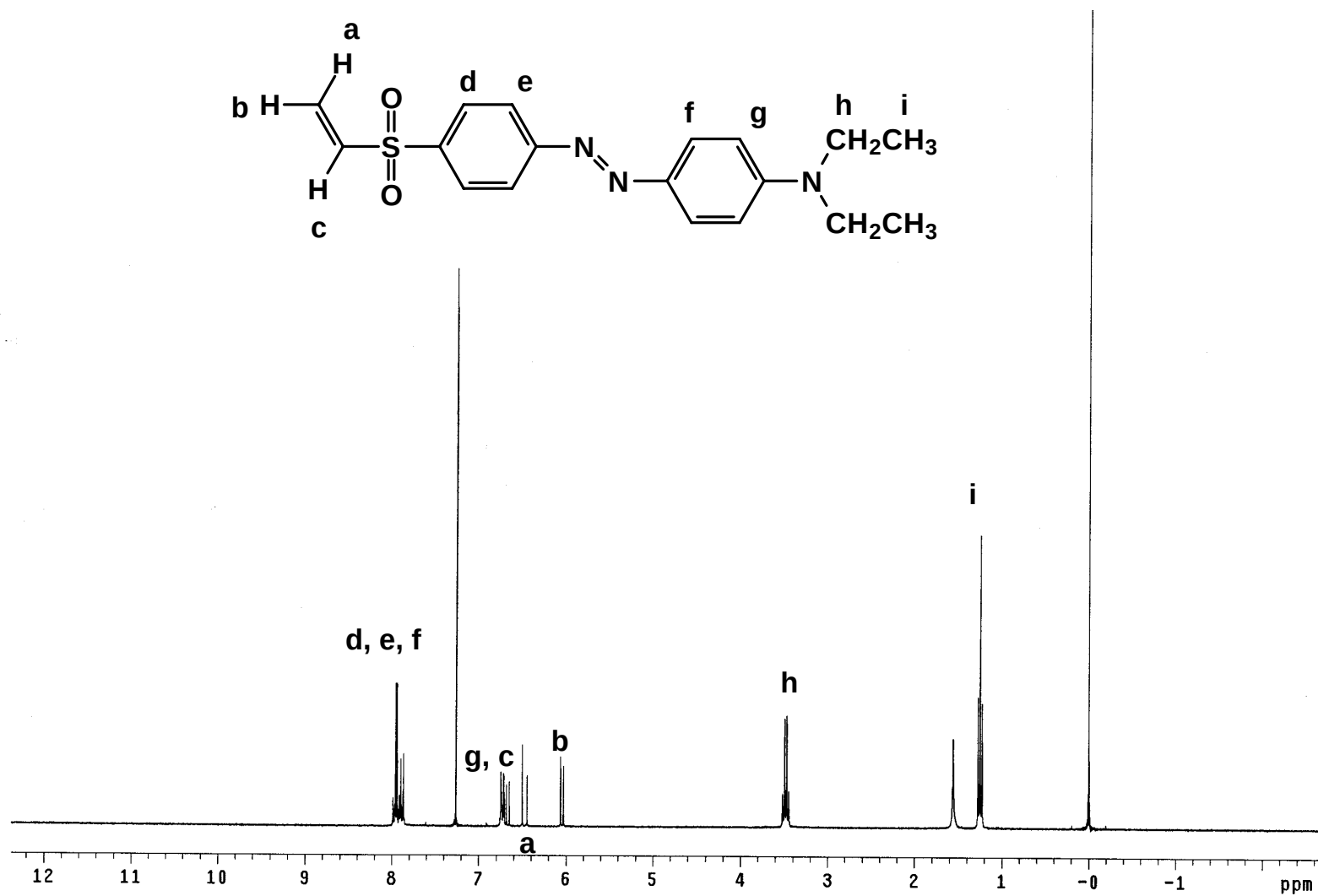


Figure A10. ^1H -NMR spectrum of dye (76) synthesized by conventional method.

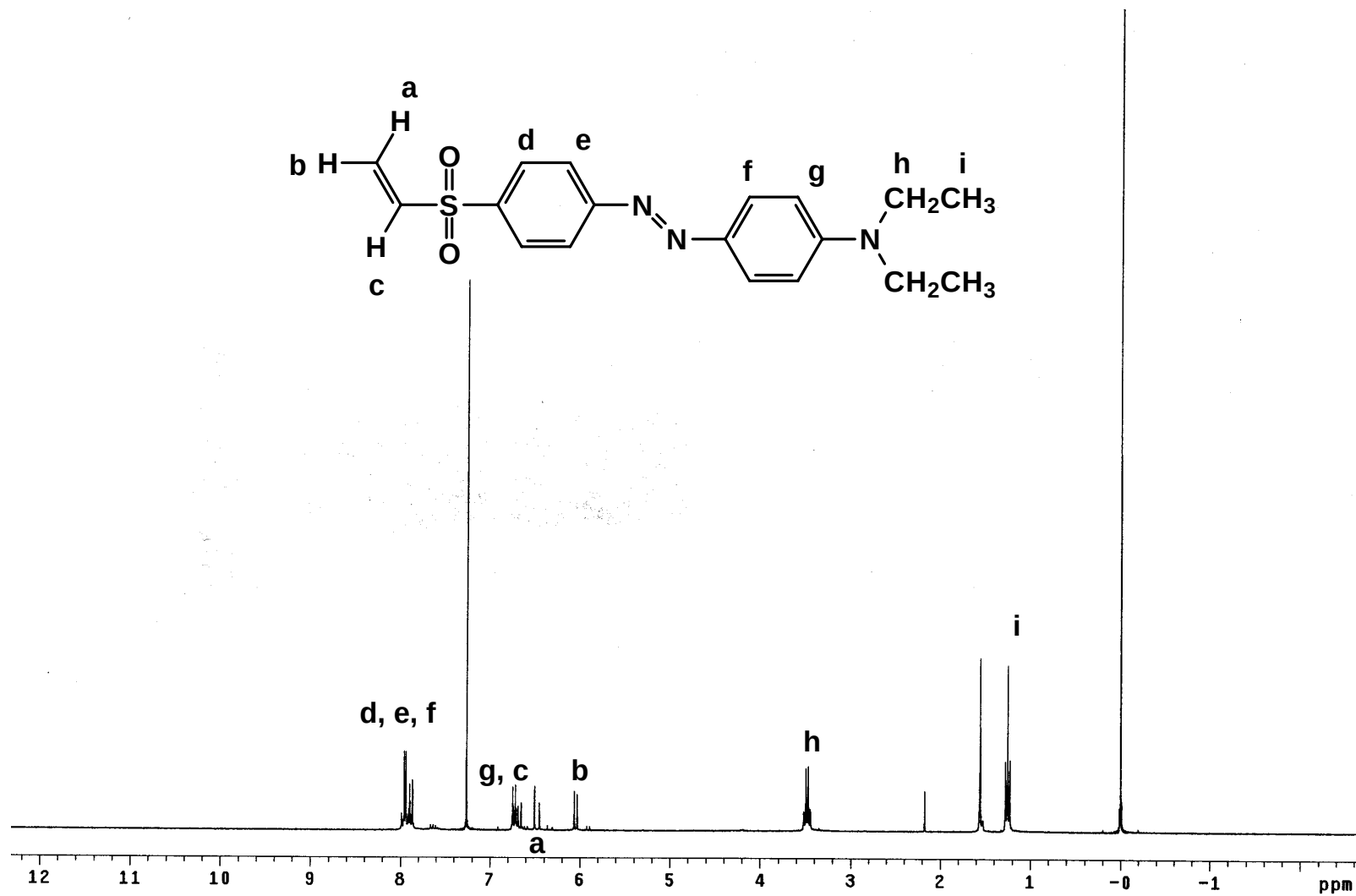


Figure A11. ^1H -NMR spectrum of dye (76) synthesized by SC-CO₂.

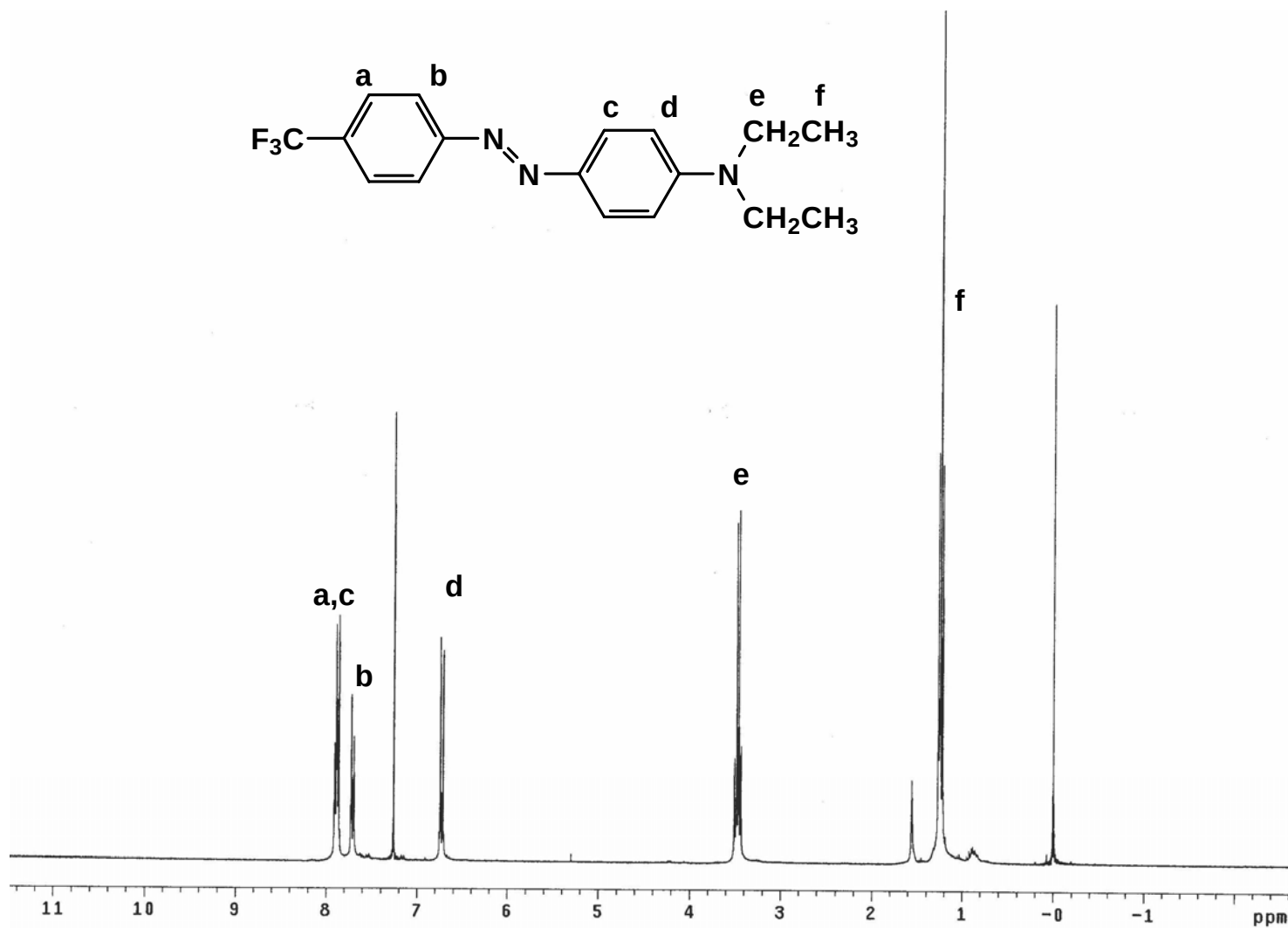


Figure A12. ^1H -NMR spectrum of dye (77) synthesized by conventional method.

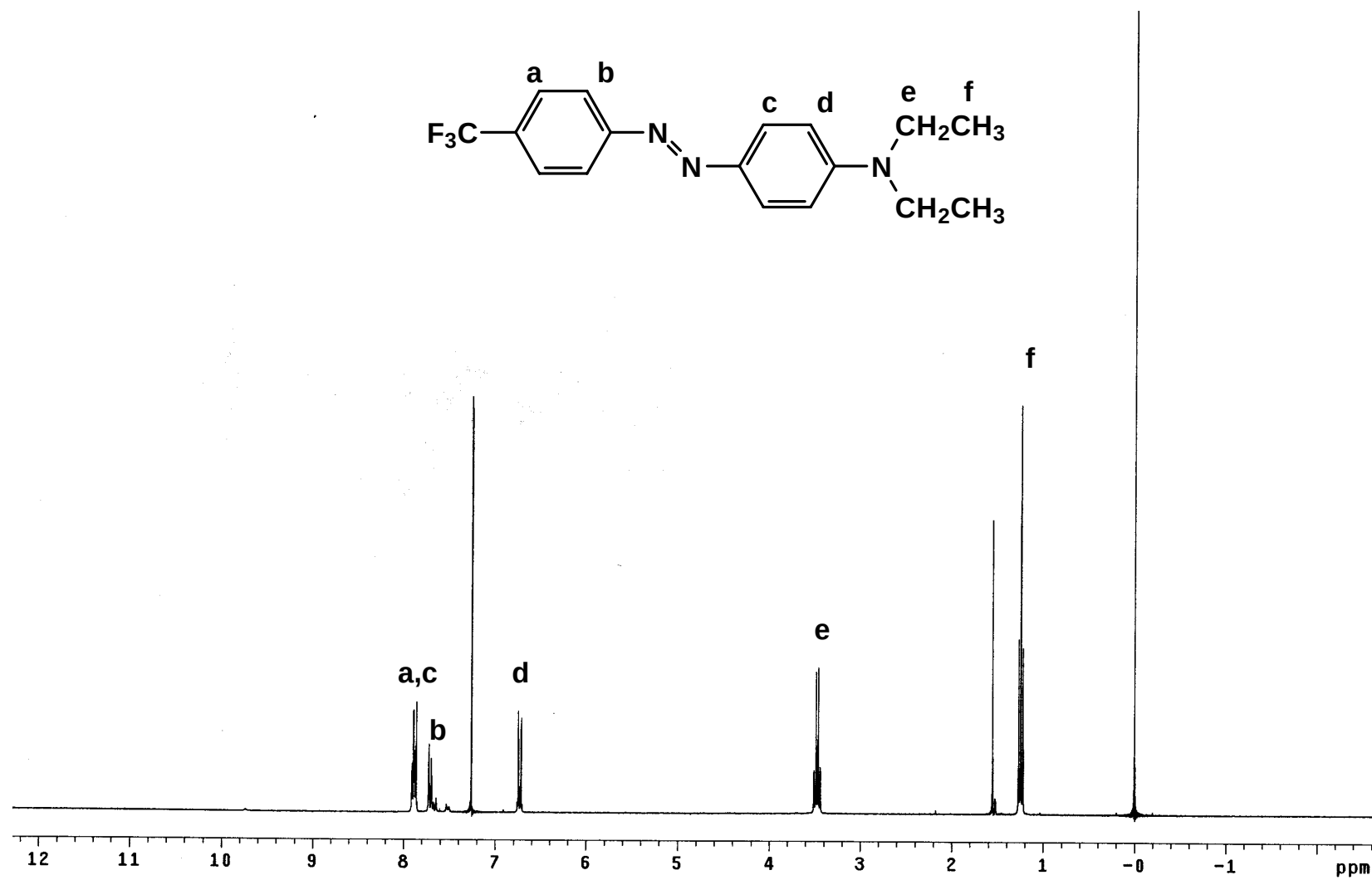


Figure A13. ^1H -NMR spectrum of dye (77) synthesized by SC-CO_2 .

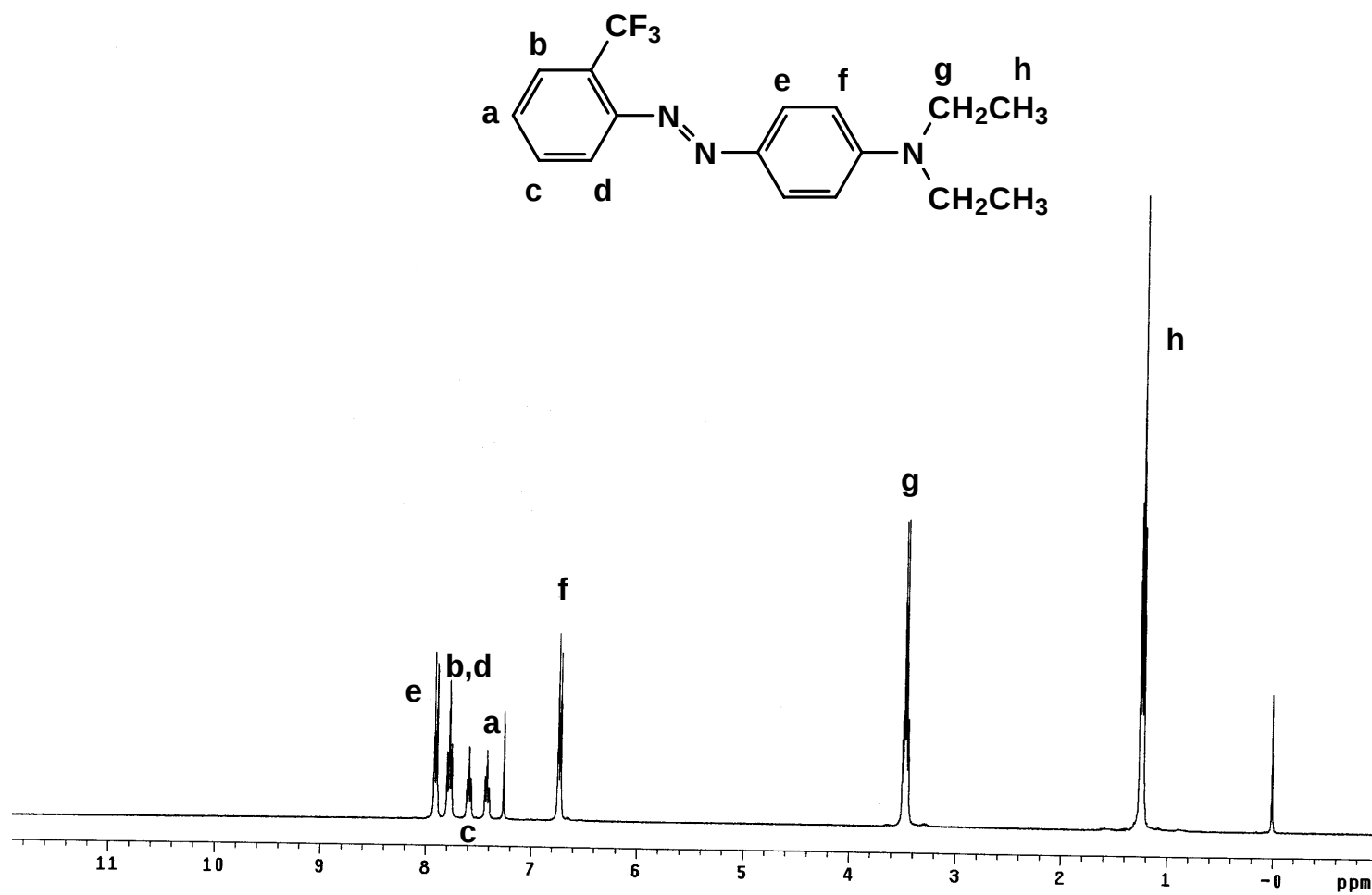


Figure A14. ^1H -NMR spectrum of dye (78) synthesized by conventional method.

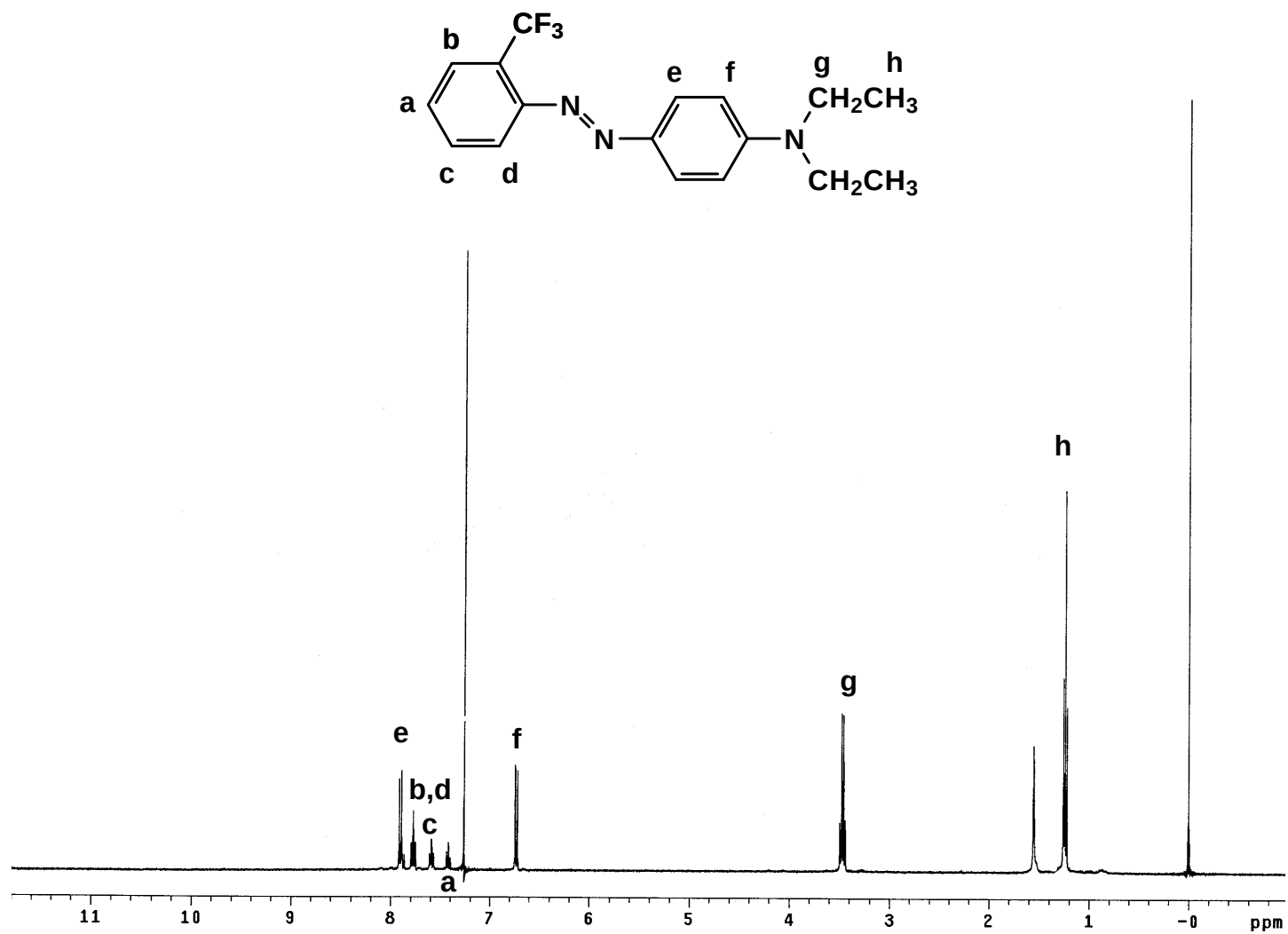


Figure A15. ^1H -NMR spectrum of dye (78) synthesized by SC- CO_2 .

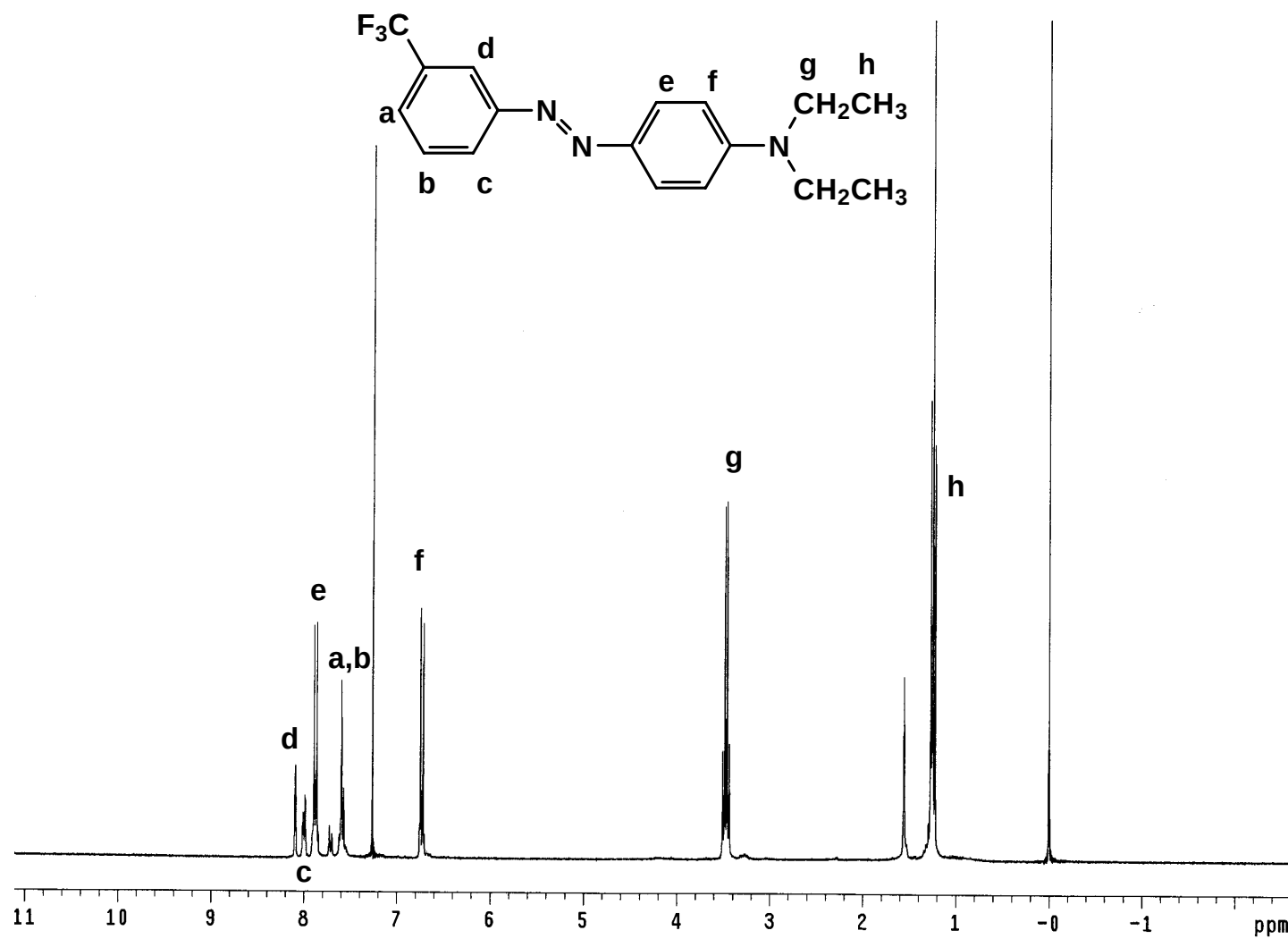


Figure A16. ^1H -NMR spectrum of dye (79) synthesized by conventional method.

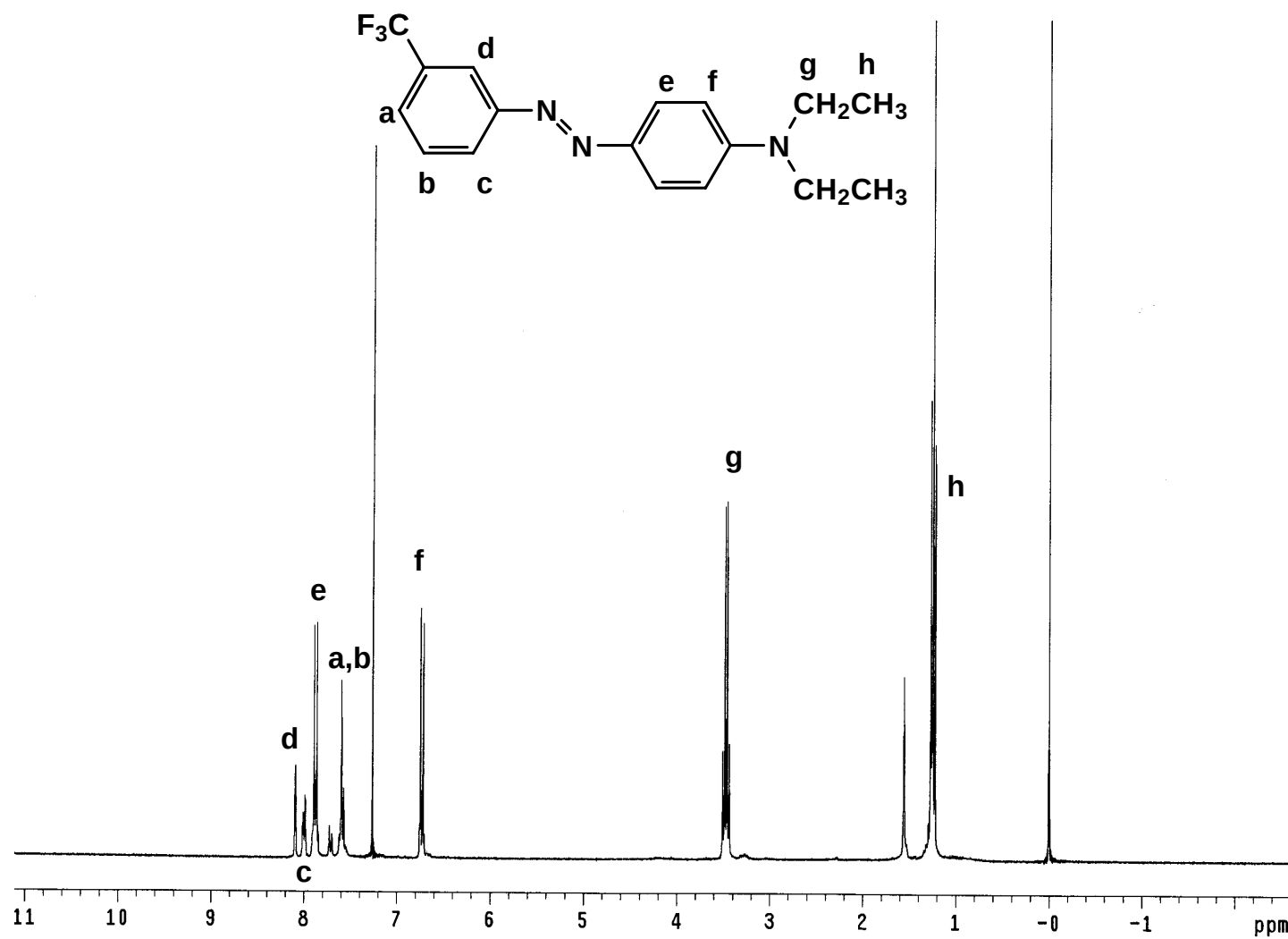


Figure A17. ^1H -NMR spectrum of dye (79) synthesized by SC- CO_2 .

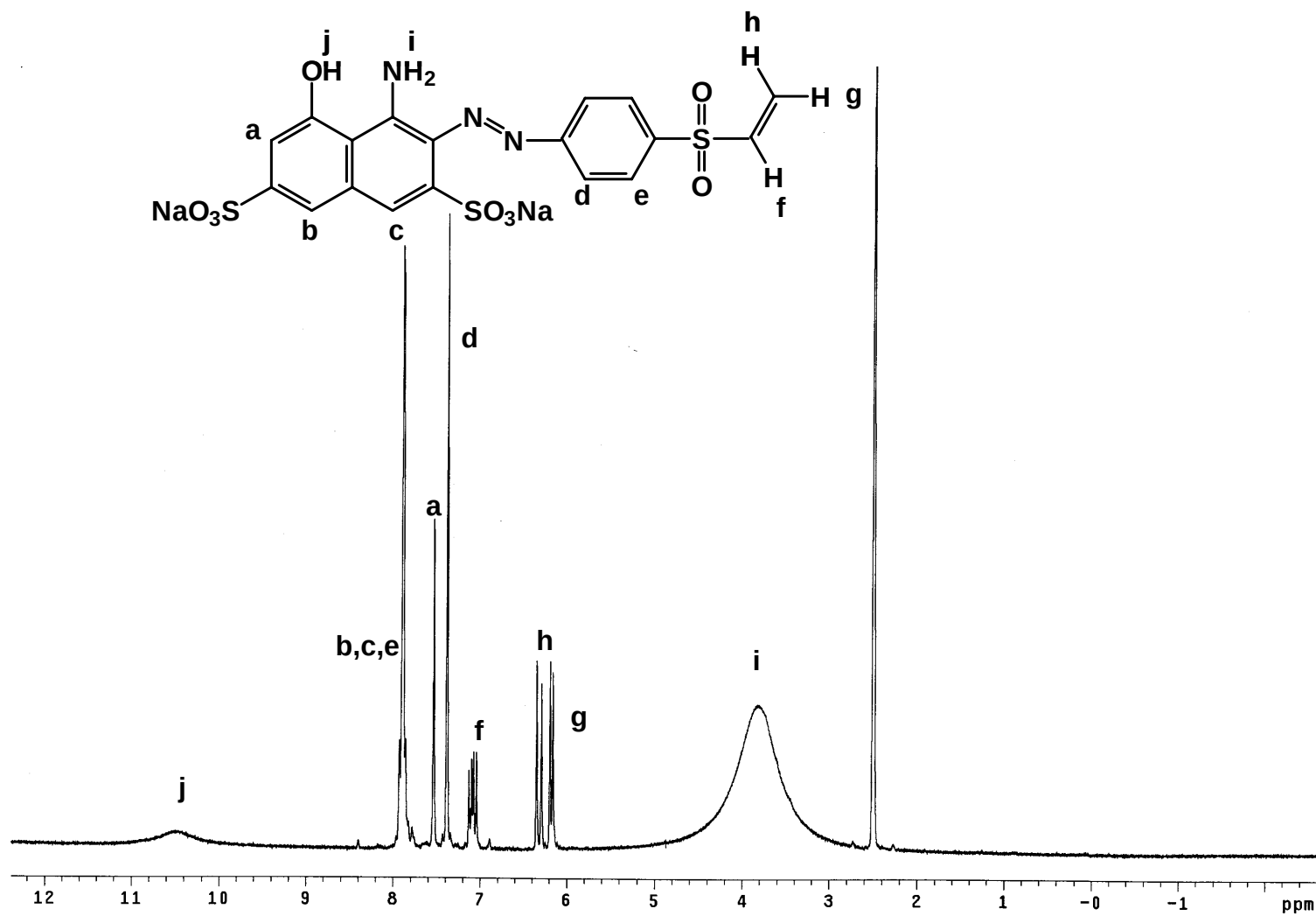


Figure A18. ^1H -NMR spectrum of dye (81) synthesized by conventional method.

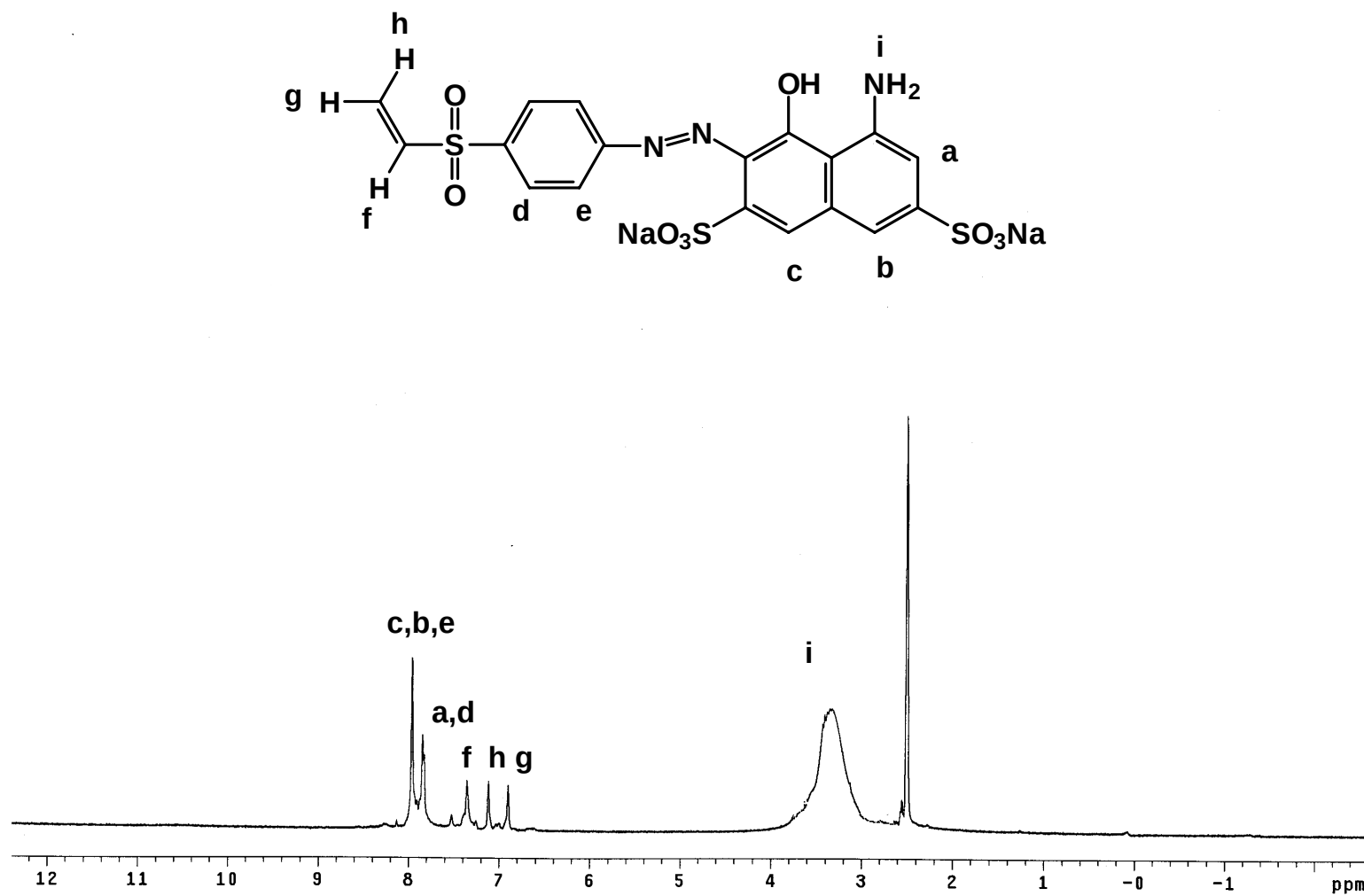


Figure A19. ^1H -NMR spectrum of dye (82) synthesized by conventional method.

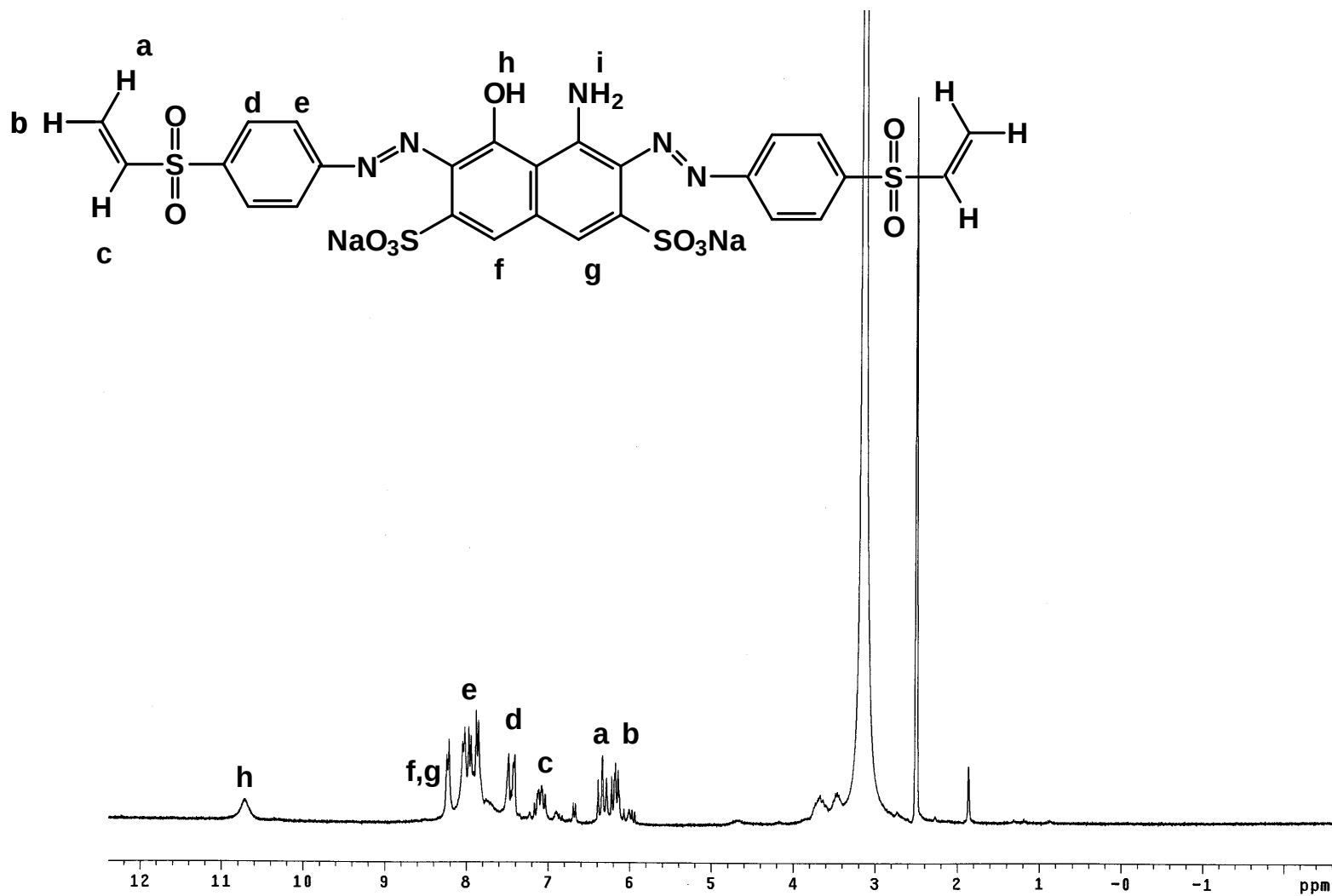


Figure A20. ^1H -NMR spectrum of dye (83) synthesized by SC- CO_2 .

Appendix B.
MASS SPECTRA

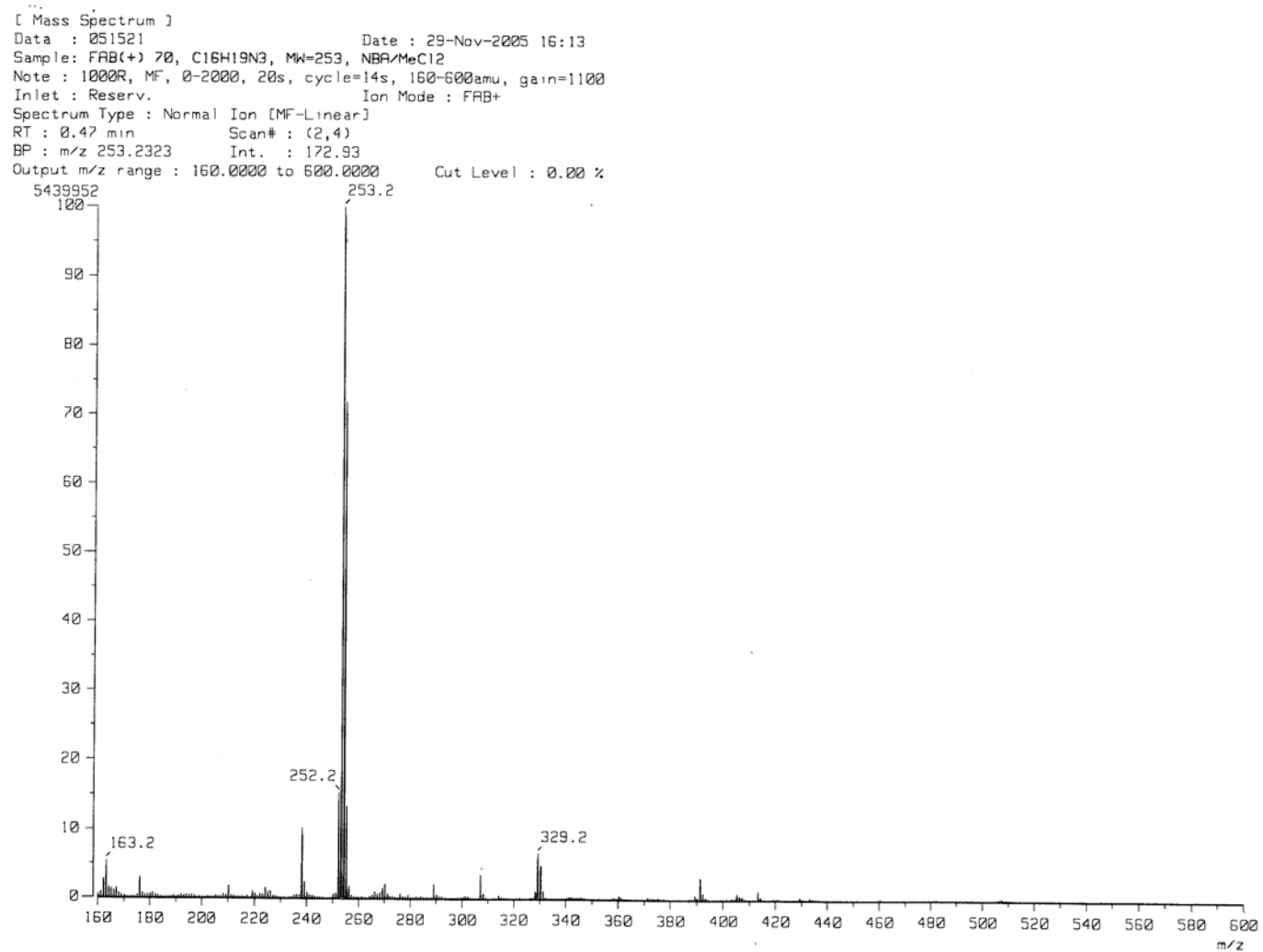


Figure B1. Positive ion FAB mass spectrum of dye (70) synthesized by SC-CO₂.

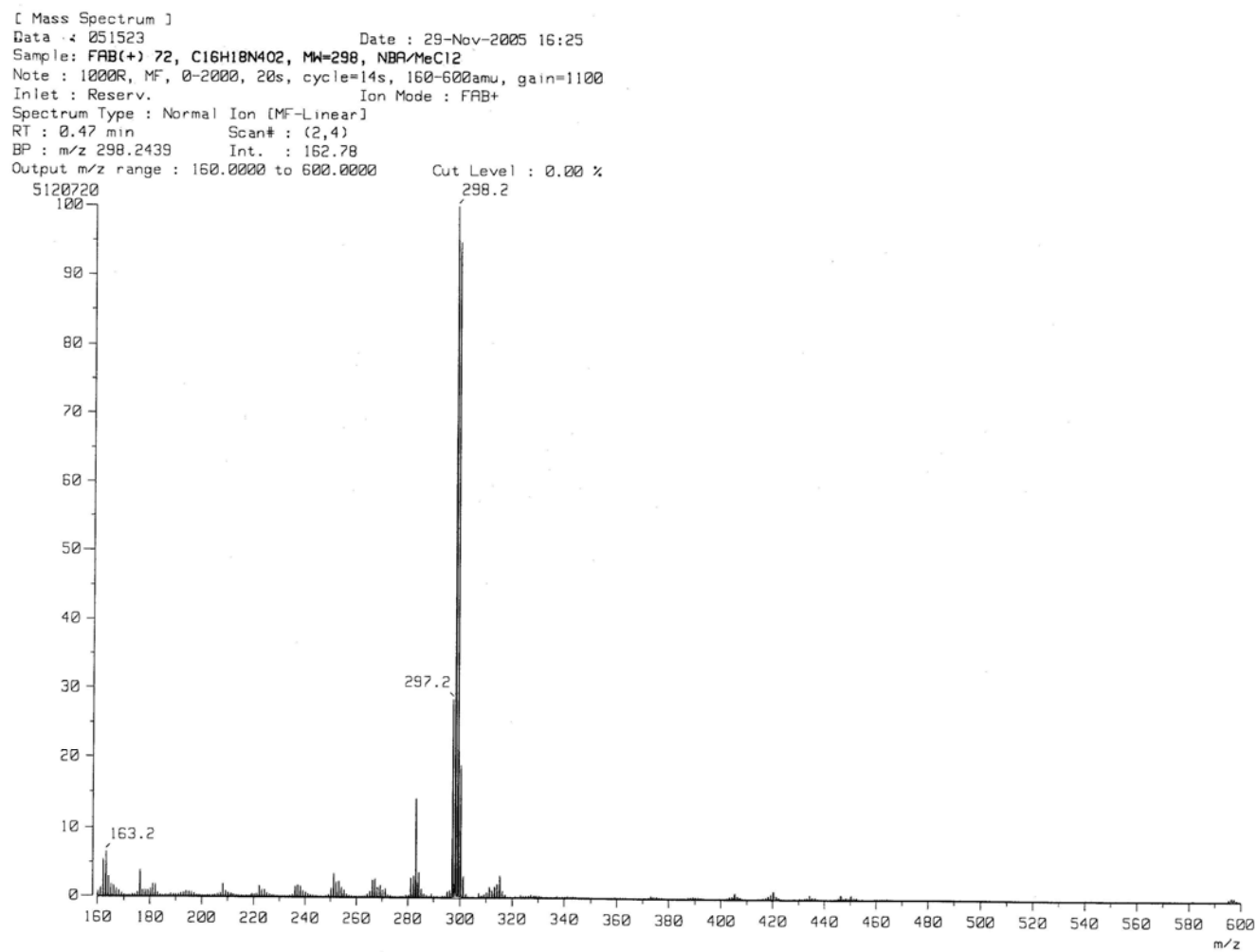


Figure B2. Positive ion FAB mass spectrum of dye (72) synthesized by SC-CO₂.

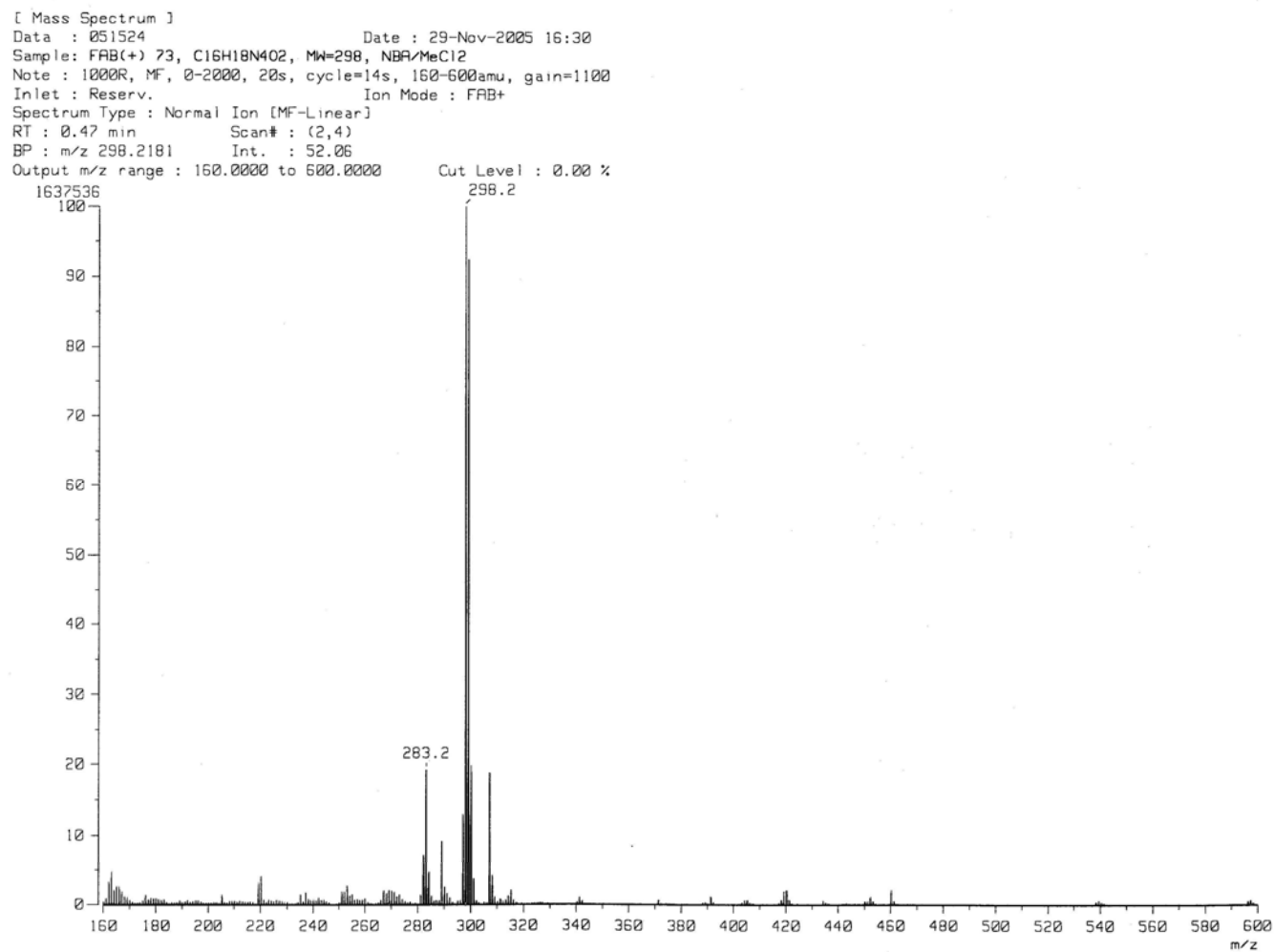


Figure B3. Positive ion FAB mass spectrum of dye (**73**) synthesized by SC-CO₂.

[Mass-Spectrum]
Data : 051525 Date : 29-Nov-2005 16:39
Sample: FAB(+) 76, C₁₈H₂₁N₃O₂S, MW=343, NBA/MeCl₂
Note : 1000R, MF, 0-2000, 20s, cycle=14s, 160-700amu, gain=1100
Inlet : Reserv. Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.47 min Scan# : (2,4)
BP : m/z 344.2317 Int. : 35.89
Output m/z range : 160.0000 to 700.0000 Cut Level : 0.00 %

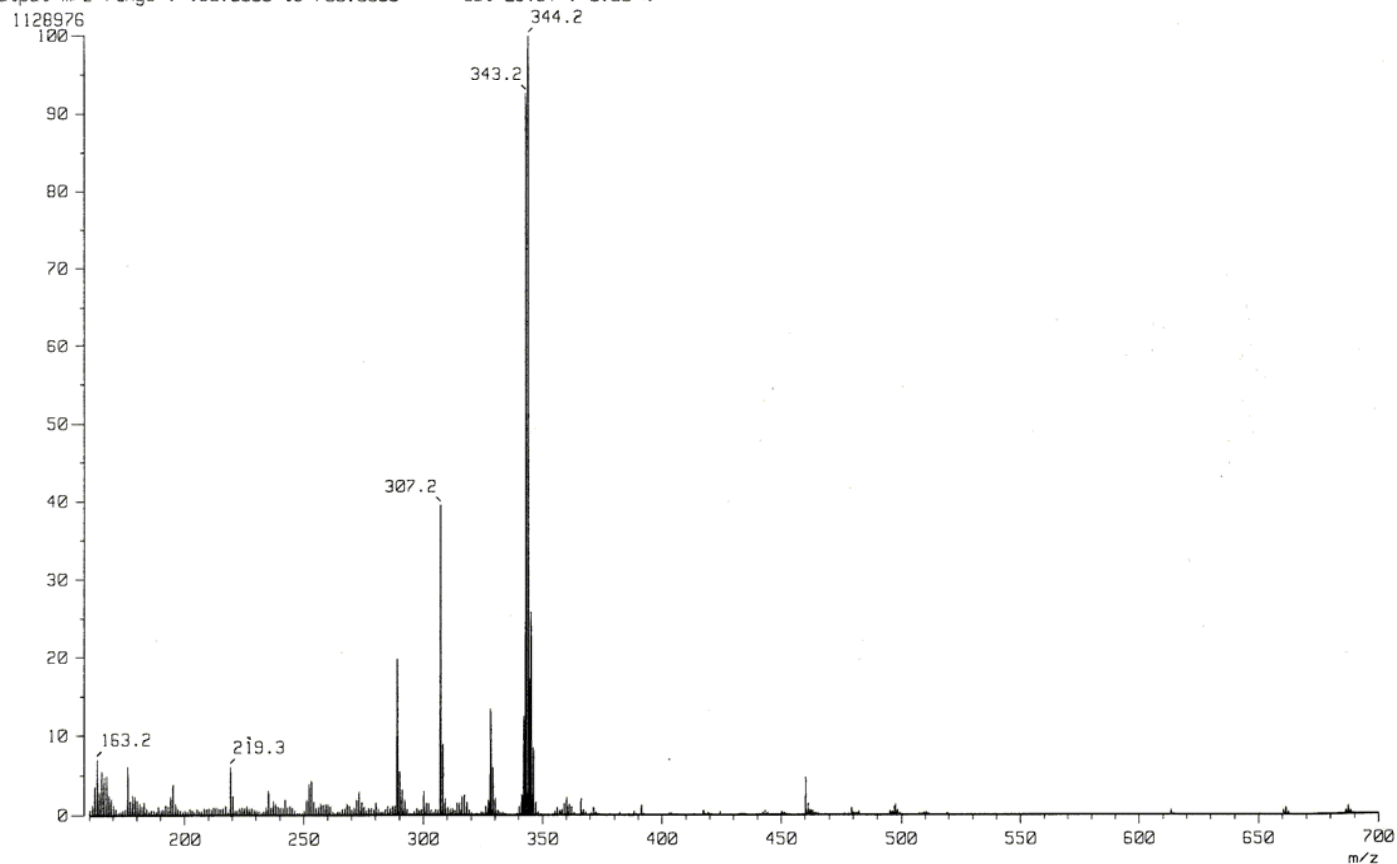


Figure B4. Positive ion FAB mass spectrum of dye (**76**) synthesized by SC-CO₂.

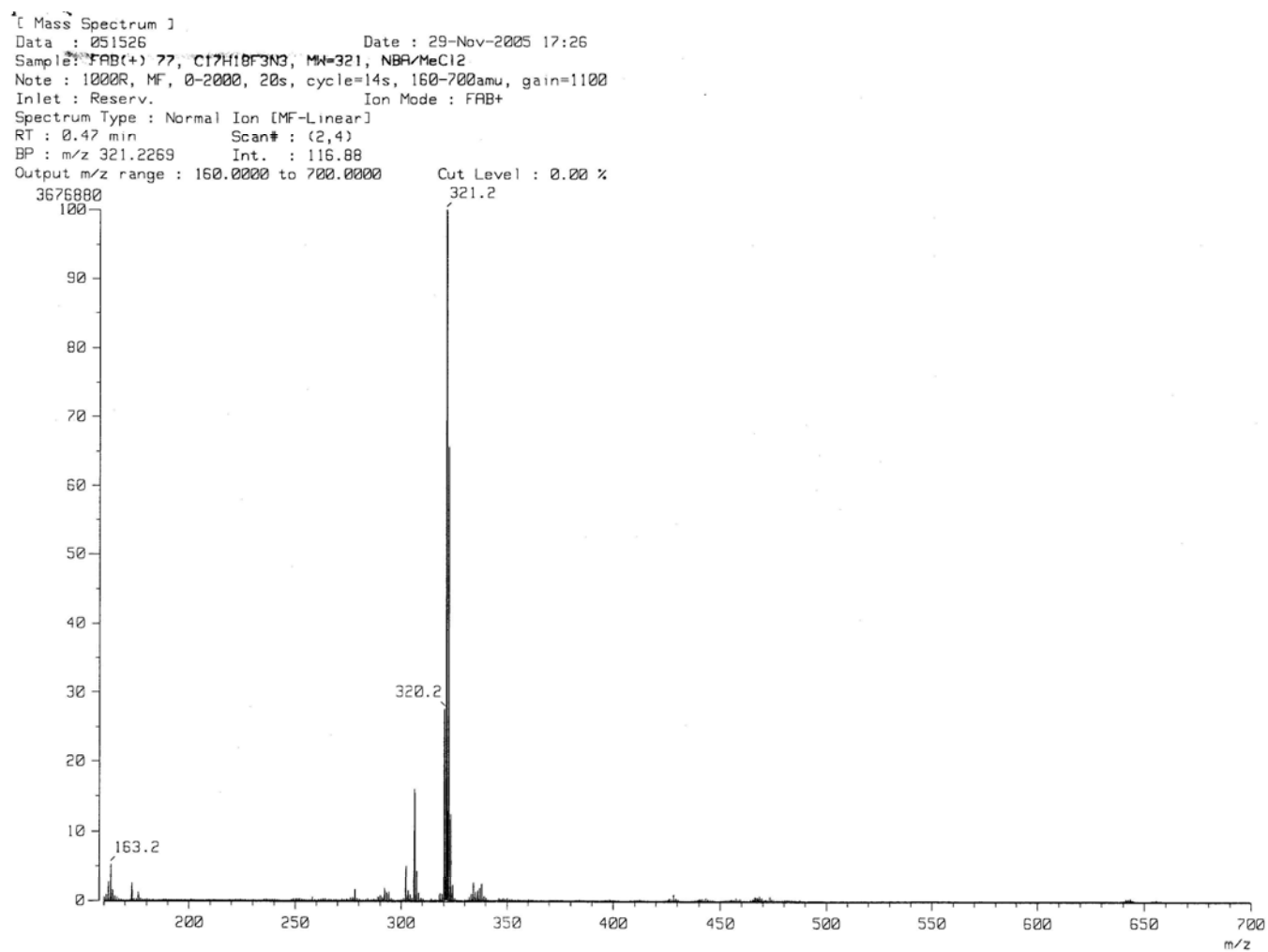


Figure B5. Positive ion FAB mass spectrum of dye (77) synthesized by SC-CO₂.

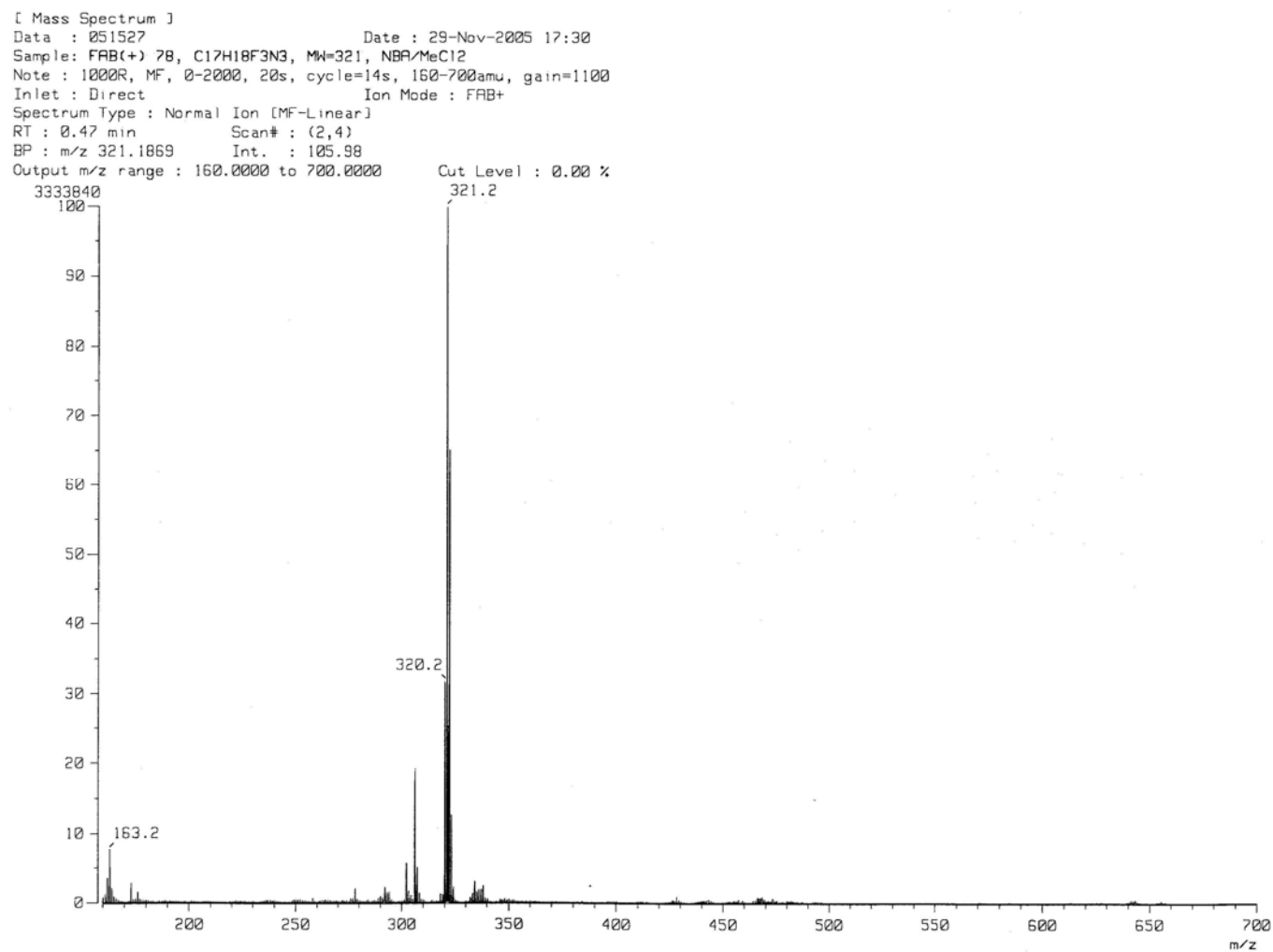


Figure B6. Positive ion FAB mass spectrum of dye (78) synthesized by SC-CO₂.

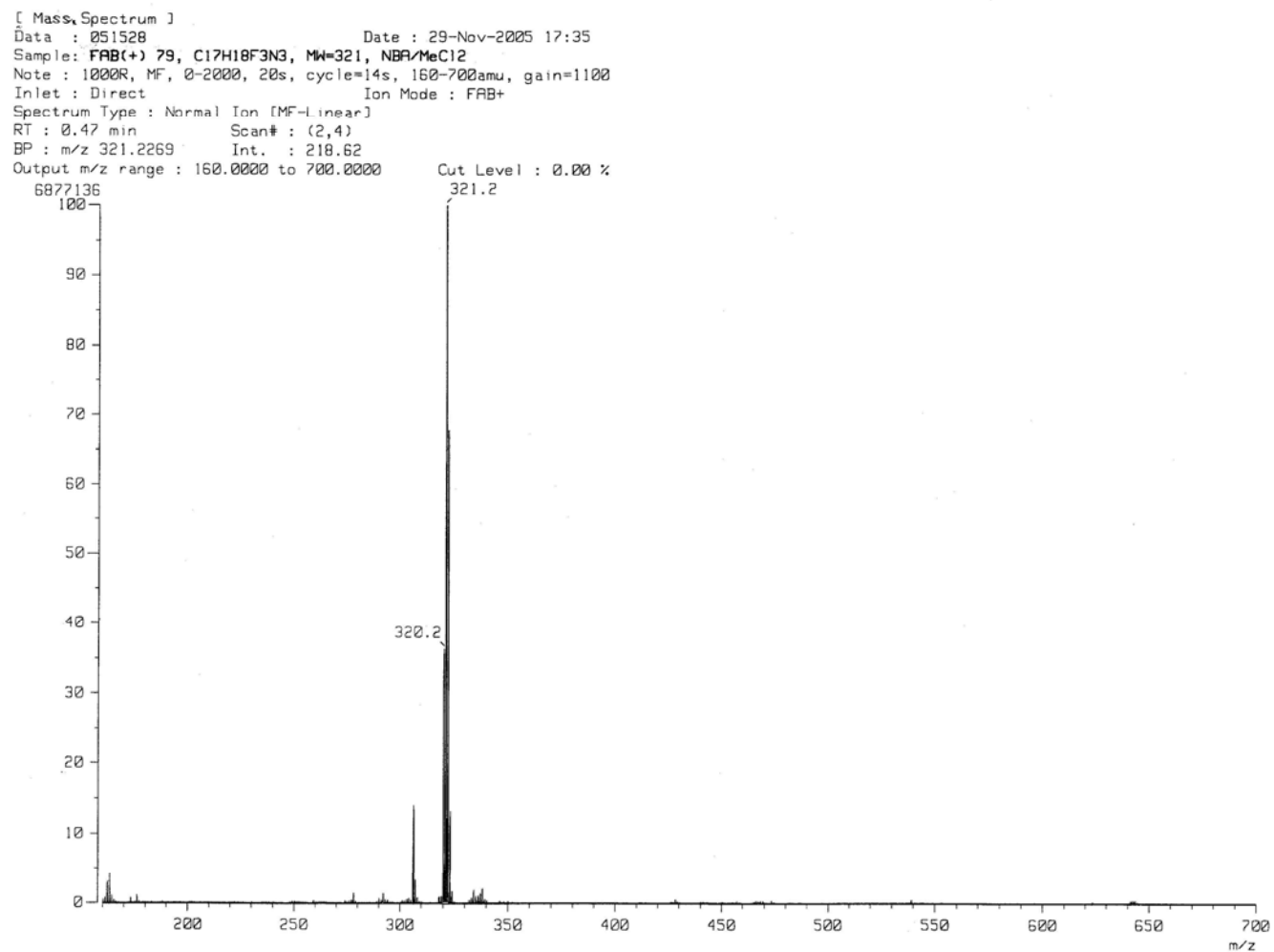


Figure B7. Positive ion FAB mass spectrum of dye (79) synthesized by SC-CO₂.