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A Kinetic Study on the Dissolution of two Naphthalimide Based Synthesized Disperse Dyestuffs in the Presence of Dispersing Agents

A. Khosravi[1*], K. Gharanjig[2], S. Moradian[3] and M. Hosseinnezhad[4]

[1] Assistant Professor, Amirkabir University of Technology, Faculty of Polymer and Color Engineering, P.O. Box: 15875-4413, Tehran, Iran.

[2] Associate Professor, Institute for Color Science and Technology, Department of Organic Colorants, P.O. Box: 16765-654, Tehran, Iran.

[3] Professor, Amirkabir University of Technology, Faculty of Polymer and Color Engineering, P.O. Box: 15875-4413, Tehran, Iran.

[4] Ph.D. Student, Amirkabir University of Technology, Faculty of Polymer and Color Engineering, P.O. Box: 15875-4413, Tehran, Iran.

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ABSTRACT

The water solubility kinetics of two synthesized mono azo naphthalimide based disperse dyestuffs in the presence of two different dispersing agents, namely Irgasol DAM and Lyoprint EV were investigated at various temperatures. An exponential equation was found to describe the dissolution process. Addition of Irgasol DAM and Lyoprint EV dispersing agents increased the dissolution rate of both synthesized dyestuffs. The dissolution of the methyl naphthalimide derived dyestuff in water as expected was more than the propylnaphthalimide derivative. The dyeing depth and the leveling properties were also higher for the methyl derivative than the propyl derivative.Prog. Color Colorants Coat. 4(2011), 107-112. Institute for Color Science and Technology.

1. Introduction

Disperse azo dyestuffs are extensively used for dyeing polyester and polyester blend fabrics. This class of dyestuffs constitute more than half of the total consumed disperse dyestuffs whilst effectively contributing to the completion of the attainable color gamut. Heterocyclic diazo and coupling components have undoubtedly contributed to such color gamut through the formation of extensive hues of high chroma [1, 2]. Heterocyclic napthalimide azo disperse dyestuffs of recent interest have good affinities for polyester fibers giving intense dyeings [3]. The hue range comprises yellowish to bluish reds of good wet and light fastness properties on polyester fibers. Although Extensive investigations on the synthesis of these dyestuffs have been done [4-6], the dyeing properties of these dyestuffs have been studied to a much lesser extent. It is shown that the dispersing dyes added to disperse dye baths stabilize the dye suspension and act as restraining and retarding agents. With some dyes, especially at low temperatures, the normal retarding effect is reversed, probably due to an increase in the rate of dissolution of dye crystalline particles in the

*Corresponding author: A.khosravi@aut.ac.ir

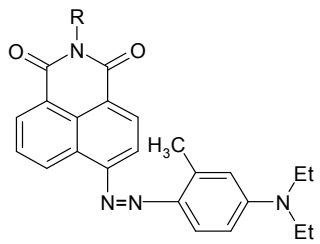
presence of dispersing agent [7, 8]. The effective parameters on dye solubility such as temperature, time and concentration of surfactants were investigated by UV-Vis spectrophotometry. The results demonstrate that the solubility of disperse dye were considerably increased at concentration above the surfactant CMC [9].

As their name implies, disperse dyestuffs are only sparingly soluble in water i.e. they disperse rather than dissolve in water. The degree of solubility of disperse dyestuffs in water will affect their dyeing properties which can be made to vary by adding dispersing agents. Although the degree of dissolution of disperse dyestuffs in water, the effect of temperature, concentration and type of dispersing agents have been extensively investigated [10, 11], it seems that the dissolution kinetics of monoazo disperse naphthalimide dyestuffs in water has not received much attention. The purpose of the present investigation was to study the influence of two different dispersing agents on the dissolution kinetics of two monoazo naphthalimide dyestuffs.

2. Experimental

All compounds used in this study are of analytical grade unless otherwise stated, and the equipments utilized in this research are as follows: UV-Vis spectrophotometry was carried out on a Cecil 9200 double beam transmission spectrophotometer. Molar extinction coefficients, absorption maxima and solvatochromic effects were also determined.

Two bluish red disperse dyestuffs i.e. dye 1 (methyl derivative) and dye 2 (propyl derivative) of the following structures were prepared in our laboratory at Amirkabir University of Technology. The synthesis of these two dyes is reported in our previous work [1]. Scheme 1 shows the chemical structures of used azo naphthalimide dyes.



For dye 1 R = CH_3 (methyl)

For dye 2 R = C_3H_7 (propyl)

Scheme 1: Chemical structure of the used azo naphthalimide dyes.

The water solubility of dye 1 (N-methyl naphthalimide-4-azo-N,N-Diethyl-m-toloidine) and dye 2 (N- propyl naphthalimide -4 –azo -N, N -Diethyl- m-toloidine) were determined by the modified Bird's method [12, 13], separately in the presence of 0.5% of Irgasol DAM and Lyoprint EV at temperatures of 25, 40 and 60 °C.

In order to investigate the dissolution kinetics, 0.02 g of each dyestuff was added to 100 ml of distilled water at the required temperature with constant shaking. Samples were drawn out from these mixtures at different time intervals. These samples were then filtered, mixed with a mixture of water and acetone (5:1) and the corresponding concentrations were determined using a Cecil 9200 UV-Visible transmission spectrophotometer.

3. Results and discussion

The kinetic isotherms (i.e. dye concentration versus time) were obtained at 60°C for dye 1 and dye 2 separately in the presence of Irgasol DAM and Lyoprint EV without dispersing agent.

The results showed that the solubility of dye 1 and dye 2 were increased in the presence of Lyoprint EV than in the presence of Irgasol DAM which in turn was greater than water alone. The solubility of dye 1 in water was greater than dye 2.

Figure 1 shows the dissolution isotherms at 60 °C for dye 1 and dye 2, respectively, in water alone in the presence of Irgasol DAM and Lyoprint EV.

It can be seen that the dissolution isotherms of the two dyestuffs in water follow an exponential function.

The dissolution kinetics of the two dispersed dyestuffs is given by the following exponential equation (1) [14]:

$$\text{Rate} = k\, S_o\, (C_s - C) \exp[-C/k] \qquad (1)$$

where k = Rate constant

S_o= Initial surface area of the solute

C_s= Saturation concentration

C = Current concentration of solute

This equation considers the surface area changes of the solute during dissolution, i.e. the change in the degree of dispersion as well as the change in the nature of the solid surface accessible to the solvent.

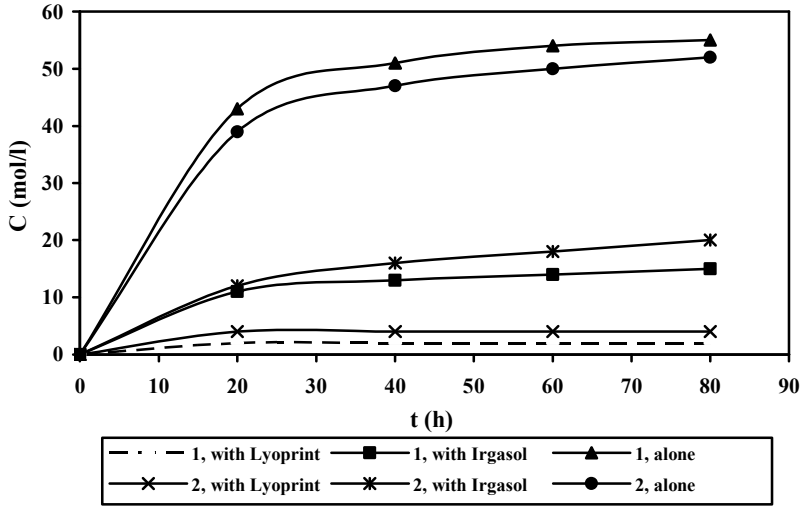


Figure 1: Kinetic isotherms of the synthesized dyestuffs

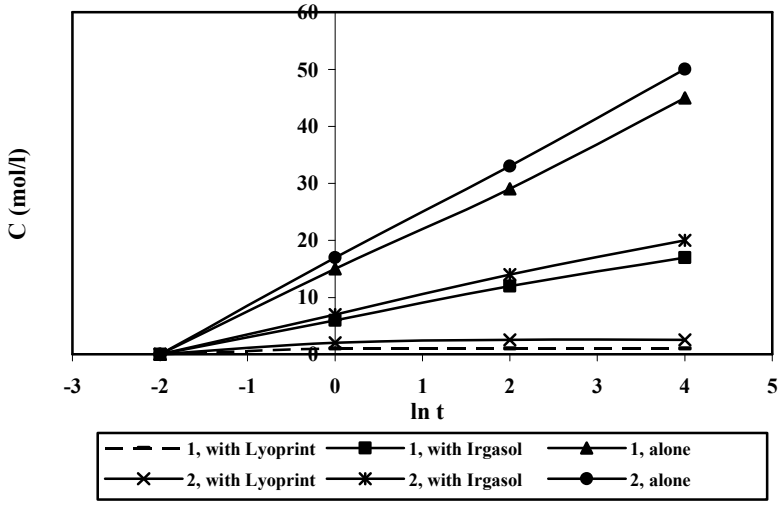


Figure 2: Variation of concentration with the logarithm of time, T= 60 ^{o}C.

When the concentration of the dye approaches the saturation, the exponential term dominates the dissolution kinetics and equation 1 can be expressed as follows:

$$r = k' \exp(-c/\kappa) \quad (2)$$

where r=Rate of dye solubilization
t= the elapsed time in minutes
k′= Constant

The approximate integral form of equation 1 (With $C/\kappa > 1$ and $\kappa/k << t$) is:

$$C = \kappa \ln k'/\kappa + \kappa \ln t \quad (3)$$

Hence, a plot of concentration versus ln t would be linear with a slope of κ and a constant of $\kappa \ln k'/\kappa$.

Such plots for dye 1 and dye 2 at 60 ^{o}C are given in Figures 1 and 2, respectively. This linearity was repeated for other investigated temperatures. Calculated values of k′ and κ are given in Table 1.

The current rates for the dissolution process were calculated using the following equation:

$$r = \kappa / t \quad (4)$$

While the initial rates for the same process were obtained from

$$r_o = K S_o C_s \quad (5)$$

The calculated values are listed in Tables 2 and 3. In order to calculate the current rate of dissolution, the Value of κ must be divided by value of time. The values of enthalpy of dissolution (i. e. ΔH) are calculated from the equations 6 and 7 and are shown in Table 4.

$$r_0 = A\exp(-\Delta H + E_0) / RT \quad (6)$$

$$r = (1/t)\, A\exp(-\Delta H/RT) \quad (7)$$

Dyestuffs 1 and 2 were then mixed separately with Irgasol and Lyoprint EV with 2:1 ratio of dyestuffs and dispersing agent in a ball mill for 48 hours. Locally produced polyester fabric was dyed separately with 0.1, 0.3, 0.5, 0.7, 1, 1.5, 2 and 4 percent on the weight of fiber (o.w.f) of each dyestuff using 0.5% (o.w.f) acetic acid and HT dyeing method. Layers of fabric with complete opacity were measured at various intervals along the surface of the fabric by Gretag-Macbeth reflectance spectrophotometer.

Investigating the dyed polyester with two dyestuffs and two dispersing agents indicates that the colour of the fabric dyed with Lyoprint EV as the dispersing

Table 1: Values of coefficients K' and κ.

Dyestuff		k′					
		25	40	60	25	40	60
Dye 1	Water alone	0.3615	0.403	0.5579	0.1998	0.278	0.3434
	With Irgasol DAM.	1.631	2.160	3.31	0.7119	0.982	1.534
	With Lyoprint EV	4.804	8.142	13.058	1.405	2.57	5.22
Dye 2	Water alone	0.4112	0.3463	0.558	0.1554	0.2111	0.3105
	With Irgasol DAM	1.089	1.603	2.536	0.869	0.965	1.427
	With Lyoprint EV	3.77	8.616	12.146	1.629	2.341	4.327

Table 2: Rates of dissolution of dyestuff 1 in water (mg/l.h).

	Without dispersing agent			With Irgasol DAM			With Lyoprint EV		
t(h)	25	40	60	25	40	60	25	40	60
0	1.24	1.66	1.92	6.14	8.43	12.9	20.79	32.75	57.15
0.25	0.622	0.84	1.24	2.85	3.93	6.12	5.62	10.28	20.88
0.5	0.311	0.42	0.621	1.42	1.96	3.06	2.81	5.14	10.44
1	0.155	0.211	0.31	0.71	0.982	1.53	1.405	2.57	5.22
2	0.078	0.11	0.155	0.36	0.49	0.765	0.70	1.28	2.61
3	0.052	0.07	0.10	0.237	0.33	0.51	0.43	0.86	1.74
4	0.039	0.053	0.078	0.179	0.245	0.38	0.35	0.64	1.305
5	0.031	0.042	0.062	0.14	0.196	0.306	0.28	0.51	1.04
6	0.026	0.035	0.052	0.119	0.164	0.255	0.234	0.43	0.87
7	0.022	0.03	0.044	0.10	0.14	0.218	0.20	0.37	0.75
8	0.019	0.026	0.039	0.089	0.122	0.19	0.175	0.32	0.65

agent is deeper than that of Irgasol DAM (Figures 2 and 3).

This is because of more improved dissolution of the dyestuff in water. According to the results shown in Tables 2 and 3, the dissolution rate of the two dyestuffs in water is more than with Irgasol DAM compare with Lyoprint EV.

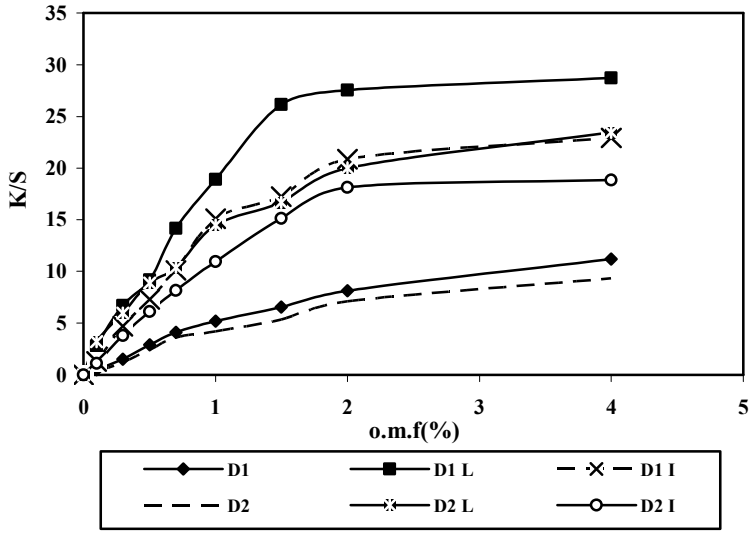


Figure 3: Dyestuffs build up on polyester fabrics.

Table 3: Rates of dissolution dyestuff 2 in water (mg/l.h)

	Without dispersing agent			With Irgasol DAM			With Lyoprint EV		
t(h)	25	40	60	25	40	60	25	40	60
0	1.25	1.42	2.13	5.7	6.72	10.10	16.86	27.32	46.70
0.25	0.62	0.84	1.24	3.48	3.86	5.71	5.62	9.36	17.3
0.5	0.31	0.42	0.621	1.74	1.93	2.85	2.81	4.68	8.65
1	0.16	0.21	0.31	0.87	0.965	1.43	1.41	2.34	4.33
2	0.08	0.106	0.16	0.43	0.48	0.71	0.70	1.17	2.16
3	0.05	0.070	0.10	0.29	0.32	0.48	0.468	0.78	1.44
4	0.04	0.053	0.078	0.217	0.24	0.36	0.35	0.59	1.08
5	0.031	0.42	0.062	0.174	0.193	0.285	0.281	0.47	0.87
6	0.26	0.035	0.052	0.145	0.16	0.238	0.234	0.39	0.72
7	0.22	0.030	0.044	0.124	0.138	0.20	0.20	0.33	0.62
8	0.019	0.026	0.039	0.11	0.120	0.178	0.176	0.29	0.54

Table 4: Dissolution enthalpy.

Dispersing agent	Enthalpy ΔH (KJ/mol)	
	Dye 1	Dye 2
Water alone	13.321	15.88
Irgasol DMA	-17.59	-12.125
Lyoprint EV	-30.27	-22.71

The dissolution of Dyestuff 1 in water is more than Dyestuff 2 which may be attributed to the less molecular weight of Dyestuff 1 in comparison with Dyestuff 2. Also, Dyestuff 2 is more hydrophobic than Dyestuff 1. The measured colour coordinates of dyed fabrics are given in Table 4.

4. Conclusions

The controlling kinetics of the water solubility of two synthesized mono azo naphthalimide based disperse dyestuffs in the presence of two different dispersing agents namely Irgasol DAM and lyoprint EV agents at various temperatures were investigated. Lyoprint EV is a non-ionic dispersing agent based on fatty alcohol ethylene oxide addition compound and is suitable for dyeing. The dissolution kinetics of azo naphthalimide dispersed dyes in the presence of dispersing agents follow an exponential rate equation.

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