

Affinity of disperse dyes on poly(ethylene terephthalate) in non-aqueous media: part 1. Adsorption and solubility properties

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Abstract

Various non-aqueous media were employed to examine the adsorption and solubility properties of disperse dyes on poly(ethylene terephthalate). The dye adsorptions in alkane media were much higher than those in other non-aqueous systems. The adsorption of disperse dyes on poly(ethylene terephthalate) increased with decreasing number of carbon atoms of alkane groups. In the case of relationships between dye adsorption and dye solubility in various non-aqueous media, the adsorption of the dye is linearly and inversely proportional to the dye solubility in the logarithmic plot. The adsorption dependency on the solubility of dyes was shown to have a similar pattern for different disperse dyes.

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1. Introduction

In the textile industries, fiber materials such as polyamide, polyester, cellulose acetate, polyacrylonitrile and polyurethane are subjected to the coloration process using various commercial dyes. In this application method, the dyes are usually dissolved or dispersed in a proper exhaustion medium and then diffused into the polymer molecules. At the end of the process, the treated effluents containing residual dyes and additives are released into the aquatic environments after complicated wastewater treatments. Although sewage treatment works are applied to the effluent, it is well accepted that this wastewater still provides eco-toxic hazard influences

to the environments [1]. In addition, although much attention has been focused on recycling of the residual dyebath, this approach has not enjoyed widespread use due to the disadvantages on the financial side.

In the other aspect, the development of non-aqueous solvent dyeing technology using tetrachloroethylene on poly(ethylene terephthalate) fiber has received much attention and numerous research articles have reviewed this topic [2–8]. However, very little of this activity has been transferred to the direct coloration applications. In this work, non-aqueous solvents with several different groups have been used to investigate the fundamental exhaustion properties of disperse dyes. In this context, a number of organic solvents were considered as possible exhaustion media and the results are discussed in terms of the adsorption of disperse dyes onto poly(ethylene terephthalate) substrate and their solubility properties.

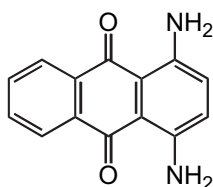
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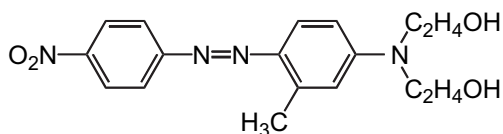
2. Experimental

2.1. Materials

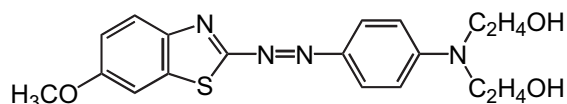
The poly(ethylene terephthalate) substrate used in this experiment was a plain-weaved fabric (75 denier/36 filaments, 106×97 yarns/inch, 70 ± 5 g/m³) which was scoured in a 0.1% non-ionic surfactant solution at 90 °C for 1 h and then rinsed with distilled water repeatedly. Acetone extraction was carried out in a soxhlet extraction apparatus to purify three commercial disperse dyes, namely C. I. Disperse Violet 1, C. I. Disperse Red 17 and C. I. Disperse Red 58 and the purified dyes were then recrystallized in ethanol. The organic solvents employed as non-aqueous media were first grade reagents and were used without further purification.



C. I. Disperse Violet 1



C. I. Disperse Red 17



C. I. Disperse Red 58

2.2. Adsorption

Disperse dyes (0.005 g) were adsorbed on poly (ethylene terephthalate) substrate (0.2 g) using non-aqueous media (50 ml) in sealed stainless steel pots at 130 °C for 1 h. Upon completion of dye adsorption, the dyed samples were completely washed with acetone and dried in a vacuum oven. The dried samples were weighed and then dyes were extracted from dyed substrates using *N,N*-dimethylformamide at 95 °C. The extracted dye concentrations were measured using a UV–vis spectrophotometer and the extent of adsorption was calculated.

2.3. Partition coefficient

Different concentrations of the dye (0.004, 0.01, 0.02, 0.03 g/l) were adsorbed on fiber substrate (0.01 g) in

non-aqueous media (50 ml). The exhaustion was carried out at 130 °C for 1 h. At the end of dyeing, an extraction of dyed samples using *N,N*-dimethylformamide was carried out. The amount of the adsorbed dyes on the substrates and the amount of the residual dyes in the solution were determined by measuring the absorbance of both dyes, respectively, using a UV–vis spectrophotometer. The adsorbed amount of dyes ($[D]_{ad}$) was plotted against the residual dye concentrations ($[D]_s$) and the partition coefficient (K) was obtained from the slope of the plots [9,10].

$$[D]_{ad} = K[D]_s \quad K = [D]_{ad}/[D]_s$$

2.4. Solubility

In order to measure the solubility of disperse dyes in non-aqueous media, an excess amount of the dyes was placed in 10 ml of the solvents at 25 °C for 48 h. The solutions were centrifuged to separate undissolved dyes and then filtered out to eliminate undissolved dye solutes. The concentration of the dyes in this solution was measured spectrophotometrically and the solubility of the dyes in each medium was then calculated.

3. Results and discussion

3.1. Adsorption of C. I. Disperse Violet 1 in non-aqueous media

To investigate the feasibility of non-aqueous media as an exhaustion bath, 29 different kinds of solvents including water were examined to determine the adsorption properties of C. I. Disperse Violet 1 on poly (ethylene terephthalate) substrate. The results for dye adsorption are shown in Fig. 1. This figure shows that the amounts of dye adsorption in most non-aqueous media were very low (0–3 mmol/kg). However, the dye adsorption in hexane was of very high value (13.18 mmol/kg) when compared to that with water (16.09 mmol/kg). This result was superior to the finding in tetrachloroethylene (1.56 mmol/kg) as a commonly considered non-aqueous bath. It is quite interesting to note from Fig. 1 that hexane was a good adsorption medium for disperse dyes on poly(ethylene terephthalate) substrate. Although tetrachloroethylene has been generally recognized as the most effective solvent for adsorption of disperse dyes on poly(ethylene terephthalate) fiber and extensive researches with tetrachloroethylene have been conducted over the last few decades [2–8], the tetrachloroethylene medium exhibited a poor adsorption result.

Consequently, several homologous series of alkanes including hexane were further investigated as shown in

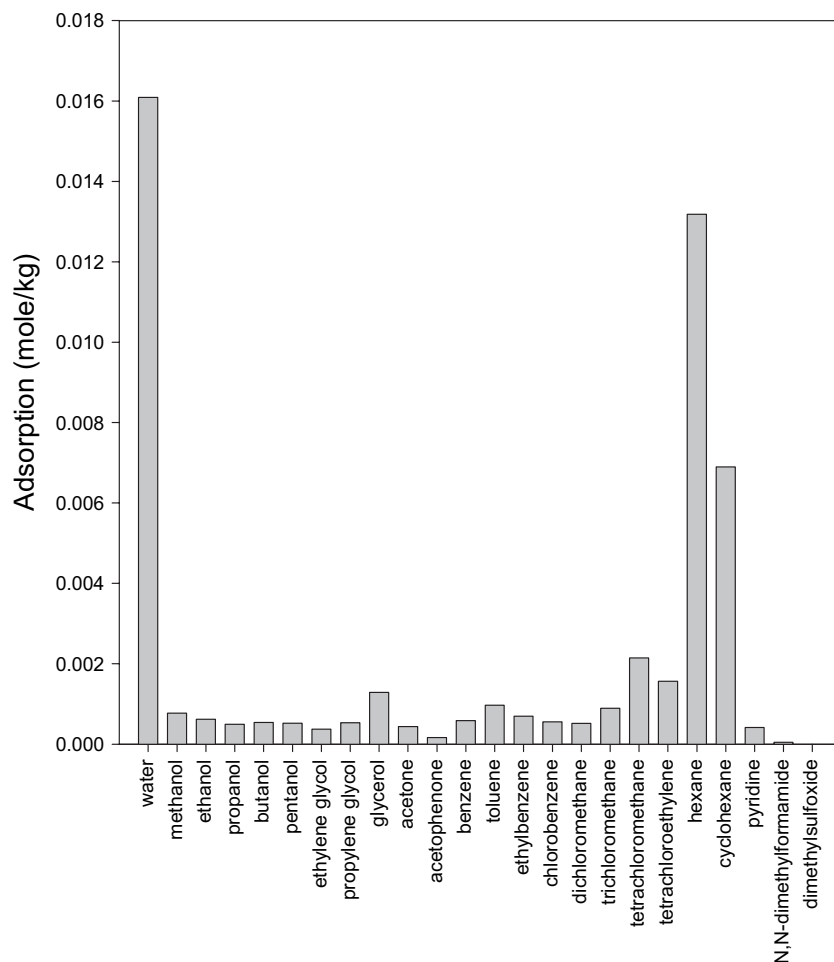


Fig. 1. Adsorption of C. I. Disperse Violet 1 on poly(ethylene terephthalate) substrate in non-aqueous media.

Fig. 2. In the range from pentane to decane, as the number of carbon atoms in the alkane decreased, the dye adsorption gradually increased and finally the amount of dye adsorption in pentane exceeded the value in water.

3.2. Partition coefficient

The adsorption mechanism of disperse dyes on hydrophobic substrates is generally explained by the solid solution theory. Regardless of the dye concentration in the adsorption medium, the dye distribution between the substrate and the adsorption medium is usually constant [10,11]. In other words, the adsorption amount of disperse dyes onto substrates is linearly proportional to the concentration of the dyes in the dye solutions at a constant temperature. This type of adsorption mechanism is well known as *Nernst's* adsorption isotherm [9,10]. The slope of this isotherm represents the corresponding partition coefficient (K) of the dyes between fiber substrate and solution. The adsorption isotherm and the partition coefficient of C. I. Disperse Violet 1 are shown in Fig. 3 and Table 1. Fig. 3 and Table 1 display that, indeed, the adsorptions of C. I.

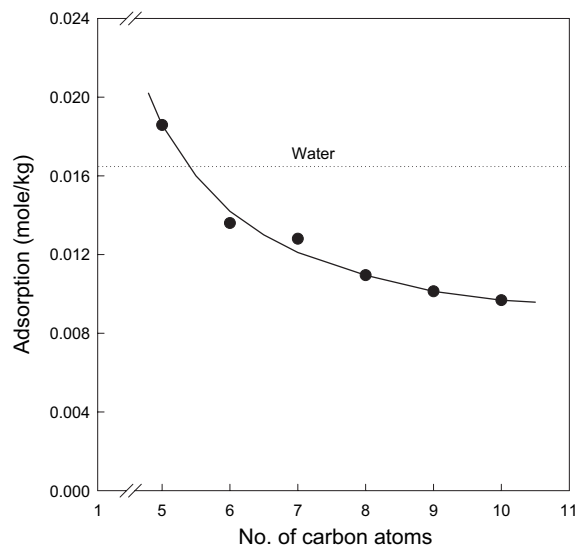


Fig. 2. Adsorption of C. I. Disperse Violet 1 on poly(ethylene terephthalate) substrate in alkane series.

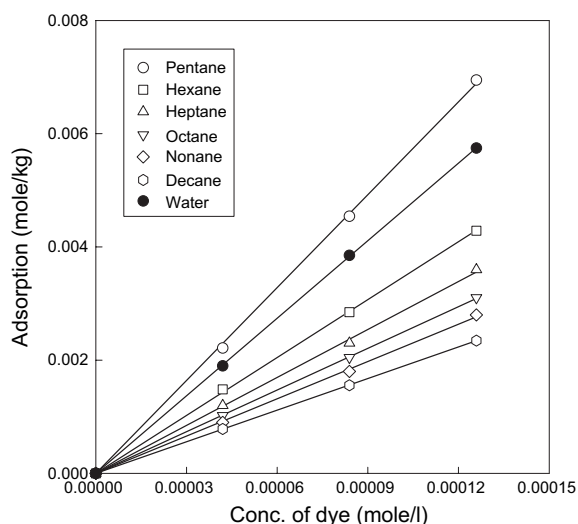


Fig. 3. Adsorption isotherms of C. I. Disperse Violet 1 on poly(ethylene terephthalate) substrate in alkane series.

Disperse Violet 1 on fiber substrates are linearly proportional to the concentrations of the dye in all adsorption media. Especially, C. I. Disperse Violet 1 shows higher affinity to the substrate in pentane medium than in water.

Table 1

Partition coefficients of C. I. Disperse Violet 1

Solvent	Partition coefficient (K)
Water	45.68
Pentane	54.71
Hexane	34.11
Heptane	28.26
Octane	24.54
Nonane	21.96
Decane	18.61

3.3. Solubility of C. I. Disperse Violet 1 in non-aqueous media

It is well known that in water, the adsorption of disperse dyes on poly(ethylene terephthalate) substrate occurs by the hydrophobic interactions between hydrophobic dyes and hydrophobic substrates. In terms of solubility of dyes, water has little effect to dissolve disperse dyes due to its characteristic as a hydrophilic dyeing medium [10,11]. Therefore, the solubility of dyes is a very important factor to determine their adsorption behaviors in a non-aqueous exhaustion system [8]. In this study dye solubility in various non-aqueous media was also measured to determine the relationship with dye adsorption. The results are displayed in Figs. 4 and 5.

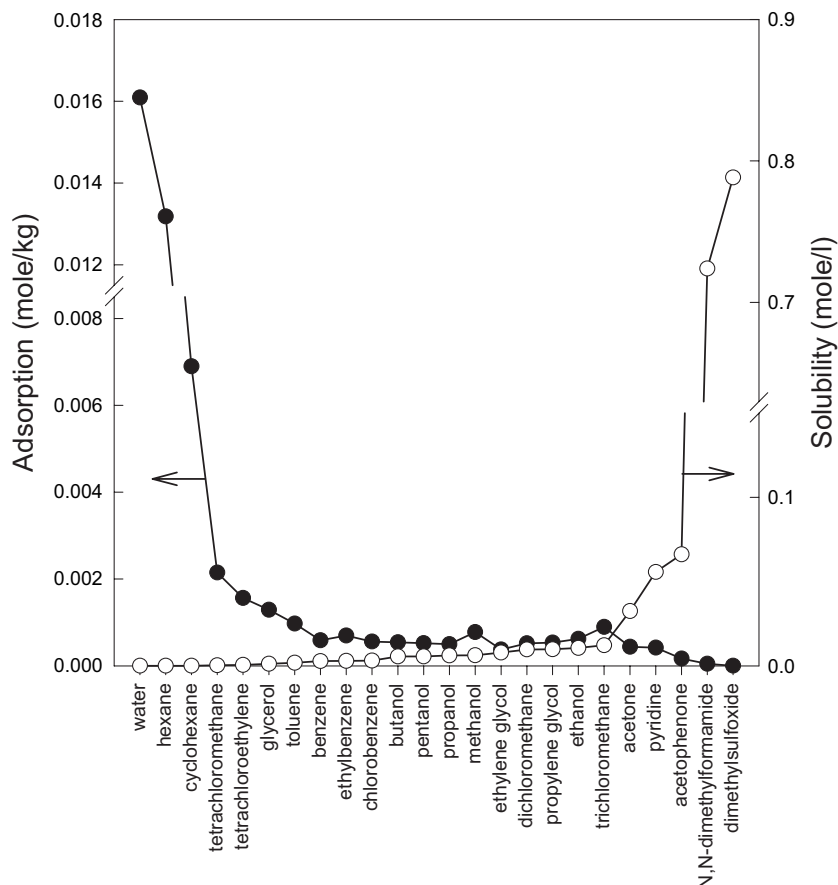


Fig. 4. Adsorption and solubility of C. I. Disperse Violet 1 on poly(ethylene terephthalate) substrate in various non-aqueous media.

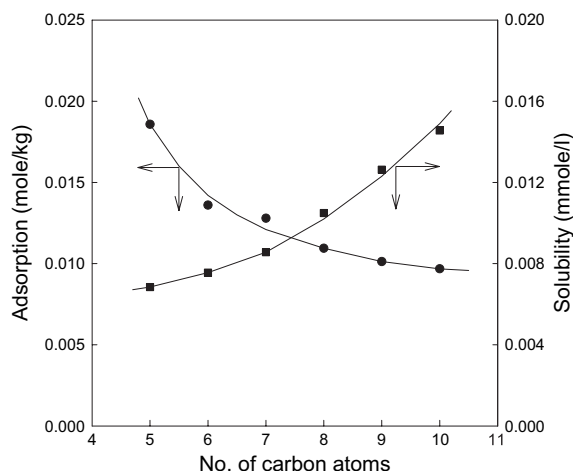


Fig. 5. Adsorption and solubility of C. I. Disperse Violet 1 on poly(ethylene terephthalate) substrate in alkane media.

Fig. 4 shows the results of non-aqueous exhaustion systems that adsorption amounts of the dye on poly(ethylene terephthalate) substrate were inversely proportional to the solubilities of the dye. The adsorption amount in water was of high value. This is attributable to the characteristic of dye solubility in water: an extremely small amount of disperse dyes could be dissolved in water. Whereas, dimethylsulfoxide system indicates the reverse observations: high dye solubility in this medium was observed and little amount of dye adsorption on fiber substrates was achieved. It is concluded from these findings that while the solubility of dyes in the bath increased, the dye adsorption onto substrate dramatically decreased.

Fig. 5 shows the further experimental results in only alkane media that the number of carbon atoms of alkanes influenced different dyeing behaviors of the dyes in terms of adsorption and solubility properties. As the number of carbon atoms of alkanes increased, solubility of the dye increased. In the case of dye adsorption, the amount of dye adsorption decreased with increasing number of carbon atoms.

3.4. Relationship between dye adsorption and dye solubility

To determine the direct relationship between dye adsorption and dye solubility, the amount of dye adsorption was plotted against the dye solubility using a logarithmic scale. Fig. 6 shows an inversely proportional relationship between dye adsorption and dye solubility. This result clearly confirms that the dye adsorptions in alkanes are much greater than those in other media and that alkane media can be considered worthwhile to be employed as an exhaustion bath. Water is the only dyeing medium that deviated from the straight line of other dyeing systems. Having ascertained

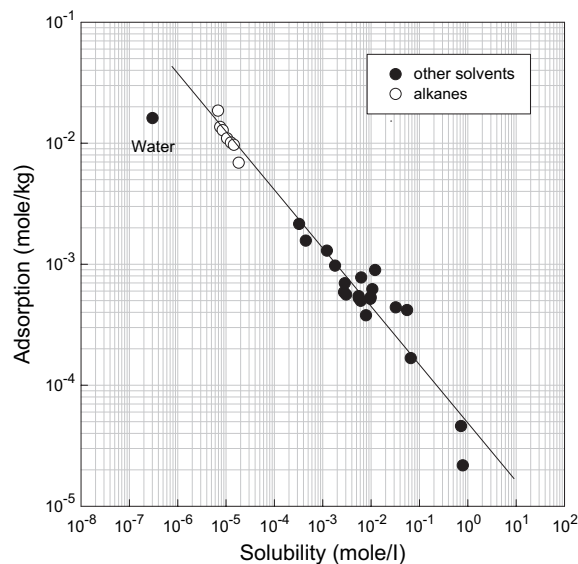


Fig. 6. Relationship between adsorption and solubility of C. I. Disperse Violet 1 in various non-aqueous systems.

the behaviors for dye adsorption and dye solubility in non-aqueous media, a further set of experiments using two other disperse dyes, namely C. I. Disperse Red 17 and C. I. Disperse Red 58, was also carried out to examine the properties of these applications. Their logarithmic plots are shown in Fig. 7. As shown in Fig. 7, for all three disperse dyes the dye adsorptions on poly(ethylene terephthalate) substrate were linearly and inversely proportional to the dye solubilities in non-aqueous media.

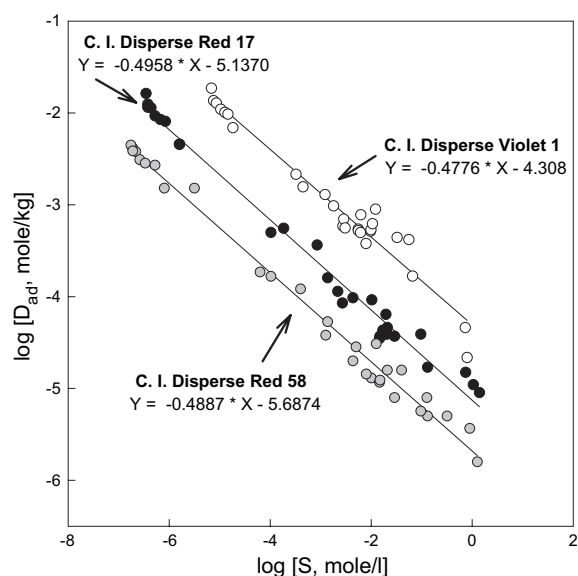


Fig. 7. Relationship between $\log D_{ad}$ and $\log S$ of disperse dyes in various non-aqueous systems: D_{ad} is the dye adsorption and the S is the dye solubility.

4. Conclusions

The adsorption properties of disperse dyes on poly(ethylene terephthalate) substrate using 29 kinds of non-aqueous media were investigated. The adsorption in alkane media was much higher than those in other non-aqueous systems. As the number of carbon atoms of the alkane series decreased, the amount of dye adsorption greatly increased. From the results of relationship between the adsorption and the solubility of disperse dyes, the findings clearly represent that the dye adsorptions onto the substrate were linearly and inversely proportional to the dye solubilities in non-aqueous media.

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