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# Affinity of disperse dyes on poly(ethylene terephthalate) in non-aqueous media. Part 2: effect of substituents

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**Abstract**

Adsorption properties of the 10 kinds of disperse dyes having different substituents were examined using several representative non-aqueous media on to poly(ethylene terephthalate) substrates. The dye adsorption amounts in pentane medium representing alkanes were much higher than those in the other non-aqueous media. In pentane medium, as the hydrophobicity of the dyes resulting from the substituents of dye molecules increased, the solubility of the dyes increased and the corresponding dye adsorption greatly decreased. This finding was coincident with the results from the previous study that the adsorption amount of disperse dyes on to substrates was inversely proportional to the solubility of the dyes. Furthermore, the hydrophobicity and the hydrophilicity of the dyes were discussed in terms of the electric dipole moments which are obtained by a semiempirical method using molecular modeling software.

*Keywords:* Adsorption; Poly(ethylene terephthalate); Disperse dyes; Non-aqueous media; Solubility

## 1. Introduction

Various attempts for non-aqueous solvent dyeing systems, especially towards poly(ethylene terephthalate) substrates, have been carried out to investigate fundamental exhaustion properties of disperse dyes [1–7]. In the previous part of this study [8], a wide range of non-aqueous solvents as possible exhaustion media was surveyed to examine the adsorption and the solubility properties. The previous results showed that the amount of dye adsorption in alkane media was much greater than those in the other media. In addition, as the number of carbon atom decreased in alkane systems, the adsorption amount of the dye greatly increased. Thus, alkane systems, especially pentane medium exhibited the highly increased adsorption properties on to poly (ethylene terephthalate) substrates.

In this work, the effects of the chemical structures of the disperse dyes on adsorption affinity were investigated with relation to hydrophobic or hydrophilic characteristics of dye substituents. Azo and anthraquinone dyes having different substituents were examined using five kinds of representative non-aqueous adsorption media and the adsorption affinity in pentane was then discussed with relation to both chemical structure and solubility of the dyes. Herein, five kinds of non-aqueous media were employed to represent each carbon compounds, namely acetone for ketone, benzene for aromatic hydrocarbon, methanol for alcohol, pentane for alkane and tetrachloroethylene (perclene) for chlorinated hydrocarbon.

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In addition, the solubility of the disperse dyes in pentane was surveyed with respect to dipole moments of the dyes caused by their dye structural substituents. Generally, the dipole moment of dyes measures the asymmetrical states in the molecular charge distribution. Also this value represents a sum of vectors from three-dimensional calculations. Therefore, it can be considered as the polarity of each molecule [9]. It is proposed that the dipole moment of the dyes resulting from the different chemical structures exhibits the changes of hydrophilicity or hydrophobicity. Consequently, the dipole moment properties provide the solubility changes of the dyes in hydrophobic pentane medium. However, it is very difficult to determine the exact dipole moments using experimental methods for the large molecules such as commercial dyes. In this context, to calculate theoretical dipole moments the current trend using computational chemistry methods has been increasing in many experimental interests such as molecular design, molecular modeling, dynamic simulation, structure analyzing and so on. In this work, the electric dipole moments of the selected dyes were obtained using molecular modeling software, *CS Chem3D*™ *Pro* (CambridgeSoft Co. USA) which is most frequently used for theoretical purposes [10]. Although the computed results are not entirely exact, a quantitative or approximate computation results can give useful insight into chemistry [11].

## 2. Experimental

### 2.1. Materials

The scoured and rinsed plain-weaved poly(ethylene terephthalate) fabrics (75 denier/36 filaments, 106 × 97 yarns/inch, $70 \pm 5$ g/m$^3$) were used. The dyes used were listed in Table 1. They were five anthraquinone and five azo disperse dyes having different substituents in the dye structures which could impart different levels of hydrophilic or hydrophobic characteristics to the dyes. Acetone extraction was carried out using a soxhlet extraction apparatus to purify the selected commercial disperse dyes, and the purified dyes were then recrystallized in ethanol. As adsorption media, the five kinds of non-aqueous representatives were employed, namely acetone, benzene, methanol, tetrachloroethylene (perclene) and pentane.

### 2.2. Adsorption

As described in the previous part of this paper [8], the disperse dyes (0.005 g) were adsorbed on poly(ethylene terephthalate) (0.2 g) using non-aqueous adsorption media (50 ml) in sealed stainless steel pots at 130 °C for 1 h. The other procedures were followed by the method mentioned in previous part.

### 2.3. Solubility determination

In order to measure the solubility of disperse dyes in pentane medium, all preparation procedures for dissolving dyes were carried out using the same method described previously [8].

### 2.4. Electric dipole moments of the dyes

In order to investigate the effect of substituent changes in the dye structures on solubility properties, a concept of the electric dipole moments of the dyes were considered and the values were theoretically obtained using molecular modeling software, *CS Chem3D*™ *Pro* (CambridgeSoft Co. USA). This electric dipole moment was computed by a semiempirical method using optional CS MOPAC system included in the molecular modeling software. To compute the dipole moments the standard parameters such as Austin Model 1 (AM1), closed shell and Mulliken charge population were selected.

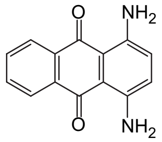
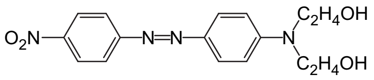
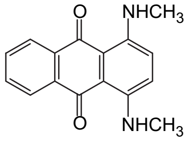
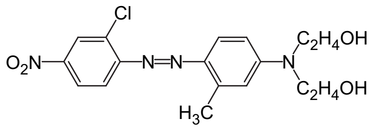
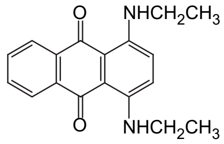
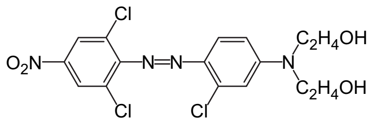
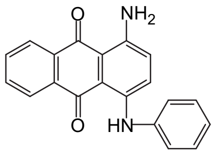
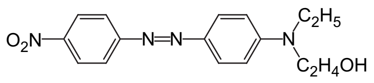
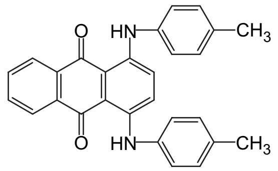
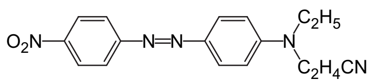
## 3. Results and discussion

### 3.1. Adsorption properties of disperse dyes in five non-aqueous media representatives

In the previous part of this study, it was concluded that the adsorption amount ($D_{ad}$) of disperse dyes towards poly(ethylene terephthalate) was inversely proportional to the solubility ($S$) of the dyes in the exhaustion media and that there was linearly and inversely proportional relationship between both parameters in their logarithmic plots as shown in Fig. 1 [8]. In addition, the adsorption amounts in alkane media were much greater than those in the other non-aqueous systems. In the range from pentane to decane, as the number of carbon atoms in the alkanes decreased, the adsorption amounts of dye gradually increased and finally the amount of dye adsorption in pentane exceeded that in water [8].

In this part of study, 10 kinds of disperse dyes were used to investigate the effect of chemical structures of disperse dyes in terms of adsorption behaviors. The dyes were selected with the standpoint of their chemical structures, namely five anthraquinone and five azo disperse dyes having different structural substituents. These substitutional effects can impart different levels of hydrophilic or hydrophobic properties to the dyes. For dye exhaustion five kinds of non-aqueous media representatives were employed, namely acetone for ketone, benzene for aromatic hydrocarbon, methanol

Table 1
Disperse dyes used

| Anthraquinone dyes | | Azo dyes | |
|---|---|---|---|
| C. I. Name (Dye No.) | Structure | C. I. Name (Dye No.) | Structure |
| Disperse Violet 1 (V01) |  | Disperse Red 19 (R19) |  |
| Disperse Blue 14 (B14) |  | Disperse Red 5 (R05) |  |
| Solvent Blue 59 (B59) |  | Disperse Brown 1 (Br01) |  |
| Disperse Blue 19 (B19) |  | Disperse Red 1 (R01) |  |
| Solvent Green 3 (G03) |  | Disperse Orange 25 (O25) |  |

for alcohol, pentane for alkane and tetrachloroethylene (perclene) for chlorinated hydrocarbon.

Fig. 2 shows the adsorption amounts of the disperse dyes in various non-aqueous media. For all disperse dyes the adsorption amounts in acetone, benzene, methanol and tetrachloroethylene were very low. However, in the case of pentane medium the various findings were appeared with relation to the chemical structures of the dyes. Blue 59 and Green 3 showed very low adsorption. Orange 25, Blue 14, Blue 19, Red 1 and Brown 1 showed middle range of adsorption. Whereas Red 5, Red 19 and Violet 1 showed very high adsorption behaviors. These corresponding results could be attributable to the effect of hydrophilic or hydrophobic characteristics caused by substitutional structure differences.

### 3.2. *Effect of dye structures on adsorption and solubility properties*

The difference of chemical structures in dye molecules could cause different levels of dye solubility in exhaustion media. As discussed in previous study [8], the adsorption amount of disperse dye was highly sensitive to the solubility of the dye in the exhaustion medium. Ten kinds of disperse dyes having various substituents within the dye molecules were classified into three groups with regard to hydrophobic or hydrophilic substituents on the basic dye structure. Especially, the adsorption properties in pentane medium ($[D]_{\mathrm{pen}}$) were discussed with relation to the solubility of the dyes ($[S]_{\mathrm{pen}}$).

Table 2 shows the adsorption and the solubility of three disperse dyes in pentane medium, which having different substituents from the basic structure of 1,4-diaminoanthraquinone. The two dyes Blue 14 and Blue 59 show two methyl and ethyl groups in the fundamental 1,4-diaminoanthraquinone structure (Violet 1), respectively. It is assumed that these substituents could increase the hydrophobic property of the dyes and that consequently the solubility of the dyes in highly hydrophobic non-aqueous pentane medium could be increased.

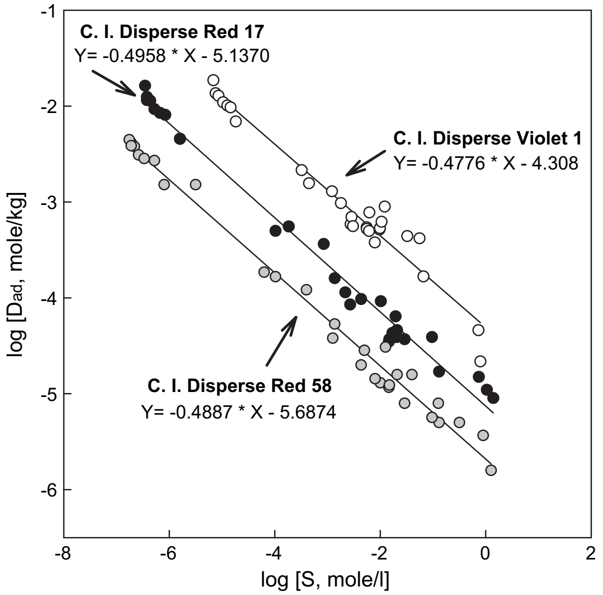


Fig. 1. Relationship between log $D_{ad}$ and log $S$ of disperse dyes in various non-aqueous systems. The $D_{ad}$ is the dye adsorption and the $S$ is the dye solubility [8].

As revealed in Table 2, the solubility of the dyes in pentane ($[S]_{pen}$) increased with substitution of hydrophobic methyl and ethyl groups to the dyes. Contrary to the solubility, the adsorption amounts ($[D]_{pen}$) were dramatically decreased. This finding was attributable to the substitution of hydrophobic groups to the dye structure, which increases hydrophobicity and solubility of the dyes in hydrophobic pentane medium.

In order to estimate hydrophobicity or hydrophilicity of the dyes, the electric dipole moment ($\mu$) of the dyes was considered. It is very well known that the dipole moment reveals the asymmetry in the molecular charge distribution and also displays a sum of charge vectors being operated in three dimension of dye molecule. Therefore, this property could be considered as a concept of the polarity of the molecule, namely hydrophilic property [9]. Table 2 also shows that the dipole moments of the disperse dyes decreased with substitution of hydrophobic methyl and ethyl groups to the dye molecules (from 1.51$D$ (Violet 1) to 1.46$D$ (Blue 59)). The decrease of dipole moment proposes that the dye molecules become more hydrophobic and that this hydrophobic alternation of the dye structures provides the increase of dye solubility in hydrophobic pentane medium.

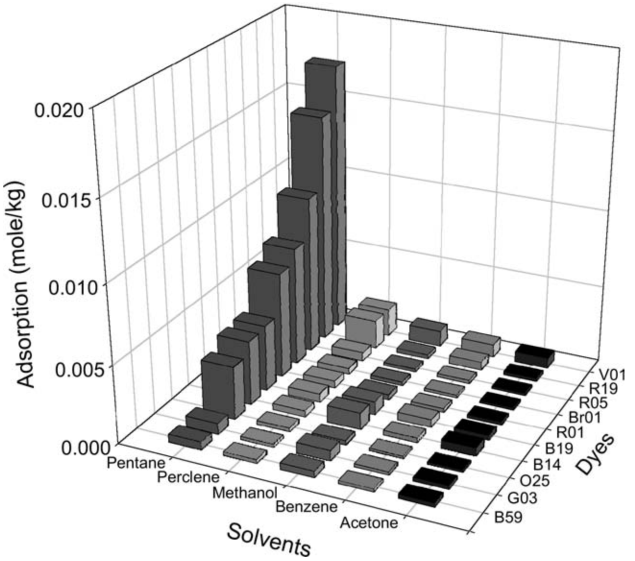


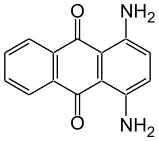
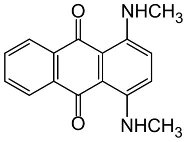
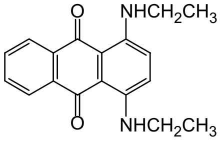
Fig. 2. Adsorption amounts of the dyes in several representative non-aqueous systems.

Table 3 also shows the adsorption amount, solubility and dipole moment of other disperse dyes having different substituents. Blue 19 and Green 3 shows one phenyl and two tolyl substituted groups to the amino groups of 1,4-diaminoanthraquinone (C. I. Disperse Violet 1), respectively. By the same reason as Table 2, it is evident that the solubility of dyes increased with substitution of hydrophobic phenyl and tolyl groups. Contrary to the solubility, the dye adsorption dramatically decreased. The dipole moments of the dyes decreased with substitution of the hydrophobic groups from 1.51$D$ (Violet 1) to 0.47$D$ (Green 3). The decrease of dipole moment resulted in the increase of solubility of the dye molecules in hydrophobic medium.

Table 4 displays the finding results of five azo type dyes having different substituents on the basic structure of 4-nitro-4′-dialkylaminoazobenzene. Red 19 possesses two hydroxyethyl groups on amino group. Red 5 and Brown 1 have methyl group and/or chlorine atoms as well as two hydroxyethyl groups on amino group. Red 1 shows one ethyl and one hydroxyethyl group. Finally, Orange 25 contains one ethyl and one propionitrile group in the structure.

As shown in Table 4, the solubility of Red 19 in pentane was very low and its adsorption was very high. It is proposed that two hydrophilic hydroxyethyl groups reduced the dye solubility in hydrophobic medium and that its property provided high adsorption affinity towards poly(ethylene terephthalate) substrates. However, Red 5 containing one methyl group and one chlorine, and Brown 1 having three chlorine atoms and two hydroxyethyl groups showed the increase of dye solubility in pentane. This corresponding solubility increase caused the decrease of dye adsorption. Meanwhile, the Red 1 showing one ethyl and one hydroxyethyl group in the structure exhibited higher solubility and lower adsorption affinity in pentane than those of Red 19 having two hydroxyethyl groups. Moreover, Orange 25 having one ethyl and one propionitrile group exhibited much higher solubility and lower adsorption property than those of Red 1. It is proposed that the

Table 2
Electric dipole moment ($\mu$), adsorption amount ($[D]_{pen}$) and solubility ($[S]_{pen}$) of disperse dyes having alkyl substituents on amino group in pentane

| Dyes | Structure | $\mu$ (debye) | $[D]_{pen}$ (mmol/kg) | $[S]_{pen}$ (mg/l) |
|---|---|---|---|---|
| C. I. Disperse Violet 1 |  | 1.51 | 17.33 | 1.63 |
| C. I. Disperse Blue 14 |  | 1.48 | 4.13 | 11.25 |
| C. I. Solvent Blue 59 |  | 1.46 | 0.51 | 27.78 |

propionitrile group is more hydrophobic characteristic than the hydroxyethyl group.

In the case of Red 5 and Brown 1, although the electronegative chlorine atoms were substituted, the solubility in hydrophobic pentane increased compared with Red 19. This finding can be explained that because the electronegative chlorines were substituted laterally to the dye molecules, it could reduce the net dipole moment of the dye molecule [9]. Consequently, the substituents decreased the polarity of the dye molecules and its changes resulted in the increase of the hydrophobicity and the solubility.

### 3.3. Relationship between the solubility and the dipole moment of disperse dyes

Fig. 3 shows the relationship between the dye solubility and the electric dipole moment of the dye molecules. Fig. 3 reveals that the solubility in pentane medium was linearly and inversely proportional to the dipole moment of the dyes. However, the sensitivity between the solubility and the dipole moment of dyes was not the same for different dye groups. The disperse dyes having alkyl substituents shown in Table 2 displayed the highest sensitivity on the solubility and

Table 3
Electric dipole moment ($\mu$), adsorption amount ($[D]_{pen}$) and solubility ($[S]_{pen}$) of disperse dyes having aromatic substituents on amino group in pentane

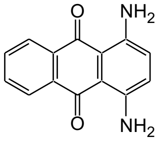
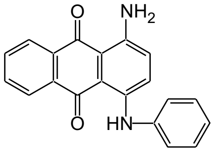
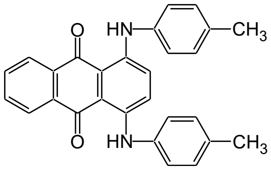
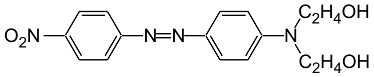
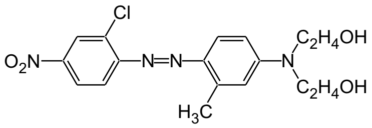
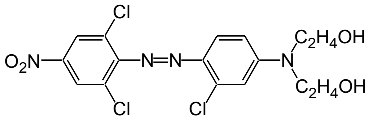
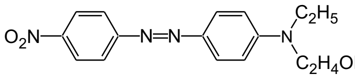
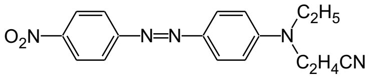
| Dyes | Structure | $\mu$ (debye) | $[D]_{pen}$ (mmol/kg) | $[S]_{pen}$ (mg/l) |
|---|---|---|---|---|
| C. I. Disperse Violet 1 |  | 1.51 | 17.33 | 1.63 |
| C. I. Disperse Blue 19 |  | 1.34 | 4.26 | 6.01 |
| C. I. Solvent Green 3 |  | 0.47 | 0.71 | 25.23 |

Table 4
Electric dipole moment ($\mu$), adsorption amount ($[D]_{pen}$) and solubility ($[S]_{pen}$) of azo disperse dyes having different substituents in pentane

| Dyes | Structure | $\mu$ (debye) | $[D]_{pen}$ (mmol/kg) | $[S]_{pen}$ (mg/l) |
|---|---|---|---|---|
| C. I. Disperse Red 19 |  | 12.85 | 14.73 | 0.10 |
| C. I. Disperse Red 5 |  | 12.45 | 10.17 | 0.67 |
| C. I. Disperse Brown 1 |  | 12.39 | 7.65 | 0.89 |
| C. I. Disperse Red 1 |  | 12.27 | 6.81 | 5.28 |
| C. I. Disperse Orange 25 |  | 10.33 | 3.39 | 20.42 |

the dipole moments and the azo dye types from Table 4 displayed the lowest corresponding results. Although the computed dipole moment values are not entirely exact, a quantitative computation results can give useful insight into chemistry in terms of solubility and adsorption.

## 4. Conclusions

Ten kinds of disperse dyes having different substituents were examined to investigate the exhaustion properties towards poly(ethylene terephthalate) substrates in several non-aqueous media. The adsorption amount of the dyes in pentane medium representing alkanes was much higher than those in other media. In terms of substitution effect within dye structures, the solubility of the dyes in pentane increased with increasing hydrophobic substituents of the dyes. On the contrary, the adsorption amounts greatly decreased with increasing hydrophobic characteristics of the dyes. Dipole moments of the dyes decreased with substitution of the hydrophobic groups to the dye molecules. The decrease of dipole moment provided the increase of dye solubility in hydrophobic pentane. The dipole moment values obtained in this work might be different from those measured experimentally. However, this computation approach could be useful to explain the exhaustion properties of dyes in terms of solubility and adsorption.

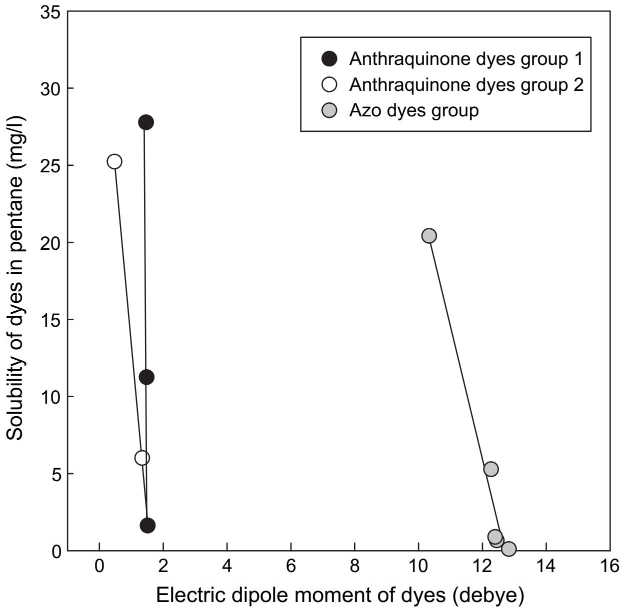


Fig. 3. Relationship between the electric dipole moments and the solubility of the disperse dyes having different substituents.

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