HEATS OF SORPTION OF ANTHRAQUINONE MODEL DISPERSE DYES ON PET FILM FROM THE VAPOR PHASE

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ABSTRACT

An investigation has been done to study the binding state of disperse dyes in poly(ethylene terephthalate) (PET) substrate. Ten anthraquinone derivatives were employed as models for disperse dyes. The equilibrium amount of sorption of these compounds on PET film was determined by vapor phase dyeing in sealed glass tubes. From these results, the heats of sorption were calculated. If necessary, the values were corrected by using the p-nitroaniline accessibility, and compared with the heats of sublimation.

From the results it was found that the main interaction between the dye molecules and PET substrate is the dispersion force and that, in the cases of the dyes having proton-donor groups such as 2-hydroxyanthraquinone, hydrogen bonding plays also an important role.

1. INTRODUCTION

The first investigation on the vapor-phase dyeing by disperse dyes has been done by Majury1). He measured the heats of sorption of the dyes on cellulose acetate film from the vapor and compared the values with the heats of sublimation, in order to get some informations on the binding state of the dye molecules in the substrate. However, he could get no significant conclusions. Jones and his coworker2) made a similar investigation, but they didn't get the expected results. Further, they measured the sublimation pressure of some disperse dyes by means of the Knudsen effusion and the torque effusion method, and from the results they concluded that the dye molecules exist as aggregate of two or three molecules in the saturated vapor3).

Contrary to Jones' conclusion, Kojima4) found from the more careful measurements of the sublimation pressure that the disperse dyes studied should be in monomolecular state in the saturated vapor phase. His conclusion has been supported by the direct measurement of visible spectrum of the vapor of 1-methylaminoanthraquinone5).

We measured the heats of sorption of some model azo disperse dyes on PET film and the heats of sublimation of these dyes6), but the accuracy of the heats of sorption was not enough to discuss in detail.

In the present study, the heats of sorption of anthraquinone model disperse dyes on PET film were measured, carefully considering the accuracy of obtained values. These values were then compared with the heats of sublimation of the dyes to discuss the binding state of the dye molecule in the PET substrate.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Model dyes

Ten anthraquinone derivatives were used as anthraquinone model disperse dyes. Table 1 shows them with the abbreviated names. Some of them were synthesized and the others were purchased. They were purified by column chromatography and/or recrystallization.
Table 1  Model disperse dyes (Anthraquinone derivatives) used.

<table>
<thead>
<tr>
<th>No.</th>
<th>Abbreviation</th>
<th>Name</th>
<th>m.p. (°C)</th>
<th>M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AQ</td>
<td>Anthraquinone</td>
<td>276-277</td>
<td>208</td>
</tr>
<tr>
<td>2</td>
<td>1-HAQ</td>
<td>1-Hydroxyanthraquinone</td>
<td>194-195</td>
<td>224</td>
</tr>
<tr>
<td>3</td>
<td>2-HAQ</td>
<td>2-Hydroxyanthraquinone</td>
<td>309.5-310</td>
<td>224</td>
</tr>
<tr>
<td>4</td>
<td>1-MAQ</td>
<td>1-Methoxyanthraquinone</td>
<td>170-170.5</td>
<td>238</td>
</tr>
<tr>
<td>5</td>
<td>2-MAQ</td>
<td>2-Methoxyanthraquinone</td>
<td>197.5-198</td>
<td>238</td>
</tr>
<tr>
<td>6</td>
<td>DHAQ</td>
<td>1,4-Dihydroxyanthraquinone</td>
<td>194-195</td>
<td>240</td>
</tr>
<tr>
<td>7</td>
<td>1-AAQ</td>
<td>1-Aminoanthraquinone</td>
<td>248.5-249.5</td>
<td>223</td>
</tr>
<tr>
<td>8</td>
<td>2-AAQ</td>
<td>2-Aminoanthraquinone</td>
<td>296-297</td>
<td>223</td>
</tr>
<tr>
<td>9</td>
<td>DAAQ</td>
<td>1,4-Diaminoanthraquinone</td>
<td>261-262</td>
<td>238</td>
</tr>
<tr>
<td>10</td>
<td>AHAQ</td>
<td>1-Amino-4-hydroxyanthraquinone</td>
<td>211-212</td>
<td>239</td>
</tr>
</tbody>
</table>

2.1.2 PET films

The PET films used were Mylar #50 from Du Pont Co. Ltd., (thickness: 13 μm, density: 1.398 g/cm³, crystallinity: 54.6%) and biaxially drawn film from Teijin Co. Ltd., (thickness: 12 μm, density: 1.407 g/cm³, crystallinity: 62.1%). They were cut in 1×6 cm sheets and treated in acetone at 30°C for 25 hrs, in order to remove the impurities and to make the physical structure of film stable. After drying, IR-spectra were measured and the trans-value (=A973/A794) and gauche-value (=A896/A794), where A is the transmittance at the wave numbers in cm⁻¹ given as suffix, were calculated. For the dyeing experiments, the films giving a limited range of trans- and gauche-values were chosen, to avoid the scatter in the dye sorption. Mylar films were used for the dye No. 1, 4, 7 and 8, and Teijin films were used for the dye No. 5, 6, 9 and 10.

2.2 Vapor phase dyeing

Dyeing of PET film was carried out from the saturated vapor of dye, by means of the sealed tube method. The procedure is shown in Fig. 1. A given amount of the acetone solution of a dye was put into a glass tubing ca. 12 cm long and the acetone was evaporated, so that the dye is adhered to the glass surface. Then, a sheet of PET film (1×6 cm) supported on a stainless steel holder was inserted in the tubing. The part ca. 4 cm down from the top of the tubing was made slender in a flame and the air in the tube was exchanged with nitrogen gas. This gas changing was repeated three times and finally the tubing was sealed in a flame under reduced pressure (~1 mmHg).

The sealed glass tubing prepared above was put into an oil bath, of which temperature was regulated within ±0.1°C, to dye the film for a given period. The dyed film was weighed and then dissolved in m-cresol. The amount of dye sorbed on film was determined spectrophotometrically.

1-MAQ and 2-MAQ were not stable against the day light. So the experiments with these two compounds were carried out under a dark condition. DAAQ was never heated above 160°C during the experiments, because of the possible decomposition above this temperature.

3. RESULTS AND DISCUSSION

3.1 Equilibrium sorption

Some examples of the dyeing rate curves are shown in Fig. 2. These are the results for 1-HAQ measured at 100 ~ 125°C. From the curves, it is clear that the equilibrium sorptions are attained in 48 hr and 2 hr at 100 and 125°C, respectively. In the experiments to measure the equilibrium dye sorption, the dyeing times twice these dyeing
The affinity $\Delta u_{\text{sub}}^0$ can be calculated by subtracting $\Delta H_{\text{sub}}^0$ values from $\Delta u_{\text{sub}}^0$ values.

The logarithmic partition coefficients were plotted against the reciprocal absolute temperature in Figs. 3 and 4 for all the model dyes used. For each of the dyes, the experimental data gave a straight line. From the slopes the heats of sorption were obtained through the equation (6). The values are summarized in Table 3. For comparison, the heats of sublimation obtained by the other measurements are given in the same table.

The affinities $\Delta u_{\text{sub}}^0$ were calculated from the partition coefficient using the equation (5).

$$ \Delta u_{\text{sub}}^0 = -2.303 RT \log K $$

The partition coefficients for 1-HAQ at various temperatures are given in Table 2 as an example, where the value of $V_a$ was assumed to be 0.340 l/kg. For the other model dyes, the similar times obtained were chosen. At each temperature, three pieces of PET film were dyed and the average amount of dye sorbed was determined. The results were within ±2%.

3.2 Affinity, heat and entropy of sorption

The partition coefficient $K$ was determined from the equilibrium sorption $[D]_{\text{sat}}^0$ obtained by the method described in 3.1 and the concentration $[D]_{\text{sat}}^0$ in the saturated vapor phase using the equation (1).

$$ K = \frac{[D]_{\text{sat}}^0}{[D]_{\text{sat}}^0 V_a} = \frac{[D]_{\text{sat}}^0}{[D]_{\text{sat}}^0 V_a} \frac{\rho_a}{1-x} $$

where, $V_a$ and $\rho_a$ are the volume (in l/kg) of the amorphous region of PET per 1 kg of the film and the density of the amorphous region (1.335 g/cm$^3$), respectively, and $x$ is the crystallinity.

The dye concentration in the saturated vapor phase is given by the following relation;

$$ \log P = -A/T + B $$

where $P$ is the sublimation pressure, $A$ and $B$ are the constants$^8)$. The heat of sublimation $\Delta H_{\text{sub}}^0$ and the entropy of sublimation $\Delta S_{\text{sub}}^0$ can be calculated using these two constants:

$$ \Delta H_{\text{sub}}^0 = 2.303 RA $$

$$ \Delta S_{\text{sub}}^0 = 2.303 R(B - 2.881) $$

In the case of 1-HAQ, $A$ and $B$ were 5924 and 13.19$^8)$, respectively.

The partition coefficients for 1-HAQ at various temperatures are given in Table 2 as an example, where the value of $V_a$ was assumed to be 0.340 l/kg$^2)$. For the other model dyes, the similar

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$[D]_{\text{sat}}^0$ (mol/l)×10$^8$</th>
<th>$[D]_{\text{sat}}^0$ (mol/kg)×10</th>
<th>$K$ (-)×10$^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>8.76</td>
<td>1.28</td>
<td>4.30</td>
</tr>
<tr>
<td>105</td>
<td>14.0</td>
<td>1.42</td>
<td>2.98</td>
</tr>
<tr>
<td>110</td>
<td>22.2</td>
<td>1.59</td>
<td>2.11</td>
</tr>
<tr>
<td>115</td>
<td>34.6</td>
<td>1.72</td>
<td>1.46</td>
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<tr>
<td>120</td>
<td>53.4</td>
<td>1.93</td>
<td>1.06</td>
</tr>
<tr>
<td>125</td>
<td>81.5</td>
<td>2.13</td>
<td>0.769</td>
</tr>
</tbody>
</table>

results were obtained.

The affinity $\Delta u_{\text{sub}}^0$ was calculated from the partition coefficient using the equation (5).

$$ \Delta u_{\text{sub}}^0 = -2.303 RT \log K $$

The logarithmic partition coefficients were plotted against the reciprocal absolute temperature in Figs. 3 and 4 for all the model dyes used. For each of the dyes, the experimental data gave a straight line. From the slopes the heats of sorption were obtained through the equation (6). The values are summarized in Table 3. For comparison, the heats of sublimation obtained by the other measurements are given in the same table.

$$ \log K = -\Delta H_{\text{sub}}^0 / 2.303 RT + \text{Const.} $$

The entropy of sorption $\Delta S_{\text{sub}}^0$ can be calculated by subtracting $\Delta H_{\text{sub}}^0$ values from $\Delta u_{\text{sub}}^0$ values.

$$ \Delta S_{\text{sub}}^0 = \Delta u_{\text{sub}}^0 / T $$

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$$ \Delta S_{\text{sub}}^0 = \Delta u_{\text{sub}}^0 / T $$

$$ \Delta S_{\text{sub}}^0 = \Delta H_{\text{sub}}^0 / T $$

$\Delta S_{\text{sub}}^0 = \Delta u_{\text{sub}}^0 / T$.

Fig. 3 Temperature dependence of partition coefficient of model disperse dyes (Δ: AQ, ○: 1-HAQ, ●: 2-HAQ, ▽: 1-MAQ, ▼: 2-MAQ) between PET and gas phase.
Fig. 4 Temperature dependence of partition coefficient of model disperse dyes (Δ: DHAQ, ○: 1-AAQ, ●: 2-AAQ, ▽: DAAQ, ▲: AHAQ) between PET and gas phase.

Table 3  Heat of sorption on PET from vapor and heat of sublimation of model disperse dyes (anthraquinone derivatives).

<table>
<thead>
<tr>
<th>No.</th>
<th>Model Dye</th>
<th>Sublimation $\delta H_{\text{sub}}^0$ (kcal/mol)</th>
<th>$\delta H_{\text{sub}}^{0*}$</th>
<th>Sorption on PET $\delta (-\Delta H_{\text{sorp}}^{0})^{**}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Model Dye 1" /></td>
<td>26.6</td>
<td>-</td>
<td>21.0 (20.7)</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Model Dye 2" /></td>
<td>27.1</td>
<td>0.5</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Model Dye 3" /></td>
<td>32.7</td>
<td>6.1</td>
<td>25.0</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Model Dye 4" /></td>
<td>30.6</td>
<td>4.0</td>
<td>23.3</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5" alt="Model Dye 5" /></td>
<td>29.8</td>
<td>3.2</td>
<td>21.4</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6" alt="Model Dye 6" /></td>
<td>27.4</td>
<td>0.8</td>
<td>21.1</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7" alt="Model Dye 7" /></td>
<td>29.1</td>
<td>2.5</td>
<td>23.2</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8" alt="Model Dye 8" /></td>
<td>32.7</td>
<td>6.1</td>
<td>26.6</td>
</tr>
<tr>
<td>9</td>
<td><img src="image9" alt="Model Dye 9" /></td>
<td>34.2</td>
<td>7.6</td>
<td>29.1</td>
</tr>
<tr>
<td>10</td>
<td><img src="image10" alt="Model Dye 10" /></td>
<td>30.4</td>
<td>3.8</td>
<td>24.2</td>
</tr>
</tbody>
</table>

$\delta H_{\text{sub}}^{0}$ = $H_{\text{sub}}^{0} - H_{\text{sub}}^{0}$ (AQ)

$\delta (-\Delta H_{\text{sorp}}^{0}) = -\Delta H_{\text{sorp}}^{0} + \Delta H_{\text{sorp}}^{0}$ (AQ)
3.3 Correction of the heat of sorption by the variable \( V_a \)-term

Before discussing the heats of sorption obtained in the previous section, it must be checked for the change in the internal effective volume, \( V_a \), for the expansion of polymer substrate due to the dye sorption. In a previous paper\(^9\), we have introduced the so-called p-nitroaniline accessibility (\( p-\text{NA}_{\text{acc}} \)), in order to examine the structural change (change in \( V_a \)-term) of polymer substrate to be caused by the large amount of sorption or by the "heat" treatment. The correction of \( V_a \) by \( p-\text{NA}_{\text{acc}} \) is given by the equation (7).

\[
V_a \text{ (correct)} = V_a \times \frac{p-\text{NA}_{\text{acc}}(t^\circ C)}{p-\text{NA}_{\text{acc}}(85^\circ C)}
\]

Eq. (7)

Here, \( p-\text{NA}_{\text{acc}}(t^\circ C) \) is the equilibrium amount of p-NA sorbed on the PET film, which was previously dyed with the dye at \( t^\circ C \) and then treated in acetone at 30°C to remove the dye sorbed. \( p-\text{NA}_{\text{acc}}(85^\circ C) \) is the \( p-\text{NA}_{\text{acc}} \) of the PET film, which was previously sorbed with p-NA at 85°C and treated in the same way as for \( p-\text{NA}_{\text{acc}}(t^\circ C) \). This method is based on the fact that the equilibrium amount of p-NA sorbed on PET can be regarded to be the quantity proportional to the \( V_a \)-term.

In Fig. 5 the equilibrium sorption (\( \bigcirc \)) of 1-AAQ on PET film and the \( p-\text{NA}_{\text{acc}}(t^\circ C) \) (\( \bigtriangleup \)) are plotted against the temperature of dyeing. The points (\( \blacktriangle \)) are the \( p-\text{NA}_{\text{acc}} \) for the film treated in the sealed glass tubing without dyestuff under the same conditions as the dyeing. The values of \( p-\text{NA}_{\text{acc}} \) for the films dyed with 1-AAQ are found to be the same as those treated under the blank conditions. In addition, the values of \( p-\text{NA}_{\text{acc}} \) decreased with increasing (dyeing or treating) temperature. This means that the polymer substrate was not expanded by the sorption of 1-AAQ, but was crystallized more highly with increasing dyeing or treating temperature.

The correction for \( V_a \)-term change can be carried out using the equation (7), and further, the affinity \( \Delta \mu_{\text{corr}}^0 \) is corrected with the corrected \( V_a \)-term. Using the corrected \( \Delta \mu_{\text{corr}}^0 \), the real heat of sorption can be obtained. For 1-AAQ, the plots of \( \Delta \mu_{\text{corr}}^0 \) vs. \( 1/T \) are shown in Fig. 6, without \( V_a \)-term correction (\( \bigcirc \)) or with the correction (\( \bullet \)). From the slopes the values of \( \Delta H_{\text{corr}}^0 \) were calculated; the corrected \( \Delta H_{\text{corr}}^0 \) was -23.0 kcal/mol, while the uncorrected one was -23.4 kcal/mol. The difference was only 0.4 kcal/mol. Since the experimental error of \( \Delta H_{\text{corr}}^0 \) is ±0.5 kcal/mol, this difference (0.4 kcal/mol) can be regarded to be within the error.

From the results of \( p-\text{NA}_{\text{acc}} \) measurements for the various sorption systems, it was known\(^10\) that the increment in \( V_a \)-term cannot be observed, until the amount of dye sorption is over ca. 5.5 wt%. Over 5.5 wt% sorption, the \( V_a \)-term increases with increasing amount of sorption and hence the real value of \( \Delta H_{\text{corr}}^0 \) should be larger than the uncorrected one. On the other hand, in such cases as the amount of sorption is below ca. 3 wt% and the dyeing temperature is relatively high (130 ~ 150°C), the decrease in \( V_a \)-term was
observed\(^{10}\)), because of the increment in crystallinity due to the “heat-treatment effect”. In this sense, it is important to know, if the correction of \(V_a\)-term is necessary to get a more reliable value of \(\Delta H^0_{\text{corr}}\). For this purpose, the equilibrium amounts of sorption at the lowest and the highest temperatures studied were checked (Table 4). Since, in the case of 1-AAQ, the decrease in \(V_a\)-term to be caused by the increment in crystallinity was very small, the correction of \(\Delta H^0_{\text{corr}}\) was not necessary. On the other hand, such correction was necessary for the cases of 1-HAQ and 1-MAQ. For 1-HAQ, whose equilibrium sorption was 6.59 wt\%, it could be expected that the corrected value of \(\Delta H^0_{\text{corr}}\) would be ca. 1 kcal/mol smaller than the uncorrected value. In the other cases, the correction was not necessary.

3.4 The heat of sorption and binding state of dye molecule

Fig. 7 shows the relationship between the heat of sorption on PET film from vapor phase and the heat of sublimation of anthraquinone model disperse dyes. A linear relation was found between them within \(\pm 1.2\) kcal/mol of scatter. This suggests

\[ \Delta H_{\text{corr}} \]

that the nature of interaction between the dye molecule and PET substrate is similar to that of intermolecular interaction of the dye molecules. In the case of AQ, the intermolecular force is considered to arise from the dispersion force alone, because its dipole moment is zero\(^{11}\). Therefore,

Table 4  Equilibrium sorptions of various model dyes at the lowest and highest temperatures to check the effect on \(\Delta H^0_{\text{corr}}\).

<table>
<thead>
<tr>
<th>No.</th>
<th>Model Dye</th>
<th>M.W.</th>
<th>Dyeing Temp.</th>
<th>(\left[D^0_{\text{stat}}\right])</th>
<th>Effect on (-\Delta H^0_{\text{corr}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>lowest (°C)</td>
<td>highest (°C)</td>
<td>mol/kg \times 10^2</td>
</tr>
<tr>
<td>1</td>
<td>AQ</td>
<td>208</td>
<td>120</td>
<td>140</td>
<td>4.13</td>
</tr>
<tr>
<td>2</td>
<td>1-HAQ</td>
<td>224</td>
<td>100</td>
<td>125</td>
<td>17.7</td>
</tr>
<tr>
<td>3</td>
<td>2-HAQ</td>
<td>224</td>
<td>125</td>
<td>145</td>
<td>2.95</td>
</tr>
<tr>
<td>4</td>
<td>1-MAQ</td>
<td>238</td>
<td>105</td>
<td>130</td>
<td>13.6</td>
</tr>
<tr>
<td>5</td>
<td>2-MAQ</td>
<td>238</td>
<td>115</td>
<td>135</td>
<td>8.38</td>
</tr>
<tr>
<td>6</td>
<td>DHAQ</td>
<td>240</td>
<td>100</td>
<td>140</td>
<td>11.1</td>
</tr>
<tr>
<td>7</td>
<td>1-AAQ</td>
<td>223</td>
<td>110</td>
<td>140</td>
<td>7.87</td>
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<tr>
<td>8</td>
<td>2-AAQ</td>
<td>223</td>
<td>110</td>
<td>140</td>
<td>2.31</td>
</tr>
<tr>
<td>9</td>
<td>DAAQ</td>
<td>238</td>
<td>100</td>
<td>140</td>
<td>4.03</td>
</tr>
<tr>
<td>10</td>
<td>AHAQ</td>
<td>239</td>
<td>100</td>
<td>140</td>
<td>9.04</td>
</tr>
</tbody>
</table>
it can be assumed that also the dye sorption on PET occurs by the dispersion force alone. The fact that the value of $-\Delta H^0_{\text{sorp}}$ is a little smaller than $\Delta H^0_{\text{sub}}$ is reasonable, considering the steric effect among them.

In the case of AQ, the value of $\Delta H^0_{\text{sorp}}$ was $-21.0$ kcal/mol. However, this value is presumably a little (ca. 0.5 kcal/mol) larger than the real one, considering the relatively large effect of the crystallinity increment caused by the "heat", which is predominant for $V_a$-change.

The value of $-\Delta H^0_{\text{sorp}}$ for 1-HAQ was 20.4 kcal/mol, which is slightly smaller than that for AQ. Since the hydrogen atom of the OH group in 1-HAQ forms an intramolecular hydrogen bond to the oxygen atom of the carbonyl group on the quinone ring, only the dispersion force comes into question as intermolecular force. Considering these, the fact that the values of $\Delta H^0_{\text{sub}}$ of 1-HAQ and AQ are almost same is quite reasonable. On the other hand, the value of $-\Delta H^0_{\text{sorp}}$ for 1-HAQ is ca. 1 kcal/mol smaller than that for AQ. This difference may come from the possible change in $V_a$-term, as discussed above.

In the case of 2-HAQ, both $-\Delta H^0_{\text{sorp}}$ and $\Delta H^0_{\text{sub}}$ are larger than those for AQ. This can be explained with the additional hydrogen bonding to be formed with the hydroxyl group in 2-position of anthraquinone ring.

Contrary to 2-HAQ, 2-MAQ which is obtained by the methyl substitution of 2-HAQ has no ability to form hydrogen bond. $-\Delta H^0_{\text{sorp}}$ for 2-MAQ is only a little (0.7 kcal/mol) larger than that for AQ. This small difference in $-\Delta H^0_{\text{sorp}}$ between 2-MAQ and AQ may be attributed to the dispersion force based on the methyl group.

Further, DHAQ has two hydroxyl groups in 1- and 4-position, which form intramolecular hydrogen bonds with oxygen atoms of the carbonyl groups. Therefore, DHAQ has no ability to form intermolecular hydrogen bonds. This explains that the value of $-\Delta H^0_{\text{sorp}}$ for DHAQ is nearly equal to those for AQ and 1-HAQ.

From these results, it can be presumed that the anthraquinone derivatives containing hydrogen group in 2- (or 3-) position have ability to form hydrogen bond with other same kind of molecules or with PET molecules.

1-AAQ has two hydrogen atoms. One of them can form intramolecular hydrogen bond, while the other one can form intermolecular hydrogen bond with other 1-AAQ molecule or with PET molecule. $-\Delta H^0_{\text{sorp}}$ for 1-AAQ is 2.5 kcal/mol, larger than that for AQ. In the case of AHAQ, which has also the ability to form one intramolecular hydrogen bond per molecule, $-\Delta H^0_{\text{sorp}}$ is 3.5 kcal/mol larger than that for AQ. Such increment (ca. 3 kcal/mol) may be attributed to the formation of the hydrogen bonding with oxygen atom of carbonyl group or $\pi$ electron of aromatic rings in PET molecules. In the case of DAAQ, the effect was about 2 times larger. The increment for 2-AAQ was 5.9 kcal/mol, while that for 2-HAQ was 4.3 kcal/mol. These values are reasonable, considering the ability of intermolecular hydrogen bond and the position of two substituents, one amino and one hydroxyl group.

The high melting points of these compounds are reasonable for these high $\Delta H^0_{\text{sub}}$.

From the above considerations, it was confirmed that the main interaction between disperse dye and PET substrate is dispersion force and that, in the cases of disperse dyes containing proton donor groups, the hydrogen bonding plays also an important role. According to the results of solubility measurements of disperse dyes in PET film using differential scanning colorimeter, the dye molecules are regarded to exist in monomolecular state in amorphous regions, in the same concentration range studied in the present paper. Therefore, it can be considered that the anthraquinone model disperse dyes used here may be in the state “molecularly adsorbed” on the PET molecular chains. Consequently, the values of $\Delta H^0_{\text{sorp}}$ obtained can be expected to correspond to the “heat of molecular adsorption”

References
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アントラキノン系モデル分散染料のPETフィルムへの収着熱

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ポリエチレンテレフタラート（PET）基質中での分散染料の結合状態を知る目的で、研究が行われた。モデル分散染料として、10種のアントラキノン誘導体を用いた。PETに対するこれらの化合物の平衡収着量は封管法で気相染色することによって求め、これらの値から、収着熱を算出した。必要に応じて、収着熱はN-ニトロアミリノ アクセシビリティを用いて補正され、昇華熱と比較した。

その結果、用いた染料とPET基質間の主な相互作用は分散力であり、2-ヒドロキシアントラキノンのようなプロトン供与性基を含む染料では基盤結合が重要な役割を演じていることが明らかになった。