

Understanding Adsorption Phenomena: Investigation of the Dye–Cellulose Interaction

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To understand the structural factors that control the adsorption of acid dyes onto cotton (cellulose), the adsorption of 15 acid dyes from water has been studied. An equilibrium exists between dye adsorbed in the cotton and dye in solution, and by measurement of the temperature dependence (277–333K) of the equilibrium constant, the enthalpy and entropy of binding are obtained. For most dyes adsorption is driven by the binding enthalpy, which is ascribed to van der Waals forces. Acid dyes consist of an aromatic core with peripheral solubilizing groups (generally sulfonates). Dyes in which the sulfonates are on one side of the molecule have the largest binding enthalpy. Assuming a binding geometry where the sulfonates protrude into water pools in the bulk amorphous regions and as much as possible of the dye core touches the surface, then a good correlation exists between the binding enthalpy and the summation of $1/r^6$ over all the C, N, and O dye atoms, where r is the distance of each atom from the cellulose surface.

1. Introduction

The ability of some molecules to either adsorb onto or absorb into substrates is extremely useful in chemistry and biology. For example, it is central to heterogeneous chemistry,¹ drives the distribution of many chemicals in the body,² and even gives the astringent flavor to red wine.³ It is also a key factor in understanding chemistry in nanoenvironments, so-called supramolecular chemistry.⁴ Much work has been done to understand such processes and it is clear that hydrogen bonding, van der Waals forces, entropy, and molecular shape are key drivers; however, which of these factor dominates and how they interrelate is generally unclear.

One of the first industrial processes to rely on adsorption was the dyeing of cotton (cellulose) by synthetic dyes⁵ and today it is used on approximately 20 million tonnes of cotton per annum.⁶ Adsorption of molecules to cellulose is important in medicine, where cellulose is often used as a polymer carrier for drugs.⁷ As well as being central to clothing production, the dyeing process represents an interesting model system for adsorption from water, as both dye and cotton have simple well-defined structures. Cotton is almost purely cellulose arranged in crystalline and amorphous regions,⁸ with the dye residing in the latter most probably on the surface of the crystallites.⁹ In the literature, dye adsorption from water has been variously ascribed to hydrogen bonding,¹⁰ dye aggregation,¹¹ and van der Waals forces;¹² additionally, QSARs have been used to try and predict behavior with limited success.¹³ Most studies have used simple measurements of adsorption efficiency, at one temperature, of a range of dyes to try to gain better insights. Clearly, enthalpy and entropy values would be more useful; however, reliable values are experimentally difficult to obtain. The simple reason for this is that most dyes adsorb either too strongly or too weakly so that the dye is almost entirely in the cotton or in the water, leaving no measurable differences. For strongly adsorbing dyes, reducing the amount of cotton does not help, as then kinetics take over and it takes days to weeks for an equilibrium to be reached.

The current study attempts to unravel the controlling factors in the adsorption of acid dyes to cotton by measurement and interpretation of the enthalpy and entropy of binding of a set of 15 acid dyes.

2. Experimental Section

The structures of the 15 dyes used are given in Table 1. The AO12 derivatives were synthesized following literature procedures¹² and all others were purchased from Aldrich and used as supplied. The adsorption of the dyes to cotton was measured by shaking aqueous dye solutions with cotton sheeting and measuring dye depletion from solution using UV–Vis spectroscopy (5 cm cells). In general, it took 1 h for equilibrium to be established. To minimize any effects of dye aggregation in solution, low dye concentrations were used such that the optical density at 5 cm was 1, corresponding to dye concentrations of 10^{-5} to 10^{-6} mol/L. As ionic strength is known to alter the adsorption, initial experiments were done at several ionic strengths in the range 0–1. Adsorption increased and then plateaued at 0.05; hence, all measurements were conducted at an ionic strength of 0.056 using a Borax buffer. Low ionic strength again reduces dye aggregation.¹⁴ It should be noted that pH in the range 7–11 had no effect on adsorption. Bleached nonmercerized cotton sheeting (e.g., Phoenix Calico) and demineralized water were used in all experiments.

3. Results

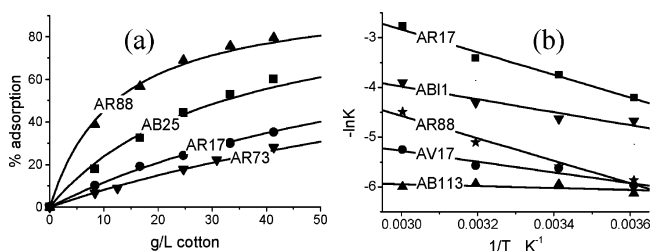
3.1. Measurement of Enthalpy and Entropy Values for Adsorption. Typical variations of dye adsorption with amount of cotton are shown in Figure 1a and as expected the dye type and amount of cotton change the adsorption. The maximum amount of dye adsorbed to the cotton was below 10^{-6} mol g⁻¹, which is well below the aggregation limit for species in cellulose¹⁴ and also far from surface coverage.¹⁵ The curve shapes are quantitatively understood on the reasonable assumption an equilibrium exists between dye in solution (dye_{aq}) and

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TABLE 1: Dye Structures, Experimental Values of K (293 K), ΔH , and ΔS for Adsorption, $\Sigma 1/r^6$, and the Calculated Dipole Moments

Dye	K (293K)	ΔH kJ/mol	ΔS J/mol/K	Dipole D	$\Sigma \frac{1}{r^6}$ 10^{57} m^{-6}
 Acid Orange 7 (AO7)	14	-16.3	-32.5	16.5	2.15
 Acid orange 12 (AO12) derivatives X=H X=Me X=MeO X=Me ₂ CH	14 30 48 33	-10.6 -17.0 -24.7 -22.7	-13.6 -28.3 -51.1 -46.3	20.2 19.5 25.2 33.2	1.77 2.12 2.48 2.83
 Acid Red 17 (AR17)	43	-18.9	-33.2	23.8	2.29
 Acid Red 27 (AR27)	4	-5	-7	8.2	1.30
 Acid Red 88 (AR88)	266	-18.7	-18.2	17.4	2.11
 Acid Red 73 (AR73)	15	-14.7	-26.8	26.4	1.50
 Acid Red 97 (AR97)	45	-31.0	-72.2	15.6*	2.96
 Acid Red 51	19	-20.1	-43.2	9.80	0.65
 Acid Black 1 (AB11)	102	-10.7	+0.9	21.9	1.46
 Acid Blue 25 (AB25)	104	-25.6	-52.1	15.7	2.52
 Acid Blue 113 (AB113)	383	-1.6	+44.5	12.7	0.85
 Acid Violet 17 (AV17)	277	-8.9	+16.9	19.4	1.41

* The value with the asterisk is the value for half of the dye.

**Figure 1.** (a) Variation of dye adsorption with dye type and amount of cotton at 293 K, with fit to eq 2. (b) Plot of $-\ln K$ vs $1/T$.

dye in cotton (dye_{cot}), such that

$$K = [\text{dye}_{\text{cot}}]/[\text{dye}_{\text{aq}}] \quad (1)$$

The percentage of dye adsorbed (% dye adsorbed) from solution is then given by

$$\% \text{ dye adsorbed} = 100 \times \left(\frac{KV_c}{V_{\text{aq}} + KV_c} \right) \quad (2)$$

where V_{aq} is the water volume and V_c is the accessible volume

of cotton obtained from the density (1.65 g/mL) and the fact that dye only deposits to the amorphous region (42% of total volume).⁸ The extracted K values show a strong variation with dye structure, Table 1. To ensure true equilibrium constants are measured, K values were also determined for five dyes by dye desorption from cotton and excellent agreement obtained between the two methods (AR73, AR17, AB25, AB11, AR88, $R^2 = 0.99$, not shown).

For each dye, the temperature dependence of K was measured in the range 277–333 K. Plotting $-\ln K$ versus $1/T$ gave a linear plot from which ΔH and ΔS are obtained by the well-known equation

$$-\ln K = -\frac{\Delta S}{R} + \frac{\Delta H}{RT} \quad (3)$$

as exemplified in Figure 1b, with values given in Table 1.

3.2. Interpretation and Discussion. The 15 dye structures are given in Table 1 and all azo dyes are drawn in their correct hydrazone tautomeric form where applicable ($=\text{N}-\text{NH}-$ not $-\text{N}=\text{N}-$).^{12,16,17} There are 5 mono-sulfonated phenyl-naphthyl mono-azo dyes (AO7 and AO12 derivatives) with different substituents and position of the sulfonate; 3 naphthyl-naphthyl

mono-azo dyes with 1,2 and 3 sulfonate groups (AR17, AR27, AR88); 4 bis-azo dyes of varying base structure (AB11, AR73, AR97, AB113); 1 xanthone (AR51); 1 anthraquinone dye (AB25); and 1 triphenylmethane dye (AV17). In terms of dye chemistry they represent a wide cross section of chromophore types which bind to cotton. Large variations in $K(293\text{ K})$, ΔH , and ΔS are found between the structures, with values varying from 4 to 383 and -5 to -33 kJ/mol and from -72 to $+44\text{ J/mol/K}$, respectively. The ΔH and ΔS values appear reasonable, as for simple adsorption slightly smaller entropies than those found for evaporation would be expected which are typically $100\text{ J mol}^{-1}\text{ K}^{-1}$ ¹⁸ and the enthalpy values match what would be expected for hydrogen bonds and dispersion forces.

For all dyes except AB113 and AV17 the adsorption is enthalpy-driven, while entropy favors desorption. There is no correlation between ΔH or ΔS and $K(293\text{ K})$: $R^2 = 0.1$ and 0.4 , respectively, vindicating the effort required to extract ΔH and ΔS rather than relying on K alone. A strong correlation between ΔH and ΔS is found ($R^2 = 0.90$) such that $\Delta H = -10.7 + 0.246\Delta S$. The reason for the correlation is unclear and may be due to the self-compensation¹⁹ and/or that the structural features that drive adsorption are also key to the entropy. Pragmatically, whatever the cause, the correlation means that if ΔH can be predicted, a reasonable estimate of ΔS and hence ΔG may be estimated for new dyes.

Assuming that the enthalpy of binding for all the dyes is predominately driven by the same interaction, the data should be examined to see if hydrogen bonding or van der Waals forces dominate. For hydrogen bonding, all the dyes contain hydrogen bond acceptors in the aromatic rings,²⁰ which could be bound to the OH groups of the cellulose, with additional contributions from the donor/acceptors N and O's of the dyes. However, using this hypothesis, it would be difficult to explain why addition of alkyl groups to AO12 increases the enthalpy, or why AB113 with an abundance of aromatic rings and N's has such a small binding enthalpy. Additionally, the OH groups of cellulose are believed to be strongly hydrogen-bonded internally and hence unavailable for bonding.⁸ Based on this qualitative reasoning, attention is directed toward van der Waals forces.

There are three types of attractive van der Waals forces: dipole/dipole, dipole/induced dipole, and induced dipole/induced dipole. All three are strongly distance-dependent such that²¹

$$\Delta H = -N_A \frac{C}{r^6} \quad (4)$$

where r is the distance separating the molecules, in this case the dye and cellulose and

$$C = \frac{2}{3} K_B T \left(\frac{\mu_1 \mu_2}{4\pi\epsilon_0} \right)^2 \quad \text{for dipole–dipole} \quad (5)$$

$$C = \frac{\mu_1^2 \alpha_2}{4\pi\epsilon_0} \quad \text{for dipole–induced dipole} \quad (6)$$

$$C = 1.5\alpha_1\alpha_2 \left(\frac{I_1 I_2}{I_1 + I_2} \right) \quad \text{for induced dipole–induced dipole} \quad (7)$$

where I_1 and I_2 are the ionization energies of the cellulose and dye, respectively; T is the temperature; α_1 and α_2 are the polarizabilities volumes; μ_1 and μ_2 are the dipole moments; N_A is Avogadro's number; ϵ_0 is the vacuum permittivity; and K_B is the Boltzmann constant.

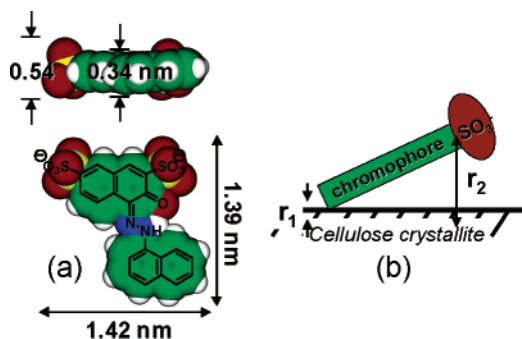


Figure 2. (a) Dimensions of Acid Red 17 (AR17) and (b) a pictorial representation of how it adsorbed to the crystallite surface.

The strong distance dependence of all three forces is especially intriguing when the dye shape is considered, exemplified by AR17, Figure 2. Most of the dyes have an essentially flat thin conjugated aromatic core, with fatter sulfonate groups on the periphery. The sulfonates are necessary to solubilize the dye in water and the aromatic core provides the color. These sulfonate groups will serve to raise the aromatic core from the cellulose surface and reduce the van der Waals forces. In part, this is due to their greater width, but also because they can interact with the water in the bulk amorphous region²² so that the hydrophobic dye core is close to the apolar crystallites and the hydrophilic sulfonates are hydrated in water pools in the bulk amorphous region. The degree to which the forces are reduced by parts of the dye rising from the surface should depend on where the/how many sulfonates are place in the molecule. Thus, in AR17 there are two sulfonates on one side, allowing the unsulfonated dye side to be close to the cellulose surface, producing an appreciable binding enthalpy. On the other hand, the two sulfonate groups in AB113 are on opposite sides of the molecule, making it impossible for most of the core to come close to the surface, and the binding enthalpy is small.

To put this hypothesis on a more quantitative basis, the distance, r , of the center of each C, N, I, and O in the aromatic core from the surface was calculated. This was done using simple geometry, assuming the cellulose surface is flat and the dye was placed on the surface, Figure 2b, as a rigid molecule. For closest contact the dye will touch the surface in at least three places; the dimensions of the dyes were calculated using a simple molecular modeling package (Molecular Modeling Pro, Chem SW) and dyes were in the conformers shown in Table 1.¹⁶ For all the dyes except AR51, when the dye touches the surface, there is a minimum distance of 0.17 nm , half the width of the aromatic core, between the surface and dye. In eq 4 the distance between the molecule centers is required, and hence the smallest value of r ($=r_1$) corresponding to the dye atoms that touch the cellulose surface is set to 0.34 nm . The other end of the dye is lifted from the surface by the sulfonates by a distance r_2 , which has a minimum value of 0.44 nm (the radius of the sulfonate + 0.17 nm), and this r_2 value varied to give the best fit to experiment. Clearly, once r_1 and r_2 are set, the distances for all atoms may be calculated. For AR51, the larger size of the iodines (diameter = 0.42 nm) must be taken into account and the carboxylated benzene ring assumed to behave similarly to the sulfonates.

The $\Sigma 1/r^6$ over all C, N, O, and I atoms gave the best correlation with the experimental, ΔH , when $r_2 = 0.8\text{ nm}$, for all but AR51, giving an R^2 of 0.91 , Figure 3. The values for $\Sigma 1/r^6$ are also given in Table 1. AR51 has quite a different structure to the other dyes, containing four large polarizable iodines, which may be the reason it appears to behave differently

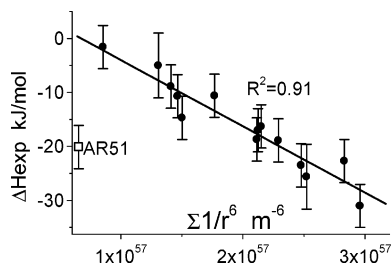


Figure 3. Correlation of ΔH with $\Sigma 1/r^6$; the dye AR51 is not included in the correlation.

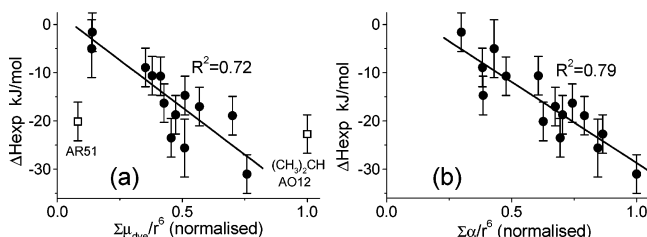


Figure 4. Correlation of ΔH with (a) $\Sigma \mu_{\text{dye}}/r^6$ and (b) $\Sigma \alpha/r^6$. The dyes AR51 and $(\text{CH}_3)_2\text{CH-AO12}$ are not included in the correlation of (a). All dyes are included in the correlation of (b).

vide infra. The correlation supports the hypothesis, and the value of r_2 agrees with the idea that the sulfonates are in water pools in the bulk amorphous regions.²² However, care must always be taken that such results are not fortuitous,²³ although the chance of obtaining a good correlation ($R^2 > 0.7$) accidentally is < 1 in 1000. Supporting the result is that the model used is physically reasonable and that such dye–cellulose geometries are already used to explain the UV–Vis spectra of acid dyes in cotton.²² It is worth noting that in a previous study of % adsorption of 52 acid dyes to cellulose analyzed using QSAR methods, the dyes AR88 and AB113 could not be fitted to any of the models, unlike in the current case.¹³

Thus, the results provide good evidence that to achieve a good enthalpy of binding, the dye core must be able to come as close as possible to the cellulose surface and that the position of the sulfonate groups is key in determining how well this can occur. If van der Waals forces are responsible for the binding, then it would be expected that correlation would also be obtained when the other variables in eqs 5–7 are included. For the dipole/dipole interaction this involves the dyes' dipole moments, which were estimated using commercial software (PEOE+ Hückel²⁴ Molecular Modelling Pro, Chem SW), with values given in Table 1. The estimated values are in reasonable agreement with literature values calculated by other methods where available.²⁵ A good correlation, $R^2 = 0.72$ ($r_2 = 0.8$ nm), Figure 4a, was found between $\Sigma \mu_{\text{dye}}/r^6$ and the binding enthalpy when the dyes AR51 and $(\text{CH}_3)_2\text{CH-AO12}$ were excluded. Allowing for the error inherent in estimating the dipole moments, the calculation itself and that the two outlier dyes are the most structurally diverse containing iodine and an isopropyl group, this shows that the results are consistent with the dipole–dipole interaction being important in the dye binding. Literature values for cellulose's dipole moment do not exist, as it is only soluble under extreme conditions; however, the dipole moment per glucose monomer has been measured for cellulose diacetate in dioxane as 2.8 D,²⁶ which also supports the dipole–dipole interaction being important.

For the dipole–induced dipole interaction, the polarizabilities volumes are central, which are approximately proportional to the molecular weight as the molecules are all predominately made from the same atom, C. This could also explain why a

good correlation is found in Figure 3 because polarizabilities volumes are effectively included by the summation. Of course, a more rigorous approach is to estimate the polarizability volumes using increments, where each N, O, and I have values of 2.8, 1.5, and 13.9, respectively, an aromatic C has 3.6, an aliphatic C has 0.28, and the value for H is 0.88. All values have units of 10^{-24} cm^3 .²⁷ Sulfonate groups have negligible polarizability using increments and H's are neglected due to their low polarizability and distance from the surface, Figure 2. The enthalpy of binding should then be given by

$$\Delta H = -N_A \frac{\mu_1^2}{4\pi\epsilon_0} \sum \frac{\alpha}{r^6} \quad (8)$$

where the summation is over all the C, N, O, and I atoms of the dye molecule. A good correlation, $R^2 = 0.79$, Figure 4b, is found between

$$\sum \frac{\alpha}{r^6}$$

and binding enthalpy with $r_2 = 0.8$ nm for the entire data set. The dye AR51 is brought back into the correlation because of the larger polarizability volume of the iodines. Consequently, the data are also consistent with the dipole–induced dipole interaction significantly contributing to the binding.

For the induced dipole–induced dipole the dye's ionization energy is important, which is difficult to measure or estimate. Oxidation potentials have been measured electrochemically for some dyes in acetonitrile and these vary by a factor of approximately 2 between triphenylmethane, mono-azo, and anthraquinone dyes.²⁸ The ionization potential of cellulose will be considerably higher than those of the dyes, further damping the effect of difference between dyes due to the

$$\frac{I_1 I_2}{I_1 + I_2}$$

factor. As such it would be expected that a correlation could also be found with eq 7, though a completely definitive statement cannot be made.

It is perhaps surprising that any correlation can be found, as it would be expected that dye adsorption is a complex process involving coadsorption/desorption of water from the cellulose surface. Recent EPR work on the adsorption of nitroxide spin probes has shown that, for the majority of adsorption sites, adsorption is independent of the cellulose water content,²⁹ indicating this does not play a major role.

4. Conclusions

Accurate measurement of the temperature dependence of acid dye adsorption onto cotton allows the enthalpy and entropy of the adsorption process to be experimentally obtained. For most dyes the adsorption is enthalpy driven, but for some it is entropy driven. The adsorption enthalpy is controlled by the position of the water-solubilizing groups on the dye as these groups lift the aromatic dye core from the cellulose surface. High adsorption enthalpies are provided by dyes which allow as much as the aromatic core to come close to the cellulose surface as possible. This observation can be effectively modeled by simply calculating the distance of each dye atom from an idealized flat surface. Further interpretation shows that such a correlation is consistent with any of the three van der Waals forces dominating the binding.

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