

A Thermodynamic Study of the Inclusion Processes of α - and β -Cyclodextrins with the Acid Forms of Methyl Orange and Methyl Yellow

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Abstract. The effect of temperature on the UV–visible spectra of the acid forms of methyl orange and methyl yellow in the presence of α - and β -cyclodextrins was analysed in terms of 1:1 inclusion processes. Three inclusion processes were considered for each azo dye/cyclodextrin system. The processes are the apparent inclusion process, the ammonium inclusion process, and the azonium inclusion process. The values of ΔH^0 and ΔS^0 are reported for each process. The inclusion complexes of the ammonium tautomer are more stable than those of the azonium tautomer and α -cyclodextrin inclusion complexes are more stable than those of β -cyclodextrin. The inclusion processes resulted in a shift in the position of the tautomeric equilibrium of an azo dye. A significant color fading was observed in α -cyclodextrin/methyl yellow solutions. No measurable changes in the absorbances were observed in the case of azo dye solutions containing γ -cyclodextrin.

Key words. Inclusion complexes, stability constants, cyclodextrins, methyl orange, methyl yellow.

1. Introduction

The inclusion processes exhibited by cyclodextrins are usually very rapid and require fast reaction techniques to reveal their kinetics [1]. However, most of the work on cyclodextrin inclusion complexes has been focused on the determination of stability constants [2]. The need for evaluating the stability constants and the thermodynamic quantities of the cyclodextrin inclusion processes with a wide range of substrate species has necessitated the use of several experimental methods such as the Benesi–Hildebrand spectrophotometric method [3], the conductance method [4], the potentiometric method [5], and the competitive indicator method [6]. The spectrophotometric method has been used for determining the stability constants of the inclusion complexes of cyclodextrins with azo dyes in acidic solutions [2, 7]. The stability constants of the inclusion complexes of α - and β -cyclodextrins with the ammonium and azonium tautomers of methyl orange and methyl yellow were previously given at 25°C [2]. The limitation to one temperature was due to the unavailability of literature information on model compounds which are usually needed for obtaining molar absorptivity data at temperatures other than 25°C.

The object of the present study is to demonstrate the application of a procedure proposed for calculating the tautomeric equilibrium constants from spectrophotometric data at several temperatures in the absence and in the presence of cyclodextrins. The results of such calculations are used in evaluating the stability constants of the inclusion complexes of the individual tautomers. The temperature depen-

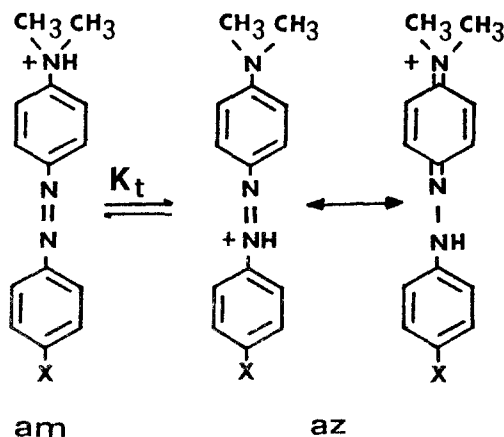


Fig. 1. Structural formulas of the ammonium tautomer (am) and the azonium tautomer (az) of the monoprotonated forms of methyl orange ($X = \text{SO}_3^-$) and methyl yellow ($X = \text{H}$).

dence of these stability constants leads to the evaluation of ΔH^0 and ΔS^0 which represent the standard change in the enthalpy and entropy of the inclusion processes of α - and β -cyclodextrins with the tautomers of methyl orange and methyl yellow. The structural formulas of these tautomers are given in Figure 1.

2. Experimental

The details of the experimental procedures concerning the preparation of stock solutions of methyl orange, methyl yellow, cyclodextrins and other preparations are the same as those reported previously [2]. The UV-visible spectra of the azo dyes were recorded in the 300–600 nm range using a double-beam spectrophotometer (DMS 100, Varian). Stopped quartz cells of 1.00 cm optical path length were used. The spectrophotometric data were obtained from absorbance measurements at 316 nm (λ_{max} for both azo dyes in the UV region) and at four other wavelengths (including λ_{max} for each azo dye) in the visible region. The effect of temperature on the inclusion processes was investigated at 15.0, 25.0, 33.0 and 40.0°C. The temperature of the water bath was controllable to $\pm 0.02^\circ\text{C}$.

3. Results and Discussion

The addition of either α -cyclodextrin or β -cyclodextrin to an acidic solution of an azo dye was found to decrease the absorbance in the visible region and to increase the absorbance in the UV region. This result is in accord with a previous study [2] and is interpreted as due to the occurrence of an inclusion process that involves the binding of an azo dye to a cyclodextrin cavity. Similar behavior was not observed for azo dye solutions containing γ -cyclodextrin even at low temperatures near 5°C. Based on this observation, it is concluded that the acid forms of methyl orange and methyl yellow do not bind to γ -cyclodextrin because of the relatively larger size of its cavity compared to that of α - or β -cyclodextrin.

Since the absorbances of the *cis* isomer of methyl orange are far less than those of the *trans* isomer [8] and the abundance of the *cis* isomer is usually less than that of the *trans* isomer, the *cis-trans* equilibrium has been neglected in the present study. The following two equilibria are proposed to account for the formation of 1:1 inclusion complexes of the tautomers



where am, az, am · CD and az · CD stand for the ammonium and azonium tautomers and their inclusion complexes, respectively. CD stands for a cyclodextrin while K_{am} and K_{az} are the stability constants of the ammonium and azonium complexes, respectively. K_{am} and K_{az} can be obtained by considering the following equilibria



where K_t and K^* are tautomeric equilibrium constants that describe the equilibria given by Equations 4 and 5, respectively.



Equation 3 gives the following relation

$$K_{\text{az}}/K_{\text{am}} = K^*/K_t \quad (6)$$

which defines the ratio $K_{\text{az}}/K_{\text{am}}$ at any temperature in terms of K^* and K_t . In order to evaluate K_{az} and K_{am} , another relation is required. If one considers an apparent inclusion process to describe the absorbance changes caused by the addition of a cyclodextrin, the following 1:1 inclusion process can be proposed.



where D, D · CD, and K stand for an azo dye, an inclusion complex, and the apparent stability constant, respectively. The equilibria of Equations 1, 2, and 7 define K_{am} and K_{az} as follows

$$K_{\text{am}} = K(1 + K_t)/(1 + K^*) \quad (8)$$

$$K_{\text{az}} = K\{(1 + K_t)/(1 + K^*)\}K^*/K_t \quad (9)$$

Based on the Benesi-Hildebrand method [3], Equation 10 was used to obtain the values of the apparent stability constant, K , from the spectrophotometric data of a given cyclodextrin/azo dye solution

$$l[\text{CD}]_0[\text{D}]_0/\Delta A = (1/K \cdot \Delta \epsilon) + [\text{CD}]_0/\Delta \epsilon \quad (10)$$

where l is the optical path length (in cm) of the cell used, $[\text{CD}]_0$ and $[\text{D}]_0$ represent the initial concentrations (in mol dm⁻³) of a cyclodextrin and an azo dye, ΔA is the

change in the absorbance of an azo dye due to the addition of a cyclodextrin, and $\Delta\epsilon$ is the difference in the molar absorptivities between the free and complexed azo dye. The absorbance data were obtained at 505 (λ_{\max}), 525, 530, 535 and 316 nm for methyl orange solutions in the presence of either α - or β -cyclodextrin. The corresponding wavelengths for methyl yellow are 518 (λ_{\max}), 525, 540, 545 and 316 nm. The data obtained at each wavelength were subjected to a linear least-squares analysis yielding values for $\Delta\epsilon$ and K from the slope and intercept of Equation 10, respectively. At least duplicate data were used for such an analysis. In the visible region, it was found that for a given data set (6–9 solutions in a set) the value of K at a certain wavelength is within $\pm 1\%$ of the mean of the set, implying that K is wavelength independent. The evaluation of K from data in the UV region at 316 nm gave results which were consistent with those obtained from the visible region except for the case of β -cyclodextrin and methyl orange where the values of K were about 40% lower than those obtained from the visible region. Such values were not considered in obtaining an average value for K . The difference is largely due to small changes in the absorbance of methyl orange at 316 nm upon the addition of β -cyclodextrin. The suitability of Equation 10 (which is based on the assumption of 1:1 inclusion processes) for analysing the spectrophotometric data of azo dye/cyclodextrin systems was discussed previously [2, 9].

The calculation of K_t at temperatures other than 25°C was carried out according to the following procedure. For azo dyes of the type investigated in this study, the maximum in the visible region is usually associated with the azonium tautomer while the maximum in the UV region is associated with the ammonium tautomer [10]. The ratio of the apparent molar absorptivities at the two maxima of an azo dye ($\epsilon_{\text{vis}}/\epsilon_{\text{UV}}$) can be considered to give a crude idea of the tautomeric equilibrium defined by Equation 4 [11]. The value of K_t at 25°C was calculated from data showing the effect of HCl concentration on K_t [12]. The calculated values of K_t are 3.46 for methyl orange and 1.33 for methyl yellow at 25°C in 0.10 mol dm⁻³ HCl. The ratio $\epsilon_{\text{vis}}/\epsilon_{\text{UV}}$ was calculated from the apparent molar absorptivities at the two maxima of each azo dye. Equation 11 was considered for calculating K_t at temperatures other than 25°C.

$$\epsilon_{\text{vis}}/\epsilon_{\text{UV}} = f \cdot K_t \quad (11)$$

where f is a factor whose value can be obtained from the given values of ϵ_{vis} , ϵ_{UV} , and K_t at 25°C. It is assumed in the present study that the factor f is temperature independent. This assumption is made since K_t is not known at temperatures different from 25°C. The factor f is 1.80 and 2.64 for methyl orange and methyl yellow at 25°C, respectively. The same argument was applied for calculating f^* for a solution that is entirely composed of complexed tautomers according to the following equation

$$\epsilon_{\text{vis}}^*/\epsilon_{\text{UV}}^* = f^* \cdot K^* \quad (12)$$

where the apparent molar absorptivities ϵ_{vis}^* and ϵ_{UV}^* are obtainable from the slope of Equation 10 and the apparent molar absorptivities, ϵ_{vis} and ϵ_{UV} , of the free azo dyes at wavelengths of maximum absorption. The calculation of K^* at 25°C was

described previously [2] from data obtained at 316 nm according to the following equation

$$K^* = \{\varepsilon_{316}^* - \varepsilon_{az}\}^{-1} \{\varepsilon_{316}(1 + K_t) - K_t \cdot \varepsilon_{az} - \varepsilon_{316}^*\} \quad (13)$$

where ε_{az} is the molar absorptivity of the azonium tautomer of an azo dye and has the value $2.0 \times 10^3 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ at 316 nm and 25°C [2]. The values of K^* at 25°C for the apparent inclusion processes of α - and β -cyclodextrins with the acid form of methyl orange are 0.267 and 0.272, respectively. The corresponding values for the inclusion processes of methyl yellow are 8.63×10^{-2} and 0.181. The factor f^* was calculated from Equation 12 at 25°C. The values obtained are 0.315 and 4.35 for the apparent inclusion process of the acid form of methyl orange with α - and β -cyclodextrins, respectively. The corresponding values for the inclusion process of methyl yellow are 0.298 and 3.45.

Tables I and II show the results of our calculations for the apparent molar absorptivities, tautomeric equilibrium constants, and the stability constants of the acid form of methyl orange and its inclusion complexes with α - and β -cyclodextrins. The data of Table I indicate that ε_{505} decreases while ε_{316} increases with increasing

Table I. The apparent molar absorptivities, tautomeric equilibrium constants and stability constants of the acid form of methyl orange and its inclusion complexes with α -cyclodextrin

Parameter	Temperature/°C			
	15.0	25.0	33.0	40.0
$10^{-4} \varepsilon_{505}/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	4.12 ± 0.03	4.01 ± 0.02	3.92 ± 0.02	3.84 ± 0.03
$10^{-3} \varepsilon_{316}/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	5.98 ± 0.30	6.43 ± 0.16	6.73 ± 0.14	7.14 ± 0.17
K_t	3.83	3.46	3.23	2.98
$10^{-3} \varepsilon_{505}^*/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	1.30 ± 0.12	1.48 ± 0.09	1.71 ± 0.13	2.04 ± 0.23
$10^{-4} \varepsilon_{316}^*/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	1.77 ± 0.01	1.76 ± 0.01	1.76 ± 0.01	1.77 ± 0.01
K^*	0.233	0.267	0.308	0.365
$10^{-2} K/\text{mol}^{-1} \text{ dm}^3$	9.27 ± 0.12	6.98 ± 0.03	5.46 ± 0.01	4.42 ± 0.03
$10^{-3} K_{am}/\text{mol}^{-1} \text{ dm}^3$	3.63	2.46	1.77	1.29
$10^{-2} K_{az}/\text{mol}^{-1} \text{ dm}^3$	2.21	1.90	1.68	1.58

Table II. The apparent molar absorptivities, tautomeric equilibrium constants and stability constants of the inclusion complexes of the acid form of methyl orange with β -cyclodextrin

Parameter	Temperature/°C			
	15.0	25.0	33.0	40.0
$10^{-4} \varepsilon_{505}^*/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	2.43 ± 0.01	2.07 ± 0.01	2.13 ± 0.03	2.06 ± 0.01
$10^{-4} \varepsilon_{316}^*/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	1.77 ± 0.02	1.75 ± 0.01	1.79 ± 0.01	1.70 ± 0.01
K^*	0.316	0.272	0.274	0.279
$10^{-2} K/\text{mol}^{-1} \text{ dm}^3$	3.24 ± 0.10	2.71 ± 0.12	2.42 ± 0.08	2.20 ± 0.15
$10^{-2} K_{am}/\text{mol}^{-1} \text{ dm}^3$	11.89	9.50	8.04	6.85
$K_{az}/\text{mol}^{-1} \text{ dm}^3$	98	75	68	64

temperature. By using the value of the factor f for methyl orange at 25°C, the values of K_t for the tautomeric equilibrium of methyl orange at temperatures other than 25°C were obtained from the temperature dependence of ϵ_{505} and ϵ_{316} as given in Table I. The temperature dependence of K_t indicates that the position of the tautomeric equilibrium of methyl orange shifts to the side of the ammonium tautomer as the temperature is increased. Table I also shows that for complexed methyl orange, ϵ_{505}^* increases while ϵ_{316}^* is nearly temperature independent. The values of K^* reported in Table I indicate that K^* increases with temperature. This leads to the conclusion that the position of the tautomeric equilibrium of the inclusion complexes of the acid form of methyl orange with α -cyclodextrin shifts to the side of the complexed azonium tautomer when the temperature is increased. Table II shows that ϵ_{316}^* is nearly temperature independent. The same applies for ϵ_{505}^* with the exception of the value at 15°C. It is concluded that the temperature has a minor effect on the position of the tautomeric equilibrium of β -cyclodextrin complexes with the acid form of methyl orange. As with regard to the apparent inclusion processes of α - and β -cyclodextrins with the acid form of methyl orange, the values of K reported in Tables I and II indicate that α -cyclodextrin forms more stable complexes than does β -cyclodextrin. The same conclusion also applies to the inclusion complexes of the individual tautomers as can be deduced from the values of K_{am} and K_{az} reported in Tables I and II. However, both α -cyclodextrin and β -cyclodextrin form more stable complexes with the ammonium tautomer than with the azonium tautomer. This result is in agreement with the increase in the absorbance at 316 nm and the decrease in the absorbance in the visible region which were observed upon the addition of either α - or β -cyclodextrin.

The molar absorptivities at 518 and 316 nm, the tautomeric equilibrium constants, and the stability constants of the inclusion processes of the acid form of methyl yellow with α - and β -cyclodextrins are given in Tables III and IV, respectively. Table III indicates that the effect of temperature on the molar absorptivities of free methyl yellow, ϵ_{518} and ϵ_{316} , is similar to the case of methyl orange in Table I. Therefore K_t for the tautomerism of methyl yellow decreases with temperature as given in Table III. The effect of temperature on ϵ_{518}^* , ϵ_{316}^* , and K^* (where the asterisk denotes quantities for a mixture of complexed tautomers) for the apparent inclusion process of α -cyclodextrin with the acid form of methyl yellow, as given in Table III, indicates that the position of the tautomeric equilibrium given by Equation 5 slightly shifts to the side of the azonium tautomer as the temperature is increased. This result is similar to that of the inclusion process of α -cyclodextrin and the acid form of methyl orange.

The data of Table IV show that ϵ_{518}^* for the apparent inclusion process of β -cyclodextrin and the acid form of methyl yellow decreases with increasing temperature, while ϵ_{316}^* is nearly constant. The corresponding values of K^* decrease with increasing temperature indicating that the position of the tautomeric equilibrium given by Equation 5 shifts to the side of the ammonium tautomer as the temperature is increased. On the basis of the values of K , K_{am} , and K_{az} given in Tables III and IV it is evident that the inclusion complexes of methyl yellow with α -cyclodextrin are more stable than those with β -cyclodextrin. As noted for methyl orange, Tables III and IV show that the inclusion complexes of the ammonium tautomer of methyl yellow are more stable than those of the azonium tautomer.

Table III. The apparent molar absorptivities, tautomeric equilibrium constants and stability constants of the acid form of methyl yellow and its inclusion complexes with α -cyclodextrin

Parameter	Temperature/ $^{\circ}\text{C}$			
	15.0	25.0	33.0	40.0
$10^{-4} \epsilon_{518}/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	3.60 ± 0.04	3.48 ± 0.05	3.40 ± 0.04	3.34 ± 0.04
$10^{-3} \epsilon_{316}/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	9.67 ± 0.22	9.91 ± 0.19	10.03 ± 0.18	10.20 ± 0.18
K_t	1.40	1.33	1.28	1.23
$10^{-2} \epsilon_{518}^*/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	3.94 ± 0.02	4.89 ± 0.05	4.82 ± 0.06	5.78 ± 0.58
$10^{-4} \epsilon_{316}^*/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	1.94 ± 0.04	1.90 ± 0.01	1.88 ± 0.02	1.89 ± 0.01
$10^2 K^*$	6.79	8.63	8.58	10.20
$10^{-3} K/\text{mol}^{-1} \text{ dm}^3$	2.94 ± 0.03	1.98 ± 0.07	1.45 ± 0.04	1.13 ± 0.01
$10^{-3} K_{\text{am}}/\text{mol}^{-1} \text{ dm}^3$	6.61	4.26	3.05	2.28
$10^{-2} K_{\text{az}}/\text{mol}^{-1} \text{ dm}^3$	3.20	2.76	2.04	1.89

Table IV. The apparent molar absorptivities, tautomeric equilibrium constants and stability constants of the inclusion complex of the acid form of methyl yellow with β -cyclodextrin

Parameter	Temperature/ $^{\circ}\text{C}$			
	15.0	25.0	33.0	40.0
$10^{-4} \epsilon_{518}^*/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	1.13 ± 0.04	1.10 ± 0.05	1.04 ± 0.04	0.99 ± 0.03
$10^{-4} \epsilon_{316}^*/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	1.74 ± 0.03	1.76 ± 0.04	1.72 ± 0.06	1.74 ± 0.04
K^*	0.188	0.181	0.175	0.165
$10^{-2} K/\text{mol}^{-1} \text{ dm}^3$	4.85 ± 0.10	4.62 ± 0.09	4.33 ± 0.10	3.95 ± 0.09
$10^{-2} K_{\text{am}}/\text{mol}^{-1} \text{ dm}^3$	9.80	9.11	8.40	7.56
$10^{-2} K_{\text{az}}/\text{mol}^{-1} \text{ dm}^3$	1.32	1.24	1.15	1.01

A quantitative comparison regarding the effect of α - and β -cyclodextrins on the position of the tautomeric equilibrium of either methyl orange or methyl yellow can be made on the basis of the following argument. If f_{am} and f_{am}^* represent the fractions of the free and complexed ammonium tautomer, while f_{az} and f_{az}^* represent the fractions of the free and complexed azonium tautomer of an azo dye, then these fractions are related to K_t and K^* as follows

$$K_t = f_{\text{az}}/f_{\text{am}} \quad (14)$$

$$K^* = f_{\text{az}}^*/f_{\text{am}}^* \quad (15)$$

Since the sum of these fractions is unity, then their dependence on the concentration of a cyclodextrin, [CD], can be given according to the following equations

$$1/f_{\text{am}} = (1 + K_t)\{1 + K[\text{CD}]\} \quad (16)$$

$$1/f_{\text{am}}^* = (1 + K^*)(1 + 1/K[\text{CD}]) \quad (17)$$

$$f_{\text{az}} = K_t\{(1 + K_t)(1 + K[\text{CD}])\}^{-1} \quad (18)$$

$$f_{\text{az}}^* = K^*\{(1 + K^*)(1 + 1/K[\text{CD}])\}^{-1} \quad (19)$$

Table V. The fractions of the ammonium and azonium tautomers of methyl orange and methyl yellow in aqueous cyclodextrin-free solutions and in the presence of 1.0×10^{-3} mol dm $^{-3}$ of either α - or β -cyclodextrin at 25°C

System ^a	f_{am}	f_{az}	f_{am}^*	f_{az}^*
MO	0.22	0.78	0	0
MO/ α -CD	0.13	0.46	0.32	0.09
MO/ β -CD	0.18	0.61	0.17	0.05
MY	0.43	0.57	0	0
MY/ α -CD	0.14	0.19	0.61	0.05
MY/ β -CD	0.29	0.39	0.27	0.05

^a MO, MY, α -CD and β -CD stand for the acid forms of methyl orange and methyl yellow, α - and β -cyclodextrins, respectively.

The solution of Equations 16–19 for $[\text{CD}] = 0$ and 1.0×10^{-3} mol dm $^{-3}$ at 25°C is given in Table V. According to this table the largest shift in the position of a tautomeric equilibrium is obtained for the methyl yellow/ α -cyclodextrin system where about 61% of methyl yellow has been converted into the colorless form via complexation of the ammonium tautomer. This result can be visually confirmed where an appreciable color fading is observed after the addition of α -cyclodextrin to the acidic solution of methyl yellow. Being the smallest, the values of ϵ_{518}^* shown in Table III for this system are consistent with this observation. The data of Table V show that, under similar conditions, the extent of complexation of an azo dye ($f_{\text{am}}^* + f_{\text{az}}^*$) by α -cyclodextrin is about twice that of β -cyclodextrin. A reasonable explanation for this result is that the relatively smaller cavity of α -cyclodextrin provides a better fit for the monomer of an azo dye.

The predominance of the ammonium inclusion process, as deduced from the f_{am}^* values given in Table V, can be explained by considering which side of an azo dye preferentially penetrates the cavity of a cyclodextrin. Information regarding the penetration of a substrate to a cyclodextrin cavity is usually obtained from a kinetic study [1]. However the data of the present equilibrium study suggest that the *N,N*-dimethyl aniline side of methyl orange or methyl yellow (see Figure 1) is not the penetrating side, instead the other side (an unsubstituted phenyl ring for methyl yellow and a phenyl ring carrying the SO_3^- group for methyl orange) is the penetrating side in both the ammonium and the azonium inclusion processes. The reasoning behind this is as follows. Since the proton of the acid form of an azo dye is attached to the azo group (most likely on the β -nitrogen) in the azonium tautomer and to the nitrogen of the *N,N*-dimethyl-aniline side in the ammonium tautomer, the bulkiness of the azo group should be determined by the location of the proton. The bulkiness of the azo group is expected to be largest in the azonium tautomer due to the attraction of water molecules by the positive charge on the azo group. Therefore the extent of cavity penetration should be largest for the inclusion of the ammonium tautomer. Considerations based on molecular models rule out the possibility of having the monomer of methyl orange or methyl yellow completely within the cavity of a cyclodextrin because the depth of the cavity is about half of the length of the azo dye. Therefore only partial penetration is possible which is affected by

the presence or absence of a positive charge on the azo group (located almost half-way from both sides of an azo dye). According to these considerations the presence of a positive charge on the azo group destabilizes the azonium inclusion complex due to steric factors resulting from the increased size of the azo group via solvolysis.

Gelb and Schwartz [13] have commented on the variations and the temperature dependence of the apparent molar absorptivities of methyl orange and its inclusion complexes with β -cyclodextrin and its derivatives. These authors reported that the molar absorptivity of the inclusion complex of the acid form of methyl orange with β -cyclodextrin is about 60% of that of the uncomplexed dye. This is in agreement with the value obtained at 15°C for the same system at 505 nm. The values of K reported in the present study at 25°C are in good agreement with literature data [2] except for the case of the α -cyclodextrin/methyl yellow system, where the present value is larger by a factor of two. The values of ϵ_{316} , ϵ_{316}^* , K^* , K_{am} , and K_{az} obtained at 25°C in the present study are somewhat different from those reported in reference [2]. The discrepancy arises from differences in the concentration of HCl which is 0.10 mol dm⁻³ in the present study, and 0.46 mol dm⁻³ in the previous work [2].

In order to evaluate the standard enthalpy change, ΔH^0 , and the standard entropy change, ΔS^0 , of the inclusion processes given by Equations 1, 2, and 7 the values of K_{am} , K_{az} , and K which were obtained at four temperatures were analysed according to the following thermodynamic equation

$$2.303R \log K = -\Delta H^0/T + \Delta S^0 \quad (20)$$

The values of K obtained from Equation 10 were found to be insensitive to variations in the ionic strength over the range 0.10–0.30 mol dm⁻³. Therefore the values of K , K_{am} , and K_{az} were used directly in Equation 20. The results of a linear least-squares analysis of the temperature dependence of K , K_{am} , and K_{az} are given in Table VI. ΔH^0 and ΔS^0 were obtained from the slope and intercept of Equation 20. It is evident from Table VI that all the inclusion processes are exothermic and the magnitude of ΔH^0 is indicative of the weak bonding involved in the formation of such inclusion complexes. All the inclusion processes of α -cyclodextrin are accompanied by a decrease in the entropy except for the azonium inclusion process with methyl orange. The opposite is true for the inclusion processes of β -cyclodextrin with the exception of the azonium inclusion process with methyl orange. Another observation to be deduced from Table VI is that the ammonium inclusion process is the most exothermic process for a given azo dye/cyclodextrin system.

The uncertainties associated with the values of the apparent molar absorptivities and the stability constants of the apparent inclusion processes which appear in Tables I–IV, are standard deviations estimated from experimental data. The remaining parameters reported in Tables I–IV were calculated from the appropriate expression in the text without specifying their uncertainties since more reliable uncertainties are required for that. The uncertainties of ΔH^0 and ΔS^0 reported in Table VI were computed from the uncertainties in the slope and intercept of Equation 20.

The temperature dependence of K_{am} and K_{az} as reported in Tables I–IV was found to fit Equation 20 with correlation coefficients ranging from 0.96 to 1.0. This

Table VI. Values of ΔH^0 (in kJ mol^{-1}) and ΔS^0 (in $\text{J mol}^{-1} \text{K}^{-1}$) for the various inclusion processes of α - and β -cyclodextrins with the acid forms of methyl orange and methyl yellow in aqueous solutions

Cyclodextrin	Azo dye	Process ^a	$-\Delta H^0$	ΔS^0
α -Cyclodextrin	Methyl orange	Apparent	22.3 ± 0.7	-20.4 ± 2.4
		Ammonium	30.9 ± 1.3	-39.1 ± 4.2
		Azonium	10.3 ± 0.6	9.2 ± 2.1
	Methyl yellow	Apparent	28.8 ± 0.3	-33.6 ± 1.0
		Ammonium	31.9 ± 0.3	-37.5 ± 0.9
		Azonium	17.0 ± 2.6	-10.7 ± 8.7
β -Cyclodextrin	Methyl orange	Apparent	11.6 ± 0.3	7.8 ± 1.2
		Ammonium	16.4 ± 0.3	1.8 ± 1.2
		Azonium	12.8 ± 2.1	-6.5 ± 7.0
	Methyl yellow	Apparent	6.0 ± 1.1	30.7 ± 3.5
		Ammonium	7.7 ± 1.1	30.8 ± 3.6
		Azonium	7.8 ± 1.6	13.9 ± 5.2

^a The apparent process refers to the equilibrium of Equation 7, while the ammonium and azonium processes refer to the equilibria given by Equations 1 and 2, respectively, in the text.

fit is very unlikely to be a coincidence. It is an indication that the assumption of the factors f and f^* being temperature independent is quite reasonable.

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