CHAPTER 3

The acid dissociation constants (pK\textsubscript{A}) of PADA

The values of pK\textsubscript{A1} and pK\textsubscript{A2} of PADA have been measured in water and in the presence of various concentrations of SDS and DTAC with the purpose of providing the coefficients that allow the conversion of pH from water to surfactant surface. Moreover, the knowledge of the pK value of a ligand can be essential for the analysis of the mechanisms of the reactions where the ligand itself is involved. Figure 3.1 shows the protonation/deprotonation steps of PADA and the protonation sites proposed by Klotz e Loh Ming (1953).

\textbf{Figure 3.1} Protonation/deprotonation steps of PADA and protonation sites.
The different extent of PADA dissociation in DTAC, H$_2$O or SDS is clearly revealed by the colour change displayed by the dye present in the three distinct media. Figure 3.2A shows that, at pH = 5, in water the dye solution is orange, corresponding to the sum of the contributions of the mono-protonated and neutral forms; in the more acidic surface of SDS the adsorbed dye impart a fucsia colour to the solution corresponding to the mono-protonated PADA; in the less acidic surface of DTAC the adsorbed dye exhibits a yellow colour corresponding to the neutral, proton free, form of PADA. The spectra of the three solutions are shown in Figure 3.2B.

![figure3.2](image)

**Figure 3.2** (A) Colour of PADA solutions in different media (respectively in H$_2$O or 0.02M SDS and 0.02M DTAC micellar systems); (B) spectral changes of PADA in the same different media. [PADA] = 1×10$^{-5}$M, pH = 5.0, T = 25°C.

### 3.1 Determination of pK$_{A1}$ and pK$_{A2}$ of PADA in water

The acid dissociation constants of PADA were measured in aqueous solution at 25°C by spectrophotometric titrations. Calibrated small amounts of HCl were sequentially added to the spectrophotometric cell containing 2.00 ml of an aqueous solution at pH = 7.0 (not buffered). Under these circumstances PADA was present essentially as the fully deprotonated species. Figure 3.3 shows the spectral changes of the dye induced by addition of HCl.
Figure 3.3 Spectral changes of $1\times10^{-5}$ M PADA in aqueous solution induced by addition of HCl at different pH values (pH = 0.4–7.0), $I = 0.1 \, M$ (NaCl), $T = 25 \, ^\circ C$; (a) pH = 7, green line, corresponding to $L$, (b) pH = 2.5 corresponding to $HL^+$ with small contribution from $H_2L^{2+}$, (c) pH = 0.4 corresponding to $H_2L^{2+}$.

The dissociation constants of PADA, $K_{A1}$ and $K_{A2}$, were evaluated using the absorbance data at $\lambda = 560 \, nm$. Figure 3.4 shows a typical titration curve which displays a biphasic behavior in agreement with the two protonation steps represented in the scheme of Figure 3.1.

Figure 3.4 Typical spectrophotometric titration curve aimed to determine the dissociation constants of PADA. $C_L = 1\times10^{-5} \, M$, $I = 0.1 \, M$ (NaCl), $\lambda = 560 \, nm$, $T = 25 \, ^\circ C$. 
The titration behavior has been analyzed using a non linear least-square treatment of data points according to equation 3.1 (see Appendix I).

\[
\frac{\Delta A}{C_L} = \frac{\Delta \varepsilon_2 K_{A_1} [H^+] + \Delta \varepsilon_1 [H^+]^2}{[H^+]^2 + K_{A_1} [H^+] + K_{A_1} K_{A_2}}
\]  

(3.1)

where \(C_L\) is the total dye concentration, \(\Delta A\) is the absorbance change \((A - A_0)\), \(\Delta \varepsilon_2 = \varepsilon_{HL} - \varepsilon_L\) and \(\Delta \varepsilon_1 = \varepsilon_{HL} - \varepsilon_L\). The continuous line in Figure 3.4 represents the best fit to data points according to equation 3.1.

### 3.2 Determination of pK\(_{A_1}\) and pK\(_{A_2}\) of PADA in SDS.

The dissociation constant of PADA in the presence of SDS were determined by the same procedure adopted for measurements in water. Figure 3.5 shows the spectral variations of PADA in 0.02 M SDS induced by increasing additions of HCl.

![Figure 3.5 Spectral changes of 1×10⁻⁵ M PADA in 0.02M SDS, induced by addition of HCl at different pH values (pH = 7+1.4), T = 25 °C; (a) pH = 7, green line, corresponding to L and HL⁺; (b) pH = 4 corresponding to HL⁺ with small contribution from H₂L²⁺; (c) pH = 1.4 corresponding to H₂L²⁺.](image)

Figure 3.6 shows a typical titration curve recorded at 560 nm.
Figure 3.6 Titration curve aimed to evaluate the dissociation constants of PADA in SDS. [PADA] = 1×10^{-5} M, [SDS] = 0.06 M, I = 0 M (NaCl), \( \lambda = 560 \text{ nm} \), \( T = 25 ^\circ \text{C} \).

The data have been processed on the basis of equation 3.1 and the values of \( K_{A1} \), \( K_{A2} \), \( pK_{A1} \) and \( pK_{A2} \) obtained at different SDS concentrations are reported in Table 3.1.

**Table 3.1 Acid dissociation constants of PADA, measured at different concentrations of SDS, \( I = 0.1 \text{M (NaCl)} \) and \( T = 25 ^\circ \text{C} \).**

<table>
<thead>
<tr>
<th>[SDS]/M</th>
<th>( K_{A1}/M )</th>
<th>( K_{A2}/M )</th>
<th>( pK_{A1} )</th>
<th>( pK_{A2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.1×10^{-2}</td>
<td>3.2×10^{-5}</td>
<td>2.0 (2.0(^a))</td>
<td>4.5 (4.5(^a))</td>
</tr>
<tr>
<td>0.01</td>
<td>1.3×10^{-3}</td>
<td>4.6×10^{-6}</td>
<td>2.89</td>
<td>5.34</td>
</tr>
<tr>
<td>0.02</td>
<td>9.1×10^{-4}</td>
<td>1.0×10^{-6}</td>
<td>3.04</td>
<td>5.99</td>
</tr>
<tr>
<td>0.03</td>
<td>7.1×10^{-4}</td>
<td>2.5×10^{-5}</td>
<td>3.15</td>
<td>4.60</td>
</tr>
<tr>
<td>0.04</td>
<td>5.5×10^{-3}</td>
<td>3.6×10^{-4}</td>
<td>2.26</td>
<td>3.44</td>
</tr>
<tr>
<td>0.05</td>
<td>1.5×10^{-2}</td>
<td>1.2×10^{-4}</td>
<td>1.81</td>
<td>3.92</td>
</tr>
<tr>
<td>0.07</td>
<td>1.3×10^{-2}</td>
<td>2.0×10^{-4}</td>
<td>1.89</td>
<td>3.70</td>
</tr>
</tbody>
</table>

\(^a\) James e Robinson, 1978
3.3 Determination of $pK_{A1}$ and $pK_{A2}$ of PADA in DTAC.

The methodology employed is the same as that used in water and SDS. Figure 3.7 shows how the spectra of PADA in DTAC change upon addition of HCl to the dye/DTAC mixture. Figure 3.8 represents a typical titration curve recorded at 560 nm. The data points have been processed again according to equation 3.1 and the values of the acid dissociation constants of PADA are represented in Table 3.2 for different DTAC concentrations.

![Figure 3.7](image1.png)

**Figure 3.7** Spectral changes of $5 \times 10^{-6}$ M PADA in the presence of 0.04 M DTAC induced by addition of HCl at different pH values ($pH = 5 \div 0.4$), $T = 25^\circ C$; (a) $pH = 5$, green line, corresponding to L, (b) $pH = 1.64$ corresponding to $HL^+$ with small contribution from $H_2L^{2+}$ and L, (c) $pH = 0.4$ corresponding to $H_2L^{2+}$.

![Figure 3.8](image2.png)

**Figure 3.8** Titration curve aimed to evaluate the dissociation constants of PADA in DTAC. $[PADA] = 1 \times 10^{-5}$ M, $[DTAC] = 0.06$ M, $I = 0.1$ M (NaCl), $\lambda = 560$ nm, $T = 25^\circ C$. 
Table 3.2 Acid dissociation constants of PADA measured at different concentrations of DTAC, $I = 0.10 \text{ M (NaCl)}$, $T = 25 \, ^\circ\text{C}$.

<table>
<thead>
<tr>
<th>[DTAC]/M</th>
<th>$K_{A1}$/M</th>
<th>$K_{A2}$/M</th>
<th>pK$_{A1}$</th>
<th>pK$_{A2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.1×10^{-2}</td>
<td>3.2×10^{-5}</td>
<td>2.0 (2.0$^a$)</td>
<td>4.5 (4.5$^a$)</td>
</tr>
<tr>
<td>0.01</td>
<td>3.9×10^{-2}</td>
<td>1.9×10^{-4}</td>
<td>1.41</td>
<td>3.72</td>
</tr>
<tr>
<td>0.02</td>
<td>4.5×10^{-2}</td>
<td>1.9×10^{-4}</td>
<td>1.35</td>
<td>3.72</td>
</tr>
<tr>
<td>0.03</td>
<td>5.0×10^{-2}</td>
<td>5.6×10^{-4}</td>
<td>1.30</td>
<td>3.25</td>
</tr>
<tr>
<td>0.04</td>
<td>5.1×10^{-2}</td>
<td>1.1×10^{-3}</td>
<td>1.29</td>
<td>2.96</td>
</tr>
<tr>
<td>0.05</td>
<td>4.8×10^{-2}</td>
<td>1.6×10^{-3}</td>
<td>1.32</td>
<td>2.80</td>
</tr>
<tr>
<td>0.06</td>
<td>4.6×10^{-2}</td>
<td>2.4×10^{-3}</td>
<td>1.34</td>
<td>2.62</td>
</tr>
</tbody>
</table>

$^a$ James e Robinson, 1978

All the results concerned with the equilibrium parameters described in this section are summarized in Table 3.3.

Table 3.3 Acid dissociation constants of PADA measured in different media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>[Surfactant]/M</th>
<th>pK$_{A1}$</th>
<th>pK$_{A2}$</th>
<th>ΔpK$_{A1}$</th>
<th>ΔpK$_{A2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0</td>
<td>1.93</td>
<td>4.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SDS</td>
<td>0.03</td>
<td>3.15</td>
<td>4.60</td>
<td>1.22</td>
<td>0.10</td>
</tr>
<tr>
<td>DTAC</td>
<td>0.03</td>
<td>1.30</td>
<td>3.25</td>
<td>-0.63</td>
<td>-1.25</td>
</tr>
</tbody>
</table>

3.4 Discussion of the results presented in Chapter 3

The data reported in Table 3.3 show that the acid dissociation constants of PADA do change in the presence of the surfactants in opposite direction. The $\Delta pK$ values ($\Delta pK = pK_{\text{surfactant}} - pK_{\text{water}}$) are positive in the presence of SDS whereas they are negative in the presence of DTAC. Denoting the deprotonated dye as L, the two acid dissociation equilibria are expressed by the reactions 3.2 and 3.3.

$$H_2L^{2+} \rightleftharpoons HL^+ + H^+ \quad (3.2)$$
The PADA/SDS system. Figure 3.9 shows the changes of $pK_{A1}$ and $pK_{A2}$ of PADA in SDS, relative to the $pK_{A1}$ and $pK_{A2}$ values in water.

![Graph showing the changes of $\Delta pK_{A1}$ and $\Delta pK_{A2}$ on the SDS concentration for the PADA/SDS system.](image)

**Figure 3.9** Dependence of $\Delta pK_{A1}$ and $\Delta pK_{A2}$ on the SDS concentration for the PADA/SDS system; (●) $\Delta pK_{A1}$, (○) $\Delta pK_{A2}$, I variable with the surfactant concentration, $T = 25^\circ C$.

The increase of both $\Delta pK_{A1}$ and $\Delta pK_{A2}$ values by about 1.5 units from [SDS] = 0 M to [SDS] = 0.02 M can be explained in terms of the electrostatic potential effect expressed by equation 3.2. The subsequent asymptotic decrease of both $\Delta pK_{A1}$ and $\Delta pK_{A2}$ observed for [SDS] > 0.02 M can be explained on the basis of a change of the surface potential of SDS as the number of surface-charges per volume unit increases. Actually, the density of the counter-ions responsible for formation of the double-layer in the vicinity of the micelle surface diminished by increasing [SDS] since the counter-ions are diluted over an enhanced number of charge-sites on the micelle surface. As a consequence, the surface potential decreases.

A kinetic explanation for the observed behavior could be forwarded. The abrupt increase of $pK_{A1}$ and $pK_{A2}$ observed up to [SDS] = 0.02 M is rationalized by:

\[
HL^+ \rightleftharpoons L + H^+ \quad (3.3)
\]
in terms of the “catalytic” effect exerted by charged micelles on reactions involving ions oppositely charged with respect to the micelle. Actually, the micelle acts as a nanoreactor where the partners of a given reaction can be concentrated so that the reaction rate is enhanced. Concerning the PADA/SDS system, the effect of SDS is to increase the specific rate of \( H_2L^{2+} \) formation (\( k_{\text{ass}} \)) because the encounter frequency between \( H^+ \) and \( HL^+ \) is enhanced, while the specific rate of \( H_2L^{2+} \) dissociation (\( k_{\text{diss}} \)) remains unchanged (being this a monomolecular step). As a consequence the equilibrium constant (\( K_{A1} = k_{\text{diss}}/k_{\text{ass}} \)) decreases and \( pK_{A1} \) increases. The decreasing trend observed for \([SDS] > 0.02 \text{ M}\) can also be explained on a kinetic ground. As \([SDS] \) increases the reaction partners distribute over a larger number of charge-sites. Such a dilution effect results in a decrease of the specific rate \( k_{\text{ass}} \) while \( k_{\text{diss}} \) remains unchanged. The obvious conclusion is that \( pK_{A1} \) experiences an asymptotic decrease.

**The PADA/DTAC system.** Figure 3.10 shows the dependence (relatives to the values in water) of \( pK_{A1} \) and \( pK_{A2} \) of PADA on the DTAC concentration.

![Figure 3.10](image)

**Figure 3.10** Dependence of \( \Delta pK_{A1} (\bullet) \) and \( \Delta pK_{A2} (\circ) \) on DTAC concentration for the PADA/DTAC system; \( I \) given by surfactant concentration, \( T = 25 ^\circ C \).
Note that pK$_{A1}$ values are independent on [DTAC]. Contrary to the case of PADA/SDS, in this case the species H$^+$, HL$^+$ and H$_2$L$^{2+}$ are repelled by the positively charged micelle. Only the neutral species L is likely transferred to the micellar pseudo-phase. Consider now the first proton transfer step (reaction 3.2). Here, all the reacting species are positively charged and stay away from the micelle. The reaction 3.2 occurs essentially in the aqueous phase and hence the equilibrium is not affected by the change of DTAC concentration as shown in Figure 3.10.

Consider now the second proton transfer step (reaction 3.3). Here H$^+$ and HL$^+$ ions are repelled by DTAC micelles and stay in the aqueous phase, but the neutral species L is likely to be at least partially absorbed on the micelles owing to its hydrophobic characteristics. Let’s define the distribution ratio as

$$R = \frac{[L]_{\text{surfactant}}}{[L]_{\text{water}}} \quad (3.4)$$

and the mass conservation equation for L as

$$[L]_T = [L]_{\text{surfactant}} + [L]_{\text{water}} \quad (3.5)$$

The overall, experimentally measured, dissociation constant of PADA is

$$K_{A2T} = [H^+]_T [L]_T/[HL]_T \quad (3.6)$$

Taking into account that $[H^+]_T = [H^+]_{\text{water}}$ and $[HL^+]_T = [HL^+]_{\text{water}}$, introduction of equation 3.4 in equation 3.5 and introduction of the result in equation (3.6) yields

$$K_{A2T} = K_{A2\text{water}} (1 + R) \quad (3.7)$$

As the DTAC concentration is raised, more and more ligand molecules will be absorbed on the micelles, so R increases up to saturation. $K_{A2T}$ will augment by
consequence according to equation 3.7 and pK_{A2} will decrease asymptotically as shown in Figure 3.10.

It has been observed that, keeping the acidity level constant (pH = 5.5), the colour of PADA changes from pink to orange on increasing the NaCl concentration (Figure 3.11). As known, PADA is a bi-protonated azo-dye that changes its colour from pink to orange and yellow upon conversion to the deprotonated, forms.

![Figure 3.11](image)

*Figure 3.11 The colour of PADA solutions, at constant hydrogen ion concentration, apparently depends on the concentration of added chloride; [PADA] = 4 \times 10^{-5} M, [SDS] = 0.02 M, pH = 5.5, T = 25 \, ^\circ C.*

An explanation for this behaviour could be found in the competition between PADA and the Na\(^+\) ions for the SDS surface. Both molecules tend to be retained on the micelle and, as [Na\(^+\)] is increased, the dye molecules, which at pH = 5.5 are present as HL\(^+\) and as H\(_2\)L\(^{2+}\), will be pushed from the SDS surface into the aqueous pseudo-phase where they deprotonate according to the ΔpK\(_A\) argument, with concomitant change of colour. A confirmation of this interpretation is provided by the picture of the three samples shown below (Figure 3.12). There, the Na\(^+\) concentration is the same (0.25 M) in the three cuvettes, while the concentration of Cl\(^-\) ions changes. The colour of the three solutions remains constant, revealing that the responsible for the observed behaviour are the Na\(^+\), and not the Cl\(^-\), ions.
Figure 3.12 The colour of PADA \((4\times10^{-5}M)\) does not change in different chloride concentrations at constant ionic strength, pH = 5.5; (a) \([\text{NaCl}] = 0.02 \, M, [\text{NaClO}_4] = 0.23 \, M\), (b) \([\text{NaCl}] = 0.10 \, M, [\text{NaClO}_4] = 0.15 \, M\), (c) \([\text{NaCl}] = 0.25 \, M\).