

# Proton transfer from 2-naphthol to aliphatic amines in supercritical CO<sub>2</sub>

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## Supporting Information

### **1: Equilibrium constant for DIEA, TEA, MP with 2-NpOH in the ground state.**

Speciation of 2-naphthol can be obtained from the UV absorption spectra. On the longer wavelength side of the spectra, we can assure that the total absorption intensity is only due to the contributions of 2-naphthol and 2-naphtholate species, equation 1, as the absorption of the amine is negligible.

$$A_T = \sum_i^{i=j} A_i = (\varepsilon_{\text{NpOH}} \cdot C_{\text{NpOH}} + \varepsilon_{\text{NpO}^-} \cdot C_{\text{NpO}^-}) \cdot l = \left[ \varepsilon_{\text{NpOH}} \cdot (1 - f_{\text{NpO}^-}) + \varepsilon_{\text{NpO}^-} \cdot f_{\text{NpO}^-} \right] \cdot C_{\text{NpOH}}^0 \cdot l \quad (1)$$

In this equation,  $\varepsilon_i$  is the absorption coefficient and  $C_i$  is the molar concentration of species  $i$ ,  $l$  is the optical path length, and  $f_{\text{NpO}^-}$  is the concentration fraction of 2-naphtholate moiety at equilibrium.

The fraction of 2-naphthol molecules in the proton transfer complex,  $f_{\text{NpO}^-}$ , for each concentration of amine in the system, can then be obtained from equation 1,

$$f_{\text{NpO}^-} = \frac{[2-\text{NpO}^- \cdots \text{AmH}^+]}{C_{\text{NpOH}}^0} = \frac{A - A_{\text{NpOH}}^0}{A_{\text{NpO}^-}^\infty - A_{\text{NpOH}}^0} = c \cdot (A - A_{\text{NpOH}}^0) \quad (2)$$

where  $A$  is the absorbance for each concentration of the amine,  $A_{\text{NpOH}}^0 = \varepsilon_{\text{NpOH}} l C_{\text{NpOH}}^0$  is the absorbance of 2-naphthol before amine injection and  $A_{\text{NpO}^-}^\infty = \varepsilon_{\text{NpO}^-} l C_{\text{NpOH}}^0$  represents the 2-naphtholate absorbance after complete conversion of 2-naphthol. Note that in equation 2 the denominator ( $A_{\text{NpO}^-}^\infty - A_{\text{NpOH}}^0$ ) does not depend on the concentration of amine, only on  $C_{\text{NpOH}}^0$ ;

therefore, for each run (constant  $C^{\circ}_{\text{NpOH}}$ ) its value was taken as a constant  $c^{-1}$ , as specified in the last term of equation 2.

To calculate the equilibrium constant of reaction (3) for proton transfer complex formation in the ground state,

$$2-\text{NpOH} + \text{Am} \leftrightarrow (2-\text{NpO}^- \cdots \text{AmH}^+) \quad K = \frac{[2-\text{NpO}^- \cdots \text{AmH}^+]}{[2-\text{NpOH}] \cdot [\text{Am}]} = \frac{f_{\text{NpO}^-}}{(1-f_{\text{NpO}^-}) \cdot [\text{Am}]} \quad (3)$$

equations 2 and 3 were combined and rearranged to yield equation 4:

$$\frac{c}{K \cdot [\text{Am}]} + c = \frac{1}{A - A^{\circ}_{\text{NpOH}}} \quad (4)$$

According to this equation, we can calculate the equilibrium constant by just fitting the experimental values of  $\frac{1}{[\text{Am}]}$  and  $\frac{1}{A - A^{\circ}_{\text{NpOH}}}$  to a linear relation.

In all cases, the absorbance,  $A$  and  $A^{\circ}_{\text{NpOH}}$ , was taken at  $\lambda = 335$  nm.

The value of the equilibrium constant does not depend on the wavelength chosen for computation.

The following table compares the results in cyclohexane obtained from the single wavelength analysis and with a bilinear regression using all the spectral range.<sup>1</sup>

Amine	Bilinear regression	$\lambda = 335$ nm
DIEA	-1.3	-1.0
TEA	-1.4	-1.5
MP	-2.5	-2.0

**Table 1:** pK values for reaction (3) in cyclohexane obtained from single wavelength analysis at 335 nm and from bilinear regression.

## 2: Speciation and correction of Stern-Volmer plots for absorption by two species

The absorbance at the excitation wavelength varies throughout the experiment. This is due to the fact that  $2-\text{NpO}^-$  builds up in the ground state by reaction with the amine, and both absorption

spectra overlap. Therefore, in order to quantify the Stern-Volmer constant,  $K_{SV}$ , a correction of the emission intensity must be performed to take into account the fraction of light absorbed by each species.

Equation 5 gives the fraction of light absorbed by 2-NpOH with respect to the incident light flux,  $I_{a,NpOH} / I_0$ ,

$$\frac{I_{a,NpOH}}{I_0} = \frac{A_{NpOH}}{A_T} \cdot (1 - 10^{-A_T}) \quad (5)$$

$A_{NpOH}$  can be expressed by means of the fraction  $f_{NpOH} = (1 - f_{NpO^-})$  and initial absorbance, of naphthol,  $A_{NpOH}^0$ .

$$\frac{I_{a,NpOH}}{I_0} = \frac{f_{NpOH} A_{NpOH}^0}{A_T} \cdot (1 - 10^{-A_T}) \quad (6)$$

On the other hand, at 335 nm only 2-NpOH emits, and then the fluorescence emission intensity can be expressed as a function of the absorbance at the excitation wavelength,  $I_{a,NpOH}(\lambda_{exc})$ , and the fluorescence quantum yield of 2-NpOH,  $\phi_{f,NpOH}$ , equation 7.

$$I_f = I_{a,NpOH}(\lambda_{exc}) \cdot \phi_{f,NpOH} \quad (7)$$

Then, assuming that  $\phi_{f,NpOH}$  is a constant, the relative fluorescence intensity can be expressed as,

$$\left( \frac{I_{f0}}{I_f} \right)_{\text{exp}} = \frac{I_{a,NpOH}^0(\lambda_{exc})}{I_{a,NpOH}(\lambda_{exc})} \cdot \frac{\phi_{f,NpOH}^0}{\phi_{f,NpOH}} = \frac{(1 - 10^{-A_{NpOH}^0})}{(1 - 10^{-A_T})} \cdot \frac{A_T}{A_{NpOH}^0} \cdot \frac{1}{f_{NpOH}} \cdot \frac{\phi_{f,NpOH}^0}{\phi_{f,NpOH}} \quad (8)$$

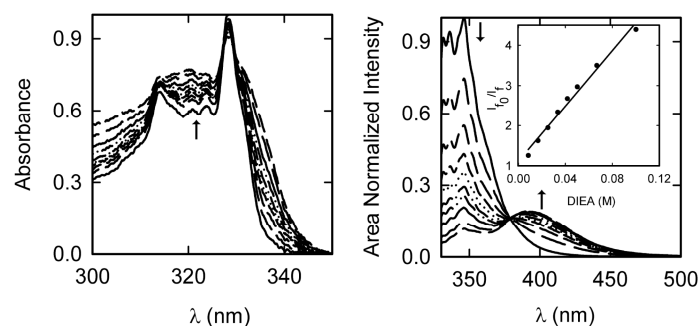
all the absorbance values are at the excitation wavelength, 312 nm. Finally, with equation 9, the fluorescence intensity of the 2-naphthol is corrected by the fraction of absorbed light of the emissive species.

$$\frac{\phi_{f,NpOH}^0}{\phi_{f,NpOH}} = \frac{\left( \frac{I_{f0}}{I_f} \right)_{\text{exp}}}{\frac{(1 - 10^{-A_{NpOH}^0})}{(1 - 10^{-A_T})} \cdot \frac{A_T}{A_{NpOH}^0 f_{NpOH}}} \quad (9)$$

This is the corrected intensity used for the S.V. plots. It takes into account the  $\text{NpOH} \rightarrow 2\text{-NpO}^-$  conversion in the ground state and the inner filter effect in the emission of 2-NpOH by 2-NpO<sup>-</sup> absorption in the ground state.

### 3: System 2-naphthol/DIEA in cyclohexane

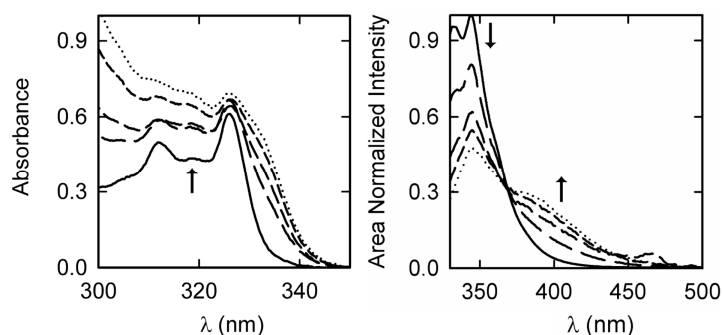
Figure 1 shows changes on the absorption and emission spectra of 2-NpOH upon addition of DIEA in cyclohexane.



**Figure 1.**-Left: Absorption spectra of mixtures of 2-naphthol and DIEA in cyclohexane (room temperature). Concentrations of amine are 0.00; 0.008; 0.017; 0.025; 0.033; 0.050; 0.067 and 0.100 M. Right: Area normalized corrected emission spectra ( $\lambda_{\text{exc}} = 312$  nm) for the same sample; inset: Stern-Volmer plot ( $K_{\text{SV}} = 36 \text{ M}^{-1}$ ).

### 4: System 2-naphthol/TEA in scCO<sub>2</sub>

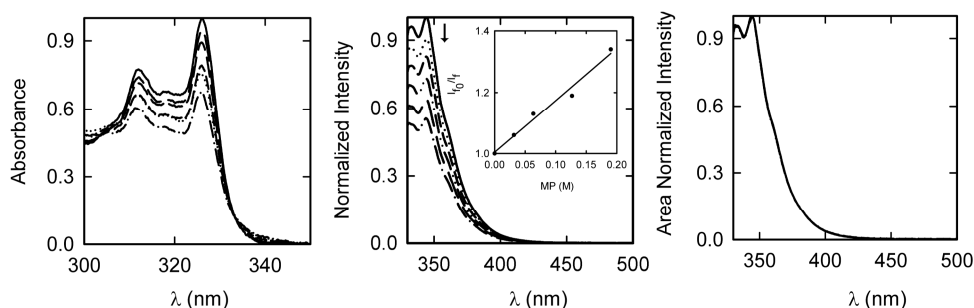
Absorption and emission spectra of 2-NpOH / TEA in scCO<sub>2</sub>.



**Figure 2.-Left:** Absorption spectra of 2-naphthol with increasing amounts of TEA in scCO<sub>2</sub> ( $\delta = 1.5 \delta_c$ ). Concentrations of amine are 0.00; 0.020; 0.041; 0.061 and 0.082 M. **Right:** Area normalized corrected emission spectra ( $\lambda_{exc} = 312$  nm) for the same sample.

## 5: System 2-naphthol/MP in scCO<sub>2</sub>

Absorption and emission spectra of 2-NpOH / MP in scCO<sub>2</sub>.



**Figure 3.-Left:** Absorption spectra of 2-naphthol with increasing amounts of MP in scCO<sub>2</sub> ( $\delta = 1.5 \delta_c$ ). Concentrations of amine are 0.00; 0.032; 0.063; 0.127; 0.190 and 0.222 M. **Center and Right:** Normalized corrected emission and area normalized corrected emission spectra ( $\lambda_{exc} = 312$  nm) for the same sample. **Inset:** Stern-Volmer plot,  $K_{SV} = 1.7 \text{ M}^{-1}$ .

The area normalized corrected emission spectra for all the concentrations of MP added superimposed.

## 6: Time resolved emission decay of 2-naphthol in the presence of amines in cyclohexane.

**Dynamic quenching rate constants.**

Amine	[Am]/M	$\tau_f$ (ns)	$k_q$ ( $10^9 \text{ M}^{-1} \text{ s}^{-1}$ )
-	0	7.6	-
DIEA	0.034	3.6	4.3
MP	0.058	3.1	3.3
TEA	0.042	2.7	5.7

**Table 2:** Rate constants for the dynamic quenching of emission of 2-naphthol by amines in cyclohexane.

### 7: Kinetic rate constants for 2-naphthol/DIEA proton transfer in the excited state.

Complex dissociation rate constant in the excited state,  $k_{dis}^*$ , was calculated by the following equation

$$k_{dis}^* = \frac{k_q}{K^*} \quad (10)$$

where  $k_q$  is the bimolecular quenching constant rate and  $K^*$  is the equilibrium constant for the proton transfer reaction of 2-NpOH/DIEA in its lowest singlet excited electronic state.

### References

- (1) San Román, E.; González, M. C. *J. Phys. Chem.* **1989**, 93, 3532-3536.