

Supporting Information

Effect of micellar and reverse micellar interface on solute location: 2,6-pyridinedicarboxylate in CTAB micelles and CTAB and AOT reverse micelles

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Supporting Information Available

Figure S1. The 400 MHz ^1H NMR spectra of H_3dipic^+ cation in CF_3COOD and D_2O mixture. Weight percent of CF_3COOD is shown next to each spectrum. Spectra were referenced against internal DSS. Hammett acidity functions (H_0) for non-deuterated CF_3COOH and H_2O mixtures with identical weight percentages shown in the figure are equal to 0.0 (12%), -0.5 (46%), -1.0 (74%), -1.5 (81%), -2 (86%), and -2.8 (96%).⁵⁵ The actual H_0 values may be different due to isotopic effects.

Figure S2. pH-variable UV spectra of 0.1 mM of H_2dipic in 30 mM NaCl (a), and 4 mM of CTAB (b).

Figure S3. Molar absorptivity of pyridine dicarboxylic acids in monocationic, neutral, monoanionic and dicationic form. Data taken from Ref.29.

Figure S4. The 300 MHz ^1H NMR spectrum of 20 mM CTAB in H_2O with proton assignment.

Figure S5. ^1H chemical shift of dipic protons is shown as a function of aqueous stock solution pH for CTAB micellar solutions (H_a and H_b) and aqueous solution (H_a^{aq} and H_b^{aq}). Data points for micellar solutions were taken from spectra shown in Figure 1 and aqueous dipic chemical shifts adjusted for the common reference standard taken from Ref. 8.

Figure S6. ^1H chemical shift of dipic protons is shown as a function of aqueous stock solution pH for CTAB reverse micellar solutions (H_a and H_b) and aqueous solution (H_a^{aq} and H_b^{aq}). Data points for reverse micellar solutions were taken from spectra shown in Figure 11 and aqueous dipic chemical shifts adjusted for the common reference standard taken from Ref. 8.

Figure S7. ^1H NMR chemical shifts of dipic^{2-} as a function of CTAB concentration. The data were obtained from spectra shown in Figure 5.

Table S1. ^1H NMR chemical shifts of dipic^{2-} and H_2dipic in various media.

Table S2. Sizes of the micellar and reverse micellar systems.

References

- (61) Spitzer, U. A.; Toone, T. W.; Stewart, R., *Can. J. Chem.* **1976**, 54, 440-447.
- (62) Dorshow, R.; Briggs, J.; Bunton, C.A.; Nicoll, D.F., *J. Phys. Chem.* **1982**, 86, 2388-2395.
- (63) Malliaris, A.; Lemoigne, J.; Sturm, J.; Zana, R., *J. Phys. Chem.* **1985**, 89, 2709-2713.
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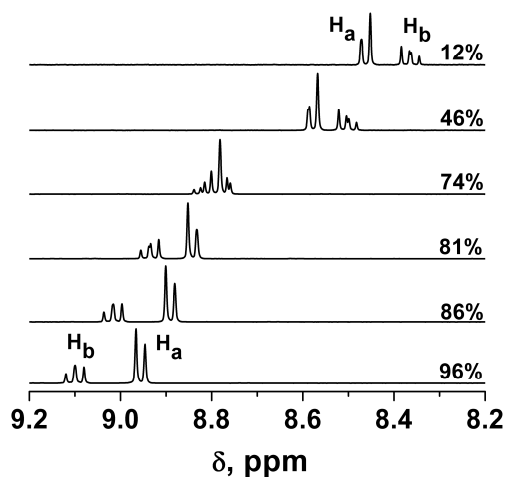


Figure S1. The 400 MHz ^1H NMR spectra of H_3dipic^+ cation in CF_3COOD and D_2O mixture. Weight percent of CF_3COOD is shown next to each spectrum. Spectra were referenced against internal DSS. Hammett acidity functions (H_0) for non-deutrated CF_3COOH and H_2O mixtures with identical weight percentages shown in the figure are equal to 0.0 (12%), -0.5 (46%), -1.0 (74%), -1.5 (81%), -2 (86%), and -2.8 (96%).⁶¹ The actual H_0 values may be different due to isotopic effects.

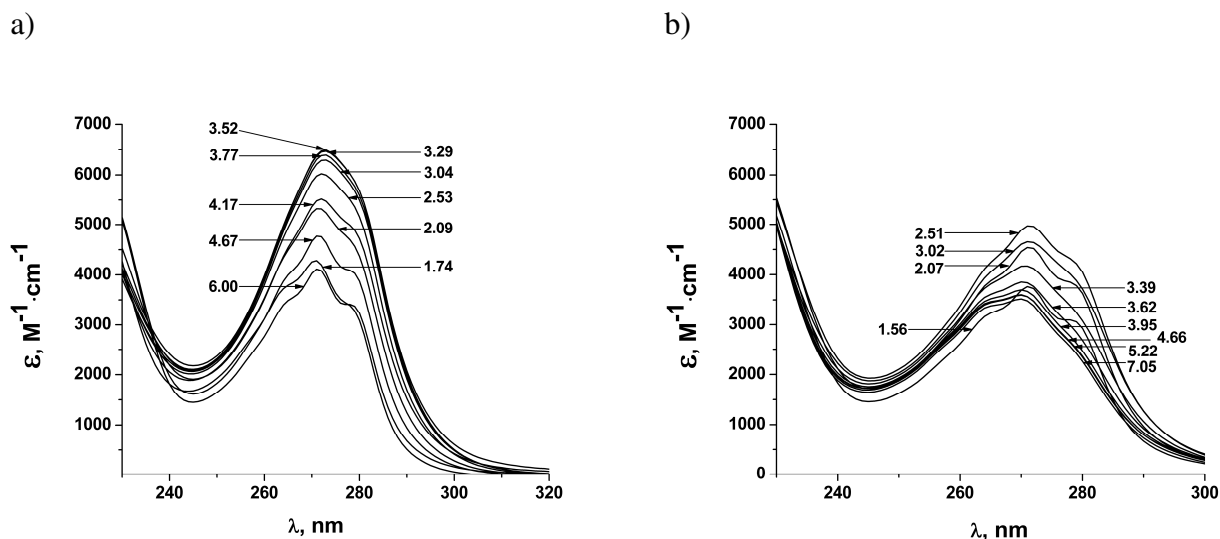


Figure S2. pH-variable UV spectra of 0.1 mM of H_2dipic in 30 mM NaCl (a), and 4 mM of CTAB (b).

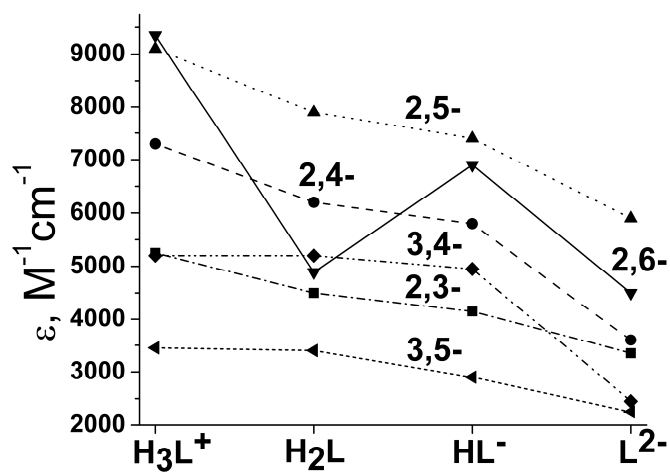


Figure S3. Molar absorptivity of pyridine dicarboxylic acids in monocationic, neutral, monoanionic and dicationic form. Data were obtained from a table in the Ref. 29 and used to construct this figure.

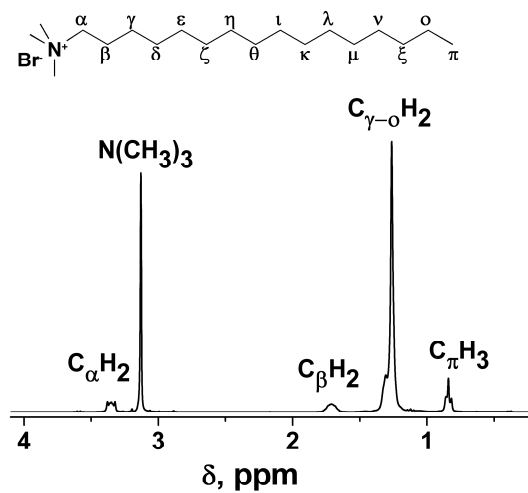


Figure S4. The 300 MHz 1H NMR spectrum of 20 mM CTAB in H_2O with proton assignment.

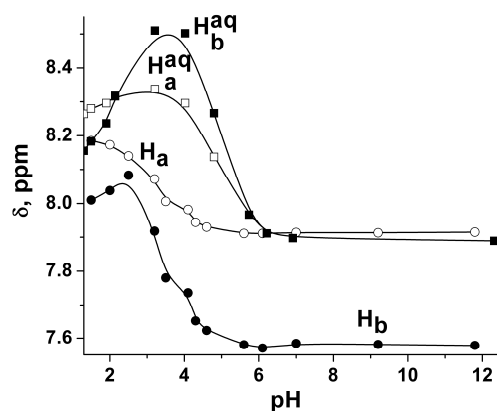


Figure S5. ^1H chemical shift of dipic protons is shown as a function of aqueous stock solution pH for CTAB micellar solutions (H_{a} and H_{b}) and aqueous solution ($\text{H}^{\text{aq}}_{\text{a}}$ and $\text{H}^{\text{aq}}_{\text{b}}$). Data points for micellar solutions were taken from spectra shown in Figure 3 and aqueous dipic chemical shifts were taken from Ref 8. The 0.10 ppm were subtracted from chemical shifts in aqueous solution to adjust to the common reference.

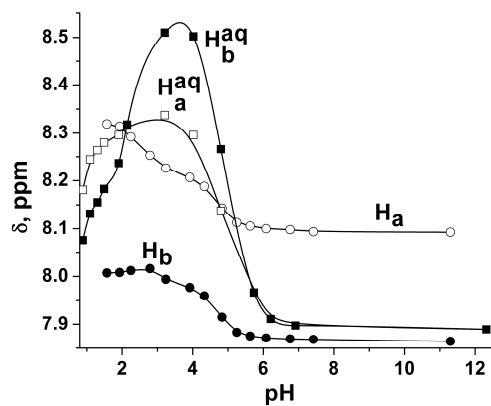


Figure S6. ^1H chemical shift of dipic protons is shown as a function of aqueous stock solution pH for CTAB reverse micellar solutions (H_{a} and H_{b}) and aqueous solution ($\text{H}^{\text{aq}}_{\text{a}}$ and $\text{H}^{\text{aq}}_{\text{b}}$). Data points for reverse micellar solutions were taken from spectra shown in Figure 7 and aqueous dipic chemical were taken from Ref. 8. The 0.10 ppm were subtracted from chemical shifts in aqueous solution to adjust to the common reference.

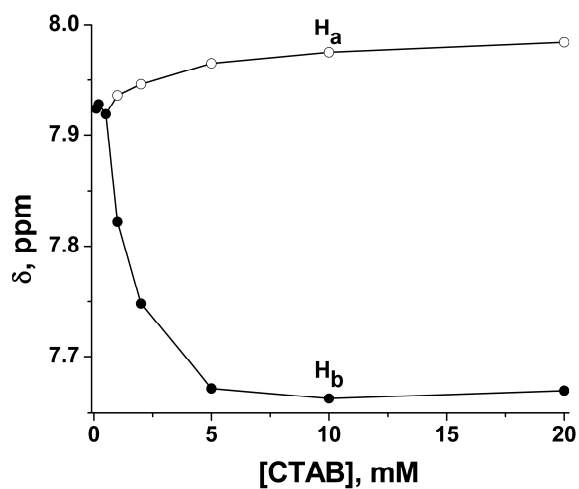


Figure S7. ^1H NMR chemical shifts of dipic^{2-} as a function of CTAB concentration. The data were obtained from spectra shown in Figure 4a.

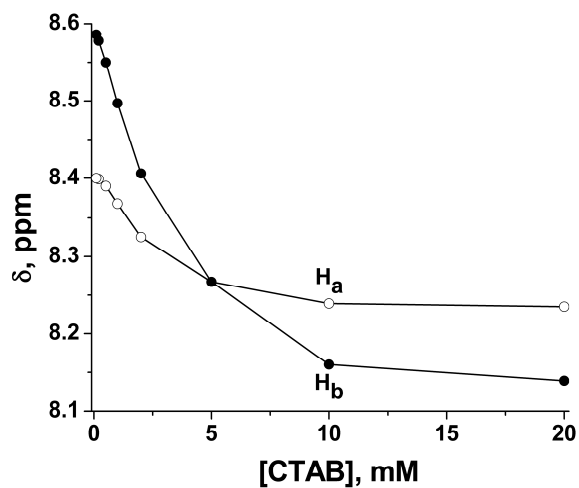


Figure S8. ^1H NMR chemical shifts of Hdipic^- as a function of CTAB concentration. The data were obtained from spectra shown in Figure 4b.

Table S1. ^1H NMR chemical shifts of dipic²⁻ and H₂dipic in various media

System	$\delta(\text{H}_a)$, ppm	$\delta(\text{H}_b)$, ppm
<i>Micellar and reverse micellar</i>		
Na ₂ dipic in H ₂ O/0.1 mM CTAB (pH 6.6)	7.92 ^a	7.92 ^a
Na ₂ dipic in H ₂ O/20 mM CTAB (pH 6.8)	7.98 ^a	7.66 ^a
Na ₂ dipic in H ₂ O (pH 6.7)/0.1 M CTAB/0.5 M 1-pentanol, w ₀ =6	8.10 ^b	7.87 ^b
Na ₂ dipic in H ₂ O (pH 6.7)/0.1 M CTAB/0.5 M 1-pentanol, w ₀ =20	8.07 ^b	7.88 ^b
<i>Aqueous</i>		
Na ₂ dipic in H ₂ O (pH 6.4)	8.005 ^c	8.027 ^c
[N(CH ₃) ₄] ₂ dipic in H ₂ O (pH 7)	8.00 ^c	8.00 ^c
H ₂ dipic in H ₂ O (pH 1.3)	8.27 ^c	8.38 ^c
<i>Organic solvent</i>		
Na ₂ dipic in CD ₃ OD	8.10 ^b	7.93 ^b
[N(CH ₃) ₄] ₂ dipic in CD ₃ OD	7.91 ^b	7.82 ^b
H ₂ dipic in CD ₃ OD	8.23 ^b	8.38 ^b

^areferenced against coaxial capillary with C₆D₆ and TMS, 35°C; ^breferenced against internal TMS, 24°C; ^creferenced against internal DSS, 24°C.

Table S2. Sizes of the micellar and reverse micellar systems.

System	Diameter (nm)	Aggregation number
CTAB micelles	5.8 ^a	~100 ^{a,b}
CTAB reverse micelles w ₀ =6	5.0 ^c	-
AOT reverse micelles w ₀ =6	5.6 ^d	50 ^d

^aRef. 62, ^bref. 63 at 35°C, ^cref. 38, ^dref. 64.