# Proximate Charge Effects. 4.<sup>1</sup> Heats of Reaction and Enthalples of Solvent Transfer of Reactants and Products in the Deprotonation of 2-Hydroxy-*N*,*N*,*N*-trimethylanllinium Ion and 3-Hydroxy-*N*-methylpyridinium Ion

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Heats of neutralization,  ${}^{+}ROH + OH^{-} \rightarrow {}^{+}RO^{-} + H_{2}O$  in water, in aqueous ethanol, and in aqueous dimethyl sulfoxide, were measured for two rigid choline analogues, namely,  ${}^{+}ROH = 2$ -hydroxy-N,N,N-trimethylanilinium ion (HOA<sup>+</sup>) and  ${}^{+}ROH = 3$ -hydroxy-N-methylpyridinium ion (HOP<sup>+</sup>). Whereas, in the case of choline ion, the change from water solvent to aqueous ethanol produced an exothermic change in the enthalpy of reaction, in the present two cases, the change was endothermic. The change from aqueous ethanol to aqueous Me<sub>2</sub>SO, which produced a large exothermic change in the enthalpy of reaction for choline (-5 kcal/mol), also produced a large exothermic effect (-9 to -7 kcal/mol) for HOA<sup>+</sup> and HOP<sup>+</sup>. Calorimetric measurements of the enthalpies of solvent transfer revealed that the endothermic  $\Delta H^{\circ}$  shift on going from water solvent. In the comparison of aqueous ethanol with aqueous Me<sub>2</sub>SO, the dominant factor was the large desolvation of both hydroxide ion and the  ${}^{-}OA^{+}$  and  ${}^{-}OP^{+}$  dipolar ions in the less H-bonding medium, as had been the case for choline. This desolvation was less pronounced for the organic dipolar ions than for OH<sup>-</sup>, thus causing the exothermic shift of the enthalpy of reaction. Of the two dipolar ions, the desolvation was less pronounced for the one ( ${}^{-}OA^{+}$ ) which is the rigid analogue of the cisoid conformation of anhydrocholine,  ${}^{+}(CH_3)_3NCH_2CH_2O^{-}$ . This is the reason that the HOA<sup>+</sup> neutralization experienced the greater exothermic shift of the enthalpy of reaction.

# Introduction

The choline-anhydrocholine equilibrium, eq 1, was re-

$$^{+}(CH_{3})_{3}NCH_{2}CH_{2}OH + OH^{-} \rightleftharpoons \\ ^{+}(CH_{3})_{3}CH_{2}CH_{2}O^{-} + H_{2}O (1)$$

cently<sup>2</sup> found to be very sensitive to a medium effect. Thus, a solvent change from water to 60 mol % aqueous ethanol produced an exothermic change in the enthalpy of reaction of about 2 kcal/mol. Going from 60 mol % aqueous ethanol to 60 mol % aqueous dimethyl sulfoxide produced a further exothermic shift of 5 kcal/mol. Measurement of the enthalpies of solvent transfer of all the participants of equilibrium 1 revealed that the enthalpy of transfer of anhydrocholine, <sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>O<sup>-</sup>, from water to aqueous ethanol was large and exothermic and was the principal cause of the exothermic shift of the enthalpy of reaction.<sup>2</sup> The enthalpy of transfer of anhydrocholine from aqueous ethanol to aqueous Me<sub>2</sub>SO was large and endothermic; however, it was 4 kcal/mol less endothermic than the corresponding enthalpy of transfer of OH<sup>-</sup>, and this was found to be the principal cause of the exothermic  $\Delta H^{\circ}$  shift in the case of these two media.<sup>2</sup>

The purpose of the present work was to determine (1) whether the above type of medium effect is found in other systems having proximate positive charges, (2) whether the enthalpies of solvent transfer of their reactants and products behave in a manner analogous to that of the choline-anhydrocholine system, and (3) how the above two effects, if any, are influenced by the distance between the proximate positive charge and the reaction center.

To address these questions, it seemed desirable to choose two systems which include the choline skeleton but are conformationally rigid. The compounds used were salts of the 2-hydroxy-N,N,N-trimethylanilinium ion (HOA<sup>+</sup>), a model for the cisoid conformation of the choline ion, and



the 3-hydroxy-N-methylpyridinium ion (HOP<sup>+</sup>), a model for the anti conformation of the choline ion.

The greater acidity of these two compounds<sup>3</sup> made it convenient to measure their heats of neutralization directly by calorimetry, rather than by way of the temperature dependence of the equilibrium constants of eq 1 as in our earlier work.<sup>2</sup>

Heats of Neutralization. The heats of neutralization were determined calorimetrically by adding a measured amount of 2-hydroxy-N,N,N-trimethylanilinium iodide (HOAI) or 3-hydroxy-N-methylpyridinium chloride (HO-PCl) to a large excess of NaOH solution or by titrating NaOH into a large excess of the salt. The results are shown in Table I. It can be seen that going from water solvent to aqueous ethanol produces a large *endothermic* shift in the enthalpy of reaction (4.5–4.8 kcal/mol). This agrees with observations on this kind of solvent effect in the neutralization of uncharged acids<sup>4</sup> but differs from the

<sup>(1) (1)</sup> Part 3: Haberfield, P.; Pessin, J. J. Am. Chem. Soc. 1983, 105, 526.

<sup>(2)</sup> Haberfield, P.; Pessin, J. J. Am. Chem. Soc. 1982, 104, 6191.

<sup>(3)</sup> HOP<sup>+</sup>,  $pK_{g} = 4.93$  (Metzler, D. E.; Harris, C. M.; Johnson, R. J.; Siano, D. B.; Thomson, J. A. *Biochemistry* 1973, 12, 5377); HOA<sup>+</sup>,  $pK_{a} = 7.4$  (Haberfield, P.; Rizzo, T., unpublished results), choline (+),  $pK_{a} = 12.8$  (ref 2).

<sup>(4)</sup> Thus, the  $\Delta H^{\circ}$  of neutralization of 4-nitrophenol is -8.67 kcal/mol in water (Fernandez, L. P.; Hepler, L. G. J. Am. Chem. Soc. 1959, 81, 1783) and -1.98 kcal/mol in methanol (taken from the heat of ionization of 4-nitrophenol in methanol,  $\Delta H_i^{\circ} = 8.25$  kcal/mol (Bolton, P. D.; Rochester, C. H.; Rossall, B. Trans. Faraday Soc. 1970, 66, 1348) and the autoprotolysis heat of methanol,  $\Delta H^{\circ} = 10.23$  kcal/mol (Leung, C. S.; Grunwald, E. J. Phys. Chem. 1970, 74, 696)).

Rechester, C. H., Rossan, B. 17013. Fundary Soc. 1970, 60, 1540, and the autoprotolysis heat of methanol,  $\Delta H^o = 10.23 \text{ kcal/mol}$  (Leung, C. S.; Grunwald, E. J. Phys. Chem. 1970, 74, 6960). (5) Dielectric constants: H<sub>2</sub>O, 78; 60 mol % aqueous ethanol, 33; 60 mol % aqueous Me<sub>2</sub>SO, 60 (Akerlof, G. J. Am. Chem. Soc. 1932, 54, 4125. Lindberg, J. J.; Kentamaa, J. Suom. Kemistil. B 1960, 33, 104. (6) This is evident from the very large transfer enthalpy of OH<sup>-</sup> ion from 60 mol % acqueous Me<sub>2</sub>SO.

<sup>(6)</sup> This is evident from the very large transfer enthalpy of OH<sup>-</sup> ion from 60 mol % aqueous ethanol to 60 mol % aqueous Me<sub>2</sub>SO,  $\Delta H_{S_1 \rightarrow S_2} =$ = 14.2 kcal/mol, or from water to 60 mol % aqueous Me<sub>2</sub>SO,  $\Delta H_{S_1 \rightarrow S_2} =$ 13.7 kcal/mol.

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TABLE I: Enthalpies (kcal/mol) of Reaction for the Process  ${}^{*}ROH + OH^{-} \rightarrow {}^{*}RO^{-} + H_{2}O$  in Several Solvents at 25.0  ${}^{\circ}C^{a}$ 

	solvent <sup>b</sup>			
⁺ROH	H <sub>2</sub> O	0.60 aq ethanol <sup>c</sup>	0.60  aq Me <sub>2</sub> SO	
HOA⁺ HOP⁺	$-7.91 \pm 0.12$ -11.84 $\pm 0.08$	$\begin{array}{r} -3.16 \pm 0.22 \\ -7.34 \pm 0.25 \end{array}$	$-12.07 \pm 0.09$ $-14.50 \pm 0.05$	

<sup>*a*</sup> Values given are the averages of 5-10 runs. The uncertainties are given as the standard deviation of the mean. <sup>*b*</sup> Solvent composition indicated as mole fraction of organic component. <sup>*c*</sup> In the case of aqueous ethanol solvent, this  $\Delta H^{\circ}$  value includes the (minor) contribution of the reaction <sup>+</sup>ROH + C<sub>2</sub>H<sub>5</sub>O<sup>-</sup>  $\rightarrow$  <sup>+</sup>RO<sup>-</sup> + C<sub>2</sub>H<sub>5</sub>OH.

effect observed in the choline cation neutralization (eq 1) where the same solvent change produced a 2 kcal/mol exothermic shift of the  $\Delta H^{\circ}$ .

On going from 60 mol % aqueous ethanol to 60 mol % aqueous Me<sub>2</sub>SO, one observes a very large (-7 to -9 kcal/mol) exothermic shift in the enthalpy of neutralization. This compares with a similar large exothermic shift (-5 kcal/mol) for the same solvent change in the case of the choline-anhydrocholine equilibrium (eq 1).<sup>2</sup> In the present case, this effect is seen to be larger for the neutralization of HOA<sup>+</sup>, which is the syn-choline model. To what extent are the above results produced by changes in the solvation of the products in these neutralization reactions?

Enthalpies of Solvent Transfer. The above question can be answered by measuring the enthalpies of transfer of the reactants in eq 2 from water to each of the other

$$^{+}ROH + OH^{-} \rightarrow ^{+}RO^{-} + H_{2}O \qquad (2)$$

two media. This, plus the  $\Delta H^{\circ}$  value for reaction 2 in each solvent, yielded the enthalpy of transfer of the products from water to the other two media. Finally, subtracting the enthalpies of transfer of H<sub>2</sub>O from those of the products yielded the enthalpies of transfer of the <sup>-</sup>OA<sup>+</sup> and <sup>-</sup>OP<sup>+</sup> dipolar ions.

The enthalpy of transfer of a compound from one solvent to another,  $\delta \Delta H_{S_1 \rightarrow S_2}$ , is the difference between the heats of solution,  $\Delta H_S$ , of the compound in the two solvents of interest:

$$\delta \Delta H_{\mathrm{S}_{1}-\mathrm{S}_{2}} = \Delta H_{\mathrm{S}_{2}} - \Delta H_{\mathrm{S}_{1}}$$

The enthalpies of transfer of the requisite compounds and ions are shown in Table II. They are listed in a rational sequence, which shows how each value was derived from the experimental data. The  $(n-C_4H_9)_4N^+-(n-C_4H_9)_4B^+$ extrathermodynamic assumption is the ultimate source of the single ion transfer enthalpies.<sup>9</sup> Table III shows the solvent transfer enthalpies of the reactants and products and of the <sup>-</sup>OA<sup>+</sup> and <sup>-</sup>OP<sup>+</sup> dipolar ions. Before we discuss these solvent transfer enthalpies, it is necessary to consider to what extent these values reflect solute-solvent interactions. Solvent transfer enthalpies consist of two contributions: (1) the difference between the solute-solvent interaction energies in the two solvents and (2) the difference between the cavity formation energies in the two solvents. One can estimate the differences in the cavity formation energies of these solvents by the use of the "benzene approximation" employed earlier.<sup>2</sup> It suggests that the enthalpy of transfer of a benzene-sized cavity from

TABLE 1	II :	Enthalpies (kcal/mol) of Solvent Transfer,
$\Delta H_{S, \rightarrow S}$	, of	Compounds and Ions at 25.0 °C

	solvent transfer <sup>a</sup>	$\Delta H_{S_1 \rightarrow S_2}$
$(n-C_4H_9)_4NI$	$H_2O \rightarrow 0.60$ aq ethanol	7.33
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	5.31
	$H_2O \rightarrow methanol$	6.9
Ι-	$H_2^{-}O \rightarrow methanol$	$-0.4^{b}$
$(n-C_4H_9)_4N^+$	$H_2O \rightarrow methanol$	7.3
	methanol $\rightarrow$ 0.60 aq ethanol	$2.0^{c}$
	$H_2O \rightarrow 0.60$ aq ethanol	9.3
	$0.60 \text{ aq ethanol} \rightarrow 0.60 \text{ aq Me}_2 SO$	$1.51^{d}$
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	10.8
I-	$H_2O \rightarrow 0.60$ aq ethanol	-2.0
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	-5.5
$HOAI^{e}$	$H_2O \rightarrow 0.60$ aq ethanol	-2.83
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	-7.76
$HOA^{+T}$	$H_2O \rightarrow 0.60$ aq ethanol	-0.8
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	-2.3
OH-	$H_2O \rightarrow 0.60$ aq ethanol	$-0.5^{c}$
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	$13.7^{c}$
HOPCl <sup>g</sup>	H₂O → 0.60 aq ethanol	-0.60
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	-1.43
Cl-	$H_2O \rightarrow 0.60$ aq ethanol	$1.6^{c}$
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	$1.9^{c}$
$HOP^{+n}$	$H_2O \rightarrow 0.60$ aq ethanol	-2.2
	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	-3.3
H <sub>2</sub> O	$H_2O \rightarrow 0.60$ aq ethanol	$-0.23^{i}$
$H_2O$	$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	-1.15'

<sup>a</sup> Solvent composition of mixed solvents indicated as mole fraction of organic solvent. <sup>b</sup> Choux, G.; Benoit, R. L., J. Am. Chem. Soc. **1969**, 91, 6221. <sup>c</sup> Haberfield, P.; Pessin, J. J. Am. Chem. Soc. **1982**, 104, 6191. <sup>d</sup> Haberfield, P.; Friedman, J.; Pinkston, M. F. J. Am. Chem. Soc. **1972**, 94, 71. <sup>e</sup> 2-Hydroxy-N,N-trimethylanilinium iodide. <sup>f</sup> 2-Hydroxy-N,N-trimethylanilinium iod. <sup>g</sup> 3-Hydroxy-Nmethylpyridinium chloride. <sup>h</sup> 3-Hydroxy-Nmethylpyridinium ion. <sup>i</sup> Lama, R. F.; Lee, C. Y. J. Chem. Eng. Data **1965**, 10, 216. <sup>j</sup> Kenttämaa, J.; Lindberg, J. J. Suom Kemistil. B **1960**, 33, 32.

TABLE III: Enthalpies (kcal/mol) of Solvent Transfer of Reactants and Products in the Reaction  $^{+}ROH + OH^{-} \rightarrow ^{+}RO^{-} + H,O$  at 25.0  $^{\circ}C$ 

		-	
	react- ants	pro- ducts	
	HOA <sup>+</sup> +	-OA* +	
	OH-	$H_2O$	⁻OA⁺
$H_2O \rightarrow 0.60$ aq ethanol	-1.3	3.5	3.7
$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	11.4	7.2	8.4
0.60 aq ethanol →	12.7	3.7	4.6
$0.60 \mathrm{aq} \mathrm{Me}_{2} \mathrm{SO}$			
	react-	pro-	
	ants	ducts	
	$HOP^+ +$	<sup>-</sup> OP <sup>+</sup> +	
	OH⁻	$H_2O$	<b>−OP</b> +
$H_2O \rightarrow 0.60$ aq ethanol	- 2.7	1.8	2.0
$H_2O \rightarrow 0.60 \text{ aq } Me_2SO$	10.4	7.7	8.9
0.60 aq ethanol $\rightarrow$	13.1	5.9	6.8
0.60 ag Me <sub>2</sub> SO			

 $\rm H_2O$  to 60 mol % aqueous ethanol is 0.5 kcal/mol and the transfer of such a cavity from 60 mol % aqueous ethanol to 60 mol % aqueous  $\rm Me_2SO$  is 0.4 mol.<sup>2</sup> This is so much smaller than the values of the product transfer enthalpies of Table III that it appears reasonable to discuss these values in terms of solute–solvent interactions.

Considering the  $H_2O \rightarrow 0.60$  aqueous ethanol solvent change first, one can see that, whereas the enthalpy of transfer of anhydrocholine was exothermic  $(-3.3 \text{ kcal/mol})^2$ into the less polar solvent, here there is an endothermic enthalpy of transfer of the dipolar ions into the less polar solvent (Table III and Figure 1). The solvent effect on

<sup>(7)</sup> Stedman, E. Biochem. J. 1926, 20, 721; Beilstein 13, II, 169.
(8) Harris, S. A.; Webb, T. J.; Folkers, K. J. Am. Chem. Soc. 1940, 62, 3198.

<sup>(9)</sup> For a discussion of this assumption, see Table II, footnote d, and the references cited therein.



**Figure 1.** Relative enthalpies of reactants and products in the neutralization reaction of 2-hydroxy-N,N,N-trimethylanilinium ion (HOA<sup>+</sup>) and 3-hydroxy-N-methylpyridinium ion (HOP<sup>+</sup>) in water and in 0.60 mole fraction aqueous ethanol at 25.0 °C.



# 0.60 aq E: OH 0.60 aq DMSO

**Figure 2.** Relative enthalpies of reactants and products in the neutralization reaction of 2-hydroxy-N,N,N-trimethylanilinium ion (HOA<sup>+</sup>) and 3-hydroxy-N-methylpyridinium ion (HOP<sup>+</sup>) in 0.60 mole fraction aqueous ethanol and 0.60 mole fraction aqueous Me<sub>2</sub>SO at 25.0 °C.

the reactants is about the same as was the case for choline and thus the net change in the  $\Delta H^{\circ}$  is caused by this difference in the enthalpy of transfer,  $H_2O \rightarrow 0.60$  aqueous ethanol, of anhydrocholine,  $^+(CH_3)_3NCH_2CH_2^-$ , vs. the present models,  $^-OA^+$  and  $^-OP^+$ . The greater hydrophilicity of anhydrocholine (by 5–7 kcal/mol) than the  $^+HOA^$ and  $^+HOP^-$  dipolar ions may be caused by the greater basicity of anhydrocholine. This conclusion is supported by the fact that the enthalpies of transfer between these two solvents of the choline cation and the  $^+HOA$  and  $^+HOP$  cations are comparable (see Table II and ref 2, Table II). Thus, it may be that the basicity difference is responsible for the different enthalpies of transfer of the conjugate bases in these equilibria and this, in turn, produces the opposite nature of the medium effect.

The medium effect on going from 60 mol % aqueous ethanol to 60 mol % aqueous  $Me_2SO$  is shown in Figure 2. As had been the case in the choline–anhydrocholine equilibrium,<sup>2</sup> this solvent change produces a far more dramatic enthalpy of transfer of both reactants and products. The 60 mol % aqueous  $Me_2SO$  medium, though it is not appreciably less polar than water,<sup>5</sup> is a very poor hydrogen-bond donor.<sup>6</sup> Consequently, there is a very large degree of desolvation of both the reactants and the products on going from 60 mol % aqueous ethanol to 60 mol

TABLE IV: Heats of Solution<sup>a</sup>

solute	solvent <sup>b</sup>	∆H <sub>S</sub> , kcal/mol
(n-C <sub>4</sub> H <sub>9</sub> )NI	H <sub>2</sub> O 0.60 aq ethanol 0.60 aq Me <sub>2</sub> SO	3.45 10.78 8.76
$\mathrm{HOAI}^d$	methanol $H_2O$ 0.60 aq ethanol 0.60 aq Me SO	10.4° 8.28 5.45 0.52
HOPCl <sup>e</sup>	$H_2O$ 0.60 aq ethanol 0.60 aq Me <sub>2</sub> SO	3.76 3.16 2.33

<sup>a</sup> Integral heats of solution, measured at concentrations of 0.001-0.01 M; standard deviations were 0.1 kcal/mol or better; temperature 25.0 °C. <sup>b</sup> Composition of mixed solvents indicated as mole fraction of organic component. <sup>c</sup> Fuchs, R.; Bear, J. L; Rodewald, R. F. J. Am. Chem. Soc. **1969**, 91, 5797. <sup>d</sup> 2-Hydroxy-N,N,N-trimethylanilinium iodide. <sup>e</sup> 3-Hydroxy-N-methylpyridinium chloride.

% aqueous Me<sub>2</sub>SO. This desolvation is far more pronounced for the reactants than it is for the products, thus causing the exothermic shift in the enthalpy of reaction. The desolvation of the products is due to the  $-OA^+$  and  $-OP^+$  dipolar ions, the other product, H<sub>2</sub>O, making a very small (-0.9 kcal/mol) contribution to the product solvent transfer enthalpies. Although the <sup>+</sup>HOA and <sup>+</sup>HOP transfer enthalpies are nearly the same (-1.5 and -1.1 kcal/mol), the  $-OA^+$  dipolar ion has a substantially less endothermic transfer enthalpy into aqueous Me<sub>2</sub>SO than the  $-OP^+$  dipolar ion (by 2.2 kcal/mol). This is clearly the consequence of the interaction between the negative charge on the <sup>+</sup>HOA<sup>-</sup> dipolar ion and its quaternary ammonium group and is the cause of the greater solvent effect experienced by the <sup>+</sup>HOA  $\Delta H^\circ$  of neutralization.

# **Experimental Section**

Materials. Dimethyl sulfoxide (Aldrich) was allowed to stand over calcium hydride overnight, decanted, and distilled at reduced pressure. Ethanol (Commercial Solvents Corp.) and NaOH (Matheson Coleman and Bell, Analyzed Reagent, ACS) were used without further purification. Tetra-*n*-butylammonium iodide (Eastman) was recrystallized from benzene and checked by titration with silver nitrate solution.

2-Hydroxy-N,N,N-trimethylanilinium iodide (HOAI) was prepared as follows. A mixture of 50 g (0.46 mol) of 2-aminophenol, 195 g (1.37 mol) of methyl iodide, and 48.6 g (0.46 mol) of anhydrous sodium carbonate in 250 mL of dry methanol was heated under reflux for 2 days. The volume was reduced by evaporation to 150 mL, the reaction mixture was cooled, and the precipitate was collected. The yield was 87 g (68%), mp 194–196 °C dec (lit.<sup>7</sup> mp 181.5–183 °C). This was recrystallized from ethanol to give material of mp 196–198 °C dec, which gave a satisfactory equivalent weight on titration with silver nitrate solution.

3-Hydroxy-N-methylpyridinium chloride (HOPCl) was prepared as follows. To 47.6 g (0.50 mol) of 3-hydroxypyridine in 400 mL of dry acetone was added 71.0 g (0.50 mol) of methyl iodide with vigorous stirring under a reflux condenser. All of the solid dissolved in about 10 min as the solution began to boil gently and a new precipitate began to appear. The reaction mixture was allowed to stand for 20 h and was then filtered to yield 83.3 g (70%) of 3-hydroxy-N-methylpyridinium iodide, mp 96-115 °C. The filtrate was concentrated to 80 mL to yield a second crop, 5.7 g (5%), mp 110-115 °C (lit.<sup>8</sup> mp 114-116 °C). This iodide (89 g, 0.38 mol) was dissolved in 100 mL of water and treated with 46 g (0.20 mol) of Ag<sub>2</sub>O. After being stirred for 1 h, the mixture was filtered and the filtrate cooled to 0 °C and acidified with 35 mL of concentrated HCl. Evaporation of the water in vacuo, followed by thorough drying of the residue at 100 °C in vacuo, yielded 40.3 g (73%) of HOPCl, mp 160–164 °C, NMR (D<sub>2</sub>O) δ 4.83 (s, 3 H), 8.50 (m, 2 H), 8.92 (m, 2 H), which gave a satisfactory equivalent weight on titration with  $AgNO_3$ .

Solution Preparation. The mixed solvents were prepared from weighed amounts of distilled water and ethanol or dimethyl sulfoxide. Dissolved carbon dioxide was removed from all solvents by passing CO<sub>2</sub>-free nitrogen gas through a sintered glass bubbler immersed in the solvent. HOAI and HOPCl solutions were prepared by weight, followed by dilution when necessary. NaOH solutions were standardized by titration with HCl.

Heats of Reaction. The heats of reaction were measured at 25.0 °C with an LKB 8700-2 titration calorimeter. Solutions of HOPCl or HOAI, 1–10 mL, at concentrations ranging from 0.005 to 0.05 M were added to 90 mL of NaOH solution having the same concentration as the phenol. In some cases, the procedure was reversed and the NaOH solution was titrated into an excess of phenol solution. Both procedures gave the same results. Heat of dilution corrections were found to be insignificant. In the aqueous cases, allowance was also made for the partial ionization of the phenol by using the ionization equilibrium constant of the phenol and the heat of dissociation of  $H_2O$ . This correction was found to be less than 1% in all cases.

*Heats of Solution*. Heats of solution were measured with an LKB 8700-1 reaction and solution calorimeter. (See Table IV.)

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# Influence of Salt, Detergent Concentration, and Temperature on the Fluorescence Quenching of 1-Methylpyrene in Sodium Dodecyl Sulfate with *m*-Dicyanobenzene

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The quenching of 1-methylpyrene by m-dicyanobenzene in sodium dodecyl sulfate micelles is studied as a function of the total detergent concentration, ionic strength, and temperature. Analysis of the time-dependent decay of the fluorescence gives information about the aggregation number and in addition permits the study of important rate constants characterizing interactions in or at the micelle. The aggregation number is found to increase either at higher scap concentration or upon adding salt. The rate constants  $k_m^+$  and  $k_m^-$  are not affected by the size of the micelle nor by the ionic strength while  $k_{qm}$  decreases as the aggregation number increases. A study of the parameters as a function of temperature shows a small decrease in aggregation number. The rate constants  $k_{\rm m}^{+}$ ,  $k_{\rm m}^{-}$ , and  $k_{\rm qm}$  increase with increasing temperature. This permits an evaluation of the activation energies. Comparison of steady-state and time-correlated fluorescence measurements shows that a fraction of the 1-methylpyrene fluorescence quenching is due to static quenching at higher quencher concentrations.

# Introduction

In the past few years the fluorescence quenching method has received much attention as a tool to study organized molecular systems. In particular, the quenching of arene fluorescence by neutral organic quenchers<sup>1</sup> and metal ions<sup>2,3</sup> has been extensively studied. The kinetic formalism of this quenching process has been described.<sup>4-6</sup> The kinetic scheme of fluorescence decay for quenching with neutral molecules in a micelle can be presented as in Scheme I, where  $P_n$  is a micelle with n quenchers and a

# Scheme I

$$\mathbf{P}_n^* \to \mathbf{P}_n \qquad k_{\mathbf{f}}[\mathbf{P}_n^*] \tag{1}$$

$$P_n^* \to P_n \qquad nk_{qm}[P_n^*]$$
 (2)

$$\mathbf{P}_n^* + \mathbf{Q}_{\mathbf{w}} \rightarrow \mathbf{P}_{n+1}^* \qquad k_{\mathbf{m}}^+ [\mathbf{P}_n^*][\mathbf{Q}_{\mathbf{w}}] \tag{3}$$

$$P_n^* \to P_{n-1}^* + Q_w \qquad nk_m^{-}[P_n^*]$$
 (4)

$$n = 0, 1, 2, ...)$$

probe,  $k_{\rm f}$  is the rate constant of fluorescence decay in a micellar solution without quencher,  $k_{am}$  is the rate constant for intramicellar quenching when only one quencher is present in the micelle,  $k_{\rm m}$  is the rate constant for a quencher to leave the micelle, and  $k_{m}^{+}$  is the rate constant for a quencher to enter the micelle.

The time-dependent fluorescence decay function is given by <sup>2,3</sup>

$$I(t) = A_1 \exp[-A_2 t - A_3 (1 - \exp(-A_4 t))]$$
(5)

$$A_1 = I(0)$$
 fluorescence intensity on  $t = 0$  (6)

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