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BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (12), 3635—3636 (1978)

Optical Spectra of the Picrate Ion in Micellar and Polymer Micellar Systems. Comment on the Solvation of Anions

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(Received January 27, 1978)

Synopsis. The optical spectra of the picrate ion in a micellar solution indicate that slightly below the CMC of CTAB surfactant the anion is relatively free and exists as an ion pair above the CMC. The hydrophobic aggregate of TMAC invariably gives free ion. The polymer micelle of quaternized poly(4-vinylpyridine) results in a tight ion pair.

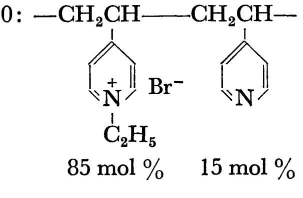
Anionic nucleophiles are activated to a great extent in cationic hydrophobic aggregates such as micelles and polymer micelles.1) The unusual activation is mainly attributed to the formation of hydrophobic ion pairs which are relatively "desolvated" in the hydrophobic domain.2–6) Thus, it would be valuable to estimate the degree of solvation as a function of surfactant concentrations. According to Bourgoin *et al.*,7) bathochromic shifts observed in the optical spectra of alkali picrates can be rationalized in terms of the formation of the free ion, and the apolar environment is characterized by a shoulder at around 400 nm. The spectrum of the picrate ion would thus be most useful for confirmation. We have measured the optical spectra of the picrate ion in the presence of hexadecyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Brij-35, trioctylmethylammonium chloride (TMAC), and the following quaternized poly(4-vinylpyridine) polymers (4VP-D-0 and 4VP-D-22).6) Typical results are summarized in Table 1.

TABLE 1. ABSORPTION MAXIMA AND SHOULDERS OF PICRATE IONS IN THE PRESENCE OF SURFACTANTSa)

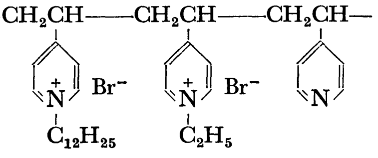
Surfactant	Concentration mM	λ_{max} nm	($\log \varepsilon_{max}$)	$\lambda_{shoulder}$b) nm	($\log \varepsilon_{max}$)
Water		355	(4.29)	—	
CTAB	0.02	355	(4.28)	—	
	0.05	360	(4.26)	—	
	0.10	380	(4.32)	+	
	0.20	360	(4.33)	422	(4.16)
	0.40	350	(4.26)	412	(4.07)
	0.80	350	(4.26)	412	(4.07)
4VP-D-0c)	5.0	355	(4.29)	—	
4VP-D-22c)	0.46	360	(4.28)	+	
	0.93	360	(4.27)	+	
	3.68	360	(4.27)	+	
SDS	15.0	355	(4.29)	—	
Brij-35	1.6	355	(4.29)	—	
TMAC	0.02	365	(4.28)	—	
	0.04	375	(4.35)	+	
	0.06	377	(4.38)	+	
	0.08	374	(4.38)	+	
	0.10	374	(4.37)	+	

a) 30 °C, pH 7.1 with 0.02 M phosphate (KH_2PO_4–K_2HPO_4) buffer, [picrate ion (added as picric acid)] = 3.90×10^{-5}M. b) "+" indicates that distinct shoulder appears but the absorption maximum cannot be determined clearly. c) The polymer concentration stands for the total concentration of monomeric units.

4VP-D-0:



4VP-D-22:



The λ_{max} of the picrate ion in an aqueous solution appeared at 355 nm. Addition of CTAB caused marked bathochromic shifts, the largest shift to 380 nm being observed at [CTAB] = 1.0×10^{-4} M. This is comparable with the λ_{max} value of triethylammonium picrate in dimethyl sulfoxide (377 nm)8) or of potassium picrate in tetrahydrofuran containing excess crown ether (380 nm).7) Since the critical micelle concentration (CMC) of CTAB (determined by use of 2,6-dichlorophenolindophenol) is 4.0×10^{-4} M, the picrate ion is relatively free slightly below this. Further increase in CTAB concentration caused hypsochromic shifts to 350 nm with a new absorption maximum at 422 nm. The final spectrum at [CTAB] = 2.0×10^{-3} M (λ_{max}, 350 and 412 nm) was similar to that in tetrahydrofuran (357 and 420 nm for the K^+ ion pair7) and 354 and 432 nm for the $HNEt_3^+$ ion pair). The results indicate that the nature of the picrate ion changes with increase in CATB concentration: hydrated (with hydrogen-bond)→dehydrated (without hydrogen-bond) and free→dehydrated and ion-paired.

No appreciable shift was observed in the presence of SDS and Brij-35 above their CMC's (Table 1).

TMAC, a typical phase transfer catalyst, forms aggregates at very low concentrations (10^{-5}—10^{-4} M). They seem to be much smaller than the conventional globular micelles and enhance the nucleophilicity of the bound anions more than the conventional cationic micelles.9) The λ_{max} values at [TMAC] = 0.04—0.1 mM always appear in the range 374—377 nm (Table 1), indicating that the TMAC aggregate provides a relatively free picrate ion. The result indicates that the nucleophilic reactivity of the anion bound to the TMAC aggregate is enhanced due to the desolvation to a greater extent than that bound to the conventional cationic micelle.[9)]

It has been established on the basis of absorption and emission spectra of dye molecules that 4VP-D-0 is classified as a simple polyelectrolyte and 4VP-D-22 as a polymer micelle which possesses the hydrophobic domain.[6,10,11)] The spectrum of the picrate ion was scarcely affected by 4VP-D-0, while addition of 4VP-D-22 caused appreciable bathochromic shifts to 360 nm accompanied by the appearance of a shoulder at around 400 nm. Further increase in the concentration of 4VP-D-22 did not change the spectrum. This indicates that the picrate ion pair formed in the polymer micelle is relatively tight.

Free, dehydrated picrate ion is formed at slightly below the CMC of CTAB. On the other hand, once the micelle formation takes place, the ion pair becomes relatively tight probably due to the apolar environment. It is suggested that the local hydrophobic domain is preferred to the globular hydrophobic domain of the micelle to produce the free ion. The TMAC aggregate may be the case.

Although the multi-phase dependence of the bimolecular reaction rate in the micellar catalysis has been rationalized in terms of concentration and dilution of reactants by micelles,[12–14)] the present study indicates that the reactivity of the anion may be also dependent on surfactant concentrations.

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