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Spectrophotometric Determination of Sodium 4-Dodecylbenzenesulfonate with 1-(*N*-Methylpyridinium-4-yl-azo)-4-(4-diethylaminophenylazo)-naphthalene Iodide

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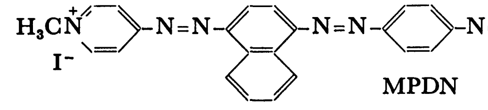
Synopsis. A new reagent, 1-(*N*-methylpyridinium-4-yl-azo)-4-(4-diethylaminophenylazo)naphthalene iodide, can react with sodium 4-dodecylbenzenesulfonate to show a color change in an aqueous phase in the presence of iodide ion. The calibration graph is straight line up to 1.2×10^{-5} M (1 M= 1 mol dm^{-3}); $\varepsilon=3.25\times10^{4}$ l mol^{-1} cm^{-1} at 580 nm.

The developmental study on the new reagent is invaluable in the determination of micro amounts of anionic surfactant in an aqueous phase.[1] A new reagent, 1-(*N*-methylpyridinium-4-yl-azo)-4-(4-diethylaminophenylazo)naphthalene iodide (MPDN), forms an ion pair with the anionic surfactants such as sodium 4-dodecylbenzenesulfonate (DBS) and dodecyl sulfate (SDS) in the presence of iodide ion. Using this phenomenon, DBS or SDS up to 1.2×10^{-5} M has been determined in an aqueous phase without extraction procedure.



MPDN

Experimental

Materials. A typical synthetic method of MPDN is as follows. A solution of 1.8 g of 4-aminopyridine in 10 ml of 85% phosphoric acid and 5 ml of concentrated nitric acid were mixed at −8 °C; sodium nitrite (1.4 g) and 25 g of ice were then added successively.[2] The solution was poured into 100 ml of ethanol containing 2.9 g of 1-naphthylamine. After the reaction, the solution was neutralized with sodium carbonate, and the precipitate was filtered off and recrystallized from benzene. The crystals of 4-(4-amino-1-naphthylazo)pyridine (ANP) were reddish violet plates. Found; C, 72.52; H, 4.56; N, 22.18%. Calcd for $C_{15}H_{12}N_4$: C, 72.60; H, 4.87; N, 22.57%.

ANP (1 g) was dissolved in 30 ml of glacial acetic acid, and diazotized with 0.28 g of sodium nitrite by adding in small portions. The solution was poured into 100 ml of ethanol containing 0.6 g of *N,N*-diethylaniline. After the reaction, the solution was neutralized with sodium carbonate, and the precipitate was filtered off and recrystallized from ethanol-water solution. The crystals of 1-(4-pyridylazo)-4-(4-diethylaminophenylazo)naphthalene (PDN) were violet needles. Found: C, 73.70; H, 6.03; N, 20.28%. Calcd for $C_{25}H_{24}N_6$: C, 73.50; H, 5.92; N, 20.58%.

PDN (0.3 g) was quarternized by refluxing with 0.2 g of methyl iodide in 30 ml of *N,N*-dimethylformamide at 50 °C for 8 h. The iodide, 1-(*N*-methylpyridinium-4-yl-azo)-4-(4-diethylaminophenylazo)naphthalene iodide (MPDN), obtained was washed with toluene until the washings were no longer colored and then dried under reduced pressure at 50 °C to a constant weight. A 6.6×10^{-4} M solution of MPDN was prepared by dissolving it in ethanol.

Anionic Surfactants. Anionic surfactants used were sodium 4-dodecylbenzenesulfonate (DBS) and dodecyl sulfate (SDS). They were dried at 50 °C under the reduced pressure to a constant weight.

Procedure. Place a suitable aliquot of the standard DBS or SDS solution, containing less than 1.2×10^{-5} M, into a 25-ml calibrated flask. Add 1 ml of 0.25M sodium iodide and 1.5 ml of 6.6×10^{-4} M MPDN solution. Dilute the solution to the mark with distilled water. Measure the absorbance at 580 nm in 1-cm cell against water as a reference.

Results and Discussion

In addition of iodide ion to the reagent solution at pH between 4 and 10, the blue color of the reagent solution changed into a reddish violet color, and the reddish violet color changed to a blue by the addition of the surfactants. The formation of the ion pair occured instantaneously, and the surfactants could be determined directly in an aqueous phase without extraction. Figure 1 shows the absorption spectra of these solutions; the wavelength of maximum absorption occurs at 620 nm for MPDN, at 520 nm for MPDN containing 10^{-2} M iodide ion, and at 575 nm for MPDN containing 10^{-2} M iodide ion and 1.2×10^{-5} M DBS, respectively. The determination was carried at 580 nm.

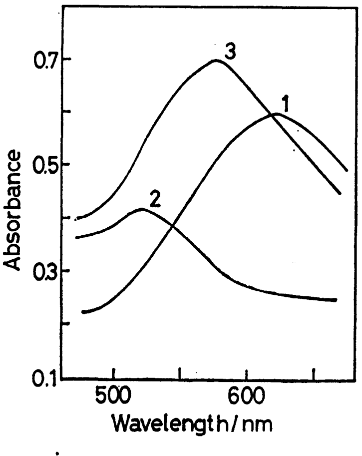


Fig. 1. Absorption spectra.
1: 3.96×10^{-5} M MPDN, 2: 3.96×10^{-5} M MPDN+ 10^{-2} M I$^-$, 3: 3.96×10^{-5} M MPDN+10^{-2} M I$^-$+ 1.2×10^{-5} M DBS.

The effect of amounts of sodium iodide on the absorbance at 580 nm was examined. The absorbance difference between the ion pair and the reagent blank was constant within 1 h when iodide ion existed from 5×10^{-3} M to 2×10^{-2} M, and above the concentration,

Table 1. Effect of anions on colouration

Anion	Concentration/M		
	10^{-1}	10^{-2}	10^{-3}
F^-	—	—	—
Cl^-	++*	+	—
Br^-	++*	++	—
I^-	++*	++	+
NO_3^-	++*	+	—
ClO_4^-	—	—	—
CH_3COO^-	—	—	—
SO_4^{2-}	++*	+	—
HPO_4^{2-}	+	—	—

++ Very good, + good, *precipitation.

very fine precipitates appeared on standing. Therefore in the following studies the concentration of iodide ion was kept at 1×10^{-2} M. The effect of other anions on coloration of the reagent solution is shown in Table 1. The most satisfactory results were obtained by use of iodide ion.

The effect of amounts of ethanol was studied. When the amount of ethanol added was 3 ml or more for the total volume of 25-ml, the both absorbances of the reagent blank and the sample solution increased gradually. And a constant absorbance difference was obtained between 1 and 2.5 ml of ethanol to 25 ml of the total solution.

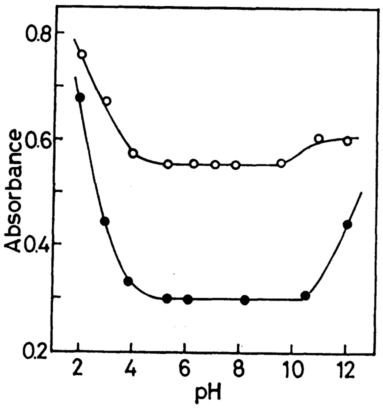


Fig. 2. Effect of pH.
—○—: MPDN-DBS, —●—: MPDN, [MPDN]=3.96×10^{-5} M, [DBS]=8.0×10^{-6} M, [I^-]=1×10^{-2} M.

Table 2. Tolerance limits for diverse ions

Ion	Tolerance limit/M	Absorbance
None		0.553
Cl^-	10^{-3}	0.558
NO_3^-	10^{-3}	0.550
HCO_3^-	10^{-3}	0.548
SO_4^{2-}	10^{-3}	0.563
HPO_4^{2-}	10^{-3}	0.549
SiO_3^{2-}	10^{-4}	0.553
Na^+	10^{-3}	0.550
K^+	10^{-3}	0.553
NH_4^+	10^{-3}	0.548
Mg^{2+}	10^{-3}	0.558
Ca^{2+}	10^{-3}	0.553
Sodium stearate	10^{-5}	0.556

The effect of pH on the absorbance is shown in Fig. 2. The optimum pH range was between pH 5 and 10. And the pH of the solutions was adjusted with hydrochloric acid or sodium hydroxide solution to avoid the interference from anions intermixed.

The calibration graph obtained by the procedure was linear up to 1.2×10^{-5} M of DBS or SDS. The practical molar absorptivities of DBS and SDS were 3.25×10^4 and 1.45×10^4 l mol^{-1} cm^{-1} at 580 nm, respectively.

The interferences due to various ions were examined, and the results obtained are shown in Table 2. The common cations and anions of 10^{-3} M levels did not interfere with the procedure. Stearate ion above 10^{-5} M caused a positive error, because the precipitate separated out gradually on standing.

References

1) Keiro Higuchi, Yasuaki Shimoishi, Haruo Miyata, and Kyoji Tôei, *Chem. Lett.*, **1981**, 711.

2) R. W. Faessinger and E. V. Brown, *Trans. Ky. Acad. Sci.*, **24**, 106 (1963).