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DIRECT SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF ALKYLBENZENESULFONATE WITH 1-(4-N-METHYLPYRIDINIUMAZO)-4-(4-AMINOPHENYLAZO) NAPHTHALENE IODIDE[1)]

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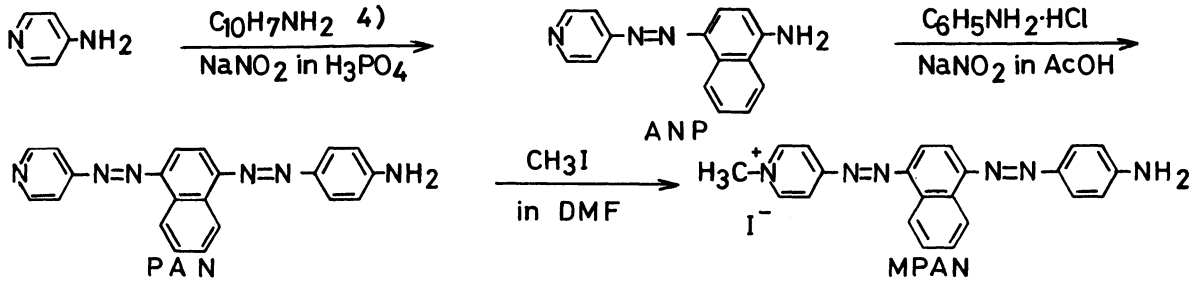
A new reagent, 1-(4-N-methylpyridiniumazo)-4-(4-aminophenylazo) naphthalene iodide, can react with sodium alkylbenzenesulfonate to show a color change in an aqueous medium. The calibration graph is straight line over the range from 8 X 10^{-6} to 3.0 X 10^{-5} M of sodium dodecylbenzenesulfonate. The practical molar absorptivity is 1.8 X 10^{4} l mol^{-1} cm^{-1} at 594 nm.

Extraction-spectrophotometric method has been widely used for the determination of anionic surfactants, such as sodium alkylbenzenesulfonate and alkylsulfate, in environmental analysis.[2,3)] On the other hand, it is interested in the developmental study on reagents which react with the anionic surfactants to show a color change in an aqueous medium. A new cationic azodye, 1-(4-N-methylpyridiniumazo)-4-(4-aminophenylazo) naphthalene iodide(MPAN) shows a color change with 10^{-5} M levels of anionic surfactants in aqueous media.

The reagent,MPAN, was obtained as depicted in the following equation.



4-(4-Aminonaphthylazo) pyridine(ANP) was obtained as reddish violet plates after the recrystallization from benzene. 1-(4-Pyridylazo)-4-(4-aminophenylazo) naphthalene(PAN) was obtained as violet needles from dioxan-water solution(1+3). PAN was quaternised by refluxing with methyl iodide in N,N-dimethylformamido in an oil bath. The iodide 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 4 X 10^{-4} M solution of MPAN was prepared by dissolving it in ethanol.

The recommended procedure is as follows; Pipet an aliquot of the standard sodium dodecylbenzenesulfonate(DBS), 3.0 X 10^{-5} M or less, into a 25-ml calibrated flask, add 1 ml of 0.1 M phosphate buffer solution(pH 8.0) and 1.2 ml of 4.0 X 10^{-4} M MPAN ethanol solution. Mix and dilute to the mark with water, and measure the absorbance at 594 nm in 1 cm cell against water as a reference.

Fig. 1 shows the absroption spectra of MPAN solution, and its solutions containing an excess of DBS, sodium dodecylsulfate(DS), or sodium stearate (SS), respectively. The wavelength at the maximum absorption of each spectrum occurs at 594 nm for MPAN, 490 nm for DBS, and 425 nm for DS or SS, respectively. And the determination of DBS was carried out at 594 nm.

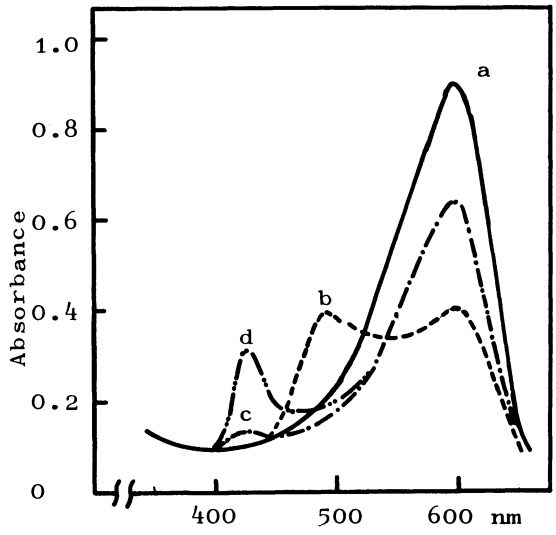


Fig. 1. Absorption spectra
a: MPAN(1.92 X 10^{-5} M)
b: MPAN + DBS(3.2 X 10^{-5} M)
c: MPAN + DS(3.2 X 10^{-5} M)
d: MPAN + SS(3.2 X 10^{-5} M)

A study of the effect of pH showed that a constant maximum absorbance was obtained between pH 7 and 9. A pH value of 8 was chosen for further work.

The absorbance was measured by the recommended procedure and the absorption differences between the reagent blank and known amounts of DBS were plotted against the DBS concentration. The calibration curve was linear in the range from 8 X 10^{-6} to 3.0 X 10^{-5} M of DBS. The practical molar absorptivity is 1.8 X 10^{4} l mol^{-1} cm^{-1} at 594 nm.

The cations(10^{-3} M levels) and anions(10^{-4}- 10^{-3} M) normally present in river waters do not interfere with the determination.

The application of the above-mentioned method for the determination of anionic surfactants in river water, and the development of the reagent synthesis are now in progress.

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