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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF HIGHER CARBOXYLIC ACIDS WITH BIS[2-(5-CHLORO-2-PYRIDYLAZO)-5-DIETHYLAMINOPHENOL] COBALT(III) CHLORIDE

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Higher carboxylic acid reacts with Bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenol] cobalt(III) chloride, Co-5-Cl-PADAP, to form a 1:1 ion-pair, which is extracted into chlorobenzene in a single extraction at pH 11. The molar absorptivities of the ion-pairs of C_{12}, C_{14}, C_{16} and C_{18} acids are 3.5, 6.6, 7.6 and 7.6 X 10^4 l mol-1 cm^{-1} at 563 nm, respectively.

Monovalent cationic dyes have become widely used in the ion-pair extraction-spectrophotometry for the determination of anionic surfactants, such as sodium alkylbenzenesulfonate and alkyl sulfate in environmental analysis.[1,2] A minute amounts of the surfactants in river waters were determined spectrophotometrically with Co-5-Cl-PADAP by Taguchi and Goto[3] at pH 1.

However, these reagents are rarely applied in the ion-pair extraction for the carboxylate anion. For its purpose, the pH value of the solution should be kept above 10 by considering their pK_a values. Under this condition, the color of the cobalt complex of pyridylazo dye[4] is more stable than that of triphenylmethane dye, such as Ethyl Violet.[5]

This paper describes a new and sensitive method for the determination of 10^{-6} M(1 M = 1 mol dm^{-3}) levels of the acids with Co-5-Cl-PADAP and their molar absorptivities in chlorobenzene at 563 nm.

The used sample solutions of the acids were 2 X 10^{-5}M of sodium hexanoate, octanoate, decanoate, laurate, myristate, palmitate and 1.3 X 10^{-5} M of sodium stearate.

The recommended procedure is as follows; Place 3 ml of a sample solution(acid content below 1 X 10^{-5} M) in a 15-ml stoppered centrifuge tube, and add 1 ml of 1 X 10^{-4} M Co-5-Cl-PADAP solution and 1 ml of borate buffer solution(pH 11). Add 5 ml of chlorobenzene and shake the tube mechanically for 5 min, and leave for 5 min. Centrifuge for 3 min at 3000 rpm, and pour the clear organic phase into a 1-cm glass cell. Measure the absorbance at 563 nm against chlorobenzene in the reference cell.

Fig. 1 shows the absorption spectra of a solution containing 6 X 10^{-6}M sodium palmitate using the described procedure. The wavelength of maximum absorption occurs at 563 nm.

A study of the effect of pH showed that a constant maximum absorbance was obtained between pH 10.5 and 13. Then, the extraction of the ion-pair into chlorobenzene was carried out at pH 11, which was adjusted with borate buffer solution.

Shaking for 5 min, standing for 5 min and centrifuging for 3 min at 3000 rpm were chosen for further work from the results of the preliminary experiments.

The stoichiometric ratio of Co-5-Cl-PADAP to calboxylate anion was found to be 1:1 by the molar ratio method.

The calibration graphs by the method were found to show a good linear relation over the range 0 to 1 X 10^{-5} M.

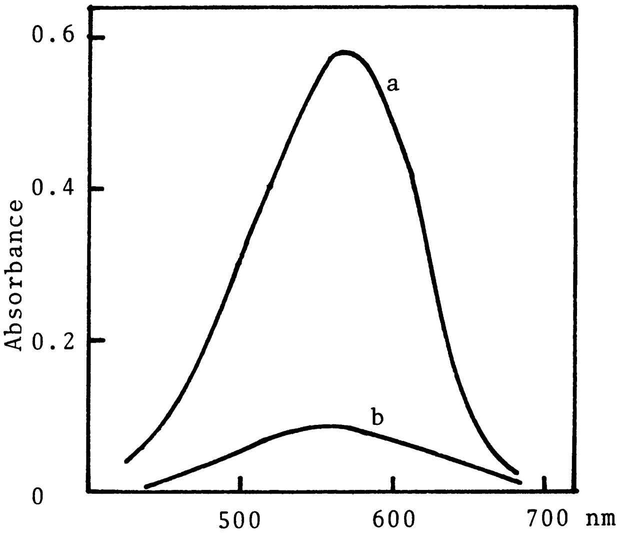

Fig. 1. Absorption spectra of ion-pair
a: Sodium palmitate 6 X 10^{-6}M
b: Reagent blank

Table 1 shows the molar absorptivities of the ion-pairs in chlorobenzene at 563 nm.

Table 1 Molar absorptivities of the ion-pairs(ε X 10^4 1 mol^{-1} cm^{-1})

Hexanoic acid	0	Myristic acid	6.6
Octanoic acid	0	Palmitic acid	7.6
Decanoic acid	0.93	Stearic acid	7.6
Lauric acid	3.5		

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 method for the determination of soap, sodium higher calboxylate, in river water is now in progress.

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References

1) Japanese Industrial Standard, K 0102, 1974.
2) K. Higuchi, Y. Shimoishi, H. Miyata, K. Tôei and T. Hayami, The Analyst, 105, 768(1980).
3) S. Taguchi and K. Goto, Talanta, 27, 289(1980).
4) S. Shibata, M. Furukawa and K. Tôei, Anal. Chim. Acta, 66, 397(1973).
5) Partly reported at the 30th Annual Meeting of the Japan Society for Analytical Chemistry, Kyoto, 1981; Abstr. No. 1B 22.

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