Batchwise and Flow-Injection Methods for the Spectrophotometric Determination of Anionic Surfactants with 4-(4-*N*,*N*-Dimethylaminophenylazo)-2-methylquinoline

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A solvent-extraction spectrophotometric method for the determination of anionic surfactants in water was developed with 4-(4-*N*,*N*-dimethylaminophenylazo)-2-methylquinoline (MQ) by batchwise and flow-injection techniques. The ion associates of MQ with anionic surfactants extracted into an organic phase showed a blue shift of the maximum absorption wavelength; their molar absorptivities were 4.5×10^4 l mol^{-1} cm^{-1} at 560 nm. In the batchwise method, a 40-fold extraction concentration was possible. In the 20-fold concentration, the calibration graph was linear at concentration ranging from 1×10^{-8} M to 7.5×10^{-7} M of anionic surfactants, and the mean absorbances of the reagent blank and the 5×10^{-7} M anionic surfactant (dodecylsulfate: LS^-) were 0.024 and 0.518, respectively; the relative standard deviation for 10 measurements of 5×10^{-7} M LS^- was 0.28%. Foreign ions generally existing in river water did not interfere with the determination. This solvent-extraction spectrophotometric method was satisfactorily applied to a flow-injection method. The reagent MQ was recycled and repeatedly used at least for 7 months, and the efficiency of the reagent has not changed during at least this period.

Keywords Spectrophotometry, ion association extraction, anionic surfactants, 4-(4-*N*,*N*-dimethylaminophenylazo)-2-methylquinoline, batchwise method, flow-injection method

Almost all of the methods for the spectrophotometric determination of anionic surfactants depend on the solvent extraction of an ion associate formed between a dye cation and an anionic surfactant. Methylene Blue is one of the most frequently used cationic dyes.[1,2] The Methylene-Blue method, however, is very troublesome and its sensitivity is low because of the small extractability of the ion associate of an anionic surfactant with Methylene Blue.

For simpler and more sensitive methods, other cationic dyes have been examined. Toei *et al.* synthesized and examined more hydrophobic cationic dyes such as Methylene-Blue analogs[3], Bindschedler's Green analogs[4] and the derivatives of 1-alkyl(or -aryl)-4-(4-*N*,*N*-diethylaminophenylazo)pyridinium cations.[5,6] Of these reagents, the dibutyl analog of Bindschedler's Green was the most sensitive reagent: the molar absorptivity was 7.1×10^4 l mol^{-1} cm^{-1} at 730 nm, though the reagent was less stable than any other reagents. Taguchi *et al.* applied the cobalt-complex cation of 2-(2-pyridylazo)-5-*N*,*N*-diethylaminophenol to the determination of anionic surfactants.[7] This cation is very stable and extractable: the ion associate of an anionic surfactant could be extracted even into benzene. The molar absorptivity was 6.1×10^4 l mol^{-1} cm^{-1} at 571 nm.

In order to improve the sensitivity, simplicity, stability and availability of a reagent, Motomizu *et al.* examined several triphenylmethane dyes; Ethyl Violet was found to be the most suitable reagent for the determination of anionic surfactants.[8] The molar absorptivity was about 1×10^5 l mol^{-1} cm^{-1} at 615 nm, and anionic surfactants were quantitatively extracted into toluene and benzene by single extraction. This Ethyl-Violet (EV) method was applied to the determination of anionic surfactants in seawater.[9,10] In all of the method using cationic dyes described above, the dyes and extraction solvents could not be recycled by a simple method and could not be repeatedly used.

The authors have studied the liquid-liquid extraction behavior of the various derivatives of phenylazopyridines and quinolines with several anions.[11,12] These reagents have been developed while aiming at reagent recycling and solvent extraction. One of the useful reagents is 4-(4-*N*,*N*-dimethylaminophenylazo)-2-methylquinoline (MQ). MQ possesses some advantages regarding practical use: it is very stable, its optimum pH range is wide, extractability and sensitivity are relatively high, and the blue shift of the maximum absorption wavelength of an ion associate is large.

In this paper the authors report on both batchwise and flow-injection methods for the spectrophotometric determination of anionic surfactants with MQ.

Experimental

Apparatus

The absorptiometric measurements were carried out on a Hitachi 100-10 spectrophotometer in glass cells of 10-mm path length. A Corning 130 pH meter equipped with a Ross combination electrode (Orion Res. Inc.), a Taiyo SR-I horizontal shaker and an Iwaki KM shaker were used.

A laboratory-made flow-injection system was used. Absorptiometric measurements were made on a Soma S-3250 visible detector with a 10-mm micro flow cell (18 μl), the peaks being recorded with a Toa Dempa FBR-251A recorder. A carrier solution and an extraction solvent were propelled using a double-plunger micro pump (Sanuki Kogyo, DM2M-1016). The segmentor was a T-shaped connector[13] in which the aqueous phase flowed straight through and the organic phase flowed at right-angles. A phase separator with porous polytetrafluoroethylene (PTFE) membranes (0.8 μm pore size)[13] was used. Samples were injected through a five-way injection valve with a loop (Sanuki Kogyo) into the carrier stream. The flow lines were made of PTFE tubing (0.5 mm i.d.). A diagram of the flow system is shown in Fig. 1.

Reagents

A standard anionic surfactant solution (10^{-3} M stock solution) was prepared by dissolving sodium dodecylsulfate (LS^-; Wako Pure Chemicals Ind., purity is more than 99.2%) in distilled water. Other anionic surfactant solutions were also prepared in a similar manner as LS^- using sodium dodecylbenzenesulfonate (DBS^-; Wako Pure Chem. Ind., purity is more than 99.0%), sodium dodecylsulfonate (DS^-; Tokyo Kasei Kogyo Co., GR) and sodium di-2-ethylhexylsulfosuccinate (SSS^-; Kanto Chem. Co., purity is 96.3%). These anionic surfactants were dried at 50°C under reduced pressure (about 3 mmHg) before being weighed. The working solutions were freshly prepared daily by accurate dilution of the stock solution.

The reagent 4-(4-*N*,*N*-dimethylaminophenylazo)-2-methylquinoline, MQ, used in this work was a reagent synthesized and used in a previous study.[12] The 2.5×10^{-5} M MQ organic solvent solution was prepared as before[12] using chloroform.

The reducing agent solution (0.1 M) was prepared from ascorbic acid. Other reagents used were of analytical-reagent grade.

Standard procedure for the batchwise method

Transfer 100 ml or less of a sample solution containing anionic surfactants into a separatory funnel, and dilute it to 100 ml with distilled water, if necessary. Add 0.5 ml of 10 M H_2SO_4 and, if necessary, add 1 ml of 0.1 M ascorbic acid. Shake it with 5 ml of a 2.5×10^{-5} M MQ chloroform solution for 5 min with an Iwaki KM shaker, and let it stand for more than 5 min. Measure the absorbance of the organic phase at 560 nm after phase separation.

When the concentration of the anionic surfactants are high, use a small sample volume, for example, 5 ml. In this (1:1) extraction, add 1 ml of a 0.5 M H_2SO_4 solution and shake with 5 ml of a 2.5×10^{-5} M MQ chloroform solution for 5 min.

Results and Discussion

Experimental variables for the batchwise method

Figure 2 shows the absorption spectra for the reagent MQ and its ion associate with LS^- in chloroform; for a comparison, the absorption spectra obtained with 4-(4-*N*,*N*-dibutylaminophenylazo)pyridine Bu_2P, which was the most extractable of the nine reagents examined in a previous study[11], are shown. In MQ, the absorption maximum of the ion associate was 560 nm, where the molar absorptivity was 4.5×10^4 l mol^{-1} cm^{-1}. The absorption maximum of MQ, itself, was 450 nm, and the absorbance of the reagent blank at 560 nm was very small. Thus, the absorbances of the ion associates with

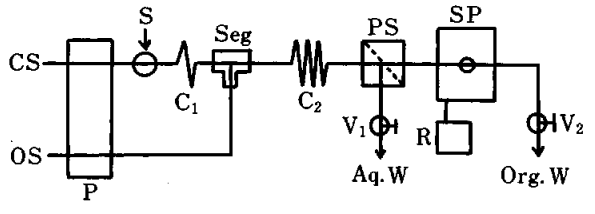

Fig. 1 Schematic diagram of the FIA system. CS, carrier solution (0.1 M H_2SO_4); OS, extraction solvent (2×10^{-5} M MQ in $CHCl_3$); P, double-plunger pump (0.8 ml min^{-1}); S, sample injection (360 μl); C_1, mixing coil (0.5 mm i.d.×30 cm); C_2, extraction coil (0.5 mm i.d.×3 m); Seg, segmentor (T-connector): PS, phase separator; SP, absorptiometric detector (560 nm); R, recorder; V_1 and V_2, needle valves; Aq.W, aqueous-phase waste; Org.W, organic-phase waste.

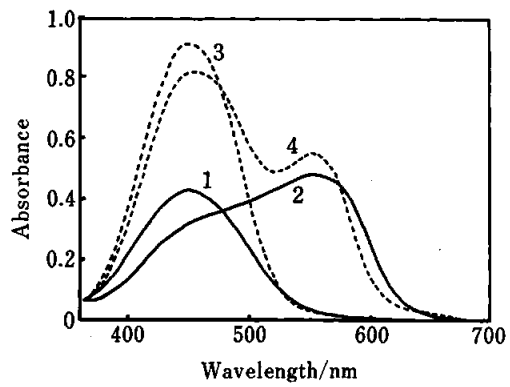

Fig. 2 Absorption spectra. (1) and (2): 2.5×10^{-5} M MQ; (3) and (4): 5.0×10^{-5} M Bu_2P; (1) and (3): reagent blank; (2) and (4): 1×10^{-5} M LS^-; pH 1.2.

anionic surfactants were measured at 560 nm. In Bu_2P, the molar absorptivity of the ion associate was 5.51×10^4 l mol^{-1} cm^{-1} at 555 nm.

The effect of the pH on the extraction of ion associates was examined; the obtained results are shown in Fig. 3. In the case of a 20-fold concentration method ((20:1) extraction), the optimum pH region was 1.2 to 2.4, while using (1:1) extraction the maximum absorbances were obtained over a wider pH range. In further experiments, the extraction was, therefore, carried out at pH 1.1 (H_2SO_4: 0.1 M) and 1.3 (H_2SO_4: 0.05 M), in (1:1) and (20:1) extraction, respectively.

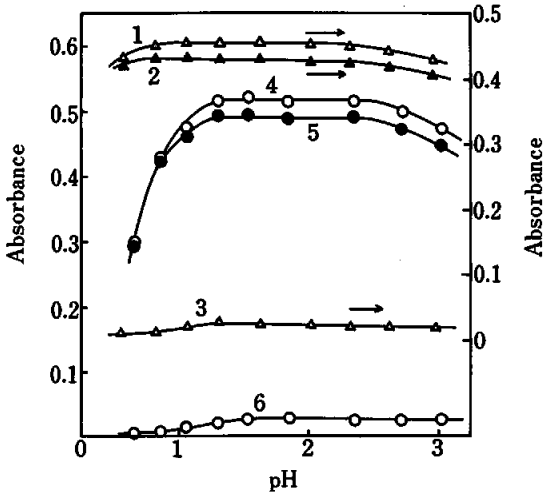

Fig. 3 Effect of pH. (1), (2) and (3): (1:1) extraction; (4), (5) and (6): (20:1) extraction; (1) and (4): 1×10^{-5} M LS^- in organic phase, ref. chloroform; (2) and (5): 1×10^{-5} M LS^- in organic phase, ref. reagent blank; (3) and (6): reagent blank, ref. chloroform; 560 nm.

The effect of the amounts of MQ was examined (Fig. 4). The higher the concentration of MQ, the larger was the absorbance of the reagent blank. In both (1:1) and (20:1) extraction methods, 2.5×10^{-5} M MQ was used.

The effect of the volume of the aqueous phase was examined. The absorbance for the samples gradually increased with increasing the volume: the increase in absorbance between 5 ml and 200 ml of aqueous phases was about 12%. This increase of the absorbance has been attributed to a decrease in the volume of the organic phase, which was ascertained by an experiment using aqueous phases saturated with chloroform.

The effect of the shaking time was examined for times between 2 and 60 min; 5 min was sufficient for quantitative extractions in both the (1:1) and (20:1) extraction procedures.

The effect of foreign ions was examined (Table 1). Inorganic ions, which generally exist in river water samples tested in this work, did not interfere with the determination of anionic surfactants. The hypochlorite

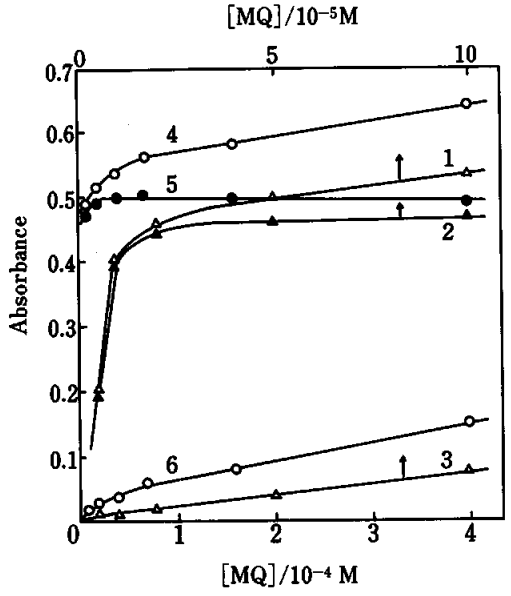

Fig. 4 Effect of amounts of the reagent, MQ. (1), (2) and (3): (1:1) extraction, pH 1.1; (4), (5) and (6): (20:1) extraction, pH 1.3; (1) and (4): 1×10^{-5} M LS^- in organic phase, ref. reagent blank; (3) and (6): reagent blank, ref. chloroform; 560 nm.

Table 1 Effect of foreign substances

Substance	Added as	Concn./M	ΔAbs.[a]
None[b]			0.000
Na^+, Cl^-	NaCl	10^{-3}	−0.008
NO_3^-	$NaNO_3$	10^{-3}	+0.037
		5×10^{-4}	+0.020
		2×10^{-4}	+0.008
NO_2^-	$NaNO_2$	10^{-3}	+0.236
		10^{-4}	+0.081
		5×10^{-5}	+0.008
HCO_3^-	$NaHCO_3$	10^{-3}	−0.006
$H_2PO_4^-$	KH_2PO_4	10^{-3}	−0.001
SiO_3^{2-}	Na_2SiO_3	10^{-3}	+0.003
ClO^-	NaClO	5×10^{-4}	+0.031[c]
		5×10^{-5}	+0.002[c]
NH_4^+	NH_4Cl	10^{-3}	+0.008
K^+	KCl	10^{-3}	+0.002
Ca^{2+}	$CaCl_2$	10^{-3}	−0.003
Mg^{2+}	$MgSO_4$	10^{-3}	−0.001
Fe^{3+}	$Fe_2(SO_4)_3$	10^{-3}	−0.008
Cu^{2+}	$CuSO_4$	10^{-3}	−0.008
Zn^{2+}	$ZnSO_4$	10^{-3}	−0.008
Humic acid		10 ppm	+0.035
		1 ppm	0.000
TX-100		1.6×10^{-3}	−0.040
		1.6×10^{-4}	−0.024
		1.6×10^{-5}	+0.001

LS^-: 5×10^{-7} M.

a. Plus and minus mean the positive and negative errors, respectively.

b. Absorbance for 5×10^{-7} M LS^-: 0.518.

c. One milliliter of 0.1 M ascorbic acid was added.

ion, which probably exists in tap water as residual chlorine, interfered with the determination. This interference, however, could be reduced by the addition of a reducing agent, such as ascorbic acid.

Calibration graphs were obtained according to the standard procedure. In (20:1) extraction, the graph was linear over the range from 1×10^{-8} to 7.5×10^{-7} M LS^-, and the absorbance of the reagent blank was on the average 0.024 for 10 determinations. The mean absorbance and the relative standard deviation for 10 measuremtents of 5×10^{-7} M LS^- were 0.518 and 0.28%, respectively.

Experimental variables for the flow-injection method

The concentration of MQ in the organic solvent was examined while being varied from 0.5×10^{-7} M to 1×10^{-4} M using the flow system shown in Fig. 1. Almost equal peak heights were obtained over the range from 2×10^{-5} M to 1×10^{-4} M; 2×10^{-5} M was chosen since the base line was stable.

The concentration of H_2SO_4 in the carrier solution was examined. The larger the concentration of H_2SO_4, the higher were the peak heights for both LS^- and the reagent blank. The reason why the peak for the reagent blank solution becomes higher with increasing H_2SO_4 concentration is as follows. The H_2SO_4 concentration of a sample zone is always lower than that of the carrier solution, itself, which results in a positive peak for a reagent blank solution. Thus, the higher the concentration of H_2SO_4 of the carrier solution, the larger is the difference in the H_2SO_4 concentration between the carrier solution and the sample zone, and the higher the peak for the reagent blank solution becomes. In this work a 10^{-1} M H_2SO_4 solution was used as a carrier solution, while considering the peak heights of the sample and the reagent blank.

The length of the mixing tubing was examined by varying it from 3 to 100 cm. The longer the tubing, the longer was the peak tailing and moreover, the first peak was always very short in a 100-cm mixing tubing. Such phenomena were attributed to an interaction between hydrophobic anionic surfactants and hydrophobic PTFE tubing. In further experiments a 30-cm tubing was chosen.

The effect of the extraction coil length was examined by varying it from 0.5 m to 5 m; the peak heights were almost identical with those of coils more than 2 m long. A 3-m coil was adopted.

Sample injection volumes were varied from 120 to 650 µl; the obtained flow signals are shown in Fig. 5. The peak height reached approximately a maximum value when 360 µl of the sample was injected.

The flow rate of the two streams was examined by varying them from 0.4 to 1.1 ml at identical flow rates. The peak heights were almost identical over the examined flow rates; 0.8 ml min^{-1} was adopted.

The reagent MQ was compared with the previously examined reagent, Bu_2P. Both flow signals are shown in Fig. 6. In the case of Bu_2P, the peak height increased

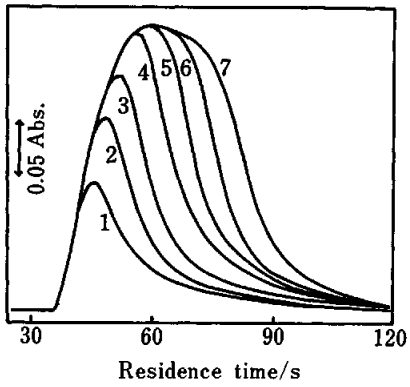

Fig. 5 Effect of the volume of sample injection. Sample volume/µl: (1) 120; (1) 200; (3) 260; (4) 360; (5) 450; (6) 550; (6) 650; (7) 750.

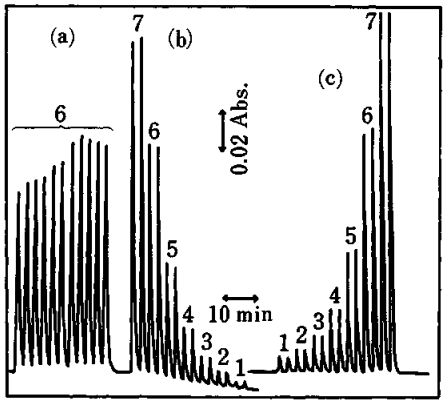

Fig. 6 Flow signals for anionic surfactants with MQ and Bu_2P. (a) and (b): Bu_2P; (c): MQ; $[LS^-]/10^{-7}$ M: (1) 0; (2) 2; (3) 5; (4) 10; (5) 20; (6) 40; (7) 60.

with an increase in the number of injection times; this is because the ion associates formed between Bu_2P and anionic surfactants are very adsorptive on the PTFE wall. Thus, MQ is preferable to Bu_2P.

The peak heights of several anionic surfactants such as LS^-, DS^-, DBS^- and SSS^- were compared with that of LS^-. The peak heights and shapes were identical for four anionic surfactants. In this work, LS^- was used as a standard anionic surfactant.

The effect of foreign ions was examined. The following ions did not interfere with the determination of anionic surfactants: Na^+, K^+, NH_4^+ and Cl^- at a concentration of 10^{-3} M; Ca^{2+}, Mg^{2+} and $H_2PO_4^-$ at a concentration of 5×10^{-4} M; NO_3^-, HCO_3^- and SiO_3^{2-} at a concentration of 10^{-4} M; and Fe^{3+} at a concentration of 5×10^{-6} M.

Determination of anionic surfactants in water samples

Anionic surfactants in water samples were determined by both the batchwise and flow injection (FIA)

Table 2 Determination of anionic surfactants in water

Sample[a]	Anionic surfactants, ppb		
	Batchwise method[b]	EV method[c]	FIA method
Zasu River at Tsushima	205 (97.2)	224	259
Sasagase River at Fujita	255 (97.4)	291	378
Kurashiki River at Kurashikigawa Bridge	320 (94.4)	352	470
Lake Kojima	162 (96.6)	183	655

a. Sampled on 6th February, 1990.
b. Twenty-fold concentration. Sample taken 25 ml. Figures in the parentheses are the values of recovery(%) obtained when 72 μg of LS^- was added to sample solutions.
c. Ref. 8.

methods. The obtained results are shown in Table 2. For a comparison, the results obtained by a batchwise EV method[8] are shown in the table. Though the results obtained by the batchwise MQ method are in good agreement with those obtained by the EV method, the results of the flow-injection method are larger than those of both batchwise methods. A similar tendency has been seen in previous flow-injection studies with Methylene Blue[14] and azo dye[15] as a counter dye ion. Such a discrepancy has been found in heavily contaminated samples: the colored precipitates occurred at the interface between an organic and an aqueous phases. This is probably because in the batchwise method some parts of the anionic surfactants sometimes form precipitates and remain on the interface between the organic and aqueous phases upon vigorous shaking. However, further experiments are necessary to study the cause of the discrepancy between the batchwise and the flow-injection methods.

Recycling the reagent solution

After a measurement of the absorbance of the organic phase, the organic and aqueous phases were collected in a separatory funnel, and then shaken after a pH adjustment to about 10. All of the reagent was transferred into the organic phase and the anionic surfactants were transferred into the aqueous phase. The organic phase, thus treated, was used repeatedly as the reagent solution for further determinations of anionic surfactants. The recycled reagent solution was sufficiently efficient for the determination of anionic surfactants after recycling 50 times over a period of 7 months.

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