

FLOW INJECTION METHOD COUPLED WITH SOLVENT EXTRACTION USING ON-TUBE VISIBLE ABSORPTION AND APPLICATION TO THE DETERMINATION OF ANIONIC SURFACTANTS

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ABSTRACT

A flow-injection spectrophotometric method using solvent extraction/on-tube visible detection was examined. The method was applied to the determination of anionic surfactants. On-tube detection technique without any phase separators was developed by using a glass capillary flow cell (inner diameter: 0.8mm). Background noises caused by the absorbance of a pairing ion, cationic dye in an aqueous phase and the difference in the index of refraction between an aqueous and an organic phase were efficiently eliminated by a digital filtering method. Two kinds of dyes were examined as a pairing ion of anionic surfactants: (1) a cationic dye, Methylene Blue (MB^+), and (2) neutral dyes, such as Rhodamine B (RhodB) and 4-(4-dimethylaminophenylazo)-2-methyl-quinoline (4-MQ). MB^+ was present in an aqueous phase as a cationic form and the ion association complexes formed between MB^+ and anionic surfactants were extracted into an organic phase. The neutral dyes were dissolved in an organic phase as an electrically neutral species. They combined with anionic surfactants in the presence of proton, and changed their color. By using the two kinds of the reagents, anionic surfactants could be determined with a low background noise.

Most of the spectrophotometric methods for the determination of anionic surfactants in water samples are based on the solvent extraction of an ion association complex formed between a cationic dye and an anionic surfactant. Methylene blue is one of the most frequently used cationic dyes in batchwise methods. The batchwise method with Methylene blue, however, is very troublesome and time-consuming, and furthermore chloroform as an extraction solvent is undesirable to our health. Recently, Motomizu et al. developed a solvent extraction-spectrophotometric method for the determination of anionic surfactants with Ethyl Violet. Ethyl Violet is a much

more extractable reagent than Methylene Blue, and therefore the method needs only a single extraction with a non-halogenated less toxic solvent, toluene.

Karlberg and Thelander[1] were the first to couple solvent extraction with flow injection analysis (FIA). Since then, a number of solvent extraction/FIA systems have been reported. Kawase et al.[2] reported a solvent extraction/FIA system using a phase separator with a polytetrafluoroethylene (PTFE) porous membrane, and applied to the determination of anionic surfactants at 10^{-3} M concentrations. Imasaka et al.[3] and Ogata et al.[4] have designed phase separators with PTFE membranes. The phase separators with PTFE membrane are more versatile than that developed by Karlberg and co-worker for solvent extraction/FIA. Later, Motomizu and Oshima[5] have developed a newly designed phase separators with PTFE membrane and applied this to the determination of trace amounts of phosphorus in water. By using this phase separator, the flow-injection methods for anionic surfactants have been developed[6-9].

These solvent extraction/FIA, however, require the use of a phase separator to recover an organic phase. When common-type flow-through cells for spectrophotometric and fluorophotometric detection are used, any pretreatment for organic-phase separation is desired to obtain reproducible signals. Kina et al. reported a simple solvent extraction/fluorophotometric method for the determination of potassium ion coupled with FIA without any phase separators[10]. Aqueous samples, which contained a fluorophor as a pairing anion, were injected into a flowing organic solvent (1,2-dichloroethane) stream containing a macrocyclic compound. This method is a very simple solvent extraction/FIA. However, the flow cell must be refreshed everytime by injecting alcohol. Motomizu and Kobayashi reported a solvent extraction/FIA using on-tube visible detector. The method was applicable only to ones with electrically neutral dyes dissolved in organic solvents.

In this work, a more versatile and useful method for solvent extraction/spectrophotometric determination of analytes extracted into organic solvents was developed.

EXPERIMENTAL

Reagents

All chemicals used were of analytical-reagent grade, except for the synthesized reagent, 4-MQ.

Standard anionic surfactant solution. Sodium dodecyl sulfate (SDS) (Wako Pure Chemicals, purity 99.2%) was dried at 50°C under reduced pressure (about 3mmHg), until a constant mass was achieved. An accurately weighed amount of SDS was dissolved in distilled water to give a $2 \times 10^{-3} \text{M}$ stock solution. The working solutions were prepared daily by accurate dilution of the stock solution.

Cationic dyes. Methylene Blue (MB) was obtained from Tokyo Kasei Kogyo, and was dissolved in distilled water to give a $5 \times 10^{-3} \text{M}$ stock solution. Rhodamine B (RhodB) purchased from Nakarai Kagaku Yakuin was dissolved in distilled water to give a $1.0 \times 10^{-3} \text{M}$ stock solution. A diluted RhodB solution was shaken with benzene: RhodB was extracted into benzene as a colorless lactone, an electrocally neutral species.

4-(4-Dimethylaminophenylazo)-2-methylquinoline(4-MQ). This was the same one as synthesized in the previous work [9]. 4-MQ was dissolved in chloroform to give a $2.0 \times 10^{-4} \text{M}$ solution.

Carrier stream and extraction solvent stream. Distilled water was used as a carrier stream. A carrier stream was merged with a solution containing acetate buffer (0.1M, pH 5) and $3 \times 10^{-4} \text{M}$ MB, and then the merged stream segmented with a stream of chloroform. Other extraction streams are $2.0 \times 10^{-4} \text{M}$ 4-MQ chloroform solution and a $1.0 \times 10^{-5} \text{M}$ RhodB benzene solution.

Recycling reagent solutions. After the measurements of absorbances of the organic phases with 4-MQ and RhodB, the organic and the aqueous phases were collected in a separatory funnel, and then shaken after the pH had been adjusted to about 10. The organic phases, thus treated, were used repeatedly as the extraction solvent stream.

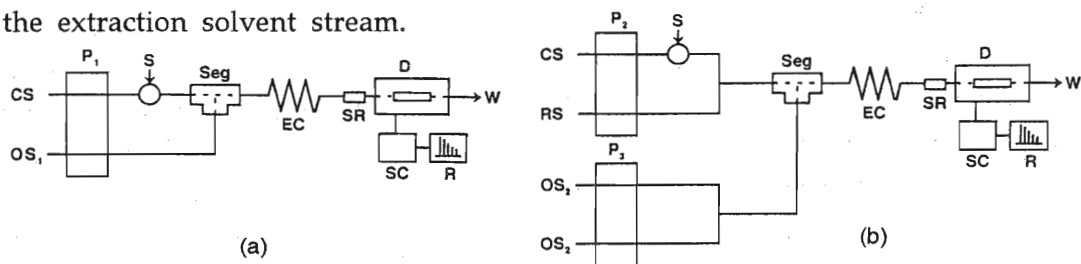


Fig.1 Flow systems for solvent extraction / Flow injection methods

(a) Rhodamine B and 4-MQ method, (b) Methylene Blue method

CS, carrier(H_2O); RS, reagent solution($3 \times 10^{-4} \text{M}$ MB, pH=5); OS₁ and OS₂, extraction solvent(OS₁: $1 \times 10^{-5} \text{M}$ RB in benzene or $2 \times 10^{-4} \text{M}$ 4-MQ in chloroform; OS₂: 1,2-dichloroethane); P₁, P₂ and P₃, double-plunger micro pump(flow rate/ml min⁻¹: P₁ 0.4, P₂ 0.3, P₃ 0.3); S, sample injection (100 μ l); Seg, segmentor(tee connector); EC,extraction coil(1.5mx0.5mm i.d.); SR; segment regulator; D, detector equipped with a capillary flowcell(MB method 660nm; Rhod B method 560nm; 4-MQ method 560nm); SC,digital filter for eliminating sharp noise; R, recorder; W, waste.

Apparatus

On-tube absorbance measurements were made at the maximum wavelength of the ion association complex in the extraction solvent on a Soma S-3250 visible detector with a laboratory-made capillary flow cell. Double-plunger micro pumps (Sanuki Kogyo DM2M-1016) were used for propelling a carrier, a reagent and an extraction solvent stream. The samples were injected by a six-way valve with a variable sample loop (100ml) into the carrier stream. Peaks were recorded with a Toa Dempa FBR-251-A recorder or a System Instruments Co. SIC Labchart TM180. Background noise was eliminated by a digital filtering method with a SIC Signal Cleaner 77 or SIC Labchart TM180. The flow systems are shown in Fig.1; the flow lines consisted of PTFE tubing (0.5mm i.d. and 1mm i.d.) with connecting parts made of poly-(chlorotrifluoroethylene) (CTFE).

Capillary flow cells used are the same as in the previous work[11], and a newly designed one is shown in Fig.2. They are made of Pyrex glass tubing (0.8mm i.d., 2mm o.d.). As is shown in Fig.2, a capillary tube is fixed on an aluminium body with new fittings. Visible light passes through a 0.3-mm diameter pinhole and the center of capillary tube, and leaves through a 2-mm diameter hole and finally reaches a silicon photodiode.

A segment regulator used is the same as in the previous work[11]. By using this, alternate regular segments can be formed.

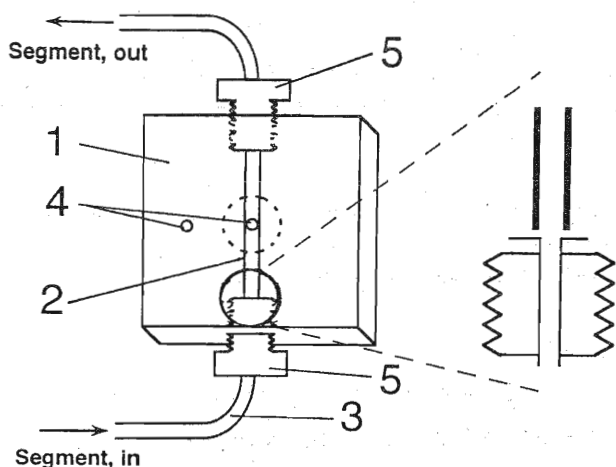


Fig.2 Capillary flow cell for absorbance measurement
1, Aluminium body;
2, capillary flow cell made of Pyrex glass (0.8mm i.d.x2mm o.d.);
3, PTFE tubing(1mm i.d.x1.5mm o.d.);
4, pinhole(0.3mm diameter);
5, screw fitting.

RESULTS AND DISCUSSION

Regular-segment flow and light scattering

A regular-segment flow is desirable to efficiently eliminate the background noises and stabilize the background. In on-tube absorbance measurements, irregular-segment flow causes irregular light scattering, which results in unstable background. By using a double plunger micro pump and the segment regulator, alternate regular segments flowed toward the flow cell; each length of the segment was about 2.5cm in a 0.5mm i.d. PTFE tubing and about 0.98cm in a 0.8mm i.d. capillary flow cell. The alternate segment flow produce periodic waves of light scattering when it passes through the capillary flow cell. Figure 3 shows the periodic waves. It can be seen that the larger the index of refraction, the larger the light scattering and its waves are. Furthermore, light absorption of dyes made the waves larger, as is shown in Fig.4. Therefore, the smaller absorbance of a reagent blank is desirable.

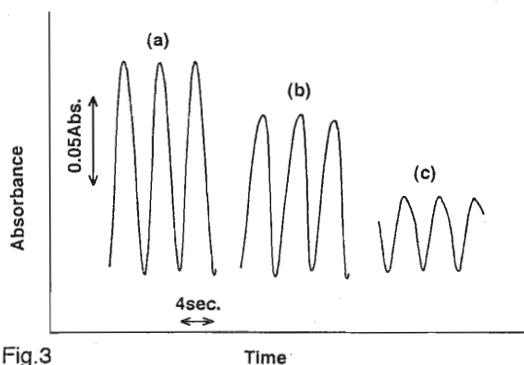


Fig.3

Time

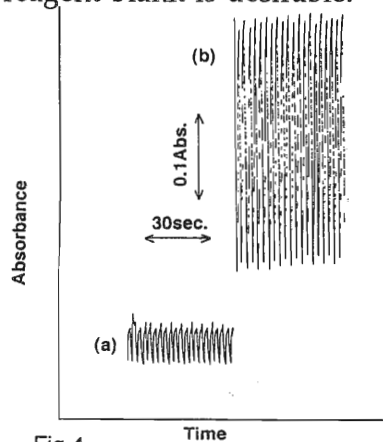


Fig.4

Time

Fig.3 Background noise caused by the difference in index of refraction (I.R.) [flow system, Fig.1(a)] Segment: (a), H₂O-chlorobenzene(I.R.=0.52); (b), H₂O-toluene(I.R.=0.49); (c), H₂O-1,2-dichloroethane (I.R.=0.44). These were recorded with a SIC Labchart TM180.

Fig.4 Effect of refraction at the interface between water and 1,2-dichloroethane(DCE) and absorbance of Methylene Blue (MB⁺) on background noise (a), water and DCE; (b), 1x10⁻⁴M MB⁺ and DCE. Flow system, Fig.1(a).

Elimination of noise with a digital filter

Usefulness of a digital filter (signal cleaner) for the elimination of sharp waves, which are the cause of background noise, was examined. Yanagi[12] developed a distortion-free digital filter for chromatography and capillary electrophoresis, and succeeded in the elimination of random and cyclic noises and spikes caused by tiny bubbles passing through the flow through cell.

By using this digital filter, the sharp waves caused by segmented flow were preferably eliminated, and the noisiness of the background was much

improved. Figure 5 shows the result of the elimination of noises. We can see that the large noise can be efficiently eliminated. In the previous work, MB^+ could not be used for a solvent extraction/FIA because of the large blank absorbance of MB^+ existing in an aqueous phase. However, by using the present flow system, anionic surfactants could be determined with MB^+ (Fig.6).

Figures 7 and 8 show examples of flow signals obtained by the RhodB and the 4-MQ methods, respectively. In these cases, background noises were much lowered, and the signal to noise ratios were much improved.

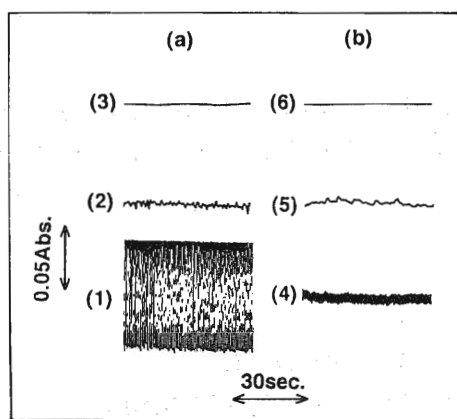


Fig.5

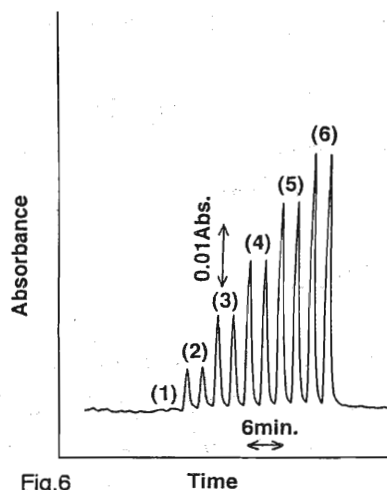


Fig.6

Fig.5 Elimination of noise due to segmented flow using digital filter

Absorbance response of detector : (a), 0.05; (b), 1.5.

Pass peak(second): (1), 0.1; (2), 6.3; (3), 102; (4), 0.1; (5), 6.3; (6), 102.

Fig.6 Flow signals for lauryl sulfate by a Methylene Blue method

Sample (lauryl sulfate, $10^{-5}M$): (1), 0; (2), 2; (3), 4; (4), 6; (5), 8; (6), 10. Flow system, Fig.1(b).

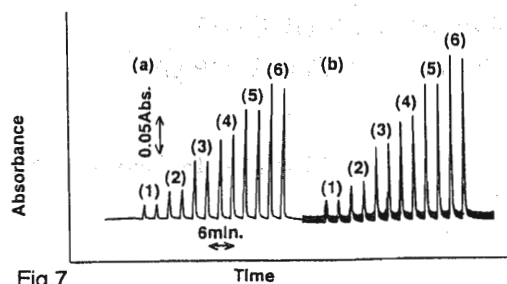


Fig.7

Fig.7 Flow signals for lauryl sulfate (LS^-) by a Rhodamine B method

(a), with signal cleaner (pass peak 102 second); (b), without signal cleaner.

Sample (LS^- , $10^{-5}M$): (1), 0; (2), 2; (3), 4; (4), 6; (5), 8; (6), 10. Flow system, Fig.1(a).

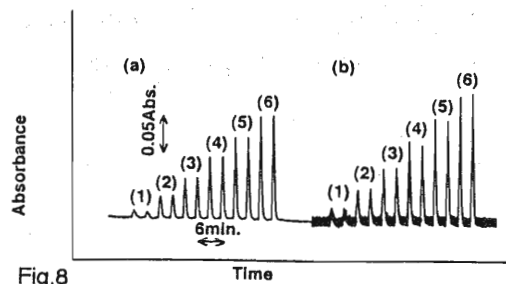


Fig.8

Fig.8 Flow signals for lauryl sulfate (LS^-) by a 4-MQ method

The conditions are the same as in Fig.6.

CONCLUSION

Solvent extraction/on-tube determination methods were examined in order to develop spectrophotometric methods by flow-injection analysis without any phase separator. The noises due to segmented flow are found to be preferably eliminated by using a digital filter, and a signal to noise ratio were much improved. On-tube detection methods recommended here will be widely applicable to a number of flow-injection methods which need solvent extraction separation techniques.

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