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Spectrophotometric Determination of Anionic Surfactant Based on Ion-pair Formation with Methylene Blue in Reversed Flow Injection Mode

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Abstract

A simple reversed flow injection system with minimal consumption of organic solvent has been developed for the spectrophotometric determination of anionic surfactant (AS) in water samples. The method is based on the ion-pair formation between anionic surfactant and Methylene Blue (MB) and its extraction to chloroform. Sodium dodecyl sulfate (SDS) is used as a model anionic surfactant. The sample and MB solutions are each delivered by two peristaltic pumps and merged to form the ion-pair of AS and MB. Small amounts of chloroform (50 mm^3) are injected every 15 s to the merged solution. The ion-pair is extracted to the chloroform phase while the solution is passing through an extraction coil. The absorbance of both phases (aqueous and organic phases) is measured sequentially at 652 nm without phase separation. Analytical parameters such as extraction coil length and MB concentration have been optimized. The dynamic ranges of calibration curves (0.1 ~ 1 and 2 ~ 8 μmol dm^{-3}) are selected depending on the analyte concentration by changing MB concentration. Calibration curves are linear ($r^2 > 0.997$) over the ranges; LOD (3.3 σ) is 0.054 μmol dm^{-3}. Relative standard deviations of repeated measurements are 2.44% (n = 8, C_{SDS} = 1 μmol dm^{-3}) and 1.46% (n = 7, C_{SDS} = 8 μmol dm^{-3}). The throughput rate of the measurement is 4 samples per minutes. The proposed method can be applied to the determination of anionic surfactant in river, pond and house sewage water samples.

Keywords: Reversed flow injection analysis, online extraction, anionic surfactant, Methylene Blue, ion-pair

1. Introduction

Anionic surfactants (AS) are the most common surfactant widely used as household cleaners, industrial detergents and so on. AS are, therefore, released to aquatic environment through both domestic and industrial waste waters. Although the biodegradability of which is relatively high [1] and the efficiency of modern sewage treatment plants to remove them is generally high, too, AS still remain in various aquatic ecosystems. Once the content of AS exceeds the self-purification capability of the systems, AS may cause harmful effect on aquatic organisms. The determination of AS in environmental water samples is, therefore, of great importance.

A lot of methods including titrimetry, spectrophotometry, nepherometry, and so forth have been developed for the determination of AS, as comprehensively described by Hummel [2]. Relatively new approaches, such as optode sensing [3], surface-plasmon resonance [4] and attenuated total reflection spectrometry [5], have also been applied to AS determination. Among them, spectrophotometry based on the ion-pair formation between AS and cationic dye is the most frequently employed method; the absorbance of the ion-pair is measured after its extraction to organic solvent. Extensive studies have been carried out in batch and flow modes. Conventional batch methods are, however, tedious and time-consuming, although some improved methods [6-8] have been proposed. On the contrary, flow methods have a lot of advantages such as simplicity, high precision and high throughput. The design of phase separator has been critical for reliability of flow methods. Motomizu *et al*. [9-11] developed a PTFE membrane separator and successfully applied to the determination of AS by FIA. Moskvin *et al*. [12] reported a chromatomembrane cell for the on-line preconcentration and extraction of the ion-pair. The phase separation devices make, however, the system complicated and accidental contamination of the other phase may cause sever interference with the determination. On-line detection with no phase separation process is a solution to prevent such potential problems. Motomizu *et al*. [13, 14] reported a capillary flow cell for the spectorphotometric determination of AS without phase separation. Liu and Dasgupta proposed dual-wavelength spectrophotometry [15] and sophisticated multiple (*i.e.*, spectrophotometry and conductometry) detection technique to identify respective phases [16].

It is preferable to reduce the consumption of harmful organic solvent. March *et al*. [17] reported a simple FIA/SIA - nephelometry system that requires no organic solvent. Ródenas-Torraba *et al*. [18] developed a multicommutated system with less organic solvent (0.7 cm^3 per AS determination). A sequential injection – Lab-at-Valve micro extraction system reported by Burakham *et al*. [19] requires only 300 mm^3 of dichloromethane per determination. It is clear that reversed FIA system, where an organic solvent is injected to the flow system, can save the solvent if a large amount of samples are available (*e.g.*, monitoring of environmental water samples).

In the present study, a simple reversed flow injection system with minimal consumption of organic solvent was investigated for the determination of AS. The method is based on the ion-pair formation between AS and Methylene Blue and its extraction to chloroform. The absorbance of chloroform phase is measured on-line without phase separation using a flow cell described before [20]. Good analytical performance was obtained; chloroform consumption: 50 mm^3 per determination; LOD (3.3 σ): 0.054 μmol dm^{-3}; throughput rate: 4 samples per minute. The proposed method was successfully applied to the determination of AS in real water samples.

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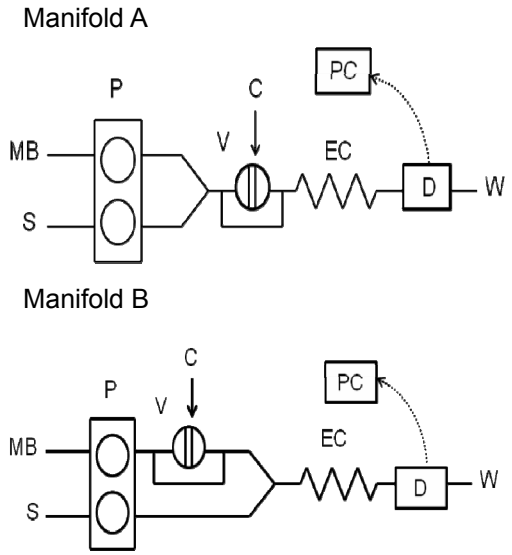

Fig. 1 Flow systems for the determination of anionic surfactant. MB, Aqueous solution of Methylene Blue; S, sample solution; P, peristaltic pump; V, six-port injection valve; C, chloroform; EC, extraction coil; D, detector; PC, personal computer; W, waste.

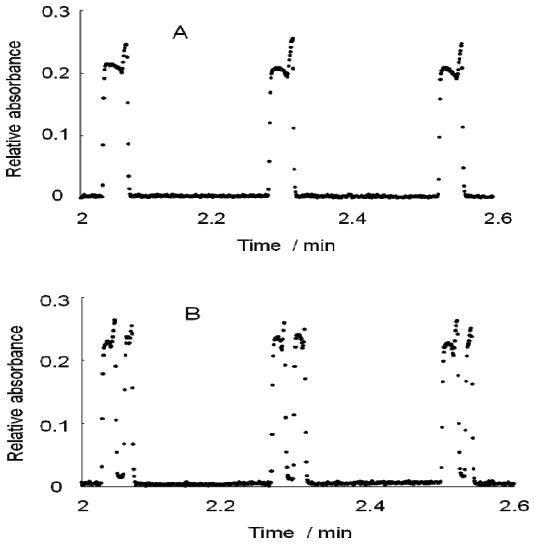

Fig. 2 Typical analytical signals obtained through Manifolds A and B. The concentrations of SDS and MB are 8 and 12 μmol dm^{-3}, respectively. Chloroform volume injected 50 mm^3; total flow rate, 0.82 cm^3 min^{-1}; extraction coil, 3 m long and 0.5 mm i.d. PTFE tubing.

2. Experimental

2.1 Materials

Sodium dodecyl sulfate (SDS), sodium sulfate and chloroform were purchashed from Kanto Chemical (Tokyo, Japan); Methylene Blue (MB) was purchased from Wako Pure Chemical Industries (Osaka, Japan); sulfuric acid was purchased from Katayama Chemical Industries (Osaka, Japan). They all were of analytical reagent grade and used without further purification. Sartorius Arium 611DI deionised water was used throughout.

Sample solutions of SDS were prepared by dissolving it with the deionised water. The stock solution of MB (0.08 mmol dm^{-3}) was prepared by dissolving 0.003 g of MB and 5 g of Na_2SO_4 in 50 cm^3 deionised water acidified with 0.686 cm^3 concentrated sulfuric acid and diluted to 100 cm^3 with deionised water [21]. The solution was kept in brown bottle at 4°C and diluted to required concentrations just before use.

2.2 Flow system

Figures 1 A and B show the schematic diagrams of flow systems examined in this study. A reagent (MB) and a sample (S) solution were each delivered with two peristaltic pumps (Rainin Dynamax RP-1, USA) at the constant flow rate of 0.39 and 0.43 cm^3 min^{-1}, respectively. Chloroform (50 mm^3) was injected manually to the mixed solution of MB and S (Manifold A) or to the MB solution before the mixing (Manifold B). Both phases (aqueous and organic phases) passed through an extraction coil (knotted PTFE tubing; 3 m long, 0.5 mm i.d.), where the ion-pair of dodecyl sulfate ion (DS) and MB formed was extracted to the chloroform phase. The liquids were then introduced to a handmade flow cell (optical path length 1 mm) [20] set in a spectrophotometer (Shimadzu SPD-6AV, Japan) without phase separation. The absorbance of both phases was each measured sequentially at 652 nm with the detector. The output signal from the detector was acquired in a computer (Toshiba Dynabook Satellite 1800 SA 70C/5, Japan) as Microsoft Excel format at the frequency of 20 Hz through an A/D-D/A converter (Measurement Computing PC-CARD-DAS16/12-AO, USA).

3. Results and Discussion

3.1 Optimization of system

Two manifolds (Figs. 1A and B), where the injection valve positions are different from each other, were examined so as to get more reliable signals. Figures 2 A and B show typical analytical signals obtained through Manifolds A and B, respectively. The absorbances of the bottom and peak plateaus correspond to those of aqueous and chloroform phases, respectively. Transit signals correspond to the absorbance of interfacial region. It is apparent that Manifold A can give more stable peak signals for chloroform phase than Manifold B. The segmentation of chloroform plug by sample solution at the confluence point is considered to be responsible for the unstable peak signals obtained from Manifold B. Manifold A was, therefore, employed for further experiments.

It was reported that the insertion of wide-bore tubing between extraction coil and detector was effective to form larger segments through the coalescence of each neighboring phases, which are more easily observable at the optical window [22]. In the present study, however, wide-bore PTFE tubings (2 mm i.d; 6.5, 10 15 and 20 cm long) did not give favorable effect but lowered the precision of the measurement. Therefore, such tubing was not employed in the present system.

The effect of total (SDS + MB) flow rate was investigated in the range from 0.58 to 1.39 cm^3 min^{-1} under holding the flow rate ratio of SDS and MB solutions at 1.1. Contrary to our expectation that the lower flow rate (*i.e.*, longer residence time

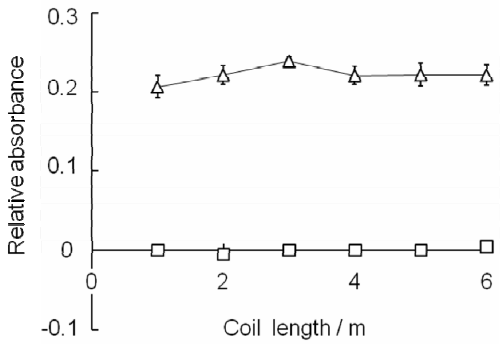

Fig. 3 Effect of extraction coil length on the absorbance of aqueous and chloroform phases. The concentration of SDS and MB are 8 and 12 μmol dm^{-3}, respectively. Injected volume of chloroform, 50 mm^3; total flow rate, 0.82 cm^3 min^{-1}; extraction coil, 0.5 mm i.d. PTFE tubing. Open squares (□), absorbance of aqueous phase; open triangles (△), absorbance of chloroform phase.

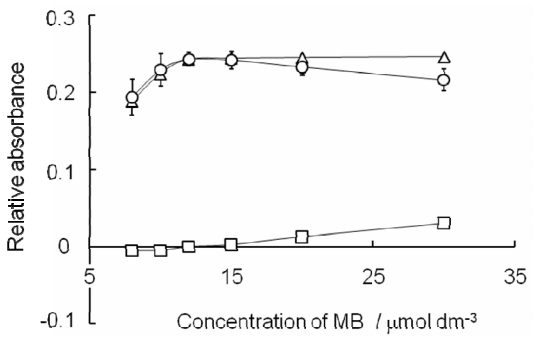

Fig. 4 Effect of MB concentration on the absorbance of aqueous and chloroform phases. The concentration of SDS, 8 μmol dm^{-3}; injected volume of chloroform, 50 mm^3; total flow rate, 0.82 cm^3 min^{-1}; extraction coil, 3 m long and 0.5 mm i.d. PTFE tubing. Open squares (□), absorbance of aqueous phase; open triangles (△), absorbance of chloroform phase; open circles (○), the difference between them.

between the injection and detection) is more preferable for the extraction, the peak height for chloroform phase increased with the flow rate. This increase can be attributed to the increase in the volume ratio of the aqueous phase (SDS + MB solutions) to the injected chloroform phase with the increase of the total flow rate. That is, the extraction equilibrium is attainable at higher analyte (*i.e.*, ion-pair of DS and MB) concentration in organic phase when aqueous/organic volume ratio becomes higher, assuming that the initial concentration of the analyte in the aqueous phase and its distribution ratio between two phases are constant. The stability of signals, however, became worse when the flow rate became higher than 0.82 cm^3 min^{-1} (data are not shown here). Therefore, 0.82 cm^3 min^{-1} was selected as the optimum total flow rate.

The effect of extraction coil length (1 ~ 6 m) was examined. The results are shown in Fig. 3, where the absorbance (arbitrary unit) of chloroform and aqueous phases is each plotted against the coil length. The effect of coil length on the absorbance seemed marginal as far as we examined. This result suggests that the extraction equilibrium is virtually attained rapidly in the extraction coil. Similar findings were obtained in the previous study on the determination of distribution coefficients by a flow analysis [23]; 50 cm long single-bead string reactor (1 mm i.d., containing 0.6 mm ϕ glass beads) or 1 m long knotted tubing (0.5 mm i.d.) were sufficient for attaining the equilibration at the total (aqueous + chloroform, in this case) flow rate of 2 cm^3 min^{-1}. In addition to the axial intra-segmental transfer, the transfer of the ion-pair from the aqueous phase to the chloroform film formed on the inner surface of hydrophobic PTFE tubing [24] is thought to be responsible for the fast attainment of the extraction equilibrium. However, too short extraction coil length (*i.e.*, <1 m) was considered to be insufficient for enough extraction. Too long coils seem not appropriate, too, because of the increase of internal pressure, which sometimes causes troubles such as leakage. The 3 m coil was selected because it gave the highest precision.

The effect of chloroform volume to be injected (50, 100 and 200 mm^3) was investigated. Even as low as 50 mm^3 of chloroform could give distinct peaks, and thus this volume was selected for minimizing organic solvent consumption.

3.2 Effect of MB concentration

The effect of MB concentration was investigated in the range from 8 to 30 μmol dm^{-3}. The concentration of SDS was kept constant at 8 μmol dm^{-3}. The results are shown in Fig. 4. Although higher concentration of MB seemed more preferable for complete ion-pair formation between DS and MB, excess MB remained in the aqueous phase. This MB rose the absorption of aqueous phase, resulting in the decrease of net increment of chloroform phase absorbance against that of aqueous phase (open circles in Fig. 4). The increment became maximum at the MB concentration of 12 μmol dm^{-3}. The precision, indicated by standard deviation (error bars), became highest at this condition. Similarly, the effect of MB concentration (1 ~ 3 μmol dm^{-3}) was investigated for lower SDS concentration (1 μmol dm^{-3}). The 1.2 μmol dm^{-3} MB was found to give the best results in this case. Consequently, 1.2 and 12 μmol dm^{-3} were selected for lower (0.1 ~ 1 μmol dm^{-3}) and higher (2 ~ 8 μmol dm^{-3}) SDS concentration ranges, respectively.

3.3 Effect of coexisting ions

The effect of diverse coexisting ions such as Na^+, Ca^{2+}, Fe^{3+}, NH_4^+, NO_3^-, HCO_3^-, Cl^-, SO_4^{2-}, $H_2PO_4^-$ and SCN^- was examined at the optimized conditions mentioned above. It is difficult to

Table 1. Tolerable limits of foreign ions

Ion	Added as	Tolerable limit / μmol dm^{-3}
Na^+	NaCl	300
Ca^{2+}	$CaCl_2$	3000
Fe^{3+}	$FeCl_3$	10
NH_4^+	NH_4Cl	10000
NO_3^-	$NaNO_3$	100
HCO_3^-	$NaHCO_3$	>10000
Cl^-	NaCl	300
SO_4^{2-}	Na_2SO_4	10000
$H_2PO_4^-$	NaH_2PO_4	>10000
SCN^-	NaSCN	1000

The concentration of SDS was 1 μmol dm^{-3}.

Table 2. Analytical results for recovery test using real water samples

Sample[a]	Spiked concentration[b] / μmol dm^{-3}	Found concentration[c] / μmol dm^{-3}	Recovery[d], %
Sako river	0	0.75 ± 0.04	–
	3	3.62 ± 0.09	95.7
	4	4.95 ± 0.14	105.0
	5	5.78 ± 0.10	100.6
Tamiya river	0	0.71 ± 0.01	–
	3	3.60 ± 0.08	96.3
	4	4.81 ± 0.14	102.5
	5	5.64 ± 0.06	98.6
House sewage	0	0.49 ± 0.04	–
	3	3.36 ± 0.08	95.6
	4	4.48 ± 0.15	99.8
	5	5.28 ± 0.19	95.8
Pond water	0	0.107 ± 0.012	–
	0.2	0.312 ± 0.009	102.5
	0.4	0.509 ± 0.016	100.5
	0.6	0.705 ± 0.017	99.7

[a] Sampled in Tokushima City area and filtered with disposable disk filters with an average pore size of 0.2 μm; [b] SDS was added as anionic surfactant; [c] Average ± SD (n = 7); [d] Recovery, % = $\{(C_{found} - C_{original}) / C_{spiked}\} \times 100\%$, where C_{found} at $C_{spiked} = 0$ are regarded as $C_{original}$.

estimate the effect of sole ion because its counter ion has some effect as well. The anions and cations were, therefore, added as sodium salts and chlorides, respectively, for better comparison. The tolerable limit was defined as the concentration of the interferent that causes 5% error in absorbance. The results are listed in Table 1. Tolerable limits obtained were 10 (Fe^{3+}), 100 (NO_3^-), 300 (Na^+, Cl^-), 1000 (SCN^-), 3000 (Ca^{2+}), 10000 (NH_4^+, SO_4^{2-}) and >10000 (HCO_3^-, $H_2PO_4^-$) μmol dm^{-3}. The limits are in the same magnitudes as those for FIA based on the extraction of the ion-pair of AS and cationic dye [9,11]. Motomizu *et al*. [9] assumed the precipitate formation of colloidal iron (III) hydroxide gave some effect on the determination.

3.4 Analytical performance of the proposed method

Under the optimization conditions described above, two calibration curves were obtained for lower and higher concentration ranges of SDS. The obtained linear regression lines are as follows: $Abs = 0.566\ C_{SDS} + 0.271$, $r^2 = 0.9971$, LOD ($3.3\ \sigma$) = 0.054 μmol dm^{-3} for the SDS concentration range of 0 ~ 1 μmol dm^{-3}; $Abs = 0.569\ C_{SDS} - 0.038$, $r^2 = 0.9995$, LOD ($3.3\ \sigma$) = 0.34 μmol dm^{-3} for the SDS concentration range of 0 ~ 8 μmol dm^{-3}. Relative standard deviations of repeated measurements were 2.44% (n = 8, C_{SDS} = 1 μmol dm^{-3}) and 1.46% (n = 7, C_{SDS} = 8 μmol dm^{-3}), respectively. The throughput rate was 4 samples per minute. Fully separated peaks shown in Fig. 2 suggest that this rate could be further improved if automatically switching valve was employed.

3.5 Application to real water samples

Fairly contaminated semi-urban river waters (Sako and Tamiya Rivers, Tokushima), House sewage water (Sako, Tokushima) and less contaminated pond water (Tokushima University) were sampled. Firstly, the amount of anionic surfactants was determined for each water samples by using the calibration curve for lower dynamic range (0 ~ 1 μmol dm^{-3}). Anionic surfactants originally contained in the samples were regarded as SDS. Then, known amounts of SDS were added to the samples. The spiked samples were analyzed by the proposed method. The calibration curve for higher range (0 ~ 8 μmol dm^{-3}) was used for the spiked samples except the pond water. The results are listed in Table 2. Good recoveries (95.6 ~ 105.0%) were obtained for all the samples examined.

4. Conclusions

A simple reversed flow injection system for the determination of anionic surfactant in water samples with minimal consumption of organic solvent is proposed. Analytical parameters such as manifold configuration and MB concentration are optimized. The limit of detection is 0.054 μmol dm^{-3}. Relative standard deviation of repeated measurements is below 2.5%. The present method is applicable to the determination of anionic surfactants in environmental water samples. Canete *et al*. [25] and Agudo *et al*. [26] reported reversed FIA systems for AS determination. The respective throughput rates were 50 and 20 samples per hour, and consumptions of chloroform were 0.49 and 0.2 cm^3 per determination. The present method has advantages in the respects of both throughput rate (4 samples per minute) and organic solvent consumption (50 mm^3 per determination).

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