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Micro-Solvent Extraction with Sequential Injection Lab-at-Valve for Successive Determination of Cationic and Nonionic Surfactants

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Abstract

A successive determination of cationic and nonionic surfactants using sequential injection lab-at-valve (SI-LAV) micro solvent extraction has been developed. The method is based on ion association formation between cationic and/or K^+-nonionic surfactant with tetrabromophenolphthalein ethyl ester (TBPE•H). The blue associate is extracted quickly into 1,2-dichloroethane (DCE) in an extraction coil which is set in a SI-LAV manifold. The segments are dispensed to a pipette tip (like a miniature separation funnel) fitted onto a port of a multi-position valve. This leads to the separation of the aqueous and organic phases. Absorbance of the DCE phase (the bottom part in the pipette tip) can be measured at 610 nm *via* optic fibers. Without the addition of KCl, absorbance of cationic surfactant can be obtained, while with adding KCl, absorbance of nonionic surfactants can be obtained. The proposed method provides an automated, novel, simple and economical strategy for simultaneous determination of cationic and nonionic surfactants without a membrane separator.

Keywords Sequential injection, lab-at-valve, solvent extraction, ion association, surfactants

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1. Introduction

In 1978, flow injection analysis-solvent extraction with chloroform was proposed for the determination of caffeine [1]. In the system, a t-connector with PTFE fibers twisted was used for a phase separator. At the same year, an extraction system using a different separation device was reported [2]. However, complete separation for aqueous and organic phases was not performed because of incorporation of aqueous moisture. To obtain the complete phase separation between organic and aqueous phases, various phase separators with hydrophobic and porous PTFE membrane have been proposed for the determination of anionic surfactants [3–9]. Although various kinds of phase separators with PTFE membrane have been designed and their efficiencies were investigated and applied, there were some problems on long-term continuous runs and permeation of small amounts of water moisture. Sakai et al. have proposed a double-membrane phase separator to prevent leakage of the aqueous phase [10,11].

As the techniques with membrane separation require skill, FIA coupled with solvent extraction without membranes have been proposed. A single plug of organic phase was inserted into the carrier stream including analyte (anionic surfactant, AS). The flow was subjected to an interactive reversal and during the reversal, the ion associate (AS-Methylene blue) was transferred into the organic phase and the extracted associate was monitored at 652 nm spectrophotometrically [12]. And also, a FI-extraction system without a segmentor, an extraction coil and a phase separator was proposed for the Hg (II)-dithizone-CCl_4 [13] system.

FIA coupled with solvent extraction has some advantages of rapidity, selectivity, simplicity and repeatability, however, all reagents are consumed continuously even without measurements. The reagents (the ion association reagent and extracting solvent) were on-line regenerated and the cyclic FIA with regenerated ones was proposed for the determination of diquat and paraquat [14] and/or methamphetamine [15]. The on-line regeneration system was feasible for continuous runs without consumption of reagents.

On the other hand, solvent extraction-SIA with wetting film formed on a Teflon tube wall was applied to the determination of bromothymol blue [16]. The extractable species in the aqueous solution was extracted into the wetting organic film and the absorbance with eluting solution was measured. And also, the wetting film extraction was applied to the determination of vanadium with a chelating reagent [17] and molybdenum with thiocyanate [18]. In the system mentioned above, the analyte is eluted with microliter volume. The method gives a big advantage on reducing the reagents consumption.

In addition, sequential injection lab-at-valve (SI-LAV) with micro-extraction was demonstrated for spectrophotometric determination of diphenhydramine hydrochloride [19] and anionic surfactant [20] with methylene blue. The aqueous and organic phases were separated in a LAV unit attached to one port of the valve and the organic solvent of 300 μL was used for the extraction.

In the FIA-solvent extraction system, there are few reports for the simultaneous determination of two or more compounds. Motomizu et al. have reported an FIA-extraction system for separation of sodium and potassium ions using silica mini-column and benzo-18-crown-6 [21].

We have reported a batch-wise ion association titration method for stepwise determination of cationic and nonionic surfactants [22].

In this study, we introduce these chemistries mentioned above into a SI-LAV-micro solvent extraction system for the successive spectrophotometric determination of cationic and nonionic surfactants.

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2. Experimental

2.1. Chemicals and reagents

All chemicals used were of analytical reagent grade and distilled water was used throughout.

A benzalkonium chloride (5×10^{-3} M) solution was prepared by dissolving 0.2241 g of benzalkonium chloride (Nakalai Tesque, Japan, MW = 448.09) in 100 mL of distilled water.

Triton X-100 (5×10^{-3} M) solution was prepared by dissolving of 0.3125 g of Triton X-100 (Sigma Ultra, USA, MW = 625.0) in 100 mL of distilled water.

Tetrabromophenolpthalein ethyl ester (TBPE•H, Wako, Japan) (1×10^{-3} M) was prepared according to the reference [23].

A buffer solution was prepared by mixing equal volumes of 0.3 M sodium dihydrogen phosphate and 0.1 M sodium tetraborate. The pH was adjusted to pH 8.0 by 1 M sodium hydroxide and 0.5 M sulfuric acid.

Potassium, sodium and calcium solutions were prepared by dissolving proper amounts of the salts (Carlo Erba, Italy) in distilled water.

1,2-Dichloroethane (DCE) (Carlo Erba, Italy) was used without purification.

2.2. Apparatus

The schematic diagram of the SI-LAV system is depicted in Fig. 1. It is consisted of a 2.50 mL syringe pump (Cavro, USA), a 10-position selection valve VICI with a microelectric actuator (Valco Instruments, USA), a D1000 CE UV-Vis light source and USB2000 spectrophotometer. The syringe pump was connected to the center of the selection valve by means of an extraction coil. A 5 mL pipette tip was modified as a separation unit situated at a fiber-optic spectrophotometer; a LAV module was placed at port-1 of the selection valve. Both instrumental control and data acquisition were manipulated *via* the FIA lab for windows 5.0 software (FIA lab Instruments, USA).

SI-LAV operation was similar to the previous report [20].

2.3. Ion associate formation procedure with TBPE•H

Chemical reactions and color development are based on the ion-associate formation with cationic surfactant (CS^+) and TBPE•H as shown in the previous paper [22]. CS^+ reacts with TBPE•H to form a blue associate. On the other hand, nonionic surfactant reacts with KCl to form K^+-nonionic complex and the cationic complex is paired with TBPE•H and the formed blue ion associate is extracted into 1,2-dichloroethane (DCE).

The chemical reaction and color development by batch-wise method are shown as follows.

First stage for cationic surfactant:

$$\underset{\text{Yellow}}{CS^+ + TBPE{\bullet}H_o} \rightleftharpoons \underset{\text{Blue, }\lambda\text{ 610 nm}}{CS^+{\cdot}TBPE^-{}_o + H^+}$$

For nonionic surfactant:

First stage:

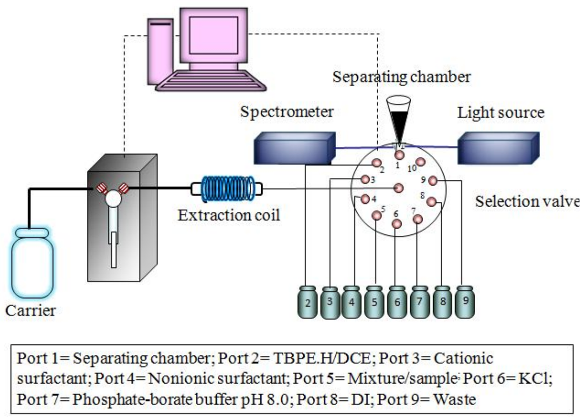
$$K^+ + \text{Nonion} \rightleftharpoons (K{\cdot}\text{Nonion})^+$$

Second stage:

$$\underset{\text{Yellow}}{(K{\cdot}\text{Nonion})^+ + TBPE{\bullet}H_o} \rightleftharpoons \underset{\text{Blue, }\lambda\text{ 610 nm}}{((K{\cdot}\text{Nonion})^+{\cdot}TBPE^-)_o + H^+}$$

Cationic surfactant can be determined at the first stage, and after addition of KCl, nonionic surfactant can be determined at the second stage.

In order to determine both surfactants simultaneously and automatically in microliter level without separation, the SI-LAV micro-solvent extraction system was assembled. As shown in Fig. 1, sample and TBPE•H/DCE are sequentially aspirated into a holding coil. Extraction in an extraction coil can be performed by using flow reversal. The aqueous phase and organic phase are separated in a conical extraction chamber modified from a pipette tip attached at one port of multi position selection valve. Absorbance is measured spectrophotometrically at 610 nm using fiber optic. Cationic and nonionic surfactants in the mixture were evaluated without and with KCl respectively.



Port 1= Separating chamber; Port 2= TBPE.H/DCE; Port 3= Cationic surfactant; Port 4= Nonionic surfactant; Port 5= Mixture/sample; Port 6= KCl; Port 7= Phosphate-borate buffer pH 8.0; Port 8= DI; Port 9= Waste

Fig. 1 Schematic diagram of SI-LAV for successive determination of cationic and non- ionic surfactants.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of the ion associate formed between benzalkonium and TBPE•H were recorded from 500 to 650 nm using the proposed SI-LAV system. The spectra with different concentrations of benzalkonium are shown in Fig. 2. The absorption maximum was observed at 610 nm.

3.2. Flow reversal and sequence order of reagent solvent

Aqueous and organic segments were formed in the holding

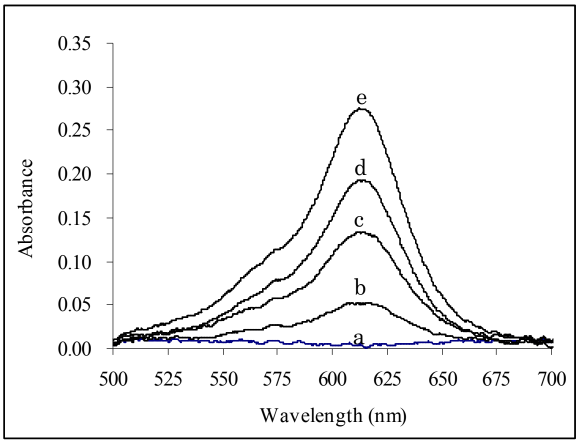


Fig. 2 Absorption spectra of benzalkonium chloride: (a) blank, (b) 1×10^{-5} M, (c) 2×10^{-5} M, (d) 3×10^{-5} M, (e) 4×10^{-5} M, 8×10^{-4} M TBPE·H/DCE, pH 8.

TBPE·H/DCE	BZ	DI	B	TBPE·H/DCE	BZ	DI	B	TBPE·H/DCE
100	100	25	75	200	100	25	75	100 µL

Fig. 3 Sequence for benzalkonium determination. BZ:benzalkonium, DI: deionized water, B: buffer solution.

TBPE·H/DCE	B	S	C	S	B	TBPE·H/DCE	B	S	C	S	B	TBPE·H/DCE
100	**	50	*	50	**	200	**	50	*	50	**	100 µL

Fig. 4 Sequence for Triton X-100 determination. *C = 50 µL of 4 M KCl, **B = 50 µL buffer solution, S = surfactant.

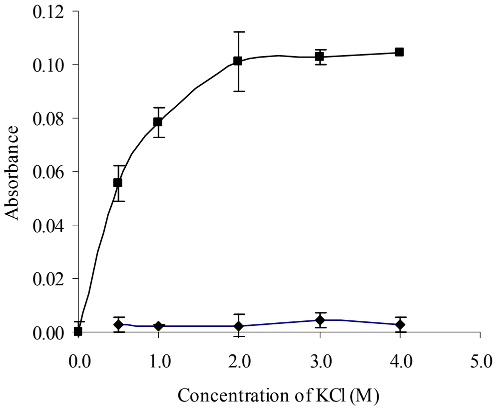


Fig. 5 Effect of concentration of KCl on formation of cationic complex; ♦Blk ■ 4×10^{-5} M Triton X-100.

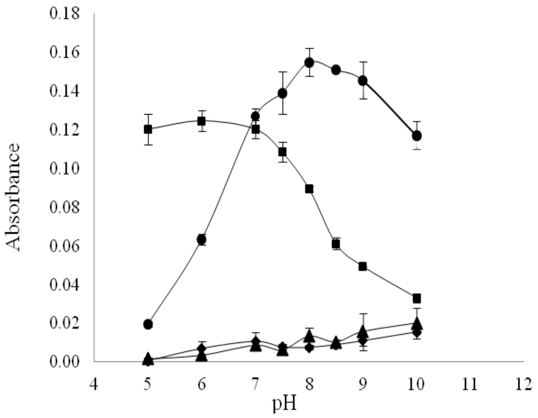


Fig. 6 Effects of pH on extraction of Triton X-100 and benzalkonium chloride; ♦blk of BZ, ▲blk of Triton X-100, ■ 2×10^{-5} M BZ, ● 4×10^{-5} M Triton X-100.

coil and extraction of the ion associate was performed with flow reversal. The number of flow reversals would affect extraction efficiency. The number of flow reversals was studied from 3 to 6 for the extraction using 4×10^{-6} M benzalkonium chloride, 5×10^{-5} M TBPE•H/DCE and phosphate-borate buffer (pH 8.0). It was found that an increase of number of flow reversal increased absorbance gradually. Four times of flow reversal resulted in higher absorbance when comparing with others. The sequence for benzalkonium chloride determination is shown in Fig.3. The aqueous zones were sandwiched by 100 µL TBPE•H/DCE.

3.3. Effect of KCl concentration

The sequence as shown in Fig.4 was used for determination of nonionic surfactant and the effect of KCl concentration was examined by varying the concentrations of KCl from 0.5 to 4 M for 4×10^{-5} M of Triton X-100. In this case, Triton X-100 (100 µL) and KCl (100 µL) were aspirated instead of BZ and DI in Fig. 3. A higher and constant absorbance was observed over 2 M KCl as shown in Fig. 5.

3.4. Effect of pH

Under the conditions established above, chemical parameters were then studied. The effect of pH on the formation of the ion associate was investigated in the range of pH 5–10. The result is shown in Fig 6. For benzalkonium chloride, the higher and constant absorbance was obtained from pH 5.0 to pH 7.0. At pH above 8.0, absorbance was slightly decreased. For Triton X-100, the greatest absorbance was obtained at pH 8.0. In order to obtain a good sensitivity, the buffer solution at pH 8.0 was selected.

3.5. Effect of TBPE·H concentration

The effect of concentration of TBPE·H (in the range of 2×10^{-4}–1×10^{-3} M) was investigated for 4×10^{-6} M benzalkonium chloride and 4×10^{-5} M Triton X-100. It was found that highest and constant absorbance was obtained above 2×10^{-4}M TBPE·H/DCE for benzalkonium chloride, while above 6×10^{-4} M TBPE·H/DCE for Triton X-100. It should be noted that absorbance of the reagent blank was also low.

3.6. Effect of Ca^{2+} and Na^+

The effects of Ca^{2+} and Na^+ ions on extraction of nonionic surfactant were studied by using 4 M of $CaCl_2$ and NaCl aspirated in the sequence instead of KCl to react with Triton X-100. It was found that no absorption at 610 nm was observed for either the extract of Triton X-100 and/or the blank. It can be concluded that Ca^{2+} and Na^+ do not behave like K^+ for the formation/extraction of Triton X-100.

Table 1 Recovery of synthetic mixtures of benzalkonium chloride and Triton X-100

Added / M		Found / M	Recovery, %
BZ	Triton X-100		
1.6×10^{-5}		1.66×10^{-5}	104
	0.8×10^{-5}	0.75×10^{-5}	94
1.6×10^{-5}		1.59×10^{-5}	99
	1.6×10^{-5}	1.74×10^{-5}	109
0.8×10^{-5}		0.79×10^{-5}	99
	0.8×10^{-5}	0.86×10^{-5}	108
2.4×10^{-5}		2.56×10^{-5}	107
	1.6×10^{-5}	1.70×10^{-5}	107

3.7. Calibration graphs

Under the proposed conditions for SI-LAV, the calibration graphs were established: $y = 5570x - 0.02$, $r^2 = 0.994$ for benzalkonium chloride (1×10^{-5}–5×10^{-5} M), while $y = 4432x + 0.006$, $r^2 = 0.988$ for Triton X-100 (1×10^{-5}–3×10^{-5} M); where x = concentration in M and y = absorbance. The sample throughput for analysis was 8 samples h^{-1}.

3.8. Determination of cationic and nonionic surfactants in synthetic mixtures

By adding known amounts of benzalkonium chloride and TritonX-100, the mixed solutions were prepared and each amount was determined using the proposed SI-LAV. The recoveries were 94–109 % as shown in Table 1.

4. Conclusion

A SI-LAV micro-solvent extraction system operated automatically was proposed for successive determination of cationic and nonionic surfactants at the microliter level. TBPE·H/DCE was employed as the extracting reagent for the determination of benzalkonium chloride and Triton X-100 as model compounds for cationic and nonionic surfactants, respectively. The proposed procedure provides an automated, novel, simple and economical strategy for determination of cationic and nonionic surfactants.

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