FLOW-INJECTION SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF ANIONIC SURFACTANTS WITH AN ANIONIC AZO DYE AND A QUATERNARY AMMONIUM ION

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Abstract - The behavior of color development of anionic azo dyes, Methyl Orange and its analogues, was examined in aqueous media by changing the micro-environment of the dyes. Organic onium ions brought about a decrease in the absorbance at wavelengths near 480 nm (pH 6.5) and 500nm (pH 2) and an increase in the absorbance at wavelengths near 400nm. On the basis of this color change phenomenon, the spectrophotometric method for the determination of anionic surfactants was developed. Anionic surfactants (AS^-) react with quaternary ammonium ion to form stable ion associates ($Q^+ \cdot AS^-$) and the residual amount of Q^+ was determined with an azo dye by measuring the absorbance at about 400nm or 500nm. This spectrophotometric method was applied to the flow injection technique.

Key words anionic surfactants, methyl orange analogues, flow injection method

Color intensity and maximum absorption wavelength of dyes are sometimes changed when the polarity of a medium is changed. Such a phenomenon is known as solvatochromism. This phenomenon has been used for analytical chemistry [1]. In the presence of micelles, sensitive spectrophotometric methods for the determination of metal ions have been developed. Another interesting analytical use of the solvatochromism is the spectrophotometric methods based on the formation of an ion association complex formed between a dye ion and its counter ion. Stelmo et al. [2] reported the spectrophotometric methods for the determination of quaternary ammonium ions with Orange G and Brij 35: the determinable concentrations were high and were $(0.1 \sim 2) \times 10^{-4}$ M.

Recently, Motomizu et al. [3] reported the principle of spectrophotometric methods for the determination of various kinds of surfactants with Methyl Orange (MO) and its analogues, and developed the batchwise and flow injection methods for the determination of quaternary ammonium ions and anionic surfactants.

In this work, the authors aim at developing a more sensitive reaction for the spectrophotometric determination of anionic surfactants.

EXPERIMENTAL

Reagents MO and its analogues were synthesized following Fieser [4]. The dyes are shown in Fig.1. They were dissolved in water with an equimolar sodium hydroxide. Alkyltrimethylammonium chloride, abbreviated as C_n TMA (Tokyo Kasei Kogyo Co.) were dissolved in water. Tri-dodecylmethylammonium chloride (TDMA, Aldrich Chem. Corp.) was dissolved in a small portion of ethanol, and the solution was diluted with water. Nonionic surfactants, Triton X-100 (TX-100, Wako Pure Chem. Ind.) was dissolved in water. Anionic surfactants were sodium dodecyl-

Fig.1 Azo dyes synthesized and examined in this work

sulfate (LS^- purity is more than 99.2%) sodium dodecylbenzenesulfonate (DBS^- , purity is more than 99.0%) sodium dodecylsulfonate (DS^- Tokyo Kasei Kogyo Co., GR) and sodium di-2-ethylhexyl-sulfosuccinate (SSS, purity is 96.3%)

Apparatus A laboratory-made flow injection system was used (Fig.2) This was assembled using a double plunger micropump (Sanuki Kogyo, DM2M-1016) a six-way sample injection valve with a loop, a visible detector with a 10-mm micro flow cell (18 μl) (Soma S-3250) and a recorder (Toa Electronics, FBR 251A) All flow lines were made of poly(tetrafluoroethylene) (PTFE) tubing (0.5mm i.d.)

Procedure for the flow injection method Use distilled water as a carrier stream and a solution containing $4.5 \times 10^{-5} \text{ M}$ MO, $4 \times 10^{-5} \text{ M}$ TDMA and 0.02% TX-100 (pH 2.2 with H_2SO_4) as a reagent stream. Inject a sample solution (100 μl) with a six-way injection valve, and measure the positive absorbance peaks at 510nm.

Fig.2 Flow injection system for the determination of anionic surfactants
Carrier: H_2O ; reagent solution: $4.5 \times 10^{-5} \text{ M}$ methyl orange + $4 \times 10^{-5} \text{ M}$ $(\text{C}_{12}\text{H}_{25})_3\text{N}(\text{CH}_3)^+$ + 0.02% Triton X-100 (pH 2.2).

Fig.3 Absorption spectra of butyl orange in the presence of octadecyltrimethylammonium ion (Q^+)
(a) pH 2.5; (b) pH 6.8, 0.002% Triton X-100; BO^- : $2.0 \times 10^{-5} \text{ M}$. Q^+ (10^{-5} M): 1, 0; 2, 1.0; 3, 1.4; 4, 2.0.

Reactivity of azo dyes (AD) with quaternary ammonium ions (Q^+) In the previous work, the reaction was carried out at pH 6.8, where AD exist in an monovalent anionic form (AD^-). However, the protonated form of azo dyes show larger molar absorptivities at the wavelengths near 500 nm. Figure 3 shows the change in the absorption spectra of BO^- by adding C_{18}TMA at pH 6.8 and 2.5. In an acidic medium, the absorbances at about 500 nm decreased and those at shorter wavelengths near 400 nm increased with increasing the amounts of Q^+ . In neutral pH regions, the decrease of absorbance at 480 nm and the increase of those at the shorter wavelengths were smaller than those obtained in an acidic medium. With respect to

high sensitivity, the reaction in an acidic medium is preferable to a neutral medium. However, the reactivity of AD with Q^+ was lowered in an acidic medium. Figure 4 shows the results of molar ratio methods for PO^- with Q^+ at pH 2.9, where 90% of PO^- are present in the protonated form (acid dissociation constant (pK_a) of PO^- : 3.85) and also shows the results obtained at pH 6.8. In both cases, the most hydrophobic cation, C_{18}TMA , reacts with PO^- to form (1:1) ion association complex, and less hydrophobic cations such as C_{10}TMA can scarcely react with PO^- at pH 2.9 and 6.8. Supposing that the molar absorptivities of ion

association complex with Q^+ are the same as that of the ion association complex formed between PO^- and C_{18}TMA , an apparent ion association constant K_{app} can be determined at each pH: K_{app} and K_{app}' are defined as the following Eqns.

$$K_{app} = \frac{[\text{Q}^+ \cdot \text{AD}^-]}{[\text{Q}^+][\text{AD}^-]} \quad (1)$$

$$K_{app}' = \frac{[\text{Q}^+ \cdot \text{AD}^-]}{(\text{C}_0 - \text{C}_{AD})} \quad (2)$$

where $[\text{Q}^+]$, $[\text{AD}^-]$ and $[\text{Q}^+ \cdot \text{AD}^-]$ are the concentration of Q^+ , AD^- and their ion association complex, and C_0 and C_{AD} are the total concentrations of Q^+ and

Fig.4 Effect of quaternary ammonium ions (Q^+) on the absorbance change of propyl orange (PO^-)
(a) pH 2.9; 510nm; 0.01% Triton X-100.
(b) pH 6.8; 490nm; 0.002% Triton X-100.
 Q^+ ($\text{C}_n\text{H}_{2n+1}\text{N}(\text{CH}_3)_3^+$): 1, n=18; 2, n=16; 3, n=14; 4, n=12; 5, n=10.

AD^- respectively. Table 1 shows K_{ass} obtained. As is expected from Fig.4, K_{ass} obtained at pH 6.8 are larger than those obtained in an acidic medium, and EO^- and MO^- did not react with Q^+ in an acidic medium. Table 1 shows that more hydrophobic ions can react strongly with more hydrophobic counter ions. As a result, BO^- is the best reagent for the determination of Q^+ in regard of the high reactivity

Table 1 Apparent ion association constants

	Log K_{ass}					
	BO^-		PO^-		EO^-	MO^-
	pH 2.5	pH 6.8	pH 2.9	pH 6.8	pH 6.8	pH 6.8
$C_{18}TMA$	6.21 ± 0.12	6.70 ± 0.21	6.23 ± 0.12	6.68 ± 0.10	6.22 ± 0.05	5.99 ± 0.05
$C_{16}TMA$	5.63 ± 0.12	6.10 ± 0.16	5.13 ± 0.10	5.89 ± 0.03	5.08 ± 0.07	4.95 ± 0.05
$C_{14}TMA$	4.22 ± 0.16	5.87 ± 0.03	3.44 ± 0.06	4.88 ± 0.04	3.75 ± 0.08	3.44 ± 0.08
$C_{12}TMA$	2.66 ± 0.03	4.79 ± 0.08	3.07 ± 0.04	3.46 ± 0.05	3.22 ± 0.04	2.5

The constants for EO^- and MO^- in an acidic medium could not be obtained because of low reactivity.

Coloration of anionic surfactants (AS^-) with an azo dye and a quaternary ammonium ion AS^- react in an aqueous medium with Q^+ to form ion association complexes: in common the reactivity becomes higher with increasing the hydrophobicity of a cation and its counter ion. Combining the reaction between AS^- and Q^+ with the reaction between Q^+ and AD^- we can design spectrophotometric methods for the determination of anionic surfactants in an aqueous medium. The reactions concerned are given in Eqns (2) and (3)

To enhance the reactivity of Q^+ with AS^- and AD^- more hydrophobic cation is preferable. In respect of the sensitive coloration of AS^- the reactivity of AD^- with Q^+ must be lower than that of AS^- with Q^+ . Therefore, MO^- seems to be the best of AD^- in Fig.1. However, as can be seen from Table 1, the reactivity of MO^- with Q^+ is very low. Therefore, other hydrophobic Q^+ were searched: they were tetradecyl- and hexadecyl-dimethylbenzylammonium ion, trioctylmethylammonium ion and tridodecylmethylammonium ion (TDMA). Of these, TDMA is found to react quantitatively with MO^- ; Fig.5 shows the change in absorption spectra of MO^- by adding TDMA. Figure 6 shows the absorbance change with increasing AS^- . It is found that the two reactions given in Eqns.(2) and (3) proceed to the completion, even in the weakest hydrophobic anionic surfactant, DS^- .

Flow injection method for the

determination of anionic surfactants Several experimental variables were examined. The most interesting result is that the order of the peak heights of AS^- did not agree with the order of the hydrophobicity of AS^- ($SSS^- > DBS^- > LS^- > DS^-$ [5])

Figure 7 shows the results obtained by varying the length of the reaction tubing. The peak height of LS^- agreed with that of DS^- using more than 230 cm

Fig.5 Absorption spectra of methyl orange (MO^-) in the presence of tridodecylmethylammonium ion (TDMA). MO^- : $2.2 \times 10^{-5} M$; 0.01% Triton X-100; pH 2.1. TDMA ($10^{-5} M$): 1, 0; 2, 0.5; 3, 1.5; 4, 2.0; 5, 2.4.

Fig.6 Effect of the amounts of anionic surfactants on the coloration. $(C_{12}H_{25})_3NCH_2^-$: $2 \times 10^{-5} M$; methyl orange: $2.2 \times 10^{-5} M$; 0.01% Triton X-100; pH 2.2; 505nm. 1, DS^- ; 2, LS^- , DBS^- and SSS^- .

Fig.7 Effect of the length of reaction tubing on the peak heights of anionic surfactants. Flow system is the same as in Fig.2, except for the reaction tubing. Anionic surfactants: $5 \times 10^{-6} M$. Sample: 1, H_2O ; 2, $5 \times 10^{-6} M$ LS^- ; 3, $5 \times 10^{-6} M$ DS^- .

reaction tubing, whereas the peak heights of SSS^- and DBS^- remained lower than those of DS^- and LS^- . This is because the exchange reaction (Eqn. (4)) is time-consuming in LS^- , DBS^- and SSS^- compared with DS^- .

Figure 8 shows the result of the effect of time on the exchange reaction obtained by a stopped flow method using each solution of AS^- and the reagent solution used in the flow injection method. It was found that the exchange reaction of LS^- was very slow, compared with DS^- . In the application of this flow injection method to the determination of AS^- in practical samples, which may contain various kinds of AS^- , there may deviate the analytical results obtained by this method from the real concentrations of given samples. Such deviations are probably less than 20%.

Calibration graph and sensitivity Figure 9 shows an example of flow signals for a calibration graph. The calibration graph was linear from 0 to 10^{-6}M of LS^- and the detection limit corresponding to the signal to noise ratio of 3 was about 10^{-7}M .

In conclusion, the proposed flow injection method is very useful in respect of the following advantages: (1) the method does not require any toxic organic solvent; (2) very simple and rapid method; (3) sensitivity is relatively high, and (4) the reagents required for this method are all available commercially.

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Fig.8 Effect of time on the exchange reaction ($\text{Q}^+\cdot\text{AD}^- + \text{AS}^- \rightleftharpoons \text{Q}^+\cdot\text{AS}^- + \text{AD}^-$) Sample solution was mixed with the reagent solution (see Fig.2) at the volume ratio of 1:1
Sample: 1, H_2O ; 2, $5 \times 10^{-6}\text{M LS}^-$; 3, $5 \times 10^{-6}\text{M DS}^-$.

Fig.9 Flow signals for the calibration graph for the determination of anionic surfactants (AS^-)
 AS^- : LS^- LS (10^{-6}M):
1, 0; 2, 2; 3, 4; 4, 6; 5, 8; 6, 10.