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## Concentration on Glass Separatory Funnel Wall of Anionic Surfactants by Ion Association with Methylene Blue

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Anionic surfactants (AS's) have been mostly determined by spectrophotometric methods based on solvent extraction of the colored ion associates of AS with a cationic dye.<sup>1-6</sup> Methylene Blue (MB) is one of the most frequently used cationic dyes. Chloroform is a common solvent for the extraction of the ion associate. The Japanese official text lists the MB-chloroform method for the determination of AS.<sup>7</sup> This method, however, is time-consuming and needs a large quantity of chloroform; moreover, the enrichment factor is two or three at most. Koga *et al.*<sup>5</sup> have recently simplified this official method and attained an enrichment factor of ten.

Although chloroform is a convenient solvent for extraction, its use is becoming regulated and restricted owing to its toxicity and its relatively large solubility in water (a 0.55 ml CHCl<sub>3</sub> dissolves in a 100 ml water). It is, therefore, desirable to analyze AS without solvent extraction. The only reports of such an analysis were made by Kamaya *et al.*<sup>8-10</sup> The ion associate formed between AS and Rhodamine 6G was adsorbed onto the wall of a PTFE vessel by vigorous shaking, followed by dissolving the ion associate with methyl cellosolve.<sup>8</sup> They have recently proposed a convenient method and applied it to determine DS in river water using MB as the counterion, a polypropylene container as a vessel, and ethanol as a dissolving solvent.<sup>10</sup>

It is interesting to study whether or not the MB-AS associate can be adsorbed onto a glass container surface. In this paper, we report that an addition of a small amount of heptane is effective to promote adsorption of the AS-MB associate onto the wall of a glass separatory funnel. It is also found that the adsorption of free MB onto the glass surface can be suppressed to a considerable extent by adding sulfuric acid. The present method can be used to determine AS (DBS or DS) of the 10- $\mu$ g/l level in tap and river water samples.

### Experimental

#### Materials and apparatus

All reagents used were of analytical grade commercially available from Wako Pure Chemical Co., and were used as received. Standard sodium salts of linear-dodecylbenzenesulfonate (DBS, F.W. 325.49) and dodecylsulfate (DS, F.W. 265.39) were used as AS's; in both

cases, the standard solution of 10<sup>-3</sup> M was diluted to prepare the working solution of 10<sup>-5</sup> M ( $f = 1.004$  for DBS and  $f = 0.983$  for DS). An MB solution was prepared by dissolving 0.25 g of MB in 1000 ml of pure water. Heptane was used to promote adsorption of the AS-MB associate onto the separatory funnel wall and ethanol was used to dissolve the associate which had adsorbed on the funnel wall.

Absorbance measurements were made on a Hitachi 100-50 spectrophotometer using glass cells of 10-mm path length.

#### Standard procedure

Transfer the sample solution of up to 300 ml containing AS of up to *ca.* 30  $\mu$ g into a 500-ml glass separatory funnel. Add 3 ml of a sulfuric acid (1 + 1) solution, 1 ml of heptane, and the MB solution (3 ml per 100 ml sample solution). Shake the funnel by hand vigorously for *ca.* 30 s to 1 min, allow the funnel to stand for a while. After the foam formed by shaking has completely disappeared (it takes a few minutes), transfer the content into a second 500-ml separatory funnel. Shake the second funnel for *ca.* 30 s to 1 min (a further addition of heptane is not necessary in this stage, since heptane added to the first funnel is mostly transferred to the second one), allow the funnel to stand for a while and discard the content. Remove a residual MB solution in the bottom of either funnel by pouring a small amount of water directly to the bottom. Rinse the wall of the first funnel with a 10-ml portion of ethanol, wipe off droplets within the stem under the stopcock with a piece of filter paper, transfer the rinsed ethanol to the second funnel, and rinse its wall. Withdraw the rinsed ethanol from the second funnel after wiping the stem, and measure the absorbance at 657 nm.

Waste solutions were stored in a large separatory funnel and the heptane phase was recovered.

### Results and Discussion

#### Adsorption characteristics

Case I: Varying aliquots of up to 10 ml of the DBS working solution we each added to a separatory funnel containing either 100 or 300 ml of water (the volume of water in this paper refers to that before additions of the AS working and any other solutions) and MB (3 ml per 100 ml water). The funnel was shaken for 30 s. After the content was withdrawn, the funnel was rinsed with a 10-ml portion of ethanol. The result is shown in Fig. 1A.

Case II: One milliliter of heptane was added to water. The

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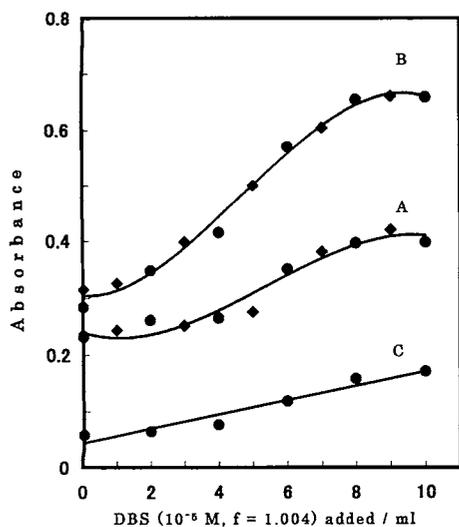


Fig. 1 Characteristics of DBS adsorption onto glass separatory funnel in the presence of MB. DBS was added to 100 ml (●) or 300 ml (◆) of water. A, Neither heptane nor sulfuric acid was added; B, heptane (1 ml) was added; C, sulfuric acid (3 ml) was added.

other conditions were the same as those of Case I. The result is shown in Fig. 1B.

Case III: Three milliliters of (1 + 1) sulfuric acid were added to 100 ml of water. The other conditions were the same as those of Case I. The result is shown in Fig. 1C.

We can see from Fig. 1 that (1) adsorption curves in the absence of sulfuric acid are sigmoid in shape and gradually approach to a plateau; (2) the slope of the sigmoid curve is steeper in the presence of heptane; and (3) adsorption is depressed in the presence of sulfuric acid and the plot is almost linear. The high adsorption activity of the glass surface toward free MB ions probably arises from negative charges due to ionization of the surface silanol groups. Protons from sulfuric acid counteract these negative charges, thus depressing adsorption of free MB.

Case IV: Both heptane (1 ml) and (1 + 1) sulfuric acid (3 ml) were added to water. The other conditions were the same as those of Case I. The results (100 and 300 ml of water) are shown by dotted lines in Fig. 2. Downward curves were obtained in this case and a difference was seen between the results of 100 ml water and 300 ml water.

Case V: Runs were made under the conditions of *Standard procedure* described in Experimental. That is, two separatory funnels were used in a series for a single run. The results are shown by solid lines in Fig. 2.

#### Calibration curves

Solid lines shown in Fig. 2 can be taken as calibration curves of DBS. The regression equations are

$$y = 0.145 + 0.0120x \quad (\gamma = 0.994)$$

for 100 ml of water and

$$y = 0.229 + 0.0160x \quad (\gamma = 0.992)$$

for 300 ml of water, where  $y$  and  $x$  refer to the absorbance and the amount of DBS in  $\mu\text{g}$ , respectively.

From calibration curves of DS, the regression equations are

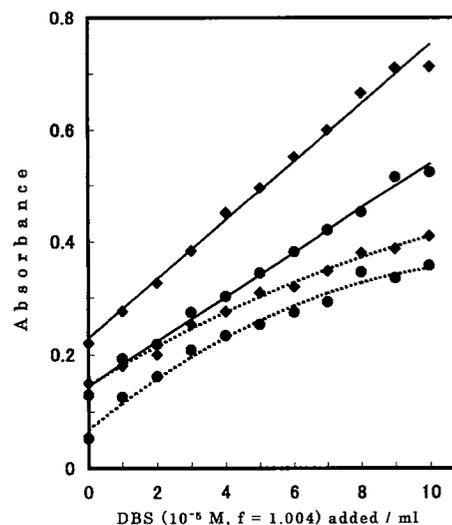


Fig. 2 Characteristics of DBS adsorption onto glass separatory funnel in the presence of MB. DBS was added to 100 ml (●) or 300 ml (◆) of water. Heptane (1 ml) and sulfuric acid (3 ml) were added together. Dotted line: one separatory funnel was used. Solid line (calibration curve): two separatory funnels were used in a series.

$$y = 0.1425 + 0.0153x \quad (\gamma = 0.996)$$

for 100 ml of water and

$$y = 0.233 + 0.0188x \quad (\gamma = 0.984)$$

for 300 ml of water.

The detection limit of the present method was *ca.* 1  $\mu\text{g}$  of AS for 300 ml sample water.

#### Recovery

Successive extraction with three 5 ml portions of  $\text{CHCl}_3$  was carried out using 4, 8, 12, and 16 ml aliquots of the working DBS and DS solutions in the presence of MB. Chloroform was expelled from the combined extracts using a rotary evaporator and the content was dissolved with ethanol. Molar absorption coefficients ( $\epsilon$ ) were estimated by absorption measurements of the ethanol solutions as follows:  $9.87 \times 10^4$  for DBS and  $9.25 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for DS. Based on these values, recoveries of AS by the present method were estimated to be 40% (100 ml) and 53% (300 ml) for DBS and 44% (100 ml) and 54% (300 ml) for DS (the volume of water is indicated in the parentheses).

Our calibration curve for DS (300 ml of water) is almost identical to that reported by Kamaya *et al.*<sup>10</sup> who have studied adsorption of the DS-MB associate onto a polypropylene container. We used two separatory funnels in a series for a single run, while they used only one container and dissolved the associate in a 5-ml portion of ethanol, just half our case. Their recovery of DS is, therefore, in almost the same level as ours.

#### Effect of experimental variables

The effect of shaking time was examined by varying the time from 15 s to 8 min under Case IV conditions. The absorbance remained almost constant after shaking for 30 s.

The effect of heptane was studied by varying its amount (0, 0.5, 1.0, and 2.0 ml) under Case V conditions using 5 ml aliquots of the DBS working solution. An addition of 1 ml of heptane to 300 ml of water was sufficient for promoting adsorption of the DBS-MB associate.

Table 1 Effect of organic solvents on promoting adsorption of DBS-MB associate onto glass separatory funnel<sup>a</sup>

Organic solvent used <sup>b</sup>	Absorbance
Hexane	0.475
Heptane	0.495
Octane	0.425
Cyclohexane	0.388
1-Octanol	0.134 (0.109)

a. A 5-ml aliquot of the DBS working solution was added to 300 ml of water.

b. A 1-ml portion of the solvent was added except for 1-octanol, where either 1 or 2 ml was used (the absorbance obtained using a 2-ml portion is given in the parentheses).

Instead of heptane, we have also tried to use hexane, octane, cyclohexane, and 1-octanol by adding 1 ml each to 300 ml of water containing a 5 ml aliquot of the DBS working solution (either 1 or 2 ml was added in the case of 1-octanol). The results are given in Table 1. As for 1-octanol, the absorbance observed is much lower than the blank value, and the absorbance obtained using 2 ml of this solvent is clearly lower than that obtained using 1 ml. The 1-octanol phase after shaking was observed to be slightly blue-colored; 1-octanol acted as a weak extractant. Among alkanes used, heptane was most effective to promote adsorption of the associate onto the funnel wall; hexane and octane were almost identical to heptane, while cyclohexane was clearly less effective.

The effect of sulfuric acid was studied under Case V conditions in the absence of AS. An addition of only 0.25 ml of (1 + 1) sulfuric acid to 100 ml of water caused a remarkable decrease in the blank absorbance. The blank absorbance decreased gradually with an increased addition of sulfuric acid. In this work we added 3 ml of the acid to 100 ml and 300 ml of water.

#### Interferences

The influence of 6 diverse ions was studied by *Standard procedure* using 100 ml of water and 3 ml aliquots of the DBS working solution, which corresponds to 9.8 µg DBS and to ca. 0.1 mg/l. Perchlorate, SCN<sup>-</sup>, I<sup>-</sup>, or NO<sub>3</sub><sup>-</sup> ion at each 10<sup>2</sup> mg/l gave 11, 14, 9.9, or 9.8 µg DBS, respectively. Nitrite at 10, 10<sup>2</sup>, and 10<sup>3</sup> mg/l gave 9.8, 2.1, and 0 µg DBS, respectively; when NO<sub>2</sub><sup>-</sup> ion was present at 10<sup>3</sup> mg/l, NO<sub>2</sub> gas was developed and the absorbance was reduced to the blank value. Chloride ions at 10<sup>3</sup> and 10<sup>4</sup> mg/l gave 9.8 and 12 µg DBS, respectively.

#### Application to tap and river water samples

Tap and river water samples of 300 ml volume were analyzed. The river water (Shirakawa River near the university) was filtered through an Advantec GF-75 glass fiber membrane (pore size 0.3 µm). The tap water supplied to our laboratory was used without filtration. The tap water were analyzed based on both the calibration curve and the standard addition methods. The results are as follows: 22 ± 1 as DBS and 17 ± 2 µg/l as DS for the tap water, 47 ± 3 as DBS and 40 ± 3 µg/l as DS for the river water. A considerable amount of AS was found in our tap water, but the amount seems to be rather lower than that reported in the results from Koga *et al.*<sup>5</sup>

#### Adsorption of AS-MB ion associate onto container wall

Kamaya *et al.*<sup>8</sup> found that, when cationic dyes were used as counter ions, the ion associates with AS were adsorbed onto the wall of vessel by shaking. They examined various vessels

including borosilicate glass, polypropylene, and PTFE, and reported that the last two gave lower blank values. In this work, we have tried using polypropylene separatory funnels of 500-ml capacity, and found that adsorption of free MB onto the funnel wall occurred to almost the same extent as in the case of glass funnels and could not be suppressed by sulfuric acid. Moreover, the addition of heptane was found not to promote adsorption of the ion associate onto the polypropylene separatory funnel wall.

It is interesting to inquire why nonpolar solvents used in this work promote adsorption of the AS-MB associate onto the glass surface. The solubility of these solvents in water is quite low (it ranges over two orders of magnitude): 6.9 × 10<sup>-4</sup> (cyclohexane), 1.3 × 10<sup>-4</sup> (hexane), 2.4 × 10<sup>-5</sup> (heptane), and 6.2 × 10<sup>-6</sup> M (octane) at 25°C.<sup>11</sup> The promoting effect of the least soluble octane is almost comparable to hexane and heptane. On the other hand, the most soluble cyclohexane is the least effective promoter. Thus, no direct relationship exists between the solubility in water and the promoting effect. It is, however, attractive to interpret the promoting effect as follows: the polarity of water surrounding the AS-MB associate, relatively polar by nature, is changed by nonpolar solvent molecules dissolved in water and the AS-MB associate is expelled out of the surrounding water-shell to the container wall surface.

On the other hand, formation of foams by shaking the funnel seems to play an important role in the promoting effect: a kind of flotation separation. Kamaya *et al.*<sup>8</sup> have observed that the AS associates with cationic dyes tend to adsorb onto the bubble surface after shaking. The reason that adsorption of the ion associate onto the polypropylene funnel wall is not promoted by heptane may be interpreted in terms of a relatively strong affinity of the solvent itself toward this polymer material.

The use of MIBK as a rinse solvent instead of ethanol gives us some information about adsorption of the AS-MB associate onto the glass surface, because free MB is insoluble in MIBK. Calibration curves were prepared according to *Standard procedure* where MIBK was used instead of ethanol and sulfuric acid was not added. Recoveries of DBS and DS increased to be 66 and 56%, respectively. This indicates that sulfuric acid suppresses, to some extent, adsorption of the AS-MB associate onto the funnel wall.

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