A Simple Determination of Polyethylene Oxide-type Non-ionic Surfactant by Adhesion Method

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Abstract: A simple and rapid method for the determination of polyethylene oxide-type non-ionic surfactants is reported herein. This method is based on the adhesion of calcium/non-ionic surfactant complexes with tetra phenyl porphine sulfonic acid (TPPS) to the wall of reaction vessel upon vigorous shaking. The ion-associate adhering to the inner wall of the vessel was dissolved with water after discarding the solution and spectrophotometrically assayed at 412 nm. From the standard curve for Triton X-100, the order of the sensitivity for different ions was as follows: $\text{Ca}^{2+} > \text{K}^{+} > \text{NH}_4^{+} > \text{Ba}^{2+}$. The proposed method does not involve extraction of the ion-associated with harmful solvents and can be simply performed by combining a procedure based on hand shaking and the use of a spectrophotometer.

Key words: Ion-associate adhesion, non-ionic surfactant detection, calcium/non-ionic surfactant complex, spectrophotometry, tetra phenyl porphine sulfonic acid.

1. Introduction

Non-ionic surfactants are widely used in industrial and domestic applications. Non-ionic surfactants account for about half of all the types of surfactants produced in Japan per year. Moreover, polyethylene oxide non-ionic surfactants occupy nearly 70% of the non-ionic surfactants used in Japan [1]. Polyethylene oxide-type non-ionic surfactants are normally determined by extraction-spectrometry [2-5]. However, these methods use a series of complicated steps and the solvents employed, such as 1, 1, 1-trichloroethane, chloroform, 1, 2-dichlorobenzene, and benzene are often potentially harmful. Therefore, simpler and more environmentally-friendly tests for the determination of non-ionic surfactants are necessary for academic and educational purposes.

In previous studies, it was found that assay of anionic surfactants can be easily performed without solvent extraction by exploiting the phenomenon of

ion association between anionic surfactants and cationic dyes. Adsorption of the ion-associate adsorption onto the copolymer of tetra fluoro ethylene and hexa fluoro phylene (FEP) test vessel was achieved by vigorous shaking. The ion-associate was then dissolved in ethanol, and the absorbance was measured [6]. In subsequent study, authors further explored the possibility of using the same principles for determination of a cationic surfactant with tetrabromophenolphthalein ethyl ester (TBPE) [7]. However, a time was required for adhesion of the ion associate. Because TBPE cannot be easily dissolved in water, ethanol was used as the solvent. However, ethanol decreased the adhesion of the ion associate on the wall of the rest vessel. Moreover, the blank value increased at the lower pH of 6. These issues were resolved by using tetra phenyl porphine sulfonic acid (TPPS) [8, 9]. In authors' latest studies, TPPS was found to be an effective counter-ion for the potassium/non-ionic surfactant complex [10, 11]. In this report, authors compare the performances of the complexes of the non-ionic surfactant Triton X-100

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with potassium, barium, calcium, ammonium, magnesium and strontium cations.

2. Materials and Methods

2.1 Reagents

All reagents were of analytical grade, and solutions were prepared with deionized water obtained from an Organo Puric-MX system. Non-ionic surfactant standard solutions were prepared by dissolving 0.100 g of polyethylene (10) octylphenyl ether (Triton X-100, Tokyo Chemical Industry Co. Ltd.), 0.100 g of polyoxyethylene sorbitan monolaurate (Tween 20, Tokyo Chemical Industry Co. Ltd.), 0.100 g of polyoxyethylene sorbitan monopalmitate (Tween 40, Tokyo Chemical Industry Co. Ltd.), 0.100 g of sorbitan monolaurate (Span 20, Tokyo Chemical Industry Co. Ltd.), and 0.100 g of sorbitan monostearate (Span 80, Tokyo Chemical Industry Co. Ltd.) in 1 L of water. The standard working solutions were prepared by accurate dilution of stock solutions with water. The complex-forming cations were dissolved by using analytical grade: potassium acetate, barium acetate, calcium chloride, magnesium nitrate, and strontium chloride. To prepare a standard $2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ solution containing the counter-ion, 0.024 g of TPPS ($> 98.0\%$, $\text{C}_{44}\text{H}_{30}\text{N}_4\text{O}_{12}\text{S}_4 \cdot 2\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; Wako Pure Chemical Industries Ltd.) was dissolved in 500 mL of water.

2.2 Apparatus

Spectrophotometric measurements were carried out with a Shimadzu UV-1800 spectrophotometer using 1 cm cells. Tetrafluoroethylene test vessels (30 mL) were obtained from Nalgene. The vessels were used for more than one experiment. A Taitec model SR-1 horizontal shaker was used to shake the 30 mL FEP test tubes.

2.3 Standard Procedure

A sample solution (5 mL) containing the non-ionic surfactant Triton X-100 was divided into six aliquots,

which were then transferred into the 30 mL FEP vessels. Subsequently, 10 mL of the required calcium chloride and 0.20 mL of TPPS solution were added into the sample. The tubes were shaken mechanically for 5 min (150 times per min). The solution was discarded, and the remaining solution was removed by tapping the vessel on a paper; the ion-associate adhering to the inner vessel wall was dissolved with 5 mL of water. The absorbance of the solution was measured at 412 nm using a 1 cm glass cell and a spectrophotometer. The sensitivity for Triton X-100 was expressed as the absorbance of a $1 \text{ mg} \cdot \text{L}^{-1}$ solution.

3. Results

3.1 Ions for Complex with Non-ionic Surfactant Triton X-100

In authors' previous study they investigated the experimental parameters influencing formation of the complex comprising non-ionic surfactants with potassium acetate and TPPS. The method could be employed to detect non-ionic surfactants containing more than seven polyethylene oxide units. In that study [10], the molar extinction coefficient for the non-ionic surfactant Triton X-100 was determined as $1.04 \times 10^5 \text{ mol}^{-1} \cdot \text{cm}^{-1}$ and the detection limit was $0.2 \text{ } \mu\text{g} \cdot \text{L}^{-1}$.

In this study, authors investigated the ability of potassium as well as other cations to complex with Triton X-100. The experiments were initiated by measuring the absorbance of the ion-associate complexes of the selected cations. The amount of Triton X-100 used was 10 μg , the concentrations of the cations varied in the range of $0.4\text{--}4 \text{ mol} \cdot \text{L}^{-1}$ (K^+ -0.4, NH_4^+ -4, and Ba^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} -2 $\text{mol} \cdot \text{L}^{-1}$; for Ba^{2+} , Sr^{2+} and Mg^{2+} ions dissolved limit was no higher than 2 $\text{mol} \cdot \text{L}^{-1}$; Fig. 1).

As shown in Fig. 1, Ba^{2+} produced the highest absorbance at 2 $\text{mol} \cdot \text{L}^{-1}$, whereas Ca^{2+} , K^+ and NH_4^+ showed high absorbance at more than 3 $\text{mol} \cdot \text{L}^{-1}$. Therefore, two concentration ranges were selected for

Fig. 1 Effect of concentration of cations (mol/L) on absorbance of ion-associate with Triton X-100 (10 µg) and TPPS.

Fig. 2 Calibration curves for Triton X-100 (mg·L⁻¹) at 2.0 mol·L⁻¹.

preparation of the calibration curves in following experiments.

In Fig. 2, authors used the results of comparing the sensitivities of 6 studied cations. Calibration curves were constructed for K⁺, Ba²⁺, Ca²⁺ and NH₄⁺ taken at concentration of 2 mol·L⁻¹, and the obtained sensitivities were approximately at the same scale. However, in the case of Sr²⁺ and Mg²⁺, there was no obvious increase in the absorbance with Triton X-100

concentration increasing. Based on the results of this experiment, it could be concluded that Sr²⁺ and Mg²⁺ did not form complexes with Triton X-100.

Then, the absorbance of Ca²⁺ (3.2 mol·L⁻¹) and NH₄⁺ (4 mol·L⁻¹) were compared (Fig. 3). The error bars in the calibration curve for Ca²⁺ showed less variation of the mean than the error bars in the calibration curve for NH₄⁺. Seen from these results, the trend in the sensitivities for Triton X-100 was as follows:

Fig. 3 Calibration curves with SD error bars for Triton X-100 (mg·L⁻¹) at NH₄⁺ (4.0 mol·L⁻¹) and Ca²⁺ (3.2 mol·L⁻¹).

Ca²⁺ > K⁺ > NH₄⁺ > Ba²⁺. Calcium ion formed a complex with Triton X-100 and showed a high sensitivity in the proposed approach. The sensitivity for Triton X-100 (expressed as absorbance of 1 mol·L⁻¹ solution) was found to be 0.146. The coefficient of variation obtained with 10 µg of Triton-X 100 was 2.7% (n = 10).

3.2 Comparative Study of Different Methods of Shaking

In the proposed method, the ability of the ion-associate of calcium-Triton X-100 with TPPS adhering to the wall of the vessel was found to be connected with the shaking parameters such as the time or speed, and method of shaking. Five minutes was established as the optimum shaking time for obtaining result when reciprocating shaker was used.

The optimum shaking speed was evaluated by the reciprocating shaker at speed of 100, 150 and 200 times per minute; it was found that 150 times per minute was the optimum speed. To evaluate the effects of different shaking, authors compared the calibration curves obtained using the reciprocating shaker,

hand-shaking, and a homogenizer. The hand-shaking method produced the most sensitive result (Fig. 4).

3.3 Comparative Study of Other Non-ionic Surfactants

Triton X-100 (polyethylene (10) octylphenyl ether) has 10 ethylene oxide units and forms complexes with alkaline and alkaline earth metal cations. The other non-ionic surfactants that were investigated are Tween 20 (polyoxyethylene sorbitan monolaurate), Tween 40 (polyoxyethylene sorbitan monopalmitate), Span 20 (sorbitan monolaurate), and Span 80 (sorbitan monostearate). Among the non-ionic surfactants evaluated, the non-ionic surfactants containing ethylene oxide units in their structure were easily determined via the proposed method (Fig. 5).

4. Discussion

In a previous approach, researchers attempted experimental designs to achieve adhesion of the ion-associate of anionic surfactants and crystal violet onto a polyvinyl chloride (PVC) film obtained by solution stirring [12]. As the next step after stirring, the film must be attached to the cell and measurement

Fig. 4 Effect of different shaking methods on absorbance with different concentration of Triton X-100, Error bar show SD : (a) hand shaking, (b) reciprocating shaking, (c) homogenizing for set-up time of 5 min.

Fig. 5 Calibration curves for Tween 40 (mg/L) and Tween 20 (mg/L): Ca^{2+} (3.2 mol/L).

carried out. Sanemura, et al. [13] use a type of separator funnel for adhesion of the ion-associates onto the inner wall of a container. However, this approach required a tedious and complicated experimental set-up and usage of small amounts of heptane.

In the present approach [14], anionic surfactant adhesion originated from a failed experimental design. An anionic surfactant was concentrated by the floatation method, which an air bubble was passed

through the sintered glass from the bottom point of the glass container (Fig. 6).

In this experiment, to obtain high anionic surfactant recovery, an ion-pair was added. Tetra-n-pentylammonium bromide gave rise to high recoveries of anionic surfactant recovery, whereas the use of Ethyl Violet in the ion-pair did not give rise to any anionic surfactant recovery because of adsorption of the ion-associate onto the glassware. Based on this failed experiment, the adhesion process was carried

Fig. 6 Schematic diagram of the system.

out by simply shaking the vessel containing the anionic surfactant and cationic dyes. The proposed method for non-ionic surfactant determination does not use utilize any organic solvent for dissolution of the ion associate. The ion associate of calcium and the non-ionic surfactant was dissolved with water because small amount water induces dissociation of the ion associate of calcium/Tween X-100 with TPPS. The trend of the sensitivity for Triton X-100 was follows: $\text{Ca}^{2+} > \text{K}^{+} > \text{NH}_4^{+} > \text{Ba}^{2+}$.

Overall, the method proposed in this work does not involve extraction of the ion-associate using harmful solvents and can be simply performed by combining a procedure based on hand shaking and the use of a spectrophotometer. In this way, this method is more rapid and simple to execute and can be packaged as a test kit. Amongst the studied non-ionic surfactants, only the polyoxyethylene-type non-ionic surfactant could be determined using the proposed method.

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References

- [1] Ministry of Economy, Trade and Industry, Japan. 2015. "Monthly Report of Current Production Statistics Survey." Minister's Secretariat of Research and Statistics Department. Accessed February 8, 2016. http://www.meti.go.jp/statistics/tyo/seidou/result/ichiran/resourceData/08_seidou/kakuho/201502/h2daa201502k.pdf.
- [2] Anderson, N., and Girling, J. 1982. "Determination of Polyoxyethylene Non-ionic Surfactants at Trace Levels." *Analyst* 107 (1276): 836-838.
- [3] Boyd-Boland, A., and Eckert, J. 1993. "Determination of Nonionic Surfactants by Spectrophotometry after Extraction with Potassium Triiodide." *Analitica Chimica Acta* 271 (2): 311-314.
- [4] Crisp, P., Eckert, J., Gibson, N., and Webster, I. 1981. "An Extraction-spectrophotometric Method for the Determination of Non-ionic Surfactants." *Analitica Chimica Acta* 123: 355-357.
- [5] Nozawa, A., and Ohnuma, T. 1976. "Re-examination of the Microanalysis of Non-ionic Surfactants that Contain Polyoxyethylene Chains by the Method Involving Solvent Extraction of the Thiocyanatecobaltate(II) Complex." *Analyst* 101 (24): 543-548.
- [6] Kamaya, M., Tomizawa, Y., and Nagashima, K. 1998. "Spectrophotometric Method for the Determination of An Anionic Surfactant without Liquid-liquid Extraction." *Analytica Chimica Acta* 362 (2-3): 157-161.
- [7] Kamaya, M., Kaneko, Y., and Nagashima, K. 1999. "Simple Method for Spectrophotometric Determination of Cationic Surfactant without Liquid-liquid Extraction." *Analitica Chimica Acta* 384 (2): 215-218.
- [8] Kamaya, M., Hashimoto, A. and Nagashima, K. 2004. "Development of A Simple Test for Ethoxylated Nonionic Surfactants." *Journal of Japanese Society of Water Environment* 27 (11): 735-740.
- [9] Kamaya, M., Takahashi J., and Nagashima, K. 2004. "Rapid and Simple Determination of A Cationic Surfactant by Adsorption induced by Vigorous Shaking." *Mikrochimica Acta* 144 (1-3): 35-39.
- [10] Kamaya, M. 2013. "Overview of Simple Test for Determination of Surfactants by Adhesion Method." *Journal of Environmental Science and Engineering* 2: 672-677.
- [11] Kamaya, M., Sugiyama, H., and Yamaguchi, Y. 2014. "A Simple and Rapid Method for the Detection of Non-ionic Surfactants." *American Journal of Analytical Chemistry* 5: 1121-1128.
- [12] Naganuma, K., Hanai, T., Li, H., Sugiyama, M., and

- Kajiyama, M. 1996. "A Simple Colorimetric Analysis for Anionic Surfactants by PVC-Film Adsorbent, the Investigation for Domestic Wastewater and Application to Environmental Education." *Kagaku to Kyoiku* 44 (5): 329-332.
- [13] Sanemura, I., Oota, A., Aoi, K., and Zheng, J. Z. 2002. "Concentration on Glass Separatory Funnel Wall of Anionic Surfactants by Ion Association with Methylene Blue." *Analytical Science* 18 (3): 347-350.
- [14] Kamaya, M., Nagashima, K., and Namiki, H. 1997. "Spectrophotometric Determination of Trace Amounts of Anionic Surfactants by Air Stripping-Ethyl Violet Method." *Journal of Environmental Chemistry* 7 (2): 291-295.