CHARACTERISTICS OF ULTRASONIC ATOMIZATION OF A SURFACTANT SOLUTION

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Abstract

Dilute aqueous solutions of dodecyl-benzenesulfonic acid sodium salt were ultrasonically atomized to examine the surfactant enrichment behavior in fine droplets. The solutions used were prepared with de-ionized water and aqueous solutions whose ion-strengths were adjusted with addition of KCl, NaCl and $CaCl_2 \cdot 2H_2O$, respectively. A high enrichment ratio was observed at low surfactant concentrations and the ratio rapidly decreased with increasing surfactant concentration. At a constant surfactant concentration, a salt addition enhanced the enrichment. A maximum enrichment was found in KCl system while the enrichment ratio reached a plateau in NaCl and $CaCl_2$ system. The behavior was discussed in view of interfacial properties such as interfacial tension and the amount of surfactant adsorbed at the interface. It was suggested that an interaction between cations and surfactant anions strongly affects the interfacial adsorption of the surfactant and also the rate of micelle breaking.

Introduction

Ultrasonic atomization has been applied for producing very fine liquid particles in such as fuel injectors, ink-jet printers, and humidifiers. A unique application of ultrasonic atomization was reported on ethanol separation of ethanol-water solutions [1]. Fine droplets of highly concentrated ethanol were produced from a solution cooled at 283 K. Some possible mechanisms were discussed, however a clear explanation was not presented. Kirpalani and Toll suggested that cavitations play an important role in ethanol concentration [2]. However, this is unlikely because of a high cavitation threshold under a frequency of 2.4 MHz [3].

Since liquid particles are formed at highly disturbed gas-liquid interface, interfacial properties like a surface adsorption should play an important role. Unlike alcohol-water system, aqueous solutions of surfactants of relatively large molecular weight are free from vaporization of the solute. Therefore, the condition is simpler than the ethanol-water system to discuss how interfacial properties are related with the separation characteristics.

For this purpose, an anionic surfactant solution was atomized ultrasonically and the enrichment ratio was examined under various conditions. A salt addition to the surfactant solution significantly changed a trend of the enrichment ratio. This fact is one of the evidence of the significance of interfacial adsorption for the separation based on ultrasonic atomization.

Experimental

The experimental apparatus is shown in Fig. 1. The atomization column is made of acrylic resin, whose diameter and height are 100 and 130 mm respectively. The ultrasonic oscillator (HM-2412, Honda electronics Co. Ltd.) mounted at the bottom of the column has a frequency of 2.4 MHz, and a diameter of 18 mm. The oscillator is driven by DC 12 W with a power supply. Pre-determined amount of dodecyl-benzenesulfonic acid sodium salt is dissolved into deionized water and used as a feed. To examine the effect of a salt addition on surfactant enrichment, prescribed amount of KCl, NaCl and $CaCl_2 \cdot 2H_2O$ was dissolved into the solution. Surface tension of the feed solution was measured with a Wilhelmy method by use of an analyzer (CBVP-A3,Kyowa Interface Sci.Co.Ltd.).

The feed is circulated between the column and a reservoir whose temperature is kept constant at 295 ± 1 K. Volume of the solution in the column is 200 cm^3, and the total amount of the solution is 600 cm^3. Droplets coming out from the tubing on the column is collected and about 2 cm^3 of the solution is taken for analysis. The surfactant concentration is determined from absorption at 261 nm by UV spectro photometer (UV-1600, Shimadzu Co. Ltd.).
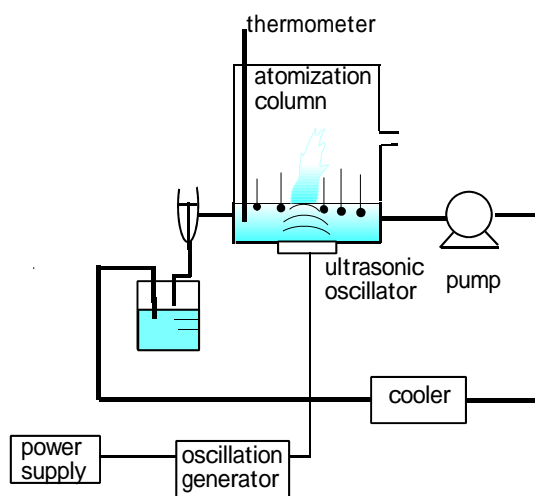

Fig.1 Schematic diagram of experimental setup

Results and discussion

Enrichment ratio of the surfactant is defined as the ratio of its concentration in collected mist droplets against that in initial solution, C_m/C_0. In Fig. 2, the ratio is plotted against a surfactant concentration in feed. A time required for collecting a sample solution for analysis was about 30 minutes. The highest enrichment was observed at very low concentrations and the ratio rapidly decreased with increasing the surfactant concentration. This fact indicates that a liquid in the vicinity of interface directly goes into droplets.
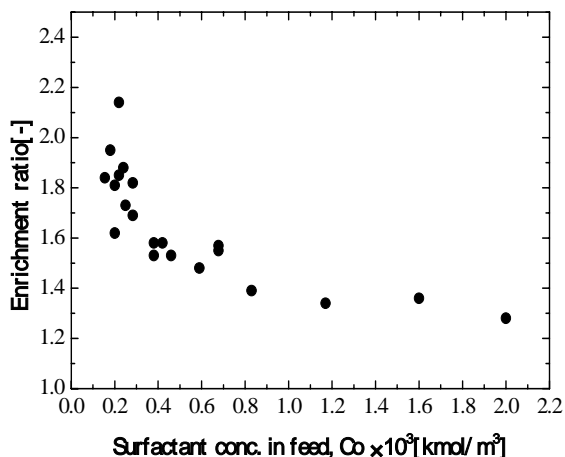

Fig.2 Enrichment ratio against surfactant concentration

Since surfactant molecules are distributed between the interface and the bulk of the solution, they are preferentially adsorbed at the interface for their concentrations lower than cmc. With increasing total surfactant concentration, the amount of surfactant in bulk solution becomes larger than the amount at the interface. Thus the increase of total surfactant concentration causes a decrease in enrichment ratio. Further increase of the surfactant leads to formation of micelles in the solution. The value of cmc for this surfactant is 3.0×10^{-3} kmol/m^3 and the range of surfactant concentration covered in Fig. 1 is lower than cmc. Although a sharp change of a trend in enhancement ratio was anticipated at cmc, the behavior unchanged at the concentration.

Addition of KCl

Effect of KCl addition to the surfactant solution on the enrichment ratio is shown in Fig. 3. The surfactant concentration was 0.46×10^{-3} kmol/m^3, which was much lower than the cmc. The enrichment ratio sharply increased with increasing KCl concentration and reached a maximum. A time for collecting a sample was about 60 minutes which was about twice as long as the time for the case without salt addition. This means finer droplets are formed in the present system. Surface tension of the solution

was also plotted in the figure. It rapidly decreases with increasing KCl concentration, which indicates that an increase of surface adsorption of the surfactant due to a charge screening effect. Since the addition of a salt to surfactant solutions also causes the lowering of cmc [4], some effects of micellar formation on the enrichment can be expected. We will discuss this point later.
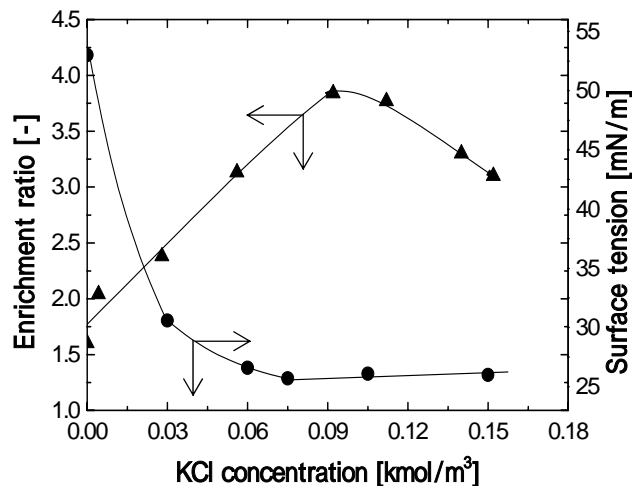

Fig.3 Effect of KCl concentration on enrichment ratio and surface tention

Addition of NaCl and CaCl$_2$

Unlike in KCl system, addition of NaCl and CaCl$_2$ to the surfactant solution gave a relatively small enhancement in the enrichment ratio. As shown in Figs. 4 and 5, the enrichment ratio reached a plateau with increasing the salt concentration. A decrease of surface tension suggests that an enhancement of surface adsorption of the surfactant by the salt addition. The reason for a constant enrichment ratio for larger salt concentrations will be discussed later.
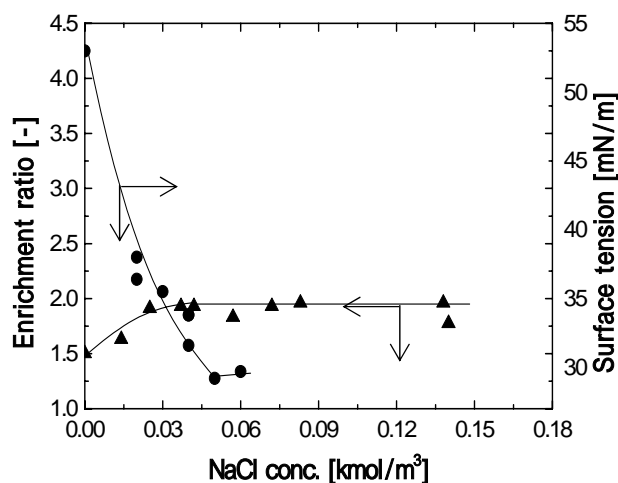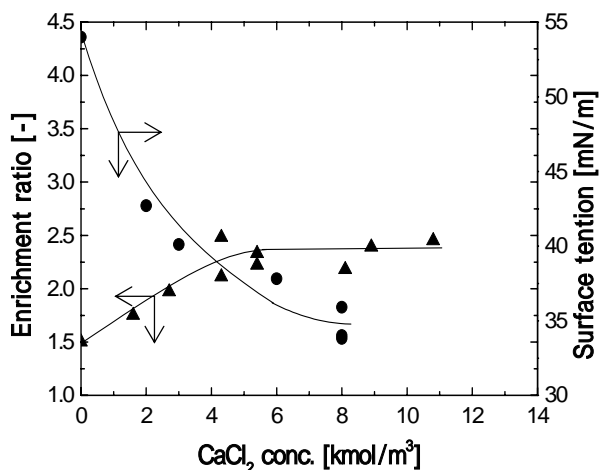

Fig.4 Effect of NaCl concentration on enrichment ratio

Fig.5 Effect of CaCl$_2$ addition on enrichment ratio

Fig.6 Change of cmc with salt addition

For NaCl system, a time for collecting droplets was about 30 minutes, which was close to that for without salt addition. The fact implies that a droplet size distribution is similar between both systems. It is noteworthy that the time for CaCl$_2$ was about 20 minutes, which suggests that formation of larger droplets.

Cmc change with salt addition

Since the addition of a salt caused an increase of the enrichment ratio, there must be some changes in interfacial properties. Figure 6 is a plot of surface tension against the surfactant concentration for various salt concentrations of KCl and NaCl. A dotted line represents the condition of the surfactant concentration for experiments in Figs. 3-5. On each curve, the cmc is designated by a large triangle. A salt addition caused a shift of cmc to lower surfactant concentration. Especially for KCl system, cmcs for both curves were lower than the dotted line. This fact suggests that micelles formation at higher than 0.05 kmol/m^3 of KCl.

Under the process of atomization, interfacial liquid is brought into droplets and a new surface is continually produced and surfactant monomers are transfered from liquid bulk to the interface. When micelles exist in liquid bulk, micelles will break into surfactant monomers to supply surfactant monomers into liquid bulk. The rate of micelles breaking can affect the supply of the surfactant to the interface. Since surfactant anions electrostatically interact with cations, it is probable that the rate depends on the cation type. When the breaking rate was low as in KCl system, amount of surfactant at the interface could decrease thus the enrichment ratio could also decrease. While in NaCl or CaCl$_2$ system, the supply of surfactant monomers can be fast enough to establish an interface saturated with surfactant monomers. This can be a reason for constant enrichment ratio at high salt concentrations.
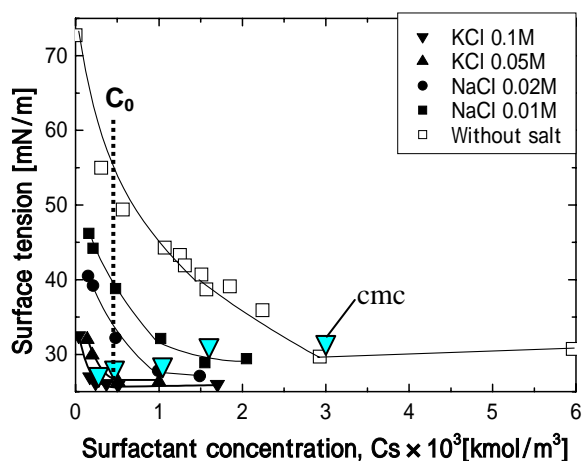
Conclusions

The surfactant was enriched in mist droplets by ultrasonic atomization. The enrichment ratio rapidly decreased with increasing surfactant concentration. A strong effect of a salt addition was observed on surfactant enrichment ratio. Addition of KCl to the surfactant solution leads to a significant increase in enrichment ratio and the ratio goes through a maximum. In NaCl and CaCl$_2$ systems, the enrichment ratio increased and reached a plateau at high salt concentrations. The increase was interpreted in terms of an enhanced adsorption of surfactant owing to a charge screening effect. At large salt concentrations, the trend of enrichment ratio was explained from a difference in breakdown rate of micelles to surfactant monomers depending on the salt type.

References

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