1704 *Bull. Chem. Soc. Jpn. Vol. 79, No. 11, 1704–1710 (2006)*

Adsorption-Equilibrium Surface Tension of Surfactant Solutions; Examination by the Drop Volume Method

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The surface tension of aqueous solutions of cationic, nonionic, and anionic surfactants was measured as a function of the size of drop formed under the tip of a glass capillary and the time for which the drop is allowed to stand by a previously developed apparatus based on the drop volume method. The surface tension of cationic and nonionic surfactant solutions was slightly dependent on the drop size and the adsorption time at low concentrations, and we could easily obtain the adsorption-equilibrium surface tension values by use of an intact capillary. However, the surface tension of anionic surfactant solutions showed a strong dependence on these factors, and the equilibrium surface tension values could not be obtained by use of the intact capillary at all. This situation was drastically improved by use of the water-repellent capillary coated with a silane-coupling reagent. We proposed that the equilibrium surface tension value of surfactant solutions can be determined by adopting the adsorption time at which the surface tension value becomes constant on the surface tension vs the drop size curves. Further, the conditions under which the equilibrium surface tension value of surfactant solutions could be acquired by means of the drop volume method were quite different than those of the Wilhelmy plate method.

Surface tension of aqueous surfactant solutions has been measured by various kinds of methods.[1,2] To acquire static surface tension values using any method, it is important to determine surface tension values after surface adsorption of the surfactant molecules reaches equilibrium. The static surface tension values can be usually obtained from values of surface tension that remain constant on the surface tension vs time curves of the surfactant solution. However, the ease with which the adsorption-equilibrium surface tension values for surfactant solutions can be acquired is dependent on kind of surfactant. With certain surfactant solutions, the surface tension values continue to increase or decrease with time, or the variation in the surface tension values for each measurement is significantly large. Equilibrium surface tension values cannot be obtained in these cases because they do not become constant. Further, the measurement methods used for the determination of surface tension also influence the acquisition of the equilibrium values. For example, it is known that with the drop volume method the surface tension of cationic surfactant solutions are easily measurable with high accuracy while reproducible surface tension values are not possible with anionic surfactant solutions.[3,4] The situation is the opposite for the Wilhelmy plate method.[5]

In the drop volume method, the surface tension values are calculated from the volume of drop formed at the end of the capillary tip of a glass syringe. The volume of the drop is determined as follows: the drop is developed rapidly to about 90–95% of its final volume and allowed to stand for about 5–10 min until adsorption equilibrium is established, and then the drop is turned off slowly.[2,6] Although the above procedure is generally acceptable to surface-chemical researchers, the conditions for the size of the drop formed and the time needed for the adsorption equilibrium are relatively empirical, and they are also ambiguous from an experimental viewpoint. The dependence of surface tension of the aqueous surfactant solutions on the drop size and the adsorption time has not been extensively studied because such surface tension measurements with the drop size and the adsorption time being controlled precisely have many difficulties which arise from the apparatus. Recently, we have developed a new apparatus based on the principle of the drop volume method for the purpose of accurate, rapid, and automatic surface tension measurements of aqueous surfactant solutions.[4,7,8] Since the apparatus can be set to the desired drop size and adsorption time, it is possible to investigate the effects of these factors on surface tension of aqueous surfactant solutions.

In the present study, we measure the surface tension of aqueous solutions of three kinds of surfactants (i.e., cationic, nonionic, and anionic) as a function of the drop size and the adsorption time by the developed apparatus. The reasons for the ease of acquisition of the adsorption-equilibrium surface tension values and the procedure to determine the equilibrium values in the drop volume method are considered. Furthermore, the time dependence of surface tension of aqueous surfactant solutions is compared with that obtained from another surface tension measurement technique, the Wilhelmy plate method. The essential differences in the conditions for acquisition of the equilibrium surface tension values between both methods are also discussed.

Experimental

Materials. Dodecyltrimethylammonium bromide (DTAB), sodium dodecyl sulfate (SDS), and decanoyl-*N*-methylgulcamide (MEGA10) were purchased from Tokyo Kasei Kogyo, Sigma-Aldrich Co., and Dojindo Laboratories, respectively. Disodium 2,3-didodecyl-1,2,3,4-butanetetracarboxylate (Geminisurf-α142: GS) was obtained from Chukyo-Yushi Co. All surfactants were used as received. Dimethylpolysiloxane (Siliconize: Fuji systems Co., Ltd.) as a silane-coupling reagent was used to make the glass capillary of syringe water-repellent. Water was triply distilled after deionization, and the second and third distillations were done from dilute alkaline permanganate solutions.

Surface Tension Measurements. The surface tension (γ) of aqueous surfactant solutions was measured by an automatic system based on the principle of the drop volume method (YTS Co.: DVS-2000). Detailed explanations for the apparatus and the measurement procedure were described elsewhere.[4,7,8] The value of γ is calculated in the drop volume method as a function of the volume (V) of the falling drop:

$$\gamma = (V \Delta \rho g / r) F, \tag{1}$$

where $\Delta \rho$ is the difference in density between aqueous solution and humid air, g is the acceleration of gravity, r is the radius of the capillary tip, and F is the correction factor[9–11] depending on the value of $r/V^{1/3}$. A glass syringe with an inner radius of 2.0 mm (inner volume: 12.57 mm^3 mm^{-1}) was used for the measurements. The r value of the capillary tip (ca. 1.0 mm) was determined from the γ measurements of pure water. A constant speed of 90 µm s^{-1}, that is, speed of volume formation = 1.131 mm^3 s^{-1}, was used to form the drop at the capillary tip and that of 5 µm s^{-1} (0.0628 mm^3 s^{-1}) in falling drop in the whole measurements. The tip of capillary was ground horizontally by an electric grinder (YTS Co.: GCS-WD10A), and the horizontal level was confirmed by using a microscope. A water-repellent glass capillary was produced using following procedure. The coating solution containing a silane-coupling reagent was prepared by the addition of 0.5 mL of dimethylpolysiloxane into 25 mL of water at ca. 343 K. The tip of the capillary was only dipped in the solution for about 10 s and, then, fully washed and rinsed with water. The syringe was heated in a drying oven at ca. 373 K for about 20 min to complete the silane-coupling reaction on the tip surface. After cooling the syringe, the base area of the tip was ground for a moment by the grinder. The treatment resulted in the circumferential sides near the tip being water-repellent while the base is water-wettable. The measurements were performed at a constant temperature of 298.15 ± 0.01 K by immersing the measurement glass cell in a thermostated water bath under atmospheric pressure.

Another γ measurement technique, the Wilhelmy plate method (Kyowa Interface Science Co., Ltd.: CVBP-A3), was also carried out so as to compare the results obtained by the drop volume method. The γ data from the apparatus was transmitted to a personal computer by a RS232C serial interface and monitored as a function of time by using data-capture software which YTS Co. developed. The temperature during the measurements was maintained within 298.1 ± 0.5 K.

Results

We started with the γ measurements of pure water prior to those of surfactant solutions. The γ values of pure water can be used as a standard γ value because it is a solvent for all surfactants. The γ values of pure water are plotted against the size of drops (s) formed under the tip of glass capillary at various times (t) for which the drop is allowed to stand in Fig. 1. Here, the drop size on the abscissa is represented by the volume percentage against the final volume of falling drop ($s = V/V_{\text{falling}}$). The γ value of pure water (71.96 mN m^{-1}) did not show any dependence on both s and t as expected since adsorption does not occur with the pure solvent.

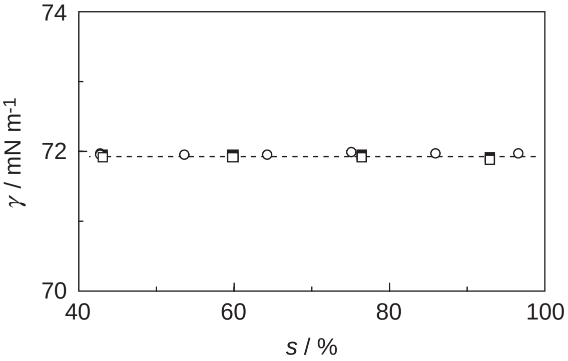

Fig. 1. Effect of the size of the drop formed under the capillary tip at constant t for which the drop is allowed to stand on the γ of pure water: (●) $t = 0$ min, (■) 3, (○) 5, (□) 10. The drop size on the abscissa is represented by the volume percentage against the final volume of falling drop ($s = V/V_{\text{falling}}$). The broken line corresponds to a value of 71.96 mN m^{-1}.

Similar γ measurements were carried out for surfactant solutions. The results for cationic surfactant DTAB solutions are shown in Fig. 2. The γ values at concentrations below the critical micelle concentration (cmc = 16 mmol kg^{-1})[12] decreased by about 0.4 mN m^{-1} during 10 min irrespective of s and remained constant at longer t (data not shown). The slight decrease in the γ value corresponds to the adsorption of DTAB molecules at the water/air interface, and the constant value can be regarded as the adsorption-equilibrium γ value of the aqueous DTAB solution. This fact clearly means that it is necessary to have an appropriate adsorption time in order to obtain equilibrium γ values at lower concentrations below the cmc. On the other hand, γ values at concentrations above the cmc were not dependent on s and t similar to pure water. Since a larger quantity of DTAB molecules exist in the bulk solution enough to form the micelles at concentrations above the cmc, it seems that adsorption is instantly completed during growth of the drop, i.e., forming a new interface on the drop. We observed in the measurements of DTAB solutions that the circumferential sides near the capillary tip do not get wet at all, and the drop grows just under the tip. This is because the cationic DTAB molecules adsorb on the surface of glass with negative charges, and thus the glass surface becomes water-repellent. The results of γ measurements for nonionic surfactant MEGA10 solutions are shown in Fig. 3. The qualitative behavior of the dependence of γ values on s and t found at concentrations below the cmc (7 mmol kg^{-1})[13] and above the cmc resembles that of the DTAB solutions, although the slight s dependence of the γ values at concentrations below the cmc was observed for larger values of s. We can say from these results that the equilibrium γ values for solutions of cationic and nonionic surfactants can be easily obtained by using an intact

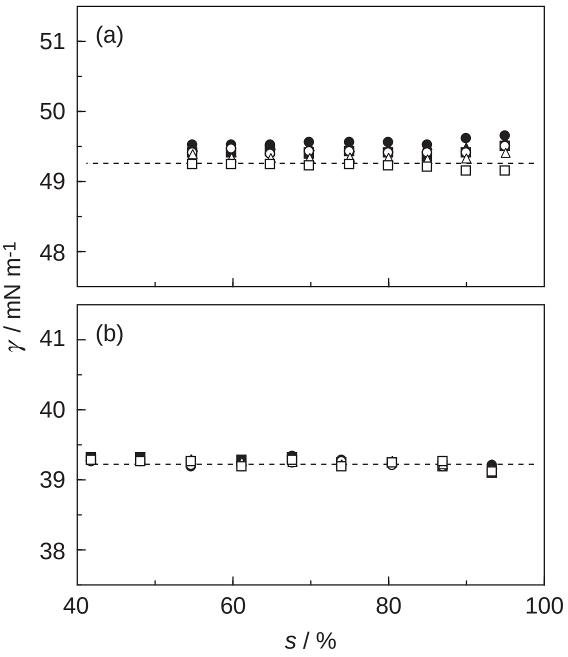

Fig. 2. Effect of the size of the drop formed under the capillary tip at constant t for which the drop is allowed to stand on the γ of aqueous DTAB solutions: (a) 8.05 mmol kg^{-1} (concentration below the cmc), (b) 19.88 mmol kg^{-1} (concentration above the cmc); (●) $t = 0$ min, (▲) 0.5, (■) 1, (○) 3, (△) 5, (□) 10. The broken lines correspond to values of adsorption equilibrium.

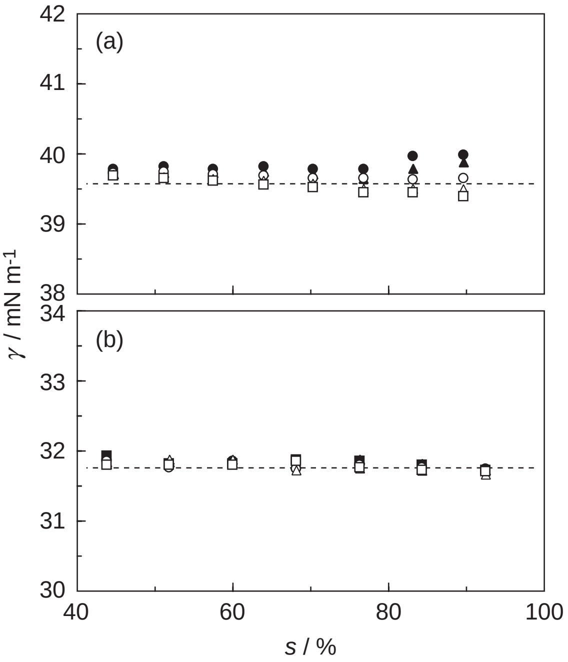

Fig. 3. Effect of the size of the drop formed under the capillary tip at constant t for which the drop is allowed to stand on the γ of aqueous MEGA10 solutions: (a) 3.01 mmol kg^{-1} (concentration below the cmc), (b) 10.01 mmol kg^{-1} (concentration above the cmc); (●) $t = 0$ min, (▲) 0.5, (■) 1, (○) 3, (△) 5, (□) 10. The broken lines correspond to values of adsorption equilibrium.

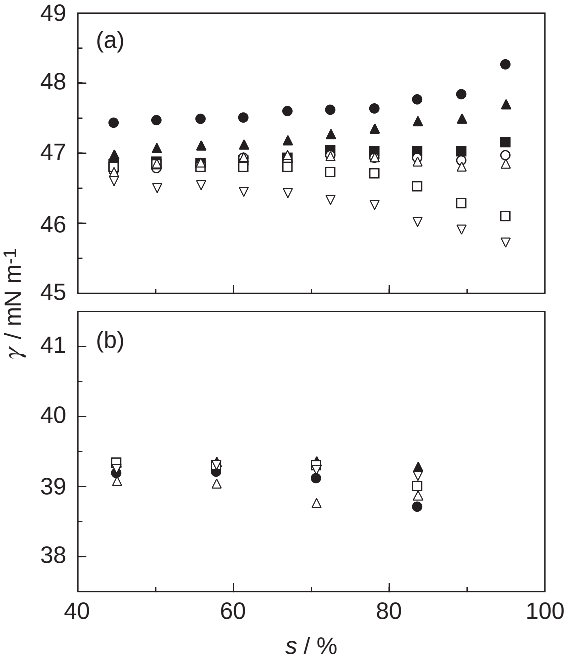

Fig. 4. Effect of the size of the drop formed under the capillary tip at constant t for which the drop is allowed to stand on the γ of aqueous SDS solutions: (a) 4.95 mmol kg^{-1} (concentration below the cmc), (b) 9.97 mmol kg^{-1} (concentration above the cmc); (●) $t = 0$ min, (▲) 0.5, (■) 1, (○) 2, (△) 3, (□) 5, (▽) 10.

glass capillary without a special treatment.

SDS is a widely used anionic surfactant in surface chemistry. Although γ of aqueous SDS solutions has been measured using various kinds of techniques, the drop volume method has been found to be inappropriate to measure the γ.[3] We performed γ measurements with aqueous SDS solutions in a similar way. The results at concentrations below the cmc (8 mmol kg^{-1})[14] and above the cmc are depicted in Fig. 4. In contrast to the cases of the DTAB and MEGA10, we found that the γ values are dependent on s and t in the region at concentrations below the cmc. In the region, the γ values increased with increasing s at short t, while they decreased with s at long t. However, the values all decreased with increasing t. The γ values at concentrations above the cmc also showed marked differences; however, we could not observe such trend at concentrations below the cmc due to the poor reproducibility of the values. The findings for the SDS solutions confirm that the equilibrium γ values in solutions of anionic surfactants cannot be obtained using the usual drop volume methods because the values continue to decrease and there are the large dispersions in the γ values.

Anionic surfactant solutions greatly wet glass surfaces unlike cationic surfactant solutions. Actually, the circumferential sides near the capillary tip become completely wet, and the drop is formed downward from the circumferential sides in the measurements of the SDS solution. In previous studies,[3,4] we found that the sign of electric charge of the surfactant ion and the state of the wetting between glass surface and surfactant solution significantly influence the γ value of the solution, and a water-repellent glass capillary should be effective

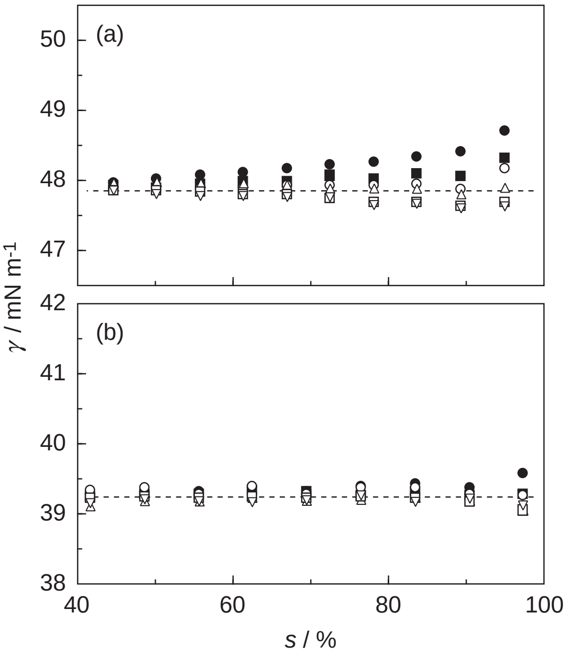

Fig. 5. Effect of the size of the drop formed under the capillary tip at constant t for which the drop is allowed to stand on the γ of aqueous SDS solutions: (a) 4.95 mmol kg^{-1} (concentration below the cmc), (b) 9.97 mmol kg^{-1} (concentration above the cmc); (●) $t = 0$ min, (■) 1, (○) 2, (△) 3, (□) 5, (▽) 10. Here, the water-repellent capillary, instead of an intact capillary, was used in the measurements (see the text). The broken lines correspond to values of adsorption equilibrium.

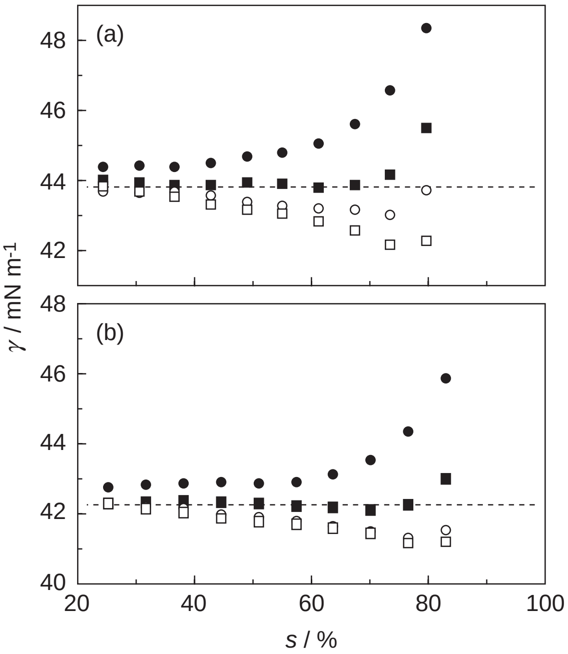

Fig. 6. Effect of the size of the drop formed under the capillary tip at constant t for which the drop is allowed to stand on the γ of aqueous GS solutions at concentrations below the cmc: (a) 0.029 mmol kg^{-1}, (b) 0.040 mmol kg^{-1}; (●) $t = 0$ min, (■) 1, (○) 2, (□) 4. The water-repellent capillary was used in the measurements. The broken lines correspond to values of adsorption equilibrium.

in the measurements of anionic surfactant solutions. Using the water-repellent capillary, γ measurements were carried out for SDS solutions with the same concentrations as shown in Fig. 4. Here, we confirmed that this water-repellent capillary produces the same γ value of pure water with high accuracy as the intact capillary before the measurements of SDS solution, and the tip was also washed out in every other measurement. Figure 5 shows the results obtained using the water-repellent capillary. There was a drastic improvement over the data shown in Fig. 4. Namely, the decrease in the γ values with increasing t became considerably small, and the dependence of the γ values on s and t was only observed in the region of larger s at concentrations below the cmc. At concentrations above the cmc, the γ values were constant irrespective of the two factors similar to the DTAB and MEGA10 solutions. The improvements by using the water-repellent capillary seem to make it possible to measure the γ of anionic surfactant solutions. We also performed γ measurements on aqueous DTAB and MEGA10 solutions with the water-repellent capillary and obtained reproducible equilibrium γ values in agreement with the results from measurements with the intact capillary in Figs. 2 and 3.

The γ values of aqueous solutions of another anionic surfactants, GS, were also measured. Since GS is a divalent anionic gemini surfactant and it has an extremely small cmc value (0.09 mmol kg^{-1}),[15] it is presumed that measuring the γ values of aqueous GS solutions is much more difficult than measuring those of the SDS solutions. The results for the aqueous GS solutions at two concentrations below the cmc are shown in Fig. 6. Although we could not measure the γ of the GS solution by using the intact capillary, reproducible results were obtained by using the water-repellent capillary. As expected, the behavior observed in the γ values of the SDS solutions with t at a large value of s was remarkably increased. In other words, it is difficult to measure the γ values of aqueous solutions of multivalent anionic surfactants with a lower cmc value because of its significant dependence on s and t.

The Wilhelmy plate method is widely used for determining the γ values. In order to determine the essential differences in the conditions for acquiring the adsorption-equilibrium γ values between the drop volume method and the Wilhelmy plate method, we compared the γ values of aqueous surfactant solutions obtained from each method. The γ values of aqueous SDS solutions at concentrations below and above the cmc, which were obtained from both measurement methods, are plotted against t in Fig. 7. Here, a frosted glass plate without any special treatment was used in the Wilhelmy plate method, and the SDS solutions of the same concentrations were measured using both methods. We observed in both methods that there was constant γ region with no t dependence, and so, it seems that equilibrium γ values are obtained. However, the absolute γ values in both methods were appreciably different; the values at concentrations below the cmc determined from the drop volume method were about 5 mN m^{-1} larger than those determined from the Wilhelmy plate method, while the values at concentrations above the cmc were about 1 mN m^{-1}

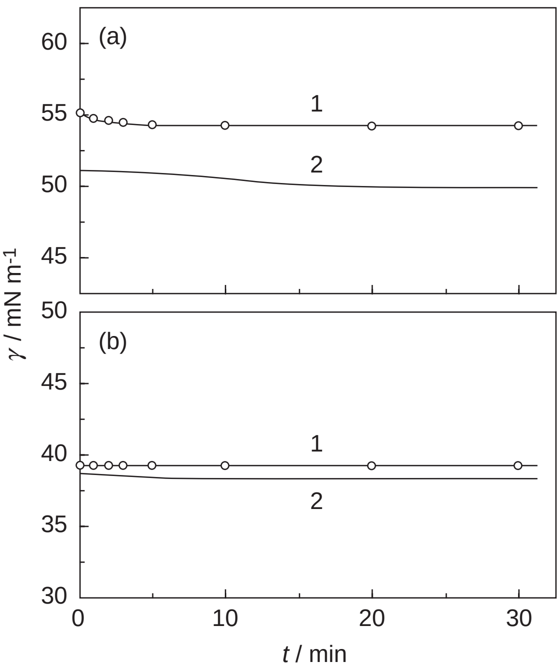

Fig. 7. Comparison of the γ of aqueous SDS solutions obtained by different measurement methods: (a) 2.98 mmol kg^{-1} (concentration below the cmc), (b) 9.92 mmol kg^{-1} (concentration above the cmc); (1) results obtained from the drop volume method, (2) results obtained from the Wilhelmy plate method.

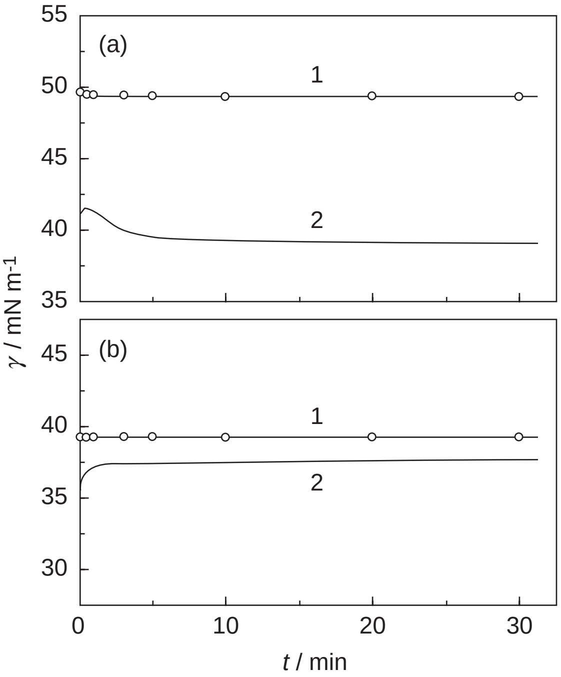

Fig. 8. Comparison of the γ of aqueous DTAB solutions obtained by different measurement methods: (a) 8.05 mmol kg^{-1} (concentration below the cmc), (b) 19.88 mmol kg^{-1} (concentration above the cmc); (1) results obtained from the drop volume method, (2) results obtained from the Wilhelmy plate method.

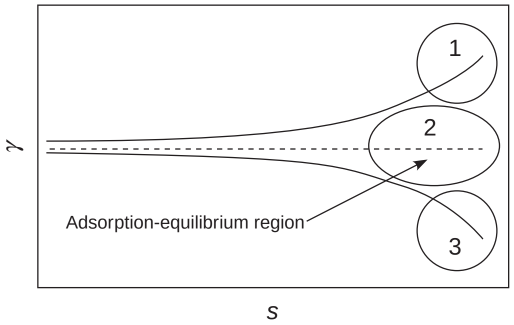

Fig. 9. Schematic drawing for the behavior of γ value observed in aqueous surfactant solutions at concentrations below the cmc: (1) short t, (2) intermediate t, (3) long t. The adsorption-equilibrium value is determined from region 2 (see the text).

larger. Similar results obtained from both methods for the γ values of aqueous SDS solution have been reported by Tajima et al.[16] We also measured the DTAB solution by using both methods, and the resulting γ vs t curves at concentrations below and above the cmc are shown in Fig. 8. The difference in the γ values for the DTAB solution between both methods was almost doubled that observed for the SDS solutions, although the t dependence of curves constructed from both methods was similar to that observed in the SDS solutions. Taking into account the difference in measurement methods, the γ values at concentrations above the cmc may be qualitatively acceptable as the equilibrium γ values in both methods, but those at concentrations below the cmc, especially in the case of the DTAB solutions, are not acceptable at all.

Discussion

The procedure to determine the adsorption-equilibrium γ values using the drop volume method on the basis of the dependence of γ values on s and t has been considered. Since the γ values for each surfactant solution at concentrations above the cmc are observed to be only slightly dependent on s and t in all surfactant solutions, the constant γ values can be considered to be the adsorption-equilibrium values. On the other hand, the γ values vary with s and t at concentrations below the cmc. From Figs. 1–6, a schematic drawing for the γ values observed generally in aqueous surfactant solutions at concentrations below the cmc is presented in the form of the γ vs s curves in Fig. 9. The dependence of γ values on s and t is divided into three patterns: the γ value increases with increasing s at shorter t (region 1), it becomes almost constant with s at intermediate t (region 2), and it decreases with increasing s at longer t (region 3). We propose to use the constant γ value in region 2 as the adsorption-equilibrium value at concentrations below the cmc. In region 1, the observed γ values become larger than the constant one at larger s and shorter t. The reason for the behavior may be that the γ value does not reach the equilibrium value with shorter t. At smaller s, the γ value seems to reach equilibrium, while the drop grows, since it has sufficient time before the drop falls. On the contrary, in region 3, the observed γ value becomes smaller than the constant value at larger s and longer t. We speculate that the phenomenon may be caused by the adsorbed film formed under the base area or on the circumferential sides of the capillary tip after the γ value reached the equilibrium one. Since it has sufficient time before the drop falls with decreasing *s*, the adsorbed film formed under or on the tip is removed with the drop growth. Therefore, we concluded that the constant γ value in region 2 of the γ vs *s* curves can be regarded as the equilibrium γ value. The constant γ values at larger *s* (more than 90%) from region 2 are probably adequate from an experimental point of view because other sources of experimental error, such as speed and time of the drop growth, are included at smaller *s*.

Eq. 1 used to calculate the γ value in the drop volume method was originally derived from the balance between upper and lower force at the capillary tip as given by[1,2]

$$(2\pi r)\gamma\phi = mg = V\Delta\rho g, \tag{2}$$

where *m* is the mass of falling drop and ϕ ($= 1/(2\pi F)$) is the correction factor for the remaining liquid under the tip, respectively. From Eq. 2, the γ value is related to the force of circumferential edges just under the tip. Judging from this fact and the γ measurements of aqueous surfactant solution as mentioned above, the ease with which the equilibrium γ values can be acquired is closely related the accuracy of the circumferential edges when the drop falls. Therefore, it is required that the circumferential sides near the tip be completely non-wettable to avoid the influence of the wetting between surfactant solution and glass surface at the sides of the tip in order to determine the equilibrium γ value by using the drop volume method.

On the other hand, the surface tension value in the Wilhelmy plate method is calculated by the equation[1,2]

$$L\gamma + Mg = P, \tag{3}$$

where *L* and *M* are the perimeter and mass of the plate, *P* is the upper force under the condition that the buoyant force of the plate is zero. The γ value is directly determined from the upper force measured by an electromicrobalance. Although it is the advantageous point in the plate method that the γ value can be obtained without any correction factor, unlike the drop volume method, the contact angle between plate surface and sample solution must be zero, that is $\cos\theta = 1$ in $\gamma\cos\theta$ in order to use Eq. 3. It is expected that the γ measurements of aqueous anionic surfactant solutions can be performed easier than those of other kinds of surfactant solutions because anionic surfactant solutions are completely wettable on glass surface and the wettability seems to lead to the condition of the contact angle zero. On the other hand, the γ values for cationic surfactant solutions cannot be determined using the plate method because the contact angle is not zero due to the adsorption of the cationic surfactant on the glass surface with negative charges. In other words, to determine the equilibrium γ values in the plate method is to make the plate completely wettable during the measurements to make the contact angle equal to zero. Interestingly, this condition is the exact opposite to that of the drop volume method. The difference between the methods explains the experimental fact that it is easy to measure the γ value of cationic surfactant solutions while it is difficult to measure the γ value of anionic surfactant solution using the drop volume method and vice versa using the plate method.

As can be seen from Figs. 7 and 8, the constant γ values are obtained by both methods; however, there is a discrepancy in the absolute γ value determined by both methods, i.e., the value is large at concentrations below the cmc and small at concentrations above the cmc. Considering that the absolute γ values obtained by the drop volume method are consistent with those obtained by using the pendant drop volume method (unpublished data), the γ values obtained by using the plate method probably correspond to the apparent values, not intrinsic ones. The smaller γ values from the plate method are attributed to the glass plate used in the measurements. The adsorption of surfactant molecules on the glass plate seems to violate the condition of a contact angle equal to zero, even in anionic surfactant solutions. The effect from surfactant adsorption becomes pronounced at low concentrations since a slight increase in surfactant concentration on the glass surface by adsorption causes a notable decrease in the γ value in the range. Moreover, in the case of cationic surfactants, the effect is synergized by stronger adsorption on the glass surface than anionic surfactants. These facts suggest that the plate method is unsuitable to determine absolute γ values of aqueous surfactant solutions. We can say that, although the plate method is a convenient method to use, and it is useful to determine the cmc values of surfactant solutions qualitatively, it is difficult to obtain intrinsic equilibrium γ values of surfactant solutions unlike the drop volume method.

Conclusion

If the γ values for aqueous surfactant solutions are obtained with high accuracy, it is possible to discuss the behavior of surfactant molecules in an oriented state at the interface and the formation of surfactant aggregates in the solution quantitatively. However, it is necessary for this purpose to determine the adsorption-equilibrium γ value for the surfactant solutions. Although every method should provide the same γ values in principle, large scattering and deviations from the intrinsic equilibrium γ value are experimentally observed depending on the kinds of surfactants and on the method used. The present study strongly suggests that great care must be used to ensure that the surfactant solution measured satisfies necessary conditions in order to obtain its intrinsic γ values.

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