

Cleaning Performance and Foaming Properties of Lauroylamidopropylbetaine/Nonionics Mixed Systems

Takamitsu Tamura^{a,*}, Tadashi Iihara^b, Shigeo Nishida^b, and Seiich Ohta^b

^aMaterial Science Research Center and ^bBetter Living Research Laboratory, Lion Corporation, Tokyo, 132, Japan

ABSTRACT: Lauroylamidopropylbetaine (LPB) has good cleaning and foaming performance with excellent low skin irritation. We have investigated the relationship between cleaning performance and foaming properties of aqueous solutions containing binary and ternary LPB/nonionic surfactant systems. Foaming properties were evaluated by observing dynamic surface tension and aqueous core thickness of a vertical foam film measured by Fourier transform infrared spectroscopy. The LPB/lauroyldiethanolamide (LDE) system has a positive synergistic effect on cleaning performance and foam stability, estimated from the grease removal test and dishwashing test for a light-duty detergent. However, this system shows very poor initial foam performance in both the sponge test and Ross-Miles foam test. This disadvantage of the LPB/LDE system was improved using C12En (polyoxyethylene dodecyl ethers). Addition of C12En promoted dynamic surface tension lowering, indicating an improvement in the initial foaming performance, while maintaining cleaning performance and foam durability. Thus, the LPB/LDE/C12En ternary system has an excellent cleaning and foam performance as a light-duty liquid detergent.

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KEY WORDS: Detergency, dishwashing performance, dynamic surface tension, drainage, foaming, lauroylamidopropylbetaine, liquid detergent, nonionic surfactant, surface tension, surfactant.

Lauroylamidopropylbetaine (LPB) is an amphoteric surfactant obtained from natural resources such as fatty methyl esters or fatty acids (1). Since LPB has good cleaning and foaming performance with low skin irritation, it has been widely used in shampoos and light-duty detergents along with anionic surfactants (2,3). Many studies of anionic/amphoteric surfactant mixed systems have been reported (4–8). Lauroyldiethanolamide (LDE) has also been widely used in many detergents as a nonionic surfactant for increasing foaming performance (9). We have studied the relationship between cleaning performance and foam film properties of LPB/nonionic surfactant binary mixed systems and compared properties against LPB and alkyl ether sulfate (AES) as the anionic surfactant. Superior cleaning performance

and foaming properties as a light-duty liquid detergent were observed, particularly for a LPB/LDE/nonionic surfactant ternary system. This paper discusses the synergistic effect of the mixed system using foam formation and foam stability methods. Foam formation was estimated by dynamic surface tension based on the maximal bubble pressure method, and foam stability was estimated by evaluating the aqueous core thickness of vertical foam films measured by Fourier transform infrared (FT-IR) spectroscopy.

EXPERIMENTAL PROCEDURES

Materials. Surfactants were commercial products from Lion Co., Ltd. (Tokyo, Japan). LPB [$C_{11}H_{23}CONHC_3H_6N^+-(CH_3)_2CH_2COO^-$, ENAGICOL L30-B, >95%], LDE [$C_{11}H_{23}CON(C_2H_4OH)_2$, >95%], polyoxyethylene dodecyl ethers C12E5, C12E9, C12E15 [$C_{12}H_{25}O(C_2H_4O)_nH$, where $n = 5, 9, \text{ or } 15$, >95%] and trioxyethylene dodecyl sulfate AE3S [$C_{12}H_{25}O(C_2H_4O)_3SO_3Na$, >95%] were used without further purification.

Grease removal test. This grease removal test, also known as the cup test, determines the ability to remove greasy soils from hydrophobic surfaces. One gram of butter was homogeneously spread on the inside of a polypropylene cup (300 mL). Then 290 mL of a surfactant solution (1.7 wt%) was poured into the cup at 25°C. The solution was stirred for 3 min with a rectangular metal plate (20 × 30 mm) at 250 rpm. After stirring, the solution was poured out and the cup was dried. The residual amount of grease was then weighed and percentage soil removal was calculated.

Dishwashing test. This dishwashing test provides cleaning and foam performance for light-duty liquid detergents. Surfactant solution (40 mL, 1.7 wt%) at 25°C was added to a sponge (70 × 120 × 30 mm). Each 20-cm diameter plate was coated with 0.5 g of butter was successively washed by this sponge, and the process was continued until foaming ceased. The number of plates cleaned was then counted.

Initial foam volume test. Surfactant solution (40 mL, 1.7 wt%) at 25°C was added to a sponge. The experimental conditions were identical to those described for the dishwashing test. The sponge was squeezed by hand several times, and the foam on the sponge was photographically recorded.

*To whom correspondence should be addressed at Material Science Research Center, Lion Corporation, 7-13-12, Hirai, Edogawa-ku, Tokyo, 132, Japan.
E-mail: tmr-3378@lion.co.jp

The Ross-Miles foam test was carried out to quantitatively measure the initial foam volume (10,11). A thermostated Ross-Miles apparatus was used, and the initial foam height was measured.

Vertical foam film stability. An amount of surfactant solution (1.7 wt%) was placed in a glass container and a Pt frame 15 mm wide and 39 mm high was dipped into the solution at 21°C. The frame was constructed of 1-mm diameter rod. After 30 min, the relative humidity reached 100%. The frame was then pulled up at a constant speed and a foam film was formed on the rectangular Pt frame. The film drainage pattern was observed based on features of the interference fringes. Film stability was expressed in terms of film lifetime until rupture.

FT-IR measurements were done as previously described using a System 2000 FT-IR (Perkin-Elmer Co., Ltd., Tokyo, Japan) to determine the aqueous core thickness (d_2) of vertical foam films (12). A rectangular frame 18 mm wide and 15 mm high, which was hollowed out of a G4 sintered glass plate (32 mm wide, 30 mm high, and 2 mm thick), was used to support the foam films. The aqueous core thickness was determined from absorbance at 3450 cm^{-1} , which is assigned to the OH stretching vibration of water molecules. The molar absorption coefficient of $1.449 \times 10^{-5}\text{ M}^{-1}\text{ nm}^{-1}$ was used to calculate the thickness (13). The infrared beam passed through the foam film center.

Surface shear viscosity. Surface shear viscosity measurements were done using the oscillation torsion pendulum method with a surface viscoelastimeter (Model SVR-A; Kyowa Interface Science Co., Ltd., Tokyo, Japan) (13,14).

Dynamic surface tension measurement. Dynamic surface tension (γ_t) was measured using the maximal bubble pressure method (13,14). Nitrogen gas was fed into a silicone-treated glass capillary (inner diameter, $122.4\text{ }\mu\text{m}$) through a precision pressure transducer (Model DP15; Validayne Co., Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

Cleaning performances of LPB/nonionics binary systems. Percentage soil removal in the grease test as a function of the weight ratio of LPB and other surfactants is shown in Figure 1. The lowest soil removal was observed for LPB/C12E9, LPB/C12E15, and LPB/AE3S regardless of mixing ratio. A slight increase was observed for LPB/C12E5 with an increase in the C12E5 fraction. However, high detergency was observed for LPB/LDE. Highest performance was maintained with an increase in the LDE fraction.

The number of washed plates during the dishwashing test as a function of LPB weight ratio and other surfactants is shown in Figure 2. Although the dependence of ethylene oxide (EO) chain length on detergency was observed for the LPB/C12En system in the order of C12E5 > C12E9 > C12E15, a poor synergistic effect was observed. However, a positive synergistic effect on detergency was observed for

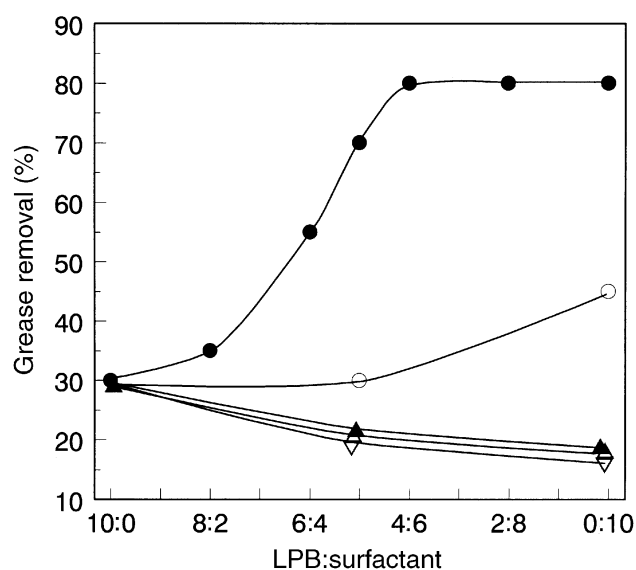


FIG. 1. Effect of lauroylamidopropylbetaine (LPB)/surfactant weight ratio on grease removal for 1.7 wt% aqueous surfactant solutions at 25°C. ●, LPB/LDE; ○, LPB/C12E5; △, LPB/C12E9; ▽, LPB/C12E15; ▲, LPB/AE3S. LDE, lauroyldiethanolamide; C12E5, C12E9 and C12E15, polyoxyethylene dodecyl ethers; AE3S, trioxyethylene dodecyl sulfate.

LPB/LDE and LPB/AE3S. The graph shows that the performance of LPB/LDE is significantly better compared to LPB/C12En and LPB/AE3S. Based on these results, the LPB/LDE mixed system shows excellent cleaning and foaming performance.

However, the data show that the initial foam volume for LPB/LDE was very low. Figure 3A illustrates visual features of foam generated for each surfactant solution using

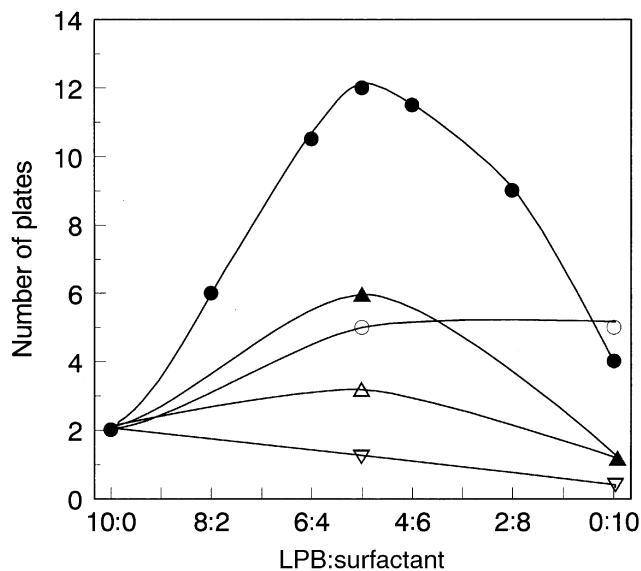


FIG. 2. Effect of LPB/surfactant weight ratio on dishwashing for 1.7 wt% aqueous surfactant solutions at 25°C. ●, LPB/LDE; ○, LPB/C12E5; △, LPB/C12E9; ▽, LPB/C12E15; ▲, LPB/AE3S. See Figure 1 for abbreviations.

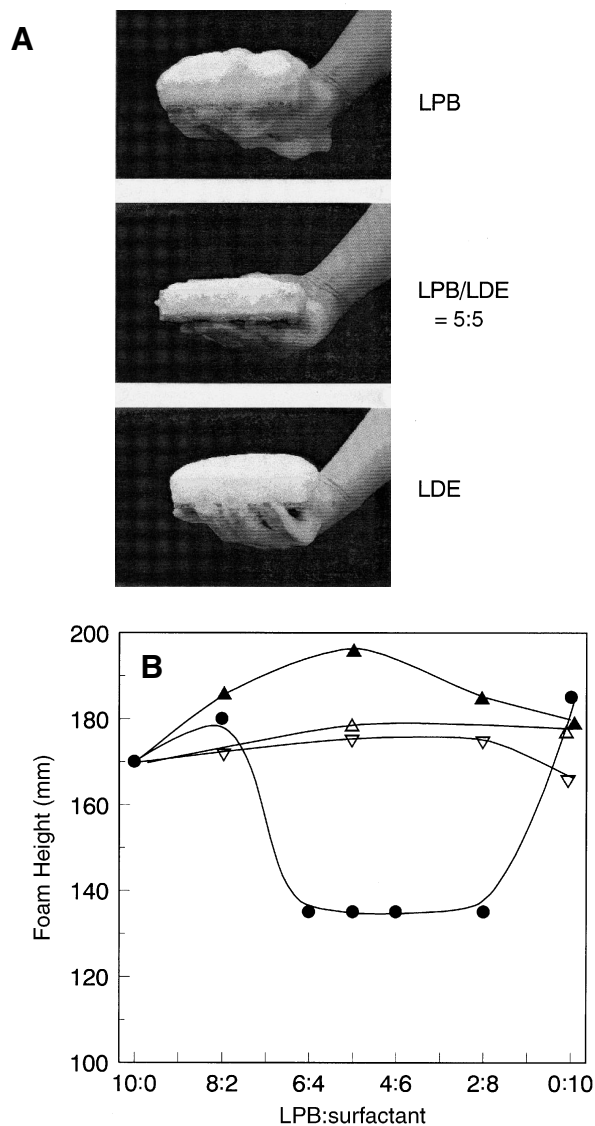


FIG. 3. (A) Initial foam volume for LPB, LPB/LDE (5:5), and LDE systems at 25°C and 1.7 wt%. (B) Effect of LPB/surfactant weight ratio on foaming for 1.7 wt% aqueous surfactant solutions at 25°C [●, LPB/LDE; △, LPB/C12E9; ▽, LPB/C12E15; ▲, LPB/AE3S]. For abbreviations see Figure 1.

a sponge (initial volume test). LPB/LDE showed very poor initial foam performance compared to LPB or LDE alone.

The Ross-Miles foam test was performed to quantify initial foam performance. Initial foam heights from the test as a function of the weight ratio of LPB and other surfactants are shown in Figure 3B. Foam is generated at constant volume for the systems of C12En regardless of their mixed ratio. A slight synergistic increase in foam was observed for LPB/AE3S at equal weight fraction. On the other hand, it was apparent that LPB/LDE showed negative synergistic performance on foam generation compared to other mixed systems.

To summarize the cleaning performance data, we found that the LPB/LDE system showed superior cleaning per-

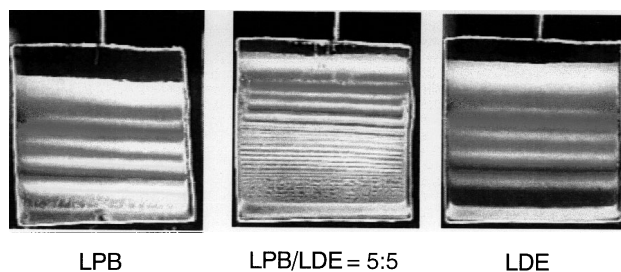
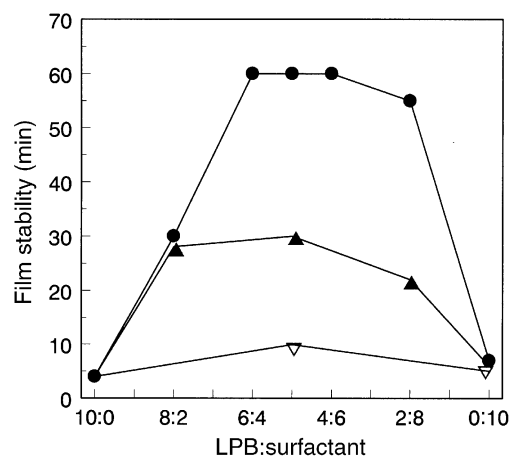


FIG. 4. (Upper) Effect of LPB/surfactant weight ratio on vertical foam film stability for 1.7 wt% aqueous surfactant solutions using Pt frame at 25°C. [●, LPB/LDE; ▽, LPB/C12E15; ▲, LPB/AE3S]. (Lower) Feature of interference fringes on the vertical foam films photographed at 3 min after pulling up. For abbreviations see Figure 1.

formance and foam stability for a light-duty detergent, but this system had a very poor initial foam performance compared to other systems.

Foam film properties of LPB/nonionics binary systems. Cleaning performance was investigated using foam film stability and adsorption dynamics of the surfactant solutions. Film lifetimes on the rectangular Pt frame as a function of the weight ratio of LPB and other surfactants are shown in Figure 4. Features of interference fringes on the vertical films photographed 3 min after pulling up are inserted in this figure. When the film thickness is over 100 nm, it is easily detected by observing the interference fringe. A silver film appeared at thicknesses under 100 nm and a black film at 50 nm. In Figure 4, although both vertical films of LPB and LDE alone rapidly appeared as silver and black films, stable interference fringes were observed only for the LPB/LDE film. A poor synergistic effect on the film lifetime was observed for LPB/C12E15, whereas a synergistic effect was seen for LPB/LDE and LPB/AE3S. Performance of LPB/LDE was significantly higher compared to the LPB/C12En and LPB/AE3S systems.

Thinning behavior of vertical foam films as a function of time is shown in Figure 5. Drainage and drainage speed increased in the order, LPB/LDE (5:5) > LPB > LDE. Vertical films and black films for LPB and LDE alone appeared within 10 min, however, a black film for LPB/LDE was not

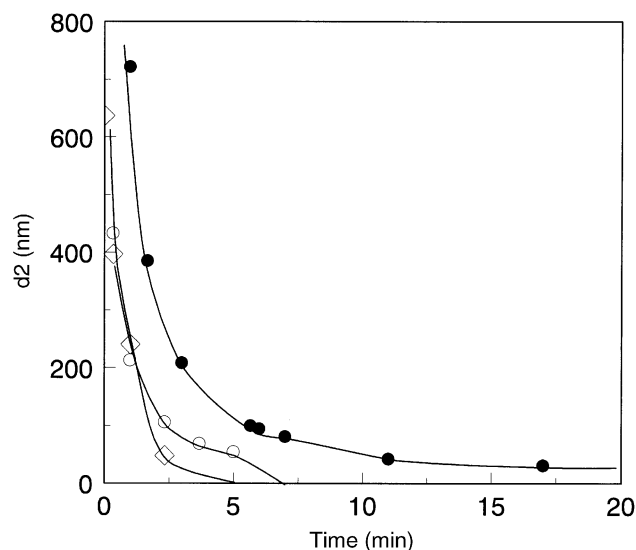


FIG. 5. Aqueous core thickness (d_2) of the vertical foam films for 1.7 wt% aqueous surfactant solutions at 20°C. ●, LPB/LDE = 5:5; ○, LPB; ◇, LDE. For abbreviations see Figure 1.

observed. Furthermore, the effect of surface shear viscosity on drainage was measured for these solutions. Surface shear viscosity remarkably increased in the order of LPB/LDE (5:5) > LDE > LPB = 725 > 91.3 > 10.4 $\mu\text{N}\cdot\text{s}\cdot\text{m}^{-1}$. To summarize data for vertical foam film properties, LPB/LDE has a superior film stability compared to other systems. In other words, LPB/LDE formed more stable foam films than LPB or LDE alone. This effect is attributed to high cleaning performance and foam durability.

The poor initial foam volume of LPB/LDE cannot be explained using vertical foam film stability data. As a result, dynamic surface tension was measured. The γ_t values of surfactant solutions as a function of time are shown in Figure 6. In the relatively longer time region (>1 s), the γ_t values for LPB alone were higher compared to LPB/LDE and LDE alone. In the relatively shorter time region (<100 ms), however, γ_t values for LPB/LDE (5:5) were significantly

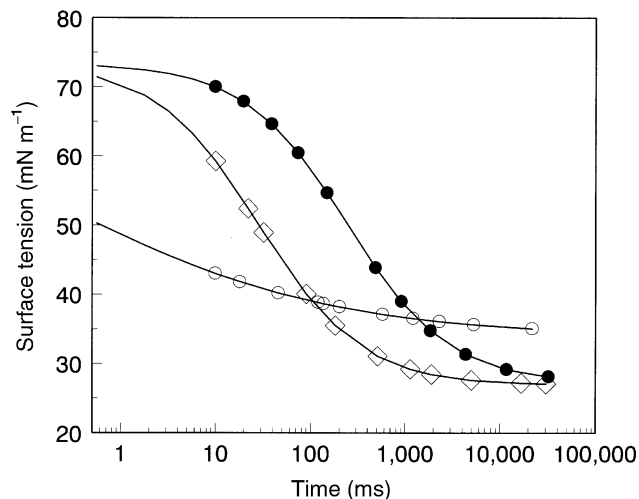


FIG. 6. Dynamic surface tension of 1.7 wt% aqueous surfactant solutions vs. time at 20°C. ●, LPB/LDE = 5:5; ○, LPB; ◇, LDE. For abbreviations see Figure 1.

higher than those for LPB and LDE alone. In our previous paper (14), we demonstrated that the initial foam height from the Ross-Miles foam test was in good agreement with the rate of decrease in surface tension. Thus, the rate of decrease in surface tension for both the LPB and LDE systems was greater compared to LPB/LDE (5:5). This result indicates that the adsorption rate of surfactants in LPB/LDE (5:5) at the air/water interface is very slow, confirming initial foam volume experiments.

Cleaning performance of LPB/LDE/C12En ternary systems. Some disadvantages in cleaning performance of LPB/LDE were improved by use of C12En. Cleaning performance of LPB/LDE = 5:5, LPB/LDE/C12E15 = 4:4:2, and LPB/AE3S = 5:5 at 1.7 wt% are shown in Figures 7A–C. Figures 7A and 7B show little influence on grease removal and dishwashing by adding C12E15 to LPB/LDE. Figure 7C, on the other hand, shows a synergistic increase in initial foam volume by addition of C12E15 to LPB/LDE. These results

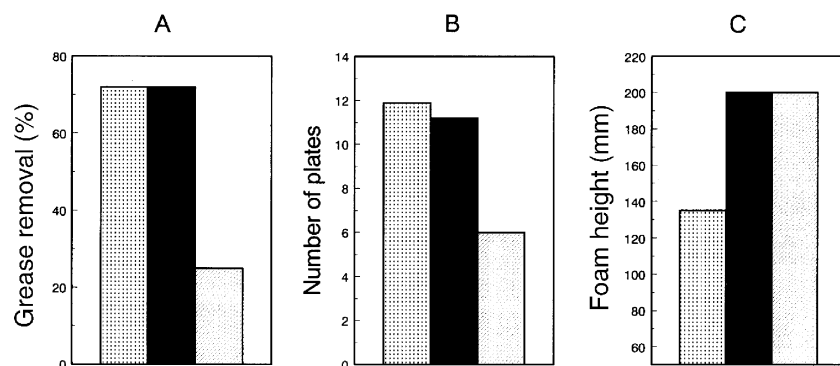


FIG. 7. Cleaning and foaming performance of three systems at 25°C. (A) Grease removal test, (B) dishwashing test; and (C) Ross-Miles foam test. Stippled bars, LPB/LDE = 5:5; solid bars, LPB/LDE/C12E15 = 2:4:2; lined bars, LPB/AE3 = 5:5. For abbreviations see Figure 1.

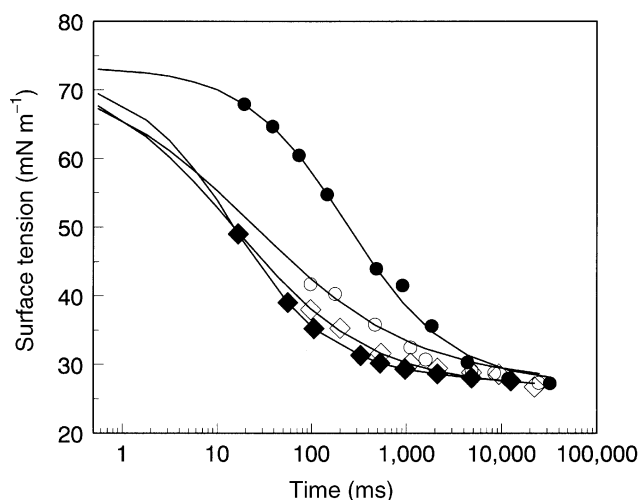


FIG. 8. Dynamic surface tension of 1.7 wt% aqueous surfactant solutions as a function time at 20°C at 4:4:2 ratio. ●, LPB/LDE = 5:5; ○, LPB/LDE/C12E5; ◇, LPB/LDE/C12E9; ◆, LPB/LDE/C12E15. For abbreviations see Figure 1.

show that the LPB/LDE/C12E15 ternary system maintains cleaning performance, foam durability and excellent initial foam generation performance.

Foam film properties of LPB/LDE/C12En ternary systems. To elucidate the reason for improved ternary system cleaning performance, foam film stability and adsorption dynamics were investigated for surfactant solutions. The lifetime of films formed on the rectangular Pt frame was 60 min for the LPB/LDE/C12E5 = 4:4:2 system, which is equal to the film lifetime for the LPB/LDE = 5:5 system (Fig. 4). This result shows that there was no change in the film upon addition of C12E15 to the LPB/LDE binary system.

The γ_t values of the ternary systems (LPB/LDE/C12En = 4:4:2) as a function of time are shown in Figure 8. A dramatic decrease in the rate of surface tension was observed for each ternary system. Although EO chain length had some influence on the rate of decrease in surface tension detergency, the LPB/LDE/C12E15 system had the fastest adsorption rate. This indicates that adsorption of surfactants at the air/water interface is improved with the use of C12E5, and as a result the foam volume for the LPB/LDE system is improved.

In conclusion, the LPB/LDE system has a synergistic effect on foam film stability, whereas addition of highly ethoxylated dodecyl ethers lowers the dynamic surface tension maintaining foam stability. As a result, the LPB/LDE/C12En ternary system exhibits excellent cleaning and foaming performance as a light-duty liquid detergent.

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Takamitsu Tamura, born in 1956, graduated from the Science University of Tokyo in 1980. He is associate senior research manager of Lion Corporation, Material Science Research Center. His research field is colloid and surface science.

Tadashi Iihara, born in 1962, graduated from Tokyo University in 1986. He is assistant research manager of Lion Corporation, Better-Living Research Laboratories. His research field is the development of liquid detergents.

Shigeo Nishida, born in 1949, graduated from Waseda University in 1973. He is research manager of Lion Corporation, Better-Living Research Laboratories. His research field is the development of liquid detergents.

Seiichi Ohta, born in 1947, graduated from Kyoto University in 1971. He is Director of Beauty-Care Research Laboratories in Lion Corporation. His research field is the development of detergents.