Surface-Active N-Acylglutamate: IV. Physicochemical Properties of Triethanolamine Long Chain N-Acylglutamates

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ABSTRACT

The physicochemical properties of triethanolamine long chain N-acylglutamates are described. The monotriethanolamine salts were less soluble in water and superior in surface activity, compared with the corresponding ditriethanolamine salts. The monotriethanolamine salt showed weak acidity in an aqueous solution. There were some differences between optically active and racemic N-acylglutamates, especially in the values of critical micelle concentration.

INTRODUCTION

The salts of long chain N-acylglutamic acids are surfactants derived from glutamic acid (1,2). They are less irritating on the skin than other synthetic surfactants, such as sodium lauryl sulfate (SLS) (3,4). In previous articles (5,6), the physicochemical properties of sodium N-acylglutamates (AGS_n) were described. The N-acylglutamates displayed different characteristics varying with the classes of acyl radicals and bases in the structures. Monosodium N-lauroyl-L-glutamate showed excellent lowering power of surface tension, foaming power, wetting power, and emulsifying power. Disodium N-palmitoyl or stearoylglutamate was superior in dispersing power to the powder of carbon black. The monosodium salts (AGS) were less soluble in water with the exception of monosodium N-oleoylglutamate, whereas the disodium salts (AGS_2) were highly soluble. AGS generally showed weak acidity in an aqueous solution, the pH of which was almost equal to that of the human skin.

In this article, the physicochemical properties of triethanolamine N-acylglutamates (AGT_n) are described. Triethanolamine salts of anionic surfactants are generally more soluble in water and less irritating on the skin, compared with the corresponding sodium salts and are often used as materials of liquid detergents like shampoo. It was expected that, if these AGT_n had good surface activities in their aqueous solutions, they could be adapted for similar usages. The various AGT_n were abbreviated with the methods described previously.

METHODS AND RESULTS

Solubility

When a diluted aqueous solution of AGS was allowed to stand at room temperature, the crystals of N-acylglutamic acid (AGA) precipitated as the result of hydrolysis of AGS, and an uncommon solubility-temperature curve was obtained. This phenomenon also was observed in aqueous solutions of monotriethanolamine N-acylglutamate (AGT). The solubility-temperature curve was obtained by a method, as described previously. Aqueous solutions with an appointed concentration were added into test tubes and were cooled sufficiently to recrystallize. The tubes were agitated under a gradually raising temperature, and the temperatures were noted at which the suspensions became clear solutions. The curves obtained are shown in Figure 1.

In higher concentration ranges (above ca. 50 mmol/liter), AGT had a temperature that the solubility increased sharply (Krafft point). Whereas in low concentration ranges, the aqueous solution became gelatinous above the

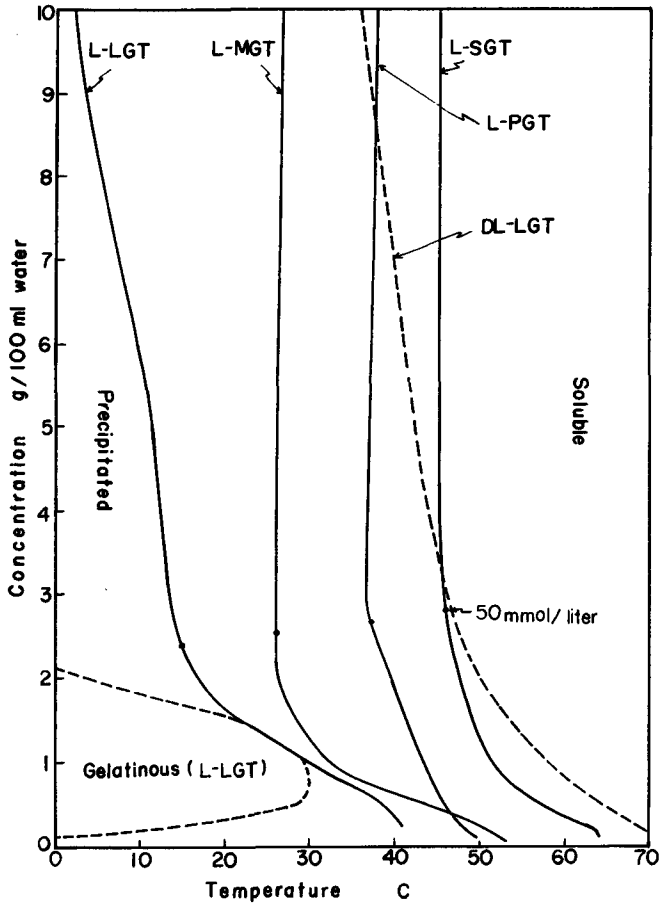

FIG. 1. Solubility-temperature curves of monotriethanolamine N-acylglutamate (AGT).

temperatures considered as the Krafft point. Of AGT tested, monotriethanolamine N-lauroyl-L-glutamate (L-LGT) was relatively soluble, but the gelantinous range was broad, especially at lower temperatures. Monotriethanolamine N-oleoyl-L-glutamate (L-OGT) was highly soluble and no crystals precipitated from the aqueous solution, even when cooled at 0 C. DL-LGT hydrolyzed greatly, and the solubility curve was peculiar. In L-AGT series, a linear relation was observed between the clear point and the length of an acyl radical at the concentration of 50 mmol/liter. When aqueous solutions of AGT were prepared freshly, no hydrolysis occurred for a while and no precipitates appeared. Surface activity measurements were conducted during the solutions kept clear.

AGT_n was generally insoluble in organic solvent, except lower alcohols and chloroform. Among the other salts of AGA, triethylamine salts were comparatively soluble in various solvents. For example, triethylamine N-lauroyl-L-glutamate was soluble in methanol, ethanol, ethyl acetate, toluene, methylethylketone, dioxane, and chloroform at the concentration of 1% but was insoluble in benzine petroleum.

pH Value

Aqueous solutions of N-acylglutamates generally showed

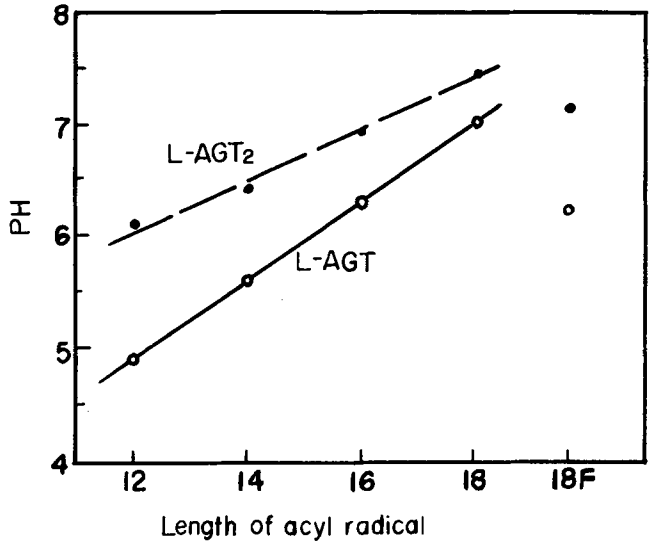

FIG. 2. Relation between pH and acyl length of triethanolamine N-acylglutamate (AGT_n) (concentration 10 mmol/liter, at 40 C).

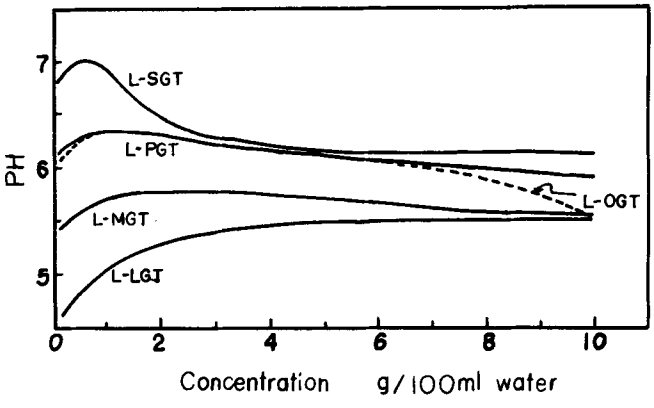

FIG. 3. Relation between pH and concentration of monotriethanolamine N-acylglutamate (AGT) (at 40 C).

TABLE I

Critical Micelle Concentration of Triethanolamine N-Acylglutamate

Samples	Critical Micelle Concentration, mmol/liter 40 C	60 C
L-LGT	5.4	6
L-MGT	5.0	5
L-PGT		4
L-SGT		3
$L\text{-}LGT_2$	27	
$L\text{-}MGT_2$	11.5	
$L\text{-}PGT_2$	5.0	
$L\text{-}SGT_2$	2.2-2.5	
$DL\text{-}LGT_2$	31	
$DL\text{-}MGT_2$	13	
$DL\text{-}PGT_2$	5.4	
$DL\text{-}SGT_2$	2.5	

weak acid or neutral pH, which varied with a degree of neutralization, concentration, and temperature. The changes in the pH values of 10 mmol/liter aqueous solutions of $L\text{-}AGT_n$ at 40 C are shown in Figure 2. Ca. linear correlation was observed between the pH values and the acyl lengths in AGT and in the ditriethanolamine salt (AGT_2) too. The pH values of L-AGT were measured as a function of concentration and the results are shown in Figure 3. The maximum value was obtained at ca. 1% concentration and, in higher concentration ranges, the pH values became gradually lower.

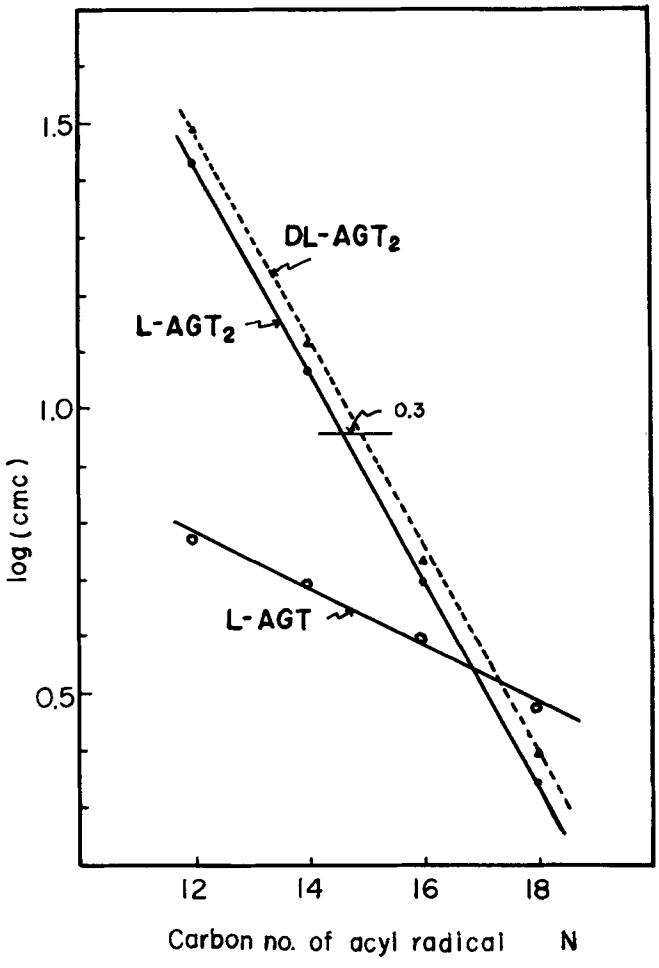

FIG. 4. Relation between log critical micelle concentration and carbon number of acyl radical.

Critical Micelle Concentration (CMC)

CMC of AGT and AGT_2 were determined by a dye method (7). When rhodamine 6G was added in an aqueous solution of an anionic surfactant, the solution became orange in color and fluorescent above the CMC. As the solution was diluted at the constant dye concentration (0.1 mmol/liter), the color changed to red at the CMC, and the fluorescence disappeared. The aqueous solutions of AGT and AGT_2 changed sharply in color in the test and the CMC were determined easily, as shown in Table I. When the logarithm of CMC value (mmol/liter) was plotted against the carbon number of acyl radical (N), a linear relationship was obtained, as is indicated in Figure 4. From these results, the following equation was conducted respectively: for L-AGT series, log (CMC) = 1.39 - 0.05N; for $L\text{-}AGT_2$ series, log (CMC) = 3.60 - 0.181N; and for $DL\text{-}AGT_2$ series, log (CMC) = 3.65 - 0.181N.

In AGT series, the CMC values did not vary largely, although the length of the acyl radical became longer. The slope of the straight line was abnormally gentle (the value of the slope constant was -0.05). Same relation also was observed in AGS series. These unusual relations seem to be caused by the abnormal structure, i.e. these monoequivalent salts have a carboxyl radical unneutralized and hydrolyze partially to AGA and AGT_2 in the aqueous solutions. Therefore, it seemed that the salts showed unusual micelle states. In $L\text{-}AGT_2$ and $DL\text{-}AGT_2$ series, the value of the slope constant was -0.181 and was ca. similar to the value in AGS_2 series (-0.169). However, these values were small when compared with the general value (-0.301) which was observed in a series of surfactants having a straight alkyl chain and a univalent counter ion. An interesting new fact

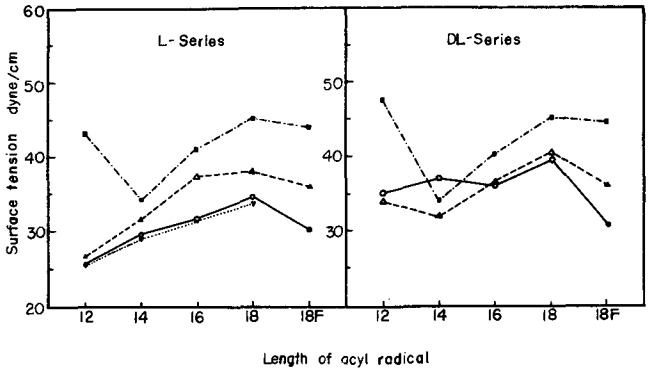

FIG. 5. Surface tensions of triethanolamine N-acylglutamate (AGT_n) (concentration 10 mmol/liter, at 40 C). —●— = monotriethanolamine salt (AGT); —▲— = sesquitriethanolamine salt ($AGT_{1.5}$); —■— = ditriethanolamine salt (AGT_2); ●,▲,■ = soluble; ○,△,□ = cloudy; —▼— = surface tensions of L-AGT measured at 50 C.

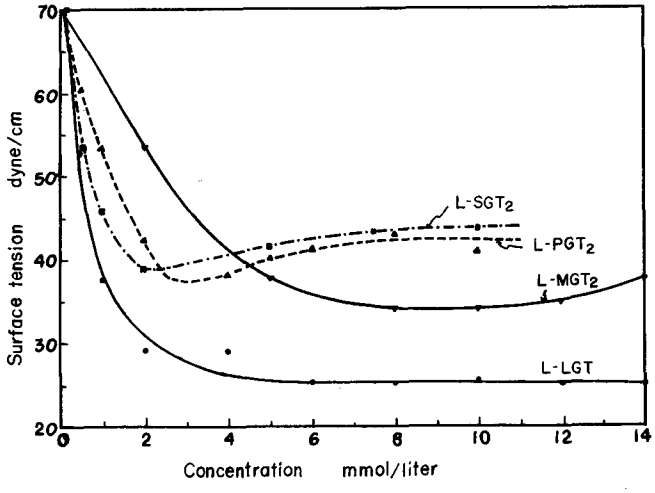

FIG. 6. Relation between surface tensions of triethanolamine N-acylglutamate (AGT_n) and concentration (at 40 C).

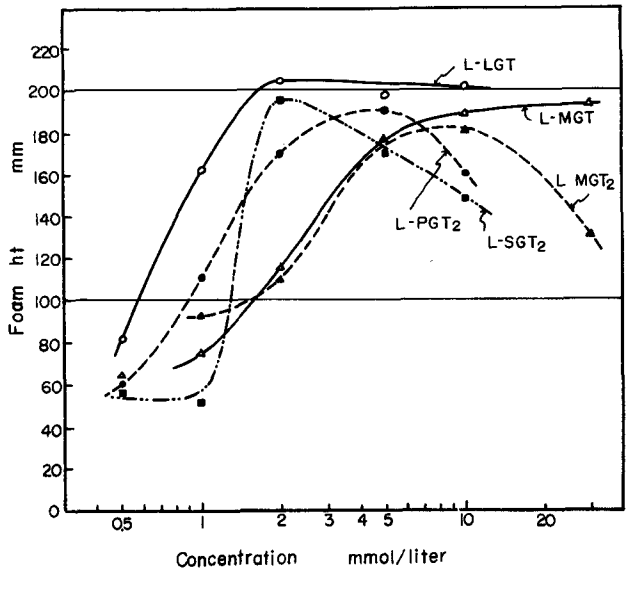

FIG. 7. Relation between foam ht and concentration (at 40 C, value after 5 min).

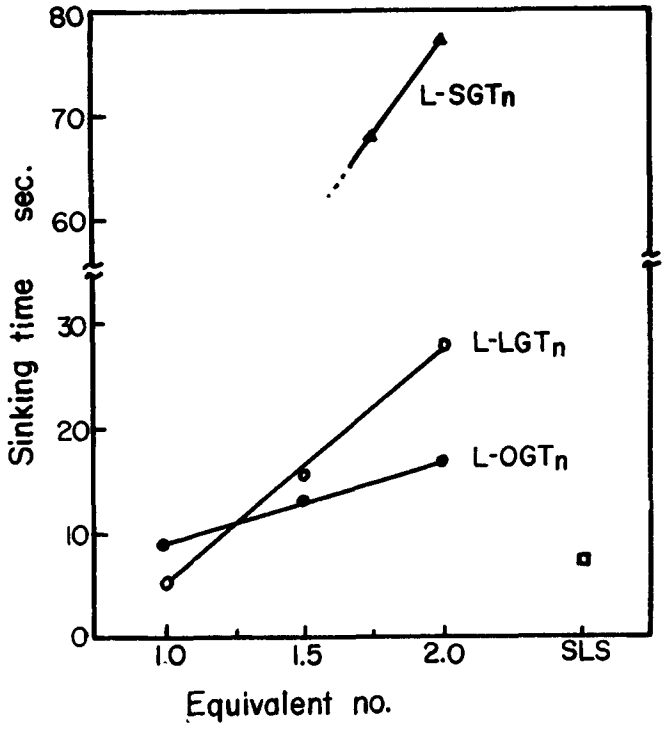

FIG. 8. Wetting powers. Relation between sinking time and equivalent number of triethanolamine salts (concentration 10 mmol/liter, at 40 C).

TABLE II

Foaming Property of Triethanolamine N-Acylglutamate[a]

Acyl[b]	Neutralization[c] equivalent	Foam ht, mm 0	5	30 min
L Series				
L	1.0	225	201	191
	1.5	217	194	182
	2.0	140	126	105
M	1.0	255	228	222
	1.5	210	180	154
	2.0	205	180	175
P	1.0	250	223	212
	1.5	226	193	192
	2.0	180	160	39
S	1.0	207	180	174
	1.5	195	167	159
	2.0	175	148	51
O	1.0	190	162	157
	1.5	210	183	101
	2.0	175	154	31
DL Series				
L	1.0	150	83	57
	1.5	160	148	142
	2.0	101	50	20
M	1.0	28	10	10
	1.5	230	202	190
	2.0	202	197	170
P	1.0	70	57	30
	1.5	185	52	20
	2.0	205	174	157
S	1.0	133	118	112
	1.5	207	175	164
	2.0	185	150	128
O	1.0	220	194	193
	1.5	200	178	166
	2.0	207	180	164
Comparison SLS[d]		205	186	181

[a]Concentration 10 mmol/liter at 40 C.

[b]L = lauroyl, M = myristoyl, P = palmitoyl, S = stearoyl, and O = oleoyl.

[c]1.0, monoequivalent salt; 1.5, sesquiequivalent salt; and 2.0, diequivalent salt.

[d]SLS = sodium lauryl sulfate.

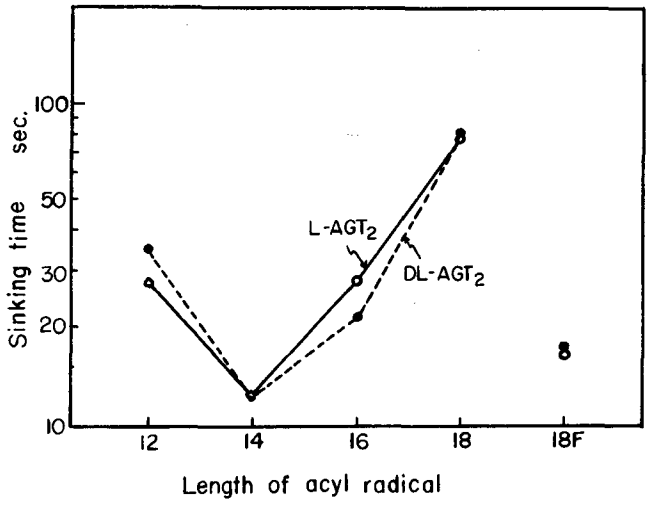

FIG. 9. Wetting power. Relation between sinking time and acyl length of ditriethanolamine N-acylglutamate (AGT_2) (concentration 10 mmol/liter, at 40 C).

TABLE III

Emulsion Stability of Toluene and Aqueous Solution of Triethanolamine N-Acylglutamate[a]

Acyl[b]	Neutralization equivalent	L-Series 5 min	L-Series 15 min	DL-Series 5 min	DL-Series 15 min
L	1.0	0.9	2.5	-	-
	1.5	1.9	4.5	1.6	4.0
	2.0	10.0	10.0	10.0	10.0
M	1.5	4.0	6.7	-	-
	2.0	6.6	8.3	5.7	7.9
P	2.0	7.1	8.6	6.9	8.6
S	2.0	7.3	8.8	7.5	8.8
O	1.0	3.9	6.7	2.1	5.5
	1.5	6.4	7.8	4.7	7.4
	2.0	7.2	8.6	6.5	8.3
Comparison					
SLS[c]		5.7	7.7		

[a]Concentration 10 mmol/liter at 40 C. Values indicate volume (ml) of aqueous solution separated from emulsion.

[b]L = lauroyl, M = myristoyl, P = palmitoyl, S = stearoyl, and O = oleoyl.

[c]SLS = sodium lauryl sulfate.

TABLE IV

Calcium Ion Stability of Triethanolamine N-Acylglutamate[a]

Acyl[b]	Neutralization equivalent	L-AGT_n	DL-AGT_n
L	1.0	531	-
	1.5	310	-
	2.0	158	188
M	2.0	124	138
P	2.0	348	385
S	2.0	164	264
O	1.0	244	284
	1.5	284	284
	2.0	323	284
Comparison			
SLS		2000	
Soap		Under 20	

[a]Concentration 10 mmol/liter at 40 C. Values indicate concentration (ppm) calculated as $CaCO_3$.

[b]L = lauroyl, M = myristoyl, P = palmitoyl, S = stearoyl, and O = oleoyl.

was observed: there was some difference for the CMC value between DL-AGT_2 and L-AGT_2.

Racemic AGT_2 indicated the CMC value larger than the corresponding optically active AGT_2. As is shown in Figure 4, a horizontal distance between the straight lines of L- and DL-AGT_2 was observed, the value of which corresponded to ca. 0.3 unit of carbon number of the acyl radical. It indicates that the use of racemate, instead of active form, effects lowering the hydrophobic property of the acyl radical. It has not been known that optical isomers of surfactants indicate different CMC values in their aqueous solutions.

Surface Tension

Surface tension of AGT_n was measured at the concentration of 10 mmol/liter by using Traube's stalagmometer at 40 C (8). Although some aqueous solutions of AGT and sesquiequivalent salts ($AGT_{1.5}$) were cloudy at 40 C, the measurement was made to the extent possible. Surface tension of L-AGT in 10 mmol/liter solution was measured at 50 C at which the L-AGT dissolved clearly. The results obtained are summarized in Figure 5. The monoequivalent salts showed the values lower than the corresponding diequivalent salts. In a series of L-AGT, L-LGT showed the smallest value, eq. 25.6 dyne/cm at 40 C. As the acyl length was longer, the value was larger. Since DL-AGT hydrolyzed easily and formed a suspension at the concentration of 10 mmol/liter, the values obtained did not show clear tendencies. In a series of AGT_2, ditriethanolamine N-myristoylglutamate showed the smallest value. The surface tensions of L-LGT and L-AGT_2 were measured at various concentrations, and the results are shown in Figure 6. These curves were relatively normal patterns, i.e. the values were minimal at the CMC and became larger at the lower concentrations.

Foaming Property

Foaming property was estimated by using the Ross-Miles method (9). The foam heights of AGT_n were measured at the concentration of 10 mmol/liter at 40 C and the results are summarized in Table II. The foaming power of AGT_n was somewhat better than that of the corresponding AGS_n, and the foam sizes were smaller. Especially, L-LGT and monotriethanolamine N-myristoyl-L-glutamate (L-MGT) had the excellent foaming powers and stabilities. DL-AGT hydrolyzed easily in the aqueous solution to liberate the crystals of free AGA, and the crystals broke the foams. Although the aqueous solutions of disodium salts of L-LGA and L-MGA hardly foamed, those of the corresponding L-LGT_2 and L-MGT_2 foamed well. The foams of L-AGT_2 seemed to be less stable than those of DL-AGT_2. The relations between the foaming powers and the concentrations of these AGT_n were measured with the soluble compounds at 40 C, and the values obtained are drawn in Figure 7. Each AGT_n had the best foaming power at the CMC and formed the most stable foams.

Wetting Power

As described previously, a wetting power was estimated from the time that a felt disk immersed in a test solution began to sink by its wt (10). The measurements were performed at the concentration of 10 mmol/liter and 40 C, and the results are shown in Figure 8 and 9. No large differences were observed in wetting powers between AGT and AGT_2. In a series of AGT_2, MGT_2 had the shortest sinking time among AGT_2, and these tendencies were identical with those of AGS_2.

Emulsifying Power

The emulsifying powers of AGT_n were estimated with the aqueous solutions of the concentration of 10 mmol/liter and toluene at 40 C (11). Each emulsion was made by inverting a test tube into which 10 ml oil and 10 ml test solution were added. After holding 5 and 15 min in a thermostat, the volume of the aqueous solution, separated from the emulsion, was measured. The results are summarized in Table III. The aqueous solutions of AGT_2 had almost equal

emulsifying powers to those of the corresponding AGS_2. L-LGT gave the best emulsion among AGT_n measured.

Calcium Ion Stability

In the previous report, it was described that the sodium salts (AGS_n), when tested at the concentration of 10 mmol/liter, were generally stable under the concentration of ca. 300 ppm calculated as $CaCO_3$. The calcium ion stabilities of the aqueous solutions of AGT_n were measured by the same method at the concentration of 10 mmol/liter at 40 C (6). A test solution (20 ml) was titrated with an aqueous solution of 0.1 mol/liter calcium chloride, and a point at which the solution became cloudy was determined. Then the amount of calcium ions in the resultant solution was indicated as the concentration (ppm) of calcium carbonate.

As summarized in Table IV, there were some differences in calcium ion stabilities between L-series and DL-series. The DL-series showed the values better than the L-series. L-LGT and L-PGT_2 showed the best stability to calcium ions among AGT and AGT_2, respectively. In general, AGT_n could be used with water having a hardness of 200-300 ppm calculated as $CaCO_3$.

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