Surface Active N-Acylglutamate: II. Physicochemical Properties of Long Chain N-Acylglutamic Acids and Their Sodium Salts

MASAHIRO TAKEHARA, HIROFUMI MORIYUKI, IPPEI YOSHIMURA, and RYONOSUKE YOSHIDA, The Central Research Laboratories of Ajinomoto Co., Inc., Suzuki-cho, Kawasaki, Japan

ABSTRACT

The physicochemical properties of long chain N-acylglutamic acids (AGA) and their sodium salts (AGS_n) are described. The solubility, Krafft point, pH value, critical micelle concentration, surface tension and foaming power were measured. The properties of the optically active AGA or AGS_n differed from those of the corresponding racemates, especially in solubility. The monosodium salts generally had high Krafft points, but monosodium N-oleoylglutamate had a low Krafft point. The monosodium salts hydrolyzed in the diluted aqueous solution to liberate the AGA. The aqueous solutions of the monosodium salts had low surface tensions and good foaming properties. The disodium salts were highly soluble in water, while surface tensions and foaming properties were inferior to those of the corresponding monosodium salts.

INTRODUCTION

The salts of long chain N-acylamino acids have been known as surface active agents, however they have not been used commercially except for a few compounds, e.g., sodium N-acylsarcosinate. Long chain N-acyl derivatives of glutamic acid, one of the most popular amino acids, have also been recognized as having surface activities. Kester (1) reported that the salts of long chain N-acylglutamic acids could be used as wetting agents, foaming agents or detergents. Fieser et al. (2) examined an emulsifying property of N-stearoyl-L-glutamic acid in a series of synthetic emulsifying agents. Komatsu et al. (3) described in their patent that the salts of long chain N-acylglutamates had good detergencies and protected the human skin from the irritation caused by sodium alkylbenzene sulfonate or sodium lauryl sulfate when used as the mixture. Moreover,

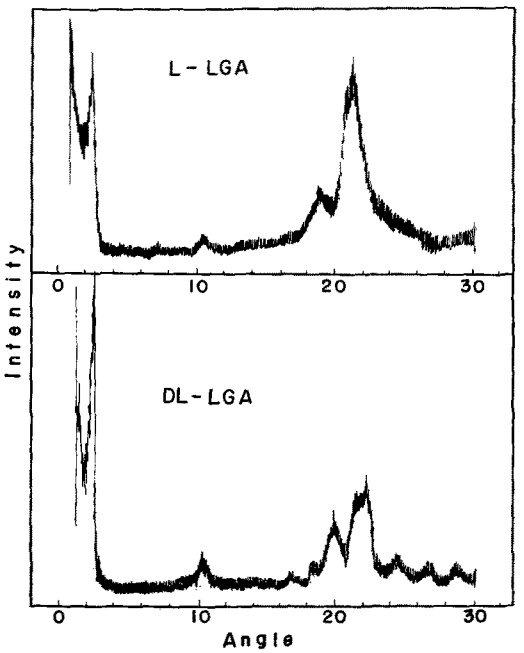

FIG. 1. X-ray diffraction spectra of N-lauroyl-L-glutamic acid (L-LGA) and N-lauroyl-DL-glutamic acid (DL-LGA).

TABLE I

Analyses of N-Acylglutamic Acids

Acyl	Distribution of acyl radical, C_n %	Average molecular weight	Fatty acids, % content	Neutralization equivalence, %	Melting point, C	Optical rotation $[\alpha]_D^{20}$ [a]
L Series						
L	8-0.1 10-0.1 12-97.3 14-2.5	330.1	0.85	100.4	101-104	-10.5
M	10-0.1 12-1.8 14-97.8 16-0.3	357.0	0.15	95.7	106-109	-10.3
P	12-1.7 14-0.4 16-97.9	384.5	0.20	93.0	111-114	-7.0
S	18-99.0 18F-1.0	413.2	0.85	100.1	114-116	-6.3
O	18F-97.8 $18F_2$-2.2	411.5	0.52	98.4	87-91	-5.8
DL Series						
L	8-1.4 10-0.6 12-95.0 14-3.0	329.3	0.20	98.5	116-119	
M	12-3.5 14-93.6 16-2.9	357.3	0.60	99.1	117-120	
P	12-0.6 14-0.9 16-98.5	384.2	0.05	98.3	125-128	
S	18-99.0 18F-1.0	413.2	0.55	100.0	128-129	
O	18F-98.0 $18F_2$-2.0	411.5	1.64	99.8	104-107	

[a]Measured in methanol solution.

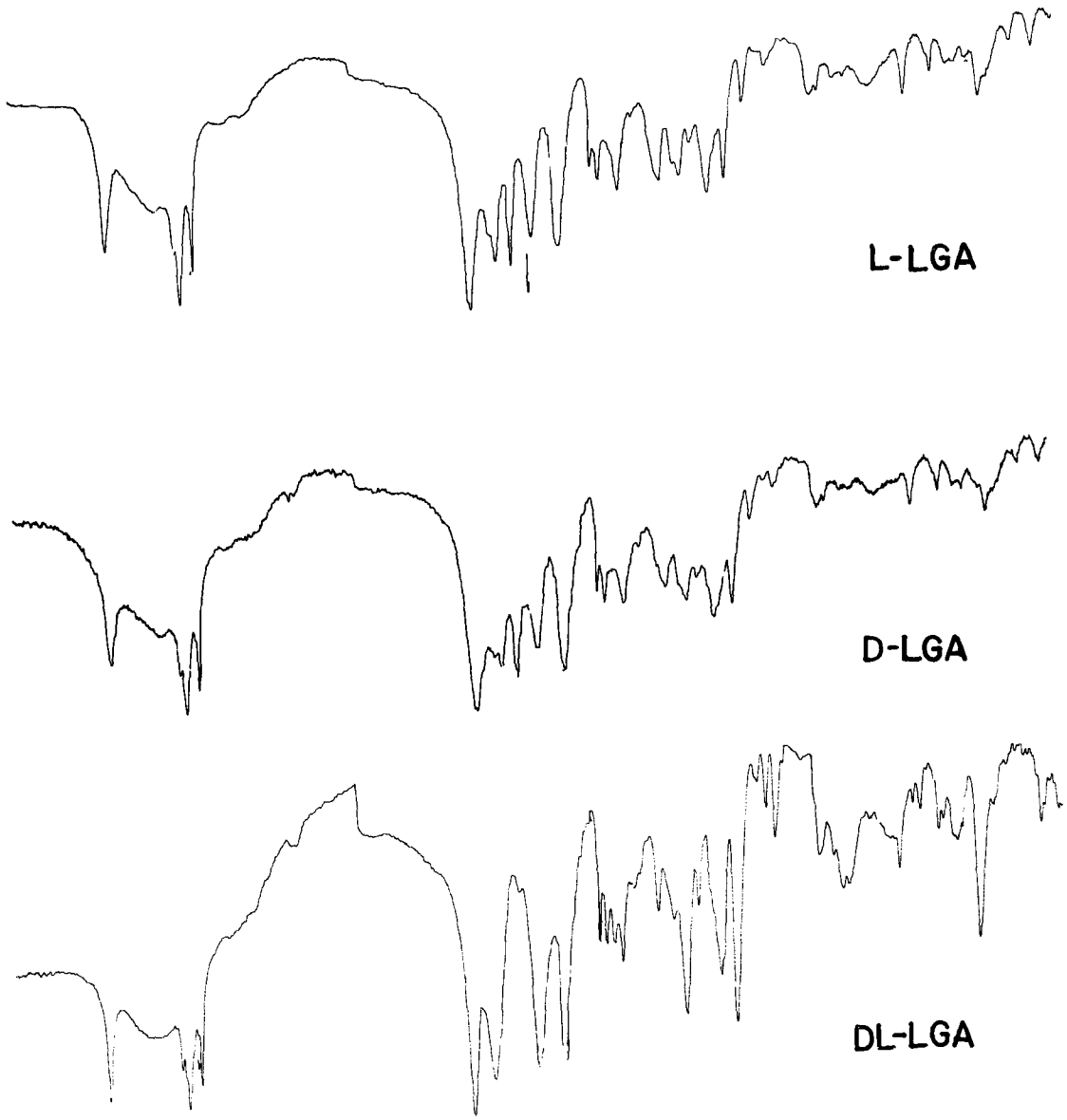

FIG. 2. Infrared spectra of N-lauroyl-L-glutamic acid (L-LGA), N-lauroyl-D-glutamic acid (D-LGA), and N-lauroyl-DL-glutamic acid (DL-LGA).

Fosdick et al. (4) examined the anticaries action of N-stearoylglutamic acid as one of many compounds. Ueda et al. (5,6) described an antivirus action of N-acylglutamic acid. There is also a patent that piperazine salt of N-acylglutamic acid can be used as a low toxic anthelmintic (7). Recently Shimizu and Narui (8) suggested that long chain N-acylglutamic acids had antibacterial actions.

In part I of this report, the authors reported that the long chain N-acylglutamic acids could be prepared by the condensation of glutamic acid and chlorides of higher fatty acids in the presence of a base in high yields. The results of the analyses of the N-acylglutamic acids are shown in Table I. In this report, the physicochemical properties of sodium long chain N-acylglutamates are systematically described.

TABLE II

Solubilities of N-Acylglutamic Acid (AGA)[a,b]

Solvent \ AGA	L Series			DL Series		
	L	O	S	L	O	S
Water	PS	GC	I	I	I	I
Methanol	S	S	S	S	S	S
Ethanol	S	S	S	S	S	S
Petroleum benzine	I	I	I	I	I	I
Ethyl acetate	S	S	I	I	S	I
Benzene	I	I	I	I	I	I
Acetone	S	S	PS	S	S	PS
Ethyl ether	I	S	I	I	S	I
Tetrahydrofuran	S	S	S	S	S	S
Dioxane	S	S	S	S	S	S
Dimethyl sulfoxide	S	S	S	S	S	S
Dimethyl formamide	S	S	S	S	S	S
Acetic acid	S	S	S	S	S	S
Pyridine	S	S	S	S	S	S

[a]Measured at 40 C, except ethyl ether at 30 C; concentration 1%.

[b]S, soluble; PS, partially soluble; I, slightly soluble or insoluble; G, gelatinous; C, cloudy.

ABBREVIATIONS

N-acylglutamic acid and its sodium salts are abbreviated as follows:

Acyl radicals: L, lauroyl; M, myristoyl; P, palmitoyl; S, stearoyl; O, oleoyl.

N-Acylglutamic acid (AGA): GA meaning glutamic acid is suffixed to the abbreviation of the acyl radical. For example: LGA, N-lauroylglutamic acid; MGA, N-myristoylglutamic acid.

Sodium salts: The following abbreviations are suffixed to that of acylglutamate (AG): S_n, sodium salt; S, monosodium salt; $S_{1.5}$, sesquisodium salt; S_2, disodium salt. For example: LGS, monosodium N-lauroylglutamate; AGS_n, sodium N-acylglutamate.

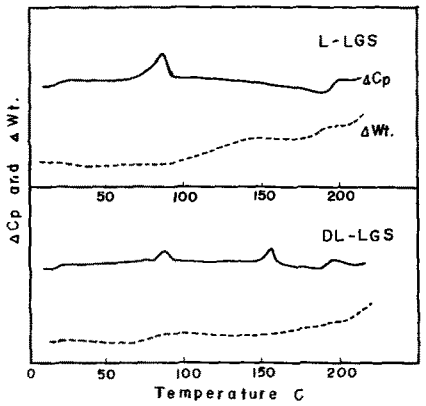

FIG. 3. Differential thermal analysis (DTA) curves of monosodium N-lauroyl-L-glutamate (L-LGS) and monosodium N-lauroyl-DL-glutamate (DL-LGS).

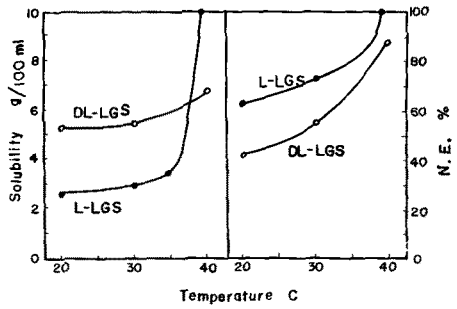

FIG. 4. Solubility and neutralization equivalence (NE) of monosodium N-lauroyl-L-glutamate (L-LGS) and monosodium N-lauroyl-DLglutamate (DL-LGS) (concentration 10 g/100 ml water).

Optical isomer of glutamate: The following prefixes are added to the abbreviation of the corresponding glutamate: L-, L-isomer; D-, D-isomer; DL-, racemic compound. For example: L-LGS, monosodium N-lauroyl-L-glutamate.

Commercially available surfactants: SLS, sodium lauryl sulfate; SLS_a, sodium N-lauroylsarcosinate.

GENERAL PROPERTIES OF AGA

AGA generally occurs as white crystals and has a melting point of about 100 C, which is about 50 C higher than the corresponding fatty acid. An optically active AGA differs from a racemic AGA in physicochemical properties as the melting point of L-isomer is lower than that of the racemate.

The x-ray spectra (Fig. 1) show that the state of the crystals of L-isomer is more highly diffracted and looser than that of the crystals of the racemate. When the recrystallization of AGA is performed with a certain solvent, the crystals of the racemate are easily obtained while the crystals of the optically active AGA become gelatinous by inclusion of the solvent. The IR spectra shown in Figure 2 indicate that the spectrum of L-isomer differs from that of the racemate especially in the IR absorptions of an acyl radical whereas that of D-isomer is equal to L-isomer. It may be expected from these results that the state of micelles in an aqueous solution of the salt of L-AGA will differ from that of the salt of the recemate.

The solubilities of AGA in water and some organic solvents were examined at 1% (w/v) concentration and the results are indicated in Table II. In water, DL-AGA is insoluble and the crystals come to the surface as so-called scums; however L-AGA and especially L-OGA have an affinity with water and the crystals become gelatinous in low concentration ranges. In organic solvents, the optically active compounds are more soluble than the corresponding racemic compounds and as the acyl radical becomes longer

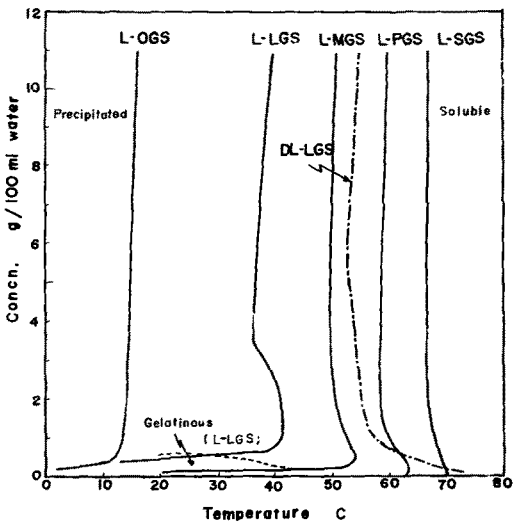

FIG. 5. Solubility-temperature curves of monosodium acylglutamate (AGS).

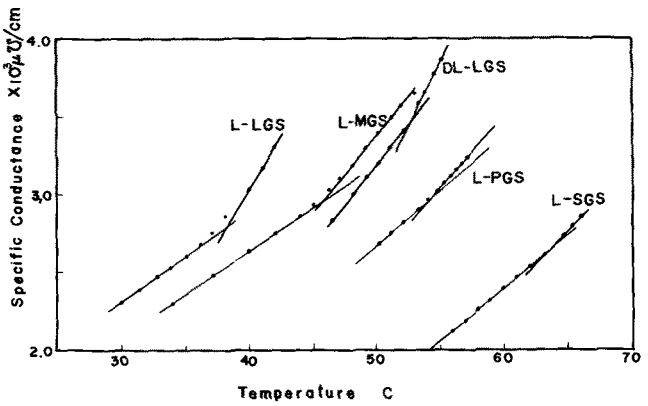

FIG. 6. Krafft points of monosodium acylglutamate (AGS). Relation between specific conductance of AGS aqueous mixture and temperature (concentration 50 mmoles/liter).

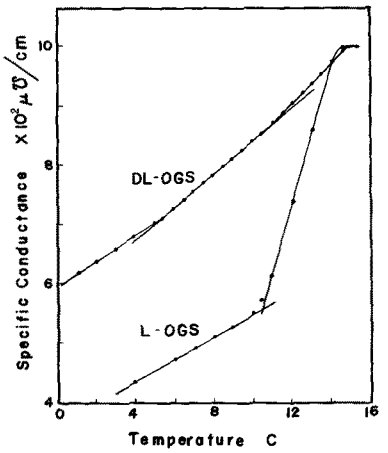

FIG. 7. Krafft points of monosodium oleoylglutamate (OGS). Relation between specific conductance of OGS aqueous mixture and temperature (concentration 50 mmoles/liter).

AGA becomes less soluble. The unsaturated acyl compounds such as L-OGA are more soluble than the saturated acyl compounds.

PREPARATION OF SALTS OF AGA

AGA is a dibasic acid having two carboxyl radicals in a molecule and it is possible to obtain the various equivalent

TABLE III

Krafft Points (KP) and Clear Points (CP) of Monosodium Salts of N-Acylglutamic Acids (AGS)[a]

L-AGS	KP, C	CP, C	DL-AGS	KP, C	CP, C
L-LGS	38.1	42.0	DL-LGS	52.9	56.4
L-MGS	45.8	50.5	DL-MGS	---	63.7
L-PGS	54.2	58.3	DL-PGS	---	68.0
L-SGS	62.5	66.0	DL-SGS	---	74.5
L-OGS	10.5	14.2	DL-OGS	11.3	15.0

[a]Concentration 50 mmoles/liter.

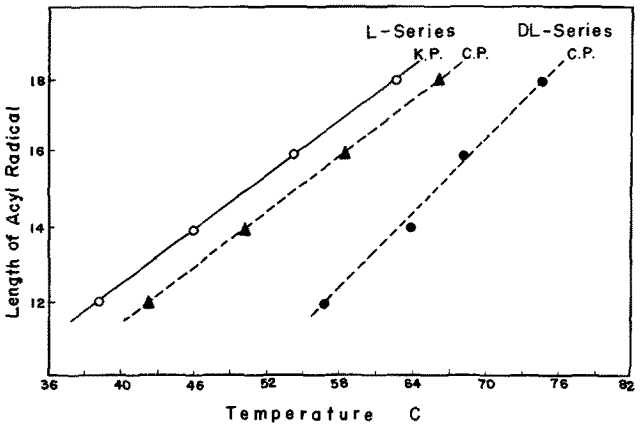

FIG. 8. Krafft point (KP) and clear point (CP) of monosodium acylglutamate (AGS) and number of carbon atoms in acyl radical (concentration 50 mmoles/liter).

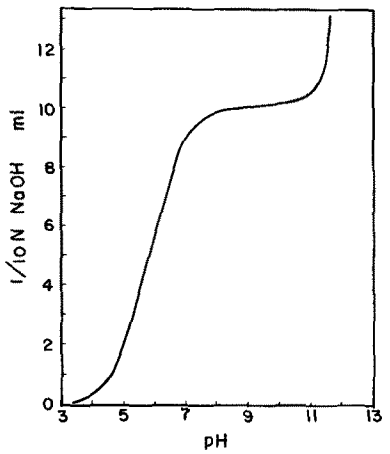

FIG. 9. Neutralization equivalence curve of N-lauroyl-L-glutamic acid (L-LGA) (concentration 0.5 mmole/10 ml methanol).

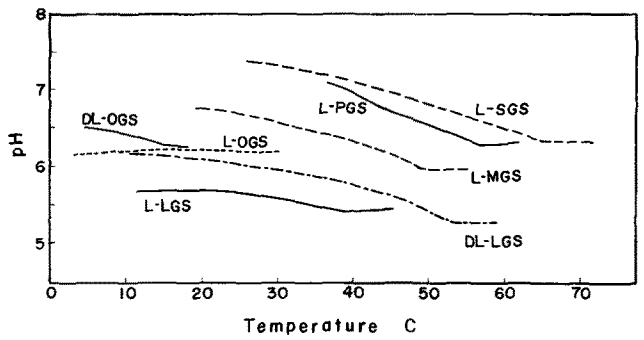

FIG. 10. Relation between pH of monosodium acylglutamate (AGS) aqueous mixture and temperature (concentration 50 mmoles/liter).

salts such as mono-, sesqui-, and di-equivalent salts. To prepare crystals of AGS_n the following method is employed: An alcoholic solution of AGA is neutralized with a calculated amount of alcoholic sodium methoxide or concentrated aqueous sodium hydroxide and the crystals precipitated by adding a large amount of acetone are filtered off. When the mother liquor is concentrated and acetone is added to the concentrate, additional crystals are obtained. The disodium salts could be obtained homogeneously by this method; however the monosodium salts, especially the salt that is highly soluble in alcohol, could not be obtained as homogeneous crystals because of a disproportional reaction of AGS. Namely, the crystals obtained contain disodium salts and have a neutralization equivalence value lower than the calculated value, while the additional crystals obtained from the mother liquor have a higher neutralization equivalence value because of the existence of unneutralized AGA. In order to prepare the homogeneous powders of AGS_n, the aqueous solution of AGS_n prepared by neutralization of AGA with a calculated amount of aqueous sodium hydroxide must be evaporated to dryness by using a spray dryer. When an appointed concentration of the aqueous solution of AGS_n is prepared, a standard amount of AGA may be dissolved in a calculated volume of an alkaline solution.

The sodium salt generally decomposes above 200 C without melting. The results of differential thermal analyses (DTA) of L-LGS and DL-LGS showed there was little phase transition (Fig. 3).

SOLUBILITIES AND KRAFFT POINTS

An ionic surfactant has a generally low aqueous solubility at low temperatures and micelles are not formed. As the temperature is raised the solubility slowly rises, and at a temperature known as the Krafft point the aqueous solubility increases rapidly and the micelles are formed at a concentration called the critical micelle concentration (CMC). To estimate the aqueous solubilities of AGS_n, the saturation solubilities of L-LGS and DL-LGS were first measured by a generally known method. An aqueous mixture containing an excess surfactant in a 100 ml test tube was stirred at a constant temperature for 6 hr and the supernatant solution was pipetted off with a cotton plugged pipette. The solution, after being weighed, was evaporated to dryness and the dissolved surfactant was measured. A curious phenomenon was observed: when the amount of L-LGS or DL-LGS added in water was varied, the value of the saturation solubility also varied greatly. And the constant value could not be obtained. To avoid this variation, the saturation solubility of L-LGS and DL-LGS was measured in an aqueous mixture of an appointed concentration (10 g AGS/100 ml water) and at the same time the neutralization equivalence of the dissolved AGS was measured. It was found as shown in Figure 4 that L-LGS and DL-LGS had comparatively good solubilities even at lower temperatures, however the neutralization equivalences of the dissolved AGS showed values lower than the calculated values. As the temperature was raised

TABLE IV

Critical Micelle Concentration (CMC) of Sodium Salts of N-Acylglutamic Acids (AGS_n)

Samples	CMC, mmoles/liter: By conductivity method	By dye method	Temperature, C
L-LGS	10.6	---	40
L-MGS	7.2	6.2-6.4	60
L-PGS	5-6	5.0	60
L-OGS	---	3.3	40
DL-LGS	10.6	---	60
DL-OGS	---	3.8	40
$L\text{-}MGS_2$	21	---	40
$L\text{-}PGS_2$	9.8	---	40
$L\text{-}SGS_2$	4.5	---	40
$L\text{-}OGS_2$	---	5.2-5.9	40

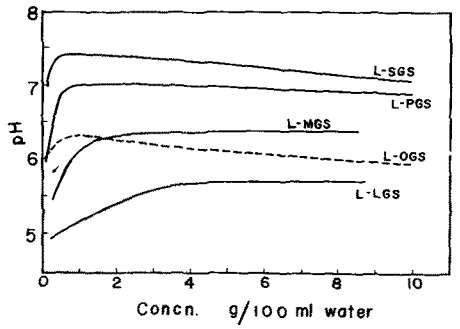

FIG. 11. Relation between pH and concentration of monosodium acylglutamate (AGS) (at 40 C).

the solubilities increased and the values of neutralization equivalence were larger, and at the temperature at which the salts completely dissolved the values became equal to the calculated values. These phenomena can be explained in terms of the hydrolysis of AGS. That is, AGS partially hydrolyzes to AGA and sodium hydroxide in an aqueous solution and the resultant AGA precipitates as crystals. On the other hand, sodium hydroxide is neutralized with AGS to form AGS_2 which is highly soluble in water.

$$2H^+[{}^-OOCCH_2CH_2\underset{\displaystyle NHCOR}{\underset{|}{C}}HCOO^-]\,Na^+ \longrightarrow$$

$$HOOCCH_2CH_2\underset{\displaystyle NHCOR}{\underset{|}{C}}HCOOH + NaOOCCH_2CH_2\underset{\displaystyle NHCOR}{\underset{|}{C}}HCOONa$$

The following experiment was carried out to obtain the solubility-temperature curve of AGS. An increasing amount of crystalline AGS and a standard volume (20 ml) of water were mixed into a number of test tubes. The tubes were gently agitated in a thermostat. The temperature was raised gradually (about 1 C per day) and, for each tube, the temperature was noted at which the mixture became a clear solution. The obtained temperature-solubility curves of AGS are shown in Figure 5. In a series of L-AGS, a curious kink was observed on each curve at some concentrations and those L-AGS became thixotropic or gelatinous solutions at low concentrations. The curve of the racemic compound DL-LGS was more curious; that is, when the concentration of the surfactant became lower, precipitates appeared from the clear solution and it was found that the precipitates were mainly crystals of AGA.

These unusual curves are caused by the hydrolysis of AGS as mentioned above and the difference between the solubility curves of L-AGS and of DL-AGS may be derived from the difference of the solubilities of the precipitated AGA. DL-AGA liberated by the hydrolysis is entirely

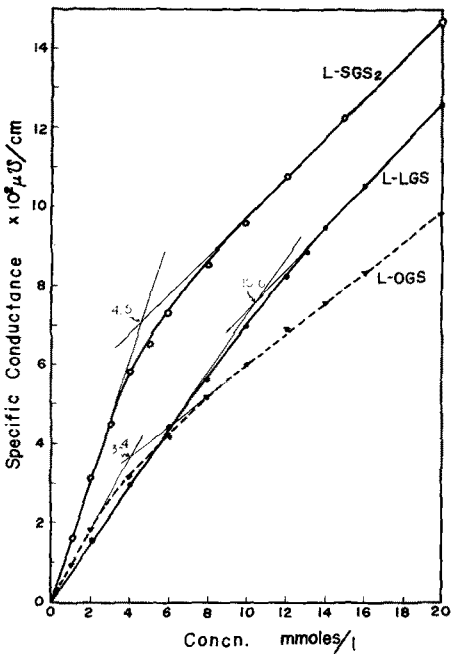

FIG. 12. Relation between specific conductance and concentration (at 40 C).

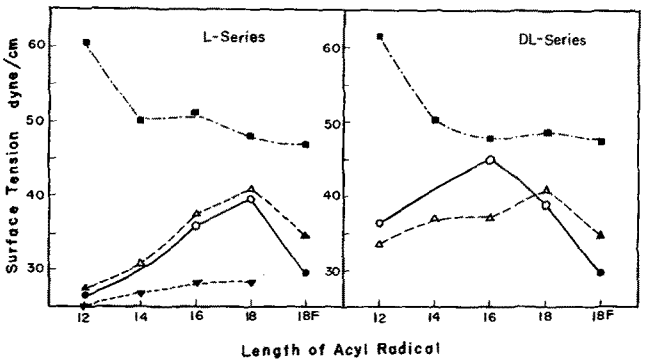

FIG. 13. Surface tensions of sodium N-acylglutamate (AGS_n) (concentration 10 mmoles/liter at 40 C) —●—; monosodium acylglutamate (AGS) —▲—; sesquisodium acylglutamate ($AGS_{1.5}$) —■—; disodium acylglutamate (AGS_2) ●, ▲, ■, soluble, ○, △, □, cloudy; -▼-, surface tensions of sodium L-acylglutamate (L-AGS) measured at 70 C.

insoluble in water and precipitates at the lower concentrations even at temperatures above the Krafft point. As the concentration increases, the precipitates are solubilized by the dissolved AGS and as a result the mixture becomes a clear solution. On the other hand, L-AGA liberated by the hydrolysis is soluble or gelatinous in water at the lower concentrations and the aqueous solution of the L-AGS becomes clear or gelatinous. However, as the concentration becomes higher at a few degrees above the Krafft point, the L-AGA liberated begins to precipitate. At the higher concentrations the precipitating L-AGA is solubilized again by the dissolved AGS to become a clear solution. L-OGS hardly hydrolyzed because the L-OGA had an affinity with water and the normal solubility curve was obtained.

Krafft points of AGS were determined by electric conductivity method (9), although those values could be estimated from the solubility-temperature curves referred to above. A standard amount (50 mmoles) of surfactant and 50 ml of water are added to a test tube (35 mm^{ϕ} x 130 mm^{h}) and the mixture is dissolved by heating. The solution obtained is cooled in a water bath to recrystallize and a conductivity measuring cell is immersed in the tube. The tube is warmed gradually with stirring (about 1 C per min)

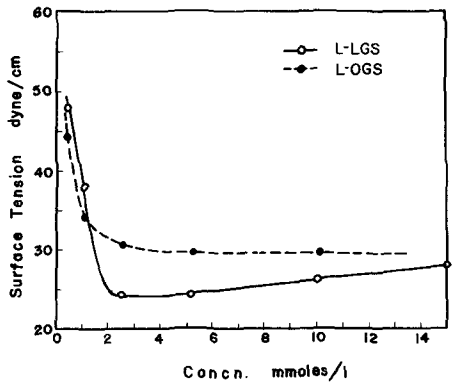

FIG. 14. Relation between surface tension of monosodium N-lauroyl-L-glutamate (L-LGS) monosodium N-oleoyl-L-glutamate (L-OGS) and concentration (at 40 C).

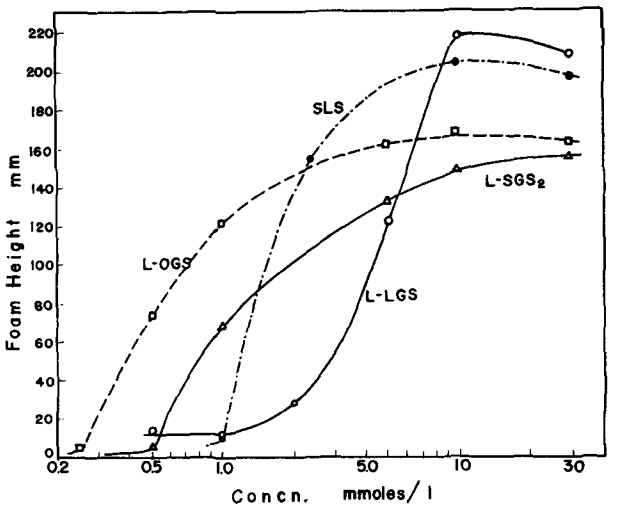

FIG. 15. Relation between foam height and concentration (at 40 C, value after 5 min).

and the specific electric conductivities are continuously measured. At the Krafft point the specific electric conductivities begin to change sharply upwards because of the rapid increase in solubility. When the values of the specific conductance are plotted against increasing temperature, a curve having an abrupt inflection at the Krafft point is generally obtained. The curves measured in this way are shown in Figures 6 and 7.

The curve of L-OGS showed a typical pattern and the Krafft point could be exactly measured. However, the other AGS had relatively high specific conductances in low temperature ranges and each curve obtained showed only a small inflection at the Krafft point, which was a few degrees below the clear point at which the surfactant dissolved completely. It seems that sodium ions which make a great contribution to the electric conductivity exist in large quantities in water even at low temperatures because of the hydrolysis of AGS. L-OGS hardly hydrolyzed in the aqueous solution and had a curve having an abrupt inflection. The electric conductivities of DL-AGS could not be exactly measured because of the extensive hydrolysis and only the clear points were observed. The results obtained are shown in Table III and the relation between the Krafft point and the clear point of AGS and the length of an acyl radical in AGS are shown in Figure 8. AGS_2 was sufficiently soluble in water even at 0C, that is it had a Krafft point under 0 C.

Sodium salts of AGA were generally insoluble in organic solvents, with the exception of alcohol.

pH VALUES

A Neutralization equivalence curve of L-LGA was first determined. One mmole of L-LGA was dissolved with 20 ml of methanol and the pH values of the solution were continuously measured under a gradual addition of 1/10N sodium hydroxide at room temperature. The pH value as a function of the added 1/10N sodium hydroxide is shown in Figure 9. In the aqueous solution the disodium salts showed a pH of 8-9 which was the same value as a sodium salt of carboxylic acid. The monosidum salt when dissolved showed pH 5-6.5 and had the buffer capacity of an unneutralized carboxylic acid.

When the pH values of an aqueous mixture containing 50 mmoles/liter of AGS were continously measured under a gradually increasing temperature, pH-temperature curves shown in Figure 10 were obtained. The aqueous mixture of AGS showed lowering pH values as the temperature was increased and constant pH values at temperatures over the clear point.

The relation of pH-concentration was also measured and the results are shown in Figure 11. When the concentration of AGS was increased, the aqueous mixture of L-LGS or L-MGS showed increasing pH, with L-OGS, L-PGS, or L-SGS showing the maximum pH at about 1% concentration.

CRITICAL MICELLE CONCENTRATION

The critical micelle concentrations (cmc) of AGS and AGS_2 were estimated by a conductivity method (10) and a dye method (11). When specific electric conductivities are plotted against the various concentrations of an aqueous solution, two extrapolated straight lines are obtained and the concentration of the intersection is defined as the cmc. The dye method is as follows: When rhodamine 6G used as a dye is added in an aqueous solution of an anionic surfactant the solution becomes orange in color and fluorescent above the cmc. As the solution is diluted at the constant dye concentration the color changes to red and the fluorescence disappears at the cmc. The specific conductances of the aqueous solutions of AGS and AGS_2, especially L-PGS, L-OGS, or DL-OGS having a low cmc, showed gentle changes at the cmc and it was difficult to estimate the exact cmc (Fig. 12). In the dye method, color changes were also gentle and the exact cmc could not be obtained.

The cmc values that were obtained are listed in Table IV. The following relationship between cmc value and length of the acyl radical of AGS_2 was obtained:

$$\log (\text{cmc}) = 3.70 - 0.159\ N$$

where N is the carbon number of an acyl radical.

SURFACE TENSIONS

For a comparison of the surface activities among the various AGS_n, surface tensions of the aqueous solutions were first measured. The measurements of the surface tensions were performed in an aqueous solution (10 mmoles/liter by using a stalagmometer at 40 C (12). Although some compounds did not dissolve completely, the measurements were performed to the extent possible. The surface tensions of AGS in 10 mmoles/liter solutions were measured at 70 C at which the AGS dissolved clearly. The values obtained are shown in Figure 13. The surface tension of the aqueous solution of L-LGS was 26.4 dyne/cm at 40 C and lower than that of SLS (32.0 dyne/cm) and SLS_a (40.8 dyne/cm). In a series of monosodium salts, as the acyl radicals became longer the surface tensions became larger. The values of the disodium salts were less than those of the monosodium salts, especially for LGS_2 which had hardly

TABLE V

Foaming Properties of Sodium Salts of N-Acylglutamic Acids (AGS_n)[a]

Acyl	Neutralization equivalence	Foam height, mm			Foam stability, %
		0	5	30 min	
L Series					
L	1.0	250	219	212	84.8
	1.5	225	194	178	79.1
	2.0	40	10	0	0.0
M	1.0	235	212	211	89.8
	1.5	220	195	183	83.2
	2.0	140	10	0	0.0
P	1.0	205	176	170	82.8
	1.5	190	165	143	75.3
	2.0	195	42	21	10.8
S	1.0	165	139	137	83.1
	1.5	160	140	130	81.3
	2.0	175	149	147	84.0
O	1.0	188	169	164	87.2
	1.5	202	177	153	75.7
	2.0	167	142	125	74.8
DL Series					
L	1.0	50	42	35	75.0
	1.5	112	101	95	84.8
	2.0	35	10	0	0.0
M	1.0	35	31	26	74.3
	1.5	185	160	150	81.1
	2.0	45	35	28	62.2
P	1.0	170	145	144	84.7
	1.5	195	171	160	82.0
	2.0	165	137	107	64.9
S	1.0	172	160	147	85.5
	1.5	173	153	145	83.8
	2.0	150	140	125	80.0
O	1.0	202	168	159	78.7
	1.5	177	161	155	87.6
	2.0	170	141	120	70.7
Comparison					
SLS		205	186	181	88.3
SLS_a		167	141	120	71.8

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

any surface activity. In a clear solution there was little difference between the L-series and DL-series, but there was a difference in solutions in which the surfactant did not dissolve completely. This may only be due to the difference in solubility between the L-series and DL-series.

The surface tensions of the aqueous solutions of L-LGS and L-OGS were measured for the various concentrations. The curves obtained are shown in Figure 14. As the aqueous solution of L-LGS was diluted the surface tension decreased gradually and did not increase even at the concentrations below the cmc. At the concentration of about 2 mmoles/liter a minimum surface tension was obtained and in the lower concentration ranges the values became larger. This is due to hydrolysis of L-LGS and liberation of L-LGA whose hydrophobic molecules come to the aqueous surface, causing the surface tension to decrease even at the lower concentrations. The aqueous solution of L-OGS had a comparatively normal curve.

FOAMING PROPERTIES

Foaming powers and stabilities were measured by the Ross-Miles method at 40 C (13). Foaming heights were recorded immediately (A), after 5 min (B), and after 30 min (C). The foaming power was represented as (A) or (B) and the foam stability (FS) was represented by the following formula (14):

$$FS\% = \frac{A - C}{A} \times 100$$

The measurements were carried out at the concentration of 10 mmoles/liter at which, however, a number of compounds did not dissolve completely. The results are summarized in Table V. In a series of the optically active compounds, mono- and sesqui-sodium salts had good foaming powers and stabilities at 10 mmoles/liter concentration, and as the acyl radicals became longer the foaming powers decreased while the foam sizes became fine. In the case of DL-LGS and DL-MGS, scumlike crystals of AGA were liberated from the solution and broke the foams.

The relation between foaming power and concentration of AGS_n were evaluated with some soluble compounds (L-LGS, L-SGS_2 and L-OGS). The curves obtained when the foaming powers were plotted against the logarithm of the concentration are shown in Figure 15. The foaming powers of AGS were generally less than those of AGS_2 at the extremely low concentrations. When the aqueous solution of L-LGS was diluted the foaming power fell rapidly and became zero at about 1 mmole/liter concentration. The concentration at which foams began to form largely was defined as the critical foam concentration (cfc) (15). The cfc of L-SGS_2 and L-OGS was 0.5 mmole/liter and 0.25 mmole/liter respectively, while the cfc of SLS was about 1.0 mmole/liter.

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