· Technical

Surface Active N-Acylglutamate: III. Physicochemical Properties of Sodium Long Chain N-Acylglutamates

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ABSTRACT

The physicochemical properties of sodium long chain N-acylglutamate (AGS_n) are described. The wetting power, emulsifying power, dispersing power and calcium ion stability were measured. Monosodium N-lauroyl-L-glutamate (L-LGS) had good wetting and emulsifying properties, but disodium N-acylglutamate (AGS_2) was inferior to L-LGS in those properties. In the dispersing power using carbon black as powder, L-LGS was inferior but AGS_2, having a palmitoyl or stearoyl radical, was excellent. The AGS_n with a few exceptions had good calcium ion stabilities.

INTRODUCTION

The salts of long chain N-acylglutamic acids are excellent surface active agents derived from the amino acid. They are synthesized by condensation of glutamic acid with long chain fatty acid chloride, followed by neutralization of the condensation product with alkalies (1).

In part II of this report (2), the physicochemical properties of N-acylglutamic acids (AGA) and their sodium salts (AGS_n) were described. Some differences, especially in solubility, were shown between optically active and racemic AGA or AGS_n. The monosodium salt (AGS) generally had a high Krafft point and hydrolyzed in the diluted aqueous solution to liberate the corresponding acid. Of AGS tested, monosodium N-lauroyl-L-glutamate (L-LGS) and monosodium N-oleoyl-L-glutamate (L-OGS) showed the highest surface activity. The disodium salts (AGS_2) were highly soluble in water but inferior in their lowering power of surface tension and foaming power, compared with those of the corresponding AGS. In this report the physicochemical properties of sodium N-acylglutamate, such as wetting power, emulsifying power, dispersing power and calcium ion stability, are described further. The abbreviations of AGS_n were described in the previous report.

METHODS AND RESULTS

Wetting Power

The wetting powers of AGS_n were estimated by a horizontal semimicro felt disk method (3). Each 50 ml aqueous solution of a surfactant was added to a beaker (42 mm^{Φ} x 65 mm^h). A felt disk (Nikke's roller cloth 20 oz, 1 $in.^{\Phi}$, 2 mm thick, ca. 0.45 g) was forced to immerse in the solution by using an inverted gooch filter funnel (34 mm^{Φ}), and the time that the disk began to sink was measured. In a surfactant solution with wetting property, the disk began to sink in a moment since the solution penetrated rapidly into the disk. The times measured in the 10 mmol/liter aqueous solution at 40 C are plotted in Figures 1 and 2. The AGS_n tested were limited to the soluble ones at the concentration of 10 mmol/liter at 40 C.

AGS had better wetting powers than the corresponding

TABLE I

Emulsion Stability of Toluene or Liquid Paraffin and Aqueous Solution[a]

Acyl[b]	Neutralization equivalent	Toluene				Liquid paraffin			
		L-AGS_n		DL-AGS_n		L-AGS_n		DL-AGS_n	
		Min				Min			
		5	15	5	15	5	15	5	15
L	1.0	0.7	1.8	2.1	3.7[c]	7.4	8.8	9.0	9.0[c]
	1.5	1.9	4.2	1.2	3.2[c]	7.7	8.7	9.6	9.7
	2.0	10.0	10.0	10.0	10.0	9.6	10.0	9.7	10.0
M	2.0	9.7	9.8	10.0	10.0	8.9	9.6	9.5	9.8
P	1.75	8.9	9.6	7.5	8.9	8.9	9.6	9.1	9.5
	2.0	9.0	9.6	8.7	9.5	9.0	9.6	9.5	9.7
S	2.0	8.3	9.3	8.5	9.3	9.3	9.6	9.0	9.5
O	1.0	2.6	5.8	2.4	5.7	7.9	9.2	7.4	8.8
	1.5	6.3	8.1	5.8	7.9	8.4	9.5	8.4	9.4
	2.0	9.1	9.7	8.1	9.1	8.7	9.6	9.0	9.6
SLS		5.5	7.7			9.1	9.7		
SLS_a		7.0	8.6			9.3	9.8		

[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; O, oleoyl.

[c] Sample used does not dissolve completely.

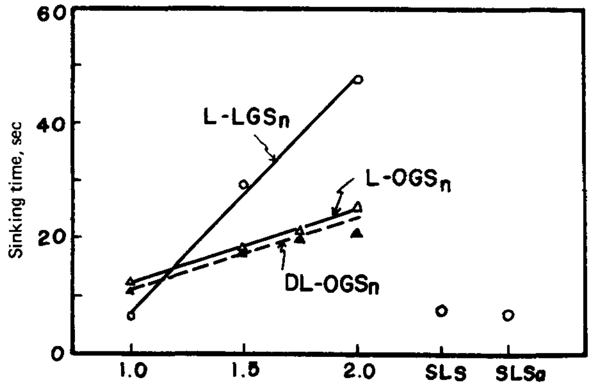

FIG. 1. Wetting powers. Relation between sinking time and equivalent number of sodium salts (concentration 10 mmol/liter, at 40 C).

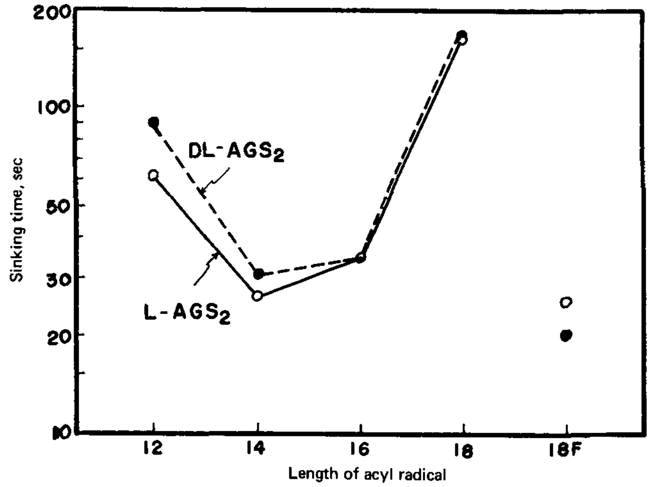

FIG. 2. Wetting powers of disodium N-acylglutamates (AGS_2). Relation between sinking time and length of acyl radical of AGS_2 (concentration 10 mmol/liter, at 40 C).

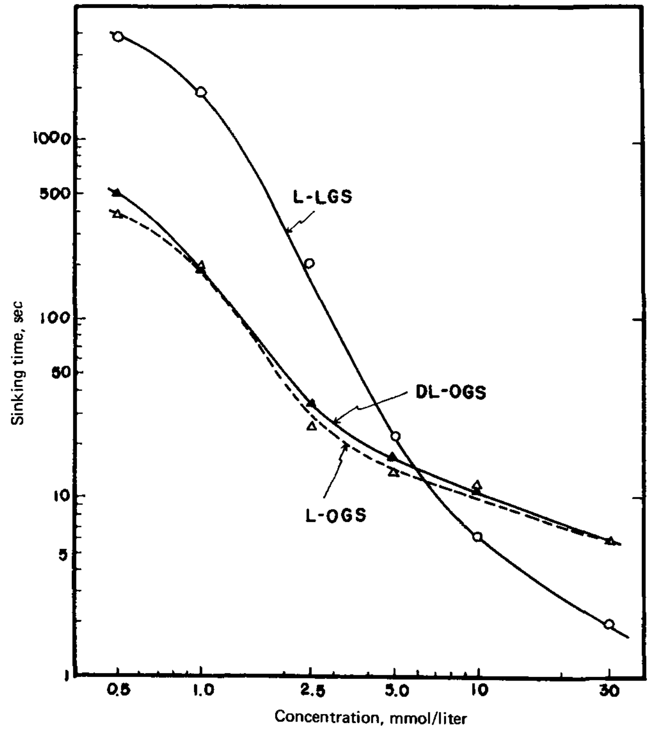

FIG. 3. Wetting powers. Relation between sinking time and concentration of monosodium N-acylglutamates (AGS) (at 40 C).

TABLE II

Emulsion Stability of Lanolin and Aqueous Solution[a]

	Volume of aqueous solution, ml	
	Min	
Samples	5	15
L-LGS	8.8	9.3
L-OGS	8.7	9.4
$L\text{-}OGS_2$	8.1	9.7
$L\text{-}SGS_2$	0.0	0.0
SLS	0.0	0.0
Soap	0.0	0.0

[a] Concentration 0.25%, at 60 C.

disodium salts (AGS_2); notably, the wetting power of L-LGS was equal to that of sodium lauryl sulfate (SLS) or sodium N-lauroylsarcosinate (SLS_a) (Fig. 1). In a series of disodium salts, disodium N-myristoylglutamate (MGS_2) had the shortest sinking time and AGS_2, having other longer or shorter acyl radicals, showed inferior values (Fig. 2). It seemed that there was little difference in wetting powers between the optically active and racemic forms of AGS_n. The relation between the wetting power and the concentration is shown in Figure 3 with L-LGS, L-OGS and DL-OGS. The wetting powers decreased with the dilution of the aqueous solutions below the critical micelle concentrations.

Emulsifying Power

The emulsifying powers of AGS_n were measured as follows (4). Ten milliliters of oil and 10 ml of a 10 mmol/liter aqueous test solution were added to a glass-stoppered test tube (10 mm^{ϕ} x 390 mm^{h}), and the test tube was quickly inverted 30 times at 40 C. The emulsion obtained was held at 40 C, and the volume of the aqueous solution separated from the emulsion layer was measured after 5 and 15 min. In these experiments, toluene, liquid paraffin or lanolin was used as oil.

Table I shows the experimental data of the emulsifying powers of the 10 mmol/liter aqueous solution of AGS_n with toluene or liquid paraffin. L-LGS gave the best emulsion with toluene and was more emulsive than SLS. AGS_2 were generally less emulsive than AGS. The tendency to emulsify liquid paraffin and water was almost equal with the case of toluene and water. Table II shows the results of tests similarly conducted using lanolin at 60 C. L-LGS, L-OGS and disodium N-oleoyl-L-glutamate ($L\text{-}OGS_2$) are less emulsive than SLS and soap, but disodium N-stearoyl-L-glutamate ($L\text{-}SGS_2$) is as emulsive as SLS and soap. The emulsifying properties of $L\text{-}SGS_2$ and soap are partially due

TABLE III

Dispersing Powers of Sodium N-Acylglutamates (AGS_n) Using Furnace Carbon Black[a,b]

Acyl	Equivalent	$L\text{-}AGS_n$	$DL\text{-}AGS_n$
L	1.0	0.92 (5.0)	---
	1.5	1.11 (5.4)	---
	2.0	0.41 (7.2)	0.49 (7.0)
M	2.0	1.22 (8.0)	0.68 (7.3)
P	2.0	9.75 (9.8)	9.06 (9.1)
S	2.0	6.54 (8.3)	6.05 (8.6)
O	1.0	1.40 (6.1)	1.10 (6.0)
	1.5	1.75 (7.0)	1.65 (6.7)
	2.0	3.65 (8.6)	3.42 (7.8)
SLS		2.17 (6.8)	
SLS_a		1.08 (6.8)	

[a] Concentration 10 mmol/liter, at 40 C. Values indicate absorbance of solution sampled.

[b] Values in brackets indicate pH of dispersion.

TABLE IV

Dispersing Powers of Sodium N-Acylglutamates (AGS_n) Using Titanium Oxide or Ferric Oxide[a]

Powder	L-LGS	L-OGS	L-LGS_2	L-MGS_2	L-PGS_2	L-SGS_2	L-OGS_2	SLS
Titanium oxide	0.68	0.83	0.46	0.52	0.57	0.62	0.58	0.78
Ferric oxide	0.90	0.75	0.07	0.25	0.58	0.61	0.63	0.73

[a]Concentration 10 mmol/liter, at 40 C. Values indicate absorbance of solution sampled.

to their alkalinity in aqueous solution, because lanolin is easily emulsified with aqueous alkali.

Dispersing Power

The dispersing property of an aqueous solution of a surfactant generally depends on the nature of the powder to be dispersed. The powders used here were furnace carbon black (Mitsubishi Kasei's no. MA100), titanium white and ferric oxide (rouge). They were passed through a sieve of 250 mesh to remove the larger grains and then dried. Twenty milliliters of an aqueous solution of a surfactant was put in a 25 ml glass-stoppered graduated test tube (18 mm$^{\Phi}$ x 165 mm^{h}) containing 5 mg (0.25%) of the powder to be tested. The test tube was agitated by a vibratory mixer for 2 min to disperse powder and was allowed to stand for 2 hr at 40 C. Then 3 ml of the suspension was pipetted carefully at the height of 15 ml, and the absorbance (A=-logT) was measured at 520 ± 5mμ (carbon black and titanium white) or 580 ± 5 mμ (ferric oxide). When the absorbance showed the value larger than 0.8, the suspension pipeted was diluted with the aqueous solution of the surfactant until the absorbance indicated the value below 0.8 and the value measured was corrected to obtain the absorbance value required.

Table III shows the results of the tests using 10 mmol/liter aqueous solution of AGS_n and carbon black. The higher absorbance means stronger dispersing power. PGS_2 and SGS_2, which were weaker in lowering power of surface tension and emulsifying power, showed the strongest dispersing power even when compared with SLS.

The dispersing powers of AGS_n to titanium oxide and ferric oxide are shown in Table IV. Unlike the case of carbon black, AGS_n with higher lowering power of surface tension and emulsifying power showed higher dispersing power.

Calcium Ion Stability

The calcium ion stability was examined as follows: To 20 ml of a 10 mmol/liter aqueous solution of a surfactant, an aqueous solution of 0.1 mol/liter calcium chloride was added dropwise at 40 C until an insoluble salt began to precipitate. The amount of calcium ions in the resultant solution was indicated as the concentration (ppm) of calcium carbonate.

The results are shown in Table V. The 10 mmol/liter aqueous solution of AGS_n was generally stable below the concentration of 300 ppm calculated as $CaCO_3$. The stability of L-LGS to calcium ions was as excellent as that of sodium linear-alkylbenzenesulfonate (LAS) or SLS_a, while that of the corresponding disodium salt (L-LGS_2) was inferior. Of the disodium salts, MGS_2 showed the lowest stability, and as the acyl radical became longer the stabilities became higher.

TABLE V

Calcium Ion Stability of Sodium N-Acylglutamates (AGS_n)[a]

Acyl	Neutralization equivalent	L-AGS_n	DL-AGS_n
L	1.0	414	---
	1.5	250	---
	2.0	158	158
M	2.0	32	32
P	2.0	310	300
S	2.0	439	400
O	1.0	244	244
	1.5	284	329
	1.75	292	323
	2.0	323	323
SLS		2000	
LAS		385	
Soap		Under 20	
SLS_a		340	

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

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