Surface Active N-Acylglutamate: V. Application of N-Acylglutamates to Detergent Bars

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ABSTRACT

An application of sodium N-acyl-L-glutamate for detergent bars is described. The acyl radicals of cocoyl, hydrogenated tallowyl, semihydrogenated tallowyl, and lauroyl were used in the glutamates. The powder of sodium N-acyl-L-glutamate was mixed with a suitable amount of water and milled; then the mixture was extruded and stamped into a bar. Bars were examined relating composition of acyl radicals of sodium N-acyl-L-glutamates and properties of the bars or milling and molding properties. The other characteristics of the detergent bars were examined. It was found that attractive detergent bars can be made by using monosodium N-acyl-L-glutamate as a component; that hardness, solubility, and lather characteristics of bars can be controlled by blending various monosodium N-acyl-L-glutamates and adding moisture; that adjuvant can be used to improve the milling and stamping properties and characteristics of the monosodium N-acyl-L-glutamate bar; and that the bars are less irritating and leave the skin feeling good.

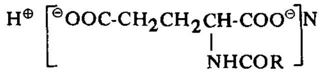
INTRODUCTION

Preparation and physicochemical properties of long chain N-acylglutamates were reported in our previous papers (1-4). In this paper, an application of N-acyl-L-glutamates to preparation of detergent bars is described. When the soap bar, easily soluble in soft water, is used in hard water, its performance is markedly reduced. In addition, weakly alkaline in its aqueous solution, it neutralizes the acid mantle of the human skin. Those having delicate skin should use neutral or weakly acid detergents.

Recently, various synthetic detergent bars have been produced and are in practical use (5,6). Although these bars have excellent detergency, they usually require superfatting agents and other additives to give desirable characteristics for toilet use. Moreover, these bars have an inferior feeling on the skin as compared with ordinary soap bars.

The authors have been trying to prepare a detergent bar using monosodium N-acyl-L-glutamates (AGS). It has been found that the pH value for this detergent bar (AGS bar) is between 5.5–6.5 in water, similar to the value for skin, and the bar can be employed in hard water. Moreover, it leaves skin feeling comfortable. Much less irritating to the skin, this type of bar can be satisfactorily used by patients suffering from skin diseases (7-8).

Sodium N-acyl-L-glutamates can be represented as follows:



$$H^{\oplus}\left[{}^{\ominus}OOC\text{-}CH_2CH_2\underset{\displaystyle NHCOR}{\underset{|}{CH}}\text{-}COO^{\ominus}\right]Na^{\oplus}$$

-COR: Acyl radicals

MATERIALS AND METHODS

Properties of Sodium N-Acyl-L-glutamates (Powder)

The physicochemical properties of AGS with a single acyl radical were reported previously (2,3). Properties of N-acyl-L-glutamic acids and their sodium salts are shown in Tables I and II. Acyl groups derived from natural fatty acids were used. Sodium N-cocoyl-L-glutamate (CGS), sodium N-tallowyl-L-glutamate (TGS), sodium N-semihydrogenated tallowyl-L-glutamate (RGS), and sodium N-hydrogenated tallowyl-L-glutamate (HGS) showed a marked difference in solubility, and the foams produced therefrom have a good appearance. It was expected that blending

TABLE I

Analyses of N-Acyl-L-glutamic Acids

Acyl[a]	Distribution of acyl radicals (C % by wt)	Average mol wt	Fatty acids contents (%)	Neutralization equivalent (%)	Melting point (C)	Optical[b] rotation $[\alpha]^{20}_{D}$
C	8-3.3, 10-7.7, 12-57.8, 14-18.1, 16-8.7, 18-3.6, 18Fx2-0.8[c]	340	0.21	92.3	94-97.5	-11.0
L	8-0.1, 10-0.1, 12-97.3, 14-2.5	330	0.85	100.4	101-104	-10.5
T	12-0.4, 14-4.0, 16-30.8, 18-20.6, 14F-0.8, 16F-4.3, 18F-31.2, 14Fx2-0.7, 16Fxn-2.7, 18Fxn-4.5	399	1.05	93.4	98-104	-6.0
R	12-0.2, 14-4.4, 16-29.8, 18-42.5, 14F-0.8, 16F-3.2, 18F-16.9, 14Fxn-0.9, 16Fxn-0.8, 18Fxn-0.5	400	0.39	99.7	109-112	-10.3
H	12-0.6, 14-1.7, 16-18.5, 18-78.4, 14F-0.7	406	1.35	98.7	115-119	-8.0
Soap	8-1.0, 10-1.1, 12-8.9, 14-6.2, 16-24.9, 18-52.3, 14F-1.3, 16F-1.7, 18F-2.9	285	(Water, 15.3%)	15.3		

[a] L = lauroyl, C = cocoyl, T = tallowyl, R = semihydrogenated tallowyl (iodine value 25), H = hydrogenated tallowyl.

[b] Measured in methanol solution.

[c] Fxn = unsaturated fatty acyl which has more than two double bonds.

TABLE II

Properties of Monosodium N-Acyl-L-glutamates (AGS)

	Solubility			Foam height (mm)[e]			Foam stability	Foam appearance	Relative[e] surface tension	Wetting[e] power
AGS[a]	Temp[c] (C)	40 C[b]	pH[d]	0 (min)	5 (min)	30 (min)	(%)			(sec)
L	39	S	5.0	250	219	212	84.8	bulky	0.379	6.5
C	23	S	5.2	245	203	197	80.4	bulky	0.374	9.8
T	38	P	6.5	220	188	182	82.7	medium	0.428	34.2
R	53	P	6.3	210	185	180	85.7	fine	0.452	---
H	60	P	6.6	205	176	176	86.0	fine	0.481	---
SLS	---	S	7.0	205	186	181	88.3	bulky	0.460	7.4
LAS	---	S	6.8	210	195	190	90.5	bulky	0.471	3.1
SLSa	---	S	6.9	167	141	120	71.8	bulky	0.587	6.7
Soap	---	Sc	10.1	220	181	177	80.4	fine	0.358	244

[a] L = lauroyl, C = cocoyl, T = tallowyl, R = semihydrogenated tallowyl (iodine value 25), H = hydrogenated tallowyl, SLS = sodium lauryl sulfate, LAS = sodium linear alkylbenzene sulfonate, SLSa = sodium N-lauroyl sarcosinate.

[b] S = soluble, P = partially soluble, C = cloudy.

[c] Temperature at which a 10% turbid dispersion became a clear solution on gradual heating.

[d] Concentration 10 mmol/liter at 35 C.

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

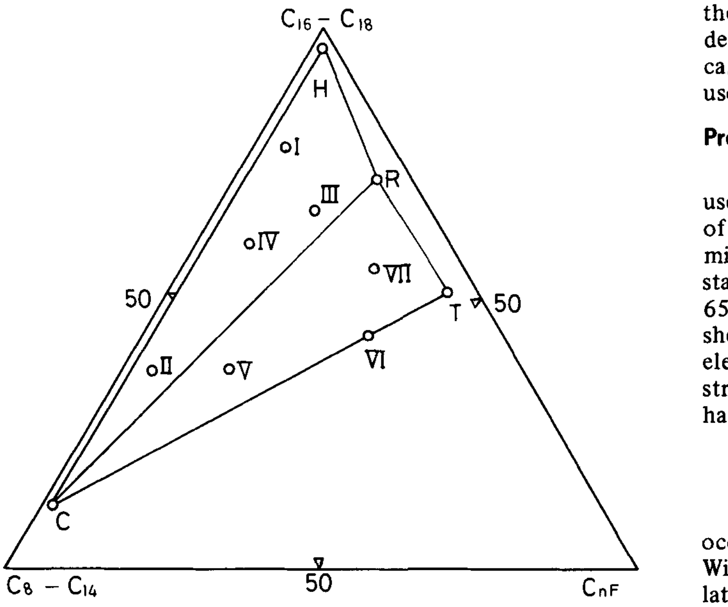


FIG. 1. Composition of acyl radicals of monosodium N-acyl-L-glutamate. C_8–C_{14} = total amount of octanoyl, decanoyl, lauroyl, and myristoyl; C_{16}–C_{18} = total amount of palmitoyl and stearoyl; C_nF = total amount of unsaturated fatty acyls; H = hydrogenated tallowyl; C = cocoyl; and T = tallowyl. The axes from C_{16}–C_{18} to C_8–C_{14}, C_8–C_{14} to C_nF, and C_nF to C_{16}–C_{18} are shown the ratios of acyl radicals C_{16}–C_{18}/C_8–C_{14}, C_8–C_{14}/C_nF, and C_nF/C_{16}–C_{18}, respectively, and the apexes of triangle mean 100% of C_{16}–C_{18}, C_8–C_{14}, and C_nF.

these materials would produce characteristics required for detergent bars. Because the calcium ion tolerance of AGS is ca. 300 ppm as calcium carbonate, the AGS bar is good for use with hard water.

Preparation of Detergent Bar

An apparatus for forming ordinary small bar soaps was used. Powdered AGS was added to an appropriate amount of water with or without other additives. The mixture was milled from two to six times on a small roller having three stainless steel cylinders with rotation speeds of 16, 32, and 65 rpm, respectively. The milled material, formed into sheets, was then processed through an extruder at an elevated temperature and made into a strand. The extruded strand was stamped into bars (50 x 35 x 12 mm, 25 g) in a hand stamping machine.

RESULTS AND DISCUSSION

AGS bars incorporating compounds having naturally occurring acyl radicals showed the following properties: With HGS a hard brittle bar of poor solubility and low lathering power was produced, but the lather was relatively good. Monosodium N-lauroyl-L-glutamate (LGS) gave a chalky, firm bar with good lathering, but it disintegrated easily and was gritty on the skin during hand washing. CGS made a bar of good solubility that had sufficient lathering power but was slightly sticky to the metal pattern of the stamping machine as well as when used for hand washing. RGS gave a firm bar that was subject to cracking when left standing for a long time after use. To eliminate these defects, AGSs were mixed at various ratios, shown in the

TABLE III

Mixing Ratio of Sodium N-Acyl -L-glutamates (AGS)

Point in Figure 1	Mixed ratio of AGS				Composition of acyl radicals (%)		
	H	R	C	T	C_{8-14}	C_{16-18}	Unsaturated
H	100	---	---	---	2.3	96.9	0.8
R	---	100	---	---	4.6	72.3	23.1
C	---	---	100	---	86.9	12.3	0.8
T	---	---	---	100	4.4	51.4	44.2
I	66	17	17	---	17.1	78.3	4.6
II	17	17	66	---	58.5	36.9	4.6
III	17	66	17	---	18.2	66.3	15.5
IV	33.3	33.3	33.3	---	31.3	60.5	8.2
V	---	25	50	25	45.7	37.1	17.2
VI	---	---	20	80	20.9	43.6	35.5
VII	---	46.6	11.6	41.8	14.1	56.6	29.3

TABLE IV

Properties of Detergent Bar

Point in Figure 1	Added water by wt (parts)	Appearance of detergent bar	Milling[a] and stamping properties	Solubility[b] by rubbing	Disintegration[c] value (%)	Lather in hand washing test
L	24.0	Chalky	O	155	-13.6	Flash lather
H	25.0	Shiny hard	O	95	+ 4.3	Slow foaming like soap
R	20.0	Firm smooth	O	60	+ 8.3	Slow foaming like soap
C	5.0	Semitransparent sticky	X	90	-23.4	Flash lather
I	16.7	Hard	X	80	+13.9	Slow foaming
II	3.0	Semitransparent sticky	O	90	+ 6.6	Flash lather
III	16.0	Smooth firm	O	90	+14.2	Slightly slow foaming
IV	20.0	Firm	O	90	+16.9	Flash lather
V	15.0	Semitransparent sticky	O	113	+16.6	Flash lather
VI	10.0	Soft sticky	O	102	+26.4	Flash lather like soap
VII	18.0	Like soap	O	95	+21.6	Flash lather like soap
Soap	---	---	O	55	+10.0	---

[a] O = good, X = some tendency to stick to the mold.

[b] The bar was rubbed on the polyethylene sheet wetted in warm water (40 C), modified method of JIS K-3304 (9).

[c] The sample was immersed into water for 60 min and the percentage of wt difference was calculated; + represents swelling and – disintegration.

TABLE V

Effect of Additives

Additives added[a] (parts)	Added water (parts)	Appearance	Milling[b] and stamping properties	Solubility by rubbing	Disintegration value	Lather in hand washing
Cetyl alcohol 5	10	Slightly firm	⊙	59	+11.5	Flash and slightly thick lather
Amisol LDE 10	10	Like soap	O	71	+13.8	Thick lather
Amisol CME 5	11	Slightly firm	O	71.5	+ 9.8	Slightly thick lather
Propylene glycol 10	0	Smooth but firm	O	100	+ 0.1	Poor
Polyethylene glycol 400 10	0	Smooth but firm	O	115	+ 0.2	Flash but not thick lather
Polyethylene glycol 400 10	10	Smooth	O	120	+ 0.1	Flash but not thick lather
Amizett 5C 5	10	Like soap	O	110	+ 0.1	Slightly thick lather
Cetyl alcohol 10	15	Like soap	⊙	83.5	+ 9.9	Flash and slightly thick lather

[a] Amisol LDE = lauroyl diethanolamide, amisol CME = cocoyl monoethanolamide, amizett 5C = polyoxyethylene cocoyl monoethanolamide.

[b] ⊙ = very good, O = good.

triangular diagram (Fig. 1) and Table III. Properties of the mixed AGS bars are summarized in Table IV.

AGS mixtures with compositions shown at points I, II, and III in the diagram gave bars having the corresponding desirable characteristic associated with HGS, CGS, and RGS. A mixture of CGS, HGS, and RGS in equal amounts (IV in the diagram) also gave good bars. The AGS mixture (VI) having acyl radicals nearly equal to ordinary soaps in its fatty acid composition produced a soft bar. However, bars given by AGS mixtures V and VII, having a little more saturated fatty acid than AGS V and VII, having a little more saturated fatty acid than AGS VI, were slightly harder than VI. Therefore, a desired AGS bar can be made by selecting ratios of the acyl radicals that fall inside the region enclosed within the line connecting the points in the order of I, II, V, VII, III, and back to I.

Effects produced by the addition of adjuvants were examined. An adjuvant was added to the AGS powder of the composition under VII in the diagram, and the mixture was milled, plodded, and stamped. The bar obtained was compared to the bar without adjuvant. The results are presented in Table V.

Cetyl alcohol was the most effective adjuvant for the AGS bars.

A close relationship existed between the properties of the AGS mixtures during milling and stamping and the temperatures at which the mixture was milled, as well as the amounts of water added before milling. To make these relations clear, the plasticity torque of the AGS sheets was measured on a Brabender Plastograph (Figs. 2 and 3). The AGS sheets were prepared by milling the AGS powder of the composition under VII in the diagram with cetyl alcohol (7.5% of the AGS powder) and an appropriate amount of water. Under the same thermal conditions, the plasticity torque rose as the moisture of the AGS sheets decreased. When the moisture level of the AGS sheets was held constant, the plasticity torque decreased as the temperature of the mixture rose. The plasticity torque of the AGS sheets was higher than that of ordinary soaps when the moisture contents were at the same level. The curves demonstrating temperature/plasticity torque relation for the AGS sheets, however, were similar to those for ordinary soaps, indicating that none of the factors–plasticity torque, moisture content, and temperature at which sheets are ex-

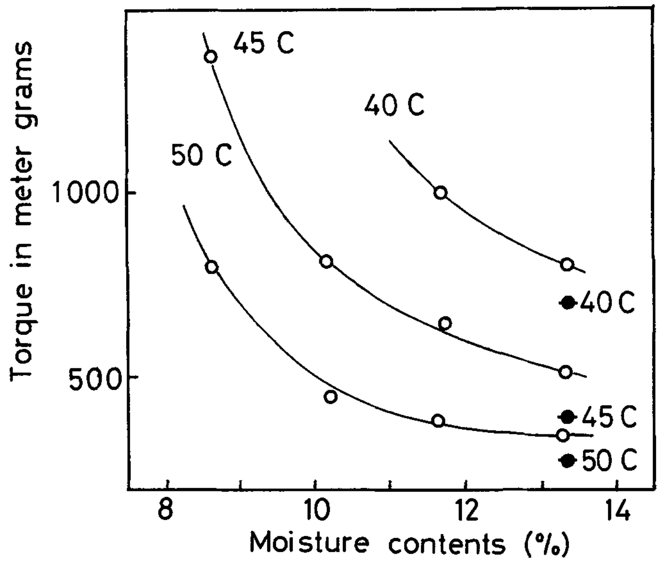


FIG. 2. Plasticity torque of monosodium N-acyl-L-glutamate (AGS) bar. Relation between moisture content and torque. Measured on a Brabender Plastograph. Roller mixers' motor speed 30 rpm. —o— AGS bar, —●— soap (toilet bar).

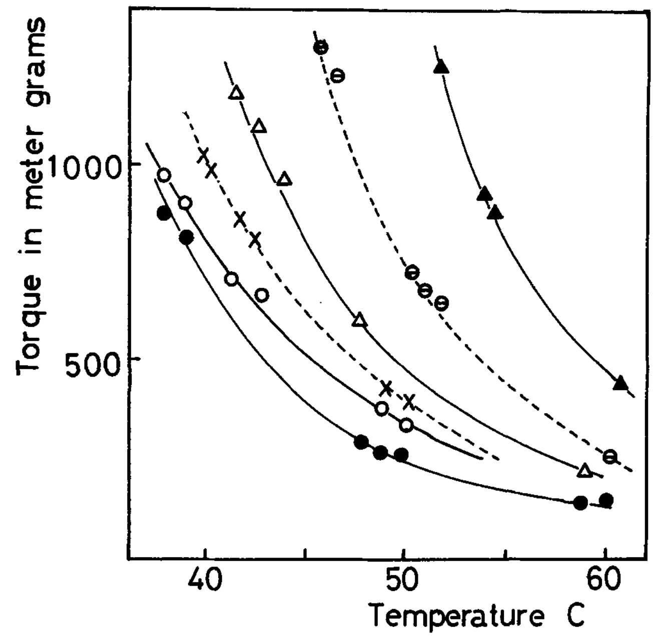


FIG. 3. Plasticity torque of monosodium N-acyl-L-glutamate bar. Relation between temperature and torque. Measured on a Brabender Plastograph. Moisture contents: —o— 13.3%, —X— 11.7%, —△— 10.2%, —⊖— 8.7%, —▲— 6.6%, and soap (toilet bar) —●—.

truded—are independent but are all closely related. In conclusion, the AGS sheets could be milled and plodded on any equipment similar to that used for manufacturing ordinary soap bars.

Hardness of the detergent bars was determined on a Shore Durometer (10), but here the AGS bar was pressed for 1 min with a steel ball (20 mm in diameter and 1.5 kg in wt), and the diameter of the depression produced by the ball was measured. The diameter corresponds inversely to the hardness of the AGS bar. The relation between the moisture added and the diameter of the dent was shown in Figure 4. AGS bars of 9-13% moisture content were softer than ordinary soaps, but they could be used in the same manner.

The stability of the AGS bar was also investigated. Covered with parchment paper, the bar was kept under ordinary laboratory conditions for 500 days. At the termination of the test period, the color, odor, and wt of the test bars were carefully examined. The color remained almost the same (Table VI). In odor, the product had an appeal equal to a fresh bar. Losses in wt of the test bars are presented in Figure 5.

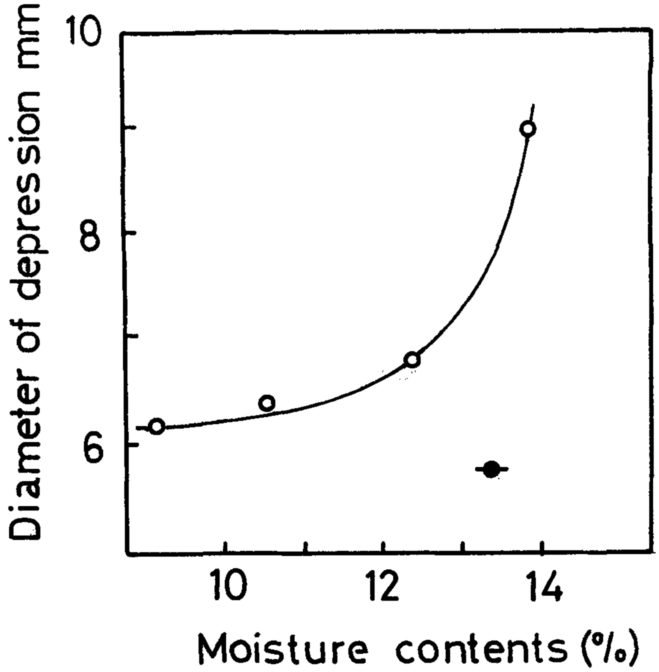


FIG. 4. Hardness of monosodium N-acyl-L-glutamate (AGS) bar. Relation between moisture contents and diameters of depression. The AGS bar was pressed for 1 min with a steel ball (20 min in diameter and 1.5 kg in wt) and the depression produced by ball was measured. —o— AGS bar, —●— soap (toilet bar).

TABLE VI

Stability of Monosodium N-Acyl-L-glutamate (AGS) Bar (Brightness by Hunter)[a]

Days	0	30	60	90	120	196
Brightness (%)	86.5	85.9	84.4	84.8	84.2	83.7

[a] The AGS bar tested was prepared by milling the AGS powder of the composition under VII in the diagram with cetyl alcohol (7.5% of the AGS powder), titanium oxide (0.1%), and an appropriate amount of water.

Measured by color and color difference meter.

Standard (100%) = standard plate of magnesium oxide.

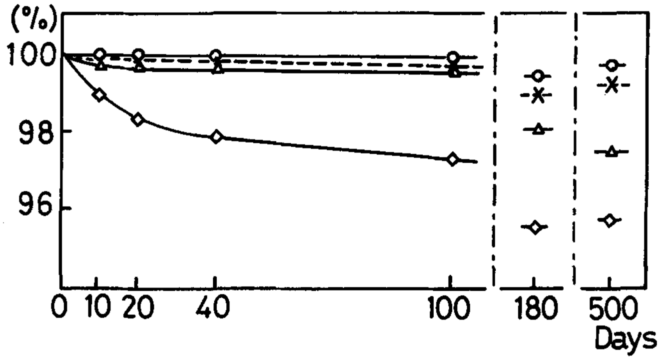


FIG. 5. Stability of monosodium N-acyl-L-glutamate (AGS) bar at room temperature. (AGS composition under VII in Fig. 1. with cetyl alcohol [7.5%], titanium oxide [0.1%], and water.) Moisture of AGS bar: —o— 9.1%, –X– 10.7%, —△— 12.8%, —◇— 13.8%.

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