Preparation and Surfactant Properties of Diglycerol Esters of Fatty Acids

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Fatty acid mono- and diesters of diglycerol constitute the major portion of commercial polyglycerol esters; hence, their composition influences the performance of the latter as emulsifiers. The correlation of structure of the fatty acids in the mono- and diesters with surfactant properties is of interest. Linear diglycerol was isolated from polymerized glycerol by acetonation, fractional distillation and regeneration. Diglycerol mono- and diesters of undecenoic, lauric, stearic, oleic and ricinoleic acids were prepared by reacting diglycerol and fatty acids in a refluxing mixture of acetonitrile-tetrahydrofuran (75:25) in the presence of p-toluenesulfonic acid and molecular sieves. Mono- and diesters were separated by silica gel column chromatography, and their purities were ascertained by thin layer chromatography and determination of saponification value. The structures were confirmed by periodic acid oxidation, chemical-ionization mass spectrometry and ^{13}C-NMR spectroscopy. Surfactant properties of the esters were determined. Monoesters showed higher ability in surface tension reduction, emulsification and foaming than the diesters. Short-chain fatty acid esters showed better surfactant properties than the long-chain fatty acid esters. The presence of a central double bond in the lipophilic part of the monoesters reduced emulsion stability. The presence of a hydroxy group in acyl chain retarded foaming and surface tension reducing power.

Polyglycerol partial esters of fatty acids, classified as nonionic food emulsifiers, are available commercially. Polyglycerols consist of homologs of polymerized glycerol units. Linear diglycerol is a major constituent of commercial polyglycerol mixtures (1). The surfactant properties of pure diglycerol esters of fatty acids would therefore be interesting. Linear diglycerol was synthesized (2,3) as well as isolated from polyglycerol mixtures obtained by polymerization of glycerol (4—6). Di-and monoesters of diglycerol have been synthesized and their physical constants determined (4,5). This communication reports the preparation of pure diglycerol and its mono- and diesters of some selected fatty acids differing in chain length, unsaturation and functional groups, characterization of diglycerol esters by chemical, chromatographic and spectral methods, determination of their surfactant properties, and correlation of structure with the surfactant properties.

MATERIALS AND METHODS

Lauric acid and undecenoic acid were purchased from Godrej Soaps Ltd., Bombay, India. Oleic acid (Reidel, Hanover, W. Germany) was enriched by urea adduction. The acid was dissolved in methanol and urea was added slowly (acid:urea:methanol, 1:1:3, wt/wt/vol). The contents were heated in a steam bath for 30 min and cooled to room temperature overnight. The adduct was filtered, and the procedure was repeated twice with filtrate to remove saturated fatty acids as adduct and once more (fatty acid:urea:methanol, 1:5:5) to remove linoleic acid as filtrate. Ricinoleic acid was obtained from castor oil by cold saponification and acidification of soap. The mixed fatty acids were partitioned between petroleum ether (40—60°C) and 80% methanol, which initially were equilibrated with each other. After repeated extractions the nonhydroxy fatty acids were separated and ricinoleic acid was enriched.

Gas liquid chromatography (GLC). Methyl esters of fatty acids were analyzed using a Hewlett-Packard 5840 A gas chromatograph fitted with a hydrogen flame ionization detector and a data processor. The column was maintained at 220 C and the detector and injection port at 260 C. Nitrogen was used as carrier gas (60 ml/min). Chart speed was one cm/min. Peaks were identified by comparison of their retention times with those of standard fatty acid methyl esters. The columns used were (i) a stainless steel column (2.4 m × 3.2 mm) packed with 15% EGSS-X Gaschrom Q (80-100 mesh); (ii) a glass column (1.8 m × 6 mm) packed with Silar 10C on Chromosorb-W HP (80-100 mesh), and (iii) a glass column (1.8 m × 6 mm) packed with SE-30 on Chromosorb W-H P (80-100 mesh). All the fatty acid methyl esters were found to be more than 98% pure by GLC.

High performance liquid chromatography (HPLC). HPLC was carried out using a Waters Associates model ALC/GPC 244 equipped with a Model 6000 A pump, a U6K injector, a model R 401 differential refractometer and Shimadzu Chromatopak E1-A integrator. A Waters Associates Carbohydrate column (30 cm × 3.9 mm id., 10 μ) was used. The mobile phase was acetonitrile-water (83:17, v/v) at a flow rate of 1.5 ml/min under a pressure of ca. 1,000 psig. The detector attenuation was 8 ×, and the recorder chart speed was 1.5 cm/min.

Mass spectrometry. The mass spectra were recorded on a VG micromass 7070 H high resolution mass spectrometer equipped with a combined chemical (CH_4) ionization/electron impact source. The samples were inserted in glass capillaries and introduced by direct insertion probe.

NMR spectroscopy. The ^{13}C-NMR spectra were obtained on dimethyl sulfoxide -d_6 solution (1M) using a Jeol FX 90Q spectrometer in FT mode operating at 22.4 MHZ. Chemical shifts are given in δ-ppm, downward from tetramethylsilane peak.

Preparation of polyglycerols. Glycerol (500 g) was polymerized (7) at 250 C for two hr under stirring and nitrogen bubbling in a four-necked flask coupled with Dean-Stark apparatus, using sodium hydroxide (1% w/w) as catalyst and a trace quantity of magnesium

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powder. After neutralizing the catalyst with dilute hydrochloric acid the product was analyzed by HPLC (8) using glycerol, cyclic diglycerol, linear diglycerol and triglycerol as standards. This product contained 37% diglycerol, 9.2% triglycerol, 53% unreacted glycerol and trace quantities of higher polymers.

Preparation of isopropylidene derivatives. Unconverted glycerol (230 g) was removed at 115 C/0.5 mm Hg. The enriched polyglycerol mixture was stirred vigorously at room temperature with a mixture of acetone (two l) and sulfuric acid (10 ml) in a two-necked round-bottomed flask fitted with a calcium chloride guard tube. The contents of the flask were cooled externally to control the initial raise in temperature due to the exothermic reaction. Anhydrous magnesium sulfate powder (400 g) was added after one hr, and the reaction was continued for 24 hr. The acetone-soluble portion was decanted, neutralized and filtered. The acetonation procedure was repeated with the gummy residue and the two acetone-soluble fractions were pooled.

Fractionation of isopropylidene derivatives. The isopropylidene derivatives were fractionally distilled using a Vigreux column (15 cm) under reduced pressure. The first fraction, isopropylidene glycerol (2 g), was collected at 60 C/0.5 mm Hg, and the second fraction, diisopropylidene diglycerol (180 g), was distilled at 90 C/0.3 mm Hg.

Regeneration of diglycerol. Diglycerol was regenerated by hydrolyzing the diisopropylidene diglycerol with 100 ml of 20% (v/v) sulfuric acid over a steam bath for 30 min. Linear diglycerol was distilled (110 g) at 190 C/0.1 mm Hg.

Preparation of diglycerol esters. Diglycerol was dissolved in acetonitrile-tetrahydrofuran (75:25, v/v) solvent mixture for better contact of reactants and placed in a round-bottomed flask. The flask was attached to a column packed with molecular seives (Linde & Co., 4 Å, 1/16″ pellets). The column was connected to a calcium chloride guard tube. After addition of fatty acid and p-toluenesulfonic acid, the mixture was refluxed. Monitoring of the reaction was carried out by thin layer chromatography (TLC) of the reactant mixture on silica gel G. At the end of the reaction, solvent was removed under reduced pressure and the product was extracted with diethyl ether. The unreacted diglycerol and catalyst were washed with distilled water. The purity of the products was checked by silica gel G TLC using benzene-methanol-acetic acid (85:14:1, v/v/v) mixture for nonhydroxy esters and benzene-diethyl ether-ethyl acetate (50:25:25, v/v/v) mixture for ricinoleic acid esters.

Analysis of diglycerol esters. Pure diglycerol mono- and diesters were separated by column chromatography. The separations were carried out over a silica gel (ACME Synthetic Chemicals, Bombay, India) column (30 × 4 cm). Nonhydroxy fatty acid esters were eluted with n-hexane-diethyl ether (50:50, v/v) solvent system. For hydroxy fatty acid esters, benzene-diethyl ether-ethyl acetate (60:25:15, v/v/v) solvent mixture was used as the eluent. The free fatty acids were eluted first, then diesters and finally monoesters. The identity of the fractions was confirmed by determination of saponification value and chemical ionization (methane) mass spectrometry. The position of the ester groups was determined by testing with periodic acid (9).

Surfactant properties. Surfactant properties of the esters at 0.1, 0.05, 0.025 and 0.01% concentrations were measured. Surface tension (ST) measurements were made using a DuNouy tensiometer at room temperature (25 C). At this temperature distilled water showed a value of 72 dynes/cm. Emulsifying property (10) was determined by giving 10 downward shakes to a mixture of 40 ml surfactant solution and 40 ml liquid paraffin taken in a 250-ml stoppered conical flask immediately followed by pouring the emulsion into a 100-ml measuring cylinder. The time taken for separation of 10 ml of the aqueous phase was recorded. Foaming properties were determined using a Ross-Miles (11) foam apparatus.

RESULTS AND DISCUSSION

Preparation of diglycerol. Glycerol was polymerized under controlled conditions. The product containing 37% diglycerol was reacted with acetone to yield isopropylidene derivatives from unreacted glycerol and linear di- and polyglycerols. The linear diglycerol de-

TABLE 1

Preparation of Diglycerol esters

Compound	Diglycerol (mmol)	Fatty acid (mmol)	Catalyst[a] (mmol)	Solvent[b] (ml)	Reaction time (hr)	Yield %	
						Monoester	Diester
Monoesters							
Laurate	12.12	12.01	1.75	300	24	55.0	Nil
Undecenoate	13.12	12.12	1.41	300	24	59.0	Nil
Oleate	13.90	13.00	1.52	350	24	40.0	Nil
Stearate	15.20	14.79	1.63	350	24	38.5	Nil
Ricinoleate	13.10	13.00	1.40	350	24	31.0	Nil
Diesters							
Laurate	11.56	22.15	2.62	350	32	21.0	49.0
Undecenoate	12.12	23.13	2.62	350	32	20.2	47.0
Oleate	12.93	24.89	2.45	375	36	32.7	20.5
Stearate	13.20	24.65	2.91	375	36	33.5	19.8
Ricinoleate	15.55	29.26	3.41	375	44	15.5	27.1

[a]p-Toluenesulfonic acid.
[b]Acetonitrile-tetrahydrofuran (75:25, v/v).

rivative was separated by fractional distillation. The diglycerol was regenerated and checked for purity by HPLC and found to be pure (99.9%).

Although linear diglycerol contains six carbon atoms, because of its symmetrical structure it gave only three signals for three different carbon atoms in ^{13}C-NMR spectrum. The characteristic signals which appeared at 62.7 δ (carbon-bearing primary hydroxyl group), 70.2 δ (ether-linked carbon atoms) and 72.0 δ (carbon-bearing secondary hydroxyl) are in agreement with the symmetrical structure of diglycerol.

Esterification of diglycerol. The esterification between diglycerol and fatty acids in the absence of solvent was found to be nonselective (unpublished observation). In the presence of acetonitrile-tetrahydrofuran (75:25, v/v) solvent mixture, the reaction was selective though slow (Table 1). The reaction was specific for primary hydroxyls. The preparation of monoesters led to a single product, whereas preparation of diesters led to formation of a considerable amount of monoesters. In the case of hydroxy fatty acids, trace amounts of estolides also were formed. The observed saponification values for the esters were in agreement with the theoretical values.

Mass spectral analysis of diglycerol esters. Because the compounds are relatively less volatile, chemical ionization was used for mass spectrometry. The spectra of mono- and dilaurates of diglycerol were studied as examples. Monolaurate of diglycerol gave a molecular ion peak at m/z 349 (Fig. 1). Due to the loss of one molecule of water, the base peak was obtained at m/z 331. The m/z 257 peak was obtained from the fragmentation of one glycerol moiety from molecular ion. In the spectrum of dilaurate (Fig. 2), the molecular ion peak was obtained at m/z 531 and the molecule was fragmented at the ether linkage, either side giving an m/z 257 peak. Loss of one fatty acid from the molecular ion gave the m/z 349 peak. A peak at m/z 331 was obtained from the loss of one water molecule from the m/z 349 fragment.

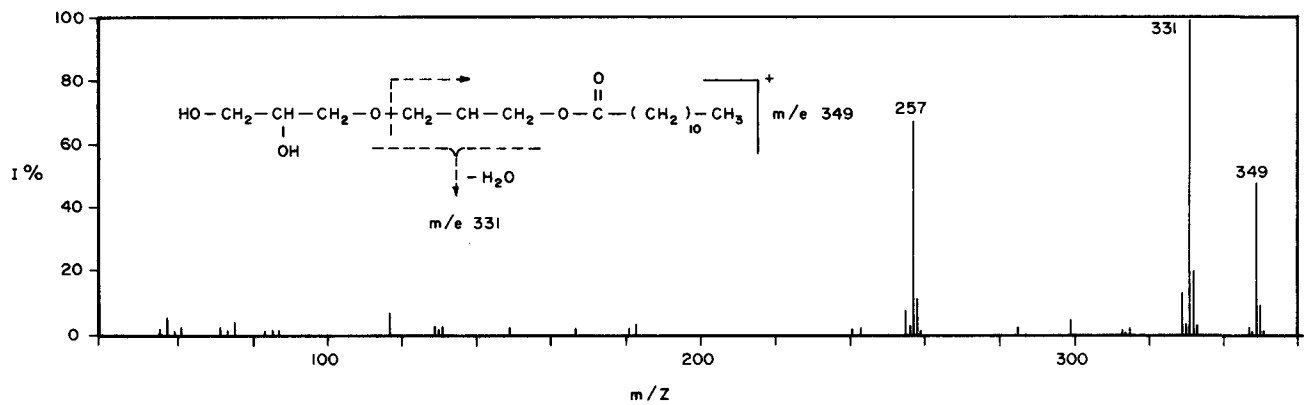

FIG. 1. Mass spectrum and fragmentation of diglycerol monolaurate.

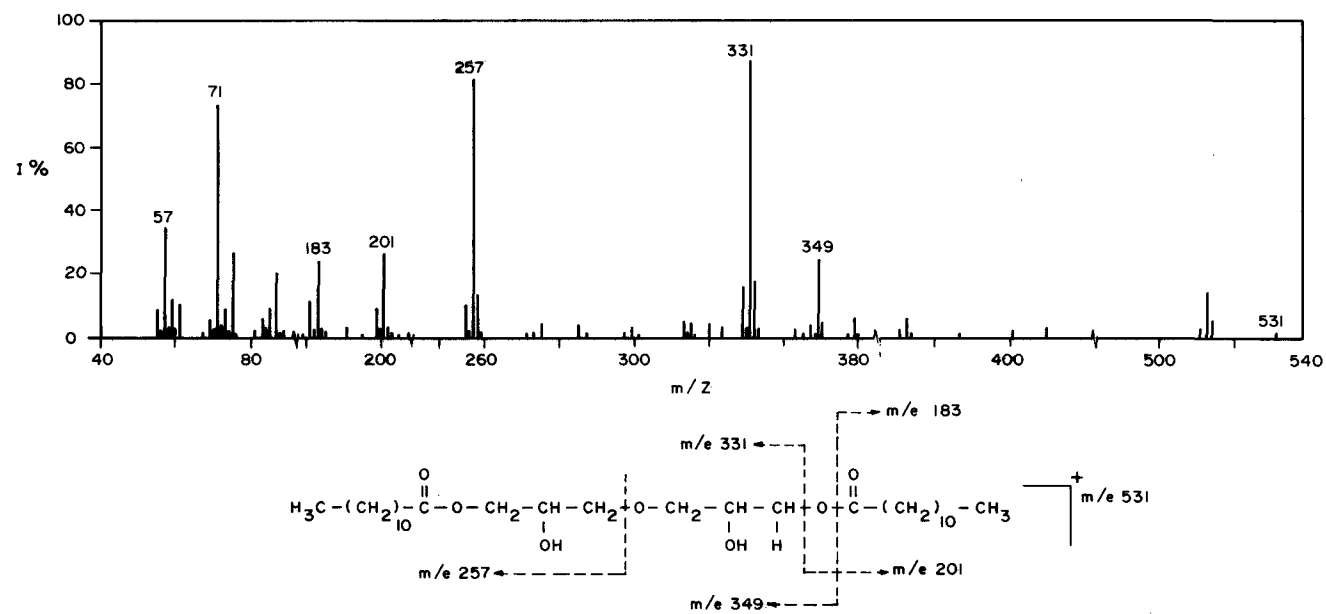

FIG. 2. Mass spectrum and fragmentation of diglycerol dilaurate.

TABLE 2

Surfactant Properties of Diglycerol Esters

Compound	Surface tension (dynes/cm)				Emulsion stability (sec)				Foam height (mm)							
									0.1%		0.05%		0.025%		0.01%	
	0.1%	0.05%	0.025%	0.01%	0.1%	0.05%	0.025%	0.01%	I	F	I	F	I	F	I	F
Monoesters																
Laurate	27.0	28.5	29.0	29.5	240	85	40	20	50	46	38	35	36	30	27	25
Undecenoate	31.0	32.0	32.5	37.5	100	50	20	10	93	83	40	18	28	7	20	5
Oleate	31.5	32.5	34.0	35.0	35	15	7	5	14	4	7	4	3	0	<1	
Stearate	32.0	34.0	37.0	38.5	60	35	20	10	50	39	35	29	32	17	25	10
Ricinoleate	36.0	37.0	37.5	38.5	30	20	17	15	<1		<1		<1		<1	
Diesters																
Laurate	32.0	34.5	37.5	39.0	50	25	17	15	25	12	22	18	14	12	9	4
Undecenoate	39.0	39.5	41.0	42.0	45	17	5	<1	9	0	3	0	<1		<1	
Oleate	35.0	38.5	40.0	43.0	30	15	8	<1	14	7	12	4	<1		<1	
Stearate	40.0	41.0	45.0	50.0	30	10	<1	<1	14	4	7	3	3	1	<1	
Ricinoleate	41.5	42.0	43.0	47.5	35	30	25	15	<1		<1		<1		<1	

[a]I, initial; F, final.

Position of esterified hydroxyl groups. The periodic acid test for diglycerol monolaurate was positive, confirming the presence of a vicinal diol group. The ^{13}C-NMR spectrum of monolaurate showed signals at 172.0 δ for the esterified carbon of the fatty acid moiety, 72.2 δ for the carbon having a secondary hydroxyl group on the monoesterified portion of the diglycerol molecule. The signal at 72.0 δ corresponds to a carbon bearing a secondary hydroxyl in the esterified side of the diglycerol molecule. The 67.0 δ signal was assigned to the ether carbon present at the nonesterified portion of diglycerol. The signal at 66.0 δ was assigned to the ether carbon present on the acylated side of the diglycerol, and the 62.7 δ signal was assigned to the free primary hydroxyl-bearing carbon. Because the diesters of diglycerol did not give positive response to the periodic test it was concluded that the two ester functions were placed on either side of the molecule. The ^{13}C-NMR spectrum of diglycerol dilaurate showed three characteristic signals for acylated diglycerol. The diester of diglycerol is a symmetrical molecule, and ^{13}C-NMR signals appeared at 172.2 δ, accounting for the ester carbon of fatty acid radical, and 72.0 δ peak, accounting for the carbon-bearing secondary hydroxyl group. The peak at 66.9 δ accounted for the ether-linked carbons of diglycerol and 64.2 δ for the carbons of diglycerol bearing the acylated primary hydroxyls. Thus, ^{13}C-NMR confirmed linear and symmetrical structure for diglycerol diester.

Surfactant properties. The ST reduction, emulsification and foaming properties of mono- and diesters of diglycerols are recorded in Table 2. The ST reducing ability of the monoesters was found to be higher than that of the diesters. The shorter-chain fatty acid ester (laurate) reduced the ST of water to a greater extent than the longer chain ester (stearate). Undecenoate, though a short chain fatty acid ester, did not reduce ST as much as laurate. But oleate performed better than stearate. Therefore, unsaturation at the terminal position did not have any effect on the ST reduction property, whereas the unsaturation in the middle of the hydrophobic chain of the surfactant molecule showed a greater effect in reducing the ST. The presence of a hydroxyl group in hydrophobic moiety of diglycerol monoester retarded the ST-reducing ability. Comparatively, diglycerol monolaurate was found to be better than the long-chain fatty acid esters.

The emulsion stability of the diglycerol monoesters varied considerably with fatty acid. Diglycerol monolaurate showed much higher stability than the other esters. The presence of either a terminal double bond in diglycerol monoundecenoate compared to laurate or a central double bond in oleate resulted in less emulsification when compared to laurate and stearate, respectively. The presence of a hydroxy group in the hydrophobic moiety of diglycerol monoester also reduced the emulsion stability. The short-chain fatty acid esters performed better at emulsion stabilization than the long-chain fatty acid diglycerol esters. All the long-chain fatty acid monoesters of diglycerol were found to be poor emulsifiers. The foaming property of diglycerol monoesters of fatty acids was moderate. The monoundecenoate, because of its terminal unsaturation, gave stable foam. The saturated esters showed similar foaming ability. In oleate, the presence of unsaturation in the middle of the hydrophobic group decreased the foaming ability. The foaming ability was further reduced in monoricinoleate because of the presence of a hydroxy group in the hydrophobic moiety.

The dilaurate reduced the ST of water more than the other diesters of diglycerol. All the diesters exhibited poor performance in emulsification compared to corresponding monoesters. The diricinoleate showed better emulsion stability than the other diesters. Foaming ability was poor for all the diesters, compared to the corresponding monoesters.

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REFERENCES

1. Aitzetmuller, K., M. Bohrs and E. Arzberger, *Fette, Seifen, Anstrichm. 81*:436 (1979).
2. Stewart, M.F., *Chem and Ind.* 2030 (1966).
3. Wittcoff, H., *J. Am. Chem. Soc. 71*:2666 (1949).
4. Istin, M., *Ann. Fac. Sci. Marseille 13*:5 (1940); *Chem. Abstr. 41*:2392 (1947).
5. Neissner, R., *Fette, Seifen, Anstrichm. 82*:93 (1980).
6. Witticoff, H., *J. Am. Chem. Soc. 69*:2655 (1947).
7. Garti, N., A. Aserin and B. Zaidman, *J. Am. Oil Chem. Soc. 58*:873 (1981).
8. Kumar, T.N., Y.S.R. Sastry and G. Lakshminarayana, *J. Chromatogr. 298*:360 (1984).
9. Vogel, A.I., *A Textbook of Practical Organic Chemistry Including Qualitative Analysis,* Longman, Green and Co., London, 1948, p. 1070.
10. Wrigley, A.N., F.D. Smith and A.J. Stirton, *J. Am. Oil Chem. Soc. 34*:39 (1957).
11. Ross, J., and G.D. Miles, *Oil and Soap 18*:99 (1941).

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