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Synthesis of Some Phosphated Fatty acyl Derivatives of Mannitol and Their Evaluation

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Abstract ☐ Sodium salts of phosphated capric and myristic acyl derivatives of mannitol were prepared and evaluated for surface activity, foam characteristics and emulsifying properties. Triacyl mannitols of capric and myristic acid have better emulsifying property than the corresponding di and monocompounds.

Key words ☐ Mannitol, capric acid, myristic acid.

The best known and most widely used surfactants are the esters of the sugar alcohols, sorbitol and mannitol. The spans are representative of this series. The mannitan esters can be prepared by direct esterification with fatty acids at high temperatures[1]. They can also be prepared by ester interchange with a lower alkyl fatty ester such as methyl oleate or by reaction of the mannitan with a fatty acid chloride[2]. Since mannitol and mannitan contain more than one hydroxyl group, the possibility exists of producing di and poly esters[3]. These compounds are not sufficiently water soluble to be used as surfactants, and it is preferable to have only one fatty acyl radical per mannitan group.

Synthesis of phosphated fatty acyl derivatives of mannitol was undertaken with a view to develop a single step process. The products synthesized were evaluated for different surfactant properties.

EXPERIMENTAL METHODS

Preparation of phosphated ester of mannitol

Utilizing the process of copper[4] mono ester of mannitol was prepared. Phosphoric anhydride (0.025 mol) was added in samll portions to 50 m*l*. Solution of mannitol (0.05 mol) in chloroform and the reaction mixture was then stirred for 12 hr in order to complete the reaction. The reaction temperature was not allowed to rise above 50°C. The solvent was removed under reduced pressure to get the mono ester of mannitol in 94% yield.

Preparation of phosphated fatty acyl mannitols s

Capric acid chloride, 8.6 g (0.05 mol) for mono, 17.2 g (0.1 mol) for di and 25.8 g (0.15 mol) for tricapric acyl mannitol was added slowly to a solution of mono phosphated ester of mannitol 13.1 g (0.05 mol) in pyridine with constant stirring. The solvent was removed under reduced pressure.

Phosphated myristic acyl mannitols were also prepared similarly by taking myristic acid chloride 12.34 g (0.05 mol) for mono, 24.68 g (0.1 mol) for di and 37.02 g (0.15 mol) for tri myristic acyl mannitols. Yield: 1) phosphated capric acyl mannitols-mono, 18.74 g; di, 37.82 g; tri, 57.10 g, and 2) phosphated myristic acyl mannitols-mono, 20.10 g; di, 43.68 g; tri, 66.22 g.

Neutralization of phosphated fatty acyl mannitols

Reaction mixture from second step was dissolved in cold rectified spirit and neutralized with concentrated sodium hydroxide. During the neutralization the temperature was kept below 20° and the mixture was subsequently filtered. Alcohol was finally removed by vacuum distillation at 60-70°.

All the synthesized compounds were analysed for the phosphate group content[5] and total fatty acid[6]. Using modified procedure for sodium lauryl sulphate. The results are given in Table I.

Evaluation of surfactants

The surfactants were evaluated for the following properties:

1) Surface tension

Surface tension of 0.1% and 0.01% aqueous solutions of surfactants were determined using Fischer's surface tensiometer. Results are recorded in Table I.

Table I. Characteristics and surface properties of phosphated fatty acyl mannitols

	Sodium salt of phosphated*						
	MCM	DCM	TCM	MMM	DMMM	TMM	SLS
% total fatty acid							
Found	34.84	53.22	64.98	40.2	59.84	80.3	—
Calculated	35.68	54.08	65.31	42.38	60.96	83.4	—
% total phosphate group							
Found	18.98	14.3	11.88	17.2	12.4	9.76	—
Calculated	19.70	14.93	12.02	17.65	12.70	9.91	—
Surface tension**							
0.1%	52.6	54.8	55.5	36.64	38.5	39.06	40.2
0.02%	67.4	68.2	70.1	51.16	53.9	55.00	49.9
Interfacial tension**							
0.1%	31.8	32.4	32.6	19.4	21.2	23.8	21.8
0.01%	34.8	35.7	38.3	30.2	34.6	38.3	38.9
Foaming power at 25°							
Initial ht in cm	2.6	2.1	1.3	10.4	8.7	8.2	30.4
$T_{1/2}$ in min	75	95	98	65	70	80	35
Emulsion stability at 256°							
1 min***	2.3	2.5	2.1	1.8	2.0	2.2	3.5
60 min***	4.1	3.8	3.2	4.5	3.4	3.1	5.75

*MCM= Mono-, DCM = Di-, TCM = Tri capric acyl mannltol; MMM = Mono-, DMM = Di-, TMM = Trimyristic acyl mannitol; SLS = Sodium lsuryl sulphate.

**Surface tension and interfacial tension expressed as dynes/cm at 20°.

***Height of separated aquous phase in cm at interval of 1 and 60 min, respectively.

2) Interfacial tension

Interfacial tension of 0.1% and 0.01% aqueous solutions of the surfactants were determined against liquid paraffin by Traube's stalagmometer method[7]. The interfacial tension of liquid paraffin against water was taken as 53.1 dynes/cm at 20° as given in Table I.

3) Foam characteristics

The stability and height of foam produced by the aqueous solution of surfactants were determined using modified method of Ross and Miles[8]. The measurements were carried out by delivering 150 ml 0.2% aqueous solution of the surfactant from a seperating funnel (1.0 mm discharge nozzle) into a calibrated measuring cylinder (4.4 cm inner diameter). The height of the tip of the nozzle from the base of the cylinder was 80 cm. Initial foam height, after five minutes and half life (*i.e.* the time required to reduce the foam volume to half its initial volume) of the foam was noted recorded.

4) Emulsifying properties

Since creaming and settling are generally considered to be indices of emulsion stability even though they are not necessarily correlated with breaking of the emulsion. These effects are frequently used as guidelines in the study of the stability of emulsion. The emulsion stability can be determined by noting the height of the seperated phases. The surfactant (20 ml of 0.5% solution) was shaken with 15 ml of liquid paraffin in a 50 ml measuring cylinder (inner diameter 2.1 cm) for one hour in a shaker which imparted an average 110 longitudinal vibrations per minute, amplitude of vibration being 11 cm. The height of the aqueous layer was noted at different time intervals during an hour.

RESULTS

The surface tension and interfacial tension of aqueous solutions of series of surfactants derived from saturated fatty acids decrease with increase in concentration. There is an increase in surface tension and interfacial tension from phosphated mono to tri capric and myristic acyl mannitols.

The phosphated tri acyl mannitols of capric and myristic acid have better emulsifying property than the corresponding di and mono compounds.

DISCUSSION

The decrease in surface tension and interfacial tension of aqueous solutions of series of surfactants derived from saturated fatty acids with increase in concentration shows that the orientation of the surfactant molecules at the surface and interface is almost similar.

It seems that the surfactant molecules orient themselves slowly both at the surface and interface of dispersed phase and dispersion medium in such a way to have maximum contact angle by changing their relative conformations.

CONCLUSION

The present method is quite satisfactory for the preparation of phosphated fatty acyl derivatives of polyols. The use of other fatty acids or mixed fatty acids can also be tried instead of pure fatty acids.

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