Preparation and Emulsifying Properties of Polyethylene Glycol (1500) Diesters of Fatty Acids

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ABSTRACT

Oil soluble polyethylene glycol (PEG-1500) diesters of stearic, 12-hydroxystearic, oleic and 12-hydroxy oleic (ricinoleic) acids were prepared by standard condensation reaction procedure. The surface active/emulsifying properties of the products were evaluated by determining interfacial tension and through performance test in making water-in-oil emulsion. The presence of double bond or hydroxyl group in the C_{18} acids, PEG content of reacting mixture, and nature and concentration of the catalyst in preparing the emulsifier all were found to have great bearing on the emulsifying property and stability of w/o emulsions, particularly when the aqueous phase contained a significant quantity of ions. Only the first factor, the effect of double bond and/or the hydroxyl group, is discussed in this paper.

INTRODUCTION

Polyethylene glycol (PEG-1500) diesters of long chain fatty acids of low HLB are non-ionic oil soluble emulsifiers and are used extensively in a variety of applications such as in emulsion paints, emulsifiable solvent cleaners and other emulsion dispersions/formulations. PEG fatty acid esters can be prepared by either ethoxylation (1,2) or esterification (3). The latter process is safer as it does not involve the handling of hazardous ethylene oxide and is more easily controllable by changing the reaction parameters. Because polyethylene glycol has two hydroxyl groups available to react with the carboxylic acid, both mono- and diesters can be formed. The relative contents of monoester and diester in the equilibrium mixture depend upon the ratio of the reactants (4).

An equimolar ratio of fatty acid and polyethylene glycol results in a mixture which is predominant in monoester. Pure monoester also can be obtained by reacting the PEG with boric acid, esterifying the resultant borate with fatty acids and selectively hydrolyzing the borate ester (5). A higher molar ratio of fatty acid to polyethylene glycol favors greater concentration of diester in the mixture. The mole ratio of the reactants also governs the solubility of the product, which ranges from complete oil solubility to complete water solubility. It has been observed that the desired oil solubility is achieved when PEG is allowed to react with excess fatty acid. Expressed in terms of ethylene oxide, generally the addition of 1 to 8 moles of EO gives a product which is completely oil soluble and also completely soluble in hydrocarbons. For such products, PEG content usually is kept below 40% (on weight basis).

Keeping the above in view, PEG-1500 diesters of four fatty acids, viz. stearic, 12-hydroxy stearic, oleic and 12-hydroxy oleic (ricinoleic), have been prepared to correlate the structural differences in the hydrophobic moiety with the surface active properties, with specific reference to the emulsifying property of the products in the presence of high ionic concentration.

EXPERIMENTAL

Materials

The fatty acids' sources and purity as checked by GLC follow:

Fatty Acid Type	Source	Purity (%)
Stearic	Bombay Oil Industries Pvt Ltd	Technical grade
12-Hydroxy stearic	—do—	85
Oleic	ACME Synthetic Chemicals, Bombay	96
Ricinoleic	Godrej Soaps Ltd, Bombay	80

The acids were used without any further purification.

PEG-1500 was obtained from Petrochemicals Division, ICI, United Kingdom. Xylene was reagent grade (Glaxo Laboratories Limited, India). The nitrogen used was of high purity (99.5%) IOLAR (The Indian Oxygen Limited), and the Ti-alkoxide catalyst was obtained from Paints Division, ICI, United Kingdom. The inorganic salts used in the aqueous phase for the emulsification study, viz. NH_4Cl, NaCl and $Ca(NO_3)_2$, were of technical grade. The oil phase in the water-in-oil emulsion (w/o) was a mixture of diesel oil and paraffin wax (1:1), and the commercially available materials were used without further purification. The diesel oil was mostly paraffinic in nature and the analysis results as per IP-156 were: paraffins + naphthenes – 77%, aromatics 22% and olefins 1%—all the results being expressed in volume basis (v/v). The paraffin wax had a melting point in the range of 59-61 C. The paraffin oil used for surface tension/interfacial tension was of medicinal grade, and its paraffinic content was more than 99%.

Methods and Apparatus

Preparation of PEG esters. The general procedure for preparing the PEG diester consisted of reacting PEG with excess of long chain fatty acid (Acid:PEG 12:1). As the reaction is reversible, it is essential that the water of reaction be continuously removed from the system to maintain the reaction in the forward direction. This was achieved through the use of xylene as an entraining solvent and the Dean and Stark apparatus to trap the water. Following is a typical recipe for the preparation of a 1 kg batch involving PEG-1500 and 12-HSA.

300 g of PEG-1500 (0.2 mole) pre-dissolved in 200 ml xylene was added to 700 g of 12-HSA (2.33 mole) also diluted with 250 ml xylene and maintained at 60 C. These were mixed together in a 4-necked RB flask under nitrogen flow. The temperature of the flask, kept in an oil bath, gradually was raised to 230 C over a period of 3 hours. Xylene mixed with water started distilling off at 125-130 C. The water was trapped in the Dean and Stark attachment while xylene flowed back into the reaction flask. Periodically the water was drained off.

The refluxing was continued at 230 C for 3 hours during which samples were drawn periodically to monitor the progress of reaction by IR spectroscopy and acid value (AV) determination. The reaction was followed until the AV of the product dropped below 30. At this stage 0.05% (on the basis of the weight of the reactants) of titanium alkoxide catalyst was incorporated and the refluxing was continued until the acid value was around 10. The product was cooled under nitrogen and recovered from the flask.

Analysis of the product. The products were analyzed in terms of the various molecular species present, and their concentrations and molecular weights were determined by HPLC/GPC techniques using ALC/GPC Model No. 244 of Waters Associates having a differential refractometer, R-401 detector and three styragel columns, viz. 1000 A°, 500 A° and 100 A° in series. THF was used as eluting solvent. All experiments were done at room temperature (25 C).

The concentrations were determined by using the area normalization method; the Model 730 Data Module with the GPC option was used to calculate the average molecular weight of each species using the standard calibration curve of PEG (Range 200-10,000).

Surface active properties. Interfacial tension (γ) measurements of the PEG alkyds in paraffin oil + diesel oil (1:1) against distilled water were made using a Du Nuoy Tensiometer. Critical micelle concentration (CMC) was determined from the plot of γ vs concentration (log C) at the point of inflection. The surface excess concentration of the surfactant, Γ and the area (A) occupied by each molecule, were calculated from the slope of the straight line in the γ-log C plots below CMC using the form of the Gibbs adsorption isotherm equation (6) assuming unit activity coefficient for the PEG esters. The surface pressure, Π values were obtained by subtracting γ values from γ_0, the observed interfacial tension in the absence of surfactants.

Emulsifying properties. The emulsifying properties of the products were checked by finding out their capability to emulsify an aqueous solution of electrolyte(s) into an oil (mixture of paraffin wax and diesel oil).

Exact compositions of the aqeuous phase and oil phase are:

Ingredient	Composition, % (w/w)
Aqueous Phase	
Ammonium chloride	24
Sodium chloride	3
Calcium nitrate	12
Water	55
Oil Phase	
Diesel oil	2.0
Paraffin wax	2.0
Emulsifier	2.0
	100.0

The emulsification was achieved by gradual addition of hot aqueous phase at 70 C into the oil phase, maintained at the same temperature, with continuous stirring. Once the emulsification took place, the material was cooled progressively to achieve a good homogeneous consistency.

RESULTS AND DISCUSSION

The yield of diesters obtained with various acids, the acid value, the average molecular weight and the molecular composition of the products are shown in Tables IA-IB.

It is seen that the yields of the diester in the cases of stearic and oleic acid are of the order of 50%, whereas the corresponding hydroxy acids give much higher yield, around 80%. The reason for this variation becomes apparent by recognizing the presence of high acid: PEG mole ratio in the reacting mixture. Excess unreacted acid present in the first two cases as manifested in the high acid value, is bringing down the proportion of the diester. This does not happen with the hydroxy acids. Because of their bifunctional nature, intermolecular condensation/polymerization is possible leading to oligomers which eventually react with the PEG. This is reflected in much higher molecular weights of the diesters with hydroxy acids as shown in Table IA. The presence of residual oligomers in the finished products also could be detected by HPLC analysis as could be seen from the results in Table IB. Formation of oligomers in situ with both hydroxy stearic and hydroxy oleic acids was confirmed by carrying out separate experiments with the acids without using any PEG-1500. GPC analysis of the products clearly revealed the presence of various oligomers as presented in Figure 1. As an example, the structure of one of the oligomers, trimer of 12-HSA, also is included in Figure 1.

Data on interfacial tension of the 4 PEG-1500 esters in (DO + PO) mixture against water are given in Table II. In each case, the concentration of the surfactant has been varied by a factor of 200, from 0.025 g/100 ml to 5.00 g/100 ml. For all the systems, the control value of interfacial tension, i.e. for paraffin oil and diesel oil mixture against water without any surfactant, was determined at 25 C and the mean value was found to be 24.6 dyne cm^{-1}.

Values of interfacial tension, γ have been plotted against log concentration as depicted in Figure 2. The values CMC, γCMC, Γ, 'C' at Π = 20 and 'A' values derived from the plots are presented in Table III, which also contains the

TABLE IA

Yield and Properties of PEG-1500 and Fatty Acid Condensation Products

Fatty acid	Product code name	Mole ratio[a] (Acid:PEG)	Yield (%)	Av. mol wt	Acid value
Stearic acid	ACM-88	12.32:1	47	2250	99.6
Oleic acid	ACM-89	12.30:1	49	2250	88.1
12-Hydroxy Stearic acid	ACM-84	11.66:1	84	3300	11.3
Ricinoleic (12-Hydroxy oleic acid)	ACM-76	11.60:1	80	3300	8.1

[a] The weight ratio was always maintained at Acid:PEG = 70:30.

TABLE IB

Molecular Composition of PEG-1500 and Fatty Acid Condensation Products

	Composition (%)					
		Oligomers				
Product	Diester	Dimer	Trimer	Tetramer	Unreacted acid	Unknown
ACM-88	45	–	–	–	53	2
ACM-89	47	–	–	–	51	2
ACM-84	83	4.4	5.6	3.1	1.8	2.1
ACM-76	80	4.0	4.5	4.5	4.0	3

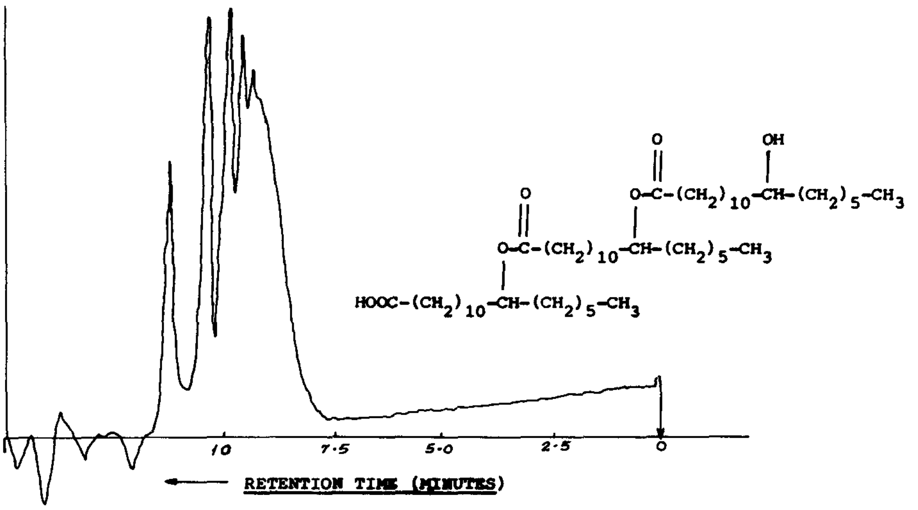

FIG. 1. Gel permeation chromatogram and planar structure of 12-hydroxy stearic acid oligomer.

TABLE II

Data on Interfacial Tension of PEG-1500 Esters in (DO + PO) Mixture Against Water at 25 C

Concentration (g/100 ml)	Interfacial tension (γ)			
	ACM-88 dyne/cm	ACM-89 dyne/cm	ACM-84 dyne/cm	ACM-76 dyne/cm
0.025	6.5	6.3	16.6	9.4
0.035	6.7	5.1	14.1	6.5
0.050	5.9	5.0	14.1	5.1
0.060	–	–	10.8	–
0.075	4.1	3.5	9.6	3.3
0.100	3.2	3.0	6.8	2.5
0.150	2.2	2.1	5.5	0.7
0.250	1.8	1.5	4.2	0.6
0.500	1.7	1.3	3.3	0.4
0.750	1.5	1.0	3.3	0.4
5.000	1.4	0.8	2.7	0.5

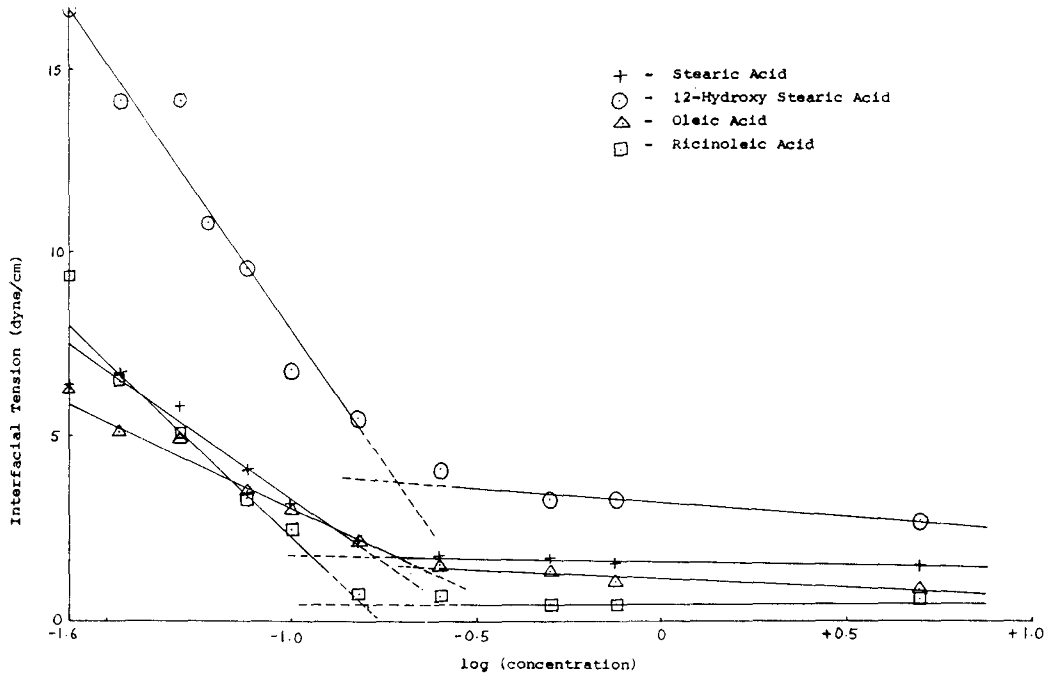

FIG. 2. Interfacial tension vs log concentration plots of PEG-1500 esters with various fatty acids. + = Stearic acid; ○ = 12-hydroxy stearic acid; △ = oleic acid, and □ = ricinoleic acid.

TABLE III

Surface Active Properties/Adsorption Parameters of PEG-1500 Esters

PEG-1500 ester based on (Code Name)	GPC mol wt	Drop in interfacial tension for 0.1% soln. (%)	CMC (g/100 ml)	γCMC (dyne/cm)	Conc. at Π =20 (g/100 ml)	Γ (mole/cm²) × 10¹⁰	A (A°)²	Brookfield viscosity (cp × 10³)	
								Fresh	6 months
Stearic acid (ACM-88)	2250	87.1	0.17	1.75	0.07	1.22	136	58	CPS[a]
12-Hydroxy stearic acid (ACM-84)	3300	72.9	0.19	3.75	0.17	2.54	65	>200	98
Oleic acid (ACM-89)	2250	87.4	0.22	1.45	0.06	0.82	202	42	CPS[a]
12-Hydroxy oleic acid (ricinoleic acid) (ACM-76)	3300	90.1	0.16	0.45	0.06	1.66	100	>200	112 TPS[b]

[a] Complete phase separation.

[b] Tendency of phase separation.

GPC mol wt of the products. The last two columns of Table III include the Brookfield Viscosity of the emulsion batches at 25 C in the fresh condition and after six months storage.

The high drop in interfacial tension/low value in γCMC or low value of surfactant concentration at Π = 20 are not the only criteria for a good emulsion, particularly in respect of its stability. Surface excess concentration, Γ should be high and the area per molecule, A should be low which are not so, especially with ACM-89, and as such its performance was very poor. The importance of this limiting area has been demonstrated elsewhere (7,8). The higher value of CMC of ACM-89 compared to that of ACM-76 presumably was because of its higher solubility in the oil phase. Similar finding on the CMC was made earlier with sorbitan esters of some fatty acids (9).

Going from stearic acid to 12-HSA or from oleic acid to ricinoleic acid, the changes in the surface active properties followed similar trends. In both cases, PEG esters based on hydroxy acids are far superior to those without OH-group in the hydrophobic chain. Bifunctionality achieved in the hydroxy acids through the OH-group made the intermolecular condensation polymerization possible. This resulted in the increase in molecular weight of the product, which is important for improved surface active property. Unfolding of the bulkier molecules at the oil-water interface will be more restricted with the hydroxy acid-based PEG-esters than the smaller molecules of the products with stearic acid or oleic acid. This restriction would minimize the coalescence of the droplets of the aqueous phase and bring an overall improvement in emulsification/stability. A similar explanation has been offered by Lankveld and Lyklema (10) in their studies with polyvinyl acetate.

The effect of introducing one double bond in the lipophilic part on the surface active and emulsifying properties is clearly manifested by comparing results between ACM-88 and ACM-89 or ACM-84 and ACM-76. Presence of unsaturation in the hydrophobic moiety makes the molecule more flat and less vertically oriented at the interface, thereby causing less efficient anchoring of the 2 phases. This is reflected in the increase in area per molecule.

Comparing the results between ACM-76 and ACM-84, it is seen that γCMC for the ricinoleic acid based product is much lower than that of the ester with 12-HSA. Since γ gives a measure of interfacial energy, thermodynamically this would imply that emulsion formation with ACM-76 would be easier. This was found to be the case. With minimum shear, PEG-ester with ricinoleic acid could emulsify the aqueous phase, yielding a good emulsion.

However, the emulsion was not very stable and within 6 months there was phase separation which was not the case with the 12-HSA based product. Increased stability in the latter case is attributed to the higher surface excess concentration (Γ), lower area per molecule (A) and more vertical orientation of the surfactant molecule at the interface.

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