

Ecofriendly Polymeric surfactants based on Polyethylene Glycol and Glycerol

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Abstract: In last five decades there is a common trend too used petroleum products as ingredients in commercial products like Liquid laundry detergents, cosmetics and textiles auxiliaries. The present research work is aimed at developing polymeric surfactant based on glycerol and polyethylene glycol .The ecofriendly polymers from glycerol and small quantity of polyethylene glycol have been synthesized by reaction with maleic anhydride, phthalic anhydride and citric acid. The mole ratios, order of addition of ingredients have been standardized to get polymer of desired acid value and viscosity. The selected polymer has been used as replacement of acid slurry and alpha olefin sulphonate in the formulation of liquid laundry detergents.

Key Words-Glycerol, Polyethylene Glycol, Eco-friendly, Detergent.

Introduction

In the present generation of commercial liquid, powder and cake detergents are based on the active ingredients like acid slurry and alpha olefin sulphonate. These raw materials are of petroleum origin. The price of crude petroleum is quite high. The stock of crude petroleum is soaring year after year. So we must develop bio-renewable agro-based alternative for these conventional petroleum based surfactants. Every industry today is searching for alternative renewable source of vegetable origin as the petroleum products are souring in price and availability

In this context we decided to design novel polymeric surfactants compositions based on glycerol and polyethylene glycol (mol.wt-400). The glycerol is by-product of bio-diesel industry, It is biodegradable and non toxic in nature. The Polyethylene glycol (400) contains Oxirane Oxygen group when it is arranged in polymeric linkages. The combination of glycerol and polyethylene glycol (400) in polymeric surfactant may give us products which replace acid slurry and alpha olefin sulphonate. In our earlier experiments we have developed polymers based on Starch, Sorbitol¹, Malenized oil² which can successfully replace 50-70% of acid Slurry and alpha olefin sulphonate from detergent compositions. The selected Polymer has been used as partial replacement of acid slurry and alpha olifine sulphonet in the liquid laundry detergent composition. The physicochemical characteristic of polymer like pH, sap-value, viscosity and H.L.B value have been studied initially and selected polymers have also been studied by I.R. and N.M.R. spectroscopy.

Experimental

The synthesis has been workout in a four neck glass reactor of 2 liter capacity .The central neck has a stirrer with speed regulator. The right neck is having a thermometer. One opening is reserved for addition of reactants .weighted quantity of various ingredients was introduced from this opening. The heating was started

slowly and steadily. The temperature of 120-130⁰c is achieved in about 90 minutes by electric heating mantle with temperature controlling regulator ($\pm 3^0$ c). The regulator can efficiently manage the desired temperature. The heating is continued for three hours and then the mass was cooled to 80⁰c. The samples were stored in tightly corked bottles. These Polymer samples were systematically analyzed for acid value, viscosity, surface tension, % oxirane oxygen value. The sample was systematically tested for %solids, foam, pH and sap-value by standard laboratory methods⁽³⁻⁸⁾. They were also analysed by I.R⁽⁹⁾, N.M.R⁽¹⁰⁾ spectroscopy to know the finger print of ester group, ether group, free-OH groups and free acid groups.

This study indicates that sample G26 based on citric acid was most suitable for formulation of liquid laundry detergent. Liquid laundry detergents based on combination of acid slurry, sodium lauryl ether sulphate (S.L.E.S), sodium lauryl sulphate(S.L.S) and Polymer G26 were prepared. Significant amount of G26 (10-15%) has been used.

The liquid laundry detergent were again systematically tested for pH, % Solids, Foaming characteristics, surface tension and cleaning of cotton cloths for stains of soil, tea, coffee and spinach(palak) by standard laboratory techniques. The result have been compared with standard commercial products in the market to know the practical viability of composition

Analysis and Testing of Liquid Detergent^{(8, 11, 12, 13):}

Liquid detergents (3 samples) were prepared using different concentrations of polymer with sodium lauryl ether sulphate (S.L.E.S), sorbitol, sodium lauryl sulphate (S.L.S), polyvinyl alcohol(P.V.A), sodium carbonate and acid slurry in a beaker and stirring was continued for 30 min (Table 3). The sample was stored overnight at 10⁰c in refrigerator. A clear solution of liquid detergent was obtained after filtration. The surface tension of liquid detergents was measured using stalagnometer. Foam was measured by using mechanical agitation in a closed glass cylinder of 1litre capacity. The analysis of different liquid stain remover sample is given in table 5 and 6.

Stain Preparation: The soil Medium of following composition is prepared.

Component Weight %-Carbon Black (28.4%), Coconut Oil(35.8%), Lauric Acid(17.9%), Mineral Oil (17.9%). The mixture of carbon black and Lauric acid along with mineral oil is taken in a pastel mortar. Coconut oil is added slowly to form a thick paste. All the components are ground in pastel mortar for 1-2 hours till we get a fine grinding. The fine grinding is indicated by smooth feel of the paste medium.

Soil Solution: This is prepared by adding 2gm of above paste in 500ml of carbon tetrachloride. Mix it well and use for staining cloth sample preparation. The solution is kept in packed bottles.

Tea Stain Solution: The tea is prepared with following composition. Tea(Taj Mahal)(2.2%), Sugar(8.0%), Milk(38.4%), Water(51.4%). Take 25gm of water and warm it to 35 to 40⁰c then add Taj mahal brand tea and sugar heat it up to 80⁰c till it starts boiling add milk and continue heating at boiling temperature for next 5 minutes, stop heating and pass the tea through a Steiner. Use this as tea medium.

Preparation of Coffee Medium: The coffee of following composition is prepared. Coffee(1%), Sugar (8.1%), Milk(51.9%), Water(39 %). Take 25gms of milk and water in a beaker warm it to 35-45⁰c than add coffee and sugar continue heating in boiling conditions for 5 minutes, stop heating and use this coffee as staining medium.

Preparation of Palak (Spinach) Medium: The Palak(spinach) medium is prepared of following composition, Oil (1.34%), Spinach (9%), Water(89.66%) heat the oil and then add spinach to it and fry for 5 minutes. To this add half cup of water cook it for 10 minutes after the preparation it is stored in tight bottle.

Method of application of soil: The cloth of size 24 x 32 cm² were prepared. Take 50ml of soil solution in a beaker; dip the cloth sample in it for 5 minutes. This is kept outside for drying in open atmosphere for 2 hours. Then this cloth is cut in size of 6x8 cm² and samples are used for washing.

Method of Washing^{(14,15):} The solutions of different concentration were prepared. Heat that solution to temperature of 60⁰c. Dip soiled cloth sample in it for 5 minutes and give to and fro 10 hand washes.

Method of application of (Spinach, Tea and Coffee): The cotton cloths of size 24 x 32 cm² were taken and make checks with the help of size 6 x 8 cm². Then take the above staining solution in a pipette and add in a

center of checks one drop and then kept the stain cloth sample in an oven at $55 - 60^{\circ}\text{C}$ for $\frac{1}{2}$ hr. then this stain cloth is cut into test sample size and these were used for stain removal testing.

Table No 1:-Composition of Polymer

Sr.No.	Polymer (Ingredients in %)	G25	G26	G27
1	Glycerol	50	50	50
2	Polyethylene glycol (Molecular weight 400)	20	20	20
3	Sorbitol	10	10	10
4	Maleic anhydride	---	---	20
5	Phthalic anhydride	20	---	---
6	Citric acid	---	20	---

Note:- 2.5% NaHSO_3 , 2.5% NaHSO_4 and 1% Conc..HCl used as catalyst in all batches.

Table No 2:- Physicochemical Analysis of Polymers

Sr.No.	Polymer	G25	G26	G27
1	Surface tension(dyne/cm)	66.34	71.23	66.45
2	Density(g/cc)	1.11	1.15	1.12
3	% solids	90.15	86.55	87.45
4	pH(1% solution)	3.08	3.32	2.80
5	Acid value	93.60	71.17	86.14
6	Foam Volume (cm^3)	100	100	100
7	Viscosity (Seconds -by ford cup No 4 at 30°C .)	220	210	210
8	Sap. Value	128.68	144.7	189.92
9	H.L.B Ratio	16.5	16.3	16.6
10	Oxirane oxygen	3.69	4.54	2.78

Table No 3:-Composition of Liquid Detergent

Sr.No	Ingredients in %	G 26L1	G 26L2	G 26L3
1	Acid Slurry	10	11	12.5
2	Polymer	15	14	12.5
3	S.L.S(30% Solids)	1	1	1
4	S.L.E.S(38% Solids)	11	11	11
5	Sorbitol(70% Solids)	3	3	3
6	Sod. Carbonate	5.5	5.5	5.5
7	Urea	0.5	0.5	0.5
8	Distilled Water	54	54	54

Table No 4:-Physicochemical Properties of Liquid Detergent

Sr.No	Properties	G 26 L1	G 26 L 2	G 26L3	CS
1	pH	8.5	8.3	8.5	5.2
2	Viscosity(Seconds)	148	150	154	289
3	Appearance Of Liquid	Transparent Liquid	Transparent Liquid	Transparent Liquid	White Liquid

Note: CS- Commercial Liquid laundry detergent Sample.

Table No 5:-Physicochemical Analysis of Liquid Detergent

Concentration	Sample	Foam Volume (cm ³)			Density (g/cc)	Surface Tension (dyne/cm)
		0min	10min	30min		
1%	G26 L1	1000	900	343	1.03	31.75
	G26 L2	1000	895	340	1.03	36.00
	G26 L3	1000	890	340	1.02	27.73
	CS	370	225	100	1.03	28.08
0.5%	G26 L1	1000	900	342	1.02	30.71
	G26 L2	1000	880	336	1.03	36.65
	G26 L3	920	810	315	1.02	36.97
	CS	200	140	100	1.02	29.79
0.25 %	G26 L1	820	720	310	1.02	35.00
	G26 L2	800	695	305	1.01	34.06
	G26 L3	590	530	300	1.02	36.61
	CS	170	120	100	1.02	33.27

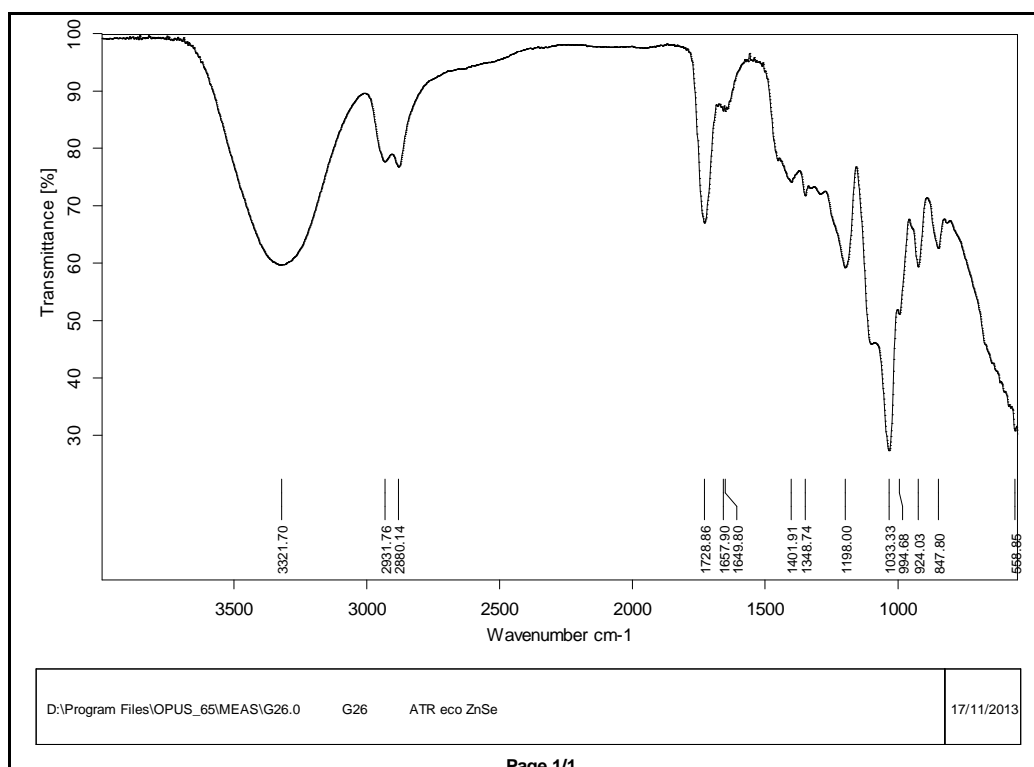
Table No 6:-Cleaning Analysis for 1% Consantration

Powder No	Stain medium For Cotton Cloth				Total Point
	Soil	Tea	Coffee	Palak(spinach)	
G26 L1	4	4	4	3	15
G26 L2	4	4	4	4	16
G 26L3	4	4	3	3	14
CS	2	4	4	3	13

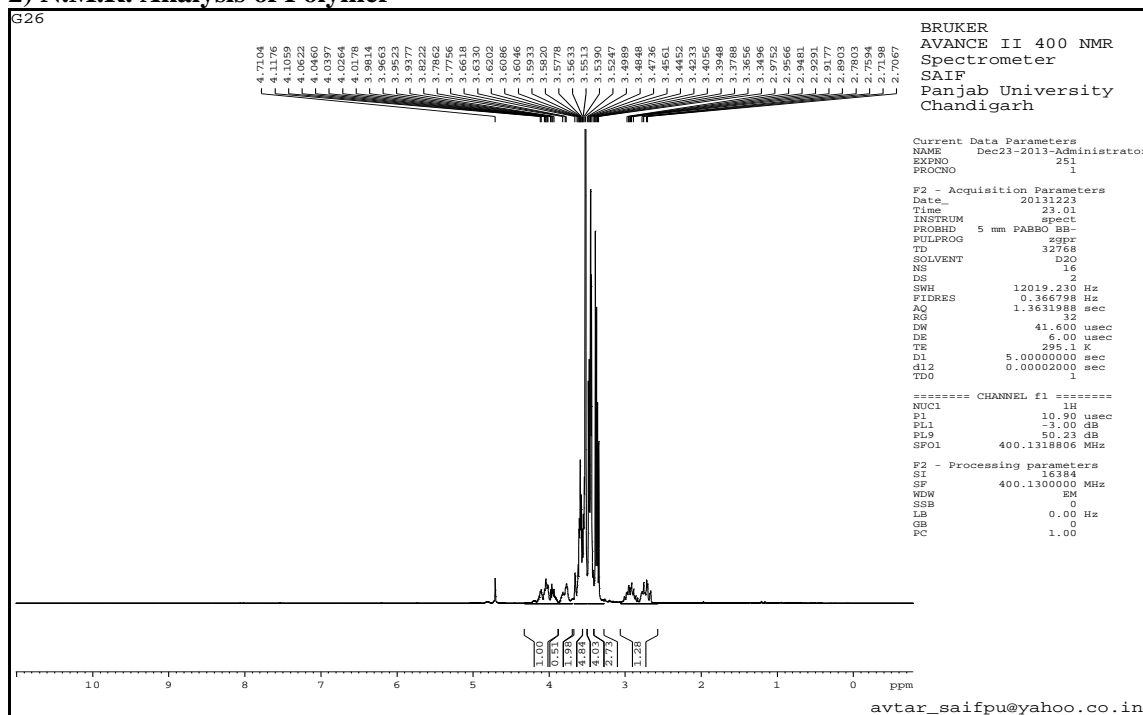
Cleaning Points:- 0- no cleaning, 1-25%, Cleaning,2- 50 %, Cleaning, 3- 74 % Cleaning, 4-100% Cleaning.

Table No 7:- Spectroscopical Analysis of Polymer

1) FT-I.R Analysis of Polymer



2) N.M.R. Analysis of Polymer



Result and Discussion

The composition of various polymers based mainly on Glycerol and Polyethylene glycol are given in Table 1. All samples contain 50% Glycerol and 20% Polyethylene glycol. These polyols were reacted with phthalic anhydride, maleic anhydride and citric acid. Same catalysts have been used in all the samples.

The Physicochemical analysis of various polymers is given in Table 2. 86 to 91% solids are present in all compositions. The acid value varies between 71 to 94. All samples have pH range of 2.80 to 3.08. All samples have excellent viscosity more than 210 seconds. The H.L.B value and oxirane oxygen indicate that sample G26 based on citric acid should be used in formulation of liquid detergents.

Liquid laundry detergent based on combination of acid slurry, sodium lauryl ether sulphate, sodium lauryl sulphate and polymer G26(10-15%) have been prepared as given in Table 3.

All samples have an alkaline pH and give excellent result of foaming, surface tension and stain removing properties for stains of soil, tea, coffee and spinach (palak). The sample is not only comparable but sometimes better than available commercial samples in the market as given in Table-4, 5 and 6.

Analysis of FT-IR spectroscopy shows presence of ester group (1728.86), ether group(1198.00), free-OH groups(3321.07) and free acid groups(2880.14). N.M.R spectra of polymer show presence of ester group formed by the reaction between alcoholic OH group and carboxylic acid group. Ether groups indicate the condensation of OH groups to form polymeric linkage. The peaks at 4.84 ppm are due to ester linkage as given in Table no7.

Conclusion

- (1) Excellent polymeric surfactant can be synthesized based on glycerol and polyethylene glycol by treating with citric acid, phthalic anhydride and maleic anhydride. Mole ratios of reactants, catalyst, time of reaction and order of addition of reactant have been standardized to get desired acid value, H.L.B Ratio and viscosity.
- (2) The Physicochemical analysis of polymers given in Table 2, indicate that these samples can be used in liquid laundry detergents. The % solids in the final product is about 86-91%. All samples are clear, transparent, with good flow and viscosity characteristics.

- (3) The polymer samples have been analysis by I.R. and N.M.R. spectra and these spectral studies indicate the presence of ether, ester, free hydroxyl group and acid groups present in polymer.
- (4) Liquid detergent base on G26 using 10-15% polymer give excellent performance characteristics comparable to available commercial products.
- (5) The product should be tried on pilot plant and commercial scale as they are techno-economically viable preposition. The use of polymeric surfactant will reduced the consumption of acid slurry as well as crude petroleum based surfactants.

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