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RESEARCH ARTICLE

Special eco-friendly liquid laundry detergents for washing machines

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ABSTRACT

The use of washing machines in India and third world countries is increasing very fast. Special ecofriendly moderate foaming and high efficiency liquid laundry detergents must be developed which are moderate in cost yet effective in performance. In the present work efficient polymeric surfactants based mainly on sorbitol, polyethylene glycol and maleic anhydride have been synthesized. The polymeric synthesis process has been standardized properly so that we can use it in washing machines detergents. The physicochemical and spectral properties of polymers suggest its selection in liquid detergent formulations. Liquid detergents were formulated using 14to20 % of this novel polymer along with other conventional ingredients. The prepared compositions were compared with commercial liquid laundry detergents. The result suggests use of this formulation on pilot plant & commercial scale.

Keywords: HLB ratio, % detergency, saponification value, polymeric surfactants.

INTRODUCTION

All cleaning compositions like powder, cake and liquid detergents, floor and glass cleansers, utensil cleansers are based mainly on linear alkyl benzene sulphonate (LABS) or alpha olefin sulphonate (AOS) which are of petroleum origin. The total dependence of various cleansing preparations on petroleum products is not a wise investment and we must develop ecofriendly surfactants which can partly or totally replace active materials of petroleum origin. We have successfully developed polymers based on sorbitol, glycerol, malenized oil and starch for powder and liquid detergents. In the present work the intention is to

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develop high efficiency active material which will give moderate foaming (High foaming is totally undesirable for washing machine) and excellent performance characteristics.

A special polymer has been synthesized based on sorbitol, polyethylene glycol (400) and maleic anhydride. A slightly higher amount of maleic anhydride has been used as this gives higher cleaning and stain removing efficiency. The polymers were systematically analyzed for their acid value, viscosity, surface tension and other physicochemical properties. The selected polymers (14-20%) were used for preparation of moderate foaming liquid laundry detergents for washing machine. The liquid laundry detergents were analyzed systematically along with a commercial product for foaming, surface tension and soil stain removal by standard methods (Gogte and Agrawal, 2003; Maltiellow, 1944; Gogte and Donyulwar, 2004; Taylor and Marks, 1972). The special feature of product is freedom form sodium tripolyphosphate which is source of pollution and use of sorbitol which gives a soothing and non-irritating feel to the skin.

METHODS AND MATERIAL

a) Synthesis of novel polymer

The preparation of novel polymer was carried out in a glass reactor. The reactor consists of two parts. Lower part of the reactor is a round bottom glass vessel with very wide mouth having capacity of about 2 liters. The upper part of the reactor is its lid, having four necks with standard joints. The central neck has a stirrer with speed regulator arrangement. The second neck is used for mounting thermometer. A condenser is fitted with the reactor through the third neck, and the fourth neck is used for dropping the chemicals into the reactor. An electric heating mantle is used for heating the reactants. A regulator controlled the speed of the stirrer. The reaction vessel and its lids are tied together with the help of clamps. Initially, composition mentioned in Table-1 of sorbitol, polyethylene glycol, maleic anhydride was added in the reactor. Con. HCl was used as a catalyst. The temperature was raised slowly and slowly to 130^0c. The reaction was continued for 3 hours. The consistency of the paste was maintained by adding water. At the end of this period the batch was terminated and prepared polymer was collected in a glass stopper bottle with least air gap. The final yield of the product was measured.

b) Analysis of Novel polymer

Analysis of novel polymers were carried out by determine acid value (ASTM, standard method), saponification value (ASTM, standard method), viscosity (Melhen, 1986), oxirane oxygen (Melhen, 1986) value solid content (ASTM, standard method, 1963-74), pH value (Jefferyetal *et al*., 1989), HLB ratio (Jellinek, 1954) and % detergency (Harries, 1954).

Table 1: Composition of special polymers based on sorbitol and Polyethylene glycol.

Sr. No.	Raw material	Concentration	
		Batch-1	Batch-2
1.	Sorbitol (70%)	60	35
2.	Polyethylene glycol(400)	10	35
3.	Maleic Anhydride	30	20
4.	Citric acid	-	05
5.	Oxalic acid	-	05

Note: *Catalyst- 1% Con. HCl, 3.5% Sodium metabisulphite, 3.5% sodium bisulphate.*

Table 2: Physicochemical properties of synthesized polymers.

Sr. No.	Polymer property	Batch-1	Batch-2
1.	Acid value of polymer	136.16	138
2.	pH of 1% solution	4	4
3.	% solid	85.21	81.70
4.	Solubility 1.Water 2. Xylene	 Soluble Insoluble	 Soluble Insoluble
5.	Hydrophilic-lipophilic balance of polymer	13.21	14.98
6.	Flow time in second at 30^0c by Ford cup no. 4.	185	252
7.	Surface tension in dyne/cm.at30^0c by Ostwald's viscometer	38	34
8.	Oxiraneoxygen (%)	1.98	2.09
9.	*Foam volume in cm^3 by cylinder method	450	800

**Foam volume was measured for combination of 90% polymer and 10% linear alkyl benzene sulphonate (LABS) neutralized.*

c) Preparation of liquid detergents

Various raw materials in liquid detergent likeneutralized acid slurry, neutralized polymeric resin and conventional ingredients were taken in aglass reactor (Table-3) and homogenized by running the stirrer for about an hour, refer Table-3. The solution is cooled in refrigerator at 10^0c for 48 hours. The clear liquid solution was filtered and packed in superior grade air tight plastic containers (Garrette,1972; Puri *et al*., 1997).

Table 3: Composition of moderate foaming liquid detergents for washing machines based on Polymer batch -1 (% by weight)

S. No.	Raw material	Concentration(% by weight)			
		LF-1	LF-2	LF-3	LF-4
1.	AOS	02	01	00	01
2.	SLES	10	10	10	10
3.	Polymer	14	16	18	20
4.	Urea	02	02	02	02
5.	EDTA	01	01	01	01
6.	Sorbitol	05	04	04	04
7.	Sodium carbonate	07	07	07	07
8.	CMC	10	10	09	09
9.	Salt	02	02	02	01
10.	Water	53	53	53	53

Note; LF-1, LF-2, LF-3.LF-4 are liquid detergents based on Batch-1. AOS- Alpha olefin sulphonate, SLES- Sodium lauryl ether sulphate, EDTA- ethylene diamine tetra acetic acid.

Table 4: Analysis of liquid detergents at 1%, 0.5, 0.25% concentration.

S. No.	Liquid detergents	Concentration %	Foam volume in (cm^3) after 0,5,10 minutes.by cylinder method			Density(g/cm^3) by density bottle	Surface tension (dynes/cm)at 30^0c by Ostwald's viscometer.
1.	LF-1	1% 0.5% 0.25%	850 650 400	800 550 300	650 400 200	1.042 1.042 1.035	27.76 29.26 29.81
2.	LF-2	1% 0.5% 0.25%	650 340 240	550 260 200	400 200 100	1.052 1.028 1.046	30.30 31.09 35.40
3.	LF-3	1% 0.5% 0.25%	450 280 250	360 210 200	300 190 170	1.019 1.045 1.031	29.35 33.11 34.15
4.	LF-4	1% 0.5% 0.25%	520 250 280	480 200 210	320 160 168	1.038 1.042 1.021	31.39 35.26 35.50
5.	Commercial market liquid detergent	1% 0.5% 0.25%	750 600 500	700 550 400	550 400 320	0.910 0.913 0.941	37.42 37.69 38.50

Table 5: Stain removing properties of moderately foaming laundry liquid detergents based on novel polymer-Batch-1

Sample	Soil	Tea	Coffee	Spinach	Cleaning score
LB-1	2	4	3	4	13
LB-2	3	4	4	3	14
LB-3	2	3	3	4	12
CD-1	3	4	4	4	15
CD-2	3	4	4	4	15

RESULT AND DISCUSSION

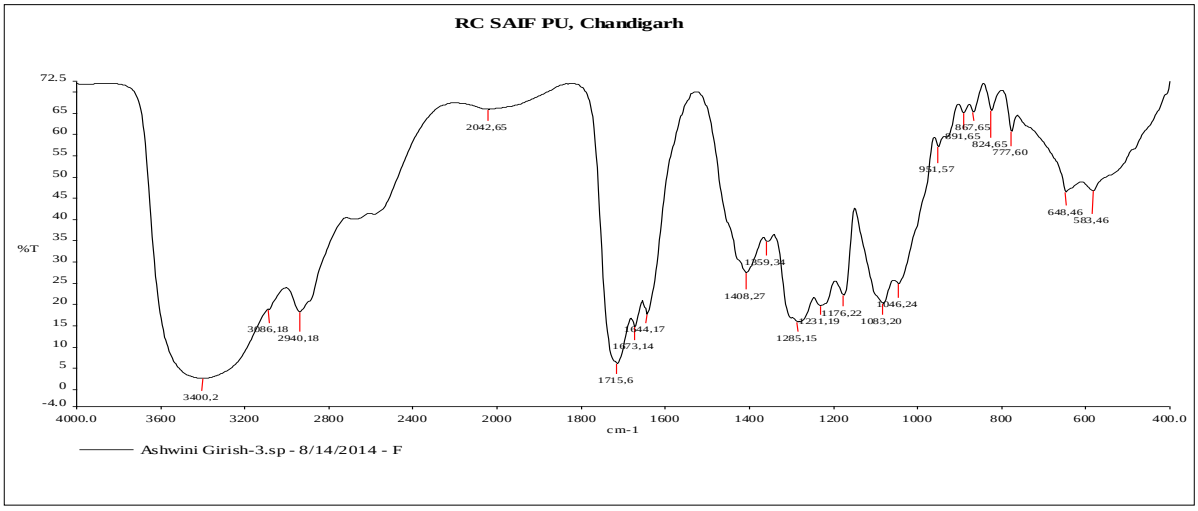

Fig.1: IR spectra of Batch-1 polymer

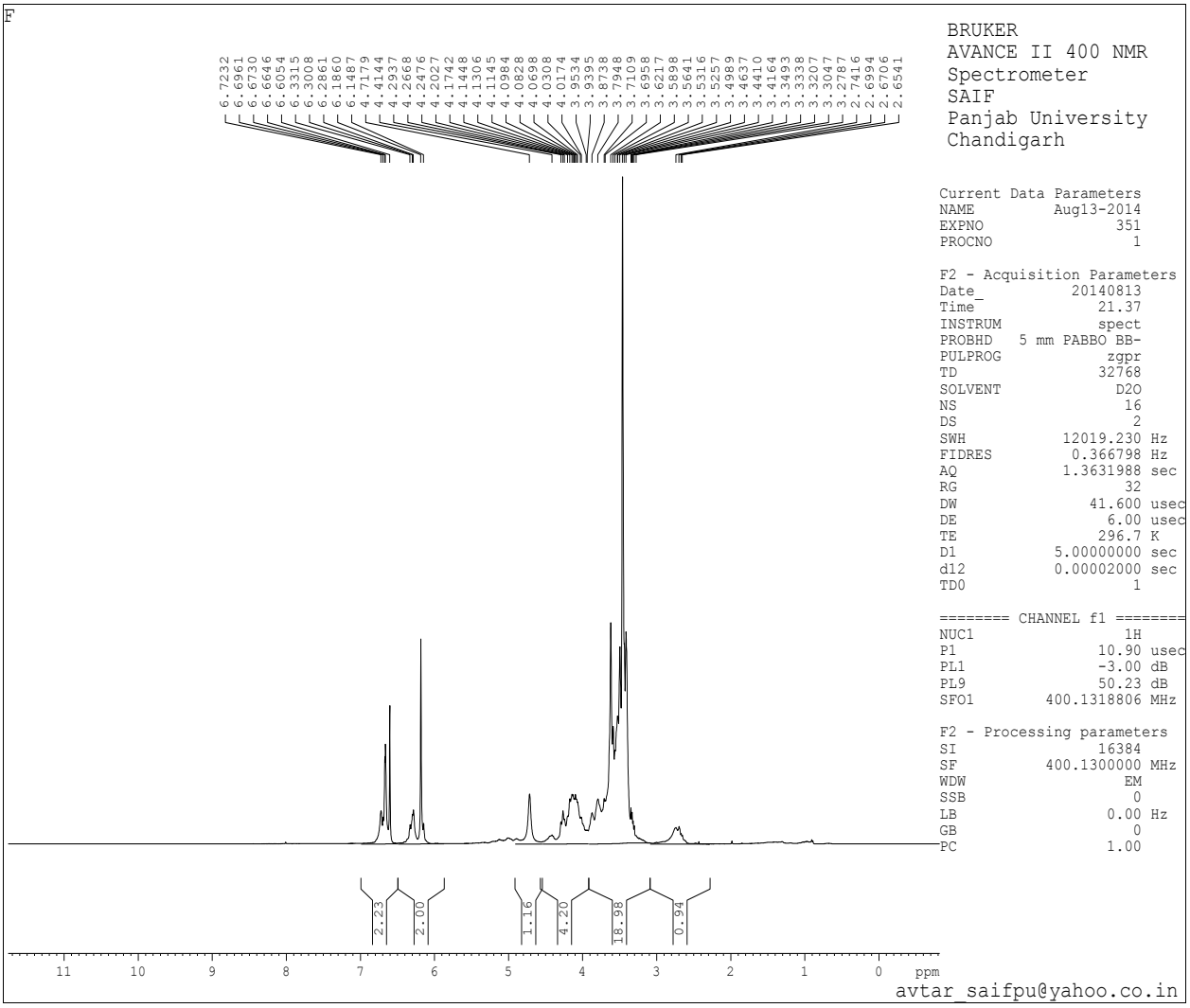

Fig. 2 :NMR spectra of Batch-1 polymer.

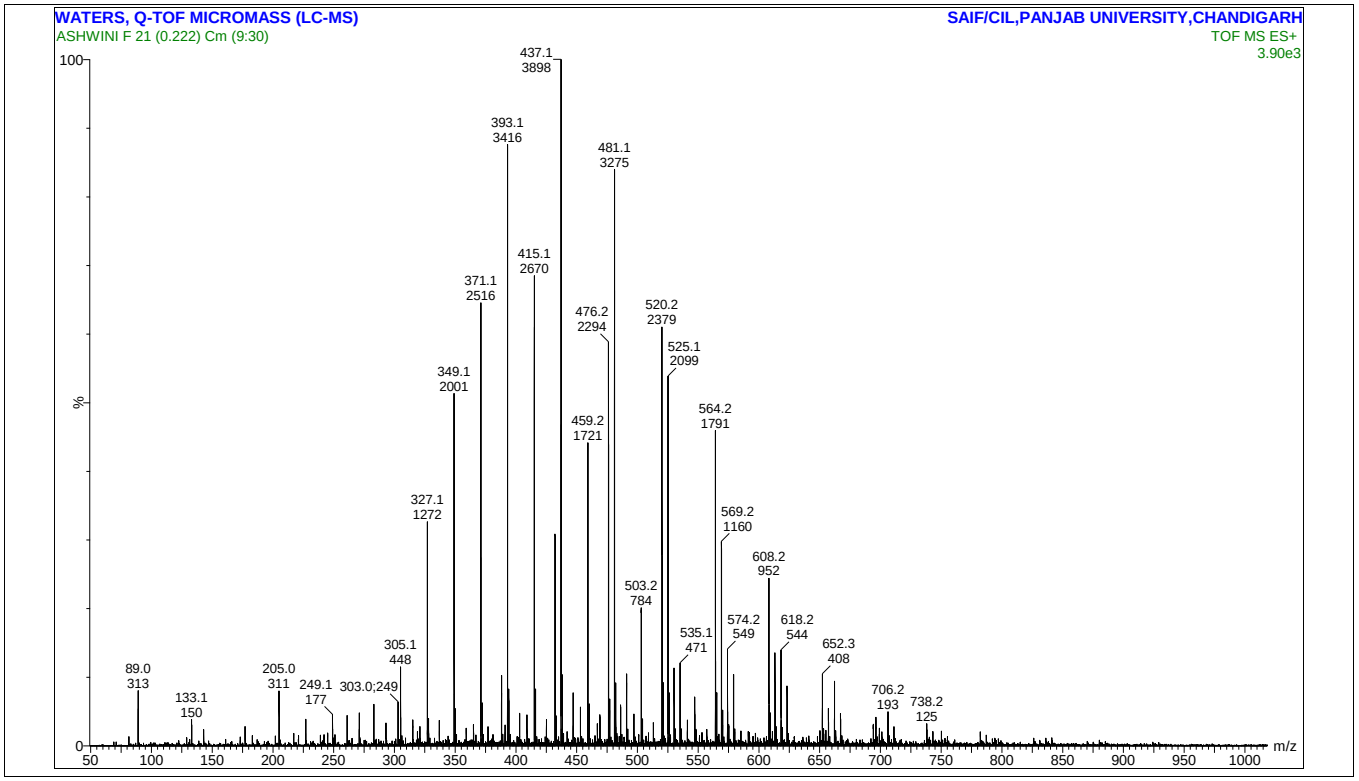

Fig. 3 : Mass spectra of Batch-1 polymer.

1. Composition of special polymers is given in Table-1.
2. A higher proportion of maleic anhydride (20-30%) has been used which may give greater cleaning efficiency to our detergent.
3. Small proportion of citric acid and oxalic acid will also help in cleaning and stain removing properties of the polymer.
4. The physicochemical properties of the polymer are reported in the Table-2.
5. The acid value of samples is significantly higher as a higher proportion of acids 30% have been used. The pH is also acidic and H.L.B. ratio suggests the use of these polymers in detergent compositions.
6. The samples are highly soluble in water and have reasonable flow and viscosity properties. Use of citric and oxalic acid give a slightly higher viscosity.
7. The surface tension reductions capacity of polymer and presence of oxiraneoxygen will certainly help the detergent to have better cleaning capacity.
8. The foaming properties were evaluated for (90:10) combination of polymer with acid slurry. The % solids are reasonably high (80-85%).
9. The composition of liquid detergents is shown in Table-3.
10. In progressive samples the percentage of polymer has been increased from 14-20%.
11. A very small percentage of alpha olefin sulphonate has been used. A constant proportion of SLES, sodium carbonate, EDTA, salt (1-2%) and sodium carbonate.
12. The pH of final sample has been maintained between 8 to 9.
13. The analysis of liquid detergents including foam stability is given in Table-4.Compared to commercial sample there is reasonable foaming property at all concentrations. The foam is reasonably stable for ten minutes and compares well with commercial sample.
14. In fact our samples have moderate foaming properties slightly lower than commercial sample. This reduced foam is a desired property for commercial application.
15. Excellent surface tension reduction at all concentrations (0.25-1%) is observed which a desirable characteristic for better performance.
16. The molecular weight of polymer is 2917(Fig.-3) and degree of polymerization is 16.

CONCLUSION

Special polymeric surfactants suitable for developing moderate foaming washing machine liquid detergent can be synthesized using mainly sorbitol and polyethylene glycol (400). The acid component is mainly maleic anhydride and minor proportions of

oxalic and citric acids have been used. The physicochemical analysis of the polymer as given in Table-2 suggests the use of this polymer is formulation of moderate foaming detergents for washing machines. Several moderate foaming detergents based on 14-20% of polymer-B1 have been formulated by standard techniques. The analysis of these samples alog with commercial sample indicates excellent foaming, surface tension reduction ans soil cleaning property. These properties are some times better than commercial sample. The manufacturing cost of our liquid detergent formulations is between 55 to 60Rs. Per Kg. So it can be marketed at Rs.100/- per Kg. Pilot scale studies on synthesis of polymers and its utilization on industrial scale must be promoted. Our samples are ecofriendly as they do not utilize any acid slurry or sodium tripolyphosphate. Spectroscopic studies indicate the presence of ester, ether, free acid and free alcohol groups.

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