



## EARTH-FRIENDLY LIQUID LAUNDRY DETERGENTS FOR WASHING MACHINES

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**KEYWORDS:** HLB ratio, % detergency, saponification value, polymeric surfactants.

### 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 oxalic acid 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.

### 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 earth-friendly 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 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 oxalic acid. 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<sup>1-4</sup> describe in the literature. The special feature of product is freedom from sodium tripolyphosphate which is source of pollution and use of sorbitol which gives a soothing and non-irritating feel to the skin.

### EXPERIMENTAL

**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 of reactants [Table-1] was added in the reactor. The temperature was raised slowly to 130<sup>0</sup>c. 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 stoppered bottle with least air gap. The final yield of the product was measured.

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

S. No.	Raw material	Concentration	
		Batch-1	Batch-2
1.	Sorbitol (70%)	55	73



2.	Polyethylene glycol(400)	10	05
3.	Oxalic acid	28	20
4	Sodium metabisulphite	3.5	01
5	Sodium bisulphate	3.5	01

**Analysis of Novel polymer-** Analysis of novel polymers were carried out by determine acid value<sup>5</sup>, saponification value<sup>5</sup>, viscosity<sup>6</sup>, oxirane oxygen<sup>6</sup> solid content<sup>7</sup>, pH value<sup>8</sup>, HLB ratio<sup>10</sup> and % detergency<sup>11</sup>

*Table-2 Physicochemical properties of synthesized polymers*

Serial No.	Polymer property	Batch-1	Batch-2
1	Acid value of polymer	116.52	63
2	pH of 1% solution	4	4
3	% solid	81.29	81.21
4	Solubility 1. Water 2. Xylene	Soluble Insoluble	Soluble Insoluble
5	Hydrophilic-lipophilic balance of polymer	12.12	13.85
6	Viscosity in second at 30 <sup>0</sup> c by Ford cup no. 4.	180	168
7	Surface tension in dyne/cm.at30 <sup>0</sup> c by Ostwald's viscometer	34	31.82
8	Oxirane oxygen (%)	2.98	2.80
9	*Foam volume in cm <sup>3</sup> by cylinder method	700	700

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

**Preparation of liquid detergents** – Various raw materials in liquid detergent like neutralized acid slurry, neutralized polymeric resin and conventional ingredients were taken in a glass reactor (Table-3) and homogenized by running the stirrer for about an hour, refer Table-3. The solution is cooled in refrigerator at 10<sup>0</sup>c for 48 hours. The clear liquid solution was filtered and packed in superior grade air tight plastic containers<sup>12-13</sup>.

*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)			
		LE-1	LE-2	LE-3	LE-4
1.	AOS	02	01	00	00
2.	SLES	10	10	10	10
3.	Polymer	14	16	18	20
4.	Urea	02	02	02	01
5.	EDTA	01	01	01	01
6.	Sorbitol	05	04	03	02
7.	Sodium carbonate	02	02	02	02



8.	CMC(10%)	04	04	04	04
9.	Salt	02	02	02	02
10.	Water	58	58	58	58

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

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

S.No.	Liquid detergents	Concentration %	Foam volume in (cm <sup>3</sup> ) after 0,5,10 minutes.by cylinder method			Density(g/cm <sup>3</sup> )by density bottle	Surface tension (dynes/cm) at 30 <sup>o</sup> c by Ostwald's viscometer.
			0	5	10		
1.	LF-1	1%	750	700	650	1.042	28.76
		0.5%	630	550	350	1.042	29.26
		0.25%	450	300	200	1.035	29.81
2.	LF-2	1%	600	530	400	1.052	31.30
		0.5%	360	280	250	1.028	32.09
		0.25%	230	180	150	1.046	34.40
3.	LF-3	1%	480	370	300	1.019	29.35
		0.5%	300	210	190	1.045	34.11
		0.25%	250	200	170	1.031	33.15
4.	LF-4	1%	580	460	320	1.038	32.39
		0.5%	290	200	160	1.042	36.26
		0.25%	280	220	168	1.021	31.50
5.	Commercial market liquid detergent	1%	750	700	550	0.910	37.42
		0.5%	600	550	400	0.913	37.69
		0.25%	500	400	320	0.941	38.50

**Fig. 1 IR spectra of Batch-1 polymer**

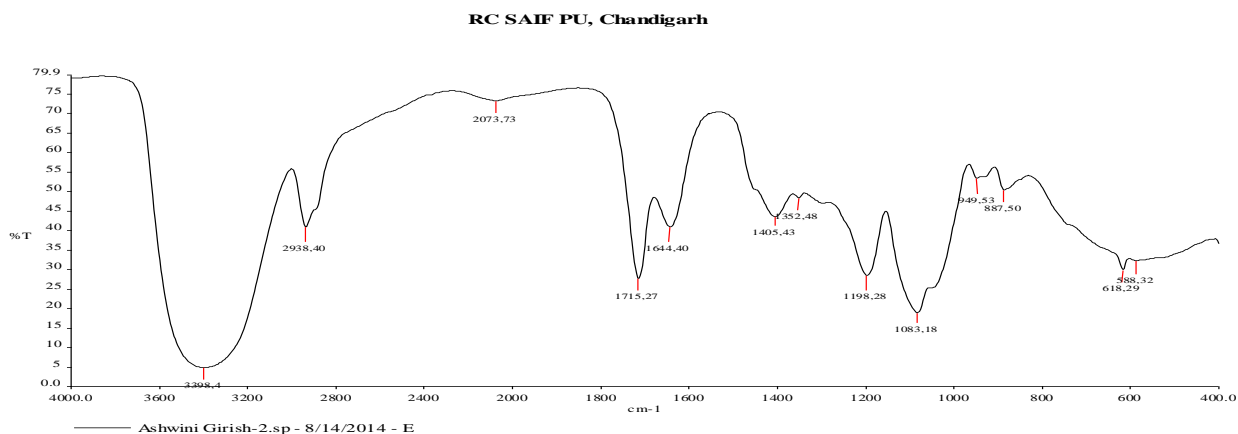




Table - 5 The prominent Peaks of the IR spectra of Novel polymer-P1

Wave No.(cm <sup>-1</sup> )	Functional group	Literature value(cm <sup>-1</sup> )
3398.4	-OH stretching	3450-3200
2938.40	-COOH stretching	2500-3000
1715.27	-COO stretching	1740-1710
1083.18	C-O-C stretching	1050-1250
887.50	=C-H bending	700-1000

Fig.2 NMR spectra of Batch-1 polymer

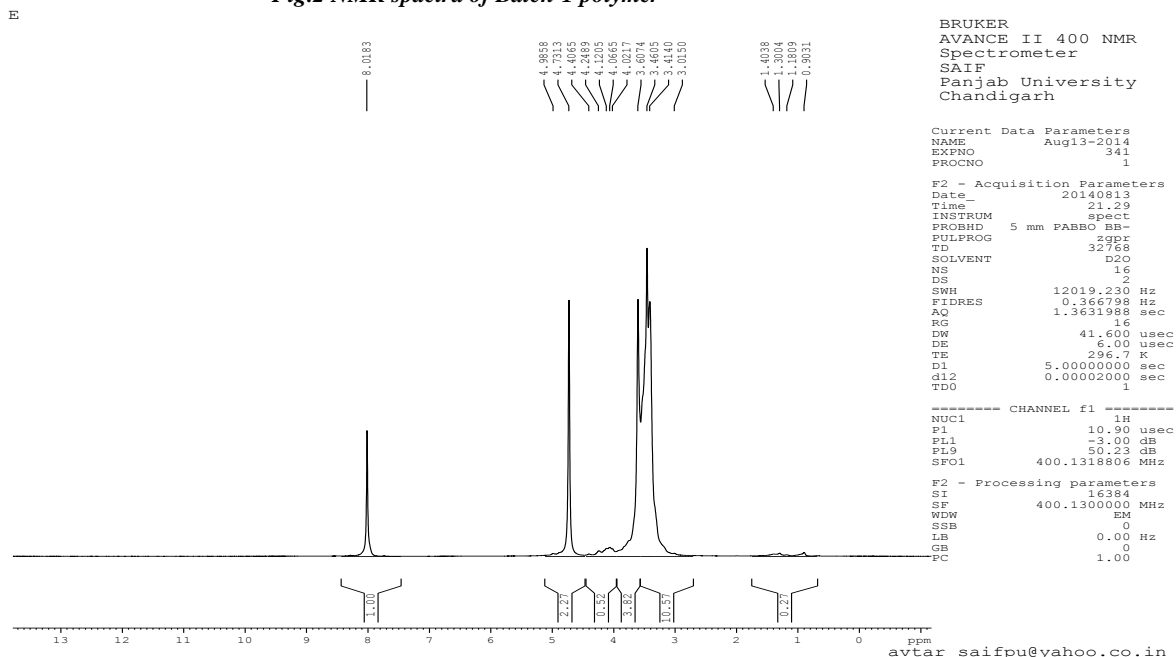


Table - 6 The prominent Peaks of the NMR spectra of Novel polymer

Range $\delta$ (ppm)	Type of proton	Literature value(ppm)
3.82	H-C-O-R(ether)	3.3-4.0
1-4	R-OH(Hydroxyl)	1-5.5
2-2.8	H-COO(ester)	2-2.2

**RESULT AND DISCUSSION**

- The use of polyethylene glycol has been especially tried as this gives enhanced water solubility cleaning and stain removing capacity to the polymer
- The polymer 1 which contains higher proportions of acids is having higher viscosity while samples containing 10% acids is slightly lower still all the samples have a reasonable viscosity so they can be handled and used in various detergent formulations.
- The acid value of samples is significantly higher as a higher proportion of acids 28% have been used. The pH is also acidic and H.L.B. ratio suggests the use of these polymers in detergent compositions.
- The surface tension reduction capacity of polymer and presence of oxirane oxygen will certainly help the detergent to have better cleaning capacity.(Table-2)
- The foaming properties were evaluated for (90:10) combination of polymer with acid slurry. The % solids are reasonably high (80-85%).
- In progressive samples the percentage of polymer has been increased from 14-20%.(Table-3)
- 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.



- 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.
- In fact our samples have moderate foaming properties slightly lower than commercial sample. This reduced foam is a desired property for washing machine application.
- The I.R. & N.M.R. spectra of polymer C confirmed the presence of ester; ether, free acid and free hydroxyl groups in the polymer (see I.R. and N.M.R. spectra-Fig.1, Fig-2.).

## CONCLUSIONS

The following conclusions can be drawn from above experimental work

- 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 oxalic acid which has established cleansing properties.
- 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-Batch-1 have been formulated by standard techniques (Table-3). The analysis of these samples along with commercial sample indicates excellent foaming, surface tension reduction and 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 earth-friendly 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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