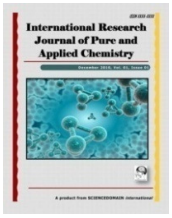

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Liquid Laundry Detergents Based on Novel Polymeric Surfactants

A. G. Deshmukh[1*], B. B. Gogte[2] and M. K. N. Yenkie[3]

[1]Department of Chemistry, Nutan Bharat Jr. College, Abhyankar Nagar, Nagpur, India.
[2]Department of Oil Tech. L.I.T., RTM, Nagpur University, Nagpur, India.
[3]Department of Chemistry, Laxminarayan Institute of Technology, RTM Nagpur University, Nagpur, India.

Authors' contributions

This work was carried out in collaborationbetween all authors. Author AGD designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors BBG and MKNY managed the analyses of the study. Author MKNY managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

A novel polymer based on sorbitol, polyethylene glycol, citric acid has been synthesized using HCl as catalyst. The experimental conditions, order of addition of ingredients, ratio of ingredients, catalyst, time and temperature have been standardized to get desired molecular weight, HLB ratio and viscosity characteristics. Spectroscopic studies of I.R. & N.M.R. of polymers has been undertaken which reveal presence of ester, ether, free Hydroxyl and free acid groups in the polymer. The selected polymer has been used as replacement of conventional linear alkyl benzenesulphonate in liquid detergent formulations. The compositions are ecofriendly and economical as they depend upon vegetable source polymers.

**Corresponding author: Email: sayalikulkarni1990@gmail.com;*

Keywords: Synthesis; polymer; sorbitol; HLB ratio; viscosity.

ABBREVIATION

Ex(excellent): 90%, stain removed, G (good): 75%, stained removed, P(poor):50%, stain removed.

1. INTRODUCTION

A large number of industrial products and surfactants are based mainly on various crude petroleum products. For in country we are importing roughly 2/3 rd. of our requirement from other countries. For a healthy and self-sufficient economy and green environment we must think of vegetable alternatives as raw materials for various products. In our laboratory we have successfully used vegetable stocks based polymeric surfactants as replacement of acid slurry to the extent of 50-60% [1]. The products like powder detergents [2] cake detergents [2] and liquid detergents [3], paints [4], wall finishes [5], have already been successfully prepared. These products compete in price and technical performance with present generation commercial products.

In the present research work we have planned to synthesize novel polymer based on polyethylene glycol which can replace 80-100% petroleum based acid slurry. Polyethylene glycol (400) is a polymer having structure:

$$HO\text{-}CH_2\text{-}(CH_2\text{-}O\text{-}CH_2)_n\text{-}CH_2\text{-}OH$$

It is prepared by polymerization of ethylene oxide. The most important properties of PEG are

a) Solubility in water making it ideally suitable for different applications.
b) Presence of oxirane oxygen may also help to get a high performance active polymeric surfactant which can replace acid slurry.
c) Presence of polyethylene glycol may help in removing stains of ink, soil, Tea, coffee, and spinach [6].

The synthesized polymers were analyzed systematically for their acid value [7,8], Saponification value [9] surface tension [10] and other physico-chemical characteristics.

2. EXPERIMENTAL DETAILS

A glass reactor fitted with stirrer, heating mantle and condenser was set up for the synthesis of the novel polymer. Initially, a stoichiometric quantity Table 1 of sorbitol, polyethylene glycol, citric acid was added in the reactor. Concentrated hydrochloric acid was used as a catalyst . The temperature was raised slowly and steadily to 130℃ for. The reaction was continued for 3 hrs. Till the desired viscosity, acid value and molecular weight were achieved. The consistency of the paste was maintained by adding additional water after 0.5 h. at the end of this period the reaction was terminated and the prepared polymer was collected in a glass-stoppered bottle with least air gap. The final yield of the product was weighed. Four different liquid detergent compositions were prepared as detailed in Table 2 these polymers sample were systematically analyzed to know acid value, molecular weight, viscosity, % oxirane oxygen value. The sample was systematically tested for % solids, foam, pH and saponification- value. They were also analyzed by IR and NMR spectroscopy to know the finger prints of ester group, ether group, free-OH groups and free acid groups.

The % of polymer and acid slurry were varied from 10 to 16 and 7-1% resp. Tables 4 and 5 describe the effect of detergent concentration on surface tension, foam height. The testing has been done as per standard methods. (stalagmometer, cylinder method, HBr method, % detergency was also determined by using Reflectance meter.)

The acid value (Bacher, 1960a), saponification value (Bacher, 1960b), oxirane oxygen by HBr method. Formulae are as follows-

$$\text{Acid value} = 56.1 \times V \times N / W$$

V= Volume of alcoholic KOH solution
N= Normality of alcoholic KOH solution
W= Weight in grams of polymer

The acid value of the polymer was determined by dissolving 1 gram of the polymer in 100 ml of neutral ethanol and solution was titrated with 0.1 N KOH solution in presence of phenolphthalein until a pale pink color was formed.

Table 1. Composition of novel polymers based on polyethylene glycol

Serial no.	Raw materials	Concentration (% by weight)		
		VI	A	B
1.	Sorbitol(70% solid)	75	80	60
2.	Polyethylene glycol(400)	05	10	30
3.	Citric acid	20	10	10

catalysts = 1% HCl, sodium metabisulphite = 3.5%, sodium bisulphate = 3.5%, isopropanol = 2% (as solvent)

Saponification value= 56.1 × (B-S)×N/W

B= Blank titration reading
S= Sample titration reading
N= Normality of alcoholic KOH solution

The saponification value of the polymer was determined by refluxing 1 gram of the polymer with 50 ml. of 0.5N HCl in presence of phenolphthalein. A blank experiment was also performed by repeating the entire process without taking the polymer.

Oxirane oxygen = V×N×1.6/W

V=Volume of HBr solution
N= Normality of HBr solution
W= Weight of polymer

The oxirane oxygen value was determined by dissolving 2 grams of sample in benzene and titrated with 0.1N HBr solution by using crystal violet indicator.

Other physical constants were determined . The polymer is believed to be an ester of carbohydrate which was confirmed by spectral studies [11,12,13]. Various peaks and interpretation of peaks indicate presence of ester (1727cm^{-1}, Figs. 1 and 2)

2.1 Analysis and Testing of Liquid Detergent

Liquid detergents (3 samples) were prepared using different concentrations of polymer with sodium lauryl ether sulphate (SLES), sorbitol, polyvinyl alcohol, sodium carbonate and Acid slurry in a beaker and stirring was continued for 30 min Table 3. The sample was stored overnight at 100℃, in oven. A clear solution of liquid detergent was obtained. The surface tension of liquid detergents was measured using stalagnometer. Foam was measured by using mechanical agitation in a closed glass cylinders of 1liter capacity. The analysis of different liquid stain removal of sample is given in Tables 5 and 6.

2.1.1 Stain preparation

The soil medium of following composition was 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 was taken in a pastel mortar. Coconut oil was added slowly to form a thick paste. All the components were ground in pastle for 1-2 hours to obtain fine paste.

2.1.2 Soil solution

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

2.1.3 Tea stain solution

The tea was prepared with following composition. Tea (TajMahal) (2.2%), sugar (8.0%), milk (38.4%), water (51.4%).

25 gms of water was warmed to 35 to 40℃ then add Tajmahal brand tea and sugar heated up to 80℃ milk was added then heating continued at boil for next 5 minutes, stop heating and pass the tea through a Steiner. Use this as tea medium.

2.1.4 Preparation of coffee medium

The Coffee of following composition was prepared, coffee (1.0%), sugar (8.1%), milk (51.9%), water (39.0%). 25gms of milk and water in a beaker warmed to 35-40℃, coffee and sugar were added and heating continued to the boil for 5 minutes.

2.1.5 Preparation of palak (spinach) medium

The palak medium was prepared as per following composition, oil (1.34%), palak (9.00%), water (89.66%) heated and fried for 5 minutes. To this add half cup of water cooked

for 10 minutes after the preparation it was stored in tight bottle.

2.1.6 Method of application of soil

The cloth of size 24 x 32 cm^2 were prepared. Took 50ml of soil solution in a beaker, the cloth sample was soaked in for 5 minutes. This is kept outside for drying in open atmosphere for 2 hours. Then this cloth was cut in size of 6 x 8cm^2 and samples were used for the washing test.

2.1.7 Method of washing

The solutions of different concentration were prepared. Heated to 60ºc. Soiled cloth sample was dipped in it for 5 minutes and given to and fro 10 hand washes.

2.1.8 Method of application of (spinach, tea and coffee)

The cotton cloths of size 24 x 32 cm^2 were taken and drawn checks of size 6 x 8 cm^2. Then took the above staining solution in a pipette and added in a center of checks one drop and then kept the stain cloth sample in an oven at 55 – 60ºc for ½ hr. then this stain cloth was cut into test sample size and these were used for stain removal testing.

2.2 Calculation for Functional Group –

2.2.1 -OH Group

In Sorbitol-
Molecular weight of sorbitol- 182
One mole of sorbitol contains 6 –OH groups
Number of –OH groups in 75 grams of sorbitol- 6×75/182 = 2.47.

2.2.2 -COOH Group-

In citric acid-
Molecular weight of citric -192.12
One mole of citric acid contains 3 _COOH groups
Number of –COOH groups in 20 grams of citric acid 3×20/192.12= 0.312
Determination of % solid-
Weigh 2 grams of polymer and heat it in oven at 100℃ for 3 hrs. Cool and weight after heating.
Weight of empty crucible-W1, Weight of crucible+ sample-W2, Weight of crucible + sample after heating-W3
% Moisture- W2-W3/W2-W1× 100, % solid content= 100-volatile content
% volatile matter=[W2-W3/W2-W1×100] - % moisture.

3. RESULTS AND DISCUSSION

Physicochemical properties of the Novel polymer are shown in Table 3. Tables 4 and 5 showed the analysis of the formulated liquid detergents (LA-1, LA-2,LA-3,LA-4) polymeric surfactants give excellent characteristics of foaming, surface tension and cleaning stains of soil, tea, coffee and spinach. Figs. 1 and 2 show the N.M.R and IR spectra of polymer VI. Various peaks and interpretation of The peaks indicated presence of ester (1727cm^{-1}), free OH (3380cm^{-1}),-COOH (1423cm^{-1}). In the synthesized polymer. The peak at 1727$cm^{-1}$is further verified by NMR spectra showing peak 3.70ppm.

Table 2. Composition of liquid detergents based on combination of Neutralized Acid slurry and novel polymer

Serial no	Raw materials	Concentration (% by weight)			
		LA-1	LA-2	LA-3	LA-4
1.	Acid slurry	7	5	3	1
2.	S.L.E.S.	20	20	20	20
3.	Polymer	10	12	14	16
4.	Sorbitol	10	10	10	10
5.	Sodium sulphate	03	03	03	03
6.	Sodium carbonate	7.5	7.0	7.6	7.5
7.	Perfume	0.5	0.5	0.5	0.5
8.	Distilled water	42.0	42.5	41.9	42.0
	Total	100	100	100	100

S.L.E.S– sodium lauryl ether sulphate, La- 1,2,3,4 - code for liquid detergents

Free OH at 3380cm^{-1} also verified by NMR by the peaks between 3 and 4 ppm. The peak 3.36 ppm which is an indication that not all the –OH groups of PEG and sorbitol are reacted. The various between the region 3.65 to 3.75 indicated the estericproton in the polymer.

Three Novel polymers have been synthesized which incorporate 10-30% polyethylene glycol. The samples also use 10-30% citric acid in different compositions. Citric acid is particularly used as it is known for its cleaning and preservative properties. If we look at the structure of citric acid it has three carboxyl groups and one OH group. This particular structure may help in developing polymer having surfactant characteristics. The catalysts used are 1% HCl and 3.5% each of sodium metabisulphite and sodium bisulphate. The yield of polymer is around 90-95% on weight basis. When we use 20% citric acid we get a polymer of higher acid value. All samples show acidic pH. The hydrophilic-lipophilic balance is very important parameter the values of hydrophilic-lipophilic balance the polymers were used in detergent. Hydrophilic-Lipophilic balance value is based mainly on saponification value and acid value of original substance. The hydrophilic-lipophilic balance of the resin is 15.19 which indicated that they can be use as active material for detergent. For detergent formulation HLB (hydrophilic-lipophilic balance) value is calculated by using formula HLB= 20{1- Sap. Value of the polymer/Acid value of the raw materials} The HLB value of our polymer is 15.19 indicating its use in detergent formulation. (HLB value of polymer for application in detergents is 13-15), indicating the use of polymer as active ingredient in liquid laundry detergents. Desired viscosity of polymer is about 300 and molecular weight is 4000.

Several liquid Laundry detergents have been formulated. An effort has been made to replace acid slurry with maximum proportion of polymer. The proportion of S.L.E.S. (38%) and sorbitol 10% has been maintained constant.

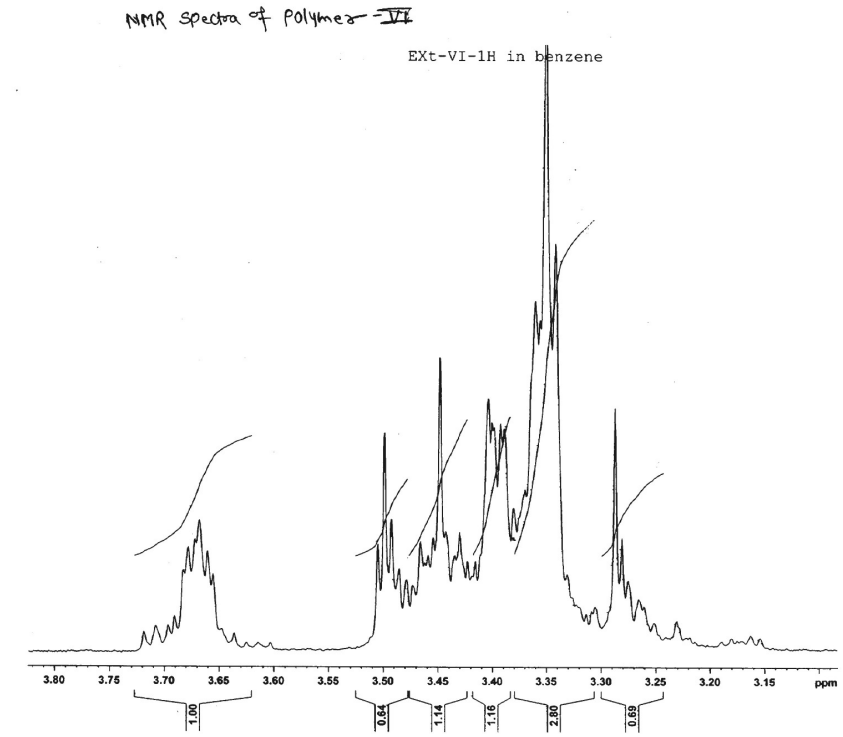
Table 3. Physicochemical properties of the synthesized polymers

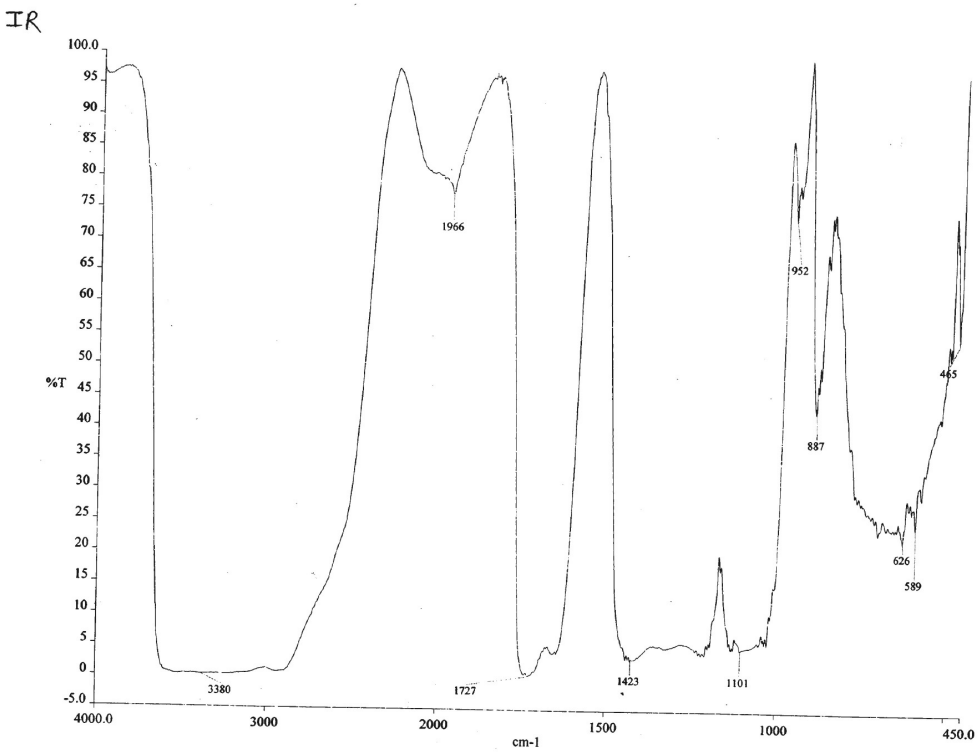
Serial no	Polymer property	Observations		
		VI	A	B
1.	Acid value of polymer	110	42.01	41.52
2.	pH value of 1% solution	4	3	3
3.	Saponification value	49.56	70.1	51.80
4.	% Solids	81.20	85.65	76.28
5.	Solubility in water	Soluble	Soluble	Soluble
	Solubility in xylene	Insoluble	Insoluble	Insoluble
6.	hydrophilic-lipophilic balance	15.19	11.32	11.43
7.	Flow time	258	258	258
	Ford cup No.4 in second at 30℃			
8	Surface Tension (in dyne/cm)By stalagmometer	27.5	24.20	19.07
9	% Oxirane oxygen(by HBr method)	3.77	2.9	3.71
10.	*Foam Volume(in cc)By cylinder method	900	950	800

Table 4. Analysis of liquid detergents at 1% concentration by weight

Detergent sample	Density (by density bottle) in g/cm^3	Surface tension (by stalagmometer) in dynes/cm	Foam height (by cylinder method) in cc	Flow time (by Ostwald's viscometer) in second
LA-1	0.9556	26.59	1000	180
LA-2	1.019	30.64	750	185
LA-3	1.003	26.59	1000	175
LA-4	1.019	34.01	800	165
Commercial	0.910	37.5	800	200

Note: Surface tension of Distilled water=72.79 Dyne/cm, the pH of all samples was 8.5-9 at 1% concentration in distilled water





Figs. 1 and 2. NMR and IR spectra of polymer VI

Table 5. Stain removal

Liquid detergents	Soil	Tea	Coffee	Spinach
LA-1	G	Ex	G	Ex
LA-2	G	Ex	G	G
LA-3	G	G	G	G
LA-4	P	P	G	P
Commercial	G	Ex	Ex	Ex

The physico- chemical and performance characteristics of Liquid detergents are shown in Table 4.

The samples were also compared with commercial laundry detergents available in the market. Our samples are at par or sometimes better than the commercial products in reference to foaming, surface tension and cleaning of the stains of soil, tea, coffee and spinach.

The costing of samples is quite satisfactory and these products can be taken on pilot plant and commercial scale.

Two possible chemical reactions occurred as follows:

1) Esterification reaction between acid group of citric acid and –OH group of sorbitol and polyethylene glycol.
2) Etherification reaction between two- OH groups of polyethylene glycol and sorbitol to produce ethoxy groups.
3) Both these reaction are expected to give good surfactant property.

4. CONCLUSION

Novel polymers based on polyethylene glycol (400) and citric acid (10-30%) has been synthesized successfully.

The available surfactants are based mainly on acid slurry (linear alkyl benzene sulphonate) ,which is based on crude petroleum. In the present work we have used very small proportion of acid slurry (3-7%) and successfully used vegetable stock based polymeric surfactants as replacement of acid slurry. The compositions are ecofriendly and economical as they depend upon vegetable source polymers.

Sorbitol in substantial quantity has been used which eliminate turbidity and transparent appearance and smooth feel to hands in washing preparation.
The pollution causing chemicals like sodium tripolyphosphate is reduced. This is step towards replacement of petroleum product with green ecofriendly renewable product.

Detergents give a very low surface tension thus they are expected to have better cleaning.

Normally we use 10-14% acid slurry in liquid laundry detergent compositions. Here we have used very small proportion of acid slurry (3 to 7%). and use of 10-14% of polymer does not practically harm the performance characteristics. In fact incorporation of polymeric surfactant gives excellent characteristics of foaming, surface tension and cleaning of stains of soil, tea, coffee and spinach see Table 4.

1) Our samples have been compared in all respects with commercial samples available in the market. Our samples stand up to the mark and sometimes perform better than commercial samples.
2) Our liquid Laundry detergents must be tried on pilot and commercial scale as they are techno economically viable compositions.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Gogte BB, Agrawal RS. Starch-sorbitol based co-polymer (a Substitute for LABS), Soaps, Detergents and toiletries Review. 2003;34(2):25-28.
2. Dontulwar JR, Gogte BB. Synthesis of eco-friendly Detergents by using white Dextrin sorbitol maleic anhydride. Asian Journal of Chemistry. 2004;16(3-4):1385-1390.
3. Agrawal RS, Kakdkar G, Gogte BB. Sorbitol based polymeric surfactant for detergent formulation. Soaps, Detergents and Toiletries Review. 2003;19:20-25.

4. Bauvy AD. Polymeric surfactant and their use in industrial product. Paint India.1993;45-52.
5. Gogte BB, Kulkarni. Paint India. 1994;44(2):89.
6. BIS methods for the test for detergency for household detergent, BIS 4995; 2000.
7. Bacher Melhlen VC. The analysis of fats and oils, Garrard publication, Champaigx llinois, 299-308(for sap. value, for acid value,103-108, for Oxirane oxygen, 558-560); 1960.
8. ASTM standard method. 6.01,D 1639-70, (For acid value of organic coating materials) published by the American society for testing materials, Philadelphia; 1981.
9. ASTM Standard method. 6.03,D1952-67, (saponification value of drying oils); 1979.
10. I.S. 5785, methods for performance tests for surface-active agents, part (Indian standards, New Delhi); 1976.
11. Silverstein RM. Spectrometric Identification of organic compounds, fifth edition John Wiley and sons. 1991;300-306.
12. Kalsi PS. Spectroscopy of organic compounds New age International Publisher Ltd. forth edition, 21-41; 1999
13. Bahl, Bahl. A text book of organic chemistry, 15 edition, S. Chand and co.

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