

LIQUID LAUNDRY DETERGENTS BASED ON NOVEL POLYMERIC SURFACTANTS

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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 reveals 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 benzene sulphonate in liquid detergent formulations. The compositions are ecofriendly and economical as they depend upon vegetable source polymers.

Keywords: Synthesis, polymer, sorbitol, HLB ratio, viscosity

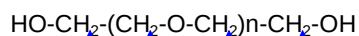
1. INTRODUCTION

A large number of industrial products and surfactants are based mainly on various crude petroleum products. For our country we are importing roughly 2/3 rd of our requirements 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 [2] cake [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 :

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

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

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

Two possible chemical reactions occurring are as follows:

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

EXPERIMENTAL DETAILS

A glass reactor fitted with stirrer, heating mantle and condenser ~~has been used was set up for the~~ ~~in 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°C~~ ^{130°C}. The reaction was continued for 3 h 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-compositions have been were~~ prepared as detailed in Table-2 these polymers sample were systematically analyzed for acid value, molecular weight, viscosity, % oxirane oxygen value. ~~The samples~~ ~~were~~ ^{as} systematically tested for % solids, foam, pH and saponification- value. they were also analysed ^{ds} by IR and NMR spectroscopy ~~to know for~~ the finger prints of ester group, ether group, free-OH groups and free acid groups

. The % of polymer and acid slurry have been varied from 10 to 16 and 7-1% resp. Table ~~nos.~~ 4 and 5 describes the effect of detergent concentration on surface tension, foam height. The testing ~~has been were~~ done as per standard methods.

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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-

Acid value= $56.1 \times v \times n / w$

Saponification value= $56.1 \times (b-s) \times n / w$

Oxirane oxygen = $v \times n \times 1.6 / w$

Other physical constants were determined . The polymer is believed to be an ester of carbohydrate which was confirmed by spectral studies[11,12,13].

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°C in refrigeratoran oven. A clear solution of liquid detergent was obtained. The surface tension of liquid detergents was measured using stalagmometer. Foam was measured by using mechanical agitation in a closed glass cylinders of 1liter capacity method. The analysis of different liquid stain removal efficiency er sample is given in Tables no.5&6.

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

Component Weight-%: Ccarbon Bblack (28.4%), Ccoconut Oil(35.8%), Llauric Acid(17.9%), Mmineral Oil(17.9%).The mixture of carbon black and Llauric acid along with mineral oil wais taken in a pastelpestle mortar. Coconut oil wais added slowly to from-form a thick paste. All the components are-were ground in the pastelpestle mortar for 1-2 hours till we get a fine grindingto obtain fine paste. The fine grinding is indicated by smooth feel of the paste medium.

Soil Solution: This wais prepared by adding 2gGms of the above paste in 500ml of carbon tetrachloride. It was Mmixed it well and used for staining cloth sample preparation. The solution wais kept in packed bottles.

Tea Stain Solution: The tea wais prepared with following composition. Tea (Taj Mahal)(2.2%),Sugar(8.0%),Milk(—38.4%),Water(51.4%). Water:Take 25gGms of water-andwas warmed-it to 35 to 40°C then add Taj mahal brand tea and sugar were added and heated-it up to 80°C. till it starts boiling-add milk was then added and continue and heating continued at the boiling temperature for next 5 minutes. The mixture was passed-stop heating-and pass the tea through a Steinerstrainer. Use this as tea medium.

Preparation of Coffee Medium: The cCoffee of the following composition wais prepared,

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112 cCoffee (1.0%), sSugar (8.1%), mMilk(51.9%),Water(39.0%).Take—Milk,
113 25gGms. of milk and water in a beaker was warmed it to 35-45°C, than add coffee
114 and sugar were added and heating continued to the boil heating in boiling conditions
115 for 5 minutes. Stop heating and use this coffee as staining medium.

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116 **Preparation of Palak (Spinach) Medium:** The Palak medium was prepared of
117 according to the following composition: Oil (1.34%),Palak(9.00%),Water(89.66%).
118 The mixture was Hheated and the oil and then add Palak to it and fryfried for 5
119 minutes. To this half add half cup of water was added and cooked it for 10 minutes.
120 afterAfter the preparation it was stored in tight bottle.

121 **Method of application of soil:** The cloth of size 24 x 32 cCm² were prepared. The
122 cloth sample was soaked inTake 50ml of the soil solution in a beaker; dip the cloth
123 sample in it for 5 minutes. This was kept outside for drying in open atmosphere for
124 2 hours. Then this cloth was cut in size of 6x8cCm² and the samples were used
125 for the washing test.

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126 **Method of Washing:** The solutions of different concentration were prepared.
127 hHeated that solution to temperature of 60°C. TheDip soiled cloth sample was
128 dipped in it for 5 minutes and given a to and fro 10 hand washes.

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129 **Method of application of (Spinach, Tea and Coffee):** The cCotton cloths of size
130 24 x 32 cm² were taken and make checks with the help of size 6 x 8 cm². Then take
131 the above staining solution in a pipette and add in a center of checks one drop and
132 then kept the stain cloth sample in an oven at 55 – 60°C for ½ hr. then this stain
133 cloth is cut into test sample size and these were used for stain removal testing.

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134 **Calculation forCalculation for functional group –**

135 **-OH group**

136 In Sorbitol-

137 Molecular weight of sorbitol- 182

138 One mole of sorbitol contains 6 –OH groups

139 Number of –OH groups in 75 grams of sorbitol- $6 \times 75 / 182 = 2.47$

140 **-COOH group-**

141 In citric acid-

142 Molecular weight of citric -192.12

143 One mole of citric acid contains 3 _COOH groups

144 Number of –COOH groups in 20 grams of citric acid $3 \times 20 / 192.12 = 0.312$

Determination of % solid-

Weigh 2 grams of polymer and heated it in an oven at 100°C 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- $\frac{W2-W3}{W2-W1} \times 100$, % solid content= 100-volatile content

% volatile matter= $[\frac{W2-W3}{W2-W1} \times 100] - \% \text{ moisture}$

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, SodiumMetabisulphite =3.5%, Sodium Bisulphate =3.5%

Isopropanol =2% (as solvent)

Table- 2

Comment [PY5]: Name the table?

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

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3. RESULTS AND DISCUSSION

Table-3.

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PHYSICOCHEMICAL PROPERTIES OF THE SYNTHESIZED POLYMERS

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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 <u>in</u> Water	Soluble	Soluble	Soluble	
	<u>Solubility in</u> Xylene	Insoluble	Insoluble	Insoluble	
6.	Hydrophilic-Lipophilic balance	15.19	11.32	11.43	

7.	Flow time Ford cup No.4 in second at 30°C	258	258	258
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

Comment [PY8]: Name the table?

Analysis of liquid detergents at 1% concentration by weight

Note: Surface tension of Distilled water=72.79 Dyne/cm

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

The pH of all samples was 8.5-9 at 1% concentration in distilled water

Table-5

Comment [PY9]: Name the table?

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

Abbreviation:

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

Physicochemical properties of the Novel polymer are shown in Table-3. Table 4,5. showed the analysis of the formulated liquid detergents(LA-1, LA-2,LA-3,LA-4) polymeric surfactants gives excellent characteristics of foaming, surface tension and cleaning of stains of soil,tea,coffee and spinach. Figure(1)and Figure(2) show the N.M.R and IR spectra of polymer VI. Various peaks and interpretation of The peaks indicate presence of ester(1727cm^{-1}), free OH(3380cm^{-1}),-COOH(1423cm^{-1}). in the synthesized polymer. The peak at 1727cm^{-1} is further verified by NMR spectra showing peak 3.70ppm. Free OH at 3380cm^{-1} also verified by NMR indicated 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 were reacted. The various values between the region 3.65 to 3.75 indicate the esteric proton 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~~ 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 ~~h~~Hydrophilic-~~L~~Lipophilic balance is very important ~~parameterparameter; depending upon~~ the values of ~~h~~Hydrophilic-~~L~~Lipophilic balance of the polymers ~~indicated that they can be are~~ used in detergent formulations. Hydrophilic-Lipophilic balance value is based mainly on saponification value and acid value of original substance. The hydrophilic-Lipophilic balance of resin is 15.19 which suggests its use as active material for detergent For detergent formulation HLB (hydrophilic-lipophilic balance) value is calculated by using formula

$$HLB = 20 \left\{ 1 - \frac{\text{Sap. Value of the polymer}}{\text{Acid value of the raw materials}} \right\}$$

The HLB value of our polymer is 15.19 ~~indicates-indicating~~ its use in detergent formulation .(HLB value of polymer for application in detergents is 13-15),indicates 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.

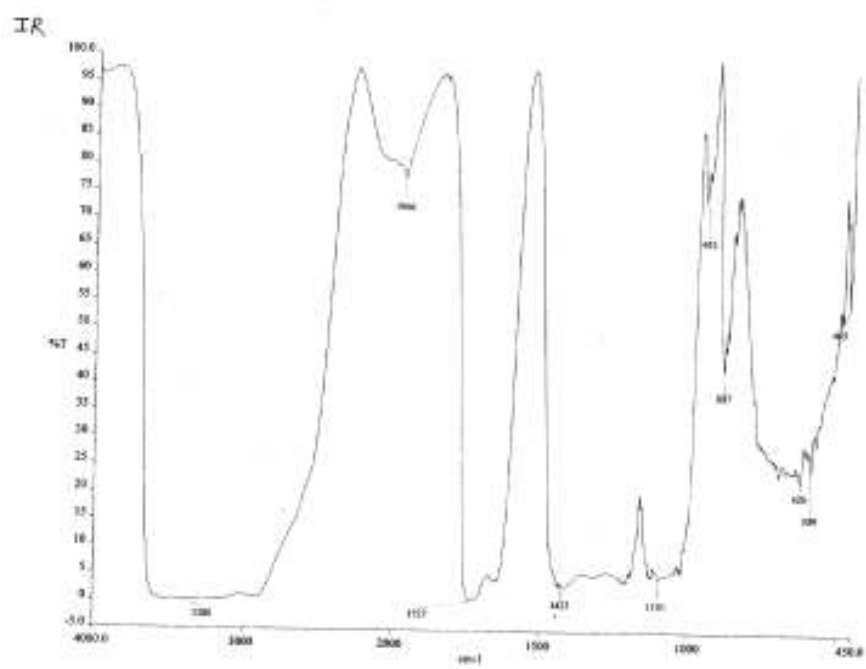
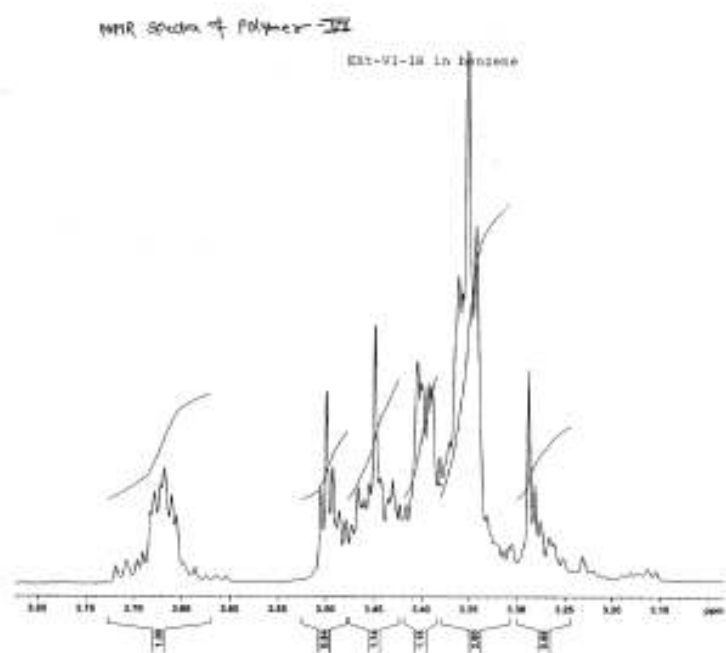
The physico- chemical and performance characteristics of Liquid detergents are shown in Table-4

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.

Fig. 1 and Fig. 2

NMR and IR spectra of polymer VI



4. CONCLUSION

Novel polymers based on polyethylene glycol(400) and citric acid (10-30%) ~~has been~~ ~~be—been~~ synthesized ~~successfully~~ ~~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 a 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 (3to7%). 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 some times perform better than commercial samples.
- 2) Our liquid Laundry detergents must be tried on pilot and commercial scale as they are technoeconomically viable compositions.

ACKNOWLEDGEMENT

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COMPETING INTERESTS

"Authors have declared that no competing interests exist."

AUTHORS' CONTRIBUTIONS

'Author A' designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. 'Author B' and 'Author C' managed the

analyses of the study. 'Author C' managed the literature searches..... All authors read and approved the final manuscript."

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

Here is the Definitions section. This is an optional section.

Term: Definition for the term

APPENDIX