

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 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 [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 :

38 $\text{HO-CH}_2\text{-(CH}_2\text{-O-CH}_2\text{)}_n\text{-CH}_2\text{-OH}$

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

41 a) Solubility in water making it ideally suitable for different applications.

42 b) Presence of oxirane oxygen may also help to get a high performance active
43 polymeric surfactant which can replace acid slurry.

44 c) Presence of polyethylene glycol may help in removing stains of ink, soil,
45 Tea, coffee, and spinach [6].

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

49 Two possible chemical reactions occurring are as follows:

50 1) Esterification reaction between acid group of citric acid and –OH group of
51 sorbitol and polyethylene glycol.

52 2) Etherification reaction between two- OH groups of polyethylene glycol and
53 sorbitol to produce ethoxy groups.

54 3) Both these reaction are expected to give good surfactant property.

55 **EXPERIMENTAL DETAILS**

56 A glass reactor fitted with stirrer, heating mantle and condenser has been used in
57 the synthesis of novel polymer. initially, a stoichiometric quantity (Table -1) of
58 sorbitol, polyethylene glycol, citric acid was added in the reactor .concentrated
59 hydrochloric acid was used as a catalyst .the temperature was raised slowly and
60 steadily to 130°C. The reaction was continued for 3 h till the desired viscosity, acid
61 value and molecular weight were achieved. The consistency of the paste was
62 maintained by adding additional water after 0.5 h. at the end of this period the
63 reaction was terminated and the prepared polymer was collected in a glass-
64 stoppered bottle with least air gap. The final yield of the product was weighed. Four
65 different liquid detergent compositions have been prepared as detailed in Table-2
66 these polymers sample were systematically analyzed for acid value, molecular
67 weight, viscosity, % oxirane oxygen value. the sample was systematically tested for
68 % solids, foam, pH and saponification- value .they were also analyses by IR and
69 NMR spectroscopy to know the finger print of ester group, ether group, free-OH
70 groups and free acid groups

71 . The % of polymer and acid slurry have been varied from 10 to 16 and 7-1% resp.
72 Table no. 4 and 5 describes the effect of detergent concentration on surface
73 tension, foam height. The testing has been done as per standard methods.(

74 stalagmometer, cylinder method, HBr method, % detergency was also determined
75 by using Reflectance meter.)

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

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

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

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

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

83 **Analysis and Testing of Liquid Detergent**

84 Liquid detergents (3 samples) were prepared using different concentrations of
85 polymer with sodium lauryl ether sulphate (SLES), sorbitol, polyvinyl alcohol, sodium
86 carbonate and Acid slurry in a beaker and stirring was continued for 30 min (Table
87 3)The sample was stored overnight at 100c in refrigerator. A clear solution of liquid
88 detergent was obtained. The surface tension of liquid detergents was measured
89 using stalagmometer. Foam was measured by using mechanical agitation in a
90 closed glass Cylinders of 1liter capacity method. The analysis of different liquid stain
91 remover sample is given in table no.5&6.

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

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

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

101 **Tea Stain Solution:** The tea is prepared with following composition. Tea (Taj
102 Mahal)(2.2%),Sugar(8.0%),Milk(38.4%),Water(51.4%).Take 25Gms of water
103 and warm it to 35 to 400C then add Taj mahal brand tea and sugar heat it up to
104 800C till it starts boiling add milk and continue heating at boiling temperature for
105 next 5 minutes, stop heating and pass the tea through a Steiner. Use this as tea
106 medium.

107 **Preparation of Coffee Medium:** The Coffee of following composition is prepared,

108 Coffee (1.0%), Sugar (8.1%), Milk(51.9%),Water(39.0%).Take 25Gms of milk and
109 water in a beaker warm it to 35-450C than add coffee and sugar continue heating in

110 boiling conditions for 5 minutes. Stop heating and use this coffee as staining
111 medium.

112 **Preparation of Palak (Spinach) Medium:** The Palak medium is prepared of
113 following composition, Oil (1.34%), Palak (9.00%), Water (89.66%) Heat the oil and then
114 add Palak to it and fry for 5 minutes. To this add half cup of water cook it for 10
115 minutes after the preparation it is stored in tight bottle.

116 **Method of application of soil:** The cloth of size 24 x 32 Cm² were prepared. Take
117 50ml of soil solution in a beaker; dip the cloth sample in it for 5 minutes. This is kept
118 outside for drying in open atmosphere for 2 hours. Then this cloth is cut in size of
119 6x8Cm² and samples are used for washing.

120 **Method of Washing:** The solutions of different concentration were prepared. Heat
121 that solution to temperature of 60°C. Dip soiled cloth sample in it for 5 minutes and
122 give to and fro 10 hand washes.

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

128 **Calculation for functional group –**

129 **-OH group**

130 **In Sorbitol-**

131 **Molecular weight of sorbitol- 182**

132 **One mole of sorbitol contains 6 –OH groups**

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

134 **-COOH group-**

135 **In citric acid-**

136 **Molecular weight of citric -192.12**

137 **One mole of citric acid contains 3 _COOH groups**

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

139 **Determination of % solid-**

140 **Weigh 2 grams of polymer and heat it in oven at 100°C for 3 hrs. Cool and weight**
141 **after heating.**

142 Weight of empty crucible-W1, Weight of crucible+ sample-W2, Weight of crucible +
143 sample after heating-W3

144 % Moisture- $\frac{W2-W3}{W2-W1} \times 100$, % solid content= 100-volatile content

145 % volatile matter= $[\frac{W2-W3}{W2-W1} \times 100] - \% \text{ moisture}$

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148 **Table-1.**

149 **Composition of novel polymers based on polyethylene glycol.**

150

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

151 Catalysts = 1% HCl, SodiumMetabisulphite =3.5%, Sodium Bisulphate =3.5%

152 Isopropanol =2% (as solvent)

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164 **Table- 2**

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166 **Composition of liquid detergents based on combination of Neutralized Acid**
167 **slurry and novel polymer**
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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

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170 S.L.E.S– Sodium Lauryl Ether sulphate LA- 1,2,3,4 - Code for Liquid detergents

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176 **3. RESULTS AND DISCUSSION**177 **Table-3.**178 **PHYSICOCHEMICAL PROPERTIES OF 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	Soluble	Soluble	Soluble	
	Water				
	Xylene	Insoluble	Insoluble	Insoluble	
6.	Hydrophilic-Lipophilic balace	15.19	11.32	11.43	
7.	Flow time	258	258	258	
	Ford cup No.4 in second at 30 ⁰ C				

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

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

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194 **Table-5**

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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

196

197 **Abbreviation:**

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

199 50%, stain removed.

200 Physicochemical properties of the Novel polymer are shown in Table-3. **Table**201 **-4,5. shown the analysis of the formulated liquid detergents(LA-1, LA-2,LA-3,LA-4)**202 **polymeric surfactants gives excellent characteristics of foaming, surface tension and**203 **cleaning of stains of soil,tea,coffee and spinach.**Figure(1)and Figure(2) show the

204 N.M.R and IR spectra of polymer VI. Various peaks and interpretation of The peaks

205 indicate presence of ester(1727cm^{-1}), free OH(3380cm^{-1}),-COOH(1423cm^{-1}). in the206 synthesized polymer.**The peak at 1727cm^{-1} is further verified by NMR spectra**207 **showing peak 3.70ppm. Free OH at 3380cm^{-1} also verified by NMR by the peaks**208 **between 3 and 4 ppm. The peak 3.36 ppm which is an indication that not all the –**209 **OH groups of PEG and sorbitol are reacted.The various between the region 3.65 to**210 **3.75 indicate the esteric proton in the polymer**

211 Three Novel polymers have been synthesized which incorporate 10-30%

212 polyethylene glycol. The samples also use 10-30% citric acid in different

213 compositions. Citric acid is particularly used as it is known for its cleaning and

214 preservative properties. If we look at the structure of citric acid it has three carboxyl

215 groups and one OH group. This particular structure may help in developing polymer

216 having surfactant characteristics. The catalysts used are 1% HCl and 3.5% each of

217 sodium metabisulphite and sodium bisulphate. The yield of polymer is around 90-

218 95% on weight basis. When we use 20% citric acid we get a polymer of higher acid

219 value. All samples show acidic pH. The Hydrophilic-Lipophilic balance is very
220 important parameter depending upon the value of Hydrophilic-Lipophilic balance the
221 polymers are used in detergent. Hydrophilic-Lipophilic balance value is based
222 mainly on saponification value and acid value of original substance. The hydrophilic-
223 Lipophilic balance of resin is 15.19 which suggest its use as active material for
224 detergent For detergent formulation HLB (hydrophilic-lipophilic balance) value is
225 calculated by using formula
226 $HLB = 20 \{1 - \frac{\text{Sap. Value of the polymer}}{\text{Acid value of the raw materials}}\}$ The HLB
227 value of our polymer is 15.19 indicates its use in detergent formulation .(HLB value
228 of polymer for application in detergents is 13-15),indicates the use of polymer as
229 active ingredient in liquid laundry detergents.Desired viscosity of polymer is about
230 300 and molecular weight is 4000.

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

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

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

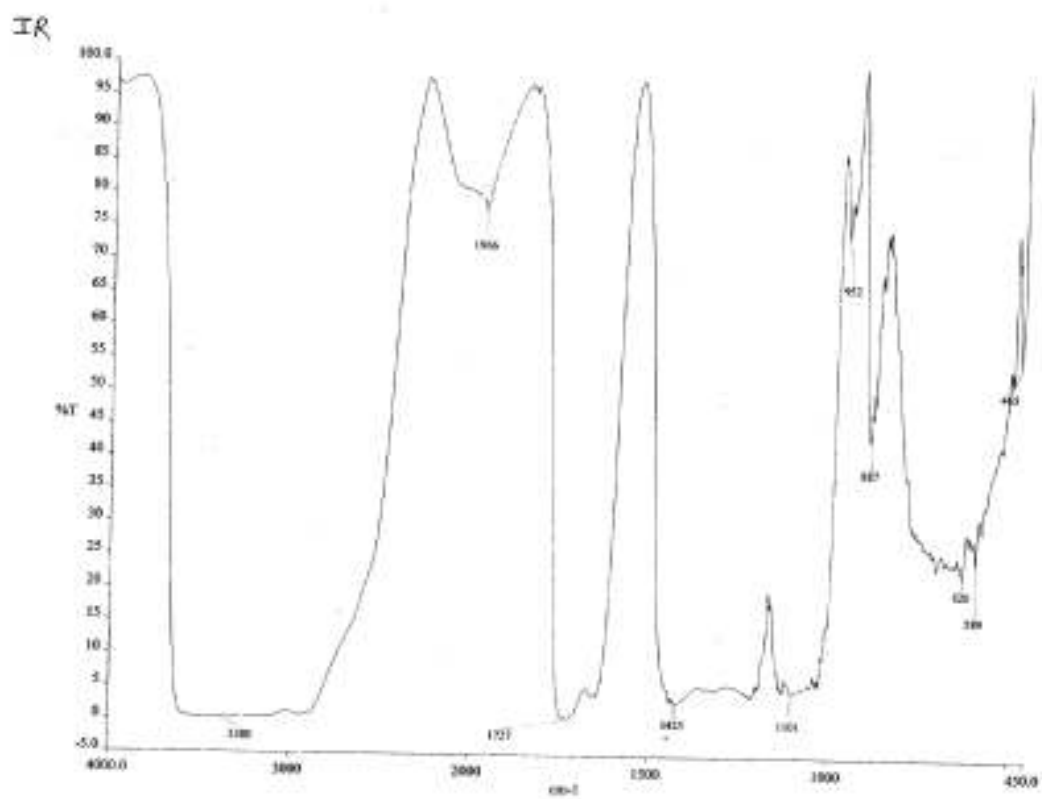
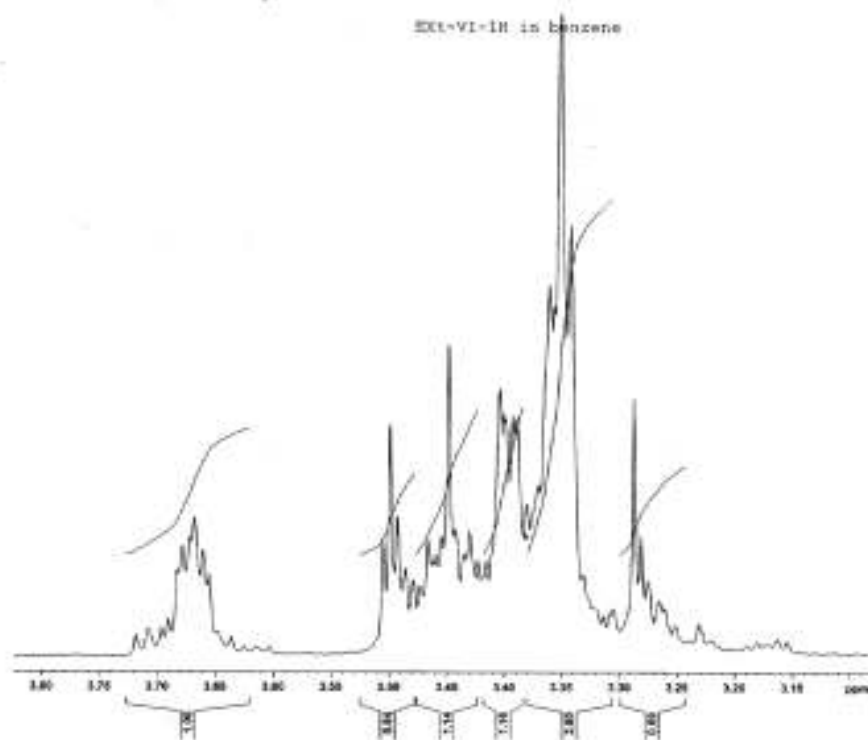
240 The costing of samples is quite satisfactory and these products can be taken on
241 pilot plant and commercial scale.

242 **Fig. 1 and Fig. 2**

243 *NMR and IR spectra of polymer VI*

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NMR spectra of polymer ~~III~~



4. CONCLUSION

Novel polymers based on polyethylene glycol(400) and citric acid (10-30%) can be 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 (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.

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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