

LIQUID LAUNDRY DETERGENTS BASED ON NOVEL POLYMERIC SURFACTANTS

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. This polymer has been used as a 70-90% 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.

Introduction:

A large number of industrial products and surfactants are based mainly on various crude petroleum products. For our country we are importing roughly 2/3rd 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%¹⁻⁵. The products like powder⁴, cake⁵ and liquid detergents, paints³, wall finishes, have already been successfully prepared^{2,12}. 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 :



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

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

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

32 c) Presence of polyethylene glycol may help in removing stains of ink³, soil⁴, Tea⁴, coffee⁴, and
33 spinach^{12,15}.

34 The synthesized polymers were analysed systematically for their acid value^{6,7}, viscosity⁹,
35 surface tension^{9,10} and other physico-chemical characteristics^{8,16,17}.

36 Two possible chemical reactions occurring are as follows:

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

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

41 Both these reaction are expected to give good surfactant properties.

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45 **Experimental :**

46 A glass reactor fitted with stirrer, heating mantle and condenser has been used in the synthesis of
47 novel polymer. Initially, a stoichiometric quantity (Table -1) of sorbitol, Polyethylene glycol,
48 citric acid was added in the reactor. Concentrated hydrochloric acid was used as a catalyst. The
49 temp. was raised slowly and steadily to 130⁰C. The reaction was continued for 3 h till the desired
50 viscosity, acid value and molecular weight were achieved. The consistency of the paste was
51 maintained by adding additional water after 0.5 h. At the end of this period the reaction was
52 terminated and the prepared polymer was collected in a glass-stoppered bottle with least air gap.
53 The final yield of the product was measured.

The acid value^{6,7}, Saponification value^{7,8}, Oxirane oxygen by HBr method and other physical constants were determined by standard methods¹⁻⁵. The polymer is believed to be an ester of carbohydrate which was confirmed by spectral studies^{16,17}

Table-1.

Composition of novel polymers based on polyethylene glycol.

S.No.	Raw material		Concentration(%by weight)		
			VI	A	B
1	Sorbitol (70% Solid)		75	80	60
2	Polyethylene glycol l(400)		5	10	30
3	Citric acid		20	10	10

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

Isopropanol =2% (as solvent)

Table: 2

Physico-chemical properties of synthesized polymers

S. No.	Polymer Property		Observation		
			Vi	A	B
1	Acid value of the polymer		110	42.01	41.52
2	pH value of 1% Sol ⁿ .		4	3	3
3	Saponification value		49.56	70.1	51.80
4	% Solids		81.20	85.65	76.28
5	SOLUBILITY				

79		In water-	Soluble	soluble	soluble
80		In Xylene-	Insoluble	insoluble	insoluble
81	6	Hydrophilic-lipophilic	15.19	11.32	11.43
82		Balance value of polymer			
83	7	Viscosity (flow time)	258	258	268
84		(In seconds, by Ford cup No. 4at 30 ⁰ C)			
85	8	Surface Tension(in dynes/cm)			
86		(By stalagmometer)	27.5	24.20	19.07
87	9	%.Oxirane Oxygen			
88		(HBr method)	3.77	2.9	3.71
89	10	Foam volume * (in cc)	900	950	800
90		(by cylinder method)			

*Foam volume was measured for combination of 90% polymer and 10% linear alkyl benzene sulphonate (LABS) neutralized to pH-8.

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Table- 3

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

98	S.No.	Raw Material	Concentration(% by wt)			
99			LA-1	LA-2	LA-3	LA-4
100	1	Acid Slurry	7	5	3	1
101	2	S.L.E.S.	20	20	20	20
102	3	Polymer	10	12	14	16
103	4	Sorbitol	10	10	10	10
104	5	Sodium sulphate	03	03	03	03

105	6	Sodium carbonate	7.5	7.0	7.6	7.5
106	7	perfume	0.5	0.5	0.5	0.5
107	8	Distilled water	42.0	42.5	41.9	42.0

108 S.L.E.S.=Sodium Lauryl Ether Sulphate.

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110 Table-4

111 Analysis of liquid detergents at 1% concentration by weight

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

113	Detergent Sample	Density	SurfaceTension	Foam height	Viscosity
114		(by density bottle)	(by stalagmometer)	(by cylinder method)	(Flow time)
115		(g/cm3)	(dynes/cm)	(cc)	(in seconds)
116	LA-1	0.9556	26.59	1000	180
117	LA-2	1.019	30.64	750	185
118	LA-3	1.003	26.59	1000	175
119	LA-4	1.019	34.01	800	165
120	Commercial	0.910	37.5	800	200

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

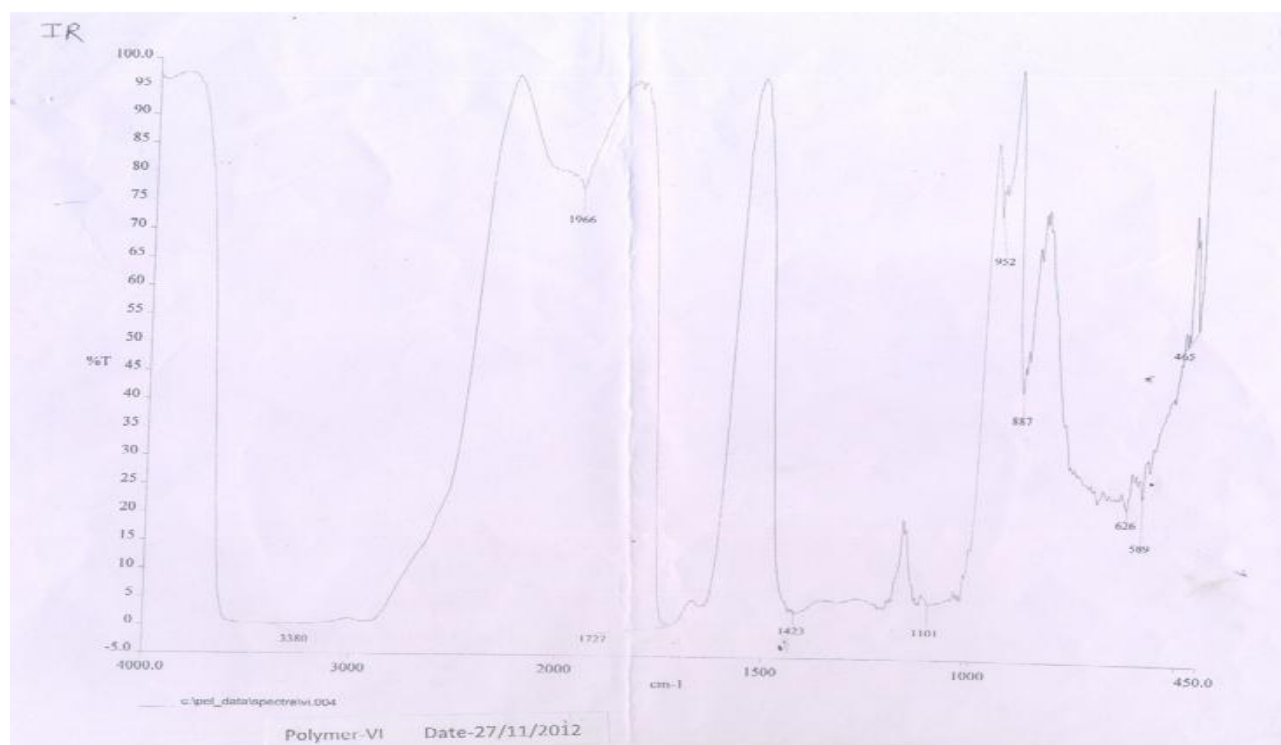
122 Table : 5

123 Stain removal (by standard procedure)

124		Soil	Tea	Coffee	Spinach
125	LA-1	G	Ex	G	Ex
126	LA-2	G	Ex	G	G
127	LA-3	G	G	G	G
128	LA-4	P	P	G	p
129	CLS	G	Ex	Ex	Ex

130 Abbreviation : Ex :90%, Stain removed,G: 75%, stained removed, P: 50%, Stain removed.

131 **Fig-1 IR Spectra** for polymer-VI



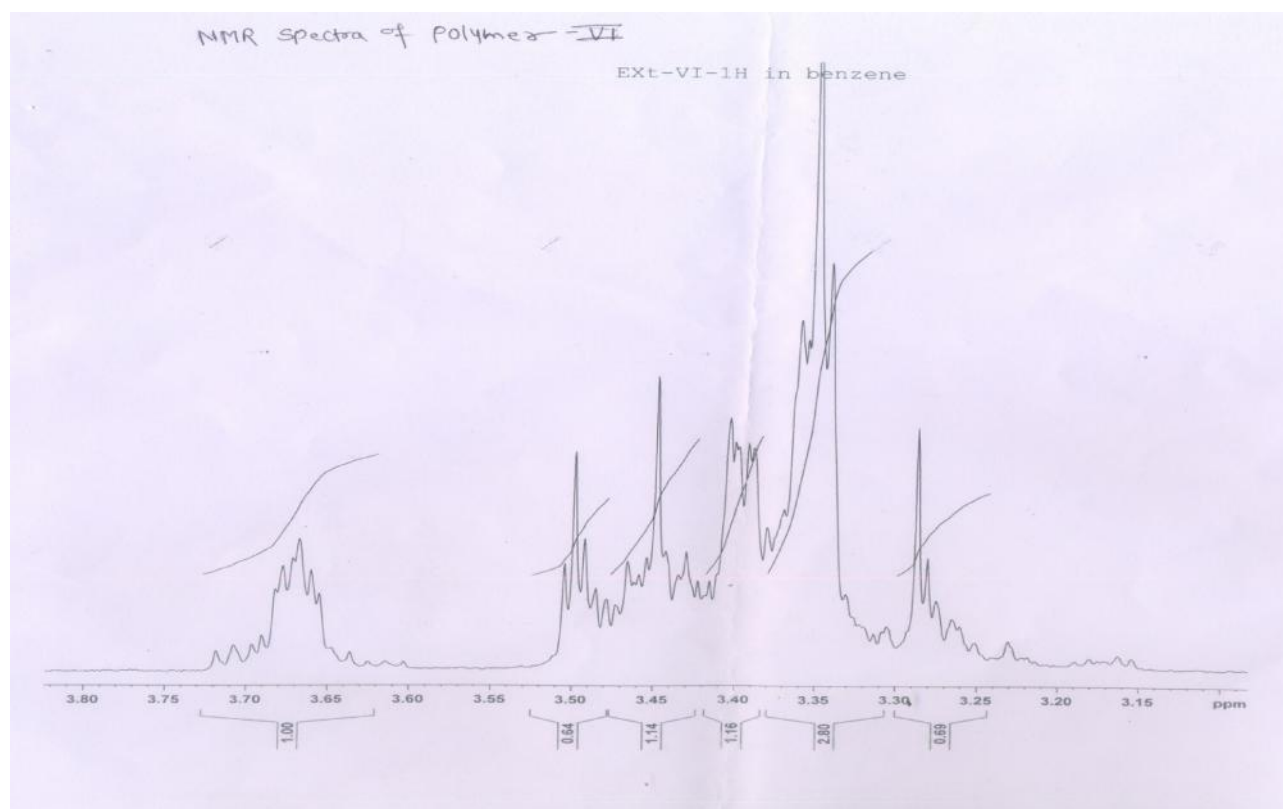
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136 **Fig-2 NMR Spectra** for polymer-VI



Results and discussion :

The Physicochemical properties of the Novel polymer are shown in Table-2. Figure(1) and Figure(2) show the I.R. and N.M.R. spectra of polymer VI. Various peaks and interpretation of peaks indicate presence of ester(1727Cm^{-1}), free OH(3380Cm^{-1}), -COOH(1423Cm^{-1}). in the synthesized polymer.

For detergent formulation HLB value is calculated by using formula

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

The HLB value of 15.19 indicates its use in detergent formulation.

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 H.L.B. value and oxirane oxygen indicate the use of polymer as active ingredient in liquid laundry detergents.

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

158 The physico- chemical and performance characteristics of Liquid detergents are shown in Table-
159 4

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

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

165 **Conclusion:**

- 166 1) Novel polymers based on polyethylene glycol(400) and citric acid (10-30%) can be
167 synthesized successfully. The mole ratio of reactants, temperature, time of reaction and
168 catalyst can be optimized to get desired acid value, H.L.B. ratio and % oxirane oxygen.
- 169 2) The yield of polymer is 90-95% which indicate the loss of 5-10% in the process of
170 esterification.
- 171 3) The catalyst most effective are 1% HCl and 3.5% each of sodium metabisulphite and
172 sodium bisulphate.
- 173 4) Composition based on sorbitol and citric acid I (Table-3)has been selected for preparation
174 of liquid laundry detergents.
- 175 5) Normally we use 10-14% acid slurry in liquid laundry detergent compositions. Here we
176 have used very small proportion of acid slurry (3to7%). and use of 10-14% of polymer
177 does not practically harm the performance characteristics. In fact incorporation of
178 polymeric surfactant gives excellent characteristics of foaming, surface tension and
179 cleaning of stains of soil, tea, coffee and spinach. (See Table-5)
- 180 6) Our samples have been compared in all respects with commercial samples available in
181 the market. Our samples stand up to the mark and some times perform better than
182 commercial samples.
- 183 7) Our liquid Laundry detergents must be tried on pilot and commercial scale as they are
184 technoeconomically viable compositions.

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186 **References :**

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