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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 2/3 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%[1-5].The products like powder[4] , cake[5] and liquid detergents, paints[3], 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 :

UNDER PEER REVIEW

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

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[3], soil[4], Tea[4], coffee[4], and spinach[12,15].

The synthesized polymers were analysed systematically for their acid value[6,7], viscosity[9], surface tension[9,10] and other physico-chemical characteristics[8,16,17].

Two possible chemical reactions occuring are 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.

Both these reaction are expected to give good surfactant properties.

Experimental :

A glass reactor fitted with stirrer, heating mantle and condenser has been used in the synthesis of 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 temp. was raised slowly and steadily to 130^0C. 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 measured.

UNDER PEER REVIEW

The acid value[6,7], Saponification value[7,8], Oxirane oxygen by HBr method and other physical constants were determined by standard methods[1-5]. 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)		
		V I	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			

UNDER PEER REVIEW

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

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

Table- 3

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

S.No.	Raw Material	Concentration(% by wt)			
		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

UNDER PEER REVIEW

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

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

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) (g/cm3)	SurfaceTension (by stalagmometer) (dynes/cm)	Foam height (by cylinder method) (cc)	Viscosity (Flow time) (in seconds)
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

Stain removal (by standard procedure)

	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
CLS	G	Ex	Ex	Ex

UNDER PEER REVIEW

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

Fig-1 IR Spectra for polymer-VI

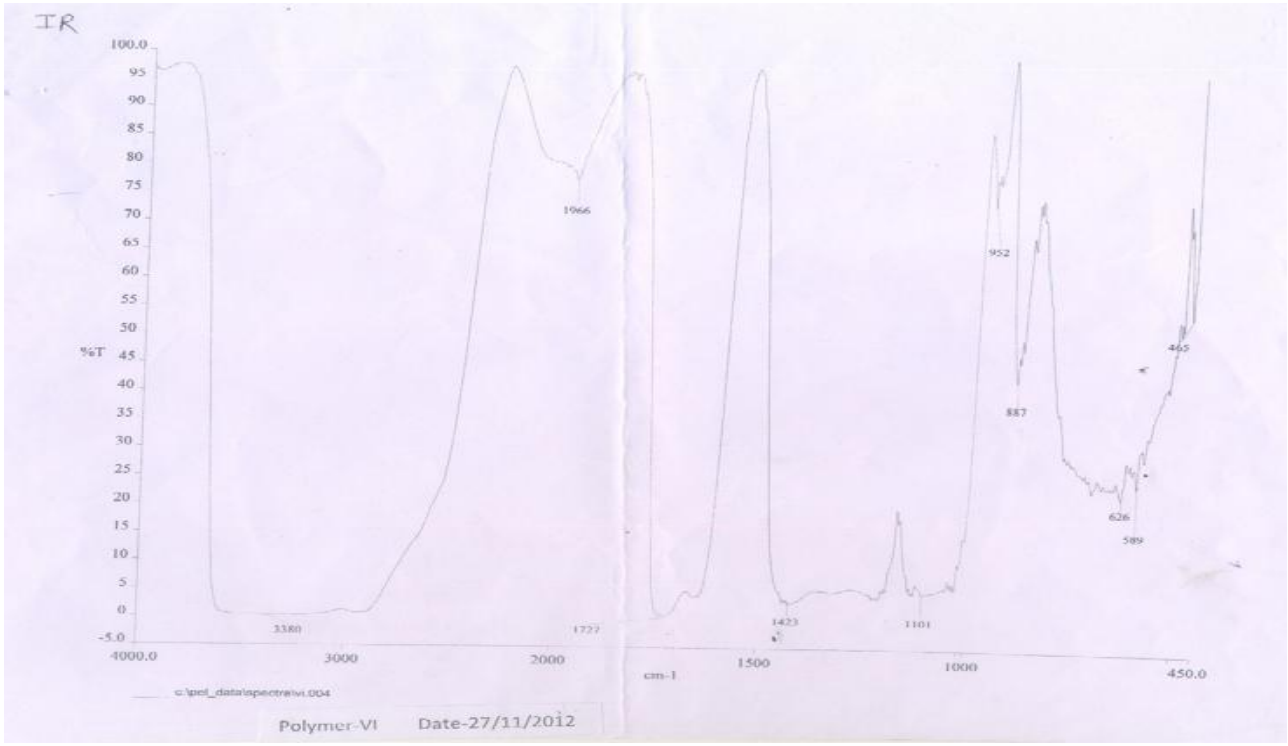
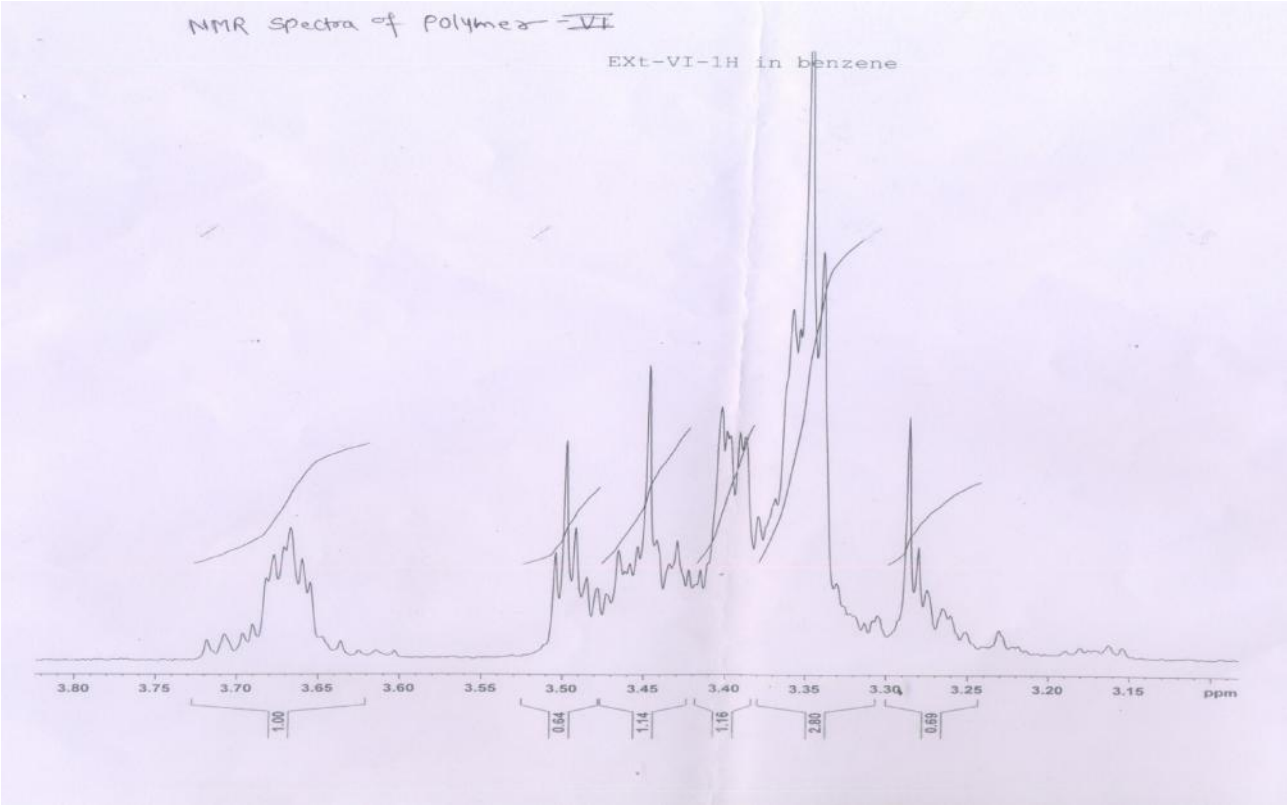


Fig-2 NMR Spectra for polymer-VI

UNDER PEER REVIEW



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

HLB= 20{1- Sap. Value of the polymer/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.

UNDER PEER REVIEW

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.

Conclusion:

1) Novel polymers based on polyethylene glycol(400) and citric acid (10-30%) can be synthesized successfully. The mole ratio of reactants, temperature, time of reaction and catalyst can be optimized to get desired acid value, H.L.B. ratio and % oxirane oxygen.
2) The yield of polymer is 90-95% which indicate the loss of 5-10% in the process of esterification.
3) The catalyst most effective are 1% HCl and 3.5% each of sodium metabisulphite and sodium bisulphate.
4) Composition based on sorbitol and citric acid I (Table-3)has been selected for preparation of liquid laundry detergents.
5) 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-5)
6) 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.
7) Our liquid Laundry detergents must be tried on pilot and commercial scale as they are technoeconomically viable compositions.

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UNDER PEER REVIEW

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