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FOAMING AND STAIN REMOVING LAUNDRY LIQUID DETERGENTS BASED ON NOVEL POLYMER AND SORBITOL

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ABSTRACT

Various liquid detergents were formulated using novel polymer of polyethylene glycol (400) and sorbitol. A combination of maleic, phthalic and citric acid have been used for esterification. Temperature, catalyst, time, ratio of ingredients require for synthesis have been standardized to get desired HLB ratio, viscosity, molecular weight. The liquid detergents were showing excellent results in terms of performance like reduction in surface tension of water, foam volume and % detergency. The results have been compared with standard market laundry detergents. These detergent formulations suggests about its efficiency and its capacity to replace the petroleum product to a considerable extent.

Key words: Catalyst, Synthesis, HLB ratio, Viscosity.

INTRODUCTION

In the last five decades there is common trend to use petroleum products as active and useful ingredients in commercial products like liquid[1] and powder[2,3] detergents, paints, inks, cosmetics. India as, a country is imparting 2/3[rd] of our requirement by way of import from other countries. Soft acid slurry and alpha olefin sulphonate are the active ingredients for powder, liquid and cake detergents. Our laboratory is working since a decade on replacing acid slurry with polymeric surfactants based on vegetable oil[1], starch[4-6], sorbitol[2,7]. In earlier work, polymeric surfactant[1-5] was used only as an additive but authors used alkyl resin as 80-90% substitute successfully.

In the present research work, we are using polyethylene glycol (400) and maleic anhydride, citric acid as novel ingredients for synthesis of polymeric surfactant. Polyethylene

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glycol with high oxirane oxygen content and citric acid with three acidic groups can give surfactant with better cleaning, ink and stain removing and foaming properties. The synthesized polymers were analysed for acid value[6,8], viscosity, surface tension[7,9], molecular weight and other physicochemical characteristics.

The possible chemical reactions in the present synthesis of polymers are –

(a) Esterification of acid groups in maleic anhydride and citric acid with –OH groups in sorbitol, polyethylene glycol.

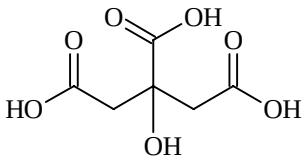
(b) Etherification between –OH groups of PEG and sorbitol to produce ethoxy groups.

Both these reactions are expected to give good surfactant properties.

Structures of polyethylene glycol (400) and citric acid are as follows –

$HOCH_2\text{-}(CH_2\text{-}O\text{-}CH_2)_n\text{-}CH_2OH$ $C_6H_8O_7$

Polyethylene glycol Citric acid



EXPERIMENTAL

In the experimental work three novel polymers have been synthesized. The mole ratio, order of addition, time of reaction and catalyst have been standardized to get desired HLB ratio, viscosity, cleaning and stain removing property.[11,12]

A two litre glass reactor fitted with stirrer, thermometer and condenser has been used. The heating was effected by an electric heating mantle with temperature regulator. A temperature control of ± 3^oC can be achieved by regulator. Calculated quantity of ingredients and catalysts are introduced step by step in the reactor. The temperature is raised slowly and steadily to 130^oC in about one hour. The heating is continued for 3-3.5 hrs till the desired viscosity and characteristics are achieved.

At the end of heating period the sample is withdrawn at 50-60^{o}C, filtered, weighed and stored in air tight bottles. The molecular weight of polymer –X is calculated from Mass spectra of polymer (Fig. 3).

Preparation of liquid laundry detergents

All the ingredients are mixed step by step with stirring. The samples are kept overnight in Refrigerator at 10^{o}C and filtered on next day. Clear transparent liquids have been analyzed for foaming, surface tension, % solids and soil, stain removing characteristics by standard methods[7,10].

Table 1: Composition of novel polymeric surfactants based on polyethylene glycol (400) and sorbitol

Ingredients	Composition (% by weight)		
	IV	**X**	**IX**
Sorbitol	74	40	75
Polyethylene glycol (400)	05	20	05
Propylene glycol	-	20	-
Maleic anhydride	07	10	-
Citric acid	05	-	-
Phthalic acid	03	10	-
Oxalic acid	05	-	20
Benzoic acid	01	-	-
Catalyst used			
1. Sodium metabisulphite	02	01	01
2. Sodium bisulphate	02	01	01
3. Conc. HCl	01	01	01

RESULTS AND DISCUSSION

The physicochemical properties of the novel polymer are shown in Table 2. Fig. 1 and 2 show the I.R. and N.M.R. spectra of polymer-X.[16,17] Fig. 3 shows Mass spectra of polymer-X. Various peaks and interpretation of peaks indicate presence of Ester (1723 cm^{-1}),

free OH (3389 cm^{-1}), -CO (1078 cm^{-1}), in the synthesized polymer. Mass spectra of polymer-X show its molecular weight 3704.

Table 2: Physicochemical analysis of novel polymer

S. No.	Polymer property	IV	X	IX
1.	Acid value	130	70.1	63
2.	Saponification value[11]	56.1	57.5	40
3.	HLB ratio	13.47	12.74	13.85
4.	Viscosity[12] (by ford cup No. 4 at 30^{o}C in second)	280	267	260
5.	% Oxirane oxygen	2.07	3.62	2.8
6.	% solid	81.03	80.22	81.21
7.	Solubility In water	Soluble	Soluble	Soluble
	In xylene	Insoluble	Insoluble	Insoluble
8.	Surface tension[13,14] (by stalagmometer in dyne/cm)	35.23	40.74	31.82
9.	Foam* volume (cc) by cylinder method[13-15]	800	900	700

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

For detergent formulation HLB value is checked by using formula –

HLB = 20 (1-Sap. value of the polymer/Acid value of the raw materials)

The HLB value of 12.74 is indicates its use in detergent formulation.

Three novel polymers have been synthesized which incorporate 10-30% polyethylene glycol. The samples also use 5% citric acid. Citric acid is particularly used as it is known for its cleaning and preservative component. 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. All samples show acidic pH. The HLB value and oxirane oxygen indicate the use of polymer as active ingredient in liquid laundry detergents. 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 physicochemical and performance characteristics of liquid detergents are shown in Table 3 and 4.

Table 3: Analysis and performance characteristics of liquid detergents based on novel polymer-X (The testing has been done at 1% concentration in distilled water)

Sample	pH (by pH meter)	Surface tension (by stalagmometer in dyne/cm)	Foam volume (by cylinder method in cc)	Density (by density bottle in gm/cc)
LX-1	8.5	33.41	950	1.031
LX-2	8.5	32.62	800	0.9742
LX-3	8.5	30.05	750	0.9391
CLS	8.5	37.4	800	0.9100

Table 4: Stain removal by standard procedure[18-20]

Sample	Soil	Tea	Coffee	Spinach
LX-1	G	Ex	Ex	G
LX-2	G	Ex	Ex	G
LX-3	P	G	G	P
CLS	G	Ex	Ex	Ex

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

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

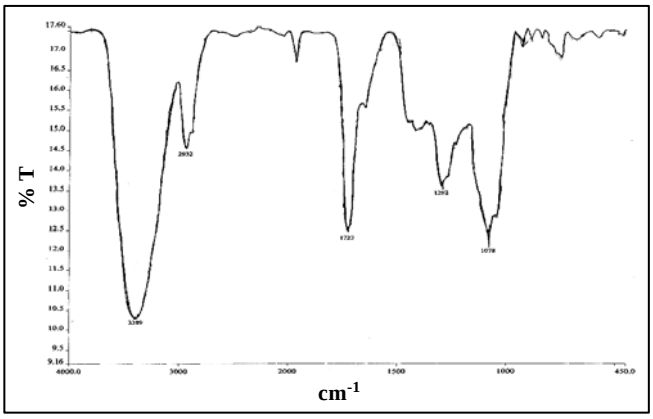


Fig. 1: IR Spectra polymer-X

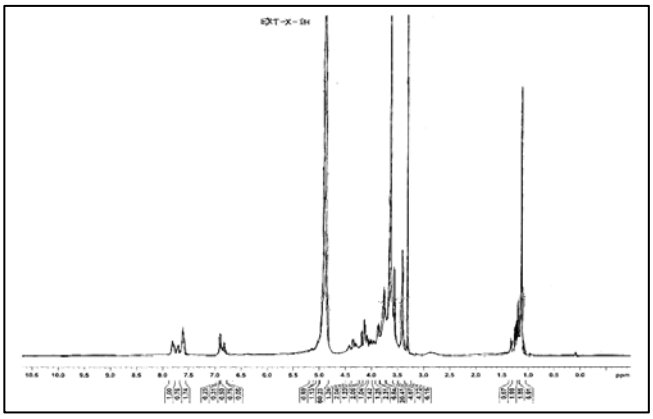


Fig. 2: NMR Spectra for polymer-X

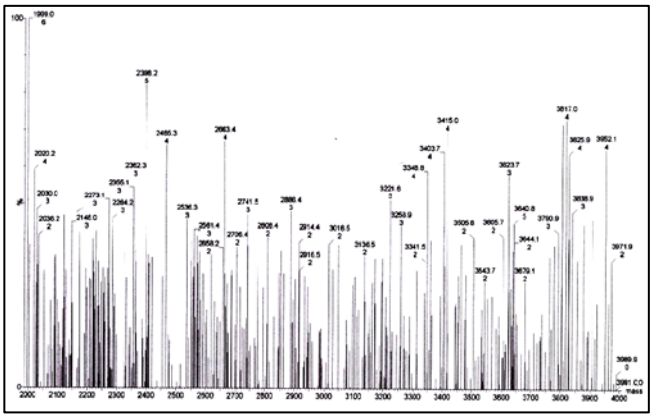


Fig. 3: Mass spectra for polymer-X

The costing of samples is quite reasonable and these products can be taken on pilot plant scale for manufacture.

CONCLUSION

(i) Novel polymers based on polyethylene glycol (400), sorbitol and citric acid 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.

(ii) The yield of polymer is 90-95% which indicate the loss of 5-10% in the process of esterification.

(iii) The catalyst most effective are 1% HCl and 3.5% each of sodium metabisulphite and sodium bisulphate.

(iv) Selected polymers have been used in formulations of liquid detergents. About 50% acid slurry has been replaced by our synthesized polymer. This substitution does not practically harm the performance characteristics. In fact incorporation of polymeric surfactant gives excellent characteristics of foaming, surface tension and cleaning of soil, tea, coffee and spinach (Table 4).

(v) 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.

(vi) Our liquid laundry detergents must be tried on pilot and commercial scale as they are technoeconomically viable compositions.

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