



---

## **Research Article**

---

Received: 25-09-2011

Accepted: 13-11-2011

Published: 29-11-2011

### **KINETIC STUDY OF NOVEL CARBOHYDRATE POLYMERS AND ITS APPLICATION IN LIQUID DETERGENT**

**Anand Deshpande** (Department of applied chemistry,CBS College of Engineering ,Amravati-444727)

**Dr.B.B.Gogte** (Department of applied chemistry,Shri ShankarPrasad Agnihotri College of Engg.Wardha-442001)

**Dr.B.W.Phate** (Department of applied chemistry,Priyadarshini Indira Gandhi College of Engg. Nagpur).

#### **\*Corresponding Author:**

*dr.gogte\_chem@rediffmail.com*

#### **ABSTRACT**

**ABSTRACT:** - Polymeric surfactant based on sorbitol, maize starch, and sugar have been synthesized and used successfully in detergent compositions. In the present piece of research work a small quantity of oxalic acid, citric acid and glycerol along with major quantity of maize starch and sugar solution has been used in synthesis of novel carbohydrate polymer .The overall idea is to develop a polymeric surfactant using higher quantity of maize starch and substantial quantity of sugar along with oxalic acid and citric acid. These polymers may be eco friendly and based totally on vegetable products. Selected novel carbohydrate polymers based on these observations have been used for the kinetic study at different temperatures and for different time durations. These novel carbohydrate polymers are then used in the preparation of powder detergent and liquid detergent .The acid slurry and Alpha Olefin Sulphonate based on crude petroleum have been successfully replaced to some extent by these novel carbohydrate polymers. Preparation of these polymers is simple and they can be recommended for commercial use .These novel polymers are comparable and suitable for commercial production. Economically they are cheaper than petroleum based products.

**Key words:** - carbohydrate polymers, sugar, starch, sorbitol.

## INTRODUCTION

As globalization and increased world population is leading world towards extinction of non renewable source mainly petroleum. This scarcity can only be full filled by modifying renewable sources to such a level that it can match up in its properties, quality and other properties with non renewable source.

Several industries like paint, detergents, inks and germicidal are mainly dependant on petroleum products, for example acrylic resin, various volatile organic solvents in paint industry. Alkyd resin one of the main ingredient of paint industry has 50% or more percentage of phthalic anhydride and maleic anhydride which are derived from petroleum origin. Organic solvents like toluene, xylene and benzene are petroleum origin and used in paint industry. Likewise linear Alkyl Benzene Sulphonate (LSBS) is used to a very large extent in detergent industry is also the example of use of petroleum products.

The present generation of surfactants is based on Linear Alkyl Benzene Sulphonate or similar materials, which are obtain from crude petroleum. The price of crude petroleum is quite high; the stock of crude petroleum is soaring year after year. So we must develop renewable vegetative base alternatives for these conventional petroleum based surfactants.

Every industry today is searching for alternative renewable resources of vegetable origin as the petroleum products are souring in price and availability. Thus biodegradable plastics, Eco- friendly surfactants and water thinnable paints are the key words in global search for alternative raw material.

### Objectives:

The present work has following objectives,

1. The basic idea of this research work is to obtain the optimize the ratio of LABS to carbohydrate based polymers, which will give the excellent technical performance. Thus we are trying to formulate Ecofriendly detergent based on renewable vegetable source like sorbitol, sugar starch, maleic anhydride, phthalic anhydride, which are having desired properties useful for products like liquid detergent.
2. These polymers will be analyzed for various physicochemical properties such as % solid, HLB, Viscosity, Molecular weight, pH, Acid value etc.
3. A combination of conventional active materials like Sodium Lauryl Sulphonate, Sodium lauryl ether sulphate, Alpha olefin Sulphonate, along with novel polymers has been used in a systematic manner to developed liquid detergents. In this way the present work is aimed at developing ecofriendly, cost effective and technically superior liquid detergents based on novel carbohydrate polymers.

## EXPERIMENTALS

### Synthesis of Novel Carbohydrate Polymers-

The polymer based on carbohydrate dates back to as early as the 1930s. Reppe (1930) was the first to synthesize vinyl saccharide monomer. He synthesized ether from glucose and fructose by alkali catalyzed addition of protected sugars to acetylene.

The esters of carbohydrates are completely soluble in water and found to be suitable in the liquid detergent formulations. The detergent made out of acid slurry cause water pollution. Acid slurry has the petroleum origin. The detergents of petroleum origin are responsible for river foaming and eutrophication. By using biodegradable polymers in detergent formulation the above mentioned problems of water pollution can be minimized to greater extent.

The polymers containing carbohydrates are potentially processable and biodegradable and biocompatible polymers. The present research work encompasses the polymer synthesis from Sugar, starch, Sorbitol, maleic anhydride and phthalic anhydride using water as solvent. Sodium bisulphate and Sodium bisulphite used as catalyst in order to formulate the ecofriendly detergents.

Surfactants can be produced from starch in combination with fatty acids and sugar. Products of these type have been known for as long as other "synthetic" surfactants formed from petrochemical-derived material. There has been a recent trend towards surfactant based on renewable sources. This trend has been supported by several commercial plants opened by Cognis (formerly Henkel). The driving force behind the trend is the number of benefits gained by starch-based surfactants. Desirable properties of these surfactants in addition to being produced from renewable sources are that they are readily biodegradable, they have low toxicity, they are produced from and degrade into materials of low toxicity, they are mild on the eyes and skin and some can perform synergistically with other surfactants. About 150,000 tons of starch-derived surfactants are produced annually worldwide. This novel carbohydrate polymer is cooked for different time periods and at different temperatures. On the basis of this kinetic study we can easily decide the cooking schedule for the preparation of novel carbohydrate polymer.

## **RESULTS AND DISCUSSIONS**

Several experiments were performed to get desired polymer of low acid value, desired molecular weight, and pale color. Two polymers with desired characteristics are reported in table no. 1. Major ingredient was sorbitol (50-55%) and sugar solution has been used (28%). The higher proportion of sugar results in charring so the limit to which sugar can be tolerated is found to be 28-30%. A small amount of starch powder (5-25%) has been used in composition B1 and S1.

A variety of catalysts have been used which include sodium bisulphite and sodium bisulphate. The preliminary physicochemical analysis is given in table no. 2. All the physicochemical analysis of both selected batches are registered after each hour. The acid values are quite low in the range of 21-19 for B1 and 40-35 for S1. This indicates esterification reaction between acidic group of phthalic & maleic anhydride and OH group of starch, sorbitol, and sugar. Compounds giving OH groups are sorbitol, sugar, and starch while component phthalic anhydride and maleic anhydride gives acid groups. It is an esterification reaction. The other possible chemical reaction is etherification between two OH groups to give an epoxy group. All the samples are highly soluble in water, alcohol, and

Sodium hydroxide. The % solids for both the batches lies between 69 to 73.pHvalue for both lies between 3-5,HLB value is reasonably good for the preparation of detergent, molecular weight of the novel carbohydrate polymer is in the range of 3997-5179 which is determined by average molecular weight determination method. All these properties are recorded in the table no.2

**Table no.1:-**Kinetic studies of two selected polymers based on Novel Carbohydrate Polymers

Sr.No.	Name of compounds	Batch B1	Batch S1
1	Sorbitol (70%)	55	51.8
2	Maleic anhydride	5	4.71
3	Phthalic anhydride	5	4.71
4	Maize starch	25	4.71
5	Oxalic acid	5	-
6	Citric acid	5	-
7	Glycerol	-	2.83
8	Sugar solution (80%)	-	28.3

**Note:** - Sodium bisulphate -1.5% and Sodium bisulphite -0.5% used as catalyst.

**Table no.2:-**Physicochemical Analysis of novel Carbohydrate Polymer

BATCH B1	After1hr	After2hr	After3hr	After4hr	After5hr
%solid	70.19	71.54	72.89	73.30	69.40
Acid value	21.87	21.19	20.17	20.26	19.20
Viscosity(by ford cup no.4 at 30°C)	54	88	163	179	223
Soluble in	Water	water	water	water	Water
PH. Value	4.99	4.95	4.91	4.89	4.31
Molecular weight	4229.64	4179.45	3994.31	3996.24	4037.24
H.L.B. ratio	14.8	14.7	15.0	15.3	15.6
oxyrene oxygen value	1.94	1.83	2.00	2.03	2.08
BATCH S1	After1hr	After2hr	After3hr	After4hr	After5hr
%solid	69.94	71.49	72.89	73.39	72.44
Acid value	40.19	39.11	35.17	37.62	35.25
Viscosity(by ford cup no.4 at 30°C)	61	199	163	310	323
Soluble in	Water	Water	water	Water	Water
PH. Value	4.71	4.70	4.91	4.42	3.35
Molecular weight	4816.97	4512.49	3994.31	5163.26	5179.14
H.L.B. ratio	13.1	13.3	15.0	13.9	14.2
oxyrene oxygen value	12.78	12.83	11.00	13.84	13.12

Five detergent samples have been prepared based on novel polymer S1 developed in the synthesis. The composition of formulated liquid detergent is given in table no.3.In this formulations acid slurry used is of 70% solid and is varied in the range 0-6 %, SLS (7.5%), SLES (10%) while the novel carbohydrate polymer used is of 72% solids this polymer is varied from 3 to 15%

Analysis of sample is given in table no. 4.

Polymer shows excellent foaming comparable to commercial sample as indicated in table no.4. The surface tension data also indicate significant lowering of surface tension in samples based on novel polymers. The results are comparable to commercial samples

**Table no 3:-**Liquid Detergent based on Novel Carbohydrate polymers (Sample Selected after 4hrs.)

SR.NO.	INGREDIENTS	LD1	LD2	LD3	LD4	LD5
1	Acid slurry (70%)	6.0	4.5	3.0	1.5	00
2	AOS	6.0	4.5	3.0	1.5	00
3	SLS	7.5	7.5	7.5	7.5	7.5
4	SLES	10	10	10	10	10
5	Sodium sulphate	05	05	05	05	05
6	Urea	03	03	03	03	03
7	Sorbitol (70%)	10	10	10	10	10
8	Polymer (S1) (72%)	3.0	6.0	9.0	12	15
9	Water	49.5	49.5	49.5	49.5	49.5

**Note:** - Acid slurry and Sorbitol used are of 70% solids, while polymer (S1) is of 72% solids

**Table no 4:-**Physicochemical properties of Liquid & Comm. Liquid Detergent

CONC	Samples	Foam Volume in cm(time in min)				density	Surface tension	% reduction in surface tension
0.1%	LD1	950	950	900	900	1.392	46.82	36.26
	LD2	650	650	600	600	1.364	46.63	34.42
	LD3	600	600	550	550	1.382	48.23	30.52
	LD4	500	450	400	400	1.392	47.59	26.18
	LD5	500	500	450	450	1.386	45.88	28.49
	CLD1	800	800	750	750	1.334	36.51	49.28
	CLD2	800	800	700	700	1.371	33.41	53.66
0.25%	LD1	850	850	800	800	1.361	44.95	39.24
	LD2	800	800	750	750	1.366	43.59	38.27
	LD3	700	700	650	650	1.359	45.24	35.29
	LD4	750	700	700	650	1.361	44.57	29.58
	LD5	700	600	600	550	1.373	42.33	31.51
	CLD1	850	850	800	800	1.346	33.62	52.65
	CLD2	850	850	850	850	1.333	30.29	54.17
0.5%	LD1	900	850	850	800	1.336	40.75	42.55
	LD2	750	750	700	700	1.359	41.65	43.29
	LD3	700	650	650	600	1.351	42.81	38.94
	LD4	600	550	500	500	1.364	40.64	33.65
	LD5	550	550	500	500	1.371	39.29	34.51
	CLD1	950	950	900	900	1.375	30.67	54.28
	CLD2	950	900	900	850	1.316	28.57	55.98
1%	LD1	950	950	900	900	1.329	38.23	44.36
	LD2	900	850	850	800	1.367	39.63	45.28
	LD3	700	650	650	600	1.372	40.58	46.39
	LD4	600	550	500	500	1.382	38.46	40.29
	LD5	550	500	500	450	1.377	37.38	39.54
	CLD1	1000	950	950	900	1.383	26.67	57.28
	CLD2	1000	950	950	900	1.334	26.33	58.03

**Note:** - CLD1 and CLD2 are commercial liquid detergent samples.

CLD1 and CLD2 tested simultaneously. Detergency testing carried out on cotton, polyester and tricot cloth sample. The soil stain removing characteristics are recorded in table no. 5 The Tea Coffee and Spinach stain removing characteristics are given in table no.6, table no. 7 and table no. 8 simultaneously. In this liquid detergent sample LD3 and LD5 gives good results in comparison with the commercial liquid detergent available in the market.

**Table no.5:-**Soil stain on Cotton, polyester and tericot sample

R0= Reflectance measured on clean cotton cloth =100

R0 =Reflectance measured on clean polyester cloth =100

R0=Reflectance measured on clean Teri cot cloth =100

Rs=Reflectance measured on Soil Stained cotton cloth =33

Rs=Reflectance measured on Soil Stained polyester cloth =43

Rs=Reflectance measured on Soil Stained Teri cot cloth =39

Sr. no.	Sample	Conc.%	Cotton		Polyester		Teri cot	
			Rw	Detergency	Rw	Detergency	Rw	Detergency
1	LD1	0.1	66	49.25	67	42.10	70	50.81
2		0.25	78	66.16	79	63.15	74	57.37
3		0.5	72	58.20	74	54.38	71	52.45
4		1.0	76	64.17	77	59.64	80	67.21
1	LD2	0.1	68	52.23	69	45.61	66	44.26
2		0.25	69	53.73	71	49.12	66	44.26
3		0.5	79	68.65	78	61.40	80	67.21
4		1.0	75	62.68	77	59.64	76	60.65
1	LD3	0.1	86	79.10	88	78.94	85	75.40
2		0.25	91	86.56	92	85.96	91	85.24
3		0.5	94	91.04	96	92.98	94	90.16
4		1.0	92	88.05	90	82.45	92	86.88
1	LD4	0.1	65	47.76	68	43.85	68	47.50
2		0.25	72	58.20	70	47.36	76	60.65
3		0.5	85	77.61	86	75.43	85	75.40
4		1.0	86	79.10	85	73.68	89	81.96
1	LD5	0.1	69	53.73	72	50.87	72	54.09
2		0.25	81	71.64	80	64.91	88	80.03
3		0.5	86	79.10	88	78.94	87	78.63
4		1.0	97	95.52	96	92.98	91	85.24
1	CD1	0.1	86	75.43	88	80.32	86	79.10
2		0.25	89	80.70	91	85.24	89	83.58
3		0.5	91	84.21	93	88.52	91	86.56
4		1.0	94	89.47	96	93.44	93	89.55
1	CD2	0.1	82	68.42	80	67.21	78	67.16
2		0.25	82	68.42	83	72.13	81	71.64
3		0.5	85	73.68	86	77.04	83	74.62
4		1.0	87	77.19	89	81.96	87	80.59

**Table no. 6:-**Tea stain on Cotton, polyester and tericot sample

R0= Reflectance measured on clean cotton cloth =100

R0 =Reflectance measured on clean polyester cloth =100

R0=Reflectance measured on clean Teri cot cloth =100

Rs=Reflectance measured on Tea cotton cloth =36

Rs=Reflectance measured on Tea polyester cloth =29

Rs=Reflectance measured on Tea Teri cot cloth =31

Sr. no.	Sample	Conc.%	Cotton		Polyester		Teri cot	
			Rw	Detergency	Rw	Detergency	Rw	Detergency
1	LD1	0.1	84	75.00	84	77.46	81	72.46
2		0.25	87	79.68	88	83.09	84	76.81
3		0.5	89	82.81	90	85.91	87	81.15
4		1.0	91	85.93	92	88.73	90	85.50
1	LD2	0.1	82	71.87	82	74.64	80	71.01
2		0.25	84	75.00	84	77.46	83	75.36
3		0.5	86	78.12	85	78.87	85	78.26
4		1.0	88	81.25	89	84.50	87	81.15
1	LD3	0.1	85	76.56	89	84.50	87	81.15
2		0.25	87	79.68	91	87.32	89	84.05
3		0.5	90	84.37	93	90.14	91	86.95
4		1.0	93	89.06	95	92.95	93	89.85
1	LD4	0.1	87	79.68	85	78.87	81	72.46
2		0.25	89	82.81	88	83.09	85	78.26
3		0.5	90	84.37	90	85.91	88	85.50
4		1.0	92	87.50	92	88.73	90	85.50
1	LD5	0.1	90	84.37	88	83.09	87	81.15
2		0.25	90	84.37	90	85.91	89	84.05
3		0.5	91	85.93	92	88.73	90	85.50
4		1.0	92	87.50	94	91.54	91	86.95
1	CD1	0.1	80	71.83	82	72.46	84	75.00
2		0.25	82	74.64	84	75.36	81	70.31
3		0.5	84	77.45	86	78.26	79	67.18
4		1.0	86	80.28	87	79.71	77	64.06
1	CD2	0.1	77	67.65	79	68.11	81	70.31
2		0.25	79	70.42	81	71.01	79	67.18
3		0.5	81	73.23	83	73.91	77	64.06
4		1.0	83	76.05	85	76.81	75	60.93

**Table no. 7:-**Coffee stain on Cotton, polyester and tricot sample

R0= Reflectance measured on clean cotton cloth =100

R0 =Reflectance measured on clean polyester cloth =100

R0=Reflectance measured on clean Teri cot cloth =100



Rs=Reflectance measured on Coffee cotton cloth =31

Rs=Reflectance measured on Coffee polyester cloth =36

Rs=Reflectance measured on Coffee Teri cot cloth =30

Sr. no.	Sample	Conc.%	Cotton		Polyester		Teri cot	
			Rw	Detergency	Rw	Detergency	Rw	Detergency
1	LD1	0.1	82	73.91	84	75.00	88	82.85
2		0.25	85	78.26	87	79.68	90	85.71
3		0.5	87	81.15	89	81.25	92	88.57
4		1.0	89	82.60	91	84.37	94	98.42
1	LD2	0.1	85	78.26	85	76.56	82	74.28
2		0.25	88	82.60	87	79.68	87	80.00
3		0.5	90	84.05	88	81.25	89	84.28
4		1.0	92	86.95	90	82.81	91	87.14
1	LD3	0.1	84	76.81	85	76.56	84	77.14
2		0.25	86	79.71	87	79.68	87	81.42
3		0.5	90	84.05	90	82.81	88	82.85
4		1.0	94	91.30	92	85.93	90	85.71
1	LD4	0.1	81	72.46	87	79.68	87	80.00
2		0.25	85	78.26	90	82.81	89	81.42
3		0.5	88	82.60	92	85.93	90	85.71
4		1.0	90	84.05	94	89.06	92	88.57
1	LD5	0.1	87	81.15	88	81.25	84	77.14
2		0.25	89	82.60	89	82.81	87	81.42
3		0.5	91	85.50	91	84.37	89	84.28
4		1.0	95	92.75	93	87.50	91	87.14
1	CD1	0.1	89	82.81	91	87.14	87	79.71
2		0.25	87	79.68	93	90.00	89	82.60
3		0.5	85	76.56	95	92.85	91	85.80
4		1.0	82	71.84	97	95.14	95	92.75
1	CD2	0.1	82	71.87	84	77.14	84	75.36
2		0.25	79	64.06	86	80.00	86	78.26
3		0.5	77	64.06	88	82.85	88	81.15
4		1.0	75	60.93	90	85.14	90	84.05

**Table no. 8:-**Spinach stain on Cotton, polyester and tericot sample

R0= Reflectance measured on clean cotton cloth =100

R0 =Reflectance measured on clean polyester cloth =100

R0=Reflectance measured on clean Teri cot cloth =100

Rs=Reflectance measured on Spinach cotton cloth =38

Rs=Reflectance measured on Spinach polyester cloth =32

Rs=Reflectance measured on Spinach Teri cot cloth =41



Sr. no.	Sample	Conc.%	Cotton		Polyester		Teri cot	
			Rw	Detergency	Rw	Detergency	Rw	Detergency
1	LD1	0.1	82	70.96	88	82.35	85	74.52
2		0.25	84	74.19	90	85.29	87	77.96
3		0.5	89	82.25	92	88.23	90	83.05
4		1.0	91	85.48	94	91.17	92	86.44
1	LD2	0.1	84	74.19	85	77.94	81	67.79
2		0.25	87	79.03	87	80.88	85	74.57
3		0.5	91	85.48	89	83.82	87	77.96
4		1.0	93	88.70	91	86.76	90	83.05
1	LD3	0.1	89	82.25	85	77.94	88	79.66
2		0.25	91	85.48	87	80.88	90	83.05
3		0.5	93	88.70	90	85.29	91	84.74
4		1.0	95	91.93	93	89.70	94	89.83
1	LD4	0.1	90	83.87	87	80.88	84	72.88
2		0.25	91	85.48	90	85.29	87	77.96
3		0.5	94	90.32	92	88.23	89	81.35
4		1.0	97	95.16	94	91.17	91	84.74
1	LD5	0.1	81	69.35	82	73.52	77	61.01
2		0.25	86	77.41	84	76.47	80	66.10
3		0.5	88	80.64	85	77.94	83	71.18
4		1.0	90	83.87	89	83.82	88	79.66
1	CD1	0.1	85	77.94	84	72.88	89	82.85
2		0.25	87	80.58	86	76.27	92	87.00
3		0.5	89	83.82	88	79.66	94	90.32
4		1.0	91	86.76	90	83.05	96	93.54
1	CD2	0.1	81	72.005	79	64.40	84	74.19
2		0.25	83	75.00	81	67.79	86	77.41
3		0.5	84	76.47	83	71.18	88	80.64
4		1.0	86	79.41	85	74.57	90	83.87

## REFERENCES

- 1 Chemistry and Technology of Surfactants by Richard J. Farn (page no.14, 46)
- 2 [http://www/google.com/polymeric surfactant/novel surfactants preparation, application and biodegradability](http://www/google.com/polymeric%20surfactant/novel%20surfactants%20preparation,%20application%20and%20biodegradability).
- 3 Bauby A., Leversidge P., "Polymeric surfactant and their use industrial application", U.S.A. 1995.
- 4 [http://www/google.com/carbohydrate polymer/soyabean, Fatty acid ester of Carbohydrate polymer](http://www/google.com/carbohydrate%20polymer/soyabean,%20Fatty%20acid%20ester%20of%20Carbohydrate%20polymer).
- 5 Gogte, B.B., Dontulwar J.R., Borikar D.K. Carbohydrate polymers 65, 2006, p.no. 207-210.
- 6 .Bhatanagar M.S., "Chemistry and Technology of polymers", S.Chand & Company Ltd, 2004, p.no.1-28.
- 7 Chattopadhyaya P.K., "Modern Technology of soaps. Detergent and Toiletries, 2nd edition p. no.8-10.
- 8 Gogte, B.B., Agrawal, RS. Journal of soaps, Detergents and Toiletries Rev., 34, 2003 p.no.25-28.
- 9 Gogte, BB, Agrawal RS., Journal of soaps, Detergents and Toiletries Rev., 34, 2003 p.no. 19-22.