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Benzylation of different mole ethoxylates of p-octyl phenol with benzyl chloride

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Abstract: The benzylation reaction of p-octyl phenol alkoxylates with alkyl halide is a crucial step in the synthesis of alkylphenol ethoxylate-based surfactants. In this research paper, we investigate the impact of different mole ratios of ethylene oxide to p-octyl phenol on the benzylation reaction and the properties of the resulting products. The reaction study involves the formation of alkoxide of different mole ratios ethoxylates of p-octyl phenol and subsequent benzylation using benzyl chloride as the alkylating agent. The mole ratios of ethylene oxide to p-octyl phenol employed for reaction study ranges 1:11 and 1:15 to 1:19. The synthesis was carried out using a batch reactor under controlled conditions. The reaction conditions, such as temperature, reaction time, and reactants mole ratio, are carefully optimized to achieve high conversion and selectivity. The products are characterized using analytical techniques such as cloud point, hydroxyl value by titration method and molecular weight of initial and synthesized product. Furthermore, the paper discusses the implications of the obtained results in terms of the potential applications and properties of the benzylation products. The modified ethoxylates could find utility as surfactants, emulsifiers, or functional additives in various industries. Overall, this research paper provides valuable insights into the benzylation of p-octyl phenol ethoxylates with benzyl chloride. The findings contribute to the understanding of this chemical modification process and offer potential avenues for the development of tailored ethoxylate-based materials with enhanced properties.

Index Terms **- Benzylation, ethoxylation, p-octyl phenol, benzyl chloride, ethylene oxide.**

I. Introduction

The modification of chemical structures through functionalization plays a crucial role in tailoring the properties of organic compounds. One such versatile approach is the synthesis of ethers by the nucleophilic substitution of alkyl or aryl halides with alkoxides. This reaction has been widely used for the synthesis of various industrially important compounds, including surfactants, pharmaceuticals, and polymers. Among the diverse range of ether-based compounds, alkylphenol ethoxylates (APEOs) have attracted significant attention due to their excellent surface-active properties and their extensive use in industrial applications such as detergents, emulsifiers, and wetting agents. A particularly significant subclass of APEOs is p-octyl phenol ethoxylates (OPEOs), which exhibit exceptional emulsifying and dispersing capabilities due to their unique hydrophilic-lipophilic balance (HLB) and surface-active properties. End-capped fatty alcohol polyglycol ethers, so-called "mixed ethers", represent an important class of nonionic surfactants which are characterized by high cleaning power with low foam development and good ecotoxicological compatibility. The products are used, for example, in the machine cleaning of beer and milk bottles [Fat. science technol. 89, 106 (1987)]. German patent specification DE-C1 37 44 525 (Henkel) discloses a process for preparing such mixed ethers, in which fatty alcohol polyglycol ethers are reacted with alkyl halides in the presence of solid alkali metal hydroxide. From the existing knowledge base, U.S. Patent No. 7,777J426J highlights a method to produce biodegradable nonionic surfactants derived from starch glycosides. This involves a two-step process: A starch is reacted with a specific amount of short-chain epoxy alkane (like ethylene oxide or propylene oxide), with the ratio being 5 to 22 moles of epoxy alkane for every mole of the anhydro glucose unit in the starch. The product from the first step is then combined with a long-chain epoxy alkane, containing between 6 to 18 carbon atoms, at a ratio of one to three moles per anhydro glucose unit. This patent points out that these nonionic surfactants contain what's termed "hemiacetal linkages" (though more accurately referred to as acetal linkages) instead of the more common polyether linkages. This unique linkage makes the surfactant more susceptible to enzymatic degradation in environments like sewage or unprocessed river water, meaning these surfactants are highly biodegradable.

Foam is highly undesired in various industrial procedures. For instance, during the cleaning of beer or milk bottles using washing machines, or while spray cleaning automobile panels, it is crucial to consider not only the effectiveness of the cleaning agents used, but also the prevention of foam formation, which can severely disrupt the functioning of the equipment. This concern is even more significant since many cases involve the use of highly active anionic surfactants that tend to produce a substantial amount of foam.

The challenge of managing foam has been recognized for some time, and as a result, several solutions have been proposed in the past. These solutions can be categorized into two main groups: The first group involves employing defoamers, which are often composed of paraffinic hydrocarbons or silicone compounds. However, for the mentioned applications, this approach is generally unfavorable. The second group consists of utilizing surface-active formulations that possess both low-foaming properties and defoaming capabilities. Typically, these formulations are nonionic surfactants or surfactant-like systems, such as fatty alcohol propylene glycol ethers or block polymers of ethylene and propylene glycol. Unfortunately, these substances lack adequate biodegradability, posing another limitation.

The control of foam in industrial processes is crucial, and while some solutions involving defoamers or low-foaming surface-active formulations have been proposed, they often have drawbacks that make them less desirable for specific applications.

In recent years, there has been growing interest in enhancing the performance and properties of OPEOs through chemical modification. One promising strategy is the benzylation of OPEOs, where a benzyl group is introduced onto the phenolic moiety of the OPEO structure. This benzyl group not only imparts enhanced lipophilicity but also introduces new functional groups, thereby broadening the range of potential applications. To systematically investigate the impact of varying ethylene oxide (EO) mole ratios on the benzylation of OPEOs, this research paper aims to explore the nucleophilic substitution reaction to achieve the desired modification. By controlling the EO mole ratios, it becomes possible to precisely adjust the degree of ethoxylation, tailoring the hydrophilic-lipophilic balance of the resulting benzylation products.

The objectives of this study are threefold: first, to optimize the reaction conditions for the benzylation of OPEOs using different EO mole ratios; second, to evaluate the influence of EO mole ratios on the physicochemical properties of the benzylation products, such as hydroxyl value, cloud point, and molecular weight; and third, to assess the impact of EO mole ratios on the surface-active properties of the modified OPEOs, including emulsifying and dispersing capabilities. By gaining a comprehensive understanding of the benzylation of OPEOs with varying EO mole ratios, this research endeavors to contribute to the design and development of tailored surfactants with improved performance characteristics for a wide range of applications. In the subsequent sections, the experimental methodology, results, and discussion will be presented, followed by the conclusions drawn from the study, providing insights into the effect of varying EO mole ratios on the benzylation of OPEOs via nucleophilic substitution reaction.

The ethoxylation of the p-octyl phenol mentioned may be carried out in known manner at temperatures of 120° to 180° C. in the presence of basic catalysts such as, for example, sodium hydroxide or sodium hydride or primarily 0.1% potassium hydroxide. Accordingly, the alkoxylates may have both a conventional and a narrow homolog distribution. It is again specifically pointed out that the catalyst of ethoxylation is critical to the performance properties of the products. As it affects the narrow or broad peak distribution in GPC which define the molecular weight of the alkoxylates. Benzyl-end-capped mixed ethers which are to be used in accordance with the invention are obtained solely based on alkyl and/or alkenyl polyglycol ethers which contain block of ethylene oxide units. Ethers based on alkyl and/or alkenyl polyglycol ethers containing on average 10 to 19 moles of ethylene oxide are particularly preferred.

The process of alkyl end capping can also be conducted using well-established methods. This involves the utilization of methyl chloride or dimethyl sulfate, following the guidelines specified in U.S. Patent No. 4,587,365 or EP-B O 302 487. It is recommended to carry out this reaction within a temperature range of 60°C to 120°C, with a preference for temperatures between 80°C and 100°C.The end capping reaction follows Williamson's ether synthesis and necessitates the presence of at least stoichiometric quantities of a potent base, such as sodium hydroxide or, more specifically, potassium hydroxide. Furthermore, it has been found advantageous to maintain a molar ratio of 1: (1.5-2.0): (1.5-2.0) between the alkyl and/or alkenyl polyglycol ether, the base, and the methylating agent.

II. Experimental Method

Materials

Ethoxylates of p-octyl phenol having degree of ethoxylation 10, 15, 16, 17, 18, 19 mole was obtained from Sterling Auxiliaries Pvt. Ltd., Sodium hydroxide in pellet form was obtained from Grasim Industries. Benzyl Chloride was obtained from Thomas Baker. Hydrochloric acid for pH adjustment was purchased from Loba chemie pvt ltd.

Methods

Laboratory scale benzylation reaction procedure

Reaction method involves the reaction of ethoxylates of p-octyl phenol with the strong base reactant like sodium hydroxide, potassium hydroxide, sodium methoxide, sodium ethoxide, etc. to form alkoxide. To avoid the dark coloration of product (yellow to brown) while formation of alkoxide the nitrogen bubbling to the inside reaction mass is preferable. Then reaction of the benzyl halide or substituted benzyl halide with the ethoxylated alcohol (alkoxide) is carried out at a temperature in the range from about 80 to 140° C., ideally from about 90 to 100 C. The temperature of the reaction is not particularly critical and can be varied outside of the stated range. The reaction gets complete at the end of about 15 minutes and the reaction time for benzylation is also depends on the quantity of reaction mass, although longer reaction times are suitable and generally employed to ensure complete reaction. After completion of the reaction, the desired product is recovered by standard procedures. Thus, the reaction mixture can be treated with DI water to affect a phase separation between a water layer and an organic layer. While addition of water into the reaction mass need to take care of reaction mass temperature must be less the 90 deg C to avoid steam formation of water and subsequent avoid the explosion. The NaCl salt formed in the reaction as by-product will get dissolve in the water layer and get separate out by phase separation technique. The organic layer can be easily separated by gravitational settling procedure, dried, and filtered to recover the novel surface-active agents of the invention.

Analytical Determination

Determination of pH Value by electrode
For the determination of pH value considered the ISO method using an electrode which is specified in ISO 10523:2008, titled "Water quality - Determination of pH." This standard provides guidelines for measuring the pH of water samples using a glass electrode or a combination electrode**.**

Determination of Cloud Point
The Cloud Point of starting material and synthesized product were analyzed by the ISO 1065:1991, non-ionic surface-active agents obtained from ethylene oxide and mixed non-ionic surface-active agents — determination of cloud point — where the 1% of surfactant in water is heated in water bath increasing the temperature of water bath as the cloudiness appears considered that temperature as the cloud point of the material. When the cloudiness of 1% of surfactant in water does not appear up to 100°C, then cloud point analyzed in 5% NaCl or 10% NaCl in water solution as the sodium chloride suppressed the cloud point of surfactants.

Determination of Hydroxyl Value by titration Method
The hydroxyl value of starting material and synthesized product were analyzed by the ISO 4327:1979 method which is normally used for the non-ionic surface-active agents — poly alkoxylates derivatives where phthalic anhydride was used for the esterification of hydroxyl group.

Determination of Molecular Weight of Non-Ionic Surfactants
To calculate the molecular weight of ethoxylates using the hydroxyl value, divide the constant 56110 by the hydroxyl value. The constant 56110 represents the molar mass of the ethylene oxide (EO) unit. The formula to calculate the molecular weight of ethoxylates using the hydroxyl value: Molecular weight = 56110 / Hydroxyl value. In this way calculated the molecular weight of p-octyl phenol ethoxylates and simply we added the molecular weight of benzyl group to the molecular weight p-octyl phenol ethoxylates for the subsequent benzylated p-octyl phenol ethoxylates.

Determination of Solid Content of material by Oven drying Method
Determined the solid content of a material using the oven drying method according to ISO 3251:2020 standards.

Determination of Dynamic Viscosity
To determine dynamic viscosity using an LVT (Low Viscosity) spindle according to ISO standards, followed the guidelines provided in ISO 2555:2018, which determine the apparent viscosity by the Brookfield test method.

Determination of Specific Gravity by Specific Gravity Bottle
For the determination of specific gravity used the specific gravity bottle method according to ISO standards used ISO 279:2004 method and it typically involves the use of a specific gravity bottle and a balance. ISO has various standards that outline the procedure for measuring specific gravity, such as ISO 279:2004, titled "Plastics - Determination of density."

Determination of Color by Tintometer
For the determination of color using a Tintometer according to ISO standards used ISO 7887:2017 method which involves tintometer instrument where color reading detects after measurement. ISO has various standards that provide guidelines for color determination, such as ISO 7887:2017, titled "Water quality - Determination of color."

Determination of NaCl Content
The sodium chloride content of the synthesized product was analyzed by the method issued by the ISO 457:1983 for soaps — determination of chloride content — titrimetric method, which also called as Mohr's method where silver nitrate used as titrant and the potassium chromate used as the indicator.

Determination of Moisture Content by Karl Fisher Method
The moisture content of starting material and the synthesized product were analyzed by the method issued by the ISO 4317:2011 - Surface-active agents and detergents — Determination of water content — Karl Fischer methods.

III. Results and Discussion

Benzylation is the reaction where the benzyl group is replaced with the hydrogen atom in any form of the alkyl reactant where alkoxide formation is the first to convert the alkyl group to the alkoxide ion by reacting with alkali hydroxide. In this study the mole ratio of ethoxylates of p-octyl phenol and the sodium hydroxide can be varied from 0.5 to 1.5, where 1.25 mole ratio found to be good conversion of alkoxide as the sodium hydroxide need to take more than 1 mole ratio to the ethoxylates. The mole ratio of alkoxide to the benzyl chloride can be varied from 0.5 to 1, where 0.85 mole ratio found to improved results as there no need to distill the unreacted benzyl chloride since all the benzyl chloride gets consumed in the reaction. The quantity of water addition for the removal of sodium chloride byproduct formed in the reaction can be calculated by the mole ratio wise formation of sodium chloride. If we add 1 mole ratio of benzyl chloride to the reaction, then exact 1 mole ratio of sodium chloride will form and saturation point of sodium chloride in water is 35 gm in 100 ml water. So, if we add 126 gm of benzyl chloride to the reaction then 58.5 gm of sodium chloride will form, and we need to add 168 gm of water to dissolve the sodium chloride according to the saturation point of sodium chloride in water. Organic and water layer of the reaction mass can be separated by the separating funnel.

To study the benzylation reaction of ethoxylates of p-octyl phenol with alkyl halide, taken the various number of degrees of ethoxylates of p-octyl phenol like 10, 15, 16, 17, 18, 19 having below listed hydroxyl value and cloud point and tabulated physical and chemical properties. The physical appearance of starting material which is ethoxylates of p-octyl phenol was clear colorless liquid, the pH was neutral in between 6-7. The cloud point was checked which was 66°C and 100°C for 10 mole and 15 mole Ethylene oxide condensates of p-octyl phenol respectively but as we go for higher mole ethylene oxide condensate the cloud point was above 100°C in 2% aqueous which was difficult to measure so also measured the cloud point in 5% NaCl salt solution and 10% NaCl salt solution which shown in below table, as the salt solution in water lower down the cloud point of same the material.

Analysis of the sample before carried out the alkoxide formation and benzylation reaction

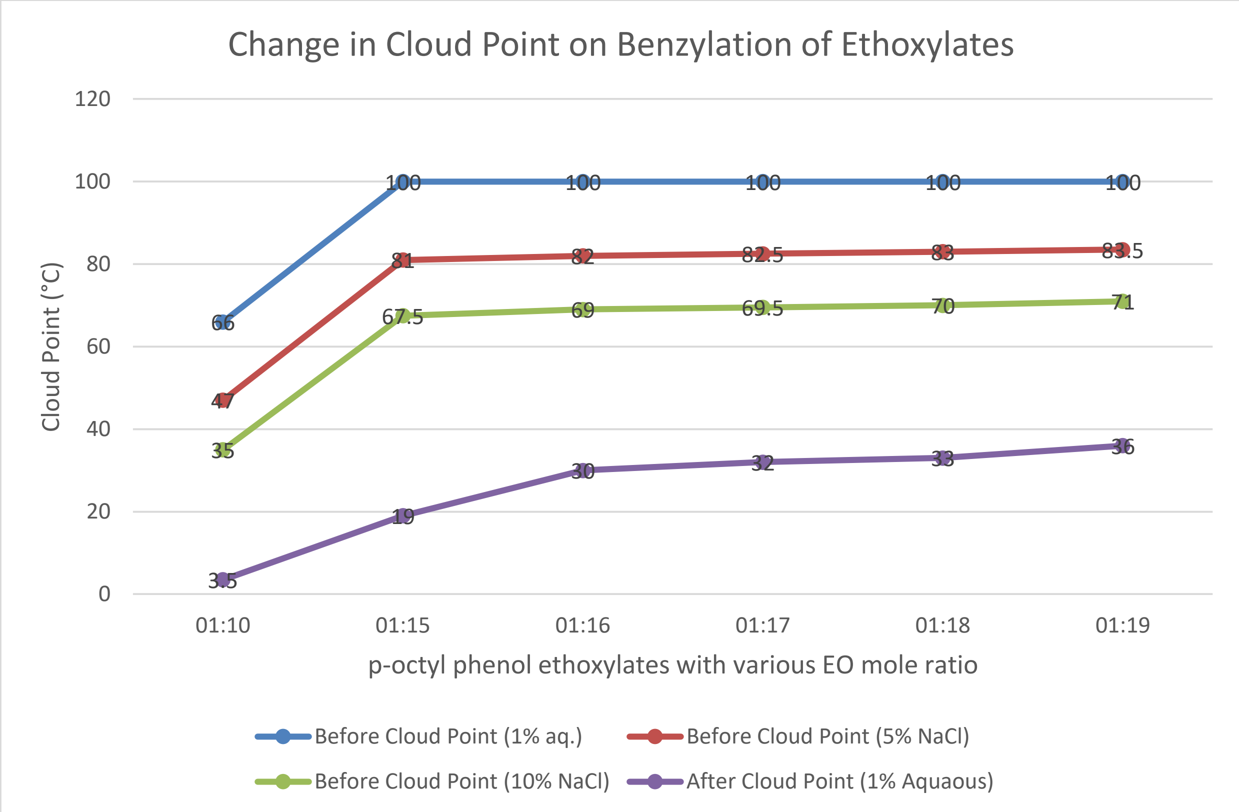
Mole of p-Octyl Phenol : Mole of Ethylene Oxide	**1:10**	**1:15**	**1:16**	**1:17**	**1:18**	**1:19**
Physical Appearance @ 25 C	Clear Liquid	Clear Liquid	Clear Liquid	Clear Liquid	Clear Liquid	Clear Liquid
Color (APHA)	36	28	51	25	25	31
pH (2% Aqueous)	6.79	6.85	6.51	6.85	6.65	6.56
Moisture Content (KF), %	0.03%	0.07%	0.01%	0.02%	0.02%	0.06%
Cloud Point (1% aq.)	66°C	100°C	above 100°C	above 100°C	above 100°C	above 100°C
Cloud Point (5% NaCl)	47°C	81°C	82°C	82.5°C	83°C	83.5°C
Cloud Point (10% NaCl)	35°C	67.5°C	69°C	69.5°C	70°C	71°C
Hydroxyl Value (mg KOH/gm)	85	65	62.01	61.83	61.33	60.5
Molecular Weight (gm/mole)	660.12	863.23	904.85	907.49	914.89	927.44

Analysis of the synthesized product after carried out the benzylation reaction

After Benzylation Parameter	**1:10**	**1:15**	**1:16**	**1:17**	**1:18**	**1:19**
Physical Appearance @ 25 C	Clear Liquid	Clear Liquid	Clear Liquid	Clear Liquid	Clear Liquid	Clear Liquid
Color (APHA)	25	46	10	25	13	41
pH (2% Aqueous)	7.06	4.2	6.66	7.05	6.48	6.12
Moisture Content (KF), %	8.02	8.04	8.00%	8.05	8.08	8.03
Solid Content (120 C/ 1hr / 2gm)	91.98	91.45	92.47%	91.95	91.92	91.97
Cloud Point (1% Aqueous)	3.5 °C	19°C	30°C	32°C	33°C	36°C
Hydroxyl Value (mg KOH / gm)	11.5	11.68	10.92	12.57	14.11	16.05
Molecular Weight (gm/mole)	755.12	958.23	999.85	1002.49	1009.89	1022.44
Dynamic Viscosity (@ 25°C /s 62/ 50 rpm)	245 cps	240 cps	258 cps	251 cps	253 cps	257 cps
Specific Gravity @25°C	1.085	1.079	1.0811	1.0854	1.0852	1.0851
NaCl Content, %	0.04	0.05	0.03	0.03%	0.06	0.045

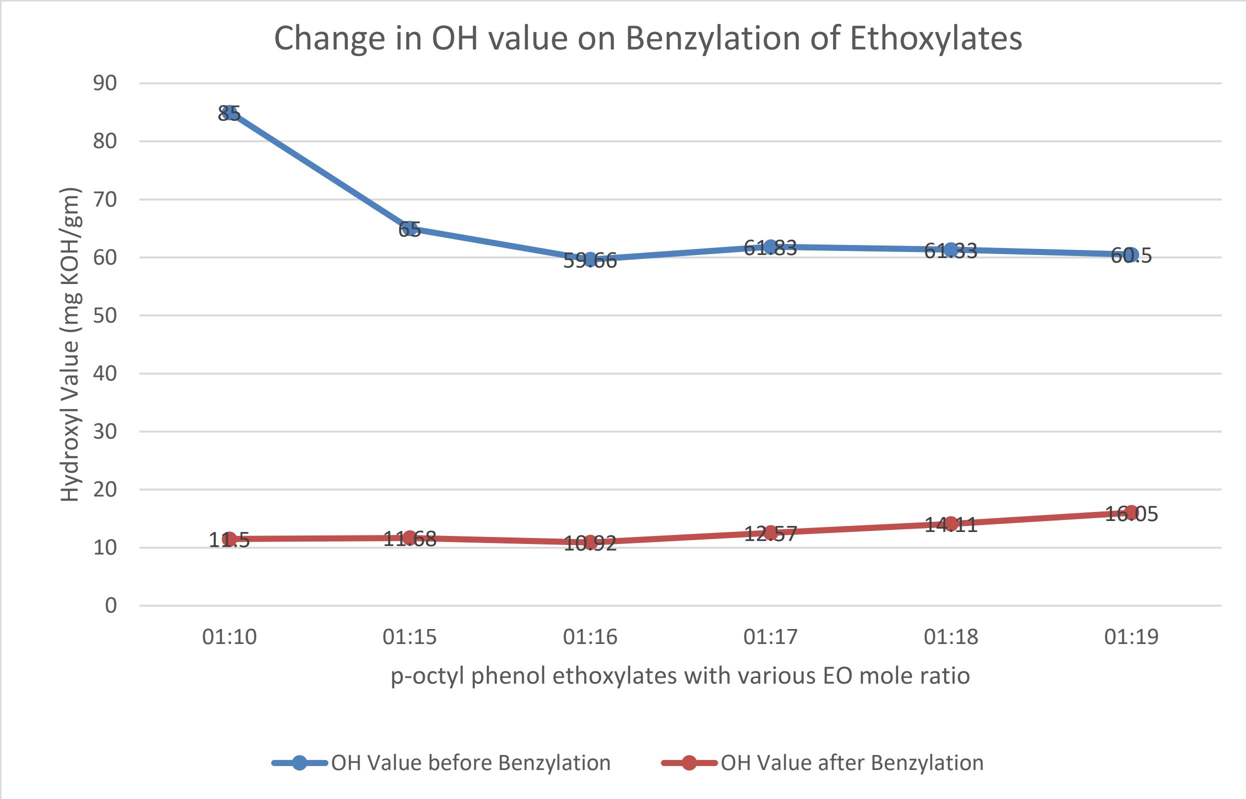
The experimental data and graphical representation of cloud point of various degree of ethoxylates of p-octyl phenol and their subsequent cloud point after benzylation reaction shown in the tabular and graphical form. It is found that after benzylation reaction the cloud point of the ethoxylates of p-octyl phenol decreases. The change in cloud point of the product is the indication of benzylation reaction means addition of benzyl group to the alcoholic end of the ethoxylates. The addition of benzyl group to the ethoxylates via alkoxide formation and benzylation is depends on the viscosity of the starting material where the viscosity of the ethoxylates increases as the degree of ethoxylation increases.

Mole of p-Octyl Phenol : Mole of Ethylene Oxide	1:10	1:15	1:16	1:17	1:18	1:19
Before Cloud Point (1% aq.)	66 °C	100 °C	Above 100 °C	Above 100 °C	Above 100 °C	Above 100 °C
Before Cloud Point (5% NaCl)	47 °C	81 °C	82 °C	82.5 °C	83 °C	83.5 °C
Before Cloud Point (10% NaCl)	35 °C	67.5 °C	69 °C	69.5 °C	70 °C	71 °C
After Benzylation Cloud Point (1% Aqueous)	3.5 °C	19 °C	30 °C	32 °C	33 °C	36 °C



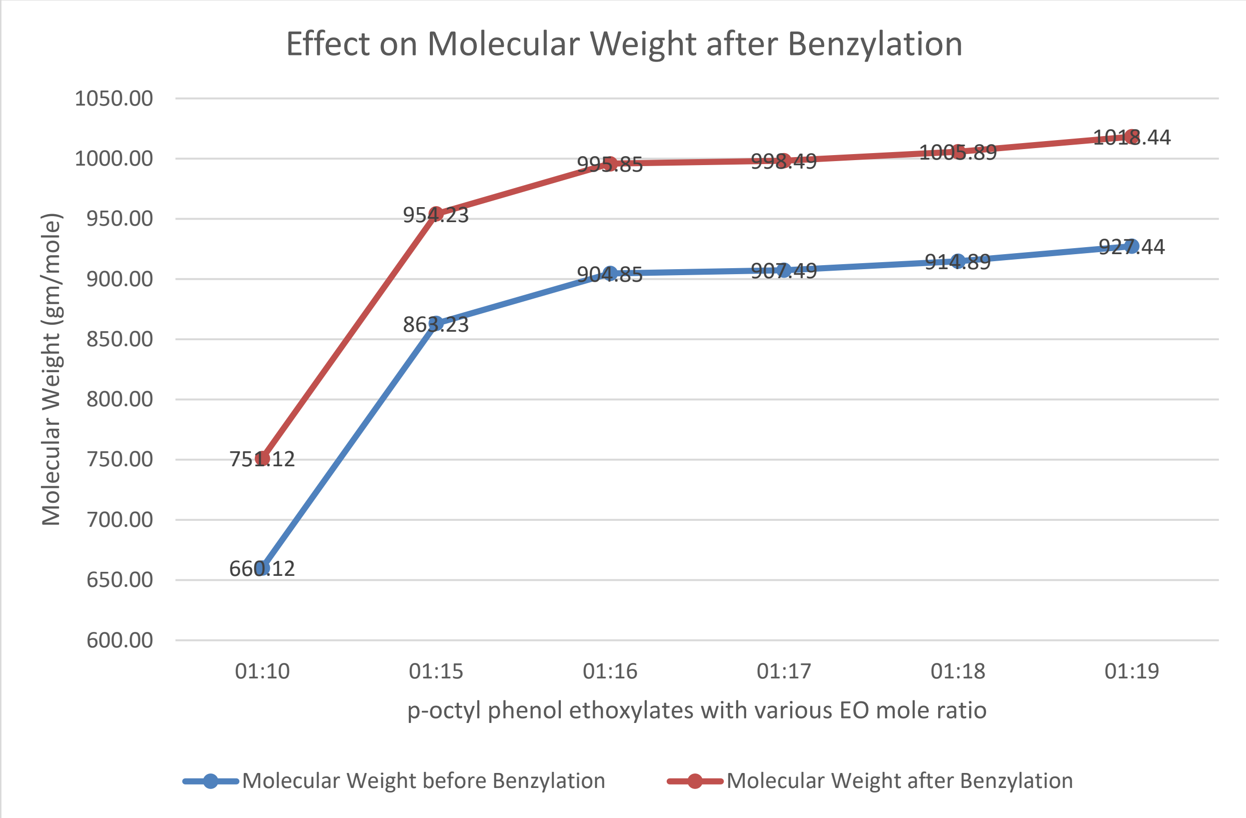
The experimental data and graphical representation of hydroxyl value of various degree of ethoxylates of p-octyl phenol and their subsequent hydroxyl value after benzylation reaction shown in the tabular and graphical form. It is found that hydroxyl value decreases after benzylation reaction. Change in hydroxyl value is the indication of benzylation reaction and degree of benzylation reaction for the respective ethoxylates. The degree of benzylation of ethoxylates is depends on viscosity of the ethoxylates, as the viscosity increases with degree of ethoxylation the benzylation rate decreases. The hydroxyl value detection method for present invention adopts phthalic anhydride-pyridine method.

Mole of p-Octyl Phenol : Mole of Ethylene Oxide	1:10	1:15	1:16	1:17	1:18	1:19
OH Value before Benzylation	85	65	59.66	61.83	61.33	60.5
OH Value after Benzylation	11.5	11.68	10.92	12.57	14.11	16.05



The experimental data and graphical representation of molecular weight of used material for the experiments, various degree of ethoxylates of p-octyl phenol and their subsequent molecular weight after benzylation reaction shown in the tabular and graphical form. The molecular weight of the ethoxylates was determined by 56110 dividing by the hydroxyl value of the respective ethoxylates and the molecular weight of benzylated product was determined by adding the molecular weight of the benzyl methyl radical which is 91 gm/mole to the molecular weight of respective ethoxylates.

Mole of p-Octyl Phenol : Mole of Ethylene Oxide	**1:10**	**1:15**	**1:16**	**1:17**	**1:18**	**1:19**
Molecular Weight before Benzylation	660.12	863.23	904.85	907.49	914.89	927.44
Molecular Weight after Benzylation	751.12	954.23	995.85	998.49	1005.89	1018.44



IV. Conclusion

The ethoxylates of p-octyl phenol with different mole ratio of ethylene oxide like 1:10, 1:15, 1:16, 1:17, 1:18, 1:19 on reaction with sodium hydroxide which was 1:1.25 mole ratio, the reaction forms the alkoxide and subsequent reaction with benzyl chloride which reaction was 1:1 mole ratio, where reaction product forms the double benzene ring structure having the superior characters than the initial ethoxylates of p-octyl phenol like hydroxyl value and cloud point in aqueous and sodium chloride solution and can be utilize for the formulation of home care product and pigment dispersion formulation. By adding the benzyl group to the hydroxyl end of ethoxylates of p-octyl phenol using benzylation reaction imparts desirable characteristics such as improved stability, enhanced hydrophobicity, and altered interfacial behavior which are suitable for the different formulations. The benzyl mixed ethers according to the invention are particularly low-foaming and are distinguished by very good defoaming properties, high cleaning power and high ecotoxicological compatibility.

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