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Some Studies on New Synthesis and Evaluation of Surface Active Agents from Byproduct Materials

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ABSTRACT

A series of nonionic compounds from coal-tar phenol, a by-product from El-Nasr Company for Manufacturing Coke and Basic Chemicals, El-Tabbin, Helwan, Egypt, was alkylated by olefine (C_{12}). The alkylated compounds were ethoxylated to nonionic surfactants by polyoxyethyleneglycols of different molecular weights, namely 2000, 1000, 400 to form new compounds having different hydrophil-lipophil balance (HLB) and hence different surface activities solubilization towards oleic acid-preparation of anionic compounds from these nonic compounds, comparison between them in surface properties and their biodegradbility in a river water.

Key words:-
Coal-tar phenol as a by-product, polyethylene glycols, chloroacetic acid, nonionic surfactants, anionic surfactants

INTRODUCTION

Many classes of nonionic surfactants will focus on alkyl phenol raw materials which have a major role in many markets [1-2]. The properties of nonionic surfactants were highly sensitive towards variation of temperature due to the nature of interaction (hydrogen bonds) between hydrophilic parts and water molecules [3-6]. These compounds used dispersion emulsion of a liquid phase into another relative immiscible phase where emulsion in the petroleum industry are undesirable[7], glycolesters are strongly lipophilic emulsifiers, opacifiers and plasticizers. They are used in textile processing and in emulsion polymerization.

Several studies on nonionic surfactants are now established. However, the comparative studies of the surface active properties of oxide linkage adducts for alcohols of aromatic compounds and their derivatives are limited. For this reason, this investigation was under-taken to study these new surfactants.

EXPERIMENTAL :-

1) Alkylation of coal-tarphenol mixtures

General procedure according to method [8]

Coal-tarphenol + dodecene ⟶ Alkylated coal-tar phenol

2) Williamson type reaction

In one litre (one mole) from alkyl coal-tar phenol (~ 110 gm), one mole from chloroactic acid (94.5 gm) and one mole of NaOH (40 gm) under refluxing for two hours. Give white waxy solid from alkyl acetoxy coal-tar phenol[9].

$$\text{Alkylated Coal-tar phenol} + Cl\text{-}CH_2\text{-}COOH \xrightarrow[\text{ii) } H^+ / H_2O]{\text{i) aqueous NaOH}} \text{Alkyl acetoxy Coal-tar phenol} + HCl$$

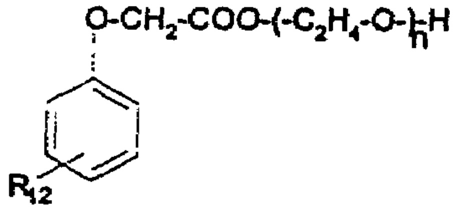
3) Estrification of alkyl acetoxy phenol

Acid catalyzed esterification of alkyl acetoxy phenol one mole and performed polyoxyethylene glycols (one mole) of different molecular weight 400 (9.9 moles). 1000 (22.72 moles), 2000 (45.45 moles) was added in a three necked flask in the presence of solid-p-Toluene sulphonic acid (0.0005) as a catalyst, the reaction mixture was heated with continuous stirring until the theoretical amounts of water was collected.

The products were purified by washing with hot solution of 5% sodium carbonate and by alcohol which then distilled off. The reaction can be forced towards the monoester by the ratio of reactants.

The ester was washed by hot water and separated by separating funnel to remove the untreated acid. The ester was viscous oily product for E.O. (9.9) to yellow waxy solid product for E.O. (45.4).

The composition of the product was confirmed by average molecular weight determination and FTIR. Average molecular weight of each prepared nonionic surfactant was determined by cryscopic method using benzene as solvent.



Where n = 9.9 moles I

= 22.72 II

= 45.45 III

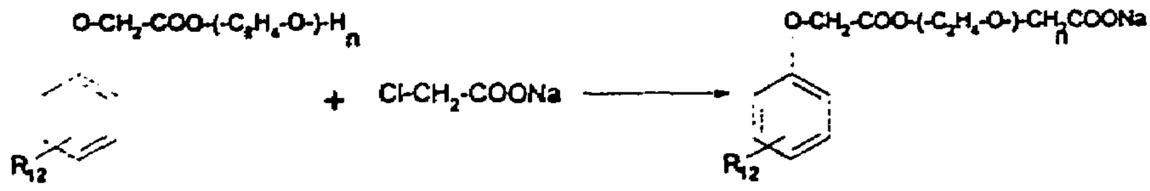
Infrared spectra

IR spectra were measured by using AVATARA 230 FTIR spectrophotometer to measure intensity of absorption band for the prepared surfactants as in table (1)

Preparation of anionic compounds form alkyl coal-tar phenol polyalkyloxy carboxylate.

One mole of each prepared polyalkoxycoal tar phenolethoxylates and sodium chloroacetate ($CLCH_2COONa$) under reflux for one hour. The product was purified by ether which then distilled off. The product yellowish waxy solid. The product are Anionic compounds but some what.

They are nonionic character due to presence of ethylene oxide linkage, these products are odorless, aqueous solution.



I, II, III　　　　IV, V, VI

The structure confirmed by FTIR, and molecular weight determination.

Evaluation of the surface active properties

1) surface and interfacial tension values of prepared nonionic, Anionic surfactants were determined by using Du-Nouy tensiometer with aplatinium ring [10].

2) **Emulsion stability:-**

The emulsion stability was performed by vigorous stirring a mixture of 10ml (0.1) surfactant solution and 10ml of parraffin oil at 25 °C. Emulsifying power, Emulsion stability of surfactants solutions was expressed as the time required for separation of –9-ml pure water soluble surfactant [11].

3) **Cloud point:-**

A freshly prepared 0.1% solution of the nonionic surfactant was placed in a test tube, then the temperature was raised using a water bath till the point at which the surfactant solution became turbid. The process was repeated several times to ensure the exact cloud point [12].

4) **Biodegradability:-**

Examination of their biodegradability properties in a medium containing ordinary river water [13,14,15].

5) **Pour point**

Polyoxyethylene dodecyl-coal-tar phenol climbs with increasing degree of polyoxyethylylation [16].

6) **Foaming**

The foam volume was measured by shaking ten vigorous shakes 100ml of 0.1% concentration of the surfactant solution in a stoppered graduated cylinder of 250ml capacity [17]

7) **Hydrophil-Lipophil Balance (HLB).**

The surfactant is usually added as emulsifiers to make the preparation of emulsion easier and to increase its stability. The firstly to reduce the interfacial tension causing a reduction in the work required to the emulsion.

The emulsifying efficiency of a surfactant was related to polarity of the molecule. So (HLB) number for nonionic surfactants were determined by this calculation.

HLB = weight % of ethylene oxide/5

Or for acid esters generally:

HLB = 20 [(MH/MH + ML)]

Where. M_H is the molecular weight of hydrophilic portion

M_L is the molecular weight of hydrophobic portion

The (HLB) is one of the most important characteristics of surfactant, which exert an effective influence on the rate of coalescence of emulsions.

Table (1) Specification of ethoxylated alklyl coal-tar phenol and sodium salt of these compounds.

Name of comp.	Average Molecular weight		Molecular weight of P.E.G	No of Ethylane oxide moles	FTIR-bands
	Found	Calculate			
I	743	741	400	9.9	1) Broad band at 3300-3455 cm^{-1} corresponding to stretching vibration of (OH) group
II	1341	1340	1000	22.72	2) stretching vib of (CH_2) (CH_3) groups appeared at 2850-2950 cm^{-1}
III	2342	2339	2000	45.44	3) strong adsorption band at 1745 cm^{-1} indicating for the presence of ester group
IV	820	821	400	9.9	
V	1422	1421	1000	22.72	4) 1540 medium 860 strong band indicating for aromatic ring (C_6H_4)-R_{12}
VI	2421	2420	2000	45.44	

Table (2) Surface properties of the prepared ethoxylates of alkylated acetoxy-Coal-tar phenol and their anionic compound

Name	Surface tension mN/m	Interfacial tension mN/m	Foaming power height vol/ml	Emulsification power tim/sec	Cloud point °C	Pour point °C	HLB
I	32.9	4.5	Poorer	130	---	0	10.7
II	36.2	7.7	foam	82	> 100	32	14.9
III	45.5	9.1	Stability	99	> 100	49	17.08
IV	30	3.2	98	102			9.7
IV	35	6.2	125	76			14.06
VI	40.3	7.2	147	61			16.515

Table (3) Biodegradability % of the prepared alkyl coal tar phenol ethoxylates and their Anionic surfactants

Name	1st	2nd	3rd	4th	5th	6th	7th	8th
I	56	61	70	78	81	85	86	89
II	42	50	57	62	69	73	76	78
IV	49	56	65	72	78	84	88	80

Aim of the work

Study the effect of molecular weight of the hydrophilic moiety on the hydrophil-lipophil balance (HLB) of the prepared nonioni c surfactants and compared between surface active properties of these non ionic compounds ınd anionic compounds of the same raw material (coal-tar phenol) mixtures.

'ESULTS AND DISCUSSION:

As an extension to our previous studies on the development of the :al industry, a new attempt was made in the present work to make use of : coal tar phenol which is considered as a by-product at "El-Nasr ınufacturing Co., for Coke and Basic Chemicals, in the preparation of ıionic and anionic surfactants.

The structure of these surfactants was confirmed by FT-IR and age molecular weight determination[18]. Polyethylene glycol esters of lated coal-tar phenol have been prepared to improve their solubility in ɔus solution of electrolytes.

The nonionic compounds of dodecyl coal-tar-phenol ethoxylates have extensively used since negative toxicological and biodegradability ·ms were pointed out. So the rate of degradation of poly oxyethylene henols from wastewater are sufficiently high to avoid accumulation in ·ironment as observed in Table (3). The cloud point is a very useful portant property of polyoxyethlene alkyl phenols. The cloud point is perature above which an aqueous solution of water-soluble nonionic nts becomes turbid. It is widely agreed that the micellar molecular ıf polyoxyethylated nonionic surfactants increases with temperature :duced surfactant solubility and increased hydrophobicity caused by on of the polyoxyethylene chain.

This increase in micellar molecular weight becomes very pronounced as the solution temperature approaches the cloud point .As temperature increases above the cloud point, the solution may separate into two phases-one surfactant-rich, the other water rich.

Pour point of polyethylene glycol of dodecyl coal tar phenol at 400 molecular weight is zero but pour point passes through an increase as the degree of ethoxylation increases.

To determine the influence of the hydrophobic moeity of the emulsification power of these surfactants, their HLB values were calculated according Griffins methodology. As in Table (2), increasing (HLB) value with increasing hydrophilicity chain of the molecules causes increased emulsification power towards paraffin oil and this agrees with results in Table (2) that emulsification power for surfactant (I is greater than II) due to its increased solubility in aqueous phase. But(II is lower than III). This may be due to an increase of coiling of the ethylene oxide linkage which increases the nonionic character and also may cause shielding of (CooNa) group. Increasing of chain length increases the hydrophobicity (HLB) , which decreases the solubility of surfactants in the solution.

Glycol esters are strongly lipophilic emulsifiers. Ethylene oxide increased linkage gives poorer foam stability, so anionic surfactant of ethoxylated coal-tarphenol was better than that nonionic in some industry. ether acetate in which the CH_2 COONa is linked to the oxygen atom of the terminal hydroxyl group so that the final product is acetate ester of the adduct.

Most of the products are good biodegradable surfactants which manifested the importance of their application in preventing pollution problems.

The results show that the products obtained have a pronounced surface activity.

CONCLUSION:

The objective of the present investigation is the preparation of some new products from a by-product at "El-Nasr Manufacturing Co. which are expected to be surface active and, determining their surface properties followed by a comparative study between their chemical structure and their surface active properties.

Alkyl coal-tar phenol fractions were esterified by polyethylene glycols of different molecular weight and their anionic compounds were prepared by using chloroacetate salt. Finally the relation between the number of E.O moles and HLB gives indication that these surfactants can be used as emulsifiers for oil/water emulsion .

REFERENCES

1) Dever. J.P, George. K.F, Hoffman W.C., and SOO. H, in Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed. Vol. 20, (M. Howe-Grant, ed.), Wiley, New York, pp. 91 5-959 (1994).

2) Anelli, F. P., 83 rd Am. Oil Chemists Soc. Annual Meeting and Expo. Tornto (1992).

3) Davidsohn, A.S. and Milwidsky, B., "Synethetic Detergents" 7th Ed. Longman, Essex England, [8] 1987.

4) Elworthy, P.H; Florence, A.T. and Macfarlane, C.B. "Solubilization by Surface Active Agents" and Its Application in Chemistry and the Biological Sciences", Chapman and Hall, London, 1968.

5) Bo, Jonsson; Bjorn Lindman; Krister Holmberg and Bengt Kronberg, "Surfactants and polymers in aqueous solutions" John Wiley and Sons, New York, 92, (1998).

6) Meguro, K. Veno, M, and Esumi, K., "Nonionic surfactant physical chemsitry". Marcel Dekker Inc. New York, 136, 1987.

7) Lis Sant, K.J., "Demulsification Industrial Application" Marcel Dekker, Inc., New York (1983).

8) Vedejs E., Organic Reaction, 22, 401 (1975).

9) Whitten, J.L., That we May Live, Van Nostrand, U.S.A., p.31, 1966.

10) Pessagno, Romina C. and Baldessari, Alicia, Fr, Patent, 433, 684 (2000).

11) Martin, H., The Scientific Principles of Crop Protection, 6th edn., Arnold, London, 1973.

12) Han. S.K, Lee. S.M, and Schott. H, J. Colloid Inter. Sci., pp. 126-393 (1988).

13) *Mounts; G.R. Warner; T.L., Heakin; AJ., J. Amer.* Oil Chem. Soc. 5592) 277 (1978).

14) Chemical Manufacturer's Association Panel of Alkylphenol ethoxylates, 1300 Wilson Boulevard, Washington, DC, 20037.

15) Naylor. C.G, Mieure. J.P, Adams. W.J., Weeks. F.J. Castalki, Ogle L.D., and Romano. R.R, J.A. Oil Chemists. Soc., 69 (1995).

16) CAMP. M. and DurHam; K.J. Physichem. 95, 993 (1995).

17) Yamauchi, K., Hashimoto, K., Kera, Y., Uemura, S., and Kajiwara, Japanese Patent 05,329. 374 Nitsusei Kagaku Kogyosho KK (1993).

18) "Handbook of chemistry and physics", 60th Edition. CRC press, (1979).