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## Surfactants & Detergents Technical

### Some Synthetic Detergents from Petroleum Products

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Deodorized and dewaxed Egyptian petroleum fraction, boiling range 200–270 C, was subjected to liquid phase oxidation at various temperatures in the presence of Co acetate as catalyst. The synthesized naphthenic acids were then converted to naphthenic acid amides and naphthenic alcohols. These products were ethoxylated to different mole ratios of ethylene oxide. The ethoxylates with an average 5 mol ethylene oxide/mol prepared hydrophobes were sulphated and phosphated to anionics.

The surface active properties of all the nonionic and anionic surfactants were evaluated.

Nonionic surfactants usually are prepared by the addition of ethylene oxide to compounds containing one or more active hydrogen atoms, such as alkyl phenols, fatty alcohols, fatty acids, fatty mercaptans, fatty amines, fatty amides and polyols. This addition reaction is one of the principal processes used to introduce hydrophilic functional groups into an organic molecule. It has been reviewed extensively in the literature (1).

The use of petroleum hydrocarbons in the manufacture

of synthetic detergents has, to a great extent, replaced those obtained from other sources. The wide variation of specific end uses in the surfactant field obtained by varying the structure of the hydrophobic base is well known. Nonionic biodegradable detergents prepared from polyethoxylated amine and polyamine derivatives of naphthenic acids have been described (2), but nothing has been published about the surface properties of ethoxylated naphthenic acids, acid amides and alcohols. For this reason, this investigation was undertaken to evaluate Egyptian petroleum as a raw material for preparing surfactants.

## EXPERIMENTAL

*Deodorization and dewaxing of the starting fraction.* Petroleum fraction, boiling range 200–270 C, was deodorized using  $H_2SO_4-P_2O_5$  (3) and dewaxed with urea as described in (4). A comparison of the characteristics of the fraction before and after treatment is given in Table 1.

*Oxidation of the naphthenic and isoparaffinic fraction.* The oxidation was done at normal pressure at a flow rate

TABLE 1  
Specifications of the Petroleum Fraction Before  
and After Deodorization and Dewaxing

	Before treatment	After treatment
Boiling range, °C/atom	200-207	197-205
Refractive index at 20 C	1.4632	1.4428
Density at 20 C	0.8219	0.8109
Mean mol wt (5)	179	178
Aromatics + olefins wt % (6)	29.7	0.6
Naphthenes wt % (7)	33.6	63.2
n-Paraffins wt % (4)	20.2	—
iso-Paraffins wt % (by difference)	15.7	36.2

of 5 l/min/100 g hydrocarbons in the presence of Co acetate (0.2 g metal content/100 g hydrocarbons) at various temperatures (110, 130 and 140 C). The extent of oxidation was followed by determining the acid value of samples withdrawn from the reaction mixture at regular intervals.

The two immiscible layers of the nonvolatile oxidate obtained in all oxidation experiments were separated. The lower layer (oxynaphthenic acids) (8) was insoluble in petroleum ether 100-120.

The upper layer was saponified and the nonacidic components were separated by extraction with petroleum ether 100-120. The alkaline solution was acidified to

liberate the acidic product. Naphthenic acids were separated from other isoparaffinic acids on the basis of solubility of their lead salts in diethyl ether (9).

The naphthenic acids produced in 17-18% yield (based on the weight of the hydrocarbons) had a boiling range 82-143 C/1 mm Hg,  $n_D^{20}$  1.4627,  $d_4^{20}$  0.9363, average mol wt 208 and acid No. 265 mg KOH/g oil.

*Methyl naphthenate.* The methyl ester of naphthenic acid was prepared in 85% yield by refluxing a mixture of the acid, absolute methanol and a few drops of concentrated sulphuric acid for six hr. The specifications determined for the prepared methyl ester were: boiling range 65-141 C/1 mm Hg,  $d_4^{20}$  0.9052,  $n_D^{20}$  1.4581 and average mol wt 219.

*Naphthenic alcohol.* The naphthenic alcohol was prepared in 89% yield by reduction of methyl ester of the naphthenic acid using  $\text{LiAlH}_4$  as described in (10). The obtained alcohol had the following specifications: boiling range 56-112 C/1 mm Hg,  $d_4^{20}$  0.8513,  $n_D^{20}$  1.4532, 1.4532, average mol wt 196, OH No. 281 and IR absorption at  $3520\text{ cm}^{-1}$  (OH).

*Naphthenic acid amide.* The amide was prepared in 81% yield by passing ammonia into the naphthenic acid at 200-210 C for 12 hr as described in (11). The product was a crystalline substance, had a melting range ca. 87-111 C, average mol wt 206 and IR absorption at  $3440\text{--}3460\text{ cm}^{-1}$  ( $\text{CONH}_2$ ).

*Condensation of the prepared hydrophobes with ethylene oxide.* Ethoxylation reaction was carried out in the presence of KOH according to (12) at 180 C. The reaction

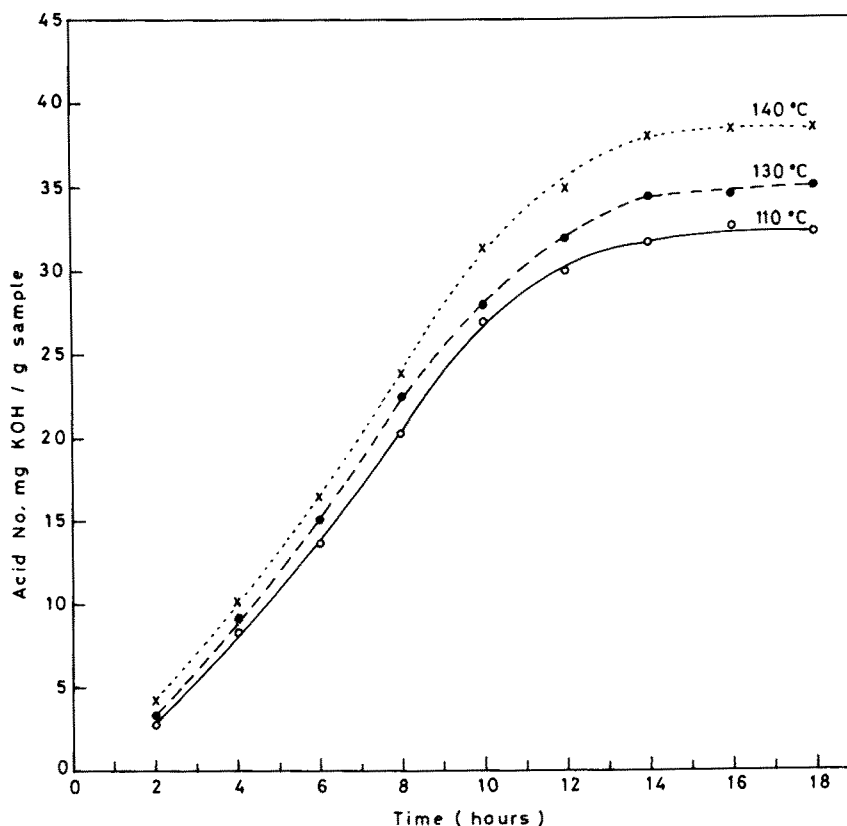


FIG. 1. Variation in acid number of the oxidized hydrocarbons with time at different temperatures using Co acetate as catalyst.

## SYNTHETIC DETERGENTS FROM PETROLEUM PRODUCTS

was run for time periods ranging from 1-5 hr.

*Sulphation and phosphorylation of the prepared ethoxylates.* The following ethoxylates were subjected to sulphation with  $\text{ClSO}_3\text{H}$  as described in (13) and to phosphorylation with  $\text{P}_2\text{O}_5$  as reported in (14):

- The naphthenic acid ethoxylate containing an average 5 mol ethylene oxide.
- The naphthenic alcohol ethoxylate containing 5 mol ethylene oxide.
- The naphthenic acid amide ethoxylate containing 5 mol ethylene oxide.

*Evaluation of the performance of the prepared surface active materials.* The solubility, cloud point, surface and interfacial tensions (15), foaming (16) and detergency powers (17) were evaluated (Tables 2 and 3).

## RESULTS AND DISCUSSION

Oxidation of naphthenic and isoparaffinic hydrocarbons in the presence of Co acetate as catalyst was attempted at different temperatures to synthesize naphthenic and isoparaffinic acids in satisfactory yields. Figure 1 shows the effect of temperature on the rate of oxidation; it was noted that the acid value increases proportionally with increases in oxidation temperature within the range 110-140 C.

The naphthenic acid was converted to the corresponding acid amide and alcohol. These products were ethoxylated to nonionic detergents to the desired content of ethylene oxide/mol of the product (Fig. 2). From this

figure it was found that the rate of ethoxylation increases in the order: naphthenic alcohols > naphthenic acid amides > naphthenic acids, showing the characteristics usually observed with long chain fatty alcohols and fatty acids (12).

The surface active and related properties of the ethoxylated naphthenic acid, acid amide and alcohol including solubility, cloud point, surface and interfacial tensions, foaming and detergency powers, were measured without removal of the small amount of the alkaline catalyst; the results are shown in Table 2 together with the results of ethoxylated lauric acid and dodecanol for comparison. This table shows that

- In general the ethoxylated naphthenic acid amide is more soluble than ethoxylated naphthenic acid and naphthenic alcohol.
- The ethoxylated amide has the highest cloud point value and the ethoxylated acid the lowest.
- The ethoxylated naphthenic acid amide has maximum surface and interfacial tensions, while minimal values were obtained with ethoxylated naphthenic acid.

Data on the foam volume indicates that ethoxylated amide has the highest value followed by the ethoxylated alcohol and then the ethoxylated acid. It is clear that the ethoxylated naphthenic alcohol has the best detergency power, while the ethoxylated naphthenic acid amide has the least.

The effect of the number of ethylene oxide moles in the

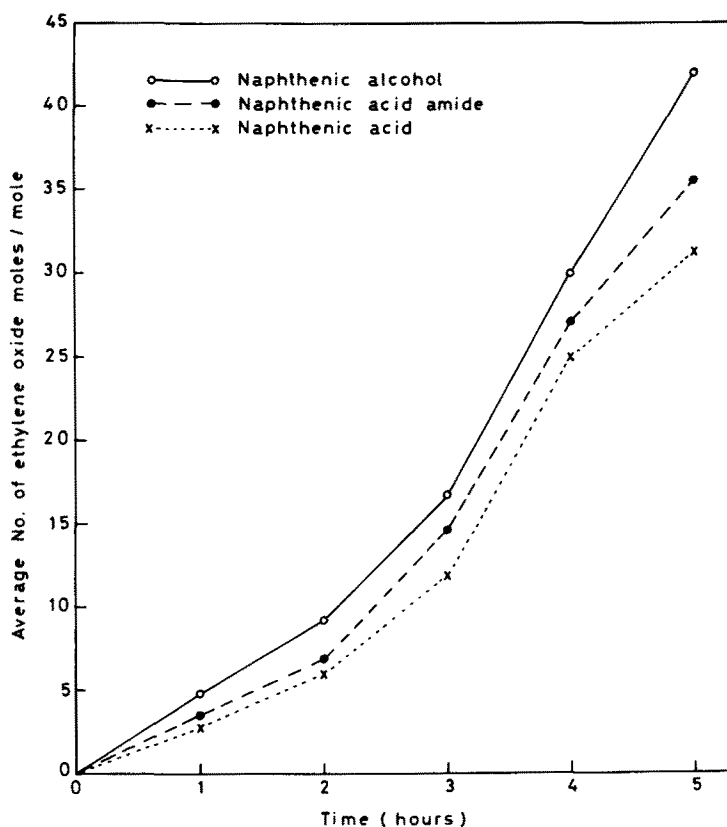


FIG. 2. Ethoxylation of the prepared hydrophobes with ethylene oxide.

TABLE 2

Surface Properties of Naphthenic Acid, Acid Amide and Alcohol Ethoxylates

Type of ethoxylate	n	Appearance at 20 C	Solubility 0.25%	Cloud point (°C) 1%	Surface tension (dynes/cm) 0.1%	Interfacial tension (dynes/cm) 0.1%	Foam height (mm) 0.1%	Detergency power 0.25%
Naphthenic acid ethoxylates	5	Clear liq.	Turbid	—	30.9	4.1	82	31.2
	10	Clear liq.	Turbid	48	33.1	5.1	120	32.6
	15	Semisolid	Slightly turbid	67	35.4	6.3	131	30.8
	20	Semisolid	Slightly turbid	80	36.5	7.3	111	28.9
Naphthenic acid amide ethoxylates	5	Semisolid	Transparent	—	34.2	5.1	93	30.6
	10	Waxy-solid	Clear	68	36.1	6.4	135	32.2
	15	Waxy-solid	Clear	93	37.8	7.2	151	29.6
	20	Waxy-solid	Clear	>100	39.9	8.3	139	28.1
Naphthenic alcohol ethoxylates	5	Clear liq.	Transparent	39	29.4	4.8	86	31.4
	10	Semi-solid	Transparent	45	35.2	5.9	124	33.6
	15	Waxy-solid	Transparent	82	36.6	6.8	146	32.6
	20	Waxy-solid	Clear	>100	38.1	7.7	138	30.6
Lauric acid ethoxylates	20		Slightly turbid	46	29.3	6.3	unstable in all cases	35.6
	15			70	30.1	4.9		36.2
	20			79	31.2	5.3		36.9
Dodecanol ethoxylates	10		Clear and transparent	88	34.6	5.2		36.2
	15			>100	36.4	6.5		36.5
	20			>100	38.2	7.5		36.9

TABLE 3

Surface Properties of the Sulphated and Phosphated Ethoxylates

Type of hydrophobe	Type of ester		Surface tension (dynes/cm) 0.1%	Interfacial tension (dynes/cm) 0.1%	Foaming power vol, ml	Detergency power %
Naphthenic acid ethoxylates	Sulphate	5	29.8	3.4	151	32.3
	Phosphate	5	32.6	4.8	109	31.9
Naphthenic acid amide ethoxylates	Sulphate	5	33.4	4.3	171	31.7
	Phosphate	5	35.4	6.3	151	30.9
Naphthenic alcohol ethoxylates	Sulphate	5	28.1	3.8	162	33.1
	Phosphate	5	30.6	5.6	133	32.3
Dodecyl benzene sodium sulphonate			34.7	7.1	230	39.1

detergents on their surface properties illustrates that, with the increase in chain length of the ethoxy groups, the cloud point, surface and interfacial tensions increased. On the other hand, the foaming power of the naphthenic acid, acid amide and alcohol increases with the increase of ethylene oxide content and reaches a maximum at  $n = 15$ , while in all types of the ethoxylates, the detergency power increases until  $n = 10$  and then decreases with the increase of ethylene oxide content.

The prepared ethoxylates having an average  $n$  equal to 5 ethylene oxide/mol of the hydrophobe were sulphated and phosphated to anionics. These are carried out with the same reagents as and under reaction conditions

similar to those used for sulphation and phosphation of long chain alcohols.

On comparing the surface active properties of the prepared ethoxylates having the lowest average number of ethylene oxide before and after sulphation or phosphation (Table 3), it is noted that

- (i) Sulphation and phosphation processes lower the surface and interfacial tensions (increase the surface activity) and increase the foaming and detergency powers.
- (ii) The sulphated ethoxylates have better surface properties than the phosphated ones.

(iii) The comparison of the results of surface tension determination with the anionic detergent sodium dodecyl benzene sulphonate shows that the products obtained have a pronounced surface activity.

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## ❁ Isotachophoretic Analysis of Surfactants

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The qualitative and quantitative determination of anionic surfactants (sodium and lithium alkylsulfate, sodium dodecylbenzenesulfonate, sodium di-2-ethylhexyl sulfosuccinate, sodium and lithium perfluoroalkylcarboxylate, and lithium perfluorooctanesulfonate) were investigated by a capillary tube isotachopheresis using a potential gradient detector. The leading electrolyte solution was the mixture of acetonitrile and aqueous solution of histidine buffer containing calcium chloride. The terminating electrolyte solution was the aqueous solution of sodium octanoate. These electrolytes were effective for the analysis of the mixtures of strongly acidic surfactants.

The quantitative determination of surfactants usually has been performed by gas chromatography, high performance liquid chromatography and other widely used methods (1,2). However, most methods are elaborate and rather time consuming. The isotachopheretic method has a large field of application of the analysis of ionic species (2-7). Many difficulties were involved in the isotachopheretic analysis of surfactant mixtures, i.e., the simultaneous separation of individual surfactants from each other and from their respective homologs. In general, the isotachopheretic separation of ionic species was achieved based on the difference in the absolute mobility or the difference in the degree of dissociation of ionic species. If an ionic species had a similar dissociation constant, the effects of addition of counterion and organic solvent usually were examined.

In this paper, we study the separation and quantifica-

tion of various ionic surfactants. A rapid and simple procedure for determination of surfactant homologs was examined by isotachopheresis.

## EXPERIMENTAL

**Materials.** Sodium perfluorooctanoate, lithium perfluorooctanesulfonate and alkylsulfate salt were the same samples as those used in the previous work (8,9). Sodium dodecylbenzenesulfonate (Kanto Chemical Co. Inc., Tokyo, Japan) and sodium di-2-ethylhexyl sulfosuccinate (Wako Pure Chemical Industries Ltd., Tokyo, Japan) were used without further purification. Lithium perfluorononanoate (Asahi Glass Co., Tokyo, Japan) was prepared by a procedure similar to that of Kunieda and Shinoda (10). Their chemical structures and abbreviations used in this study are illustrated in Table 1. All other reagents were of guaranteed grade.

**Isotachopheresis.** Isotachopherograms were recorded on a Shimadzu IP-2A equipped with a potential gradient detector. The capillary tube used consisted of a main column (150 × 0.5 mm I.D.) and a pre-column (40 × 1.0 mm I.D.) and was thermostated at 15°C. The leading electrolyte solution was prepared as follows. An aqueous solution containing 8.33 mM histidine monohydrochloride, 12.5 mM histidine and 8.33 mM calcium chloride was mixed with acetonitrile (1:1, v/v). Then the solution was degassed in vacuo. The terminating electrolyte solution was 10 mM aqueous sodium octanoate solution. The migration current was 200 μA after 250 μA for 7 min. All the sample solutions were prepared to the surfactant concentrations of 1-5 mM.

## RESULTS AND DISCUSSION

Yagi used 50% acetone aqueous solution of histidine-HCl as a leading electrolyte for the analysis of

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