TABLE II
Contamination of Unsaponifiables as Determined by Carbon-14 Analysis for Petroleum Residues

Sample	Counts min	Efficiency	cpm/gr sample	Estimated contamination
		%		%
Soybean oil	33	32.0	13.9	0
Unsaponifiables				
Hydrocarbons	8	16.0	18.2	0
Hydrocarbons	10	31.4	10.2	20
Hydrocarbons	11	36.5	11.2	20
Squalene	40	45.9	11.8	25
Pentane-hexane	0	56.7	0	100
Pentane-hexane residue	0	9.7	0	100

leum oil and this background used to correct the counting rate of the samples.

Possible contamination of the unsaponifiable hydrocarbon samples by petroleum solvent residues varied from 0 to a possible 20%. These values apparently vary within the limits of accuracy of the method as would be indicated by the squalene control sample. C^{14} counts for soybean oil and the petroleum solvent and residue showed the expected counts. Thus, hydrocarbons isolated from soybean oil deodorizer condensates are native to soybean oil and did not arise from petroleum solvents used to process the oil.

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On the Polarographic Behaviour of the Palmitates and Myristates of Copper and Cobalt

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Abstract

Pyridine complexes of myristates and palmitrates of copper and cobalt were found to be reducible at the dropping mercury electrode in 1) LiCl in 1:1 benzene methanol mixture; 2) $MeHSO_4$ in 1:1 benzene methanol mixture; and 3) KCl in glycol. The diffusion current was found to be a linear function of concentration. Hence it was concluded that this linear relationship can be successfully employed for the estimation of cobalt and copper concentration in their respective soaps.

Introduction

THE COMPLEX formation between pyridine and heavy metal soaps was pointed out by Boner (1). Recently we have done some preliminary experiments to study the polarographic (3) and spectrophotometric (4,5) behaviour of some metal soaps. It was found that these methods can be employed for the quantitative estimation of metal ions in the soaps. Due to these encouraging results it was thought worth-while to extend these studies to some other soaps such as those of cobalt and copper. The present communciation deals with the polarographic behaviour of myristates and palmitates of copper and cobalt in various nonaqueous media.

Experimental

Reagents. Palmitic and myristic acids were B.D.H, C.P. grade, used after fractionation under reduced pressure for the preparation of sodium soaps. The metal salts of copper and cobalt, pyridine, potassium chloride, lithium chloride and methyl red were B.D.H, A.R. grade. Benzene, methanol and glycol were used after extensive purification and careful drying. Triple distilled A.R. mercury was used for polarographic measurements.

Preparation of Metal Soaps. The soaps were prepared (2) by precipitation method, adding an equivalent amount of hot dilute cobalt or copper salt solution to an equivalent amount of hot dilute sodium palmitate or myristate under vigorous stirring. The precipitated soap was filtered, washed thoroughly with hot water followed by dry acetone and ether and dried in a vacuum desiccator. The copper content of the soap was found by ashing a known amount of the soap, dissolving the ash in mineral acid and titrating the copper iodometrically; the metal content was 10.98% for the palmitate [calculated for $Cu(C_{15}H_{31}COO)_2$ 11.08%] and 12.13% for the myristate [calculated for $Cu(C_{13}H_{27}COO)_2$ 12.20%]. The cobalt soaps were subjected to similar treatment and the amount of cobalt determined gravimetrically. Metal content was 11.12% for the palmitate [calculated for $Co(C_{15}H_{31}COO)_2$ 11.49%] and 10.20% for the myristate [calculated for $Co(C_{13}H_{27}COO)_2$ 10.36%].

Apparatus and Technique. The polarographic technique applied here was the same as described earlier (3). Supporting electrolytes and the solvents used were the same as in the case of nickel soaps (3). Methyl red (0.004%) was used as the maximum suppressor in 1:1 benzene-methanol mixture in the case of methyl hydrogen sulphate as supporting electrolyte. The capillary constant $m^{2/3}\ t^{1/6}$ was 1.618, 1.320, and

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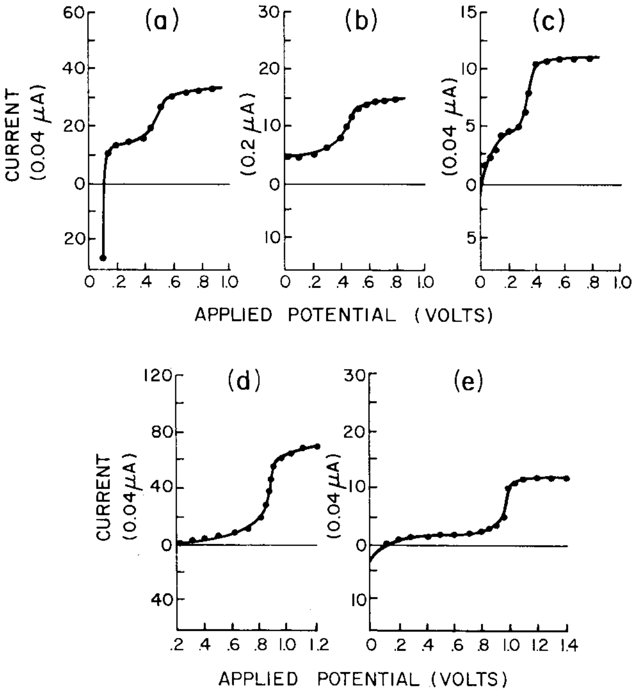

FIG. 1. Polarograms of metal soap pyridine complexes in various supporting electrolytes.

a) 0.99 mM Cu^{++} (myristate) in 4.44 x 10^{-2} M LiCl (in 1:1 benzene methanol mixture).
b) 0.98 mM Cu^{++} (palmitate) in 0.1 M $MeHSO_4$ (in 1:1 benzene methanol mixture) and 0.04% methyl red as maximum suppressor.
c) 0.98 mM Cu^{++} (palmitate) in 5.0 x 10^{-2} M KCl (in glycol).
d) 0.875 mM Co^{++} (palmitate) in 4.44 x 10^{-2} M KCl (in 1:1 benzene methanol mixture).
e) 0.646 mM Co^{++} (myristate) in 5.0 x 10^{-2} M KCl (in glycol).

TABLE I

$E_{1/2}$ and $E_{3/4}$–$E_{1/4}$ of Copper and Cobalt Soaps in Different Supporting Electrolytes

Metal soap	Concn of supporting electrolyte	$E_{1/2}$	$E_{3/4}-E_{1/4}$
		(vs. Saturated calomel electrode)	
Copper palmitate	0.044M LiCl	—0.480	—0.060
Copper palmitate	0.100M $MeHSO_4$	—0.450	—0.130
Copper palmitate	0.050M KCl	—0.385	—0.055
Copper myristate	0.044M LiCl	—0.480	—0.055
Copper myristate	0.100M MeHSO	—0.380	—0.100
Copper myristate	0.050M KCl	—0.395	—0.06
Cobalt palmitate	0.110M LiCl	—1.050	—0.07
Cobalt palmitate	0.083M KCl	—1.020	—0.07
Cobalt myristate	0.110M LiCl	—1.080	—0.09
Cobalt myristate	0.083M KCl	—1.020	—0.09

TABLE III

Diffusion Current of Cobalt Soaps at Diflerent Concn of Soaps

C	Cobalt palmitate				Cobalt myristate			
	0.111M LiCl		0.1M KCl		0.111M LiCl		0.1M KCl	
	id	id/C	id	id/C	id	id/C	id	id/C
0.646	....	....	......	....	......	....	0.48	0.741
0.776	....	....	......	....	1.30	1.675	......	....
0.875	1.6	1.828	0.48	0.549	......	....	......	....
1.400	2.8	2.000	0.78	0.557	......	....	......	....
1.552	....	....	......	....	2.8	1.804	......	....
1.616	....	....	......	....	......	....	1.28	0.792
1.750	3.2	1.828	1.00	0.571	......	....	......	....
1.940	....	....	......	....	3.4	1.753	......	....
2.100	3.8	1.809	1.24	0.590	......	....	......	....
2.370	....	....	......	....	4.3	1.814	......	....
2.450	4.2	1.714	1.40	0.571	......	....	......	....
2.584	....	....	......	....	......	....	1.96	0.759
2.625	5.0	1.905	1.48	0.564	......	....	......	....
3.004	....	....	......	....	5.4	1.798	......	....
3.232	....	....	......	....	......	....	2.60	0.803
3.858	....	....	......	....	......	....	3.00	0.778
3.880	....	....	......	....	6.6	1.701	......	....
4.848	....	....	......	....	......	....	3.6	0.743

1.610 $mg^{2/3}$ $sec^{-1/2}$ for LiCl, $MeHSO_4$ and KCl, respectively. The experiments were carried out at 25 ± 0.1C.

Procedure. A known quantity of metal soap was taken and dissolved in pure pyridine to form the metal soap pyridine complex. A known amount of this soap solution was taken and diluted to 30 ml by adding the requisite amount of 1:1 benzene-methanol mixture in the case of LiCl and $MeHSO_4$, and glycol in the case of KCl. While applying this method for metal content determination, experiments were performed under similar conditions using different concentrations of soap.

Results and Discussion

The polarograms of the metal soap in different supporting electrolytes show in Figure 1. It is evident that well defined waves in non-aqueous media are realized in almost all the cases except in cobalt soaps while using $MeHSO_4$ as supporting electrolyte. This is due to interference of the hydrogen wave. In the case of copper soaps a pronounced maximum existed in this supporting electrolyte, which was suppressed by 0.004% methyl red for low soap concn ($\leq$2.376 m.mole) only. Tome's equation (6) was applied to test the reversibility of the wave. The values of $E_{1/2}$ and $E_{3/4}$–$E_{1/4}$ for different supporting electrolytes show in Table I.

It is evident that copper and cobalt soaps are reducible at the dropping mercury electrode in presence of these electrolytes. The reduction of copper soap complex takes place in two steps, the first wave

TABLE II

Diffusion Current of Copper Soaps at Different Concn of Soaps

C	Copper palmitate						Copper myristate					
	0.111M LiCl		0.166M $MeHSO_4$		0.083M KCl		0.111M LiCl		0.166M $MeHSO_4$		0.083M KCl	
	id	id/C	id	id/C	id	id/C	id	id/C	id	id/C	id	id/C
0.680	1.2	1.765	......	....	......	....	......	....	....	....	......	....
0.970	......	....	......	....	......	....	1.00	1.030				
0.980	......	....	2.00	2.041	0.46	0.469	......	....	....	....	......	....
1.088	2.00	1.838	......	....	......	....	......	....	....	....	......	....
1.360	2.50	1.839	......	....	......	....	......	....	....	....	......	....
1.485	......	....	......	....	......	....	......	....	2.0	1.344	0.64	0.431
1.568	......	....	3.10	1.977	0.70	0.447	......	....	....	....	......	....
1.584	......	....	......	....	......	....	1.70	1.073	....	....	......	....
1.632	2.80	1.716	......	....	......	....	......	....	....	....	......	....
1.904	3.10	1.631	......	....	......	....	......	....	....	....	......	....
1.960	......	....	3.90	1.990	0.92	0.469	......	....	....	....	......	....
1.980	......	....	......	....	......	....	2.00	1.010	....	....	......	....
2.040	3.40	1.666	......	....	......	....	......	....	....	....	......	....
2.352	......	....	4.80	2.040	1.04	0.442	......	....	....	....	......	....
2.376	......	....	......	....	......	....	2.40	1.010	3.2	1.347	1.06	0.446
2.744	......	....	5.60	2.041	1.28	0.466	......	....	....	....	......	....
2.772	......	....	......	....	......	....	2.60	0.938	....	....	......	....
2.940	......	....	6.00	2.041	1.40	0.476	......	....	....	....	......	....
2.970	......	....	......	....	......	....	3.00	1.010	3.8	1.279	1.32	0.444
3.564	......	....	......	....	......	....	......	....	4.8	1.347	1.60	0.449
4.158	......	....	......	....	......	....	......	....	5.6	1.347	1.88	0.452
4.455	......	....	......	....	......	....	......	....	6.0	1.347	2.00	0.449

TABLE IV
Average Value of id/C of Different Soaps in Various Supporting Electrolytes

Soap	LiCl	id/C $MeHSO_4$	KCl
Copper palmitate	1.742	2.021	0.461
Copper myristate	1.012	1.335	0.445
Cobalt palmitate	1.847	....	0.567
Cobalt myristate	1.657	....	0.769

appears before zero voltage. The second wave is well defined. Reduction of cobalt soap takes place in only one step. The value of $E_{3/4}$–$E_{1/4}$ for copper wave ranges from −0.055 to −0.06 in KCl and LiCl indicating a reversible nature of the wave, whereas in $MeHSO_4$ the abnormally high value suggests an irreversible nature. An irreversible nature is shown for cobalt soaps in LiCl and KCl as the value is again high.

The metal concn in the soap (C) in m.moles/litre, diffusion current (id) in micro amp and id/C show in Tables II and III.

From Table III it is clear that the diffusion current is a linear function of the concn of metal in the soap, and also the value of id/C remains fairly constant. Hence, this method can be employed for the determination of the metal content in soaps. An average value of id/C in different supporting electrolytes shows in Table IV; the table also shows that the value of id/C is smaller in glycol medium. This may be due to high viscosity of glycol.

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Relative Reactivity Toward Hydrogenation of the Oleoyl Group in the 2- and 1,3-Positions of Triglycerides

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Abstract

Olive oil was hydrogenated to an iodine value (I.V.) of ca. 50 under widely differing operating conditions. Three types of catalyst were employed. Each catalyst was used at the lowest possible operating temp and at 170C. The hydrogenated samples were subjected to lipase hydrolysis to remove a portion of the acyl groups in the 1,3-positions, and the fractions obtained, as well as the unhydrolyzed samples, were analyzed for fatty acid composition and content of *trans* monoenes. From these data it was concluded that the position of the oleoyl group in the triglyceride molecule is not a factor in the rate of hydrogenation or isomerization.

Introduction

The question as to whether or not unsaturated acyl groups in the 1,3-positions of triglycerides hydrogenate more readily than do similar groups in the 2-position is both of theoretical and practical interest. Should it be possible to even partially direct the addition of hydrogen, then hydrogenation would become an even more powerful tool in the preparation of special fats.

Bushell and Hilditch (4) investigated this aspect of hydrogenation in 1937 and concluded that the position of the oleoyl group in a triglyceride did not affect the rate of hydrogenation. Some of their starting materials were synthesized by methods now open to question, and their hydrogenated products were analyzed by fractional crystallization. Since then much better instruments and techniques for carrying out work of this type have become available. After the investigation to be reported here was completed, the authors learned that Mattson and Volpenhein (10) had made a similar investigation. The latter workers randomly rearranged the acyl groups in a soybean oil and then subjected the oil to a single hydrogenation. Samples were withdrawn as the hydrogenation progressed and were analyzed for saturated acids, *trans* acids, and poly-, di-, and monounsaturated acids. Mattson and Volpenhein concluded that the position of an unsaturated acyl group did not affect its rate of hydrogenation.

The present investigation differs from the two cited above. The behavior of the oleoyl group toward both hydrogenation and geometrical isomerization was investigated. Because hydrogenation conditions have a marked effect on the course of the reaction (3,5), they were varied widely with respect to type of catalyst and temp.

Experimental

Materials. A refined and bleached olive oil was used as starting material in the hydrogenations. The fatty acid composition of this oil is recorded in Table I.

Two nickel catalysts were employed. The G-53 product, a commercial catalyst (Chemetron Corp.), was of the supported type prepared by electrolytic precipitation and dry reduction. The Raney nickel catalyst was prepared essentially according to the method given by Adkins and Billica (1) for their W-5 catalyst, which possesses a very high activity. The ethanol under which the catalyst was stored was removed before the hydrogenation was carried out.

The palladium catalyst (Baker & Co., Inc.) was of the carbon-supported type and contained 10% palladium by wt.

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