Preparation and Solubility of Metal Soaps of Wool Wax Acids[1]

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The preparation and solubility determination of the cupric, magnesium, nickel, cobalt, cadmium, lead, barium, manganous, ferric, and chromic soaps of the wool wax acid fraction are described. Solubilities, at 25°, were determined in: ethanol, methanol, isopropyl alcohol, acetone, ethyl acetate, carbon tetrachloride, and petroleum ether. Barium and cadmium soaps of hydroxy and nonhydroxy acid fractions, obtained by partitioning the whole wool wax acid fraction, were also prepared and subjected to the same study.

ALTHOUGH a considerable amount of attention has been directed toward the practical applications of wool wax acids as their soaps (8), little if any published information is available concerning some of their physical properties, e.g. solubility.

Four series of acids comprise the wool wax acid fraction. These are: normal acids, hydroxy acids, iso acids and ante-iso acids (1, 3, 4, 5, 6, 10). The acid fraction contains branched chain fatty acids amounting to at least 60% of the fraction. The acids are long chain $(C_9 - C_{34})$, singly methyl-branched with the branching in the iso or ante-iso positions. The hydroxy acids are also long chain acids of similar carbon structure with the hydroxyl group alpha to the carboxyl. With these types of structures present, it was thought that the metal soaps of the acids would have unusual properties.

As part of our program of investigations on the fractionation products of wool grease, some information on the solubility of the metal soaps was desired. The present paper describes the preparation and solubility determinations of the cupric, magnesium, nickel, cobalt, cadmium, lead, barium, manganous, ferric and chromic soaps of the wool wax acid fraction. In addition to the soaps mentioned above, the barium and cadmium soaps of the hydroxy and non-hydroxy acid fractions were also prepared. The solubility of the soaps was determined at 25°C. in the following solvents: ethanol, methanol, isopropyl alcohol, acetone, ethyl acetate, carbon tetrachloride, benzene, and petroleum ether.

Wool Wax Acids. The wool wax acids used in this investigation were prepared from USP lanolin by the saponification procedure of Barnes, Curtis, and Hatt (2). Since the acids thus obtained had an appreciable ester number, they were resaponified, and liberated as free acids in a mixture of dilute hydrochloric acid and ice in order to keep ester formation at a minimum (9). These acids are designated as whole acid fraction in Table I.

Wool Wax Acid Fractions. Wool wax acids were fractionated by partitioning their methyl esters between two immiscible solvent layers (9). This procedure produced an hydroxy ester fraction and ten non-hydroxy ester fractions. Those non-hydroxy fractions with saponification numbers of the same order of magnitude were combined to give two fractions from which the soaps were prepared. Analytical data for hydroxy, non-hydroxy, and whole acid fractions are summarized in Table I.

Metal Soap Preparation. In a typical metallic soap preparation, the fatty acids were saponified with an equivalent amount of potassium hydroxide in 50% alcohol solution for 3 to 4 hr. An equivalent amount of inorganic salt was dissolved in enough distilled water to give a solution volume equal to the volume of potassium soap solution. The two solutions, heated to prevent precipitation of the potassium soap, were added slowly at equal rates to a beaker of hot water; the contents of the beaker were stirred rapidly throughout the course of addition. Many of the product soaps were molten when prepared at these temperatures (approximately 90°C.). Those that melted were allowed to cool and then ground to a fine powder in a mortar along with some dry ice to prevent sticking and agglomeration. The product was then washed thoroughly with distilled water to remove inorganic material. After filtering and washing, the soaps were dried to constant weight at 60°C. in a vacuum oven fitted with a nitrogen bleed.

All soaps except the ferric soap were prepared by the procedure outlined above. In the latter case the soap solution was added to a ferric chloride solution. The addition was carried out in this manner in order to prevent formation of hydrated ferric oxide. Copper, nickel, and magnesium soaps were prepared from their sulfates; manganese, cobalt, and ferric from their chlorides; lead and barium from their nitrates;

TABLE I

Analytical Values of Wool Wax Acid Fractions Used in Soap Preparation

	Whole acid fraction[a]	Hydroxy acid fraction	Non-hydroxy acid fraction	
			I	II
Sapon. No.	166.1	......	......	......
Acid No.	166.2	169.9[b]	154.8[b]	190.2[b]
Percent hydroxyl	2.6	5.7	0.6	1.0

[a] Several samples of acids were used in the preparation of the soaps. The analysis represents average values.

[b] Calculated from the saponification number of the methyl ester.

TABLE II

Metal Content of Soap—Whole Acid Fraction

Metal	Found	Calc.*
	%	%
Copper	8.58	8.61
Magnesium	4.02	3.47
Nickel	7.24	8.00
Cobalt	8.07	8.01
Cadmium	15.07	14.68
Lead	24.0	23.5
Barium	16.08	16.76
Manganese	7.60	7.52
Iron	5.16	5.17
Chromium	4.93	4.83

* Based on the acid number of the fraction.

TABLE III

Metal Content—Fractionated Acids

Acid fraction	Cadmium		Barium	
	Found	Calc.*	Found	Calc.*
	%	%	%	%
Hydroxy acids	13.81	14.59	16.23	16.68
Non-Hydroxy acids, Frac. I	14.45	13.43	16.06	15.97
Non-Hydroxy acids, Frac. II	16.75	16.05	18.35	18.95

* Based on the acid number of the fraction.

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TABLE IV
Solubility of the Metal Soaps (g./1000 g. of Solvent)

Soap	CCl_4	Benzene	Absolute ethanol	Methanol	Ethyl acetate	Isopropyl alcohol	Acetone	Petroleum ether
Fe^{+++} (W)	0.17	0.29	0.47	0.39	0.23	0.41	0.27	0.30
Cr^{+++} (W)	0.37	0.50	0.43	0.38	0.33	0.41	0.37	0.35
Cu^{++} (W)	0.39	0.33	0.28	0.24	0.23	0.22	0.20	0.18
Pb^{++} (W)	0.28	0.24	0.21	0.59	0.14	0.15	0.16	0.13
Mg^{++} (W)	0.13	0.19	0.40	0.25	0.14	0.18	0.18	0.17
Ni^{++} (W)	0.11	0.19	0.39	0.67	0.23	0.23	0.21	0.19
Mn^{++} (W)	0.10	0.17	0.27	0.35	0.15	0.17	0.16	0.17
Co^{++} (W)	0.24	0.27	0.31	0.48	0.16	0.19	0.21	0.17
Ba^{++} (W)	0.36	0.15	0.19	0.32	0.13	0.12	0.14	0.16
Ba^{++} (H)	0.14	0.20	0.17	0.21	0.19	0.21	0.15	0.22
Ba^{++} (NHI)	0.08	0.04	0.07	0.13	0.09	0.07	0.06	0.05
Ba^{++} (NHII)	0.06	0.10	0.18	0.63	0.13	0.11	0.10	0.10
Cd^{++} (W)	0.15	0.23	0.27	0.33	0.23	0.25	0.23	0.24
Cd^{++} (H)	0.17	0.20	0.24	0.28	0.23	0.50	0.30	0.23
Cd^{++} (NHI)	0.22	0.05	0.12	0.12	0.07	0.08	0.06	0.05
Cd^{++} (NHII)	0.16	0.12	0.58	0.53	0.12	0.25	0.11	0.13

(W)—Soap made from whole acid fraction (Table I); (H)—Soap made from hydroxy acid fraction (Table I); (NHI)—Soap made from non-hydroxy acid fraction I (Table I); (NHII)—Soap made from non-hydroxy acid fraction II (Table I).

chromic from chrome alum; and cadmium from cadmium acetate.

Determination of Metal Content. With the exception of barium, cadmium, nickel, and cobalt soaps, metal content was determined by ignition to oxides. Barium and cadmium content was determined by ashing as sulfate in a platinum crucible. Nickel was determined as the dimethylglyoxime complex. Cobalt was determined with α-nitroso-β-naphthol.

The metal content of the individual soaps of the whole acid fraction is given in Table II. Table III lists similar data for the barium and cadmium soaps of the partitioned acid fractions.

Solubility Determination. Two hundred fifty ml. of solvent and approximately 0.2 g. of metal soap were added to a 500 ml. flask, the flask was stoppered and shaken vigorously in a constant temperature bath for 4 hr. At the end of this period the contents of the flask were poured into two 100 ml. graduate cylinders. The cylinders were then stoppered and allowed to stand in the constant temperature bath until all the solids had settled and the supernatant liquid was clear. A portion of the supernatant liquid (96 ml.) was withdrawn from the graduates with a specially designed automatic pipette (7) into a tared beaker. The beaker and solution was weighed. The solvent was evaporated. The beaker and residue were dried to constant weight and weighed. The solubility of the soap per 1000 g. of solvent was calculated from these data. The solubility data is summarized in Table IV.

From an inspection of the data given in Table IV, no hard and fast rule for solubility of the metal soaps can be established. For the most part, in any given solvent, the soaps of the trivalent metals were more soluble than those of the divalent metals. Generally, the soaps have the greatest solubility in methanol and the least solubility in carbon tetrachloride. In no instance did the solubility of any soap exceed 1 g. per 1000 g. of solvent.

Partitioning did not seem to be much of a factor in solubility. The cadmium and barium soaps of the whole acid fraction and the hydroxy acid concentrate had about equal solubility characteristics. However, chain length appears to have a greater effect than hydroxyl content. The corresponding soaps of the non-hydroxy acid fraction having a low acid number were less soluble than the whole acid fraction soaps. Those of the high acid number fraction were more soluble than the whole acid fraction soaps.

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Report of the Spectroscopy Committee, 1960-61

FOLLOWING usual custom, the Spectroscopy Committee met only once during the past year. The meeting was held during the American Oil Chemists' Society 52nd Annual Convention at the Sheraton-Jefferson Hotel, St. Louis, Mo., May 1–3, 1961. Fifteen members and guests attended the session held Monday, May 1.

A.O.C.S. Tentative Method "Isolated Trans Isomers—Infrared Spectrophotometric Method"

Announcement was made that the Uniform Methods Committee has approved the method for "Isolated *Trans* Isomers—Infrared Spectrophotometric Method," recommended by the Spectroscopy Committee. The method accepted by the Uniform Methods Committee as a tentative method of the Society is essentially that published in our report for the year 1958–1959 (1), as revised following a discussion of the problem of the direct determination of long-chain fatty acids (2). The tentative method includes provision for direct determination of *trans* isomers in long-chain fatty acids if the *trans* content is 15% or greater. If less than 15%, the method provides for conversion of the fatty acid to the methyl ester (2). The method will appear as a tentative method of the Society in the next revision of A.O.C.S. Book of Methods.

New Subcommittee to Investigate Methods for Preparing Methyl Esters from Long-Chain Fatty Acids

The provision in the revised tentative method "Isolated *Trans* Isomers—Infrared Spectrophotometric Procedure" requiring that samples of fatty acids