[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Preparation of Aluminum Di-Soaps[1]

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The existence of mono-, di- and tri-aluminum soaps has been in question for a decade. Extreme opinions on the subject have been set forth. Lawrence[4] maintains that the mono-, di- and tri-soaps of aluminum all exist and exhibit a similar behavior. He has asserted that the tri-soap is most easily prepared. Indeed a so-called tri-soap has long been an article of commerce. On the other hand, Eigenberger and Eigenberger–Bittner[5] obtained none of these soaps but only a basic compound intermediate between mono- and di-soaps, and a still more basic sorption compound. Alexander[6] suggested that only the mono-soap exists; McBain and McClatchie[7] were unable to prepare aluminum tri-palmitate even under the most anhydrous conditions. The third equivalent of fatty acid could always be immediately extracted as such by an anhydrous solvent, leaving a di-soap. Even the di-soap was partially hydrolyzed by moisture or aqueous media. Ostwald and Riedel[8] also found that precipitation from aqueous solution resulted in an aluminum di-soap. Markowicz[9] had earlier reported that aluminum palmitate, prepared in an aqueous medium, was such an aluminum dipalmitate.

In the present work the region in the immediate neighborhood of the di-soap has been explored thoroughly, that of the tri- and mono-soap less intensively. It is concluded that di-soaps such as dilaurate, $AlOHL_2$, definitely exist as chemical entities, and that the existence of the tri-soaps, AlL_3, AlP_3 and $AlStr_3$, remains unproven and improbable. On the basis of work not recorded here and of subsequent work by C. G. McGee, it is concluded that polymerized mono-soaps approximating such empirical formulas as $Al(OH)_2L$ also exist. This will be published separately.

Addition of aqueous solution of potassium soaps to an excess of aqueous solution of aluminum chloride leads to the formation of a *di-soap*. However, this is usually associated with 20–30% of free or loosely bound fatty acid which is extractable with anhydrous solvents, leaving the di-soap.

When the extraction is carried out with highly dried acetone at 20°, the first few hundred cc. of acetone used per gram of soap removed practically all the excess of fatty acid above the di-soap, showing that the excess of acid was partly free and partly merely sorbed. Only in the case of the stearate, where the stearic acid is but little soluble at 0° was the extraction slower. Further exhaustive extraction with 5 or 6 liters of acetone per gram removed very little further acid. However, extraction at 53° definitely caused further removal of acid below the di-soap which could be accounted for by hydrolysis due to the irreducible trace of water in the dried acetone. Further moisture increased the rate and amount of extraction.

Extraction of aluminum stearate with boiling anhydrous isoöctane yielded a clear jelly of aluminum distearate, $Al(OH)Str_2$, with ash value of 8.74%; calcd. 8.52%.

The present paper deals with dilaurate, distearate, dioleate, dicyclohexane carboxylate, and dinaphthenate.

Materials

Baker's C.P. Reagent grade aluminum chloride hexahydrate and potassium hydroxide were used. Lauric and stearic acids were obtained from the Eastman Kodak Company and were found to have neutralization numbers of 279.4 and 198, respectively (calcd., 277.5 and 197.3). Potassium soaps were prepared by mixing carbonate-free solutions of potassium hydroxide and fatty acid in methanol. They precipitated in a fine, white, flocculent state and filtered easily. They were washed with portions of methanol, and then with acetone to purify and dry the soap. Final drying was carried out over phosphorus pentoxide in an evacuated desiccator. The dried soaps were white, light and powdery. Kahlbaum potassium oleate was used directly.

Procedure

After numerous tests, the following standardized procedure was developed. A 2% freshly prepared aqueous solution of potassium soap was slowly added to a 1.5% solution of aluminum chloride with vigorous agitation in a blender provided with an electrically heated jacket. The amount of aluminum chloride present (in the ratio of one mole aluminum chloride to one mole potassium soap, each 0.00775 *m* in the case of stearate) was approximately twice that necessary for the complete precipitation of all the fatty acid as aluminum disoap. Under these conditions, a precipitate formed which contained all of the fatty acid either as free or loosely bound molecular fatty acid or as aluminum soap, while the mother liquor contained the chlorides of aluminum and potassium.

The precipitate was washed with water in the blender, and filtered until the filtrate gave no turbidity with a silver nitrate solution. The soap was finally dried to constant weight over phosphorus pentoxide. This was the "unextracted" soap. Extraction at 0° with acetone dried over Drierite (calcium sulfate), or with dried isooctane at room temperature, frees the aluminum soap from all free and loosely bound acid, leaving an "extracted" soap of nearly the theoretical composition of aluminum disoap.

Samples of all aluminum soaps, both extracted and unextracted, were ashed at 900–1000°, duplicate results on a given sample agreeing within 0.04%. The ash was calculated as aluminum oxide, since it was repeatedly found

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(1) Study conducted under contract OEMsr-1057 between Stanford University and the Office of Emergency Management, recommended by Division 11.3 of the National Defense Research Council, reported in P.B. 5885, and supervised by Professor J. W. McBain.

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(4) Lawrence, *J. Inst. Petroleum*, **31**, 312 (1945).

(5) Eigenberger and Eigenberger–Bittner, *Kolloid Z.*, **91**, 287 (1940).

(6) Reports to Division 11.3 N. D. R. C.

(7) McBain and McClatchie, *J. Phys. Chem.*, **36**, 2567 (1932).

(8) Ostwald and Riedel, *Kolloid Z.*, **69**, 185 (1934).

(9) Markowicz, *Farben-Ztg.*, **34**, 326, 414, 503 (1928).

to be free from water-soluble salts. Some of the aluminum soaps were also analyzed by decomposing with excess of strong acid, titrating the excess, and also determining the liberated fatty acid. Conditions of mixing and stirring have no appreciable effect on the properties of the resulting soap, nor does varying concentration of the reactants.

Aluminum Dilaurate, $AlOHL_2$.—The precipitation of aluminum laurate when carried out at 25–30° resulted in free-floating flocs that were readily filtered and washed. However, temperatures above 40° resulted in a sticky aluminum soap that on cooling became hard and brittle, necessitating grinding to permit satisfactory washing. The ash content of the dried extracted aluminum soap varied but little with the temperature of precipitation from room temperature to the boiling point, and was close to 11.56–11.62% as compared with a theoretical value[10] of 11.49 for the dilaurate, $Al(OH)L_2$, whereas that of a monolaurate, $Al(OH)_2L$, would be 19.6%. The pure aluminum dilaurate melted between 195 and 197°.

A composition much closer to the theoretical (ash contents 11.56-11.62%) was obtained if extraction was conducted so as to minimize hydrolysis, *e. g.* Soxhlet extraction with isoöctane at room temperature, or with acetone at 0°, or rapid washing in a fritted glass funnel with 80 cc. of acetone per gram of salt. The product obtained by this last method contained 89.3% of lauric acid by titration (theory 90.5) melted over a range of one degree centigrade at 193–196° and was used for most of subsequent studies.[11]

When 0.4 equivalent excess of potassium hydroxide was added to the potassium laurate used for precipitation, the ash of the resulting extracted soap was 12.4%, only about 0.8% higher than before.

Aluminum Distearate, $AlOHStr_2$.—Aluminum stearate precipitated at temperatures from 0° up to about 50–60° usually formed soft and slow-filtering sludges. However, samples prepared at a higher temperature separated easily as coagula from the clear aqueous medium. The dried aluminum soap from batches precipitated at temperatures below 50–60° was flaky and compact, whereas higher temperatures resulted in light, powdery and very finely divided aluminum soaps. The composition of extracted aluminum stearate depends largely on the temperature of precipitation; the ash content is constant at 9.55% between 0 and 40°, but then decreases linearly with temperature to 100° where it is within 0.1 to 0.15% of the theoretical value for the ash of distearate, 8.38%; the ash of monostearate would be 14.86%. The distearate melts between 175 and 177°.

Aluminum Dioleate, $AlOHOl_2$.—Dry unextracted aluminum oleate was an orange-tan, granular powder at 0–5° which became gummy when the free oleic acid was allowed to melt. The extracted soap was in the form of small friable granules, with no definite melting point. Like laurate, temperature of precipitation had but little effect on the composition of the extracted oleate. It remained close to 8.64% ash as compared with 8.42%, the theoretical value for $Al(OH)Ol_2$.

Aluminum Dicyclohexanecarboxylate, $Al(OH)(C_6H_{11}COO)_2$.—Cyclohexanecarboxylic acid (Eastman Kodak Company) differs from fatty acids in being somewhat water soluble and some part of the original precipitate of the free or loosely bound acid is removed when washing with water. The extracted, white, powdery, odorless product had an ash content of 16.95%; Calcd. for $Al(OH)(C_6H_{11}COO)_2$: 17.09%. It is insoluble and apparently inert in water, acetone, ethyl alcohol, and diethyl ether. A slight tendency toward swelling occurs in *n*-amyl alcohol, diisobutylene, cyclohexane and dioxane. It swells to a gel in carbon tetrachloride and toluene. It exhibits a remarkable thermal stability, showing no decomposition upon prolonged heating at 360° in a sealed, evacuated glass tube; but at about 450° it melts with decomposition.

Aluminum Naphthenates.—Several samples of aluminum naphthenate were prepared from purified samples of commercial naphthenic acids of different molecular weights. The sodium soaps of the naphthenic acids were prepared and then washed exhaustively with acetone. This removed most of the color and residual oil. Following this treatment, the aluminum soaps were prepared in the usual manner. Some fractionation of the original impure naphthenic acids occurs as a result of the drastic acetone extraction of the sodium naphthenates. As determined from the extracted ash value and the neutralization value of the acids freed from the finished soap, the white powdery products had a composition corresponding to about $^1/_3$ dinaphthenate and $^1/_3$ mononaphthenate.

Summary

Aluminum dilaurate, dicyclohexanecarboxylate, moderately pure dioleate, distearate and a product intermediate between dinaphthenate and mononaphthenate were prepared by aqueous precipitation, followed by thorough extraction with dried isoöctane or acetone. The original precipitates, at least of the first three, are aluminum di-soaps, together with free or loosely bound molecular fatty acid.

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RECEIVED SEPTEMBER 16, 1947

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[10] The "theoretical" compositions of all soaps in this paper are based on the actual molecular weight of the fatty acid used.

[11] J. W. McBain, K. J. Mysels, *et al*, *J. Gen. Physiol.* **30**, 159 (1946); *J. Coll. Sci.*, **2**, 265 (1947); **2**, 375 (1947); *J. Phys. Coll. Chem.*, **51**, 963 (1947); *Trans. Far. Soc.*; and unpublished work.