386. *Aluminium Tri-soaps.*

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Mehrotra's [1] claim to have prepared aluminium tristearate is confirmed by molecular-weight measurements and *X*-ray analysis. An improved synthesis enables this soap to be isolated as a crystalline pyridine complex. Some physical and chemical properties of aluminium tri-soaps are reported.

IN connection with the structure of gels formed by solutions of aluminium soaps in organic media [2] the behaviour of the neutral aluminium tri-soaps is of interest. Unsuccessful attempts [3,4] have been made to prepare these and there have been speculations [5] about the apparent difficulty of isolating them and even about their probable non-existence.[3,6]

The reaction which has received greatest attention is that of aluminium alkoxides with fatty acids. A German patent [7] describes the preparation of aluminium trioleate from oleic acid and aluminium ethoxide in xylene but no proof of the formation of the tri-soap is offered. Lawrence [8] stated that the distillation of three mols. of fatty acid with one mol.

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[1] Mehrotra, *Nature*, 1953, **172**, 74.

[2] Cf. Discussion on Hydrocarbon Gelling, *Proc. Roy. Soc.*, 1950, *A*, **200**, 135.

[3] McBain and McClatchie, *J. Amer. Chem. Soc.*, 1932, **54**, 3266.

[4] Shreve, Pomeroy, and Mysels, *J. Phys. Colloid Chem.*, 1947, **51**, 963; Mysels and Chin, *J. Amer. Chem. Soc.*, 1953, **75**, 1750.

[5] McGee, *J. Amer. Chem. Soc.*, 1949, **71**, 278.

[6] Licata, *Drugs, Oil and Paints*, 1936, **51**, 148, 150; Eigenberger and Eigenberger-Bittner, *Kolloid Z.*, 1940, **91**, 287; Gallay and Puddington, *Canad. J. Res.*, 1948, **26**, *B*, 155; Alexander, *J. Oil Colour Chemists' Assoc.*, 1954, **37**, 378.

[7] G.P. 569946/1933.

[8] Lawrence, *J. Inst. Petroleum*, 1945, **31**, 303.

of aluminium *iso*propoxide produced three mols. of *iso*propyl alcohol but this was disputed by Gray and Alexander[9] who claimed that, provided that moisture was excluded, three mols. of alcohol were only obtained by heating to the point at which pyrolysis of the residue began. Mehrotra[1] recently reported the preparation of aluminium tristearate and tripalmitate from the appropriate fatty acid and aluminium *iso*propoxide in benzene, the essential step being the distillation of the alcohol formed from the sphere of reaction and the subsequent prolonged evacuation of the product (200° and 0·2 mm. for 1 hr.) to remove any unchanged material. Whilst this probably is practicable, it is open to objection here since the only proof offered of the formation of a tri-soap is an elementary analysis for carbon, hydrogen, and aluminium. If nothing were pumped off, this will obviously be correct since the theoretical quantities were introduced initially. No properties of the products were reported.

A modification has now been devised by which aluminium tristearate was isolated as a crystalline pyridine complex. The identity of this soap with that prepared by Mehrotra's method has been established.

EXPERIMENTAL

Preparation of Some Aluminium Tri-soaps.—*Aluminium trioleate.* This soap was prepared by a method essentially that of Mehrotra[1] from pre-war " purissimus " grade Schering–Kahlbaum oleic acid and B.D.H. aluminium *iso*propoxide. The oleic acid was dried (P_2O_5 *in vacuo*) and twice distilled under reduced pressure just before use. The aluminium *iso*propoxide was dried by evacuation (120°/2 mm.) for 1 hr. followed by distillation directly into the reaction vessel. The removal of the liberated *iso*propyl alcohol in the benzene distillate was measured by refractive-index measurements. The *soap* [Found : Al, 3·12, 3·23. $Al(C_{18}H_{33}O_2)_3$ requires Al, 3·10%] was a yellow-brown material which was plastic at room temperature and became less viscous with increasing temperature.

Aluminium trilaurate. Prepared similarly from " purissimus " grade Schering–Kahlbaum fatty acid [Found : Al, 4·25, 4·27. $Al(C_{12}H_{23}O_2)_3$ requires Al, 4·32%], this *soap* was a hard white solid which softened slowly and formed a transparent viscous liquid above 110°. On cooling, opacity did not develop above 72—73° and a well-defined transition from opaque viscous liquid to a hard white solid was observed at 49·5° by temperature–time readings. Both the development of opacity and the lower transition were reproducible. The final m. p. is somewhat higher than the value of 94° reported by Glazer, McRoberts, and Schulman[10] for the product obtained from lauric acid and trimethylaluminium. This they believed to be a mixture of aluminium trilaurate with finely occluded alumina.

Aluminium dilaurate iso*propoxide.* In neither of the preceding preparations was it possible to collect the theoretical amount of *iso*propyl alcohol in the distillate. This discrepancy may have been due to the experimental error of the refractive-index method of determining the free alcohol or to its appreciable retention before the high-temperature low-pressure treatment where analysis was difficult. It was also possible that the product was not the tri-soap but the di-soap monoalkoxide, or a mixture of both compounds. To confirm that this was not so the preparation of the dilaurate *iso*propoxide was attempted. McRoberts and Schulman[11] had previously reported that aluminium dilaurate *sec.*-butoxide is formed in benzene solution from 2 mols. of lauric acid and 1 mol. of aluminium *sec.*-butoxide. We used the same method as for the trilaurate except that only 2 equiv. of lauric acid were taken. On mixing the reagents, a solution of high viscosity was obtained, distillation of which yielded 1·93 mols. of *iso*propyl alcohol and a *product* having properties totally different from those of the " tri-soap." It was a slightly opaque, rubber-like material which softened on heating but did not flow below about 150°. No arrest in the cooling curve was observed. Swelling in dry hydrocarbon solvents occurred slowly with the formation of viscous solutions which thickened rapidly on addition of water [Found : Al, 5·66. $Al(C_{12}H_{23}O_2)_2(C_3H_7O)$ requires Al, 5·57%].

Aluminium tristearate. If the alkoxide reacts with stearic acid in anhydrous pyridine, the tri-soap crystallises from the cooled reaction mixture. Hopkin and Williams's " anhydrous " grade pyridine (fresh) was distilled over aluminium *iso*propoxide in a dry atmosphere and the middle fraction collected. The reaction was carried out in an all-glass vacuum apparatus consisting of a flask with a side-arm and tap, having a Soxhlet extractor and reflux condenser fitted to its neck. A known quantity of stearic acid [Eastman Kodak, recrystallised from

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[9] Gray and Alexander, *J. Phys. Colloid Chem.*, 1949, **53**, 28.
[10] Glazer, McRoberts, and Schulman, *J.*, 1950, 2082.
[11] McRoberts and Schulman, *Proc. Roy. Soc.*, 1950, *A*, **200**, 136.

acetonitrile; found by titration with alkali (phenolphthalein) to contain 100·3 ± 0·1% of stearic acid] was placed in the flask and in the Soxhlet thimble slightly more than the theoretical amount of aluminium *iso*propoxide (Hopkin and Williams). The flask was evacuated and the acid melted by gentle warming to ensure complete dryness. The anhydrous pyridine was admitted through the side arm from a special receiver and refluxed through the extractor until all the alkoxide dissolved. Any free alumina was retained in the thimble. The soap crystallised from the reaction mixture on cooling. With a stream of dry air or nitrogen passing through the side arm into the flask, the extractor and condenser were replaced by a ground-glass joint containing a sintered-glass filter on which the soap was collected. By admission of further quantities of pyridine, the soap was then washed and recrystallised in the same flask without exposure to the atmosphere. After the final filtration, the *soap* was pumped free from pyridine [Found: Al, 3·15. $Al(C_{18}H_{35}O_2)_3$ requires Al, 3·07%]. As the soap had possibly been contaminated by the Silicone grease used to lubricate the joints and stopcocks, a further portion was hydrolysed with dilute hydrochloric acid and the aluminium content of the aqueous phase determined gravimetrically with 8-hydroxyquinoline (Found: Al, 3·07%). The tristearate was a hard white material which on heating passed into a plastic form similar to that observed in many other metal soaps by Lawrence,[12] and finally melted to a clear liquid at 117—120°. Cooling curves gave rather uncertain indications of transitions in the regions of 55° and 85°. The infrared spectra of solutions of the tristearate have been examined and details will be published elsewhere. The broad band attributed to hydroxyl in the spectrum of the monohydroxydistearate is absent from that of the tristearate.

Aluminium trisdodecylsulphate. Hot concentrated aqueous solutions of ammonium alum and sodium dodecyl sulphate were mixed in the correct proportions to form the *trisdodecylsulphate.* On cooling, a white fatty material crystallised and was filtered off and dried at room temperature [Found: Al, 3·28. $Al(C_{12}H_{25}SO_4)_3$ requires Al, 3·30%].

Solubility.—All three carboxylate soaps are very soluble in dry hydrocarbons and in carbon tetrachloride. On exposure to the atmosphere or on addition of water, the solutions are converted into viscoelastic gels, presumably because of hydrolysis of the tri-soap to the monohydroxy-di-soap. The trisdodecylsulphate is soluble in alcohol and in acetone on warming but is less soluble in non-polar solvents than the carboxylates. If this soap is heated in damp solvents (*e.g.*, acetonitrile, pyridine, benzene), opacity develops presumably owing to hydrolysis but no analogous tendency of these solutions to increase in viscosity has been observed.

X-*Ray Analysis.*—*X*-Ray-diffraction measurements were made with a Hilger HRX instrument and Unicam powder camera, Cu-*K*α radiation and a nickel filter being used. The powdered samples were enclosed in thin-walled Pyrex capillaries.

The diffraction patterns obtained with a sample of aluminium tristearate prepared by Mehrotra's method and of a sample prepared by the pyridine method are shown in Fig. 1 together with powder patterns of aluminium distearate and stearic acid. The calculated interplanar spacings ("*d*" values, in Å) are as follows: Aluminium tristearate prepared by Mehrotra's method, 6·97 (very faint), 4·37—3·86 (broad band decreasing in intensity towards the 3·86 Å edge). Aluminium tristearate prepared by our pyridine method, 7·06 (very faint), 4·33—3·82 (broad band decreasing in intensity towards the 3·82 Å edge). Aluminium distearate, 7·71, 6·67 (very faint), 5·73 (very faint), 4·70, 4·22, 3·87, 3·64. The spacings found for the distearate agree well with the data of Bauer, Fisher, Scott, and Wiberley.[13]

Molecular-weight Measurements.—The results of ebullioscopic molecular-weight measurements in carefully dried benzene in a modified Cottrell apparatus[14] are as follows (concentrations in g. per 100 ml. of solution):

Trilaurate:	Concn.	0·16	0·35	0·58	0·94	1·27	1·77	2·39	3·08	3·92	4·80	5·31
M (calc.), 624	*M* (obs.)	652	702	730	692	726	802	954	889	796	931	843
Tristearate:	Concn.	0·56	1·00	1·46	1·82	2·23						
M (calc.), 877	*M* (obs.)	1547	1214	1525	1566	1427						

Dielectric and Viscosity Measurements.—Toluene solutions of the trioleate and trilaurate have relatively high direct-current conductivities at 25°. The measuring apparatus and dielectric cell have been described previously.[15] Comparative viscosity measurements, also at 25°, were made by the capillary flow method. These solutions were mobile, with viscosities little greater than that of the solvent, but when exposed to moisture they became increasingly

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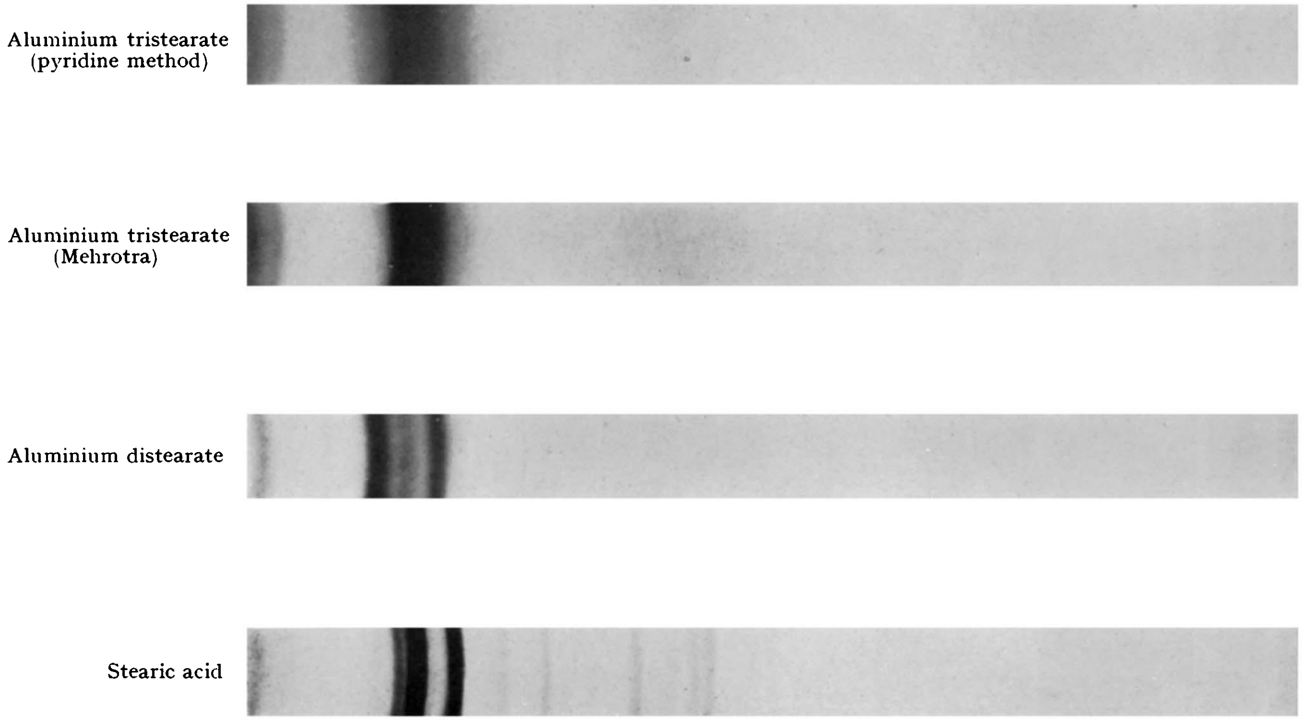
[12] Lawrence, *Trans. Faraday Soc.*, 1938, **34**, 660.

[13] Bauer, Fisher, Scott, and Wiberley, *J. Phys. Chem.*, 1955, **59**, 30.

[14] Nelson and Pink, *J.*, 1952, 1744.

[15] *Idem, ibid.*, 1954, 4412.

Fig. 1.


Aluminium tristearate (pyridine method)
Aluminium tristearate (Mehrotra)
Aluminium distearate
Stearic acid

viscous. Small, known amounts of water were therefore introduced into the anhydrous toluene solutions from a micropipette and dispersed by vigorous shaking. With increasing water content a rapid fall in direct-current conductivity was observed with a parallel increase in viscosity. A minimum conductivity and a maximum viscosity were observed when the soap and water were present in equivalent amounts, the viscosity being immeasurably high by the capillary flow method at this composition (Fig. 2). It is of interest that the fall in conductivity was accompanied by a departure of the log ε''–log f curves (ε'' = dielectric loss factor, f = frequency) from the 45° slope required for direct-current conduction. Such departures are shown by toluene solutions of the monohydroxy-di-soaps and may be accounted for in terms of the restricted displacement of ions and charged micelles in a viscous medium.[16] These effects appear to arise from the growth of extensive chains of di-soap molecules formed by the replacement of one carboxylate group in the tri-soap molecule by a hydroxyl group. The effect of water in excess of the equivalent amount is probably one of peptisation.

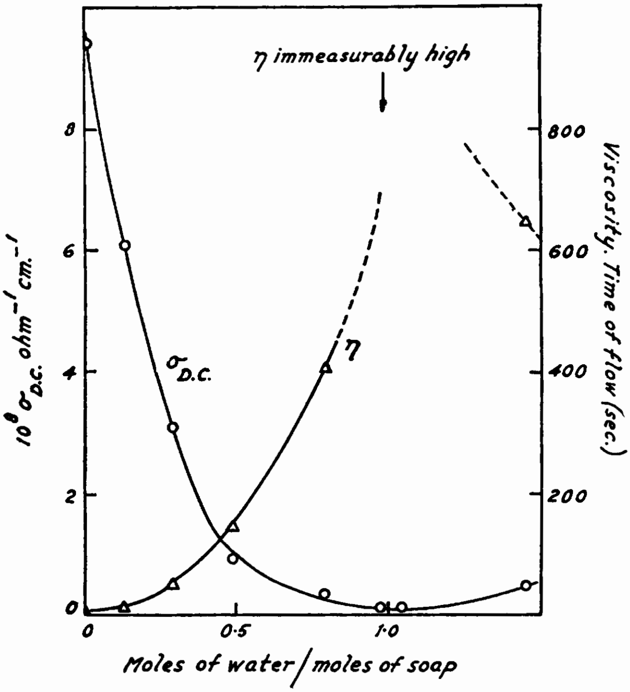


FIG. 2. *Effect of water on D.C. conductivity* ($\sigma_{D.C.}$) *and viscosity of* 3·74% *aluminium trioleate solution in toluene.*

DISCUSSION

Our preparative and analytical results provide very strong evidence for the independent existence of both aluminium tri-soaps and monoalkoxyaluminium di-soaps in addition to the monohydroxy-di-soaps. Further, comparison of the diffraction patterns establishes the identity of the two tri-soap preparations and disposes of the possibility that the aluminium tristearate is a mixture of the crystalline distearate and stearic acid. A diffuse band similar to that given by the tristearate might be obtained with an amorphous mixture of these two compounds but the presence of the faint line at 7 Å in the tri-soap pattern which is probably an order of a long spacing and which does not appear in the distearate would still require explanation. This hypothesis, therefore, seems unlikely.

The broad band at 3·8—4·3 Å in the tristearate probably arises from a short spacing at 4·3 Å in combination with a long spacing of which the faint line at 7 Å is a high order. There are, however, insufficient orders to establish this with certainty or to permit an estimate of the value of the long spacing.

The separate existence of the tri-soaps as distinct compounds is further borne out by the properties of their solutions in non-polar solvents. These solutions, which show

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[16] Nelson, Ph.D. thesis, Belfast, 1954.

viscosities very little greater than those of the pure solvents, contrast strongly with the viscoelastic gels formed by the monohydroxy di-soaps in the same media. In accordance with this observation, aggregation of the tri-soap molecules in benzene at its boiling point appears to stop at the dimer stage, a type of behaviour which parallels that of the ferric tri-soap.[17]

Moreover, anhydrous tri-soap solutions show none of the dielectric anomalies associated with the restricted movement of charged aggregates observed for dispersions of the corresponding monohydroxy di-soaps.[16]

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[17] Nelson and Pink, *Nature*, 1952, **169**, 620.