426. *The Preparation of a Stable Aluminium Dodecanoate (Laurate) with no Gelling Properties in Hydrocarbons.*

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The preparation is described of a stable aluminium dodecanoate (laurate) having no gelling properties in hydrocarbon solution. A consideration of its properties indicates that it is aluminium trilaurate; analysis indicates a small percentage of occluded alumina. The absence of gelling is attributed to the absence of intermolecular hydrogen-bond cross-links.

Previous work (McRoberts and Schulman, *Nature*, 1948, **162**, 101; *Proc. Roy. Soc., A*, Discussion on Hydrocarbon Gelling, 1949) has suggested that the gelling properties of the aluminium soaps depend upon the existence of a hydroxy-group in the molecule. It is through the agency of this group that cross-linking takes place, and the resultant hydrogen-bonded network gives rise to the observed gelling properties in hydrocarbon solvents.

Should this be so, an aluminium tri-soap, since it does not contain a hydroxy-group, should exhibit no such gelling properties. It has hitherto been impossible to test this contention since the tri-soaps cannot be prepared by any of the known methods of synthesis involving fatty acids (and their alkali-metal salts) and both inorganic aluminium salts and organic aluminium compounds of the type AlX_3, where the group X is appreciably electronegative. An attempt has now been made to prepare aluminium dodecanoate (trilaurate) by reaction of lauric acid with trimethylaluminium.

Experimental.

Trimethylaluminium, prepared according to the method of Pitzer and Gutowsky (*J. Amer. Chem. Soc.*, 1946, **68**, 2204), was treated with pure lauric acid (Verley) in dry benzene, in the absence of moisture and oxygen, and the product extracted by removing the benzene and any excess of trimethylaluminium by distillation. The product (A) was purified by trituration with dry light petroleum (b. p. 40—60°) until of constant m. p. 94° (Found : Al_2O_3, 10·3%). The same product, m. p. 94°, was obtained whether the reactants contained excess of lauric acid or of trimethylaluminium. It was a yellow, amorphous powder which dissolved easily in benzene to give a highly mobile solution, no trace of gelling being noticeable. Prolonged contact of such a solution with water did not produce any gelling tendencies; yet, when the product was heated in moist acetone or dioxan, a second product (B), m. p. 180—220° (Found: Al_2O_3, 14·3%), was formed which exhibited strong gelling properties in benzene and light petroleum.

The addition of " hydrogen-bond forming " organic liquids to gels of aluminium dilaurate in benzene and light petroleum destroyed the gel structure and produced mobility. The following liquids were effective: acetone, di*iso*propyl ketone, ether, methanol, and ethanol.

DISCUSSION.

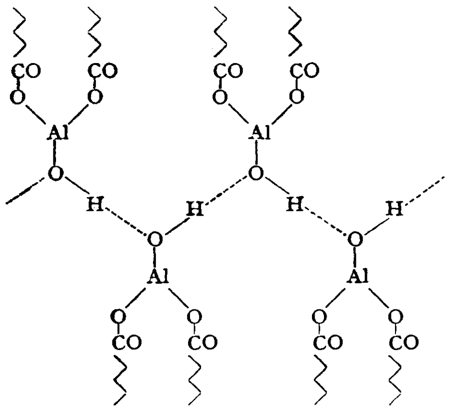
The absence of gelling properties shown by A and the strong gelling shown by B suggests that the former is the tri- and the latter the di-soap. It is known that the di-soap is a strong gelling agent in hydrocarbon solvents. However, the analytical results are clearly not in accord with the theoretical values expected for these compounds:

Compound.	Al_2O_3, %, found.	Al_2O_3, %, calc.
Product A	10·3	8·1 for tri-soap.
Product B	14·3	11·5 for di-soap.
Commercial di-soap	14·7	,, ,,

Product A was refluxed with light petroleum, the mixture filtered, and the resulting clear solution evaporated to dryness (Found: Al_2O_3, 9·9%).

The high aluminium content of product A may, *a priori*, be due to the presence of the di-soap or methylaluminium di-soap in appreciable amount, or a small (*ca.* 2%) occlusion of alumina. The absence of di-soaps is shown by the sharpness and constancy of the m. p. after repeated washing with solvent, and the complete lack of gelling properties. The existence of a stable methylaluminium di-soap is unlikely in view of the extreme instability of the known aluminium alkyls. For these reasons, we believe A to consist of the tri-soap containing a small amount of occluded alumina; such an impurity would not affect the sharpness or the constancy of the m. p. Should this be so, the di-soap derived (by hydrolysis) should retain the high aluminium content. This is borne out by the analytical results for the product B. The formation of visually transparent solutions by the tri-soap would indicate that the alumina is molecularly dispersed.

No hydrolysis takes place when a benzene solution of the tri-soap is kept in contact with water, the solution remaining perfectly mobile. This is in marked contrast with the di-soap alcoholates (McRoberts and Schulman, *loc. cit.*), where the hydrolysis proceeds immediately on the exposure to traces of atmospheric moisture. The tri-soap would appear to be more stable than has hitherto been thought. Under more drastic conditions, such as refluxing with aqueous acetone or dioxan, the tri- is hydrolysed to the di-soap. This hydrolysis product exhibits strong gelling properties in hydrocarbon dispersion.



The inset type of hydrogen-bond cross-linking is envisaged for aluminium di-soap gels. For a stable hydrogen bond of the type O–H . . . O, the inter-oxygen distance varies between 2·5 and 2·9 A. for different compounds. This requires that the cross-link direction, in a di-soap gel, is normal to the $R\cdot CO_2-Al-CO_2R$ plane, thereby allowing sufficient space in the cross-link direction to accommodate the long-chain hydrocarbon portion of the molecule. This space conception is discussed in connection with a monolayer study on the formation of metal soaps (Wolstenholme and Schulman, *Trans. Faraday Soc.*, 1950, **46**, 475). The presence of hydrogen bonds is supported by the negative streaming birefringence exhibited by hydrocarbon gels of aluminium di-soaps (O. Snellman, Uppsala, private communication).

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