237. *Studies in Water-in-oil Emulsions. Part I. Preparation of Anhydrous Magnesium Oleate.*

By Richard C. Pink.

Anhydrous and hydrated magnesium oleate have been prepared and examined. It has been shown that addition of small amounts of water to solutions of the anhydrous soap in benzene causes its precipitation in an insoluble form containing water. Such systems are not true emulsions, although appearing to be so. The results indicate that in the inversion of oil-in-water emulsions with magnesium chloride the magnesium oleate formed does not dissolve in the oil phase.

SEVERAL descriptions of the preparation and properties of magnesium oleate are recorded. Newman (*J. Physical Chem.*, 1914, **18**, 34), who first described its emulsifying powers, used a " concentrated " solution of the soap in benzene. Briggs and Schmidt (*ibid.*, 1915, **19**, 478), in a continuation of Newman's work, described it as being soluble in benzene to the extent of 1% after refluxing with benzene for one hour. Wellman and Tartar (*ibid.*, 1930, **34**, 371) claimed that the material used by them was " fairly easily dissolved by warm benzene," and more recently Parke (J., 1934, 1112) has described the preparation of a material with which he was able to prepare a 19·28% solution in benzene.

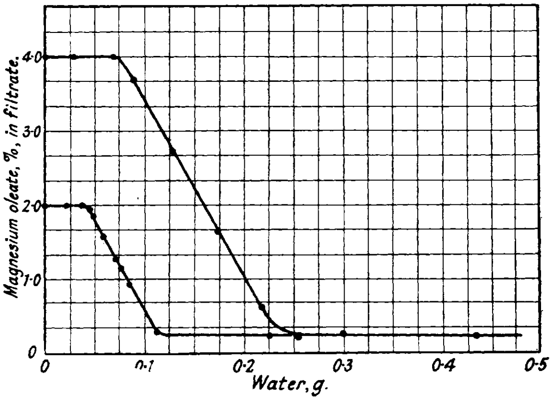
It is apparent that the various workers were dealing with different substances. Further light is thrown on the problem by the observations of Wellman and Tartar (*loc. cit.*). Solutions of their magnesium oleate in dry benzene were clear, but contact with water caused precipitation of a flocculent material, the nature of which was not investigated by them, but which they assumed was magnesium oleate. Shaking only appeared to hasten the precipitation, but was not necessary to cause the phenomenon. They considered that this fact supported the colloidal or solid-film theory of water-in-oil emulsions.

The author considered that the flocculent precipitate obtained by Wellman and Tartar was probably a hydrated form of magnesium oleate, and that the materials used by Newman and by Briggs and Schmidt may have been such a hydrated form of the soap.

EXPERIMENTAL.

Materials.—The oleic acid was from Kahlbaum, and the other chemicals were of " AnalaR " standard. Benzene (thiophen-free) was twice redistilled, kept over sodium, and redistilled immediately before use : 100 c.c. on evaporation left no residue. All the water used was freshly distilled.

Preparation of Magnesium Oleate.—Parke's method (*loc. cit.*) was followed. A solution of 50 g. of sodium oleate in 2 l. of water, prepared by exact neutralisation of 46·4 g. of oleic acid with 164·31 c.c. of N-sodium hydroxide, was heated to 90°, and 20 g. of magnesium chloride in 100 c.c. of water added dropwise. A white precipitate immediately appeared. After cooling, it was filtered off, washed free from chloride, and finally washed with alcohol. 10 G. of this material were dried over concentrated sulphuric acid in a vacuum desiccator for 4 weeks (Sample A). The remainder was refluxed with benzene for 20 minutes, and the clear yellow supernatant layer was decanted while still hot and evaporated to dryness. The residue was crystallised from benzene. It was a yellow glassy material which dissolved *readily* in cold dry benzene (Sample B) [Found, by calcination to MgO for 20 mins. at a red heat : Mg, 4·13, 4·14, 4·14. Calc. for $Mg(C_{18}H_{33}O_2)_2$: Mg, 4·14%].



Sample A, on the other hand, was a white powdery substance only *slightly* soluble in cold benzene, but it dissolved in hot benzene, this solution being opalescent on cooling. A portion of this sample was heated in an air-oven at 105° for 2 hours [Found : loss, 5·83. Calc. for $Mg(C_{18}H_{33}O_2)_2,2H_2O$: loss, 5·78%], and then resembled sample B in every way.

The hydrated material can be readily obtained by leaving the anhydrous material in contact with water for several days, filtering it off, and drying it over concentrated sulphuric acid in a desiccator. If the soap is finely powdered, absorption of water takes place much more rapidly.

It is clear that the material obtained by metathesis of sodium oleate with magnesium salts is a hydrated form of the soap, and that the combined water is removed when heated in the air-oven or when treated as described by Parke, who appears to be the first worker to have published a method for preparing a completely anhydrous form of the soap.

Precipitation of Magnesium Oleate from Benzene by Addition of Water.—To 50 c.c. portions of a 2% solution of the anhydrous soap in benzene, various amounts of water were added. The mixtures were vigorously shaken first by hand and then on a mechanical shaker for 3 hours, and kept in a thermostat at 20° for at least 12 hours. The white flocculent precipitate which was formed was collected on a dried filter-paper, and 25 c.c. of the filtrate were evaporated slowly on a hot plate and dried to constant weight in the air-oven. The percentage of magnesium oleate in the filtrate was calculated.

A similar series of experiments was carried out with a 4% solution of the soap. The results are shown below, and also graphically in the figure.

2% *Solution.*

H_2O, g.	0	0·0200	0·0373	0·0440	0·0500	0·0583	0·0720	0·0767	0·0851	0·1147	0·2270	0·2515
Soap in filtrate, %	2·000	2·000	2·000	1·972	1·918	1·570	1·266	1·164	0·933	0·324	0·229	0·183

4% *Solution.*

H_2O, g.	0	0·0300	0·0670	0·0875	0·1285	0·1720	0·2190	0·300	0·4350	1·0021
Soap in filtrate, %	4·000	4·000	4·000	3·701	2·759	1·656	0·606	0·302	0·203	0·201

Discussion.—An emulsion has been defined as a system containing two *liquid* phases, one of which is dispersed as *globules* in the other (Selmi, *Nuovi Ann. Sci. nat. Bologna*, 1845, **4**, 146; see Clayton, "Theory of Emulsions and their Technical Treatment," London, 1935, p. 1). If this definition is accepted, the benzene–magnesium oleate–water systems examined above are not true emulsions, but are suspensions of hydrated magnesium oleate in benzene. This view is confirmed by microscopic examination. There appears to be some evidence to show that such systems containing larger amounts of water are also of this type. Briggs and Schmidt (*loc. cit.*) describe them thus: "Emulsions of benzene in sodium oleate, resinate, etc., were of the usual form, consisting as they did of small spherical drops of benzene floating in an aqueous medium. . . . The internal structure of the water-in-benzene emulsions was found to be of a different nature. The magnesium oleate emulsions seemed composed of a gelatinous material containing a large proportion of water in exceedingly irregular masses. There were no sharply defined water globules as such."

Further, the soap is precipitated almost completely in an insoluble form from a benzene solution of magnesium oleate in contact with a very small amount of water. It is therefore clear that the reason for the inversion of benzene-in-water emulsions stabilised by univalent soaps on the addition of magnesium chloride cannot be, as suggested by Parsons and Wilson (*J. Ind. Eng. Chem.*, 1921, **13**, 1119), solution in the benzene of the bivalent soap formed by metathesis.

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