

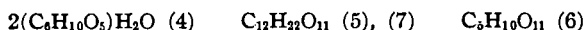
## A STUDY OF THE EMULSIFYING PROPERTIES OF CERTAIN SALTS OF ARABIC ACID.\*

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### INTRODUCTION.

The work of Harkins (1) and Langmuir (2) on the structure of liquid surfaces at a liquid-liquid interface, and the orientation theory of emulsions and emulsification, has been the object of much investigation and experimental work. Newman (3), working with Bancroft in 1914, records the observation that when a hydrocarbon, such as benzene and water are emulsified, using sodium oleate as an emulsifying agent, the hydrocarbon was emulsified in the water, the latter serving as the external phase. When, however, the oleic acid salts of metals with higher valence were employed, the water became dispersed through the benzene, and this hydrocarbon became the continuous phase. The theoretical deduction of Harkins upon the nature of emulsifying agents substantiates this observation of Bancroft and Newman. Harkins and his co-workers have proposed a theory regarding the stability of dispersed particles in an emulsion. It is their claim that this is accomplished by the orientation of the molecules at the interface with a medium of dispersion. An emulsifying agent, in light of Harkins' theory, should have a polar group in the molecule, and also a group of lesser polarity. The alkali salts of fatty acids, such as oleic acid, meets this requirement. The alkali metal serving as the polar group, and the hydrocarbon chain serving as the group of lesser polarity or the non-polar group. The emulsifying agent tends to reduce the abruptness of the transition between two liquids, and forms a film over the emulsified particles, which film, according to Harkins, must fit the curvature of the emulsified particle. Accordingly, sodium oleate reduces the free energy between benzene or an oil and water, and thus induces the emulsification of the benzene or oil-in-water, whereas, with magnesium oleate, the film of the emulsifying agent fits better the water particle, and this becomes dispersed through either the benzene or oil, which forms the outer phase of the emulsion.

In pharmacy, acacia and tragacanth are the most generally used emulsifying agents. Each of these substances produces emulsions of the oil-in-water type with a reasonable degree of stability. The general treatises on Chemistry refer to acacia as the potassium, magnesium and calcium salts of arabic acid. The following formulas have been assigned to the compound, arabic acid.



The structure of arabic acid is not definitely known, and the following references have been filed in the literature to work done on the structure of this compound. Beilstein gives the empirical formula for the acid, which has been dried at 100° C.,  $C_{18}H_{18}O_9$ ?. Neubauer (8) prepared the calcium and potassium salts, and found them to have the following compositions  $CaO \cdot 2C_{12}H_{20}O_{10}$   $K_2O \cdot (C_{12}H_{22}O_{11})_3$ ?. Heckmeyer (9) found the lead, copper and barium salts to have the following compositions  $2PbO \cdot 3C_{12}H_{20}O_{10}$ ,  $CuO \cdot C_{12}H_{20}O_{10} \cdot C_{12}H_{22}O_{11}$ ,  $BaO \cdot 2C_{12}H_{20}O_{10}$ . O'Sullivan (10) prepared the calcium and barium salts of the acid which he analyzed and as-

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signed to them the following formulas  $C_{89}H_{142}O_{74}.Ca$  and  $C_{89}H_{142}O_{74}.Ba$ . By hydrolyzing arabic acid with diluted sulphuric acid, the same investigator obtained a series of acids having 23 to 71 carbon atoms in the molecule. Bechamp (11) obtained the di- and tetra-nitro substitution products of arabic acid by treating gum arabic with hot nitric acid. These compounds were amorphous and assigned the compositions  $C_{12}H_{18}(NO_2)_2O_{10}?$  and  $C_{12}H_{16}(NO_2)_4O_{10}?$ , respectively. Likewise the same investigator succeeded in acetylizing the gum with acetic anhydride at  $105^\circ C.$  and obtained an amorphous insoluble compound of the composition  $C_{21}H_{16}(C_2H_3O)_4O_{10}?$ .

This summary indicates that little is known about the structure of arabic acid, but from the work that has been done, the compound seems to be similar to familiar carbohydrates in structure or the carboxylic acids obtained by mild oxidation of the carbohydrates.

Recent work done on the structure of tragacanth by Sullivan (12) suggests this gum to be the calcium salt of bassoric acid to which this investigator has assigned the formula  $H.C_{24}H_{34}O_{20}.H_2O$ .

With the experiences of Harkins and Newman in mind, with the oleates of sodium and magnesium as emulsifying agents, it occurred to the authors that it would be interesting to investigate the emulsifying properties of salts of arabic acid and bassoric acid, in order to determine the effect of a univalent or divalent metal combined with the acid as far as the character of the emulsion produced is concerned. The oleates of sodium and magnesium contained by one polar group in the molecule, namely, the metallic atom present, whereas, the sodium and magnesium salts of arabic or bassoric acids contain the polar metallic atom in addition to the polar hydroxyl groups which has been indicated to be present in their structure by view of their union with acetic anhydride and nitric acid.

#### EXPERIMENTAL.

##### *Materials.*

1. *Arabic Acid.*—This compound was obtained by slightly acidifying a solution of acacia in water with hydrochloric acid, dialyzing to remove soluble chlorides and precipitating the arabic acid from its aqueous solution by means of alcohol. Merck's Arabin was also employed.

2. *Magnesium Arabate.*—The compound was prepared by boiling a solution of arabic acid in water with an excess of magnesium carbonate, filtering and evaporating the filtrate to dryness over a water-bath.

Upon ignition the compound yielded 2.4 per cent of magnesium oxide.

3. *Sodium Arabate.*—The calcium present in a solution of acacia in water was precipitated by the addition of sodium carbonate and the solution brought to the neutral point. The filtrate was evaporated to dryness over a water bath.

4. *Ferric Arabate.*—A 20 per cent solution of acacia in water was treated with ferric chloride solution, added drop by drop until a gel was obtained of uniform reddish brown color and a stiff consistency. The iron (Fe) content of the gel was determined by treatment with hydrochloric acid and potassium iodide in the usual manner and titrating the liberated iodine with sodium thiosulphate solution. The gel contained 0.39 per cent of iron.

5. *Lead Arabate.*—A solution of acacia in water was treated with a solution

of lead subacetate  $\text{Pb}(\text{CH}_3\text{COO})_2$  (equivalent to 18 per cent of metallic lead), as long as precipitation occurred. The precipitate was washed free of soluble lead salts and dried to a constant weight at  $100^\circ \text{C}$ . The lead content was determined by dissolving about one Gm. of the lead arabate in diluted nitric acid and precipitating the lead as carbonate by means of sodium carbonate, washing, filtering and igniting, weighing the lead as the monoxide. The compound contained 40.25 per cent  $\text{PbO}$ .

6. *Sodium Valerate*.—Obtained by neutralizing valeric acid with sodium bicarbonate and evaporating the solution to the crystallizing point.

7. *Magnesium Valerate*.—Prepared by dissolving magnesium borings (for Grignard reaction) in a mixture of valeric acid and water. After the reaction was complete the solution was evaporated to the crystallizing point.

8. *Zinc and Ammonium Valerates*.—These compounds were used from a supply of the salts of medicinal purity in this laboratory.

9. *Calcium Gluconate* (14).

10. *Cadmium i-Galactonate* (15).

11. *Magnesium Dioxystearate* (16).

12. The acacia and tragacanth employed met the requirements prescribed by the United States Pharmacopœia for these substances.

13. The mineral oil employed was the commercial "Nujol" and the cottonseed and olive oils met the requirements of the United States Pharmacopœia. Distilled water  $p_{\text{H}}$  5.8 to 6.4 was employed.

#### CERTAIN OLEATES AS EMULSIFYING AGENTS.

Using mineral oil and water as two immiscible liquids, sodium oleate, magnesium oleate, calcium oleate, manganese oleate, cobaltous oleate, nickelous oleate and aluminum oleate were employed, respectively, as emulsifying agents. Similar to the observation of Newman and Harkins with benzene, sodium oleate yielded an emulsion in which the oil was the inner phase, whereas, the emulsions prepared with the oleates of the divalent metals, and aluminum produced emulsions of the water-in-oil type.

#### VALERATES AS EMULSIFYING AGENTS.

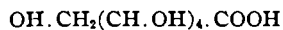
The simplest possible formula assigned to arabic acid was  $\text{C}_6\text{H}_{10}\text{O}_{11}$ . Five carbon atoms in the molecule were selected as the starting place for study. This acid, namely, valeric acid, in the form of its sodium and ammonium salts, produced emulsions of the oil-in-water type. The procedure employed was to place one Gm. of the salt in a mortar, add 5 cc. of oil and 5 cc. of water, and triturate briskly until the mixture was homogeneous. These emulsions were not very stable and, upon standing twelve to eighteen hours, the oil and water separated. Yet upon agitation the oil was again dispersed through the water. The zinc and magnesium salts of valeric acid, used in place of the sodium and ammonium salts in the foregoing experiments, yielded emulsions of the water-in-oil type. These emulsions, like those produced with the sodium and ammonium salts, were quite unstable, and yet permitted liberal dilution with oil and no dilution with water.

## ARABATES AS EMULSIFYING AGENTS.

Having observed the characteristics of the emulsions prepared by certain salts of valeric acid, the next step in this investigation was to employ as emulsifying agents certain salts of arabic acid. With arabic acid sodium and magnesium arabates, emulsions of the oil-in-water type were obtained. The procedure employed was to triturate 10 cc. of the oil with 2.5 Gm. of the emulsifying agent and add in one portion 5 cc. of water. Then after brisk trituration and the formation of the emulsion, the remainder of the water was added slowly with continued trituration until 40-cc. volume was obtained. Thus in each case a 25 per cent oil-in-water emulsion was prepared. The arabic acid, iron gel, produced an emulsion of the oil-in-water type. Using 15 Gm. of the gel, 5 cc. of water and 10 cc. of oil, and briskly triturating until emulsification took place. These emulsions were stable over a period of several months. Experiments with lead arabate showed this substance to be quite incapable of producing emulsions of water-in-oil, or of oil-in-water. These experiments indicate that although the magnesium and zinc salts of valeric acid yield emulsions of the water-in-oil type, the magnesium and iron salts of arabic acid gave a normal oil-in-water emulsion.

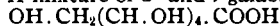
## COMPOUNDS RELATED TO ARABIC ACID AS EMULSIFYING AGENTS.

The next step in the experimental work was to select a number of acids of definite structure, having hydroxyl groups in the molecule, and to determine the nature of emulsions prepared with the di-valent salts of these acids. The salts of the following acids were employed:

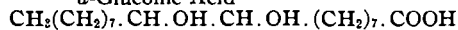


*i*-Galactonic Acid

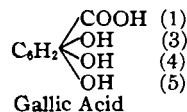
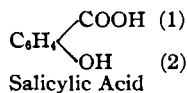
A mixture of *d*- and *l*-galactonic acids.



*d*-Gluconic Acid



Dihydroxystearic Acid



*Salts of Gluconic Acid.*—Similar to the sodium salts of valeric acid, the sodium salt of gluconic acid produced emulsions of the oil-in-water type. Five Gm. of the compound were necessary to disperse 10 cc. of oil through 10 cc. of water, producing an emulsion which was very viscid, yet upon standing for a period of an hour, began to separate. The calcium salt of gluconic acid was treated as follows: 1 Gm. of the salt was rubbed with 5 cc. of oil, and water was added gradually with brisk trituration, 5 cc. of water in all. This procedure yielded an emulsion of the water-in-oil type, as was shown by a microscopic examination of the mixture. Changing the foregoing procedure of mixing, and employing the same emulsifying agent, namely, calcium gluconate, an emulsion of the oil-in-water type was obtained. The particles of oil emulsions were somewhat larger than those found in most emulsions of this type, and upon standing the oil and water separated, but not completely, and there remained an emulsion nucleus which was shown by the fact that upon simple agitation the emulsion was restored to its normal condition.

*i*-Galactonic Acid.—Similar to the sodium salt of gluconic acid the sodium salt of *i*-galactonic acid produces dispersions of oil-in-water, whereas the cadmium salt

of this compound, like the calcium salt of gluconic acid, exhibited the capacity of dispersing oil-in-water or water-in-oil.

*Dioxystearic Acid.*—Having observed the capacity of each of these acids to form oil-in-water and water-in-oil emulsions, the next compound prepared and studied was di-hydroxystearic acid, which has but two hydroxyl groups in a molecule containing a chain of seventeen carbon atoms. The sodium salt of di-hydroxystearic acid produced very stable emulsions of the oil-in-water type, whereas the magnesium salt of this acid produced emulsions of the water-in-oil type. Under no circumstances was it found possible to prepare emulsions with magnesium dioxystearate of the oil-in-water type. Thus the di-hydroxyl acid combined with a divalent metal behaved like a normal stearic acid salt, whereas the polyhydroxyl compounds *i*-galactonic and gluconic acids showed the property of emulsifying water-in-oil and also oil-in-water.

*Salicylic Acid.*—Having observed the influence of hydroxyl groups in the straight chain acids, the next step was to study the influence of the introduction of hydroxyl groups into acids containing cyclic groups. Accordingly sodium salicylate was found to produce emulsions which were unstable, but always of the oil-in-water type. Calcium salicylate, on the other hand, produced rather stable emulsions of water-in-oil, although the water particles were quite large. Employing the procedures described under the gluconic acid salts, attempts were made to prepare emulsions of the oil-in-water type, and although the particles of oil were exceedingly large and rapidly separated, there is undoubtedly some tendency on the part of calcium salicylate to form emulsions of the oil-in-water type.

*Gallic Acid.*—The sodium salt of gallic acid, although a poor emulsifying agent, was shown to invariably produce dispersions of the oil-in-water type. The calcium salt of gallic acid produced rather stable emulsions of the water-in-oil type and also served, to a greater degree than did calcium salicylate, to produce emulsions of the oil-in-water type. From the observations made with gluconic and *i*-galactonic acids in the form of their divalent salts, this is the behavior that might have been anticipated.

TABLE I.

SUMMARY OF RESULTS.

Emulsifying agent.	Type of emulsion.			Emulsifying agent.	Type of emulsion.		
	Oil-in-water.	Ampho-teric properties.	Water-in-oil.		Oil-in-water.	Ampho-teric properties.	Water-in-oil.
Sodium oleate	X			Magnesium valerate			X
Magnesium oleate			X	Zinc valerate			X
Calcium oleate			X	Sodium gluconate	X		
Cobaltous oleate			X	Calcium gluconate		X	
Nickelous oleate			X	Sodium <i>i</i> -galactonate	X		
Manganese oleate			X	Cadmium <i>i</i> -galactonate		X	
Aluminum oleate			X	Sodium dihydroxystearate	X		
Arabic acid	X			Magnesium dihydroxystearate			X
Sodium arabate	X			Sodium salicylate	X		
Magnesium arabate	X			Calcium salicylate		X	
Ferric arabate	X			Sodium gallate	X		
Ammonium valerate	X			Calcium gallate		X	
Sodium valerate	X			Lead arabate			Did not serve as an emulsifying agent.

## THEORETICAL CONSIDERATIONS.

The results of these experiments indicate that when several hydroxyl groups are present in the molecule as exemplified in the molecule of gluconic acid, thus having two or more polar groups present in the same molecule, the divalent salts of such acids show amphoteric emulsion characteristics, that is, they produce oil-in-water or water-in-oil emulsions. With arabic acid combined with iron and magnesium, emulsions of oil-in-water were obtained. Thus, it is entirely possible that the presence of hydroxyl groups in the arabic acid molecule, in addition to the fact that there is present in acacia some univalent salts of arabic acid, are responsible for the production of oil-in-water emulsions with this compound. Likewise similar reasons could be assigned to the production of oil-in-water emulsions by tragacanth.

According to the postulates of Harkins and his associates, when the cross-section of the hydrocarbon chain of an emulsifying agent, and the metallic end of the molecule are of the same magnitude, there is little or no tendency to curvature and hence, no stable emulsion will result. With the univalent salts of these acids containing hydroxyl groups, the packing of the emulsifying agent molecules need not be altered because the polar metallic atoms, and also the polar hydroxyl groups dip into the water. When, however, these compounds are attached to a divalent metal, the hydroxyl groups so increase the magnitude of the hydrocarbon chain that there is little tendency to curvature, and the emulsions obtained are not very stable. It is probable that the presence of so many polar groups in the molecule makes the production of emulsions of oil-in-water or water-in-oil possible.

## CONCLUSIONS.

1. The character of emulsions prepared with certain salts of arabic acid and certain compounds assumed to be related, has been studied.
2. An explanation for the production of oil-in-water emulsions by acacia and tragacanth has been proposed.

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