In view of the lack of a simple valence relation between the atoms, complex atom-groups may be formed in sodium cadmide in a way similar to the formation of $Pb_2^-$ ions in a solution of sodium plumbide, $NaPb_2$, in liquid ammonia,[9] preventing a simplicity of structure.

## Summary

Crystals of the intermetallic compound magnesium stannide, $Mg_2Sn$, have been prepared and investigated by means of Laue and spectral photographs with the aid of the theory of space-groups. The intermetallic compound has been found to have the calcium fluoride structure, with $d_{100} = 6.78 \pm 0.02$ Å. U. The closest approach of tin and magnesium atoms is $2.94 \pm 0.01$ Å. U.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# THE THEORY OF EMULSIFICATION[1]

BY PHILIP FINKLE, HAL D. DRAPER AND JOEL H. HILDEBRAND

RECEIVED JUNE 6, 1923

To disperse one liquid in another in the form of an emulsion requires the doing of work upon the system equal to the product of the interfacial tension multiplied by the increase in surface. An emulsion produced by the mechanical agitation of two pure, incompletely miscible liquids is, therefore, always unstable, the drops of dispersed liquid coalescing upon contact to decrease the interfacial area. To stabilize an emulsion a suitable third substance must be added. Many very effective emulsifiers are known but there has been thus far no altogether satisfactory way to predict the relative powers of different emulsifying agents, either to stabilize the emulsions or to determine which of the two liquids shall be dispersed in the other. Some very useful criteria yielded by experience are more in the nature of rules than theories. We will refer to some of these briefly and then proceed to elaborate an hypothesis which seems to account for the behavior of all emulsifying agents for which we have the data to apply it.

To form a stable foam or emulsion requires that the films of enclosing liquid which separate the bubbles or drops, respectively, shall be stable. This cannot be the case with a pure liquid, since a film represents a surface which is far from the minimum possible. It was shown by Rayleigh that a film is stabilized by the addition of some substance which, by virtue of high adsorption at the surface, greatly lowers the surface tension. In such a case the surface tension is larger at a fresh surface than at an old surface, at which there has been time for the adsorption to take place by diffusion,

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[9] Kraus, THIS JOURNAL, 29, 1557 (1907).

[1] Presented at the Colloid Symposium held at Madison, Wis., in June, 1923, under the auspices of the Department of Chemistry of the University of Wisconsin.

so that if an old surface is threatened with rupture, the new surface thereby formed is stronger than the old, and further strain is diverted from the threatened point. This is the effect of soap in stabilizing the water films between the bubbles in soap suds. Since the globules of dispersed liquid in an emulsion must likewise be held apart by a stable film of the enclosing liquid, the presence of a solute which is highly adsorbed at the interface stabilizes the film and prevents the coalescence of the drops. Thus, soap, which is adsorbed at a water-oil surface as well as at a water-air surface, stabilizes a water-oil emulsion as it does a water-air "emulsion." The difficulty enters when we consider the difference in the type of the emulsion produced by soaps of the alkali metals on the one hand, which disperse the oil in the water, and heavier metal soaps on the other hand, which disperse the water in the oil, for we have adsorption and lowering of the interfacial tension in both cases, and might expect either an oil or a water film to be stabilized.

Bancroft[2] connects the type of emulsion with the phase which is the best solvent for the emulsifying agent. He says,

> "If the adsorption of the emulsifying agent lowers the surface tension on the water side of the interface more than it does on the oil side, the interface will tend to curve so as to be convex on the water side, and we shall have a tendency to emulsify oil in water. If the adsorption of the emulsifying agent lowers the surface tension on the oil side of the interface more than it does on the water side, the interface will tend to curve so as to be concave on the water side, and we shall have a tendency to emulsify water in oil. The simplest way, then, to emulsify oil in water is to add a water-soluble colloid which is adsorbed strongly at the interface and the simplest way to emulsify water in oil is to add an oil-soluble colloid which is adsorbed strongly in the interface."

The idea of a film with two surface tensions, one on the oil side and another on the water side, is rather disconcerting, for no one is likely to measure separately the surface tensions on two sides of an interface, and we have evidence, furthermore, that the emulsifying agent may form films at the interface which are but one molecule thick.[3] The general rule which this theory implies, that the external phase is the one which is the best solvent for the emulsifier is undoubtedly true in most instances. Thus, the alkali metal soaps are soluble in water and disperse oil in water, while the soaps of iron, zinc, aluminum, etc., which are more soluble in benzene and other solvents of low polarity, disperse the water in the other liquid. A contradiction exists, however, in the case of a fatty acid, such as oleic acid, which, though soluble in benzene and not in water, gives an unstable emulsion of benzene in water.

Bhatnagar,[4] on the basis of considerable experimental data, has arrived

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[2] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1922.

[3] Langmuir, (a) *Met. Chem. Eng.*, **15**, 468 (1916); (b) THIS JOURNAL, **39**, 1848 (1917); (c) Adam, *Proc. Roy. Soc. London*, **99A**, 336 (1921); (d) **101A**, 452 (1922); (e) Griffin, THIS JOURNAL, **45**, 1648 (1923).

[4] Bhatnagar, *J. Chem. Soc.*, **119**, 61, 1760 (1921).

at what may likewise be regarded as a rule rather than a theory. "All emulsifying agents having an excess of negative ions adsorbed on them and wetted by water will yield oil-in-water, emulsions, while those having an excess of adsorbed positive ions and wetted by oil give water-in-oil emulsions."

The role played by the orientation of the molecules in the interface in determining the direction of curvature was suggested by Langmuir,[3a] who said,

> "This theory also affords an explanation of the mechanism by which colloids are formed. If a film of closely packed oleic acid molecules covers the surface of water to which sodium hydroxide has been added, OH groups are adsorbed by the COOH radicals, causing an expansion of the lower side of the film without a corresponding expansion of the upper side. This results in the bulging of the film downwards in spots so that it finally detaches itself in the form of particles, the outer surfaces of which consist of COOH groups together with the adsorbed OH, while the interior consists of the long hydrocarbon chains.
>
> "The size of the colloidal particles is determined by the difference in size between the two ends of the molecules, just as the size of an arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed."

Harkins, Davies and Clark[5] applied essentially the same view to explain the reversal of type in emulsions connecting the differences between sodium and potassium oleates as emulsifying agents with the number of oleate radicals in the molecule of the soap.

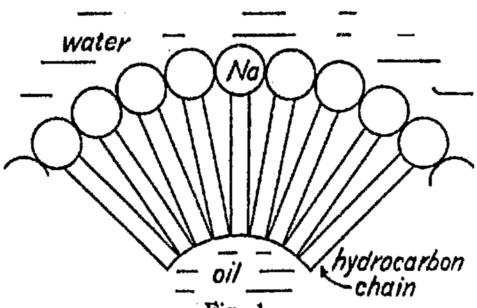

Fig. 1

It is possible to test the orientation hypothesis in a very striking way in the case of the soaps, where the work of Langmuir and of Harkins and co-workers seems amply to justify the assumption that at an interface between water and some liquid of low polarity, such as benzene, any soap would form an interfacial film, which might be as little as one molecule thick, whose molecules would be oriented with the non-polar hydrocarbon chain in the benzene and the polar metallic end in the water.

Now, if the polar group, in the water, occupies more space than is necessary for the closest packing of the hydrocarbon chain, the latter can be packed more closely if the film is convex on the water side, as illustrated in Fig. 1, in a highly idealized form. It is obvious that the direction and degree of curvature, if this hypothesis is correct, should vary, first, with the atomic volume of the metal, being more convex the larger this volume, and second, with the number of hydrocarbon chains attached to a

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[5] Harkins, Davies and Clark, This Journal, 39, 354, 541 (1917).

single metallic atom, according to its valence. Zinc soap, for example, would correspond to Fig. 2, making the interface convex towards the "oil" side; while an aluminum soap should give still more curvature and more stable emulsions of water in oil. Where the cross section of the hydrocarbon chain and of the metallic end are of the same magnitude, there will be no tendency to curvature, and no very stable emulsion, in spite of the high adsorption at the interface which is still possible.

The relative sizes of the metallic atoms in the various soaps may be inferred from the atomic volumes of the metals, and from their atomic diameters in the free state and in compounds. Values are given in Table I. The atomic diameters are according to Hull,[6] Bragg,[7] and Richards,[8] respectively. Of course, hydration may modify the effective atomic domain, but since, for example, the hydration of silver ion can hardly be as great as that of sodium ion, this factor may be expected to increase rather than to oppose the effect of the differences evident in Table I.

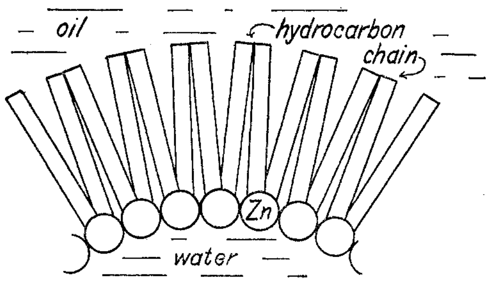

Fig. 2

TABLE I

RELATIVE SIZES OF ATOMS

| | Atomic diameters | | | |
|---|---|---|---|---|
| | In metal | In halides | | |
| Element | Hull | Bragg | Richards | Atomic volumes |
| Cs | .. | 4.75 | 3.8 | 70.6 |
| K | .. | 4.15 | 3.46 (in KCl) | 45.3 |
| Na | 3.72 | 3.55 | 2.85 (in NaCl) | 22.9 |
| Ag | 2.87 | 3.55 | .. | 10.3 |
| Ca | 3.93 | 3.40 | .. | 12.6 |
| Mg | 3.22 | 2.85 | .. | 7.0 |
| Zn | 2.67 | 2.65 | .. | 4.6 |
| Al | 2.86 | 2.70 | .. | 3.4 |
| Fe | 2.48 | 2.80 | .. | 2.3 |

Application of the theory to these figures would indicate that the ability of soaps of calcium, potassium, sodium and silver to emulsify oil in water would *decrease* in the order given; or, viewed from the other angle, their ability to emulsify water in oil should *increase* in this order; that the soaps of the divalent metals, calcium, magnesium and zinc, should have much *less*

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[6] Hull, *Proc. Am. Inst. Elec. Eng.*, **38**, 1171 (1919); *Science*, **52**, 227 (1920).

[7] Bragg, *Phil. Mag.*, [6] **40**, 169 (1920).

[8] Richards, THIS JOURNAL, **45**, 422 (1923).

ability to emulsify oil in water or much *greater* ability to emulsify water in oil, and further, that they should vary in these respects in the order given. The soaps of the trivalent metals aluminum and iron, should exhibit the greatest tendency to emulsify water in oil. The values in the several columns for the relative sizes of iron and aluminum atoms do not all agree, so that the relative emulsifying powers are not definitely indicated by these figures. In general, the values for the atomic diameters of the free metals are most reliable, since the values for the atomic diameters in compounds involve two variables which require some further consideration for their determination. On the other hand, there may be doubt that the elementary atom with its electrons occupies the same domain as does the atomic kernel in the compounds. However, there are enough uncertain factors involved to deter us from attempting to make any very fine distinctions on the basis of existing figures for atomic diameters.

To confirm the difference between the volumes of the metallic end of the molecule in Na and Ag soaps we made approximate determinations of the molecular volumes of their stearates as follows.

MOLECULAR VOLUMES IN SATURATED SOLUTIONS

| Stearate | Acetone | Benzene | Methyl alcohol | Av. |
|---|---|---|---|---|
| Na | 338 | 330 | ... | 334 |
| Ag | 309 | ... | 291 | 300 |

There were known, previous to our own study of this subject, some facts which support this theory of the action of soaps. The soaps of the alkali metals are very effective in stabilizing oil-in-water emulsions, potassium soaps being more effective than sodium soaps.[9] Magnesium soaps emulsify water in oil,[10] salts of the trivalent metals, aluminum and iron, are especially effective in reversing oil-in-water emulsions stabilized by soaps of the alkali metals.[4] Emulsions of oil in water stabilized by sodium oleate are reversed by adding magnesium, aluminum, ferrous or ferric salts in amounts chemically equivalent to the sodium oleate used.[11]

These facts encouraged us to undertake a more systematic study of the applicability of the theory here outlined. Stearates and oleates of the metals listed in Table I were used to prepare several series of emulsions, in which the concentrations of soap, the relative amounts of oil and water used and the degrees of shaking were varied for the different series, but composed of equivalent amounts of soaps in any one series. One liquid was always water, the other benzene, xylene or hexane.

Each group of emulsions was placed in a thermostat maintained at 23° and the time noted when each emulsion began visibly to break down.

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[9] Neunier and Maury, *Collegium*, **1910**, 277; *Chem. Zentr.*, **1910**, II, 1416.

[10] Newman, *J. Phys. Chem.*, **18**, 34 (1914).

[11] Parsons and Wilson, *J. Ind. Eng. Chem.*, **13**, 1116 (1921).

Table II gives the results of a typical series. Other series using stearates in place of oleates, and still others using xylene or hexane in place of benzene gave results so entirely in accord with those here given that their detailed reproduction is hardly necessary. The correspondence in all cases was far more closely in accord with the theory than we had dared to anticipate.

Table II

Types and Stabilities of Emulsions

| | Dispersed phase, Benzene | | | Dispersed phase, Water | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Oleate of | Cs | K | Na | Ca | Ag | Mg | Zn | Al | Fe |
| Approx. life of emuls. | 8 wk. | 8 wk. | 6 wk. | 1 hr. | 1 d. | 2 d. | 24 d. | 7 d. | 10 d. |

The results in these cases are also in accord with the rule that the external phase is the one which is the better solvent for the emulsifier. The soaps of the alkali metals are more soluble in water, the others more soluble in the non-polar liquid. The soaps of iron and aluminum have more symmetrical and less polar molecules and would, therefore, be expected to dissolve best in solvents of low polarity, while the alkali-metal soaps, consisting of a single chain with a highly polar end, cannot dissolve considerably in non-polar liquids but can, on the other hand, form clusters with the hydrocarbon chains in the interior, which can then dissolve "colloidally" in water.

If the orientation theory is correct, the different degrees of curvature natural to films of different soaps should yield drops of different sizes. Since the shaking would never produce drops of uniform size in any emulsion, it was necessary to determine the distribution of a large number of drops between different size intervals. (To take the mean size would obviously give abnormal weight to the occasional very large drops.) A micrometer microscope was used, and the diameter of all drops in the field measured, the field being altered often enough to get a total of 100 drops. The operator did not know which emulsion he was measuring until after he had finished.

Four different series of emulsions with cesium, potassium and sodium stearates were thus measured, the conditions in all series being identical except for the kind of soap used. Table III and Fig. 3 represent the results with one series. The size intervals are represented in scale divisions of the microscope micrometer, of which 60 div. = 0.01 mm. The other series showed a similar displacement of the maxima, although due to differences in shaking, etc., among the different series, the soap did not yield the same maximum each time.

The flatness of the curve for sodium stearate in Fig. 3 evidently has no significance in view of the relatively small number of drops counted. In the other series no such marked difference occurred.

It is evident from these data that the cesium soap gives the smallest drops and the sodium soap the largest, so that the curvatures of the films actually differ in the predicted direction and, therefore, support the theory.

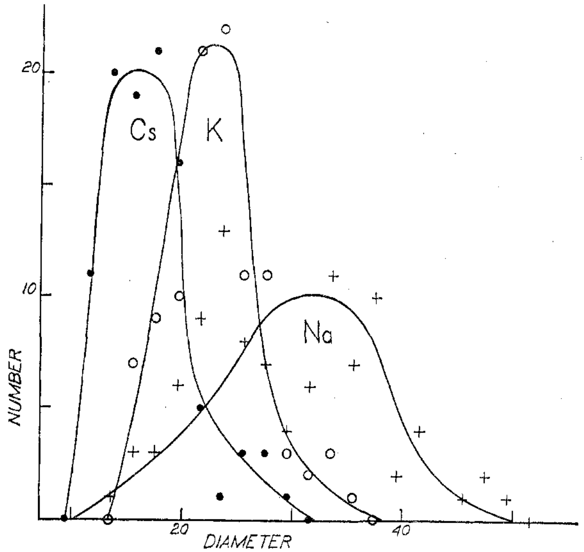

Fig. 3

Many powdered solids have been shown to be capable of stabilizing emulsions.[12] It seems to be possible to account for the type of emulsion produced by the following hypothesis. It is obvious, first, that the powder must collect at the interface in order to be effective. Now, this will occur

Table III

Relation of Drop Size to the Kind of Soap Used

| | No. of drops | | |
|---|---|---|---|
| Size interval | Cesium soap | Potassium soap | Sodium soap |
| 9–10 | 0 | 0 | 0 |
| 11–12 | 11 | 0 | 0 |
| 13–14 | 20 | 0 | 1 |
| 15–16 | 19 | 7 | 3 |
| 17–18 | 21 | 9 | 3 |
| 19–20 | 16 | 10 | 6 |
| 21–22 | 5 | 21 | 9 |
| 23–24 | 1 | 22 | 13 |
| 25–26 | 3 | 11 | 8 |
| 27–28 | 3 | 11 | 7 |
| 29–30 | 1 | 3 | 4 |
| 31–32 | 0 | 2 | 6 |
| 33–34 | 0 | 3 | 11 |
| 35–36 | 0 | 1 | 7 |
| 37–38 | 0 | 0 | 10 |
| 39–40 | 0 | 0 | 2 |
| 41–42 | 0 | 0 | 4 |
| 43–44 | 0 | 0 | 0 |
| 45–46 | 0 | 0 | 1 |
| 47–48 | 0 | 0 | 2 |
| 49–50 | 0 | 0 | 1 |

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[12] Compare Pickering, *J. Chem. Soc.*, **91**, 2010 (1907); *Kolloid Z.*, **7**, 11 (1910). Sheppard, *J. Phys. Chem.*, **23**, 634 (1919). Schlaepfer, *J. Chem. Soc.*, **113**, 522 (1918). Moore, This Journal, **41**, 940 (1919).

only when the solid is wetted by both liquids, with a finite angle of contact of the interface with the solid. In general, one liquid will wet the solid better than the other, as represented in Fig. 4, so that the particles will be drawn more largely into the former. If there are enough solid particles to fill the interface the tendency of the interface to contract will cause it to bend, as shown in Fig. 4, in the direction of the more poorly wetting liquid, which makes it easy for the latter to become the enclosed phase. Of course, a solid, in order to behave in this way, must be easily dispersed in the outer liquid, its particles not tending to agglomerate therein or to stick together when serving as protective armor for emulsified drops. One should, therefore, be able to predict whether or not a given solid powder can stabilize an emulsion, and also which liquid will become the dispersed phase, by noting the angle of contact of the interface with the solid. Data upon this point are not abundant but seem to be altogether confirmatory, and a microscopic examination of an emulsion of water in benzene stabilized by lampblack confirmed the picture given in Fig. 4.

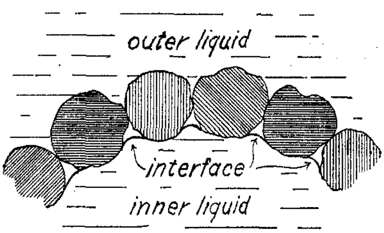

Fig. 4

We suggest that this picture may serve to explain the Bancroft rule that a colloid emulsifier causes the phase in which it is soluble to be external. A colloidal particle with only a few polar groups upon it would remain largely in the oil phase and *vice versa*, so that the natural curvature of the surface may be determined in much the same way as with powdered emulsifiers.

## Summary

1. The present status of the theory of emulsification has been outlined.

2. The types and relative stabilities of emulsions formed by the aid of various soaps have been explained by the aid of the theory of orientation of the soap molecules in the interface.

3. The curvature of the film of soap adsorbed at the interface is more convex toward the water, yielding more stable emulsions of the oil-enclosed type, the larger the metal atom in the soap.

4. As the number of hydrocarbon chains attached to a single metallic atom increases (with the valence of the metal) the curvature is reversed, becoming strongly convex towards the oil phase with soaps of the trivalent metals, aluminum and iron, which yield the most stable emulsions of water in oil.

5. Experimental data upon the type and relative stabilities of emulsions of various liquids with water show that the transition from the most stable oil-enclosed to the most stable water-enclosed emulsion for both stearates

and oleates follows the order: cesium, potassium, sodium, calcium, silver, magnesium, zinc, aluminum, iron. This order is in accord with the valences and atomic diameters of the metals, as interpreted by the orientation theory.

6. It is suggested that the type of emulsion produced by a solid powder is determined by the angle of contact of the interface with the solid. In order for the powder to remain in the interface the angle must be finite, and unless the angle is 90°, the interface will be on one side or the other of the points of contact of the particles, and its tension will cause the film to be concave on that side.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 35]

# DISPLACEMENT OF METALS FROM SOLUTIONS OF THEIR SALTS BY LESS ELECTROPOSITIVE ELEMENTS

## I. THE REPLACEMENT OF SODIUM AND POTASSIUM BY MAGNESIUM AND ALUMINUM

BY F. W. BERGSTROM[1]

RECEIVED JUNE 22, 1923

### Introduction

Franklin[2] found that a solution of potassium amide in liquid ammonia reacts readily with magnesium to form an opaque blue solution, which disappears within a few hours leaving a precipitate of the sparingly soluble potassium ammono-magnesiate, $Mg(NHK)_2.2NH_3$.[3] During the preparation in an analogous manner of potassium and sodium ammono-aluminates the author observed the production of similar intermediate blue solutions. The present work, which was undertaken primarily for the purpose of accounting for the phenomena observed, and of establishing the equations for the reactions, is a portion of a general investigation dealing with the action of potassium and potassium amide upon the elements.

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[1] National Research Council Fellow.

[2] Franklin, THIS JOURNAL, **35**, 1463 (1913).

[3] Potassium and sodium amides are bases of the ammonia system, and behave in this solvent just as potassium and sodium hydroxides behave in water. Thus an aqueous solution of potassium hydroxide dissolves aluminum and zinc to form, respectively, potassium aquo-aluminate and potassium aquo-zincate, while a liquid ammonia solution of potassium amide dissolves aluminum to form a potassium ammono-aluminate, and reacts with zinc to form a sparingly soluble potassium ammono-zincate. Potassium ammono-magnesiate, on the other hand, has no analog in the water system, because the much greater solvolytic power of water relative to that of ammonia renders its existence impossible. Reactions thus occur in ammonia that cannot take place in water. For a further explanation of the ammonia system of acids, bases and salts, see *Am. Chem. J.*, **47**, 285 (1912); *Proc. Eighth Int. Cong. Appl. Chem.*, **6**, 119 (1912).