ORGANOPHILIC COLLOIDAL CLAY

AS AN

EMULSIFIER

by

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Submitted in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Chemistry

from the
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Signature of Author

Department of Chemistry May 20, 1949

Signature of Professor in
Charge of Research

Signature of Head
of Department
May 20, 1949

Professor J. S. Newell
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Dear Sir:

In partial fulfillment of the requirements for the degree of bachelor of science in chemistry from the Massachusetts Institute of Technology, I herewith submit this thesis entitled, *Organophilic Colloidal Clay as an Emulsifier*.

Very truly yours,

Mary C. Cretella
ACKNOWLEDGEMENT

I should like to express my gratitude to Professor Ernst A. Hauser for suggesting the subject of this thesis, and for his help, suggestions and encouragement.
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I. SUMMARY

The purpose of this work was to ascertain if an organophilic colloidal clay could be used as an emulsifying agent to produce a water-in-oil emulsion, since natural colloidal clay exhibiting hydrophilic properties has been successfully used as an oil-in-water emulsifier.

Natural bentonite was converted by base exchange reaction into an organophilic one and used as an emulsifier in a water/oil system. Results have proven that so treated clay causes the formation of water-in-oil emulsions.
II. INTRODUCTION

A. GENERAL THEORY OF EMULSIONS

Emulsions are intimate mixtures of two immiscible liquids, one of them being dispersed in the other in the form of droplets. Two pure liquids, e.g. benzene (C₆H₆) and water when agitated by shaking or in some other manner will temporarily produce an emulsion, but as soon as agitation ceases, the droplets of each liquid coalesce and reseparation into separate layers occurs. Such a system as this lacks stability. Therefore, there are three constituents necessary to form an emulsion, two immiscible liquids and a substance which helps to promote the dispersion of one of the liquids in the other and to maintain the dispersed condition—an emulsifying agent.

In each emulsion there are two phases, the internal or discontinuous phase and the external or continuous phase. The former is the dispersed liquid and the latter is the dispersion medium. In the majority of emulsions one of the phases is water or an aqueous solution of salts, water soluble organics, etc. This phase is commonly denoted as the water phases. The other phase, called the oil phase, comprises materials such as hydrocarbons, resins, waxes, and nitrocellulose solutions, all of which have in common one important factor, their insolubility in water. Those substances exhibiting an affinity towards water have been labeled hydrophilic substances.
The other group showing an affinity for oil or oil-like substances, and a hostility towards water are called hydrophobic substances.

With any given pair of immiscible liquids, two types of emulsions are possible. One type is that in which the water is the external phase and the oil is the internal phase, known as an oil-in-water emulsion symbolized by (O/W). The other type with oil as the external and water as the internal phase is known as a water-in-oil emulsion (W/O). There is no general law regulating the type obtainable. The determination of the internal phase depends on the prevailing conditions, the emulsifying agent, the phase-volume ratios, and the means of introducing and incorporating the components.

The properties of the resulting solution are determined by the external phase. Consider as an example an emulsion where water is the external phase (an O/W emulsion). Here the properties of water govern. The emulsion can be diluted with water, but not with oil or oil-like substances. It will conduct an electric current since the water phase is continuous, and the emulsion can be colored with water soluble dyes. This latter property is useful in identifying the emulsion type.

B. EMULSIFYING AGENTS

One of the factors which hinders emulsification is high interfacial tension. When a liquid is in contact with another liquid or solid as in emulsions, the boundaries are termed interfaces. The tension occurring at the
interfaces are then called interfacial tensions. Water and oil have a high interfacial tension and to reduce this tension sufficiently for emulsification requires the use of an emulsifying agent. Its use is thus. The polar end of the emulsifying agent's molecule with a strong affinity toward the polar liquid (water) will tend to pull the molecules into the water phase, while the non-polar end will tend to draw the molecules into the non-polar, oil phase. If each force is equally strong, neither will succeed and there will result an accumulation between the boundaries of the two surfaces with a resultant reduction of interfacial tension.

```
  □ □ □ □  Non-polar liquid
  □ □ □ □  Emulsifying Agent
      □ □ □ □  Polar liquid
```

Figure 1. Orientation at the interfacial film

The interfacial film is comprised of at least three layers of molecules oriented as shown in Figure 1. A balance like this is maintained, as mentioned before, only if the two portions of the molecule are balanced. If one portion is much more dominant, e.g., the polar end, the molecule will be completely adsorbed in the polar phase.

The type of emulsion produced depends on the agent employed. If both forces, polar and non-polar are uniformly distributed in the molecule, the agent will not tend to
promote either type of emulsion. However, if one portion is only very slightly more dominant, there will be a greater affinity towards that prominent phase and the agent will accumulate with the bulk of its volume at that phase side. Agents which thus promote O/W emulsions are termed hydrophilic; agents promoting W/O, hydrophobic.

A substance employed as an emulsifying agent must at least fulfil these two conditions.

1. It must reduce the interfacial tension.
2. It must stabilize the emulsion.

In addition:

3. It should be chemically stable.
4. It is desirable that it be selective, promoting very definitely one and only one type of emulsion, either O/W or W/O.
5. It is advantageous that it be nearly colorless, fairly odorless, and cheap in use.

In certain instances finely divided solids may act as emulsifying agents. Pickering found that the basic sulphates of iron, copper, nickel, zinc, and aluminum act as efficient emulsifying agents for mineral oil in water. He also believed that the success and efficiency of emulsification depended on the size of the solid particle employed.

A North African argillaceous earth was found which readily emulsified oils in water. Briggs and Schmidt found that hydrous ferric oxide in aqueous suspension
was a "fairly good" emulsifier for benzene. On the other hand, carbon black and mercuric iodide promotes the emulsification of water in benzene. A conclusion in this respect was reached by Schaepler who in 1918 formulated that "insoluble particles, which are more easily moistened by oil than by water, will have a tendency to facilitate the emulsification of water in oil". Moore found that the amount of carbon used varied inversely as the diameter of the emulsified water globules.

Colloidal clay as an efficient emulsifying agent for oils has been investigated by Weston. He contends that colloidal clay may give either an O/W or a W/O emulsion. Since it is generally understood that a given emulsifying agent will promote only one type of emulsion with any two given liquids to be emulsified, further investigation is indicated. So far colloidal clays have only given oil in water type emulsions.

C. PURPOSE

It therefore is proposed to prove by demonstration that with an ordinary alkali base montmorillonite colloidal clay, only one type of emulsion is possible—oil-in-water.

It therefore seemed of interest to ascertain if a bentonitic clay having been rendered organophilic would act as a water-in-oil emulsifying agent.
III. PROCEDURE

The colloidal clays used throughout are sodium montmorillonite and dietyldodecyl ammonium bentonite (Bentone 18)*. Water used in mixing the emulsions, unless otherwise indicated, is distilled water; oil used, unless otherwise stated, is benzene. The apparatus used in mixing the emulsions is a Waring blender which for most efficiency is used at low speed.

A. DETERMINATION OF INFLUENCING FACTORS.

(1) Size of particles in solid emulsifier.

The effectiveness of a solid emulsifier varies inversely as the particle size. The greater the surface, i.e. the smaller the particle, the more of the internal phase may coat it and become more easily emulsified. Since the size of the particles of clay employed were of colloidal dimensions, there already exists optimum conditions and further investigation is unnecessary.

(2) Concentration of Solid

The conclusion has been made that emulsification depends upon the amount of solid used, varying in direct proportion. However, there is an optimum concentration which is most effective. This optimum was found by maintaining a constant ratio of oil and water and varying the concentration of solid

* Supplied by the National Lead Company
until the peak of efficiency was determined.

(3) Relative proportions of emulsifying liquids.

The relative proportion of oil and water affects the stability of the emulsion. If oil and water start out in a certain ratio with oil as the external phase, the addition of more water will vary the stability. The determination of the most durable ratio of oil and water was found in each type of emulsion by holding the amount of one constituent constant and varying the other until the breakdown of the emulsion indicated instability. The amount of clay used was the value determined in III-A2. This latter value was rechecked when the ratio of greatest stability had been determined.

(4) Relative wetting of colloidal clay and previous wetting of surfaces in contact with emulsion.

Pickering has pointed out the condition that for finely divided solid emulsifiers used in preparing oil-in-water emulsions, the agent must be more readily wetted by water than by oil. It follows then, that in preparing emulsions of the water-in-oil variety, the emulsifier should be more readily wetted by the oil than by the water. This factor was investigated by conducting two series of experiments with each clay. In the first series, the clay was dispersed in oil (oil
being the phase desired as external), and an emulsifier formed by the addition of water. In the second series, the clay was dispersed first in water (water here being the desired external phase) and the emulsion was formed by the addition of oil.

Also it has been suggested that the emulsification is assisted if the surfaces in direct contact are first coated with the desired external phase. This was investigated by rinsing the emulsifying apparatus, before each use, with the desired external phase liquid.

(5) Method of Agitation

Various proposals have been made for mixing emulsions. One suggestion was intermittent shaking by hand.

Using a test tube, a steady shaking of one-half to one and one-half minutes in one-half minute steps was tried. Also a thirty second shake followed by a thirty second rest; a thirty second shake followed by a ten second rest.

The Waring blender was also tried using the high speed and then again using the low speed.

In each of these cases, the amounts of each of the substituent used were those found in III-A2 and III-A3.

(6) Method of Introduction of Ingredients
The effectiveness of the previous wetting of the emulsifying agent has already been explored. However, the method of introduction of the second liquid, the internal phase, might cause some difference in the emulsion results. To explore this possibility three methods of addition were devised:

a) The second phase was introduced by rapid pouring while the other phase was being agitated.

b) One quarter of the amount of the second phase was introduced, allowed to mix in and then the remainder was added.

c) The whole amount of liquid was allowed to run in at a slow trickle.

B. INVESTIGATION OF POSSIBILITIES OF O/W EMULSION USING DIETHYL-DODECYL AMMONIUM BENTONITE.

In order to encourage the formation of an O/W emulsion, the diethyl-dodecylammonium bentonite was treated as an O/W emulsifier. That is, in accordance with the results obtained from III-A (See IV-A) the emulsions were prepared and mixed.

To further influence the possibilities of an O/W emulsion using the diethyl-dodecylammonium bentonite as the emulsifying agent the use of auxiliary emulsifiers was employed. Both gum arabic and dimethyl phthalate have been identified as aiding the emulsification of oil in water. Both of these agents were used separately and together in addition
to the clay and emulsions of the W/O type were attempted.
IV RESULTS

A. INFLUENCING FACTORS

Investigation showed that in order to facilitate the formation of an O/W emulsion the addition as an auxiliary emulsifying agent of 1CC of dimethyl phthalate was necessary. When this was not added, the clay particles tended to agglutinate when mixed with the water.

The ideal method for mixing the emulsions was determined to be as follows:

With the water and oil in a one-to-one ratio 0.6 grams of the clay was added to one of the liquid constituents. It did not matter to which one, but to facilitate matters it was added to the constituent comprising the external phase. This dispersion was then added to the Waring blender, which did not require previous surface coating with the external phase liquid and agitated for about ten seconds to thoroughly disperse any clay particles which may have tended to settle. The internal phase liquid was then added, while agitation continued, at a slow trickle and the whole mixture was allowed to agitate at low speed for approximately fifty seconds.

A complete tabulation of the procedure outlined in II-A2, III-A3 and III-A4 will be found in the appendix (VII).

B. POSSIBILITIES OF O/W EMULSIONS USING DIETHYL DODECYLAMMONIUM BENTONITE

The results of this investigation were decidedly negative. Neither the gum arabic nor the dimethyl phthalate
had any effect on the type of emulsion formed. In each case the type was W/O with no appreciable change in apparent stability.

The use of adverse conditions for W/O formation had no effect on its final type.

In all cases, the tests used to determine the emulsion type were: (1) one drop of emulsion in distilled water and one drop in benzene—dilution occurs with the liquid forming the outer phase; (2) addition of a crystal of water soluble violet dye (3 mg/l00CC).
V. DISCUSSION OF RESULTS

The organophilic clay, diethyldecylammonium bentonite, results from the base exchange of an alkali ion by ammonium ion. The clay therefore has a sufficient non-polar tendency to enable it to act as a hydrophobic agent. The non-polarity is dominant enough to render inversion an impossibility.

The fact that variations in the factors discussed in III-A and IV-A resulted in no change in emulsion type, but merely caused the stability to fluctuate further indicates that the emulsifying agent is the prime factor in deciding emulsification type.
VI. CONCLUSION

It is now established irrevocably that diethyldodecyl-ammonium bentonite is able to form a W/O emulsion and not just that, but also it cannot under any conditions be made to form one of the O/W type.

For the first time, ammonium ion substituted clay as an emulsifying agent has produced a water-in-oil emulsion.
Table 1

A. Tests for Optimum Concentration of Solid.

<table>
<thead>
<tr>
<th>No.</th>
<th>cc Bz</th>
<th>mg Clay</th>
<th>cc H₂O</th>
<th>Emulsion Type</th>
<th>Emulsion Comment</th>
<th>Per cent Breakdown</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1811</td>
<td>35</td>
<td>100</td>
<td>35</td>
<td>W/O</td>
<td>Thin</td>
<td>23.0 per cent</td>
</tr>
<tr>
<td>B1812</td>
<td>35</td>
<td>200</td>
<td>35</td>
<td>W/O</td>
<td>Medium</td>
<td>9.6 per cent</td>
</tr>
<tr>
<td>B1813</td>
<td>35</td>
<td>300</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>10.5 per cent</td>
</tr>
<tr>
<td>B1814</td>
<td>35</td>
<td>400</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>10.4 per cent</td>
</tr>
<tr>
<td>B1815</td>
<td>35</td>
<td>500</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>10.0 per cent</td>
</tr>
<tr>
<td>B1816</td>
<td>35</td>
<td>600</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>8.9 per cent</td>
</tr>
<tr>
<td>B1817</td>
<td>35</td>
<td>700</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>20.0 per cent</td>
</tr>
<tr>
<td>B1818</td>
<td>35</td>
<td>800</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>21.4 per cent</td>
</tr>
</tbody>
</table>

B. Recheck as in III-A3

<table>
<thead>
<tr>
<th>No.</th>
<th>cc Bz</th>
<th>mg Clay</th>
<th>cc H₂O</th>
<th>Emulsion Type</th>
<th>Emulsion Comment</th>
<th>Per cent Breakdown</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1821</td>
<td>35</td>
<td>800</td>
<td>35</td>
<td>W/O</td>
<td>Thin</td>
<td>23.6 per cent</td>
</tr>
<tr>
<td>B1822</td>
<td>35</td>
<td>900</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>13.0 per cent</td>
</tr>
<tr>
<td>B1823</td>
<td>35</td>
<td>1000</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>11.0 per cent</td>
</tr>
<tr>
<td>B1824</td>
<td>35</td>
<td>1100</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>10.8 per cent</td>
</tr>
<tr>
<td>B1825</td>
<td>35</td>
<td>1200</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>9.4 per cent</td>
</tr>
<tr>
<td>B1826</td>
<td>35</td>
<td>1300</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>8.6 per cent</td>
</tr>
<tr>
<td>B1827</td>
<td>35</td>
<td>1400</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>8.6 per cent</td>
</tr>
<tr>
<td>B1828</td>
<td>35</td>
<td>1500</td>
<td>35</td>
<td>W/O</td>
<td>Viscous</td>
<td>22.0 per cent</td>
</tr>
</tbody>
</table>
Graph of Table I

Per cent Breakdown

Milligrams of Clay
Table II-A
Proportions of Oil and Water

A. Using 0.6 grams Sodium Montmorillonite and 1cc of Dimethyl Phthalate

<table>
<thead>
<tr>
<th>No.</th>
<th>cc Bz</th>
<th>cc H₂O</th>
<th>Emulsion Type</th>
<th>Comment</th>
<th>Per cent Emulsified</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1830</td>
<td>35</td>
<td>45</td>
<td>O/W</td>
<td>Fair</td>
<td>66.7 per cent</td>
</tr>
<tr>
<td>B1831</td>
<td>35</td>
<td>35</td>
<td>O/W</td>
<td>Good</td>
<td>91.8 per cent</td>
</tr>
<tr>
<td>B1832</td>
<td>35</td>
<td>20</td>
<td>O/W</td>
<td>Poor</td>
<td>58.7 per cent</td>
</tr>
<tr>
<td>B1833</td>
<td>35</td>
<td>10</td>
<td>O/W</td>
<td>Very Poor</td>
<td>20.0 per cent</td>
</tr>
<tr>
<td>B1834</td>
<td>35</td>
<td>5</td>
<td>O/W</td>
<td>No emulsion</td>
<td>none</td>
</tr>
<tr>
<td>B1835</td>
<td>35</td>
<td>45</td>
<td>O/W</td>
<td>Fair</td>
<td>64.0 per cent</td>
</tr>
<tr>
<td>B1836</td>
<td>35</td>
<td>35</td>
<td>O/W</td>
<td>Good</td>
<td>90.5 per cent</td>
</tr>
<tr>
<td>B1837</td>
<td>35</td>
<td>20</td>
<td>O/W</td>
<td>Poor</td>
<td>60.1 per cent</td>
</tr>
<tr>
<td>B1838</td>
<td>35</td>
<td>10</td>
<td>O/W</td>
<td>Very poor</td>
<td>20.5 per cent</td>
</tr>
<tr>
<td>B1839</td>
<td>35</td>
<td>5</td>
<td>O/W</td>
<td>No emulsion</td>
<td>none</td>
</tr>
</tbody>
</table>
Graph of Table II-A

Per cent of Emulsification

Milliliters of Benzene
### Table II-B
Proportions of Oil and Water

B. Using 0.6 grams Diethyldodecylammonium Bentonite

<table>
<thead>
<tr>
<th>No.</th>
<th>cc Bz</th>
<th>cc H₂O</th>
<th>Emulsion Type</th>
<th>Comment</th>
<th>per cent breakdown</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL840</td>
<td>45</td>
<td>35</td>
<td>W/O</td>
<td>Fair</td>
<td>65.0 per cent</td>
</tr>
<tr>
<td>BL841</td>
<td>35</td>
<td>35</td>
<td>W/O</td>
<td>Good</td>
<td>93.0 per cent</td>
</tr>
<tr>
<td>BL842</td>
<td>20</td>
<td>35</td>
<td>W/O</td>
<td>Poor</td>
<td>60.0 per cent</td>
</tr>
<tr>
<td>BL843</td>
<td>10</td>
<td>35</td>
<td>W/O</td>
<td>Very poor</td>
<td>19.0 per cent</td>
</tr>
<tr>
<td>BL844</td>
<td>5</td>
<td>35</td>
<td>W/O</td>
<td>No emulsion</td>
<td>none</td>
</tr>
<tr>
<td>BL845</td>
<td>45</td>
<td>35</td>
<td>W/O</td>
<td>Fair</td>
<td>63.2 per cent</td>
</tr>
<tr>
<td>BL846</td>
<td>35</td>
<td>35</td>
<td>W/O</td>
<td>Good</td>
<td>91.5 per cent</td>
</tr>
<tr>
<td>BL847</td>
<td>20</td>
<td>35</td>
<td>W/O</td>
<td>Poor</td>
<td>62.3 per cent</td>
</tr>
<tr>
<td>BL848</td>
<td>10</td>
<td>35</td>
<td>W/O</td>
<td>Very poor</td>
<td>22.1 per cent</td>
</tr>
<tr>
<td>BL849</td>
<td>5</td>
<td>35</td>
<td>W/O</td>
<td>No emulsion</td>
<td>none</td>
</tr>
</tbody>
</table>
Graph of Table II-B
### Table III
(See III-A4)

#### A. Clay used is Sodium Montmorillonite

<table>
<thead>
<tr>
<th>No.</th>
<th>grams clay</th>
<th>cc DMP*</th>
<th>cc Bz</th>
<th>cc H₂O</th>
<th>Type</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1851</td>
<td>0.6</td>
<td>1cc</td>
<td>35</td>
<td>35</td>
<td>O/W</td>
<td>Clay and DMP dispersed in oil</td>
</tr>
<tr>
<td>B1852</td>
<td>0.6</td>
<td>1cc</td>
<td>35</td>
<td>35</td>
<td>O/W</td>
<td>Clay and DMP dispersed in H₂O</td>
</tr>
<tr>
<td>B1853</td>
<td>0.6</td>
<td>1cc</td>
<td>35</td>
<td>35</td>
<td>O/W</td>
<td>Condition of B1851 with previous oil rinsing</td>
</tr>
<tr>
<td>B1854</td>
<td>0.6</td>
<td>1cc</td>
<td>35</td>
<td>35</td>
<td>O/W</td>
<td>Cond. of B1851 with previous water rinsing</td>
</tr>
<tr>
<td>B1855</td>
<td>0.6</td>
<td>1cc</td>
<td>35</td>
<td>35</td>
<td>O/W</td>
<td>Cond. of B1852 plus cond. of B1853</td>
</tr>
<tr>
<td>B1856</td>
<td>0.6</td>
<td>1cc</td>
<td>35</td>
<td>35</td>
<td>O/W</td>
<td>Cond. of B1852 plus cond. of B1854</td>
</tr>
</tbody>
</table>

* DMP = Dimethyl Phthalate

#### B. Clay used in Diethyldecylammonium Bentonite

<table>
<thead>
<tr>
<th>No.</th>
<th>grams clay</th>
<th>cc Bz</th>
<th>cc H₂O</th>
<th>Type</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1861</td>
<td>0.6</td>
<td>--</td>
<td>35</td>
<td>35</td>
<td>W/O</td>
</tr>
<tr>
<td>B1862</td>
<td>0.6</td>
<td>--</td>
<td>35</td>
<td>35</td>
<td>W/O</td>
</tr>
<tr>
<td>B1863</td>
<td>0.6</td>
<td>--</td>
<td>35</td>
<td>35</td>
<td>W/O</td>
</tr>
<tr>
<td>B1864</td>
<td>0.6</td>
<td>--</td>
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VIII  BIBLIOGRAPHY


2. Clayton, W.: Theory of Emulsions and Emulsification


