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The Stability Characteristics of
Monodisperse Hydrophobic Soln

by
Paul Elliott Merrifield, M.A.

A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
Doctor of Philosophy

Houston, Texas
May, 1951
DEDICATED

to

DR. HARRY B. WEISER
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I. INTRODUCTION
I. INTRODUCTION

Various theories for the stability of hydrophobic colloid systems have been advanced throughout the years. W.C.M. Lewis (12), Derjaguin (2), Langmuir (10), Levine and Dube (11), Gouy and Chapman (6), Debye and Hückel (1), all have made their contributions to a clearer understanding of colloid stability. Recently, however, Verwey and Overbeek (14) have proposed a theory, new in the sense that it makes use of the better features put forth by the above-mentioned authors, which gives us a criterion for colloid stability and a clear picture of the mechanism of the coagulation process. In this report the theory of Verwey and Overbeek will be discussed and evaluated.

Colloid stability is influenced by two factors which must be considered separately.

1. A sol acquires stability by the formation of a double layer of sufficient strength to prevent agglomeration.
2. A sol once formed loses stability by the addition of foreign electrolytes which ultimately leads to complete coagulation.

Stability then is not just a function of the interaction of point charges but rather a function of the interaction of the double layers surrounding the colloidal particles. This interaction of double layers will be
considered for the case of spherical particles which is a
good approximation to the shape of colloidal particles
actually encountered.

The potential energy of interaction is made up of
two parts: the attractive potential $V_a$ which is based
entirely on the London-Van der Waals forces, and the
repulsive potential $V_r$ which is calculated from free
energy considerations. $V = V_a + V_r$ Derivations of the
respective equations for $V_a$ and $V_r$ will not be given here.
The expressions and definitions of symbols used are as
follows:

$$V_a = -\frac{A}{6} \left( \frac{2}{S^2} + \frac{2}{S^2} + \ln \frac{S^2 - 4}{S^2} \right)$$

$$V_r = \frac{D a \gamma_o^2}{2} \ln \left( 1 + e^{-\tau(s-2)} \right) \text{ for } \tau > 2.5$$

$$V_r = \frac{D a \gamma_o^2}{S} e^{-\tau(s-2)} \quad \text{ for } \tau < 2.5$$

where $A = 2 \times 10^{-12}$ (evaluated by Hamaker) - best
value by Overbeek

$S = \frac{R}{a} \quad R =$ distance between centers $\quad a =$ particle radius

$D =$ dielectric constant $\quad \gamma_o =$ surface potential of particles

$\tau = \chi \rho^2 = \frac{8 \pi n e^2 v^2}{D k T} \quad \text{ (from Debye-Hückel)}$

When two spherical particles are close together

$V_a$ behaves in the following manner. Setting $S = 2a + H$
where \( H \) is the shortest distance between the two spheres and assuming \( H \ll a \), \( V_a \) is approximated by

\[
V_a = \frac{-4a}{12H} = \frac{-4}{12(S-2)}
\]

and varies reciprocally as the distance between spheres.

The repulsive potential \( V_r \) is always positive and decreases with increasing \( S \). A plot of total potential energy of interaction \( V \) versus \( S \) contains three variable quantities, namely \( a, V_0, \) and \( \chi \). Therefore we must necessarily have three graphs of \( V \) vs. \( S \) showing the variations with (1) the particle size, (2) the surface potential, and (3) the quantity \( \chi \) which is proportional to the concentration of coagulating electrolyte.

From these curves of potential energy of interaction it is possible to derive a criterion for colloid stability. Qualitatively it will be noticed that a sol has stability only if the curves have a maximum which must be of the order of \( kT \) (4.2 x 10^{-14} \text{ ergs}) to prevent coagulation.

Treating the coagulation process as a diffusion problem as done by Fuchs (5), a more quantitative expression for stability may be found. If one of the particles is considered fixed, the question is how many other particles touch it in one second. This assumes that every collision leads to agglomeration. The number of particles making collision is determined by two factors; the diffusion
under the influence of concentration gradients, and the displacement caused by the interaction of two particles. The number of particles, \( G \), may be calculated from the following equation:

\[
G = 4\pi R^2 (d \oint n/R + n/\rho \oint V/R)
\]

where \( R \) is the distance from the center of the fixed particle; \( d \), the diffusion constant; \( n \), the number of particles per cm\(^3\); \( \rho \) the friction constant \((\sim 6\pi \eta a)\); and \( V \) the energy of interaction of two particles at a distance \( R \).

This equation must be solved with the boundary conditions

\[
n = 0 \quad \text{when} \quad R = 2a
\]

and

\[
n = n_0 \quad \text{when} \quad R = \infty
\]

According to Einstein (3), \( d = kT/\rho \). If the central particle is no longer considered fixed but also free to move, the diffusion constant is doubled or \( d' = 2d \). Also the interaction force is doubled or \( \rho' = \rho/2 \).

With \( V_{\infty} = 0 \) and replacing \( d \) by \( 2d \) and \( \rho \) by \( kT/2d \) the solution of the equation becomes

\[
n = n_0 e^{-V/kT} + Ge^{-V/kT} \int_{\infty}^{R} e^{V/kT} \frac{dR}{R^2}
\]

To satisfy the condition for \( R = 2a \), \( G \) must equal

\[
G = \frac{4\pi d'n_0}{\int_{2a}^{\infty} e^{V/kT} \frac{dR}{R^2}}
\]
G is a direct measure of the flocculation velocity. The value of G when \( V = 0 \) (no interaction between particles except for a very steep attraction when the particles touch) is equal to \( G_{V=0} = 8 \pi \delta^2 n_0 \) and is a measure of rapid coagulation.

The interaction \( V \) diminishes the velocity of coagulation by a factor

\[
\nu = 2a \int_2^\infty \frac{V/kT}{R^2} \, dR = 2 \int_2^\infty \frac{V/kT}{S^2} \, dS \quad \text{(since } S = R/a) 
\]

The time of coagulation of a rapidly coagulating sol as derived by Von Smoluchowski (15) and confirmed by Kruyt and Van Arkel (6) is \( t = 1/8 \pi \delta \nu n_0 \). As before \( d = kT/\nu = kT/6 \pi \nu a \) and the time of coagulation becomes

\[
t = \frac{3\pi}{4kTn_0}
\]

which for water as the dispersion medium and \( T = 305^\circ \), is equal to \( t = 1.37 \times 10^{11} \). For a typical gold sol containing 57 mg/l with a particle radius of 25 millimicrons, the value of \( n_0 \) is \( 4.51 \times 10^{10} \) and \( t \) is the order of 3 seconds.

A sol may be considered reasonably stable if it does not coagulate in a month's time which means that the flocculation time should be greater than \( 2.6 \times 10^6 \) seconds. Thus \( W \), the ratio between slow and fast coagulation must have the value of \( 8.5 \times 10^5 \) to insure reasonable stability. A concentrated sol seldom has
no > 10^{14}, and the stability ratio in this case should
then be of the order of 10^9. Therefore our criterion for
stability is that W should fall within the range 10^5 to 10^9
depending on the concentration of the sol.

The problem then resolves itself into the evaluation
of W. This may be done by graphical integration of a plot
of eV/kT/ s^2 vs. S. As one performs this integration, it
becomes obvious that the most important factor in the
evaluation of W is the maximum of the potential energy
of interaction curve. Once again qualitatively speaking
V_{max} must equal 15kT to 25kT for W to equal 10^5 to 10^9.

The preceding discussion has been a condensation of
the theory of Verwey and Overbeek. An extension of the
table to include zeta potential, in order that
electrophoresis data may be employed, follows logically.
In the Gouy-Chapman (6) picture of the double layer, zeta-
potential is the variable portion of total surface potential,
and therefore direct substitution of \zeta for \psi is not
unreasonable. In fact Overbeek suggests in his theory
that since \psi is not a constant but varies with concen-
tration of electrolyte, the Stern (13) correction should
be applied, namely that \psi be used instead of \psi.

Stern's \psi and the zeta-potential if not identical certainly
vary in the same manner. The validity of the substitution
of \zeta for \psi withstands numerical evaluation, as completely
analogous results are obtained for V and W.
The advantage in using zeta-potential values is that the number of variables involved in V and W may be reduced. Recall that in Overbeek's theory V (and thus W) varied with \( a \), the particle radius; \( \psi_0 \), the surface potential; and \( X \), which is a function of concentration and valency of electrolyte. In electrophoresis measurements, we determine the variation of \( \psi \) with respect to \( X \); and for each case, we may actually find an equation for this variation, and express \( \psi \) in terms of \( X \).

Of the three variables under consideration, the particle radius is the most nearly constant. During a coagulation process the particle size certainly increases with increasing concentration of electrolyte. However, until coagulation actually occurs, it is essentially impossible to observe this change by any known method. Analyzing the equation for the repulsive potential, 

\[
V_r = \text{Da} \frac{\psi_0^2}{2} \ln(1 + e^{-Ta(S-2)}),
\]

any slight change in \( a \) influences the equation in two ways. First, it increases the coefficient of the logarithmic term, thus increasing \( V_r \). Second, it increases the negative exponential producing a decrease in \( V_r \). The net effect is an increase at low values of \( S \) and a decrease at high values of \( S \). Therefore by considering \( a \) to be constant, the total potential peak is lowered and thus the value of \( W \) is somewhat small.
With the above assumptions, \( V \) now varies with \( \mathbf{x} \) only. Previously \( V = f(\psi, \mathbf{x}, a) \). Substituting \( \psi \) for \( \psi_e \) and observing that \( \psi = f'(\mathbf{x}) \), \( V = f'(\mathbf{x}, a) \).

Assuming \( a \) to be a constant, \( V = a f'(\mathbf{x}) \).

The goal of this research is therefore to observe the variation of the zeta-potential with the concentration and valency of coagulating electrolyte.

Using this data, the validity of Verwey and Overbeek's theory will be tested to determine whether or not the stability ratio \( W \) is a satisfactory criterion of colloid stability.
II. EXPERIMENTAL
II. EXPERIMENTAL

Three colloidal solutions have been investigated in this test of the new theory. The mobilities of two negative sols, gold and selenium, and one positive sol, ferric oxide, have been measured; the zeta-potentials calculated by the formula $\zeta = 4\pi n \mu /\epsilon\eta$; the particle radii determined by the ultracentrifuge and the electron microscope; and the stability ratio, $W$, then evaluated.

PREPARATION OF SOLS

Gold: The gold sol was prepared by the method of Faraday (4) with a saturated solution of phosphorous in ether as the reducing agent. The exact amounts of the materials used were identical with those employed previously by the author in this laboratory and reference is made to an earlier publication (16) for this data. Analysis showed the concentration of the gold to be 50.9 milligrams/liter.

Selenium: Preparation of the selenium sol involved the use of the method of Kruyt and Van Arkel (9), reducing a solution of selenium dioxide with hydrazine hydrate. This method also had been used previously, and found to give a very satisfactory sol (16). The concentration of selenium in this sol was 184 milligrams/liter.
Ferric oxide: The method of preparing the ferric oxide sol was quite unique. In three liters of water, 6.06 grams of Fe(NO$_3$)$_3$·9H$_2$O were dissolved and this solution was treated with an ion exchange resin (Amberlite - IR - 4 - B) which is made up in the free base form. The pH value of successive samples was measured during the time of exposure to the anion exchange resin. The resulting sol was decanted after a pH value of 4.65 was attained. It was observed in preliminary experiments that above a pH of 5.0 the sol coagulated. After decantation the sol was tested for free ferric ion and gave a negative test with potassium ferrocyanide. Analysis showed that the concentration of ferric oxide was 508 milligrams/liter.

These three sols were selected because of their monodisperse character. The first test of monodispersity is a visual test. If the sol is clear, it is relatively monodisperse and if it is cloudy, it is definitely polydisperse and therefore discarded. Uniform particle size is desired thus validating our assumption of constant radius at least in the original sol when the concentration of coagulating electrolyte is zero.
MOBILITY MEASUREMENTS

The apparatus used in measuring mobility has been described in detail in the previous publication (16). Suffice to say here that it is a modified Burton U-tube employing the moving boundary technique. The U-tubes are immersed in a glass constant temperature bath maintained at 36° C. The distance through which the boundary moves is measured by a telescope mounted on a cathetometer capable of determining a change of 0.005 cm. Parallax through the glass and water was found to be non-existent.

An interesting sidelight concerning the accuracy in this measurement of the distance was observed. During an experimental "run," it was necessary to measure the applied voltage, the time, and the distance, having previously determined the length of the U-tube between electrodes. Allowing the following error: .5 volt in a total of 135 volts, .2 second in 1800 seconds, and .3 cm in the length of the U-tube; and observing that the experimental reproducibility of zeta-potential is 1 millivolt, it is only necessary to measure the moving boundary distance with an accuracy of .025 - .030 cm. This is 5 - 6 times the actual capability of the cathetometer, and such a lee-way in this measurement
compensates for the usual diffuseness of the boundary.

PARTICLE SIZE DETERMINATION

The electron microscope was the best tool in the determination of particle radii. Samples for electron microscopy were prepared from the sols by evaporating a drop of diluted sol on a thin collodion membrane. During an evaporation process, some agglomeration occurs, however it is possible to distinguish the agglomerates from the independent particles. Measuring the diameters from an enlarged photograph for a number of particles gives an average particle size. The total magnification factor including enlargement was 43000.

Gold and selenium sols gave excellent electron micrographs and values for their radii were determined in the manner just described. The ferric oxide was not particularly suited for electron microscopy giving huge agglomerates at various dilutions.

Observance of the sedimentation rate in the ultracentrifuge also yields values for particle size. The three sols were subjected to a centrifugal force of \( \approx 750 \) times gravity (corresponding to 3480 rpm) in a Fisher-Stern ultracentrifuge. The ferric oxide particles completely sedimented in 1.5 minutes at this rotational speed indicating a minimum radius of \( \approx 85 \) millimicrons. The few small particles of ferric oxide that could be
observed on the viewing screen of the electron microscope were approximately 100 millimicrons in radius. For the purpose of calculations of the stability ratio, \( W \), this latter value was selected.
III. RESULTS
III. RESULTS

The tables and graphs presented in this section are nearly self-explanatory and require only slight clarification. Tables I, II, and III contain the experimental data obtained during the mobility measurements of the selenium, gold, and ferric oxide sols respectively. Calculated values of the zeta-potential, $X$, and $\tau$ are also included. At the bottom of each table is listed the surprising agreement with the empirical rule postulated by Whetham (17). This empirical rule states that the ratio of the reciprocals of the coagulation values varies as $1 : X : X^2$ for mono-, bi-, and trivalent electrolytes.

Figures I, II, and III are plots of the zeta-potential values versus the quantity $\tau$. The equation of $S$ as a function of $\tau$ is given for each curve. $S_0$ is the value of the zeta-potential at zero concentration of electrolyte.

In figures IV, V, and VI are plotted the total potential energies of interaction, $V$, versus $S$ for various values of $\tau$. Recall that $V = V_a + V_r$. Hamaker’s (7) $A$, which is constant for each sol is also designated.
Figures VII, VIII, and IX show the variation of \( \log W \) with \( \Upsilon \) for the three sols. \( W \) is obtained by graphic integration of \( \frac{e^{V/kT}}{S^2} \) versus \( S \).

In figure X are shown the electron micrographs of selenium and gold. The average particle radius is indicated in each case.
# TABLE I

<table>
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<tr>
<th></th>
<th>Conc. 184 mg/l</th>
<th>$\gamma = 38.5 , \mu$</th>
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<td>$\chi^2 = 8v_n e^{2v^2/D_K}$</td>
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<th>$\xi$</th>
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<td>/s</td>
<td>volts/cm</td>
<td>mV</td>
<td>cm$^{-1}$</td>
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$1/c_1 : 1/c_2 : 1/c_3 \quad 1/20 : 1/2 : 1/0.2254 \quad 1 : X : X^{1.948}$
### TABLE II

Gold Sol

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<tr>
<th>( \zeta ) = 107.34 u/H</th>
<th>( T^2 = 3.8 \times 10^{-3} )</th>
<th>( \rightarrow )</th>
<th>Conc. 50.9 mg/l</th>
<th>( \tau = \chi / \omega )</th>
<th>a 36.0 mμ</th>
</tr>
</thead>
</table>

\[
\begin{array}{cccccc}
\text{Ba(NO₃)₂} & \text{u} & \text{H} & \zeta & \chi \times 10^{-5} & \tau \\
\text{millimols/l} & \text{/sec} & \text{volts/cm} & \text{mV} & \text{cm}^{-1} & \\
0.00 & 6.50 & 1.745 & 40.0 & 0.00 & 0.00 \\
0.20 & 4.61 & 1.977 & 25.0 & 9.35 & 3.36 \\
0.40 & 3.96 & 1.758 & 24.2 & 13.24 & 4.77 \\
0.60 & 4.11 & 1.962 & 22.5 & 16.24 & 5.85 \\
0.80 & 3.54 & 1.745 & 21.8 & 18.74 & 6.75 \\
1.00 & 3.25 & 1.962 & 17.8 & 20.97 & 7.55 \\
\rightarrow 1.20 & 2.67 & 1.745 & 18.4 & 22.95 & 8.26 \\
\end{array}
\]

Al(NO₃)₃

\[
\begin{array}{cccccc}
\text{millimols/l} &
\end{array}
\]

\[
\begin{array}{cccccc}
0.0000 & 7.30 & 1.977 & 39.1 & 0.00 & 0.00 \\
0.0088 & 6.05 & 1.962 & 33.1 & 3.10 & 1.12 \\
0.0294 & 5.14 & 1.962 & 29.1 & 5.38 & 1.94 \\
0.0588 & 4.08 & 1.758 & 26.0 & 7.81 & 2.74 \\
0.1176 & 3.04 & 1.758 & 18.8 & 10.74 & 3.87 \\
\rightarrow 0.1764 & 3.08 & 1.969 & 16.7 & 13.19 & 4.75 \\
\end{array}
\]

\[
\frac{1}{v_2} : \frac{1}{v_3} \quad \frac{1}{1.20} : \frac{1}{0.1764} \quad \chi : \chi^{1.905}
\]
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<th>Table III</th>
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<td>0.0000600</td>
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$1/c_1:1/c_2:1/c_3 = 1:1.00:1/0.038:1/0.0016 = 1:X:X^1.947$
Figure I

\[ \xi = \xi_0 + (1 - \exp^{-4.5 \tau}) \]

\[ \xi = \xi_0 + (1 - \exp^{-2.4 \tau}) \]

\[ \xi = \xi_0 + (1 - \exp^{-1.8 \tau}) \]

\( \xi_0 = 25.8 \text{ mv} \)
IV. DISCUSSION
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The results obtained in this research agree remarkably with the calculated examples contained in Verwey and Overbeek's book (14). There are two slight deviations from the theory that should be noted.

First, recall the qualitative statement in the introduction that a sol has stability only if the maximum of the $V$ versus $S$ curve is of the order of $kT (4.27 \times 10^{-14} \text{ erg})$. In one instance, namely the curve in Figure VI where $T = 1.25$ with potassium ferricyanide as the coagulating electrolyte for the ferric oxide sol, a maximum of $17.8 \text{ kT}$ exists. This value of $T$ corresponds to a concentration of potassium ferricyanide which is close to the coagulation value and the sol at this point has only temporary stability. Therefore the maximum should occur at approximately $1kT$ rather than at such a high value. However this is the only instance of this type of deviation and should not be considered as a reflection on the general theory.

Secondly, Verwey and Overbeek designated the best value of $A$, the constant in the expression for the attractive potential, as $2 \times 10^{-12} \text{ erg}$. It was found in the evaluations of the stability ratio, $W$, for the individual sols that a best value of $A$ certainly exists, but that it varies with each colloidal system. This is
more in accordance with Hamaker's (7) original evaluation, wherein it was stated that A may vary between $10^{-14}$ and $10^{-11}$ erg but usually lies between $10^{-13}$ and $10^{-12}$ erg.

In the introduction, the ratio between a month's time and the time of coagulation of a rapidly coagulating sol, was calculated, and this ratio was used as a value for $W$ to insure reasonable stability ($W > 10^5$). In the light of this research, it is quite obvious that this is only a starting point to determine an order of magnitude. At least, we are not justified in back calculating in an attempt to determine time of stability. For instance, making a rough calculation on the gold sol (Figure VIII), the high value of $W$ ($> 10^{12}$) indicates that this gold sol with no electrolyte present should be stable for $10^6$ months or approximately $10^5$ years. Likewise for low values of $W$ ($< 10$), attempting to back calculate yields a stability time of less than 90 seconds. Both of these values are ridiculous. In the second case, with $W < 10$, the sol was stable for at least one hour as the mobility measurements consumed that amount of time. Therefore $W$ can be considered only as a relative factor as far as actual time of stability is concerned. The working value of $W = 10^5$ for reasonable stability appears to be a good middle point, and in the final analysis, all that can be
said is that if \( W > 10^5 \) a colloidal system is quite stable, and as \( W \) approaches 10, a region of instability is being approached.

In conclusion, it is noted that experimental results obtained in this laboratory are in reasonable agreement with the theory of Verwey and Overbeek. The stability ratio, \( W \), may be considered qualitatively as a relative measure of stability.
V. ACKNOWLEDGMENT
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VI. BIBLIOGRAPHY
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