Electrolyte coagulation and stability of calcium caprylate stabilized o/w emulsions

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With 6 figures and 2 tables

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Introduction

Soap stabilized emulsions are of topical importance from technological point of view and have been a subject of many investigations. It was observed by Smith and Keaton (1) that the dirt, rust and marine growth could be removed from the metallic surfaces by wetting with an emulsifying agent, comprising fatty acid soap of alkaline earth metals. Polyvalent metal soaps of small chain fatty acids are water soluble and have good emulsifying power in promoting o/w emulsion like monovalent metal soaps of long chain acids. Similar effects have been observed by Wellman and Tartar (2) who obtained stable o/w emulsions by shaking equal volumes of benzene and dilute aqueous solutions of calcium valerate, magnesium heptylate, caproate, etc. Bhatnagar (3) reported that oleates of calcium, magnesium and barium were fairly soluble in water to stabilize emulsions of o/w type.

In the present work, an attempt has been made to study the electrolyte flocculation of calcium caprylate stabilized o/w emulsions in the light of the Derjaguin, Landau, Verwey, and Overbeek (4–6) theory.

Theoretical

The following theoretical aspects were considered before explaining the results of these investigations. In order to apply DLVO theory to the present system, the interaction energies $V_I$, which is the sum of attraction energies $V_A$ and repulsion energies $V_R$, have been calculated using following equations.

$$V_R = \frac{\alpha \psi^{s_2}}{2} \ln(1 + e^{-\kappa H}) \quad [1]$$

$$V_A = \frac{-Aa}{12H}. \quad [2]$$

Where the notations have their usual meanings.

In $V_A$ calculations $A$, the van der Waals constant has been taken equal to $3.16 \times 10^{-13}$ erg, the value for xylene droplets dispersed in water with the help of optical data (7) – and the retardation correction was applied using the following approximate equations due to Schenkel and Kitchener (8)

$$V_A \approx \frac{-Aa}{\pi} \left\{ \frac{2.45\lambda}{120H^2} - \frac{\lambda^2}{1045H^3} + \frac{\lambda^3}{5.62 \times 10^4 H^4} \right\} \quad [3]$$

valid for $H > 150 \text{ Å}$

$$V_A \approx \frac{-Aa}{12H} \left\{ \frac{\lambda}{\lambda + 3.54H\pi} \right\} \quad [4]$$

valid for $H < 150 \text{ Å}$

Where $\lambda$ is the wavelength of the London frequency, equal to 1000 Å.

The charge density in the Gouy layer, $\sigma_2$ has been calculated using the corrected equation.

$$\sigma_2 = \frac{\varepsilon \alpha}{4\pi} \frac{kT}{e} 2^{1/2} \times \left\{ \exp\left(\frac{z_- \varepsilon^2}{kT}\right) - 1 \right\} \left\{ \exp\left(\frac{-z_+ \varepsilon^2}{kT}\right) - 1 \right\} \quad [5]$$

Where $Z_{\pm}$ are valencies of anions and cations, $K$ the Boltzmann constant and $e$ the elementary charge.

Charge density of an emulsion droplet by adding small quantities of inorganic electrolytes
is given by Stern equation

\[
\sigma_s = \frac{N_1 e Z}{1 + \frac{55.6}{c} \exp(\frac{AG}{kT})}
\]  

where \( c \) is the molar concentration, \( N_1 \) the binding sites per cm\(^2\) and \( AG \) the free energy of adsorption per molecule. The same equation can be written in the form (9–10)

\[
\sigma_s = \frac{k_1 c}{1 + k_2 c}
\]

\[
k_1 = N_1 k_2 e^Z
\]

\[
k_1 \text{ and } k_2 \text{ are the adsorption constants which have been calculated from the treatment given by Srivastava (11) at isoelectric point of the system which finally yields the following equations:}
\]

\[
\frac{1}{c} = \frac{4\pi e Z N_1 k_2}{\varepsilon \varepsilon_0 \delta} - k_2
\]

\[
\left(\frac{d\psi_\delta}{d \ln c}\right)_{\psi_\delta = 0} = \left\{\frac{\varepsilon \varepsilon_0 \delta}{4\pi e Z N_1} - 1\right\} \psi_\delta^0
\]

Where \( Z \) is the valency and \( \left(\frac{d\psi_\delta}{d \ln c}\right)_{\psi_\delta = 0} \) is the slope of the zeta potential log \( C \) curves (assuming \( \psi_\delta^0 = \zeta^0 \)), \( C \) is the flocculating concentration of the electrolytes.

**Experimental**

**Materials**

The emulgent, calcium caprylate was prepared by direct metathesis of sodium caprylate (prepared in this lab.) with the required amount of calcium hydroxide at 50–55 °C. The precipitated soap was washed with distilled water and then with alcohol to remove the free precipitant and acid respectively. After initial drying in air oven at 100–105 °C it was again dried under reduced pressure.

Xylene used as oil phase in the emulsification was of AR (BDH) quality. All the flocculating electrolytes were Anala-R reagents. Double distilled water was always used throughout the experiment.

**Method**

**Preparation of emulsion**

The emulsions were prepared by suspending 1.0 % by volume of xylene in a 0.01 % aqueous solution of calcium caprylate in 0.01 M KCl. The mixture was first hand shaken for about fifteen minutes and finally homogenized well in a stainless steel homogenizer (Schaar Scientific Co., Chicago). The freshly prepared emulsion was kept for about half an hour and then creamed layer was skimmed off. Care was taken for preparing emulsion samples under similar conditions.

Measurements of globule mobility were made microelectrophoretically using Northrup-Kunitz type cell by diluting the emulsion ten times with 0.01 M KCl solution. The electrophoretic mobility (\( \nu \)) was calculated from \( v/\chi \), where \( v \) is the mean velocity of at least ten particles and \( \chi \) is the field strength. As the observed particles had large radii compared with the Debye-Hückel parameter \( 1/\kappa \), the zeta potentials (to be identified with surface potential) were calculated using the Helmholtz-Smoluchowski equation.

For the size of drops the microphotograph was taken using a magnification of 15 x 40 times. The size distribution curve was plotted and the average particle diameter was found to be 1.15 \( \mu \) (fig. 1).

![Fig. 1. Size frequency curves average particle radius = 0.55 \( \mu \)](image-url)