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EVALUATION OF THE MOONEY VISCOSITY/CONCENTRATION EQUATION FOR LIQUID–LIQUID EMULSIONS

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Mooney's viscosity equation, originally proposed for concentrated solids in liquid suspensions, has been tested for stable liquid in liquid emulsions. Nine different emulsion systems have been considered. In none of the cases considered, Mooney's equation is found to adequately describe the viscosity/concentration behavior. However, the modified form of the Mooney's equation \( \eta = \exp\left[K_1 \phi/(1 - K_2 \phi)\right] \) is found to fit the data quite well. The \( K_1 \) varies from 2.2 to 5.0 depending on the emulsion system; the \( K_2 \) varies from 0.6 to 2.1.

KEYWORDS Mooney Viscosity Equation Concentration Emulsions.

INTRODUCTION

Emulsions are dispersions of two immiscible liquids, usually oil and water. Two types of emulsions are possible—oil in water (o/w) and water in oil (w/o) emulsions. In the former case, oil is the dispersed phase and in the latter case, water is the dispersed phase. Emulsions normally contain a third component, emulsifying agent or emulsifier, which has two principal functions: (1) to decrease the interfacial tension between oil and water, thereby enabling easier formation of the emulsion, and (2) to stabilize the dispersed phase against coalescence once it is formed.

The viscosity of concentrated emulsions is of considerable importance because of the many industrial applications of emulsions. The important factors which affect the relative viscosity (the ratio of the viscosity of the emulsion to that of the continuous phase) of emulsions are:

1. volume fraction of dispersed phase
2. the ratio of dispersed phase viscosity to continuous phase viscosity
3. interfacial tension
4. size and distribution of dispersed particles

In the absence of an emulsifier, the dispersed particles of an emulsion exhibit internal circulation; also, deformation of the dispersed particles is important. Consequently, the relative viscosity of emulsion is strongly influenced by the ratio of dispersed phase viscosity to continuous phase viscosity and the interfacial
tension. However, when an emulsifier is present in the emulsion system the viscosity ratio and the interfacial tension are less important. This is due to two reasons—the presence of emulsifier on the surface of the dispersed particles prevents internal circulation (Sherman, 1983), and the particles produced in the presence of an emulsifier are usually very small (few microns) so that they do not suffer much deformation even at high rates of shear. Thus, we can regard the dispersed particles of emulsifier-stabilized emulsions as rigid particles.

In light of the above discussion, the relative viscosity versus dispersed phase concentration behavior of stable emulsions is usually described by the equations originally proposed for solids in liquid suspensions.

The most popular relative viscosity/concentration equation in the emulsion literature (Sherman, 1983) is the Mooney's equation (1951). Using functional analysis, Mooney derived the following equation to describe the relative viscosity/concentration behavior of rigid, spherical particles:

$$\eta_r = \exp\left[\frac{2.5\phi}{(1 - a_M\phi)}\right]$$

(1)

where $\eta_r$ is the relative viscosity, $\phi$ is the volume fraction of the solids, and $a_M$ is the geometric crowding factor which varies in the range $1.35 < a_M < 1.91$.

The objective of this paper is to test the validity of Mooney's equation for a large body of experimental data obtained on the emulsifier-stabilized o/w and w/o emulsions.

EMULSION VISCOSITY DATA

Viscosity/concentration data of nine different emulsion systems are considered. Six of these systems were studied by the present author (Pal, 1987), rest three were studied by the other workers (Sibree, 1930; Broughton and Squires, 1938; Van der Waarden, 1954). Following is the brief description of the various emulsion systems considered (for details, see the original references):

Emulsion System 1 (Pal's data): The emulsions were o/w type. The dispersed phase was Shell Vitrea oil 220 and the continuous phase was 0.5% by volume solution of Triton X-100 (emulsifier) in water. The dispersed phase concentration was varied from 39% to 68.6% by volume.

Emulsion System 2 (Pal's data): The emulsions were o/w type. The dispersed phase was Diesel oil No. 2 and the continuous phase was 1% by volume solution of Triton X-100 (emulsifier) in water. The dispersed phase concentration was varied from 25% to 70% by volume.

Emulsion System 3 (Pal's data): The emulsions were o/w type. The dispersed phase was Bayol-35 (white mineral oil) and the continuous phase was 0.5% by volume solution of Triton X-100 in water. The dispersed phase concentration was varied from 30% to 69% by volume.

Emulsion System 4 (Pal's data): The emulsions were w/o type. The dispersed phase was water and the continuous phase was 2% by volume solution of Span-85 (emulsifier) in Diesel oil No. 2. The dispersed phase concentration was varied from 5% to 70% by volume.
LIQUID–LIQUID EMULSIONS

Emulsion System 5 (Pal's data): The emulsions were w/o type. The dispersed phase was water and the continuous phase was 2% by volume solution of Span-80 (emulsifier) in Furnace oil No. 2. The dispersed phase concentration was varied from 5% to 70% by volume.

Emulsion System 6 (Pal's data): The emulsions were w/o type. The dispersed phase was water and the continuous phase was 1.5% by volume solution of Span-80 in Bayol-35/CCl₄ mixture (Carbon tetra chloride is soluble in Bayol-35; the mixture contained 26.5% by volume CCl₄). The dispersed phase concentration was varied from 30% to 70% by volume.

Emulsion System 7 (Sibree's data): The emulsions were o/w type. The dispersed phase was paraffin oil and the continuous phase was 1% by volume solution of Sodium oleate (emulsifier) in water. The dispersed phase concentration was varied from 50% to 75% by volume.

Emulsion System 8 (Broughton and Squires' data): The emulsions were o/w type. The dispersed phase was Nujol and the continuous phase was 2% by volume solution of Saponin (emulsifier) in water. The dispersed phase concentration was varied from 50% to 75% by volume.

Emulsion System 9 (Van der Waarden's data): The emulsions were o/w type. The dispersed phase was Medicinal oil containing 35% by weight of Sodium naptha sulfonates (emulsifier) and the continuous phase was water. The dispersed phase concentration was varied from 5.3% to 31.3% by volume.

EVALUATION OF MOONEY EQUATION

Mooney's equation can be re-written as:

\[
\frac{(\ln \eta_r)}{\phi} - 2.5 = a_M \ln \eta_r \tag{2}
\]

According to this relation, \((\ln \eta_r)/\phi - 2.5\) versus \(\ln \eta_r\) data should be linear, having the slope \(a_M\), and should pass through the origin.

Figures 1 to 3 compare the experimental data of emulsions with Eq. (2). It should be mentioned that emulsions, in general, were Newtonian at low dispersed phase concentrations and non-Newtonian pseudoplastic at high concentrations. In the latter case, the high shear-rate \((1000 \text{ s}^{-1})\) viscosity was used in Figures 1 to 3. It is clear from the Figures that Mooney's equation does not adequately describe the viscosity/concentration behavior of emulsions. In most cases, the experimental data fall below the Mooney's equation. However, the data of Van der Waarden (System 9) fall above the Mooney's equation.

The data of Figures 1 to 3 are re-analyzed in terms of the modified Mooney's equation:

\[
\eta_r = \exp[K_1 \phi/(1 - K_2 \phi)] \tag{3a}
\]

or,

\[
(\ln \eta_r)/\phi = K_1 + K_2 \ln \eta_r \tag{3b}
\]

where \(K_1\) and \(K_2\) vary from one emulsion system to another. It is found that all the data can be fitted satisfactorily by the above equation. Figure 4 shows the
FIGURE 1  o/w emulsion data of Pal.

FIGURE 2  w/o emulsion data of Pal.

FIGURE 3  Literature data on emulsions.
typical plots. The data of \( \ln \eta_r/\phi \) versus \( \ln \eta_r \) are linear; the slope \( (K_2) \) and the intercept \( (K_1) \) vary from system to system.

Table I summarizes the values of \( K_1 \) and \( K_2 \) for the various emulsion systems. In most cases the value of \( K_1 \) is close to 2.5 (Einstein's theoretical prediction). Van der Waarden's emulsions have a very high value of \( K_1 (=5) \). The dispersed particles (oil droplets) of Van der Waarden's emulsions had a strong negative charge on their surface. The charge originated from strongly ionized surfactant (sodium naptha sulfonate) molecules adsorbed at the oil-water interface. The presence of charge on the surface of the dispersed particles caused "electroviscous effect". The high value of \( K_1 \) is likely due to the electroviscous effect.

The value of \( K_2 \) ranges from 0.6 to 2.1. However, in most cases the value of \( K_2 \) is close to 0.7. It should be mentioned that the reported literature values of \( K_2 \) for solids in liquid suspensions cover a wide range. On the basis of a large body of suspension viscosity data, Barnea and Mizrahi (1973) found that \( K_2 = 1.0 \). According to Mooney (1951), \( K_2 \) varies from 1.35 to 1.91. Thus, it is difficult to

### Table I

Summary of the values of \( K_1 \) and \( K_2 \)

<table>
<thead>
<tr>
<th>Emulsion system</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.66 ± 0.2</td>
<td>0.80 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>2.74 ± 0.2</td>
<td>0.61 ± 0.1</td>
</tr>
<tr>
<td>3</td>
<td>2.59 ± 0.2</td>
<td>0.69 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>2.53 ± 0.2</td>
<td>0.69 ± 0.1</td>
</tr>
<tr>
<td>5</td>
<td>2.48 ± 0.1</td>
<td>0.64 ± 0.1</td>
</tr>
<tr>
<td>6</td>
<td>2.50 ± 0.3</td>
<td>0.76 ± 0.1</td>
</tr>
<tr>
<td>7</td>
<td>2.26 ± 0.3</td>
<td>0.84 ± 0.1</td>
</tr>
<tr>
<td>8</td>
<td>3.24 ± 1.7</td>
<td>0.70 ± 0.4</td>
</tr>
<tr>
<td>9</td>
<td>5.00 ± 0.2</td>
<td>2.10 ± 0.1</td>
</tr>
</tbody>
</table>
give exact physical interpretation of $K_2$. However, there is enough evidence in the literature to show that $K_2$ is a function of particle size distribution, particle shape, interparticle affinity and electric charge on particles (Wildemuth and Williams, 1985). The variation in $K_2$ observed in the case of present emulsions is likely due to variations in some of these factors.

NOMENCLATURE

$a_M$ geometric crowding factor, Eq. (1)

$K_1$ constant in Eq. (3)

$K_2$ constant in Eq. (3)

o/w oil in water

w/o water in oil

Greek Symbols

$\eta_r$ relative viscosity

REFERENCES


