CHAPTER 13

ULTRASONIC STUDY OF SUSPENSIONS OF SMALL PARTICLES OF SULPHUR

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13.1 Introduction

In recent years there has been increasing interest in the use of ultrasonics as a probe of suspensions and emulsions, especially by means of ultrasonic velocity measurements. Such measurements offer a means of determining volume fractions or compressibilities of dispersed phase in many systems and in special cases may even be used as a means of particle sizing or for determining disperse or continuous phase viscosities (1). Ultrasonic techniques have also been widely used in the studies of physical properties of micellar solutions (2). There are many equations in the literature for the prediction of the sound velocity in suspensions (3-11). A number of these equations were reviewed by Kuster and Toksoz (11). Urick and Ament (4) have derived a sound velocity formula for rigid particle suspension from scattering theory. Ahuja (8) has derived a wave equation for the propagation of sound in suspensions and emulsions taking into account the different viscosities and thermodynamic properties of components of the suspension. Ultrasonic measurements have been used to determine the compressibilities of blood and blood components such as erythrocytes (3,12). Urick was the first investigator (3) to use a sound velocity method to measure the compressibility.
of red blood cells. This technique stems from the fact that if the scattering of sound waves in a suspension of a solid phase in a liquid medium is negligible, the compressibilities can be calculated from the ultrasonic velocity based upon the assumption that the density and compressibility of the system are additive properties of the individual components. Urick showed (3) that the sound velocity $V_o$ in a suspension is

$$V_o = (1/p_o k_o)^{1/2} \quad \text{............(1)}$$

and

$$p_o = B p_2 + p_1 (1-B) \quad \text{............(2)}$$

$$k_o = B k_2 + k_1 (1-B)$$

where $p_o$, $p_1$ and $p_2$ are the densities of the suspension, suspending medium and the suspended particles respectively, $k_o$, $k_1$ and $k_2$ are the corresponding compressibilities.

$$B = (p_o-p_1)/(p_2-p_1) \quad \text{............(3)}$$

is the volume percentage of the particles. Substituting eqn.(2) in eqn.(1), and rearranging, we get,

$$k_2 = k_1/B \left(1/V_o^2 \left[B \left(p_2/p_1 - 1\right) + 1\right]^{-1} + B-1\right) \quad \text{............(4)}$$
This is the simplification of a more accurate relation which takes into account the viscosity of the suspending medium (13), given by

\[ k_2 = k_1/B \left[ \left( \frac{V_1}{V_0} \right)^2 \frac{A^{-1}}{1 + B^{-1}} \right] \]  \hspace{1cm} \text{(5)}

Where \( A \) is a factor which depends on the kinematic viscosity of the suspending fluid, the radius of the particles, and the angular frequency of the sound wave. Sung et al (14) have shown that the compressibility of erythrocytes calculated from eqn.(4) is within 0.1% of that obtained using eqn.(5). The aim of the present investigation is to study the physical properties of the colloidal system consisting of sulphur dispersed in water-methanol mixture. The aggregation and vibrational properties of this system have been studied and discussed in chapter 5 and chapter 7 respectively. In this study, the ultrasonic velocity of suspensions of sulphur particles of various concentrations have been studied by a pulse-echo technique using KRAUTKRAMER USIP - 12 with DTM 12 module, which permits a direct reading of the ultrasonic velocity on feeding the ultrasonic path length. The densities of the suspension and the suspension medium have been determined. These data have been used to calculate the adiabatic compressibility of the suspension and the suspended particles using eqns. (1) and (4) respectively.
13.2 Experiment and Observation

Suspensions of sulphur used in the present investigation were prepared as discussed in section 1 of chapter 5 (15). Suspensions consisting of sulphur particles of different particle size and varying volume fractions of the dispersed phase were prepared. Size of the sulphur particles was found to decrease with decrease in volume fraction of the sulphur solution. (For example, the average particle size obtained from the TEM micrographs were found to be 30 nm for particles in suspensions of volume fraction 2:1 and 16 nm for particles in suspensions of volume fraction 4:1 respectively.) (refer chapter 5 section 1) A liquid cell of variable path length for the ultrasonic measurements was constructed. The ultrasonic velocity in these suspensions was determined by ultrasonic pulse technique using KRAUTKRAMER USIP-12 with DTM 12 module and using a single probe of frequency 2MHz (K2N 53 905) and diameter 10mm. The path length of the liquid cell for ultrasonic waves was determined by filling the liquid cell with distilled water and feeding the corresponding ultrasonic velocity obtained from the literature (16). The path length between the probe and the reflector was found to be 40.45 ± 0.01 mm. The temperature of the liquid cell was kept fixed at 30±1°C. The liquid cell was then filled with the suspension, taking care to avoid air bubbles, and the
velocity was obtained by feeding the path length. This was repeated for suspensions of different concentrations. Then the ultrasonic velocities in water-methanol mixtures of different concentrations which were used as the suspension media were determined. The densities of the suspensions and the suspension media (water-methanol) for different volume fractions are determined using pyknometer. The volume percentages of the particles were calculated using eqn.(3). The adiabatic compressibilities of the suspension and the particles were then calculated.

13.3 Discussion

The measured values of ultrasonic velocity of the suspensions were found to decrease with decrease in the volume fraction of the sulphur solution (Table 13.1). The calculated volume percentages of sulphur in the suspensions is very low, still the acoustic velocity in the suspension is found appreciably lower than that of the suspension medium (Fig 13.1).

Piotrowska (17) has shown that sound velocity in a suspension of certain inorganic pigments was less than that in the dispersion fluid at low concentrations. The results of the present investigation also indicate that the velocity in the suspensions is lower than that in the suspension.
Table 13.1  Compressibility of Small Particles of Sulphur

<table>
<thead>
<tr>
<th>Ratio of water to sulphur solution</th>
<th>V0</th>
<th>V1</th>
<th>P0</th>
<th>P1</th>
<th>B</th>
<th>K0</th>
<th>K1</th>
<th>K2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm/sec</td>
<td>cm/sec</td>
<td>gm/cm³</td>
<td>gm/cm³</td>
<td>cm²/dyne</td>
<td>cm²/dyne</td>
<td>cm²/dyne</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>1563</td>
<td>1570</td>
<td>0.960</td>
<td>0.959</td>
<td>1.040</td>
<td>4.264</td>
<td>4.230</td>
<td>36.453</td>
</tr>
<tr>
<td>1:4</td>
<td>1559</td>
<td>1564</td>
<td>0.968</td>
<td>0.967</td>
<td>1.049</td>
<td>4.250</td>
<td>4.228</td>
<td>25.92</td>
</tr>
<tr>
<td>1:5</td>
<td>1555</td>
<td>1559</td>
<td>0.971</td>
<td>0.970</td>
<td>1.052</td>
<td>4.259</td>
<td>4.242</td>
<td>20.82</td>
</tr>
<tr>
<td>1:7</td>
<td>1543</td>
<td>1544</td>
<td>0.976</td>
<td>0.975</td>
<td>1.058</td>
<td>4.303</td>
<td>4.302</td>
<td>5.403</td>
</tr>
</tbody>
</table>
Fig. 13.1. Variation of Ultrasonic velocity with (a) volume percentage of sulphur solution in the suspension (b) volume percentage of methanol as the suspension medium.
medium. In the case of nucleation of a substance from a solution, smaller the solubility of the substance, larger will be the number of nuclei formed. As the volume of the methanol in the suspension fluid is decreased, the solubility of sulphur is decreased and hence a large number of nuclei will be formed. Hence the size of the particles will be smaller for smaller volume fraction of the sulphur solution in the suspension. The size of sulphur particles obtained from the TEM micrographs justifies this result. Hence the decrease in particle size with decrease in volume percentage of sulphur solution may also play a role in lowering the ultrasonic velocity.

The calculated values of compressibility of the suspended particles show an increase with decrease in volume percentage of sulphur solution (Fig.13.2). A particle of a substance in a suspension may be made up of a group of atoms or molecules not bound together as strongly as they are bound in a crystal (17). In such a case the compressibility of a particle will be greater than that of a fine powder of the same substance. The observation that compressibility increases with decrease in volume percentage of sulphur solution indicate that the atoms in the particles are less and less strongly bound together as the volume percentage of sulphur solution is decreased.
Fig. 13.2. Variation of compressibility of sulphur particles with volume percentage of sulphur solution in the suspension.
13.4 Conclusion

Ultrasonic velocity in colloidal systems of sulphur in water-methanol mixture have been determined for various volume fractions of sulphur solutions. The compressibility of the particles have been calculated and has been found to increase with decrease in volume fraction of the sulphur solution. It is inferred that the sulphur atoms forming the particles are more and more loosely bound as the volume fraction of sulphur solution decreases.
References

17. A.Piotrowska, Ultrasonics, October, 9 (1971)236.