On the Question of a Separation in a Field of Stationary Ultrasonic Waves

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A well established fact is that stationary ultrasonic waves in a liquid suspension will cause the suspended matter to move into planes separated by half sound wave lengths. It has been shown that the disperse phase will accumulate in the velocity nodes when it is of a less density than the solvent and vice versa ^{1,2}.

Could this separating effect of the ultrasonic waves be reproduced even on a molecular scale? — No doubt it would be of a great interest if it were possible to establish permanent concentration changes in a true solution subjected to stationary ultrasonic waves. In the literature there are some indications that this might be true but as yet definite evidence is lacking.

PREVIOUS OBSERVATIONS

Young and Kersten obtained ripples on the cathode in the electrolytic deposition in an ultrasonic field ³. The distances between these ripples corresponded to half sound wave lengths. The authors concluded that a possible explanation is that concentration differences are set up in the ultrasonorated electrolyte. In a separate study the present author, however, has tried to show that this suggestion is not very plausible and that the effect in question may be looked upon as a pure electrochemical phenomenon ⁴.

Ernst made an interesting observation when he determined the sound velocity in some binary solutions according to a striation method ⁵. A solution of 80 weight % paraffin oil in chloroform did not give the usual line structure but showed a definite brick-stone pattern. At this concentration there was also a distinct maximum in the sound velocity. The most interesting thing, however, is that the structure was frozen in for several hours after the ultrasonic treatment had been interrupted.

Partly analogous results were obtained by Frei and Schiffer who worked with aqueous glycerol solutions and a solution of hexane in paraffin oil ⁶. In their experiments the "Toepler's Schlieren" in the nodal planes were recognized up to 24 hours after the ultrasonic treatment.

Frei and Schiffer as well as Ernst state that their results seem to indicate a separating action of the ultrasonic waves. It is also pointed out by the above authors that this is contradictory to theoretical considerations by Herzfeld.⁷

However, this is apparently not true. The separating effect treated by Herzfeld and found to be negligible does not seem to be of the permanent type here dealt with (Herzfeld's considerations refer to the possibility of temporary concentration changes within a volume element with the same frequency as the ultrasonic waves; the time mean value of these rapid variations, however, being constant and equal to the initial value. This effect is thus seen to be analogous with the wellknown Debye effect. — In the permanent separation, on the other hand, it is assumed a resulting uneven concentration distribution in the acoustic field, which should be detectable even after the interruption of the sound.)

Summing up, there seems to be no theoretical account on the type of permanent separation which is the subject of this paper. The cited observations on the other hand give some circumstantial evidence that the effect in question can take place. These reasons and the importance of the effect if real were the motives for the following study.

THERMODYNAMIC CALCULATION

In the following treatment we restrict ourselves to the conditions in the proper nodal and antinodal planes. (With nodes we will mean the velocity nodes, *viz.* where the particle velocity always is zero but pressure and temperature oscillate with maximum amplitudes). We may thus represent the system by two thin plane compartments, one for the nodal and the other for the antinodal plane, which are connected with a small channel in order to permit changes in concentration.

The liquid mixture is made up of the two components M_1 and M_2 , where this symbol also stands for the molecular weight. Consider the process 1 mole M_2 being transferred from the node to the antinode.

Of the two additional subscripts n stands for the node and a for the antinode.

In order to keep the volume of the system constant the corresponding volume of M_1 must simultaneously be transferred from the antinode to the node.

Partial molar quantities are approximated with molar quantities throughout in this preliminary treatment, and thus $q = V_2/V_1 = M_2 \varrho_1/M_1 \varrho_2$, where V refers to the molar volume and ϱ to the density of the pure components.

The proper process will be the sum of the two processes (1) and (2)

$$M_{2n} + q M_{1a} \rightarrow M_{2a} + q M_{1n} \quad (3)$$

In the state of equilibrium the free energy change, ΔF , of the process is zero, or

$$\Delta F = \mu_{2a} + q \mu_{1n} - \mu_{2n} - q \mu_{1a} = 0 \quad (4)$$

where μ designates the time mean values of the corresponding chemical potentials per mole under the prevailing conditions in the ultrasonic field. It is convenient to define the standard conditions as the unit concentration of 1 mole/cm³, and the pressure P_s and temperature T_s where P_s and T_s are the time mean values of these quantities in the actual ultrasonic field. It is to be noted that the P_s and T_s as defined here are constant during any one experiment but may have other values for different experiments. Furthermore we impose the condition that the particle velocity is zero.

Let us first examine the free energy change which will accompany the transformation of P_s and T_s into the corresponding oscillating variables. The changes of state in the ideal acoustic wave are processes that occur at constant entropy. It can easily be shown that the appropriate thermodynamic formulae are ¹⁰

$$\left(\frac{\partial F}{\partial T}\right)_S = \frac{V \cdot C_p}{T \cdot \left(\frac{\partial V}{\partial T}\right)_P} - S \text{ and } \left(\frac{\partial F}{\partial P}\right)_S = V - \frac{S \cdot T}{C_p} \cdot \left(\frac{\partial V}{\partial T}\right)_P \quad (5)$$

From these expressions is inferred that the derivatives $\left(\frac{\partial F}{\partial T}\right)_S$ and $\left(\frac{\partial F}{\partial P}\right)_S$ may be assumed to be very near constant in this ideal case; the pressure and temperature variations amount to some atmospheres and some tenths of a degree centigrade respectively. As the equations thus will be linear there is a negligible change in the free energy when we change the stationary conditions, P_s and T_s , into oscillating ones with the same time mean values. Furthermore P_s and T_s are assumed to be the same in the nodes and the antinodes (the mean pressure equals the static pressure plus the sound pressure). It is now recognized that with the chosen set of standard conditions the pressure and temperature fluctuations in the ideal case will not affect the chemical potentials in question. — It remains, however, to obtain expressions for the influence of the particle velocity in the antinodes.

The displacements of the particles are considered to be reversible and thus the increase in the free energy of the substance is equal to the work done upon it. This quantity is here negative since work is done on the surroundings of the oscillating particles. If x is the displacement and ρ is the density we can write for 1 cm³ of the substance in the antinode

$$dF = \rho \cdot \frac{\partial^2 x}{\partial t^2} \cdot dx = \rho \cdot \frac{\partial^2 x}{\partial t^2} \cdot \frac{\partial x}{\partial t} \cdot dt \quad (6)$$

The acoustic displacements are written under the form

$$x = A \cdot \sin (\omega \cdot t) \quad (7)$$

where A is the amplitude. Accordingly we obtain the derivatives

$$\frac{\partial x}{\partial t} = A\omega \cos(\omega t) \text{ and } \frac{\partial^2 x}{\partial t^2} = -A\omega^2 \sin(\omega t) \quad (8)$$

Insertion of these expressions gives

$$dF = -\frac{1}{2} \cdot \rho \cdot A^2 \cdot \omega^3 \cdot \sin(2\omega t) \cdot dt \quad (9)$$

which on integration yields

$$\Delta F = \frac{1}{4} \cdot \rho \cdot A^2 \cdot \omega^2 \cdot (\cos(2\omega t) - 1) \quad (10)$$

The time mean value of the increase in free energy can then easily be shown to be

$$\Delta F = -\frac{1}{4} \cdot \rho \cdot A^2 \cdot \omega^2 \quad (11)$$

the absolute value of which thus is seen to be equal to either the kinetic or the potential part of the mean energy density in the acoustic field.

The parallelism between this "acoustic potential" and the centrifugal potential may be pointed out for the sake of clarity. If a particle is transferred from any position where it is at rest to some position in a centrifugal field the increase in the free energy is also negative as in this case¹⁰. As a matter of fact the movement in the acoustic field constitutes the one dimensional projection of the two dimensional movement in the centrifugal field.

The free energy increase *per cm³* is divided between the two components in the quantities

$$\Delta F_1 = -\frac{1}{4} \cdot c_{1s} \cdot M_1 \cdot \omega^2 \cdot A^2 \text{ and } \Delta F_2 = -\frac{1}{4} \cdot c_{2s} \cdot M_2 \cdot \omega^2 \cdot A^2 \quad (12)$$

where c stands for the concentration in moles/cm³.

The acoustic intensity, J , can be expressed by $J = \frac{1}{2} \cdot \rho \cdot \omega^2 \cdot A^2 \cdot v$, where v is the sound velocity. (The formula is strictly valid for progressive waves. In a stationary field, however, the concept of intensity seems to be unclear. In this work it is rather convenient to define J also for the resonance field according to the given progressive field relation.) Utilizing this it is possible to write the free energy increase *per mole* as

$$\Delta F_1 = -\frac{1}{2} \cdot \frac{J}{v} \cdot \frac{M_1}{\rho} \text{ and } \Delta F_2 = -\frac{1}{2} \cdot \frac{J}{v} \cdot \frac{M_2}{\rho} \quad (13)$$

The appropriate chemical potentials are now computed to be

$$\begin{aligned}
 \mu_{2n} &= \mu_2^0 + RT \ln c_{1a} \\
 \mu_{1a} &= \mu_1^0 + RT \ln c_{1a} - \frac{1}{2} \cdot \frac{J}{v} \cdot \frac{M_1}{\varrho} \\
 \mu_{2a} &= \mu_2^0 + RT \ln c_{2a} - \frac{1}{2} \cdot \frac{J}{v} \cdot \frac{M_2}{\varrho} \\
 \mu_{1n} &= \mu_1^0 + RT \ln c_{1n}
 \end{aligned} \tag{14}$$

Applying the equilibrium condition that the free energy change should be zero (4), gives as a result

$$RT \ln \frac{(c_{1n})^q \cdot (c_{2a})}{(c_{1a})^q \cdot (c_{2n})} = \frac{1}{2} \cdot \frac{J}{v} \cdot \frac{M_2}{\varrho} (1 - \varrho_1/\varrho_2) \tag{15}$$

Insertion of $\Delta c_2 = c_{2a} - c_{2n}$ and repeated approximations lead to the more convenient expression

$$\Delta c_2 = \frac{1}{2} \cdot \frac{J}{v} \cdot \frac{1}{RT} \cdot \frac{M_2}{\varrho} \cdot \frac{c_1 c_2}{c_1 + q^2 \cdot c_2} \cdot (1 - \frac{\varrho_1}{\varrho_2}) \tag{16}$$

As a practical example we may consider an aqueous glycerol solution with 50 vol % glycerol at the (rather high) acoustic intensity of 10 W/cm². Insertion of the numerical values gives for this case

$$\Delta c_2 = 3 \cdot 10^{-10} \text{ or } \frac{\Delta c_2}{c_2} = 5 \cdot 10^{-8}$$

This separation corresponds to a change in the refractive index of $5 \cdot 10^{-9}$, which is too small to be observed by the present "Schlieren" methods (the resolution of which may be put equal to $5 \cdot 10^{-7}$). In passing it can be noted that the value for the relative *temporary* separation in a case comparative to the above example is computed to be of the order of $5 \cdot 10^{-12}$ by means of Herzfeld's formula ⁷.

The approximate treatment performed above has led to small values for the separation too small to be detected by experiments *e. g.* of the kind described by Frei and Schiffer ⁵ and Ernst ⁶. The computed effects are, however, not of an infinitesimally small magnitude.

Here it has to be remembered that there often is a very poor accordance between ultrasonic parameters as determined by experiments and calculated with the aid of the present theories. For example the experimental absorption coefficients are in some cases higher than the "theoretical values" by a factor of 1 000. These circumstances clearly indicate that in an ultrasonic field processes might occur about which at present little is known. Therefore it still seemed worth while trying some experimental approaches to this problem in

spite of the negative result of the calculation. This especially as the published results referred to above constitute a rather strong support to the idea of a separation.

EXPERIMENTAL DETERMINATIONS

The direct way of measuring any concentration changes set up in the ultrasonic field is to take out thin layers of the liquid column in the stationary ultrasonic field and analyse them. This could be done by means of a special technique: the separation cell was equipped with a small pile of filter papers; after the ultrasonic treatment the papers were separated and analysed.

Necessary for this to work well is that there is a negligible absorption of sound in the filter paper pile. In separate experiments this was demonstrated to be true; *e. g.* a pile of 20 papers in water showed a value for the transmission of $91 \pm 2\%$ at 700 kc/s, 1.5 W/cm², 25 °C and a dry weight of 8.15 mg/cm² per paper. Since in the experiments reported here the pile consisted of 5–6 papers it is realized that absorption and reflection in the pile may not have caused any influence on the results.

The general experimental arrangements were the same as described in ⁴. The utilized separation cell is shown in Figure 1. The paper pile covers the region between the reflector node and the nearest antinode $1/4 \lambda$ from there. Thermostated oil is circulated not only around the cell but also in the reflector assembly in order to obtain as good a temperature control as possible within the essential part of the cell.

For the choice of the analytical procedure one has to consider the following main requirements. Since evaporation from the papers is the most important source of error the analytic method must be very rapid. It is also wished that the result will be received in terms of concentration and not as absolute amounts. The refractometric method could fulfill these requirements.

A special feature with the refractometric method was that it was possible to perform the measurements directly on the filter paper. — A strip was snipped off from the filter paper and placed between the prisms of the Abbe refractometer. The borderline between the dark and light fields in the ocular was of course not so sharp as in measurements on a proper liquid object. The error obtained in the described procedure, however, was found to be less than the error when one pressed some liquid from the paper and made the measurements on this liquid sample.

A typical experiment was conducted in the following way. Before the experiment the filter papers were soaked in the experiment solution and the whole put under the vacuum for 3–4 hours in order to remove the gas in the papers and in the solution. The proper number of degassed papers were then quickly placed in position on the reflector and the assembly inserted in the cell. The cell was filled with some more solution and mounted on its place on the frame above the piezo quartz. — After the ultrasonic treatment this procedure was repeated in the reverse order. The cell was inverted to permit the surplus solution to run away and then dismounted. After removal of any adhering surplus solution with a strip of filter paper the papers in the pile were taken away one by one by means of sharp tweezers and put into separate small weighing glasses with covers.

The refractometric analyses were performed in a special order and at a controlled speed in order to obtain mean values as free from non-statistical error as possible. (The analyses

Figure 1. Separation cell with a thin acoustic window of stainless steel.

were made in the order paper No. 1, 2, 3 ... 3, 2, 1. Thus two strips were snipped off from each paper; on every strip 10 single readings were made.)

The experiments were performed on aqueous glycerol solutions, about 50 % glycerol, so as to fit with the experiments of Frei and Schiffer⁶ referred to above; and on ferric nitrate solutions, 80 mg Fe^{+++} /ml, so as to compare with the electrochemical phenomena³. The ultrasonic treatments were performed at varying times and acoustic intensities, max. being 400 minutes at $\sim 3\text{W}/\text{cm}^2$, most often 100 minutes at $\sim 7\text{W}/\text{cm}^2$. These experiments were supplemented with quite analogous runs but with no sound.

No separation could, however, be detected. The experimental error amounted in the case of the glycerol solution to ± 0.0002 in the refractive index or $< 0.2\%$ in the concentration, and in the iron solution to ± 0.0005 in the refractive index or $< 2\%$ in the concentration.

DISCUSSION

From the above results one must conclude that the electrochemical phenomena are not caused by separation but must depend on some other influence on the electrode potential, as also could be inferred from a separate study on this⁴. The effects observed *e. g.* the production of ripples in electrolysis should namely, if separation were the cause, be connected with a high degree of separation, far above the experimental error in the direct concentration determinations.

Concerning the glycerol solutions we must confine ourselves to noting the experimental result that the separation, if real, must be very small and $< 0.2\%$ in these experiments. There is however still the possibility to be discussed that separation might occur to a smaller degree and be observed by Schlieren methods as has been reported^{5,6}. The calculations, however, show

that the separation should be less than what is detectable even in this way. The reported results ^{5,6} therefore probably depends either on some unknown effect promoting separation or on structure changes in the liquid.

Contrary to a statement in the literature ⁶ it does not seem probable that separation by ultrasonic waves might constitute an alternative to the other methods for separation, *e.g.* thermal diffusion.*

SUMMARY

An approximate formula for the permanent separation is derived where is utilized the concept of an acoustic potential, which is partly analogous with the thermodynamic centrifugal potential. The separation effect as calculated with this formula is found to be less than what seems possible to detect by experiments. The performed experiments which were made in spite of the result of this calculation have given negative results.

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