

LETTER TO THE EDITOR

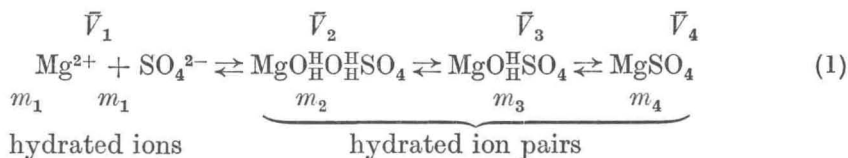
Effect of pressure on sulfate ion association and ultrasonic absorption in sea water

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Abstract—Recent studies on sea water indicated that an increase in pressure of 1000 atm produces a small increase in the concentration of MgSO_4 ion-pairs; this is opposite to the effect observed in aqueous solutions of MgSO_4 alone. This increase has been assumed to imply a corresponding increase with pressure of ultrasonic absorption due to MgSO_4 in sea water, in contrast to the large decrease observed in aqueous solutions. A detailed calculation based on the Eigen and Tamm multistate dissociation model shows, however, that a decrease in ultrasonic absorption with pressure still occurs even though the concentration of ion-pairs increases

KESTER and PYTKOWICZ (1970) reported that the effect of pressure on dissociation of NaSO_4^- ion-pairs in sea water produces an increase in the concentration of MgSO_4^0 ion-pairs in contrast to the decrease (FISHER, 1962) observed for aqueous MgSO_4 solutions. For a pressure change of 1000 atm at 2° they calculate an increase of SO_4^{2-} paired with Mg^{2+} from 21 per cent (0.0072 molal) to 24 per cent (0.0082 molal) of the total sulfate. KESTER and PYTKOWICZ assumed that their data suggested an increase of ultrasonic absorption with depth in the ocean. At constant pressure KURTZE and TAMM (1953) have shown such an increase upon addition of a common ion. However, such a conclusion about the effect of pressure is unwarranted because the ultrasonic absorption depends on the relative distribution of the different species of MgSO_4 ion-pairs (EIGEN and TAMM, 1962). While ultrasonic absorption has been used to calculate ion-pairing in sea water at atmospheric pressure (FISHER, 1967), the pressure calculation is not as simple. For example, in aqueous solutions of MgSO_4 a pressure increase of 1000 atm produces a 60 per cent decrease in ultrasonic absorption and only a 10 per cent decrease in MgSO_4^0 ion-pairs (FISHER, 1965).

These apparently contradictory effects are resolved by the EIGEN and TAMM (1962) multistate dissociation theory in which three forms of ion-pairs interact through two pressure dependent chemical reactions shown below



where m_1 represents the concentration of each of the electrically conducting hydrated ions; m_2 , m_3 and m_4 are the concentrations of the various ion-pairs which differ in the number of water molecules separating the ions. For the corresponding partial molal volumes EIGEN and TAMM calculated $\bar{V}_1 \leq \bar{V}_2 < \bar{V}_3 < \bar{V}_4$. The transition from state 4 to state 3 is the reaction which essentially controls the relaxation frequency ($\sim 10^5$ Hz) observed in the ocean and aqueous solutions. An increase in

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hydrostatic pressure will shift the equilibria to the left in the above equation, that is, towards the states with smaller partial molal volumes. An increase in the concentration of either the Mg^{2+} or SO_4^{2-} ions will shift the equilibria towards the right. However, even if the pressure-induced increase in the SO_4^{2-} concentration produces a small increase in the overall concentration of ion-pairs, $m_2 + m_3 + m_4$, the sound absorption will still decrease because m_4 decreases substantially.

To illustrate this, assume that the values of $m_2 + m_3 + m_4$ calculated by KESTER and PYTKOWICZ for MgSO_4^0 can be used at 20–25°. Using these concentrations and the multistate parameters selected on the basis of acoustic and conductance data (FISHER, 1965), the concentration m_4 shown in Table 1 can be calculated as a function of pressure with the equation (HARNED and OWEN, 1958)

$$\left(\frac{\partial \ln K_{ij}}{\partial p}\right)_T = -\frac{\Delta V_{ij}}{RT}, \quad (2)$$

where the K_{ij} are the equilibrium constants and the ΔV_{ij} are the volume changes for the reactions. It is the large volume change, $\Delta V_{23} = \bar{V}_2 - \bar{V}_3$, that is responsible for the large decrease in m_4 .

Table 1. Illustrative calculation of pressure dependence of K_{ij} and m_4 for MgSO_4 in sea water

K_{ij}	1 atm	1000 atm	ΔV_{ij} cm ³ /mole
$K_{23} = \frac{m_2}{m_3}$	1	2.1	$\Delta V_{23} = -18$
$K_{34} = \frac{m_3}{m_4}$	9	10.2	$\Delta V_{34} = -3$
$m_2 + m_3 + m_4$	0.0072	0.0082	
m_4	0.00038	0.00025	

Because m_4 is only a small fraction (<6%) of the MgSO_4 ion-pair concentration, the ultrasonic absorption is proportional to the concentration m_4 (FISHER, 1965). From the decrease in m_4 shown in Table 1, it can be concluded that there will still be a decrease of ultrasonic absorption with depth in the ocean despite a small increase in the total ion-pair concentration. The decrease will not be as great as that in m_4 because of increases in sound velocity and density; however, there will be an overall net decrease. How closely these calculations correspond to reality is another question which can only be resolved by ultrasonic experiments at sea.

In conclusion, there is no basis for prediction of an increase in ultrasonic absorption with depth in the ocean on the basis of a small increase in MgSO_4^0 ion-pairs due to NaSO_4^- dissociation.

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REFERENCES

- EIGEN M. and TAMM K. (1962) Schallabsorption in Elektrolytlosungen als folge chemischer Relaxation. *Z. Elektrochem.* **66**, 93-121.
- FISHER F. H. (1962) The effect of pressure on the equilibrium of magnesium sulfate. *J. Phys. Chem.* **66**, 1607-1611.
- FISHER F. H. (1965) Ultrasonic absorption in MgSO_4 solutions as a function of pressure and dielectric constant. *J. Acoust. Soc. Amer.* **38**, 805-812.
- FISHER F. H. (1967) Ion-pairing of magnesium sulfate in seawater: determined by ultrasonic absorption. *Science* **157**, 823.
- HARNED H. S. and OWEN B. B. (1958) *The Physical Chemistry of Electrolytic Solutions*, 3rd edition, 803 pp. Reinhold.
- KESTER D. R. and PYTKOWICZ R. M. (1970) Effect of temperature and pressure on sulfate ion association in sea water. *Geochim. Cosmochim. Acta* **34**, 1039-1051.