

THE JOURNAL
OF THE
ACOUSTICAL SOCIETY OF AMERICA



Volume 46 Number 3

(Part 2)

SEPTEMBER 1969

10.5

Received 12 March 1968

Effect of Pressure on Ultrasonic Absorption, Multistate Dissociation, and Chemical Equilibrium in MnSO_4 Solutions*

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Measurements were made on the effect of pressure on ultrasonic absorption in a 0.5M aqueous solution of manganese sulfate at 25°C. A cylindrical resonant cavity was used for obtaining absorption in the frequency regions of 300 and 500 kHz, at pressures up to 20 000 psi. Results are similar to those obtained for MgSO_4 , in that absorption decreases by a factor of about 3 for a pressure increase of 15 000 psi. Independent conductivity data show nearly the same behavior for MnSO_4 as for MgSO_4 solutions, namely, an increase of only about 14% in the concentration of dissociated ions for the same pressure increase. These results for MnSO_4 appear to be inconsistent with the model used by Atkinson and Kor to analyze their data. The large effect of pressure on ultrasonic absorption is similar to that observed by Carnevale for 0.1M MnSO_4 at 60°C from 9 to 75 MHz.

INTRODUCTION

The extensive acoustic absorption measurements of Kurtze and Tamm¹ in aqueous solutions of divalent sulfates demonstrated that these electrolytes exhibited pronounced acoustic relaxation frequencies. The high-frequency relaxation was nearly the same ($\nu_1 \cong 200$ MHz) for all the salts but the low relaxation frequency varied over a wide range as the cation varied from Be through Ni, Mg, Co, and Mn ($\nu_{\text{III}} = 10^3 - 5 \times 10^6$ Hz). The acoustic properties exhibited by these solutions have been explained by Eigen and Tamm² in terms of a multistate dissociation theory, in which a series of pressure-dependent chemical reactions are coupled together. This theory postulates three forms for an electrically neutral ion pair, in which the successive stepwise addition of water molecules between the ions constitutes the reactions giving rise to the observed acoustic absorption; ultimately, the ion pair dissociates into electrically conducting hydrated ions.

The multistate dissociation theory was developed to account for acoustic absorption at atmospheric pressure, in particular, for solutions of MgSO_4 , the salt that is

responsible for the high sound absorption in sea water below ~ 100 kHz.³ This theory also accounts for the contrasting pressure dependence observed for acoustic absorption and electrical conductivity of MgSO_4 solutions⁴; a pressure increase of 15 000 psi produces a decrease in sound absorption of about 67%, whereas only a 10% increase is observed in electrical conductance.⁵

Because of the large difference (~ 130 kHz vs ~ 5 MHz) in the acoustic relaxation frequency ν_{III} , observed at atmospheric pressure for MgSO_4 and MnSO_4 solutions, a set of experiments was performed in 1958 at the Acoustic Research Laboratory at Harvard in order to compare the effect of pressure on ultrasonic absorption for aqueous solutions of these two salts. Because of the large difference in the relaxation frequency, ν_{III} for MgSO_4 and MnSO_4 , we wished to determine if this difference might have any relation to the pressure dependence of sound absorption.

In 1958, Carnevale⁶ reported pressure data on ultrasonic absorption in aqueous MnSO_4 solutions at 60°

* O. B. Wilson and R. W. Leonard, *J. Acoust. Soc. Amer.* **26**, 223-226 (1954).

† F. H. Fisher, *J. Acoust. Soc. Amer.* **38**, 805-812 (1965).

‡ F. H. Fisher, *J. Phys. Chem.* **66**, 1607-1611 (1962).

§ E. H. Carnevale, "Effect of Pressure on Ultrasonic Relaxation in Electrolytes," PhD thesis, Catholic University of America Press (1958).

* Contribution of Scripps Inst. of Oceanogr., new series.

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¹ G. Kurtze and K. Tamm, *Acustica* **3**, 33-48 (1953).

² M. Eigen and K. Tamm, *Z. Elektrochem.* **66**, 93-121 (1962).

ULTRASONIC ABSORPTION IN $MnSO_4$ SOLUTIONS

 TABLE I. Summary of present absorption data of 0.5M $MnSO_4$ at 25°C and atmospheric pressure.^a

| | | 327 kHz | 500 kHz |
|-------------------------------|--|------------------------|------------------------|
| α' | (dB/sec) | 2269 ± 231 | 3991 ± 263 |
| λ | (cm) | 0.471 | 0.308 |
| α | (Np/cm) | 1.696×10^{-3} | 2.983×10^{-3} |
| $\alpha\lambda$ | (Np) | 0.799×10^{-3} | 0.919×10^{-3} |
| $(\alpha/f^2) \times 10^{17}$ | (Np cm ⁻¹ · sec ⁻²) | (1590 ± 159) | 1190 ± 79 |
| $(Q\lambda) \times 10^{32}$ | (m ²) | 531 ± 53 | 610 ± 40 |

^a $\alpha' = 8.686\alpha c$, $c = 154\,000$ cm/sec, $Q\lambda = 2\alpha\lambda/NA$, where N is concentration in moles/cubic meter and A is Avogadro's number.

over a frequency range from 9.0 to 75 MHz and up to pressures of about 60 000 psi; for a pressure increase of ~15 000 psi, he observed a large decrease in absorption similar to that observed for $MgSO_4$ at 25° and a slight increase, about 15%, in relaxation frequency. However, because of the large temperature difference, it was not possible to compare the results between $MgSO_4$ and $MnSO_4$ solutions.

At the time this work was performed, no quantitative model had been proposed for $MnSO_4$, and the multistate dissociation theory had not yet appeared in detail, although its basic features had been outlined.⁷ The results for the pressure dependence of sound absorption in $MnSO_4$ solutions were similar to but less accurate than those obtained in $MgSO_4$ solutions. Results for the pressure dependence of electrical conductivity for $MnSO_4$ solutions⁸ were also nearly the same as for $MgSO_4$.⁵ The recent work of Atkinson and Kor⁹ on $MnSO_4$, as well as the work of Bechtler at Tamm's laboratory, stimulated the reexamination of these 10-year-old data.

The present experimental results are discussed in relation to a critical test of a multistate dissociation model proposed by Atkinson and Kor⁹ for $MnSO_4$ solutions at 25°.

I. EXPERIMENTAL MEASUREMENTS AND RESULTS

Measurements of ultrasonic absorption were made in two frequency regions, using the resonant-cavity technique described in relation to the $MgSO_4$ work.⁴ The results were converted to single-frequency data as a function of pressure¹⁰ by means of Eq. 1,

$$2\alpha = \beta_{III}\rho c [2\pi\nu_{III}f^2 / (f^2 + \nu_{III}^2)], \quad (1)$$

where α is absorption in nepers/centimeter; β_{III} , the chemical compressibility in square centimeters/dyne; ρ , the density in grams/cubic centimeter; c , the sound speed in centimeters/second; f , the acoustic frequency

⁷ M. Eigen, Discussions Faraday Soc. 24, 25-36 (1957).

⁸ F. H. Fisher and D. F. Davis, J. Phys. Chem. 69, 2595-2598 (1965).

⁹ G. Atkinson and S. K. Kor, J. Phys. Chem. 71, 673-677 (1967).

¹⁰ The resonant mode frequency varies with pressure, owing to changes in sound velocity and cavity dimensions.

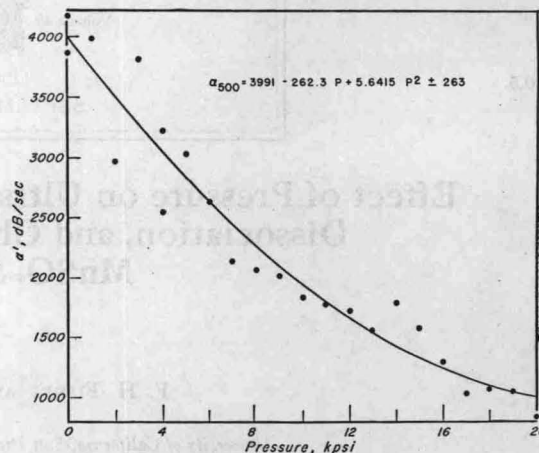


FIG. 1. Sound absorption at 327 kHz vs pressure for 0.5M $MnSO_4$ aqueous solution at 25°C.

in hertz; and ν_{III} , the relaxation frequency. At a given pressure ν_{III} , β_{III} , ρ , and c are constant, so

$$\frac{\alpha_1}{\alpha_2} = \left(\frac{f_1}{f_2}\right)^2 \left(\frac{f_2^2 + \nu_{III}^2}{f_1^2 + \nu_{III}^2}\right). \quad (2)$$

If ν_{III} is known, then absorption at frequency f_1 can be converted to that at f_2 with this equation. Since data in this work were obtained at frequencies well below the low relaxation frequency reported in the literature, it makes little difference for this conversion which value of ν_{III} is used. Because of the negligible pressure dependence observed for ν_{III} in $MgSO_4$ solutions at this concentration,⁴ ν_{III} was assumed to be pressure independent for $MnSO_4$. This assumption for 25° is not in substantial disagreement with Carnevale's work, in which he calculated a slight change of 15% for a pressure increase of about 15 000 psi.

The absorption results, reduced to fixed frequency through use of Eq. 2, are shown in Figs. 1 and 2. To facilitate comparison of these results with those of other

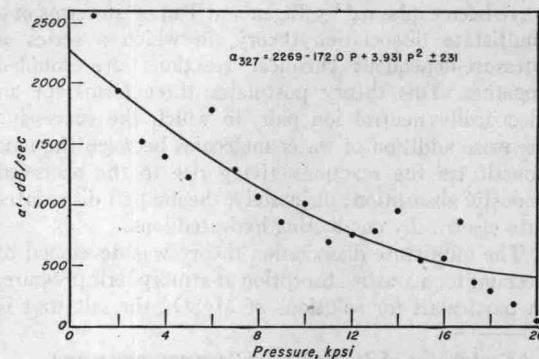


FIG. 2. Sound absorption at 500 kHz vs pressure for 0.5M $MnSO_4$ aqueous solution at 25°C.