Origin of the low-frequency sound absorption in sea water

Ernest Yeager
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

F. H. Fisher
Marine Physical Laboratory of the Scripps Institution of Oceanography, University of California, San Diego, California 92152

John Miceli and Robert Bressel
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

(Received 21 December 1972)

Temperature-jump measurements in sea water over the time domain 10^{-5} to 10^{-2} sec reveal a single relaxation of 1.5×10^{-4} sec at 9.7°C, which appears to correspond to the $\sim$1 kHz relaxation found from long-range sound propagation. Laboratory measurements indicate the relaxation to originate from boron with the $B(OH)_3-B(OH)_4^-$ equilibrium the likely relaxation process.

Subject Classification: 13.2.

Sea water exhibits large excess acoustical absorption at frequencies below 100 kHz because of a chemical relaxation involving magnesium sulfate with a relaxation frequency f_r of $\sim$70 kHz or a relaxation time $\tau=\frac{1}{2}\pi f_r=2.3$ μsec.[1] From analysis of long-range acoustic propagation in the deep-ocean sound channel (depth 1300 m at $\sim$4°C), Thorp[2] has concluded that sea water has an additional relaxation at $\sim$1 kHz ($\tau=\sim160$ μsec) which further increases the absorption by a factor of $\sim$10 over the magnesium-sulfate absorption. Long-range sound-propagation studies in Lake Superior and Lake Tanganyika have also been reported[3] to yield similar excess absorption at frequencies below 1 kHz but these absorption data are far less certain and remain to be confirmed.

The acoustical absorption of sea water has not been measured in the laboratory at such low frequencies because of the very small attenuation coefficients (i.e., 10^{-1} dB/km at 1 kHz). Other relaxation methods, however, can be used to obtain information concerning the origin of this low-frequency acoustic relaxation. This communication reports laboratory measurements on standard sea water[4] and synthetic sea water by the temperature-jump[5] relaxation method which confirm the existence of a relaxation in sea water of the proper relaxation time and identifies the boric-acid–borate system as responsible for this low-frequency relaxation.

The relaxation spectrum of sea water was examined in the range 10^{-5}–10^{-2} sec with temperature-jump apparatus (Messanlagen Studiengesellschaft)[5] in which a temperature rise of $\sim$3°C is produced in $<10^{-6}$ sec by a condenser discharge through the solution. The subsequent relaxation is followed optically by means of a hydrogen ion sensitive color indicator (2.0×10^{-5} M phenol red unless otherwise noted). Only one relaxation was found with $\tau=107$ μsec at 25.5°C. Modification of the pH of the sea water by small additions of HCl or KOH had no effect on the relaxation time over the pH range 7.2 to 8.7. At a pH of 9.46, the relaxation time increased to 153 μsec, using 2.0×10^{-5} M thymol blue as the indicator to give adequate sensitivity at the higher pH (see Table I).

Dilution of sea water by a factor of two with a solution consisting of 0.7M NaCl plus sufficient $NaHCO_3$ to yield a final pH of 7.66 increased τ to 164 μsec at 25.5°C. For a similar dilution by five fold, τ increased to 456 μsec. Upon restoring the total boron concentration to the normal sea water value of 4×10^{-4}

TABLE I. Relaxation times measured with the temperature-jump method[a] and the corresponding relaxation frequencies.

A. pH dependence of τ in sea water[b] at 25.5°C

pH	7.17	7.66	8.54	9.48
τ(μsec)	107	107	107	153
f_r(kHz)	1.49	1.49	1.49	1.04

B. Concentration dependence of τ at 25.5°C in sea water[b] diluted with 0.7 M NaCl and sufficient $NaHCO_3$ added to adjust the final pH to 7.66.

% (volume) sea water	100	50	20
τ(μsec)	107	164	456
f_r(kHz)	1.49	0.97	0.35

C. Temperature dependence of τ in sea water[b]

temperature	25.5°C	9.7°C
τ(μsec)	107	150
f_r(kHz)	1.49	1.06

[a] Temperature rise: $\sim$3°C; indicator: 2×10^{-5} M phenol red, except at pH 9.46, indicator: 2×10^{-5} M thymol blue. Temperatures listed are final values following temperature rise.

[b] Sea water sample obtained from Standard Sea Water Service, I.A.P.S.O., Charlottenlund, Denmark, Chlorinity: 19.375‰, 12–13 June 1971.

M by adding $Na_2B_4O_7$, the relaxation time of the fivefold diluted sea water decreased from 456 to 118 μsec, a value essentially the same as that of undiluted sea water. Lowering the temperature to 9.7°C increased the relaxation time of undiluted sea water to 150 μsec, which compares favorably with the value of 160 μsec calculated from Thorp's analysis from long-range acoustic propagation data at ~4°C.

To establish further that the boric-acid–borate system is responsible for the observed relaxation, synthetic sea water was prepared according to the Lyman–Fleming formulation[6] but without any borates or boric acid added. This formulation includes only constituents at concentrations above 1 ppm.[7] Such boron-free synthetic sea water did not exhibit any relaxation in the temperature-jump apparatus in the 10^{-5} to 10^{-2} sec range. Upon addition of sufficient boric acid to duplicate the total boron concentration in standard sea water, the relaxation reappeared with $\tau = 92$ μsec. Similar results are to be expected with the addition of sodium tetraborate in place of boric acid since the tetraborate anion is in equilibrium with the $B(OH)_4^-$ anion and boric acid. Only the *p*H will differ and then only by a few tenths of a *p*H unit over a range where the relaxation time appears to be relatively insensitive to *p*H in sea water.

Anderson *et al.*[8] have examined the relaxation spectra of boric acid in $0.1M$ $NaClO_4$ solutions using the temperature-jump method. The total boron concentrations, however, were in the range 0.06 to $0.6M$, which is much higher than in sea water or used in the present study. These authors observed a concentration-dependent relaxation time with a value of 12.9 msec at $0.06M$ total boron concentration at 25°C. At lower concentrations, this relaxation time should become even longer and hence be far longer than the sea water acoustic relaxation time. Anderson *et al.* assigned the relaxation which they observed to the reaction

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O. \quad (1)$$

At the high concentrations and low *p*H involved in their studies, the concentration of the polymeric species $B_3O_3(OH)_4^-$ as well as boric acid should be appreciable. At the total boron concentrations and *p*H of sea water, however, the equilibrium constant data of Ingri *et al.*[9–11] indicate that the concentrations of the various polymeric borates [e.g., $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$] should be far too small to account for the excess acoustic absorption of sea water below 1 kHz or the relaxation effects observed in the present work.

Knoche[12] has proposed that the relaxation of an aluminum sulfate complex is responsible for the excess sound absorption in sea water below a few kilohertz. Knoche's proposal is based on a sea water concentration for aluminum in solution of ~1 mg/liter or $\sim 4\times10^{-5}M$. This value is to be compared with the 0.5 mg/liter given by Haendler and Thompson[13] in 1939; 0.16 to 1.9 mg/liter listed by Sverdrup, Johnson, and Fleming[14] in 1942; 0.001 to 0.01 mg/liter given by Durum and Haffty[15] in 1963; and 0.01 mg/liter listed by Sillen[16] in 1961 and also Goldberg[7] in 1965. This large range of values probably reflects the difficulty in differentiating analytically between Al ions in solution, Al in colloidal form, and even possibly Al adsorbed on the surface of colloidal particles in sea water. The 0.01 mg/liter value is probably a better indication of the concentration of Al in solution and a more appropriate value to be used for calculation of the low-frequency acoustical relaxation properties of sea water than the value of 1 mg/liter used by Knoche.

If the excess absorption is calculated using the rate constants obtained by Kalidas, Knoche, and Papadopoulos[17] and the value listed by Goldberg[7] for the concentration of aluminum in sea water (0.01 mg/liter or $4\times10^{-7}M$), the predicted excess absorption to be expected is far too small to explain the observed absorption. To check further on the possible contribution of Al to the excess low-frequency absorption, a solution containing 0.5 mg/liter of Al was prepared using the Lyman–Fleming[6] formulation for synthetic sea water but without any borates or boric acid added. No relaxation effect was observed in the range 10^{-2} to 10^{-5} sec. Further, the omission or addition of Al^{3+} at 0.01 mg/liter to the artificial sea water also had no effect on the relaxation observed by the temperature-jump method with boron present.

The chemical process responsible for the excess acoustic absorption in sea water and the relaxation observed in the present study is believed to involve an acid–base equilibrium between $B(OH)_3$ and $B(OH)_4^-$ of the form

$$B(OH)_3 + N + H_2O \rightleftharpoons B(OH)_4^- + (HN)^+, \quad (2)$$

where N is a Lewis base such as OH^- or $CO_3^=$. Reaction Eq. 2 may proceed through two steps as suggested by Muetterties[18] with the slow step involving the rearrangement from a trigonal to tetrahedral distribution of oxygen around boron. This rearrangement should result in a substantial contribution to the activation free energy for the acid–base conversion with the result that the overall $B(OH)_3 - B(OH)_4^-$ conversion should be much slower than expected on the basis of simple diffusion control.

In sea water, the reaction, Eq. 2, will be coupled to other processes involving OH^- and H^+ ions, including the $CO_3^= - HCO_3^- - H_2CO_3$ equilibria[19,20] which in turn are coupled to such processes as the formation of $MgCO_3$ and $CaCO_3$ complexes.[19,20] The complete analysis of the boric-acid–borate relaxation in sea water is expected to be quite complicated and will be the subject of a further investigation. A preliminary analysis, however, indicates that the data in Table I are reasonable for the reaction in Eq. 2 as the slow relaxing process.

While the relaxation time from the temperature-jump corresponds to that from the long-range acoustic-propagation studies in sea water, the temperature-jump method does not yield information concerning the volume change (ΔV) of the relaxing process. Such is needed to calculate the excess acoustical absorption to be expected from the relaxation. Efforts are in progress to determine ΔV using the pressure shock wave relaxation method[21] with the conductivity read-out normally used with this method replaced with an optical read-out similar to that involved in the temperature-jump studies.

ACKNOWLEDGMENTS

This research has been supported by the Office of Naval Research. The authors express appreciation to Prof. J. Stuehr of Case Western Reserve University for the use of temperature-jump equipment in his laboratory and to Dr. H. Hoffmann of the University of Erlangen for his help in the design and use of the pressure-shock apparatus.

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