THE BRINE CONTENT OF SEA ICE MEASURED WITH A NUCLEAR MAGNETIC RESONANCE SPECTROMETER

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ABSTRACT. Nuclear magnetic properties of hydrogen are used for the quantitative analysis of the water content of sea ice from 0° C. to −40° C. The data on water content are utilized to calculate the brine volume and brine weight content of the samples. Over a range of water contents of 2% to 96% the standard deviation of the nuclear magnetic resonance data from chemical analysis data is ±0·6%. An estimate of water content in a sample of sea ice at −70° C. is given, and the value of nuclear magnetic resonance measurements for field studies is discussed.

RÉSUMÉ. *La teneur en saumure de la glace de mer mesurée avec un spectromètre nucléaire à résonnance magnétique.* Les propriétés magnétiques nucléaires de l'hydrogène sont utilisées pour l'analyse quantitative de l'eau contenue dans la glace de mer de 0° C à −40° C. Les valeurs de la teneur en eau sont utilisées pour calculer le volume et le poids de saumure des échantillons. Pour des valeurs de rétention entre 2% à 96%, la déviation moyenne de la R.M.N. des analyses chimiques est de ±0,6%. Une estimation de l'eau de rétention d'un seul échantillon de glace de mer à −70° C est donnée, et la valeur des mesures de R.M.N. pour des études en campagne est discutée.

ZUSAMMENFASSUNG. *Der Salzwassergehalt von Meereis, gemessen mit einem kernmagnetischen Resonanz-Spektrometer.* Zur quantitativen Analyse des Wassergehaltes von Meereis bei 0° bis −40° C werden die kernmagnetischen Eigenschaften des Wasserstoffes herangezogen. Die Wassergehaltswerte werden zur Berechnung des Salzwasservolumens und -gewichtes der Proben benutzt. Für einen Bereich von 2–96% Wassergehalt beträgt der mittlere Fehler der Ergebnisse aus der kernmagnetischen Resonanz gegenüber der chemischen Analyse ±0,6%. Nach einer Abschätzung des Wassergehaltes einer Meer-Eisprobe von −70° C wird der Wert der kernmagnetischen Resonanzmessung für Feldarbeiten erörtert.

INTRODUCTION

In the realm of solids, sea ice occupies a rather unique position. Physically it is an extremely complicated material which is always at its melting point, thus always in a state of quasi equilibrium at any given temperature. These equilibria are formed between the solid ice, the precipitated salts and the liquid brine solution. The dissolved salts and gases present in sea-water are not admitted to the ice lattice but are either expelled or entrapped in the interstitial and sub-crystal regions in the form of cells. The quantity, composition and distribution of these entrapped materials acutely affect the grain boundaries, thereby controlling the behavior and physical properties of the solid. Thus, any investigation of sea ice must be accompanied by a study of the phase composition.

The method commonly used by most investigators (Zubov, 1945, p. 143–4; Anderson, 1958, p. 148; Assur, 1958, p. 117; Brown, 1963, p. 81 and many others) to determine the amount of liquid phase (brine) present in a sample of sea ice is based upon the experimental data of Ringer (1906) and the later work of Nelson and Thompson (1954). This method assumes that the total amount of the salts in sea ice does not change when the concentration of brine changes with temperature.

Thus, if a sample of n grams of sea ice at a temperature T contains b grams of brine with a salinity S_b, then

$$n(S_m - S_s) = bS_b \qquad (1)$$

where S_m is the salinity of the melt water and S_s is the amount of the precipitated salts per gram of sea ice.

The brine content β_w (grams/kilogram of ice) is then given by

$$\beta_w = b/n = \frac{S_m - S_s}{S_b}. \tag{2}$$

Using the Nelson–Thompson data and equation (2), a number of authors (Anderson, 1958, p. 149–50; Assur, 1958, p. 124 and 138) have tabulated brine content, (β_w, the weight ratio, and β, the volume ratio) as a function of ice temperature and the salinity of the melt water of the sample.

The use of such a closed-system model for naturally-formed sea ice has certain drawbacks; e.g. the oceanic system of sea-ice formation is not a simple closed system. Ice formation in the open sea rarely takes place as undisturbed accretion from below. Water movements break up the initial sheet; collisions then bring about rafting; wave action splashes sea-water on top of the segments, all of which tend to produce a somewhat chaotic growth situation. Operating over and above these conditions to produce internal changes in the ion content are the processes of brine expulsion and migration (Lewis and Thompson, 1950; Zubov, 1945; Korolev, 1937). Thus, except for those brine cells which are totally enclosed by the ice crystals, the regime is an open one, particularly the lower sea-water–ice interface, where circulation effects maintain an almost constant salinity (Zubov, 1945, p. 140).

Therefore, it seems highly probable that in the course of one or two years' growth a variation in the ion ratios (from those in normal sea-water) occurs in natural sea ice. (There are experiments which support this view and some others which refute it.) Such changes in the ion ratio would alter the definition of salinity for the melt water.

A second drawback is that the salinity measurement requires a fairly large sample; therefore, the brine content is based upon an averaged salinity, i.e. the average of many crystal and liquid regions. Often the sample used for the salinity measurement is not directly involved in the physical experiment. And, finally, it is always desirable to measure an important quantity, such as brine content, directly rather than relying on the work of others and an indirect measurement as well.

Nuclear magnetic resonance (N. M. R.) techniques for measuring liquid phase content appear to offer a method which obviates these drawbacks. It measures the liquid phase content of a sample of sea ice with virtually no errors due to variations in the ion ratios or errors in salinity measurements. It measures the liquid content directly, and the sample size required for the measurement is comparable to the size of some of the smallest sea-ice crystals (on the order of 300 mg. or less).

Description of Nuclear Magnetic Resonance

The quantum-mechanical theory and the mathematical analysis of N. M. R. have been presented by Bloembergen and others, 1948; Pake, 1950; and Andrew, 1955; but, for the purposes of this paper, a brief descriptive model of the system may better serve as an introduction to the techniques.

Consider the hydrogen nuclei in a sample of water and imagine each nucleus to be a simple bar magnet which is spinning about its longitudinal axis. If the sample is now placed in a constant magnetic field, each nuclear magnet will precess about an axis which is in the direction of the constant field. The angular velocity of this precession will be proportional to the strength of the constant field. Now, if a second magnetic field is superimposed upon the system, and this new field is an oscillating one whose direction is perpendicular to that of the constant field, the precessing angle of the nuclei will be altered. If the frequency of the oscillating field is the same as that of the precessing nuclei, the disturbance of the precessing angle will be a maximum and a resonance will be developed. These disturbed nuclei will absorb energy from the oscillating field and the reduction in energy will be proportional to the number of nuclei present.

If the nuclei are in liquid form, their longitudinal axes will have a random distribution of direction and their own magnetic fields will tend to cancel each other. The resonance frequency band will be very narrow for a liquid. If the nuclei are in a frozen or solid state, the thermal movements of the nuclei will be greatly restricted. The axes distribution will no longer be random, and the magnetic field of each nucleus will influence the magnetic field of its neighbors. Over the whole sample the summation of these variations will result in a resonance band many hundred times wider than that of the liquid. As a result a combined system of liquid and solid nuclei produce a resonance curve similar to Figure 1. (Note: The liquid signal is highly exaggerated in width.) Over the narrow band width of the liquid signal, the solid signal may be assumed constant and the N. M. R. spectrometer may be set to scan only the very narrow segment of the frequency band containing the liquid signal. The intensity of the liquid signal is directly related to the amount of liquid present.

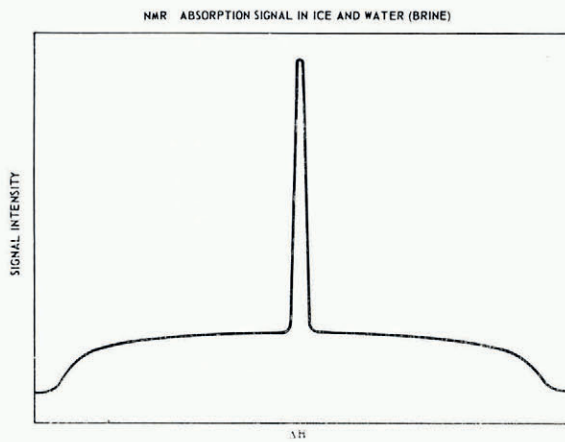NMR ABSORPTION SIGNAL IN ICE AND WATER (BRINE)

SIGNAL INTENSITY

ΔH

Fig. 1. Schematic of N. M. R. absorption signals of protons. The broad, flat signal is due to the protons in the solid ice. The sharp peak in the center is associated with the protons in the liquid brine solution. Note: This pulse is highly exaggerated in width for pictorial purposes, ratio of widths is actually about 100 to 1

THEORETICAL CONSIDERATIONS

Faraday's Law for the induced voltage in the receiver coil of the N. M. R. spectrometer is given by

$$V = -K \frac{dM_y}{dt} \tag{3}$$

where K is a function of the coil geometry and a filling factor associated with the sample, and M_y is the y component of the magnetic moment, (the y-axis is the axis of the receiver coil).

The solution of Equation (3) (see Pople and others, 1959, p. 39) is

$$V = C \frac{N H_1 \omega T_2}{T[1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2]} \tag{4}$$

where C includes the various nuclear and instrumental constants, T is the absolute temperature, N is the number of protons per unit volume, H_1 is the oscillating radio-frequency field, T_2 and T_1 are relaxation times, ω is the angular frequency of H_1 about the z-axis and at

resonance equals ω_0, the angular frequency of Larmor precession, given by $\omega_0 = \gamma H_0$ where H_0 is the uniform magnetic field in the z direction and γ is the magnetogyric ratio.

The peak voltage occurs at resonance and is given by

$$V_p = C\frac{NH_1\omega_0 T_2}{T(1+\gamma^2 H_1^2 T_1 T_2)}.$$

Several investigators have used peak measurements for moisture analysis (Shaw and Elsken, 1950; Rollwitz and O'Meara*); however, the dependence on the unknown quantities of the relaxation times (T_2 and T_1) produce rather large errors. Other investigators (e.g. Shaw and others, 1953) utilized the pulse width measurement; but this has drawbacks also, particularly in the small range of liquid contents over which meaningful measurements can be made. In order to reduce some of the errors and extend the range of liquid content which could be measured, the integral of equation (4) was used, i.e. the area under the liquid portion of the voltage curve (Fig. 1).

If the magnetic field is assumed to be swept at a rate R where

$$R = dH/dt, \tag{5}$$

equation (4) may be integrated with respect to time, and the area under the absorption curve is given by

$$A = \int_{-\infty}^{\infty} V\,dt = C\frac{H_1 N}{RT(1+\gamma^2 H_1^2 T_1 T_2)^{\frac{1}{2}}}. \tag{6}$$

The integration of V has removed the linear dependence on T_2 and reduced its dependence on the product $T_1 T_2$ to a square root.

Equation (6) is strictly valid only under certain conditions (Paulsen and Cooke, 1964), which for the most part are not practical for actual laboratory experimentation. In practice some approximations for measuring the absolute area have been derived (Williams, 1958; Jungnickel and Forbes, 1963) which give reasonable results and at the same time permit the use of more practical laboratory procedures. However, the best results have come from measuring the relative areas, i.e. the area ratio of the unknown peak to a standard peak. This scheme has the advantage of reducing the errors as well as the utilization of commercial laboratory equipment, and, in the case of sea-ice studies, gives precisely the type of information sought. We compare the N. M. R. areas of a known quantity of melted sea ice at a temperature just above its melting point (100 per cent liquid) with the N. M. R. areas of the entrapped liquid at sub-freezing temperatures.

The ideal situation would be to choose H_1 sufficiently small, so that

$$\gamma^2 H_1^2 T_1 T_2 \ll 1. \tag{7}$$

Then equation (6) may be expanded to

$$A = \frac{CH_1 N}{RT}[1 - \tfrac{1}{2}\gamma^2 H_1^2 T_1 T_2 + \tfrac{3}{8}(\gamma^2 H_1^2 T_1 T_2)^2 - \ldots]. \tag{8}$$

Using equation (7), equation (8) is given approximately by

$$A \approx \frac{CH_1 N}{RT}. \tag{9}$$

For the samples of sea-water at $-0 \cdot 5°$ C.,

$$T_1 \approx 1 \cdot 9 \text{ sec.}, \quad T_2 \approx 1 \cdot 4 \text{ sec.}, \text{ and } \gamma = 4 \cdot 26 \times 10^3,$$

thus the term $\gamma^2 H_1^2 T_1 T_2$ in equation (7) will have a value of $0 \cdot 1$ if H_1 is set at $0 \cdot 046$ milligauss. However, signal to noise ratios at the lowest temperatures are rather poor under the best of

* Determination of moisture by nuclear magnetic resonance. Unpublished paper presented before the Division of Carbohydrate Chemistry, American Chemical Society, Chicago, Illinois, 6–11 September 1953.

conditions and so a maximum value of H_1 is desired. A compromise value for H_1 of approximately 0·09 to 0·1 milligauss was chosen. This is well below saturation but is rather large for equation (7). Below solidification temperatures the ion concentration increases rapidly, causing a broadening of the signal and a decrease in the value of T_2. T_1, on the other hand, increases but at a much slower rate than T_2 decreases, so that (7) is more applicable at the lower temperatures. The measurements of T_2 and H_1 are rather difficult to make with any high degree of accuracy; so no correction was applied to equation (9) for this choice of H_1.

In equation (9) N is associated with the total number of protons (in solution) contained in the active volume of the receiver coil, hence, with the total number of water molecules present. A quantity Q is defined as the total weight of the water molecules contained in a sample of a salt solution (brine). The brine may be entrapped in a sample of sea ice or it may be the resultant melt water of the sea-ice sample. In the later case we may write

$$Q_0 = W(1 - S_{b_0}) \qquad (10a)$$

and for the entrapped brine we write

$$Q_T = w(1 - S_{b_T}) \qquad (10b)$$

where

W is the weight of the sea ice sample, w is the weight of the entrapped brine, and S_{b_0} and S_{b_T} are the respective salinities.

Then for a sample of sea ice or melt water in the active volume of the receiver coil

$$Q \propto N.$$

Now, if T_0 is a temperature just above the total-liquid point of an ice sample, then the ratio of the amount of water in the entrapped brine at some sub-freezing temperature, T, to the amount of water in the melted sample at T_0 is given by

$$\frac{Q_T}{Q_0} \approx \frac{A_T T C_0 R_T H_{1_0}}{A_0 T_0 C_T R_0 H_{1_T}}.$$

The sweep R and the radio-frequency field H_1 may be maintained relatively constant during an experiment; and, by choosing T_0 just above the total-liquid temperature, it is possible to minimize the variations in C. Thus, the ratio can be reasonably expressed by

$$\frac{Q_T}{Q_0} \approx \frac{A_T T}{A_0 T_0}. \qquad (11)$$

The theoretical value of Q_T/Q_0 may be calculated from the Nelson-Thompson data (Nelson and Thompson, 1954), using equations (10a) and (10b).

$$\frac{Q_T}{Q_0} = \frac{w(1 - S_{b_T})}{W(1 - S_{b_0})}. \qquad (12)$$

The Nelson-Thompson data (weights of ions and water in residual brine) are given for a melt-water salinity of 34·625 ‰, the weight ratio for any other value of S_{b_0} is given by multiplying the values given by Nelson and Thompson, by the ratio of the salinities. The experiments were designed to compare the weight ratio obtained from the N. M. R. data with the calculated values. The weight ratio of water can be used in some studies of the physical properties of sea ice, but it is more useful when it serves as the basis for calculating the two other ratios β_w and β. The first of these, the brine weight ratio, is given by

$$\beta_w = \frac{w}{W}$$

$$= \frac{Q_T(1 - S_{b_0})}{Q_0(1 - S_{b_T})}$$

$$\approx \frac{A_T T(1 - S_{b_0})}{A_0 T_0(1 - S_{b_T})}. \qquad (13)$$

Hereafter we shall choose to drop the approximation designation.

The second, and most useful ratio, is the volume ratio:

$$\beta = \beta_w \left(\frac{\gamma_i}{\gamma_b}\right)_T$$

where γ_i is the density of sea ice (usually the density of sea ice is a calculated value based upon the assumption that the sea ice has no void spaces) and γ_b is the density of the brine solution, both at temperature T.

Then

$$\beta = \frac{Q_T(1-S_{b_0})}{Q_0 (1-S_{b_T})} \left(\frac{\gamma_i}{\gamma_b}\right)_T$$
$$= \frac{A_T T(1-S_{b_0})}{A_0 T_0 (1-S_{b_T})} \left(\frac{\gamma_i}{\gamma_b}\right)_T. \tag{14}$$

The variations of such bulk physical properties of sea ice as strength, thermal conductivity, etc., with changes in temperature or salinity, have been ascribed by most investigators to changes in β; hence, this term is utilized in all calculations of these bulk properties. A direct accurate measurement of this important quantity has never been made.

EXPERIMENTAL ARRANGEMENT

A Varian Associates Model 4200B (high resolution N. M. R. spectrometer) was used for the experiments. It operates at a fixed frequency of 40 Mc./sec. with a 9,500 gauss magnetic field. The absorption signal was recorded on a Minneapolis Honeywell high-speed recorder, which worked in conjunction with a Perkin-Elmer electromechanical integrator to provide a numerical value for the area under the analog of the absorption curve. This system was capable of producing repeatable N. M. R. areas of a water sample with a maximum error of 1 per cent.

The sample holder was a glass Dewar vessel into which a separate 5 mm. internal diameter glass tube containing the sample could be introduced. Tests were made to determine the position and length (vertical) associated with the active volume of the receiver coil. The Dewar vessel was designed so as to permit centering of the sample within the active volume. Sample size was chosen so that the entire sample was contained well within the limits of this volume. The samples of sea-water at 35·035 ‰ and 10·022 ‰ salinity ranged in size from 250 to 350 mg. Dry nitrogen was cooled in a heat exchanger and circulated around the sample tube. The temperature of the sample could be maintained constant at any temperature from 0 to −70° C. ±0·5° C. Two calibrated copper–constantan thermocouples were used with a Minneapolis Honeywell recorder to provide a continuous record of sample temperatures.

RESULTS AND DISCUSSION

Figure 2 summarizes the results obtained for sea-water of 35·035 ‰ salinity. The experimental data $A_T T/A_0 T_0$ is compared with a curve of Q_T/Q_0 derived from the Nelson and Thompson (1954) data. The points in Figure 2 are average values of ten or more areas: five obtained with an increasing sweep (R) and five with a decreasing sweep, thus reducing instrumental drift errors. The standard deviation of the points from the Nelson and Thompson curve is 0·6 per cent. However, at −50° C. the error exceeds 50 per cent, so that the useful range of temperature is limited to about −40° C. At this particular S_{b_0} the weight of liquid water at −40° C. represents about 2 per cent of the initial weight at T_0.
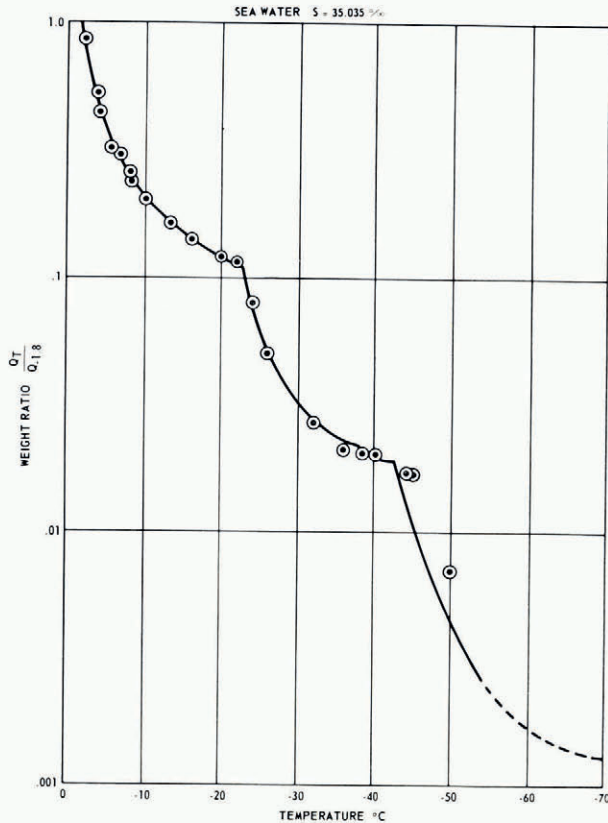
Fig. 2. *Relative water content in ‰ versus temperature for sea ice (sea-water sample 35·035 ‰ salinity). The curve is drawn from Nelson and Thompson's analytical data, the points are measured by N. M. R. techniques*

Figure 3 summarizes the results obtained for samples of sea-water with a salinity of 10·022 ‰. The curve is again derived from the Nelson and Thompson data. The standard deviation of the points from the Nelson and Thompson curve is 0·5 per cent and the range is about the same as Figure 2, 99 per cent to 2 per cent. However, due to the reduced salinity of the sample, this represents a useful range in temperature to −25° C.

The rapid increase in the errors associated with data below −40° C. is for the most part due to the experimental conditions. At −45° C. the signal to average noise ratio is approaching 5 : 1. This is well below the limits for reliable operation of the mechanical integrator. With an electronic integrator and recently developed modulation techniques for N. M. R. operation, it would appear relatively easy greatly to extend the useful range of measurements.

Figure 4 compares values of β obtained using the N. M. R. data in equation (14), with values calculated by Anderson (1960, p. 317). The usual procedure for evaluating either β_w or β for a sample of sea ice is to measure the temperature of the ice specimen and then the salinity of a melted sample which may be the test specimen or, more frequently, a core sample from the ice adjacent to the test area. In either case, the temperature and salinity are used to obtain a value of β_w or β from one of the phase diagrams given by Assur (1958, p. 138) or Anderson (1958, p. 148); Anderson (1960, p. 312). At the higher temperatures these phase diagrams have very steep slopes; thus, an error in the salinity measurement of

$\pm 0 \cdot 5 \%$ can produce an error in β of almost 10 per cent. In equation (14) the same error in salinity produces less than $0 \cdot 2$ per cent error in β.

Assuming that the ion ratios in sea ice are altered by the processes of precipitation and brine migration, the salinity of the melt water as determined by the same methods used for normal sea-water will be in error. Zubov (1945, p. 149) gives some values for the various ion ratios determined for young sea ice; using these values it is found that the salinity of the melt water could be as much as $0 \cdot 5 \%$ greater than that which was measured. This error in salinity could produce as much as 10 per cent error in β, depending upon experimental conditions.
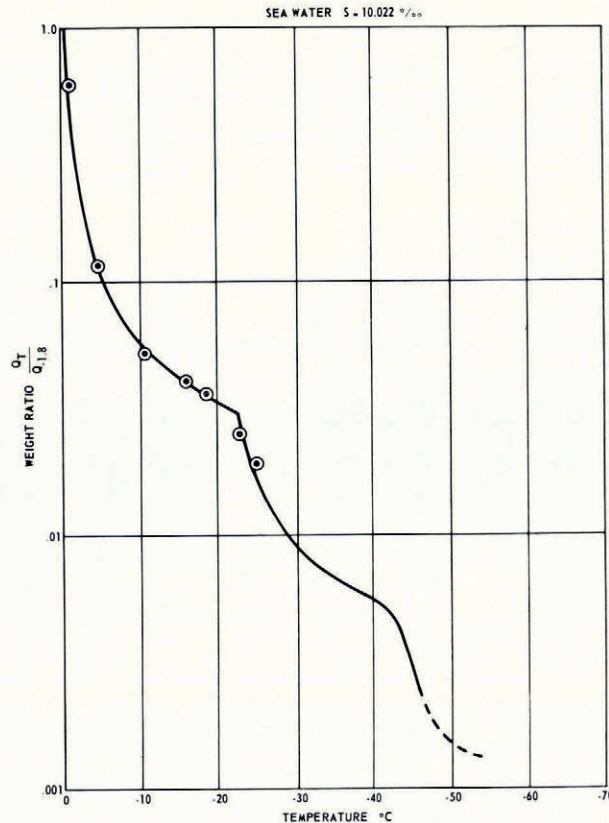

Fig. 3. Relative water content in ‰ versus temperature for sea ice (sea-water sample 10·022 ‰ salinity). The curve is drawn from Nelson and Thompson's analytical data, the points are measured by N. M. R. techniques

All of the mathematical models for the bulk properties of sea ice, such as latent heat, thermal conductivity and maximum strength, utilize some form of β. In most instances the introduction of a 10 per cent error in β results in an even larger error in the property being studied. For example, using Anderson's model for the maximum stress in sea ice (1960, p. 315, equation (3)), a 10 per cent error in β can produce errors in σ_m (the maximum stress) ranging from 8 per cent to 45 per cent, depending upon the experimental conditions. Variations of this magnitude have been reported by several investigators, although the data was supposedly collected from ice having the same history, temperature and salinity.

The basic assumption of the mathematical models is that the behavior of the whole mixture is a function of the behavior and quantity of the individual components present in

the test specimen. Thus the strength of sea ice is given as proportional to the area of ice (1—area of brine) in the "failure plane". However, none of the experiments have measured the amount of brine in the failure plane either directly or indirectly; instead they have used a sort of averaged brine content of the entire test specimen or the average content of an ice sample from the near vicinity of the test specimen. Weeks and Lee (1962, p. 106) investigated this latter process and found that the standard deviation of the salinity of closely spaced core samples in an ice sheet was equal to, or greater than, $\pm 0 \cdot 3$ ‰. In pancake ice the standard deviation rises to ± 1 ‰ or greater. Using Assur's table for β, Weeks and Lee (1962) calculated standard deviations in β of at least ± 4 per cent to ± 6 per cent and in pancake ice at least
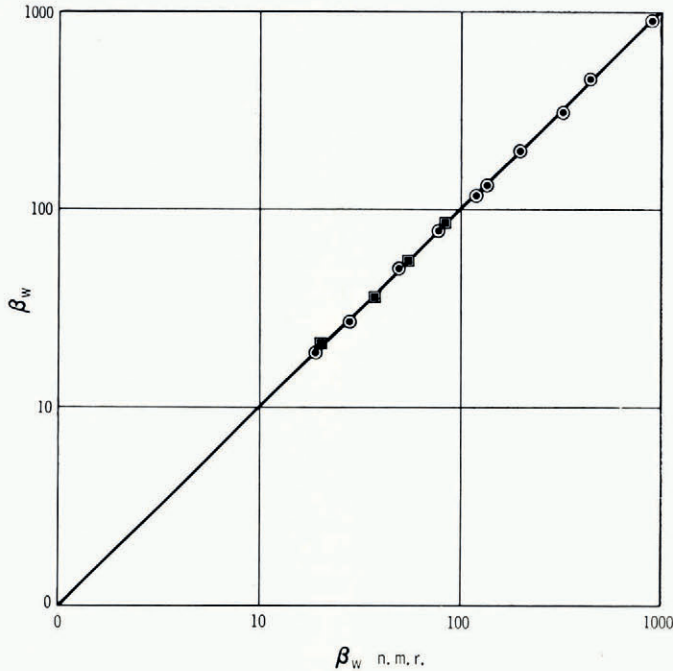

Fig. 4. A comparison of β_w, the brine weight ratio. The abscissa values were calculated by equation (13) from the N. M. R. data. The ordinate values were given by Anderson (1960, p. 317). The circle and squares represent salinity (S_{b_0}) values of 35 ‰ and 10 ‰ respectively.

± 11 per cent to ± 19 per cent. Thus the practice of utilizing adjacent cores to obtain values of β contributes sizable errors to the strength calculations and may share the responsibility for much of the scatter found in these studies.

Utilization of the entire test specimen for the salinity measurement (as is done in ring tensile strength studies) is not thought to improve the standard deviations reported above according to Weeks and Lee (1962), since the individuality of the segment of the core containing the failure plane is lost in the average salinity of the entire ring. Ultimately the salinity and the distribution of brine in the brine layers that separate the sub-plates of pure ice in a single crystal of sea ice will be required in order to determine workable mathematical models.

To date experiments are under way designed to measure the brine distribution along both the horizontal and vertical center-lines of the failure plane of a tension test bar, using a micro-corer. Cores 4 mm. in diameter and 8 mm. long are extracted. The first corer design

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was rather crude, and the N. M. R. data taken on the initial cores were erratic due primarily to thermal effects on the small sample. A second corer is now being designed which, it is hoped, will at least reduce some of these disturbances.

Since it is not readily possible to get a salinity measurement on such a small sample as that taken by the micro-corer, the terms in equation (14) dealing with salinity and density had to be eliminated. For salinities and densities encountered in natural sea ice the range of values for the product of the two terms is rather small, especially if temperature is constant. The maximum range between values at any temperature is 0·9200 to 0·9900. For any one temperature the maximum variation is 0·9270 to 0·9628, which occurs at $-2°$ C. Below $-6°$ C. the range of values is less than 0·009. Rather than substitute a single constant for the product, a median salinity of 10 ‰ was adopted, and values of the product using this salinity were tabulated (Table I) for every $2°$ C. in the range $-2°$ C. to $-50°$ C. These values can be expressed approximately (to $-45°$ C.) as a function of absolute temperature as:

$$f(T) = \frac{(1-0·01)}{(1-S_{b_T})}\left(\frac{\gamma_i}{\gamma_b}\right)_T \approx \frac{(1-S_{b_0})}{(1-S_{b_T})}\left(\frac{\gamma_i}{\gamma_b}\right)_T. \tag{15}$$

Then equation (14) may be rewritten as

$$\beta \approx \frac{A_T T}{A_0 T_0}f(T),$$

$$\approx \frac{Q_T}{Q_0}f(T). \tag{16}$$

Table I is a comparison of equation (16) results with the calculated values of β given by Anderson (1960, p. 317) and Assur (1958, p. 138). Salinities chosen were 3·0 ‰ and 20 ‰, and values of Q_T/Q_0 were calculated from the Nelson and Thompson data.

TABLE I. A COMPARISON OF VALUES OF β, THE BRINE VOLUME CONTENT OF SEA ICE, FOR SALINITIES S_{b_0}, OF 3 ‰ AND 20 ‰

$\beta_{\text{N.M.R.}}$ values were computed using equation (16)
β_{DA} are values given by Anderson (1960, p. 317) and
β_{AA} are values given by Assur (1958, p. 138).

$\frac{-T}{°\text{C.}}$	$f(T)$	S_{b_0} three parts per thousand				S_{b_0} twenty parts per thousand			
		Q_T/Q_0	β_{NMR}	β_{DA}	β_{AA}	Q_T/Q_0	β_{NMR}	β_{DA}	β_{AA}
2	0·9434	76·816	72·47	71·7	72·0	512·102	483·12	503·2	480·0
4	0·9414	39·471	37·16	37·0	37·2	263·138	247·72	254·6	248·0
6	0·9477	27·033	25·62	25·6	25·8	180·218	170·79	175·3	172·0
8	0·9594	20·693	19·85	19·9	20·0	137·952	132·35	135·5	133·4
10	0·9630	17·069	16·44	16·5	16·6	113·790	109·58	112·1	110·6
12	0·9660	14·786	14·28	14·3	14·5	98·568	95·22	97·4	96·4
14	0·9712	13·204	12·82	12·8	13·0	88·028	85·49	87·3	86·6
16	0·9752	11·997	11·70	11·7	11·8	79·978	77·99	79·7	79·0
18	0·9815	10·993	10·79	10·8	11·0	73·286	71·93	73·4	73·0
20	0·9867	10·100	9·96	10·0	10·1	67·332	66·44	67·8	67·6
22	0·9943	9·327	9·27	9·3	9·4	62·180	61·82	63·1	62·8
24	0·9941	6·635	6·60	6·6	6·7	44·230	43·97	44·8	44·8
26	0·9891	4·276	4·23	4·2	4·3	28·510	28·20	28·7	28·8
28	0·9826	3·202	3·15	3·2	3·1	21·346	20·97	21·4	21·4
30	0·9780	2·641	2·58	2·6	2·6	17·606	17·22	17·5	17·62
32	0·9742	2·319	2·26	2·3	2·3	15·462	15·06	15·3	15·46
34	0·9707	2·084	2·02	2·0	2·1	13·890	13·48	13·7	13·90
36	0·9687	1·918	1·86	1·9	1·9	12·784	12·38	12·6	12·82
38	0·9678	1·782	1·72	1·7	1·8	11·878	11·50	11·7	11·92
40	0·9656	1·660	1·60	1·6	1·7	11·050	10·67	10·9	11·10
42	0·9646	1·555	1·50	1·5	1·57	10·370	10·00	10·2	10·44

Figure 5 is presented more as an interesting observation than as factual data, since the signals were far below the noise level and no measurements were possible except for a few crude planimeter values. However, Figure 6 does present some evidence that sea ice does not totally solidify (at least to $-70°$ C.). During two experiments the sample temperatures were reduced to $-70°$ C., where a very weak but consistent liquid signal was observed. In order to insure that these signals were associated with a quantity of the liquid phase and not a product of the solid or the equipment, two solutions (sodium chloride and sodium sulfate)

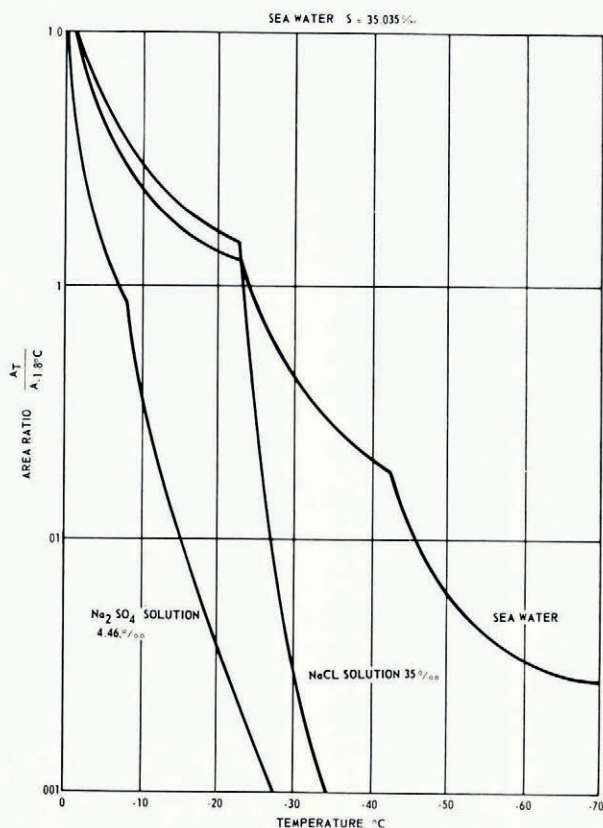*Fig. 5. The ratio of the integrated N. M. R. analog of the absorption curve for protons in the liquid state, versus the temperature ($°$ C.). Note: The area ratios below $-40°$ C. should not be taken as realistic; the errors in the measurements are very large, and the number of measurements very few, therefore the curve is only indicative of the presence of liquid water at $-70°$ C*

which were known to solidify entirely at relatively high temperatures were tested. The curves for the two solutions are included in Figure 5. Note that both curves are not realistic below the eutectic points since both solutions contained impurities. The two curves decrease to zero amplitude at complete solidification; therefore, it was concluded that the liquid signals at $-70°$ C. did result from protons in a liquid form of water. However, the chemical state of the water could not be determined, i.e. whether the water was associated with a quantity of unsaturated brine or was bound to some hydrate. It was of some interest to try to estimate the amount of water that might be involved, this turned out to be ≈ 1 g./kg.

CONCLUSIONS

The results presented demonstrate that the integrated analog of the magnetic resonance absorption due to hydrogen nuclei can be used to measure the brine content of sea ice. The range of measurements made and their accuracy is sufficient for most sea-ice studies. Extension of the range and increased accuracy are readily obtainable with new N. M. R. spectrometers, which utilize frequency modulation techniques and electronic integration.

The micro-corer in conjunction with N. M. R. techniques shows promise of providing information on the brine distribution throughout a test section of an ice sample. Ultimately the aim is to measure the brine distribution in a single crystal of sea ice. This is a necessary step toward real understanding of this complex material.

MS. received 13 December 1964 and in revised form 13 September 1965

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