

Nuclear magnetic resonance study of sea-water freezing mechanisms: 1. Temperature dependence of relative brine content in sea ice

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ABSTRACT. The results of measuring relative brine content (Q_{lm}) in the liquid phase of frozen sea water at temperatures between -2°C and -43°C with variable rate and direction of temperature change are presented. Various pulsed and steady-state nuclear magnetic resonance (NMR) methods are used and the results are compared with data in the literature. Temperature dependences of Q_{lm} in sea water with dry NaCl added are given. Quasi-hysteresis corresponding to the crystallization range of certain sea-water salts, mainly NaCl, which partially precipitates as the crystalline hydrate $\text{NaCl}\cdot 2\text{H}_2\text{O}$ at temperatures below -23°C , is detected in the temperature dependence of Q_{lm} . The reasons why Q_{lm} values, under various experimental conditions, differ from data in the literature are explained. Brine salinity (S) is calculated from the relative intensity of NMR signals of Q_l and agrees well with previously published data over a wide temperature range. It is shown that determining Q_{lm} from base measurements of Q_l in ice does not require information about brine salinity. Empirical equations for calculating brine content at different sea-water temperatures and salinity are given.

INTRODUCTION

Knowledge of brine content in sea-ice pores and brine composition under various sea-water freezing conditions is important for understanding the formation of the physico-chemical properties of sea ice. The volume of sea-ice brine and ice porosity determine heat exchange processes between sea water and atmosphere via the ice surface, especially at the polar ice caps. These processes strongly influence Earth's climate.

Numerous studies have investigated the freezing processes of sea water and aqueous solutions (e.g. Ringer, 1906; Gitterman, 1937; Nelson and Thompson, 1954; Thompson and Nelson, 1956; Assur, 1958; Pounder, 1965; Richardson and Keller, 1966; Doronin and Kheisin, 1975; Richardson, 1976; Bogorodskiy and Gavrilov, 1980; Cox and Weeks, 1983; Cho and others, 2002; Maus, 2007). The content and salinity of the liquid phase in sea-ice pores (brine) are complex functions of ice temperature, brine salinity, freezing rate and age of the ice. The mechanical strength of the ice depends on brine salinity and ice porosity. Liquid-phase salinity increases with decreasing temperature and can reach values of $\sim 218.6\text{--}226.6\text{‰}$ at temperatures below -22°C (Gitterman, 1937; Assur, 1958; Bogorodskiy and Gavrilov, 1980). Brine properties near eutectic points have been insufficiently studied even for salt and water binary systems, to say nothing of such a complex natural material as sea water. This lack of information creates problems for detailed investigations of various aspects of the interaction between water molecules and solutes in brines, especially the formation of crystalline hydrates in brine and on sea-ice pore walls, on which the thermophysical properties of ice depend. Sea-water freezing processes are most often studied in model systems. Stable thermodynamic equilibrium is usually calculated for this purpose (e.g. Herut and others, 1990; Spencer and others, 1990; Perovich and Gow, 1996; Marion and Farren, 1999; Akinfiyev and others, 2001);

experimental methods (dielectric and calorimetric measurements, including differential calorimetry) are also used (Rasmussen and others, 1997). Concepts of the sea-water freezing mechanisms differ concerning precipitating crystalline hydrates and their quantity. Thermodynamic conclusions about the formation of ice and salts are made on the basis that heat is evolved or absorbed, and by comparing sea water with solutions of individual salts. However, thermodynamic calculations cannot serve as direct proof of the formation of specific crystalline hydrates, or of their quantity and sequence of precipitation, because during heat evolution (absorption) a shift of ionic equilibrium occurs in a multi-component ionic system, which initiates new processes. Ice formation of solutions can be studied more reliably under laboratory conditions, which allow many uncontrollable factors (e.g. changes in weather conditions) to be eliminated. The method traditionally used to study brine of frozen sea water (Gitterman, 1937; Thompson and Nelson, 1956), based on analysis of the quantity and composition of drained brine, is imperfect owing to partial losses of brine. Perhaps for this reason, the results of experiments by different investigators are not always in agreement.

Nuclear magnetic resonance (NMR) by protons and other nuclei is a better method for studying sea-water freezing processes because it is non-destructive and does not require brine drainage or the addition of chemical reagents. NMR determination of brine content was first used by Richardson and Keller (1966). Results of studies of phase relationships in sea ice as a function of temperature are given by Richardson (1976). This method is presently widely used to study the porosity of natural sea ice, including under field conditions (e.g. Edelstein and Schulson, 1991; Callaghan and others, 1999; Eicken and others, 2000; Menzel and others, 2000).

Mel'nichenko and others (1981) measured the temperature dependence of the amount of liquid phase (brine Q_l) during freezing of samples of natural sea water, using the pulsed NMR method. The advantage of this method over the

steady-state method stems from the fact that the magnitude of the free induction signal, after acting on a sample with a 90° electromagnetic pulse at resonance frequency, is proportional to the quantity of protons in the liquid-phase volume, but does not depend on relaxation times (T_1 , T_2) or other factors. This is not so for determination of Q_l from the total intensity of the spectral absorption line in the steady-state NMR method as utilized by Richardson and Keller (1966).

It has been shown by Richardson (1976) that the amount of liquid phase in frozen sea water depends on the rate and direction of temperature change. The temperature dependence of Q_l near the eutectic point for NaCl exhibits hysteresis, so Q_l values do not coincide with temperature decrease or increase. The literature on brine content in frozen sea water pertains mainly to experiments in which the brine content was determined using NMR during an increase in the temperature of ice initially cooled to -60°C ; ice at -60°C was assumed to be in a completely solid state. Under natural conditions, however, sea ice forms in an environment of decreasing temperature. According to our experimental data, there is a noticeable amount of liquid phase in ice even at -70°C .

If the formation of crystalline hydrates and their subsequent precipitation in sea-ice brine pertains strictly to phase transition of the first kind, then in accordance with the laws of thermodynamics, there should not be hysteresis behavior in the temperature dependence of relative mass of brine (Q_{lm}) near the NaCl eutectic point because there is only one degree of freedom, temperature. At the same time, the pressure in ice cells can differ from the atmospheric pressure, so that squeezing of brine onto the ice surface with the formation of 'salt flowers' is often observed under natural conditions. In addition, the pressure within ice cells may differ from atmospheric pressure owing, in particular, to blockage of ice canals by precipitated salts.

Analysis of the available brine content data at temperatures between the freezing point and the NaCl eutectic temperature shows no significant differences, i.e. the brine content changes little over this temperature range. However, the data for the interval -8 to -21°C given by Richardson (1976) differ significantly from earlier data (e.g. Assur, 1958; Tsurikov and Tsurikova, 1972). It is evident that comparison of the relative brine content (Q_l) found from the relative intensity of NMR induction signals and from the Q_{lm} by chemical analysis does not show agreement and that additional experimental data are therefore needed. Moreover, published experimental eutectic temperatures (T_e) for sea water and for various NaCl solutions (corresponding to characteristic breaks in graphs of temperature dependences of Q_{lm}) differ substantially. For example, a value of T_e equal to -21°C for sea water is given by Cho and others (2002), while according to the data of Franks (1973), Doronin and Kheisin (1975) and Bogorodskiy and Gavrilov (1980), T_e values for NaCl and sea water respectively are -21.9 and -22.9°C . For this reason we conducted additional experiments varying the direction of temperature change, and not excluding the supercooled state of sea water.

To develop investigations begun earlier (Mel'nichenko and others, 1981) and to explain why data obtained on this subject by other authors differ, we present the results of additional experiments to study the temperature dependence of the relative content and mass of brine by varying the direction of temperature change. We include experiments with NaCl dissolved in the sea water before it freezes. We

study the temperature dependence of proton magnetic relaxation time in the liquid phase of frozen sea water within the temperature range of sea ice under natural conditions. This approach, combined with earlier investigations, makes it possible to detail sea-water freezing mechanisms. The main purpose of these additional experiments is to inspect the hysteresis behavior in the temperature dependence of Q_{lm} near the NaCl eutectic point.

METHODS

The method is based on measuring the amplitude of nuclear induction signals from water protons after 90° single excitation radio-frequency pulses at the resonance frequency. The amplitude of these signals is proportional to the number of resonating nuclei (protons) in the sample volume and, accordingly, to the number of water molecules. An increase in the amplitude of induction signals with decreasing temperature due to an increase of the tuned-circuit Q -factor is easily taken into account by a predetermined coefficient. The nuclear induction signals from water protons in the solid phase of ice are not recorded by the pulsed NMR method owing to the different (by 5–6 orders of magnitude) widths of the spectral lines from solid and liquid phases.

Measurements were taken on three spectrometers:

1. Measurements at St Petersburg State University were made using a coherent pulsed NMR spectrometer with a signal-to-noise (S/N) ratio of 5×10^3 from $1 \text{ cm}^3 \text{ H}_2\text{O}$ with stabilization of resonance conditions and digital indication of the amplitude of nuclear induction signals and time intervals. The errors in determining the amplitude of the signals and relaxation time were 1% and 2% respectively, and temperature errors were $<0.2 \text{ K}$. The sample was cooled using liquid nitrogen vapors that bathed the ampoule with the sample from the top and bottom to eliminate a temperature gradient along it. The temperature of the sample was taken equal to the temperature of the coolant in a Dewar flask, measured by a calibrated thermocouple located next to the lower end of the ampoule since direct measurement in the sample is impossible when the spectrometer is operating. Control measurements, using a platinum thermal resistor isolated from sea water, of the temperature of the coolant and water in the sample, taken with the spectrometer receiver and transmitter disconnected, gave a discrepancy not exceeding the indicated error at -60°C . The amplitude of the nuclear induction signals after each temperature change was measured only after establishing equilibrium, when the values did not change for 15–20 min. Surface water from the Atlantic with salinity $\approx 35\%$ was investigated. The ampoule with the sample had a diameter of 10 mm, the volume of the sample was $\sim 1 \text{ cm}^3$ and the resonance frequency for water protons was 20 MHz.
2. Analogous experiments supplemented with measurements of the relaxation rate were carried out on an apparatus assembled by the author with proton stabilization of resonance conditions and approximately the same error in determining the amplitude, relaxation time and temperature. For automatic proton stabilization we use an additional receiver magnet coil with an ampoule of LiCl solution. Signals of proton absorption are governed by current strength in the additional magnet

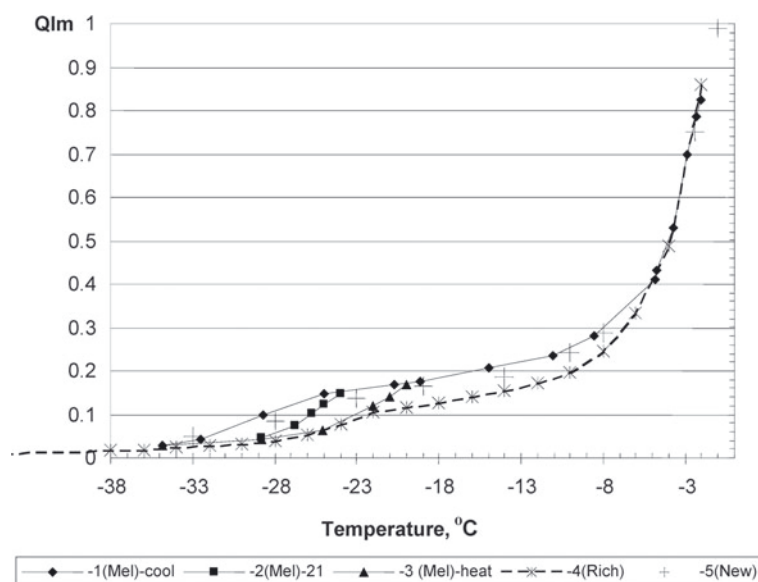


Fig. 1. Temperature dependence of relative brine content in frozen sea water given different directions of temperature change based on pulse and steady-state NMR data. Curve 1: smooth temperature decrease from -2°C , with sea-water freezing initiated by shaking the ampoule with sea water; curve 2: sharp temperature decrease to -21°C and then gradual temperature decrease; curve 3: temperature increase from -60°C ; curve 4: Richardson (1976) data; curve 5: new data for sea water with salinity 31.809‰ and temperature increasing from -45°C .

winding for cup-lock resonant conditions. The increase in error is related to a decrease in the amplitude of the nuclear induction signals due to a decrease in brine content. A technical signal accumulation procedure for increasing the S/N ratio was not used in the experiments, because this ratio is quite sufficient for these determinations. Water from the Philippine Sea with approximately the same salinity as in the experiments on the first apparatus was investigated. The inside diameter of the ampoule was 15 mm, sample volume was $\sim 1.5\text{ cm}^3$ and resonance frequency for water protons was 13.509 MHz.

- We conducted additional experiments to study the temperature dependence of Q_l in frozen sea water, on an AV-300 NMR spectrometer (Bruker spectrometer) at the Institute of Chemistry, Far East Branch, Russian Academy of Sciences, Vladivostok. The resonance frequency for protons was 300 MHz and the sample volume was $\sim 0.5\text{ cm}^3$.

The relative liquid-phase content in these experiments was determined from the total intensity of the spectral absorption line. The trend of the temperature dependence of signal intensity from room temperature to sea-water freezing temperatures, including the region of supercooled state and considering that the content of protons within the sample remains constant, was taken into account when correcting the change in signal intensity caused by an increase in the received tuned-circuit Q -factor upon a decrease in temperature. This distinguishes our method from others used in preceding work (e.g. Cho and others, 2002) in which the relative intensity was reduced to room temperature. At high frequencies the procedure used compensates the decrease in NMR signal intensity owing to dielectric losses in highly concentrated brine. The error in determining the integrated absorption line intensity was $\sim 1\%$. The temperature change of the chemical shift at a rate of -0.03 ppm K^{-1} had practically no effect on the integrated spectral absorption line intensity.

Experiments (using method 3 above) were conducted on sea water from Peter the Great Bay (salinity 31.809‰) and the Sea of Okhotsk (33.566‰) with mass 75.159 g, in which 4.3829 g NaCl of very pure grade 12 was dissolved. Oxygen dissolved and adsorbed on the ampoule glass, which had a considerable effect on relaxation rate, was thoroughly removed prior to relaxation measurements, by multiple repetition of the freezing–vacuum-pumping–thawing–heating cycle. This procedure was not used in experiments to determine the brine content by the pulsed method since, as mentioned above, the intensity of nuclear induction signals after single excitation RF pulses does not depend on relaxation time.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of Q_{lm} in frozen sea water according to averaged data from experiments on apparatuses 1 and 2 (solid curves 1–3), assuming the same errors and experimental conditions. Results of additional experiments on apparatus 3 are also included. The new results, and previous results, are in agreement with the literature data (Table 1), with account taken of the differences in sea-water salinity.

Q_l is the quantity of liquid phase in the ice volume, calculated as $Q_l = A_t/A_0$, where A_t and A_0 are amplitudes of the NMR induction signals (or integral intensity of absorption in the spectra line) at temperature t and at freezing point in liquid state. A difference between our results and Richardson's (1976) data is observed in the interval from -8 to -24°C . One possible cause of this discrepancy is a disparity between brine salinity from Nelson and Thompson (1954) and the actual salinity when calculating the mass of brine. Nelson and Thompson's salinities are lower than Gitterman's (1937) in this interval (Tsurikov and Tsurikova, 1972 table 3). In Table 1 the values of Q_l and Q_{lm} , smoothed by a polynomial dependence, are compared with the literature data. The results of additional experiments for sea water with salinity 31.809‰ are given in Figure 2, and

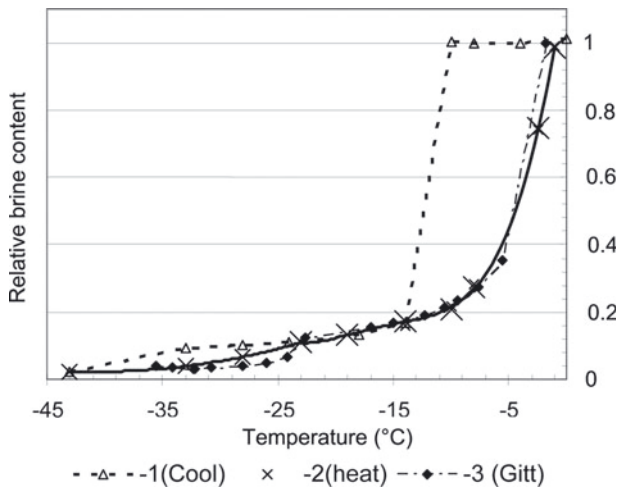


Fig. 2. Temperature dependence of relative brine content in frozen sea water ($S=31.809\text{‰}$) with different directions of temperature change based on steady-state NMR data. Curve 1: smooth temperature decrease from -2°C in sea water with added NaCl; curve 2: temperature increase in frozen sea water with added NaCl; curve 3: Gitterman (1937) data.

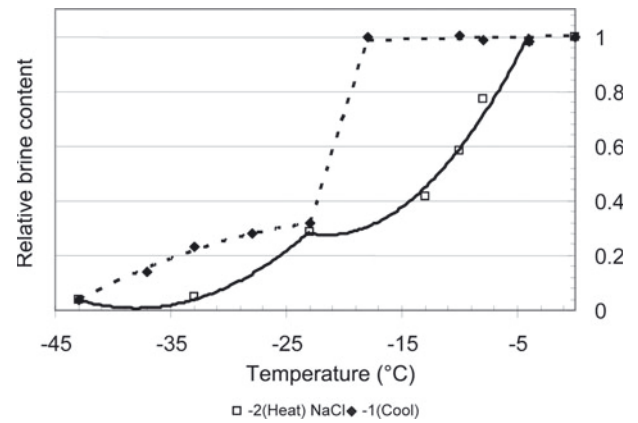


Fig. 3. Temperature dependence of relative brine content in frozen sea water with added NaCl with different directions of temperature change based on steady-state NMR data. Curve 1: smooth temperature decrease from -2°C in sea water with added NaCl; curve 2: temperature increase in frozen sea water with added NaCl.

Figure 3 presents the results of experiments with additional NaCl dissolved in sea water to a final salinity of 86.81‰ . The initial experimental data are given in Table 2. The relative mass of brine Q_{lm} was calculated on the basis of Q_l by Richardson and Keller (1966) using

$$Q_{lm}(T, S) = Q_l(1000 - S_w)/(1000 - S_{br}). \quad (1)$$

In contrast to Richardson and Keller (1966), we did not use literature data for S_{br} or density. These values are found from Q_l determinations on the basis of

$$S_{br} = S_w \cdot a_t \cdot 1000/[S_w \cdot a_t + (1000 - S_w) \cdot Q_l], \quad (2)$$

where a_t is the portion of salts remaining in brine and is unity for conditions not taking account of precipitated salts.

The dependence of the relative mass of brine on the salinity of sea water before freezing at different temperatures, according to our data and the literature data, is plotted in Figure 4. For sea-water salinity at 3‰ and 10‰ we used Richardson and Keller's (1966) data and other data in the literature, as indicated in Table 1. Differences from the linearity law may be due not only to experimental errors but also to a manifestation of the effects of achievement boundaries of complete ion hydration in brine at salinity $\sim 80\text{--}90\text{‰}$ (Mel'nichenko, 2007).

Table 1. Brine content in ice according to NMR and literature data

Temp. °C	$Q_{lw\ Mel}(\text{cool})$ $S=34.98\text{‰}$	$Q_{lm\ Mel}(\text{cool})$ $S=34.98\text{‰}$	$Q_{lm\ Mel}(\text{heat})$ $S=34.98\text{‰}$	$Q_{lm\ Asr}$ $S=34.32\text{‰}$	$Q_{lm\ Rich}$ $S=34.98\text{‰}$	$Q_{lm\ Tsur-Naz}$ $S=33.34\text{‰}$	$Q_{lw}(\text{new cool})$ $S=31.809\text{‰}$	$Q_{lm}(\text{new heat})$ $S=31.809\text{‰}$	Q_{lmR-K} $S=3\text{‰}$	Q_{lmR-K} $S=20\text{‰}$
-2	0.832	0.833	-	0.913	0.861	0.902	-	0.788	0.072	0.483
-4	0.489	0.500	-	0.486	0.489	0.458	-	0.514	0.037	0.248
-6	0.330	0.372	-	0.344	0.335	0.327	-	0.355	0.026	0.171
-8	0.256	0.303	-	0.271	0.247	0.259	-	0.272	0.020	0.132
-10	0.229	0.260	-	0.228	0.197	0.219	-	0.187	0.016	0.110
-12	0.198	0.235	-	0.201	0.173	0.195	-	0.233	0.014	0.095
-14	0.180	0.217	-	0.182	0.155	0.177	0.163	0.214	0.013	0.085
-16	0.161	0.205	-	0.168	0.140	0.161	0.151	0.200	0.012	0.078
-18	0.146	0.192	-	0.157	0.127	0.148	0.141	0.183	0.011	0.072
-20	0.135	0.177	0.171	0.146	0.116	0.138	0.131	0.162	0.010	0.066
-22	0.128	0.167	0.116	0.138	0.107	0.134	0.123	0.146	0.009	0.062
-24	0.124	0.157	0.080	0.099	0.077	0.094	0.116	0.150	0.007	0.044
-26	0.102	0.140	0.057	0.064	0.052	0.066	0.109	0.125	0.004	0.029
-28	0.080	0.113	0.045	0.048	0.039	0.047	0.104	0.104	0.003	0.021
-30	0.061	0.083	0.040	0.035	0.032	0.036	0.099	0.085	0.003	0.017
-32	0.043	0.050	0.037	0.029	0.027	0.031	0.095	0.069	0.002	0.015
-34	0.028	0.033	0.033	0.027	0.023	0.027	0.092	0.056	0.002	0.013

Notes: $Q_{lw\ Mel}(\text{cool})$ and $Q_{lm\ Mel}(\text{cool})$: relative content of water and mass content in cooling sea water from positive temperatures (1979). $Q_{lm\ Mel}(\text{heat})$: mass content in sea water from -38°C (Mel'nichenko and others, 1981). $Q_{lm\ Asr}$: Assur's (1958) data. $Q_{lm\ Rich}$: Richardson's (1976) data. $Q_{lm\ Tsur-Naz}$: Tsurikov and Tsurikova's (1972) data; Nazinsev's (1974) data. $Q_{lw}(\text{new cool})$ and $Q_{lm}(\text{new heat})$: new determinations of water and mass contents. Q_{lmR-K} (3‰ and 20‰): Richardson and Keller's (1966) data.

The temperature dependencies of Q_{lm} in frozen sea-water brine have two distinctive features: (1) a clearly expressed and sufficiently known break of the curves near the NaCl eutectic point and (2) temperature hysteresis, the extent and character of the curves of which were highly dependent on freezing conditions. We also observed temperature hysteresis in new experiments. Comparing the curves for different initial sea-water salinity (31.809‰, 35‰ and 86.81‰ before freezing), we see that the range of the hysteresis loop is proportional to the sea-water salinity (Figs 1–3).

The graph changed most abruptly upon sharp cooling of the sample to -21°C . Conversely, when freezing was initiated at -2.3°C , after holding and shaking the ampoule for 30 min, the steepness of the slope of the curves below -24°C decreased more slowly, and also decreased for the sample with a lower initial sea-water salinity (31.809‰). The steepness of this slope, also as a hysteresis loop, is in accordance with the salinity of freezing sea water. A supercooled state was observed during a smooth temperature decrease of sea and distilled water to -16 to -18°C , as in the pure-water relaxation experiments of Hindman and others (1973). We did not add a *n*-heptane emulsion sample, although this is sometimes done when studying the supercooled state of water (Mel'nichenko and others, 2009).

On average, discounting the possible influence of effects related to supercooling of sea water obtained under laboratory conditions, which does not occur under natural conditions, the eutectic point for NaCl in sea water is $\sim -23^{\circ}\text{C}$, which agrees with the bulk of literature data (e.g. Doronin and Kheisin, 1975; Bogorodskiy and Gavrilov, 1980), but not the data of Cho and others (2002; $T_e = -21^{\circ}\text{C}$). The shift of the eutectic point in sea water relative to the single-component NaCl solution, occurring at -21.9°C (Franks, 1973), is due to the combined influence of the remaining sea-water components, as noted above.

Mel'nichenko and others (1981) indicated an average temperature of the characteristic break (T_e) on the graph of temperature dependence of sea water of $\sim -24^{\circ}\text{C}$. The shift by 1°C relative to the values most often mentioned in the literature can be related both to experimental errors, due to

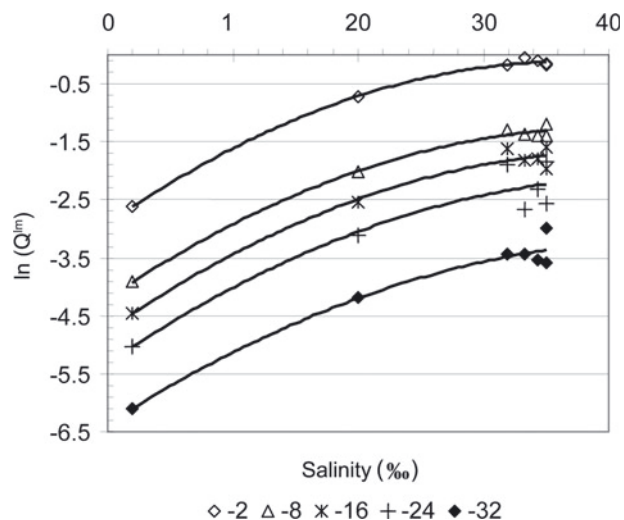


Fig. 4. Dependence of brine on salinity of sea water at different temperatures (2, 8, 16, 24 and 32°C).

lack of uniform temperature intervals between adjacent points and manual approximation of the temperature dependence graphs, and to the meta-stable character of the formation of crystalline hydrates in brine and their precipitation. This may explain why sea water $T_e = -21^{\circ}\text{C}$ is obtained in the results of experiments (Cho and others, 2002). It may also explain the break in the curve of temperature dependence of the brine content by Richardson and Keller (1966) at $\sim -22^{\circ}\text{C}$ and by Richardson (1976) at $\sim -23^{\circ}\text{C}$. According to Assur (1958), breaks occur in the sea-water phase diagram at -23°C and not at -21°C , as was also exhibited in graphs of the relative content of NaCl by Bogorodskiy and Gavrilov (1980). But according to other data, the characteristic temperature is -24°C (Ringer, 1906) and -22.4°C (Nelson and Thompson, 1954). In our experiments, a break was observed even at -25°C during a smooth temperature decrease (curve 1 in Fig. 1) and above -33°C for sea water with NaCl.

Table 2. Data of experimental determinations of relative brine content in frozen sea water by the NMR method

Cooling from -2°C		Cooling from -21°C		Heating from -60°C		Cooling from room temp. (New)		Heating from -43°C (New)		Cooling with NaCl		Heating from -43°C with NaCl	
T	Q_l	T	Q_l	T	Q_l	T	Q_l	T	Q_l	T	Q_l	T	Q_l
$^{\circ}\text{C}$		$^{\circ}\text{C}$		$^{\circ}\text{C}$		$^{\circ}\text{C}$		$^{\circ}\text{C}$		$^{\circ}\text{C}$		$^{\circ}\text{C}$	
-2.1	0.820	-25.0	0.099	-34.8	0.023	0	1.013	-43	0.020	0	1.014	-43	0.039
-2.3	0.780	-25.7	0.082	-28.8	0.035	-4	0.998	-33	0.027	-3	1.0	-33	0.046
-2.9	0.686	-26.7	0.058	-25.1	0.052	-8	0.997	-28	0.068	-8	0.988	-23	0.284
-3.7	0.514	-28.8	0.035	-21.0	0.118	-10	1.004	-23	0.120	-10	0.986	-13	0.416
-4.8	0.410			-20.0	0.143	-14	0.166	-19	0.134	-12.7	0.984	-10	0.583
-4.85	0.392					-18	0.134	-14	0.170	-14	0.964	-8	0.769
-8.5	0.253					-24	0.112	-10	0.216	-18	1.008	-4	0.982
-11.9	0.208					-28	0.102	-8	0.282	-23	0.316	0	0.999
-14.9	0.176					-33	0.093	-2.4	0.742	-28	0.281		
-19.1	0.145					-43	0.024	-1	0.990	-33	0.233		
-20.7	0.137									-43	0.039		
-25.0	0.118												
-28.7	0.078												
-32.5	0.033												
-34.9	0.023												

Cho's experimental data do not indicate the existence of hysteresis in the temperature dependences of the liquid phase in pores of frozen sea water (Cho and others, 2002, p. 11 229). Furthermore, in experiments with ^1H and ^{23}Na nuclei, the temperature at which a break occurs in the graphs for the NaCl solution and sea water coincided. For single-component aqueous solutions with an equal number of cations and anions, this is completely explicable and in agreement with the thermodynamics of phase transitions. But in a complex ion system of concentrated sea-ice brine with a diversity of ions and ion concentrations, the absence of hysteresis on the curve of the temperature dependence of the brine content is not evident.

It should be pointed out that the possible partial lack of correspondence of the ice and coolant temperatures with the natural invariability of ice temperature during phase transitions could be one of the causes of the observed hysteresis, since the temperature of the sample was taken as equal to the coolant temperature, assuming the ampoule was held for a sufficiently long time at the prescribed temperature. However, as the results of our control experiments showed, this cannot be the main cause of the observed effects.

The similar values of relative brine content and mass obtained in our experiments with ice temperature increasing from -43°C , compared with the results obtained earlier with a smooth temperature decrease from the sea-water freezing point, support the absence of hysteresis. However, the values of Q_{lm} with a temperature increase from -60°C to -24°C (curve 3 in Fig. 1) are close to Richardson's and Cho's data, even considering the differences in initial sea-water salinity. This may be a manifestation of meta-stability of the formation and dissolution of crystalline hydrates near the NaCl eutectic point, which depends on sea-water freezing conditions. An additional contribution to meta-stability may be a manifestation of the thermal-diffusion cross effects of Dufour and Soret, connected with sharp changes in salt concentration near eutectic points. The meta-stability of crystalline hydrates can explain the different slopes of the curves at temperatures close to and below the NaCl eutectic point for various sea-water freezing conditions (curves 1 and 2 in Fig. 1) and the considerable scatter in the Q_{lm} versus sea-water salinity data at $T < -24^\circ\text{C}$ (Fig. 4).

According to Tsurikov and Tsurikova (1972), the mass of brine should increase with increasing sea-water salinity. Apparently, the barely noticeable change in slope of the curves of Q_{lm} versus sea-water salinity is due to the narrow interval of sea-water salinities before freezing (31.8–35‰). Actually, dissolution in sea water of the amount of NaCl indicated above resulted in salinity increasing to 86.818‰ and Q_{lm} more than doubling.

The results of experiments with NaCl added to sea water and with natural sea water, given separately in Figure 3, showed that the limits of the region of the supercooled state with excess NaCl broadened considerably in accordance with Raoult's second law, connecting the freezing point of a water solution with its concentration. The liquid-phase content in such ice, both with a temperature decrease and increase, was about twice as high as in ice of ordinary sea water. Hysteresis behavior in Q_{l} in ice is evidenced by the discrepancies in its value at increasing and decreasing temperatures near the eutectic point of the main salt of sea water. The discrepancy in the values of Q_{l} in the hysteresis loop also increased with decreasing and increasing temperature. But the location of the eutectic point ($\sim -23^\circ\text{C}$) with

increasing temperature of frozen sea water with added NaCl remained practically unchanged compared with experiments with sea water having a natural salt content. This indicates the primary precipitation of $\text{NaCl}\cdot 2\text{H}_2\text{O}$ at this temperature.

The occurrence of a temperature hysteresis loop in the curves can be explained by two factors. The first is the non-equivalence of ion exchange during differently directed temperature actions, while the formation and dissolution of crystalline hydrates from ion composition are taken into account. This applies especially to sea water, i.e. to a solution which, unlike simple water solutions, does not solidify entirely at one temperature. That is, the eutectic point in ice brine implies the temperature only at the start of crystallization of hydrates. The second factor may be related to the meta-stability of the formation of crystalline hydrates in ice brine with a corresponding difference in heat absorption and evolution that can lead to different values of Q_{l} under different sea-water freezing conditions. The relatively weak manifestation of possible temperature hysteresis near -8°C may not have been noticed due to the substantially different amount of $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ and $\text{NaCl}\cdot 2\text{H}_2\text{O}$ precipitates. In addition, precipitated salts, mainly crystalline hydrate $\text{NaCl}\cdot 2\text{H}_2\text{O}$, may block small ice canals.

To establish the factors influencing the formation of brine salt content, we calculated brine salinity on the basis of directly measured liquid-phase content (Q_{l}), considering the initial salinity of the sea water before freezing (S_{w}) using Eqn (2). The coefficient α_{t} in this equation, corresponding to the portion of salts remaining in brine, was determined as

$$\alpha_{\text{t}} = q_{\text{l}}/q_{\text{tabl}} \quad (3)$$

in which

$$q_{\text{l}} = (1000 - S_{\text{l}})/(1000 - S_{\text{w}}) \cdot S_{\text{l}}$$

and

$$q_{\text{tabl}} = (1000 - S_{\text{tabl}})/(1000 - S_{\text{w}}) \cdot S_{\text{tabl}}$$

S_{w} and $(1000 - S_{\text{w}})$ are the masses of salts and water in 1 kg of sea water before it freezes. Assur's (1958) and Nazintsev's (1974) averaged data given in the 1977 Russian oceanographic tables can be taken as the standard (Table 3) values of S_{l} . Thus, we can calculate the value of α_{t} if we consider Cox and Weeks' (1983) data to be more accurate based on the results of Nelson and Thompson's (1954) analyses. The value of α_{t} can be taken as unity for temperatures of the order of -23 to -24°C (while there is no perceptible formation of crystalline hydrates).

The temperature dependences of salinity calculated on the basis of Q_{l} are given in Figure 5 and Table 3, along with points corresponding to ice brine salinities taken from the literature.

The calculated salinity values within temperature limits from 0°C to -23 to -24°C agree well with the literature data. The closeness of α_{t} to unity, considering the scatter of the experimental data within the error limits of the experiments, is confirmed by the data in Table 2. (The values of α_{t} calculated on the basis of salinity values according to Cox and Weeks' (1983) data and the salinity values themselves in Table 3 are marked by a prime.) As is seen from the data given above, when determining the relative mass of ice brine Q_{lm} from the results of measuring Q_{l} by the pulsed NMR method in the temperature range from 0°C to -23°C under natural conditions, there is no need to resort to brine salinity values since salinity is determined by Eqn (2) and brine mass by Eqn (1).

Tsurikov and Tsurikova (1972) provide a formula for calculating brine mass based on the sea-water freezing point. It is simpler to calculate the relative mass of brine by empirical equations of the dependence of the relative mass on ice temperature and not on the freezing point of concentrated sea water. Theoretically, we might expect temperature to decrease with brine content exponentially. But the precipitation of salt from an ionic solution is not analogous to the same process with a simple water solution, and may well be handled with more precision by a polynomial presentation.

The empirical equation error of 2% of the temperature dependence of the relative mass of brine with various initial sea-water salinities (assuming a linear dependence on salinity) for the temperature intervals -2 to -10°C , -10 to -23°C and -23 to -35°C respectively can be represented as

$$Q_{\text{lm}} = S_w \cdot (0.00389T^4 + 0.13121T^3 + 1.80091T^2 + 12.26342T + 42/14569)$$

$$Q_{\text{lm}} = S_w \cdot (0.000244T^4 + 0.015899T^3 + 0.392936T^2 + 4.587753T + 27.39897)$$

$$Q_{\text{lm}} = S_w \cdot (-0.00041415T^3 - 0.02819508T^2 - 0.23712714T + 9.26992019).$$

CONCLUSIONS

Taking into account the literature data and our results, we conclude that the main characteristic of the sea-water freezing mechanism and formation of the salt composition of ice brine is the generation of crystalline hydrates of salts, mainly $\text{NaCl}\cdot 2\text{H}_2\text{O}$, partially precipitating from brine at temperatures below -23°C . Precipitation of calcium carbonate and sodium sulfate from ice brine in the temperature interval from the freezing point to the NaCl eutectic point has practically no effect on the salinity of sea-ice brine, but the phase diagram of sea ice must be in accordance with the salinity of freezing sea water.

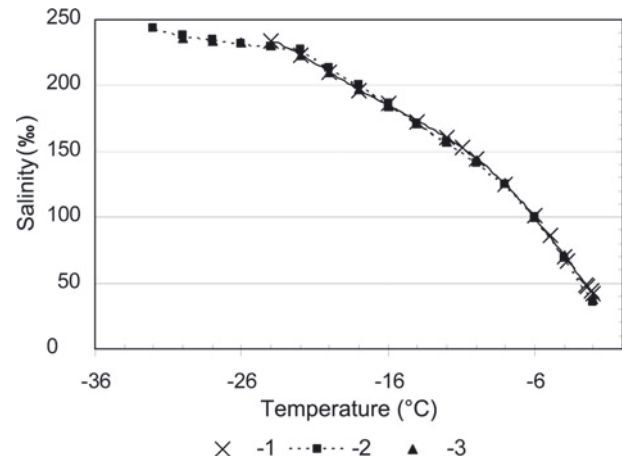


Fig. 5. Temperature dependence of brine salinity calculated on the basis of relative brine content determinations in frozen sea water according to data of various authors. Curve 1: smooth temperature decrease from -2°C with freezing initiated by shaking ampoules with sea water (Mel'nichenko and others, 1981); curve 2: Tsurikov and Tsurikova (1972) and Nazintsev's (1974) data; curve 3: Cox and Weeks' (1983) data; curve 4: data based on averaged Q_1 values from various experiments.

Hysteresis in the temperature dependence of the relative brine content and relaxation time is due to meta-stability of the formation of crystalline hydrates, which can lead to differences in the values of the content of ice brine and its salinity at the same ice temperatures near the NaCl and Na_2SO_4 eutectic points, especially when there are sharp changes in the rate of ice formation and direction of temperature change. An additional contribution to the occurrence of hysteresis may be in manifestation of thermal-diffusion cross effects near the eutectic points (Bogorodskiy and Pnyushkov, 2007) and in blocking of ice shells by precipitated salts.

Table 3. Brine salinity and relative proportion of salt remaining in brine (α) at different temperatures

Temp. °C	S_i	S'_i	S_{tabl}	α	α'	S_{Rich}	S_{avr}
-2	41.9	37.6	35.6	0.844	0.893	39.052	37.42
-4	69.1	70.6	68.8	0.995	1.023	66.752	68.72
-6	99.0	99.8	99.8	1.009	1.009	94.455	98.02
-8	124.0	126.5	125.0	1.009	1.004	122.135	124.54
-10	139.9	142.8	141.2	1.011	1.024	143.952	142.6
-12	154.7	157.6	156.8	1.016	1.021	157.728	157.4
-14	168.5	171.5	171.8	1.024	1.027	171.49	171.6
-16	183.9	184.4	186.3	1.016	1.023	184.839	185.2
-18	198.4	197.0	200.3	1.012	1.017	198.286	198.5
-20	211.1	209.9	213.9	1.017	1.018	211.685	211.8
-22	220.8	222.6	227.0	1.036	1.026	225.655	225.1
-24	226.3	230.5	229.0	1.015	1.027	231.675	230.4
-26	262.3	232.7	231.5	0.847	0.855	233.995	232.7
-28	311.9	234.1	234.4	0.675	0.681	234.57	234.4
-30	372.9	235.6	238.3	0.526	0.520	235.996	236.6
-32	457.5	-	243.5	0.382	-	245.677	243.0
-34	564.3	-	-	-	-	252.93	-

Notes: S_i : salinity of ice brine on base NMR determinations (experiment 1). S'_i : Cox and Weeks' (1983) data. S_{tabl} : data from Russian oceanographic tables (Assur, 1958; Nazintsev, 1974). α and α' : proportion of salts remaining in brine on the basis of our results and using Cox and Weeks (1983). S_{Rich} : salinity (Richardson, 1976). S_{avr} : average means (S_i , S'_i , S_{tabl}).

ACKNOWLEDGEMENTS

We thank Jack Slep for English language assistance and P.A. Stunzhas (P.P. Shirshov Institute of Oceanology, Moscow) for useful discussion. The project was supported by the Scientific Fund of the Far East Federal University.

REFERENCES

- Akin'ev NN, Mironenko MV and Grant SA (2001) Thermodynamic properties of NaCl solutions at subzero temperatures. *J. Solution Chem.*, **30**(12), 1065–1080 (doi: 10.1023/A:1014445917207)
- Assur A (1958) Composition of sea ice and its tensile strength. In *Arctic Sea Ice. Proceedings of the Conference held at Easton, Maryland, February 24–27, 1958*. (National Research Council Publication 598) U.S. National Academy of Sciences, Washington, DC, 106–138
- Bogorodskiy VV and Gavrilov VP (1980) *Led. Fizicheskiye svoystva [Ice: physical properties]*. Gidrometeoizdat, Leningrad [in Russian with English summary]
- Bogorodskiy PV and Pnyushkov AV (2007) A simple model for seawater crystallization in the temperature spectrum. *Oceanology*, **47**(4), 500–506 [Okeanologiya, **47**(4), 539–545] (doi: 10.1134/S0001437007040078)
- Callaghan PT and Eccles CD (1996) NMR studies on Antarctic sea ice. *Bull. Magn. Reson.*, **18** (1–2), 62–64
- Callaghan PT, Eccles CD and Seymour JD (1997) An earth's field nuclear magnetic resonance apparatus suitable for pulsed gradient spin echo measurements of self-diffusion under Antarctic conditions. *Rev. Sci. Instr.*, **68**(11), 4263 (doi: 10.1063/1.1148340)
- Callaghan PT, Dykstra R, Eccles CD, Haskell TG and Seymour JD (1999) A nuclear magnetic resonance study of Antarctic sea ice brine diffusivity. *Cold Reg. Sci. Technol.*, **29**(2), 153–171 (doi: 10.1016/S0165-232X(99)00024-5)
- Cho H, Shepson PB, Barrie LA, Cowin JP and Zaveri R (2002) NMR investigation of the quasi-brine layer in ice/brine mixtures. *J. Phys. Chem. B*, **106**(43), 11 226–11 232 (doi: 10.1021/jp020449+)
- Cox GFN and Weeks WF (1983) Equations for determining the gas and brine volumes in sea-ice samples. *J. Glaciol.*, **29**(102), 306–316
- Doronin YuP and Kheisin DE (1975) *Morskoi led [Sea ice]*. Gidrometeoizdat, Leningrad
- Edelstein WA and Schulson EM (1991) NMR imaging of salt-water ice. *J. Glaciol.*, **37**(125), 177–180
- Eicken H, Bock C, Wittig R, Miller H and Poertner HO (2000) Magnetic resonance imaging of sea-ice pore fluids: methods and thermal evolution of pore microstructure. *Cold Reg. Sci. Technol.*, **31**(3), 207–225 (doi: 10.1016/S0165-232X(00)00016-1)
- Franks F (1973) *Water and aqueous solution at subzero temperatures*. (A Comprehensive Treatise 7) Plenum Press, New York
- Gitterman KE (1937) Thermal analysis of seawater. *CRREL Rep.* TL 287
- Herut B, Starinsky A, Katz A and Bein A (1990) The role of seawater freezing in the formation of subsurface brines. *Geochim. Cosmochim. Acta*, **54**(11), 13–21 (doi: 10.1016/0016-7037(90)90190-V)
- Hindman JC, Svirmickas A and Wood M (1973) Relaxation processes in water. A study of the proton spin-lattice relaxation time. *J. Chem. Phys.*, **59**(3), 1517–1522 (doi: 10.1063/1.1680209)
- Marion GM and Farren RE (1999) Mineral solubilities in the Na-K-Mg-Ca-Cl-SO₄-H₂O system: a re-evaluation of the sulfate chemistry in the Spencer–Møller–Weare model. *Geochim. Cosmochim. Acta*, **63**(9), 1305–1318 (doi: 10.1016/S0016-7037(99)00102-7)
- Marion GM, Farren RE and Komrowski AJ (1999) Alternative pathways for seawater freezing. *Cold Reg. Sci. Technol.*, **29**(3), 259–266 (doi: 10.1016/S0165-232X(99)00033-6)
- Maus S (2007) *On brine entrapment in sea ice: morphological stability, microstructure and convection*. Logos, Berlin
- Mel'nichenko NA (2007) Hydration numbers of sea water basic ions found by the pulse method of proton NMR. *J. Struct. Chem.*, **48**(3), 479–485
- Mel'nichenko NA, Mihailov VI and Chizhik VI (1981) Studies of the temperature-dependence of the brine content of sea ice by the pulse NMR method. *CRREL Draft Transl.* 757 [translated from *Okeanologiya*, **19**(5) [1979], 811–814]
- Mel'nichenko NA, Chizhik VI, Vyskrebentsev AS and Tyuveev AV (2009) The temperature dependences and methods for the functional representation of the rates of proton magnetic relaxation in aqueous solutions of electrolytes. *Russ. J. Phys. Chem.*, **83**(8), 1307–1314 (doi: 10.1134/S0036024409080111)
- Menzel M, Han S, Stapf S and Blumich B (2000) NMR characterization of the pore structure and anisotropic self-diffusion in salt water. *J. Magn. Reson.*, **143**(2), 376–381
- Nazintzev UL (1974) [Quantity relations in phase composition of sea ice]. *Probl. Arkt. Antarkt.*, **45**, 62–67 [in Russian]
- Nelson KH and Thompson TG (1954) Deposition of salts from sea water by frigid concentration. *J. Mar. Res.*, **13**(2), 166–182
- Perovich DK and Gow AJ (1996) A quantitative description of sea ice inclusions. *J. Geophys. Res.*, **101**(C8), 18 327–18 343 (doi: 10.1029/96JC01688)
- Pounder ER (1965) *The physics of ice*. Pergamon Press, Oxford
- Rasmussen PH, Jørgensen B and Nielsen J (1997) Aqueous solutions of proline and NaCl studied by differential scanning calorimetry at subzero temperatures. *Thermochim. Acta*, **303**(1), 23–30 (doi: 10.1016/S0040-6031(97)00241-4)
- Richardson C (1976) Phase relationships in sea ice as a function of temperature. *J. Glaciol.*, **17**(77), 507–519
- Richardson C and Keller EE (1966) The brine content of sea ice measured with a nuclear magnetic resonance spectrometer. *J. Glaciol.*, **6**(43), 89–100
- Ringer WE (1906) De veranderingen in samenstelling van zeewater bij het bevriezen. *Chemisch Weekblad.*, **3**(15), 223–249
- Spencer RJ, Moller N and Weare JH (1990) The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO₄-H₂O system at temperatures below 25°C. *Geochim. Cosmochim. Acta*, **54**(3), 575–590 (doi: 10.1016/0016-7037(90)90354-N)
- Thompson TG and Nelson KH (1956) Concentration of brines and deposition of salts from sea water under frigid conditions. *Am. J. Sci.*, **254**(4), 227–238 (doi: 10.2475/ajs.254.4.227)
- Tsurikov VL and Tsurikova AP (1972) O sodержanii rassola v morskikh l'dakh (sostoyaniye voprosa) [On the brine content of sea ice (state of the problem)]. *Okeanologiya*, **12**(5), 792–802

MS received 17 December 2012 and accepted in revised form 22 April 2013