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Nuclear Magnetic Resonance Study of Sea Water Freezing

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ABSTRACT

Results of measuring the relative brine content (Q_l) in the liquid phase of frozen sea water (SW) at temperatures between -2°C and -43°C with variable rate and direction of temperature change and with the use of various pulsed and steady-state NMR methods are presented and compared with analogous known literature data. Hysteresis loops corresponding to the crystallization range of SW salts, mainly NaCl, which partially precipitates as the crystalline hydrate $NaCl{\cdot}2H_2O$ at temperatures below -23°C, are detected on the temperature dependence of Q_l in brine. The main causes of hysteresis are indicated. Brine salinity in pores (*S)* is calculated from the results of determining Q_l and agrees well with current literature data in a wide temperatures range. Empirical equations for determination mass of brine are given.

KEYWORDS: sea ice; brine content and it salinity; NMR method.

INTRODUCTION

Knowledge about brine content in sea ice pores and its brine composition under various conditions of sea water freezing are important for understanding the formation of the physicochemical properties of sea ice. The volumes of sea ice brine and ice porosity determine heat exchange processes between sea water and atmosphere via the ice surface, particularly at the polar caps. These processes to a considerable extent determine our planet's climate.

There have been many studies (e.g., Ringer, 1906; Gitterman, 1937; Nelson and Thompson, 1954; Thompson and Nelson, 1956; Assur, 1958; Blinov, 1965; Richardson and Keller, 1966; Nazintsev and Nazintseva, 1972; Doronin and Kheisin, 1975; Tzurikov, 1976; Richardson, 1976; Cox and Weeks, 1983; Franks, 1985; Bogorodskiy and Gavrilo, 1988; Cho et al., 2002; Maus, 2007), as well as many other publications.

It is known that the content and salinity of the liquid phase in sea **ice** pores (brine) are complex functions of ice temperature, brine salinity, freezing rate, and its age. Liquid phase salinity increases with decreasing temperature and can reach ~ 243.5‰ at -32°C (Assur, 1958; Nazintsev, 1974; and another data). Brine properties near eutectic points have been insufficiently studied, even for binary systems (salt and water), to say nothing of such a complex natural object as sea water. The mechanical strength of sea ice depends on brine salinity and ice porosity (Assur, 1958). Sea ice morphology has been studied experimentally and by various theoretical methods using computer simulation. The best and most informative experimental technique for contactless determination of brine content in sea ice pores and its study (without destroying and pouring it) is the pulsed nuclear magnetic resonance (NMR) method, which has considerable advantages over other methods, including steady-state NMR (Nelson and Thompson, 1954; Richardson and Keller, 1966; Richarson, 1976; Edelstein and Schulson, 1991; Stepnik et al, 1994; Eicken and Bock, 2000; Bock et al, 2003; Cho et al., 2002) and another woks. Determination of the liquid phase content is based on measuring the amplitude of free induction signals from hydrogen nuclei (protons) after single excitation spin system pulses (Melnichenko et al., 1979) or on determining the integrated intensity of the absorption line in NMR spectra for the steady-state method, which are proportional to the number of resonant hydrogen water nuclei in the liquid phase.

It was shown in a previous paper (Melnichenko et al., 1979) that the liquid phase quantity (Q_l) in frozen SW depends on the rate and direction of temperature change, and hysteresis during which the Q_l values don't coincide upon a decrease and increase of temperature is observed on the curve of the brine temperature dependence near the NaCl eutectic point. The available literature data on a study of temperature dependences of Q_l in frozen sea water (SW) using the NMR method mainly refer to experiments in which the brine content was determined only during an increase of temperature in ice previously cooled to about -45 to -70°C under the assumption that, in this case, sea ice is completely in a solid state. However, according to Richardson's data (1976) and our experiments, a noticeable amount of the liquid phase was observed in ice even at temperatures of about -70°C. At the same time, under natural conditions the formation of a polycrystalline ice mass and brine occurs upon a decrease in temperature and not vice versa.

An analysis of the data on Q_l presented in different literature sources indicates their sufficiently good agreement in the temperature range from the freezing point to eutectic point (T_e) of NaCl. At lower temperatures the steepness of the change in the graphs of the temperature dependence of Q_l as well as the eutectic points obtained in different experiments differ substantially. For example, Cho's work (Cho et al., 2002) gives a value of T_e for SW equal to -21°C. At the same time, T_e for NaCl and SW are equal respectively to -21.9°C and -22.9°C (Frank, 1985; Blinov, 1965; Bogorodskiy and Gavrilo, 1988; Nazintsev, 1974). Precisely for this reason we conducted additional experiments with varying the direction of temperature change,