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THE BRINE AND GAS CONTENT OF SEA ICE WITH ATTENTION TO LOW
SALINITIES AND HIGH TEMPERATURES

Matti Leppäranta and Terhikki Manninen
Finnish Institute of Marine Research
P.O. Box 33
SF-00931 Helsinki, Finland

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TO LOW SALINITIES AND HIGH TEMPERATURES

MATTI LEPPÄRANTA AND TERHIKKI MANNINEN

FINNISH INSTITUTE OF MARINE RESEARCH
P.O. BOX 33, SF-00931 HELSINKI, FINLAND

ABSTRACT

Based on the well known sea ice phase diagram, equations are derived for determining the brine and gas content of sea ice for high temperatures (range 0 to -2°C) and low salinities. The presently widely used equations of Cox and Weeks (1982) are valid only for temperatures below -2°C . Fresh-water ice is used as a boundary condition for the equations. The relative salt concentrations in brine are assumed to be the same as in normal (or standard) sea water. Two sets of equations are presented: 1) accurate formulae based on UNESCO standard sea water equations, and 2) approximate formulae based on general properties of weak solutions. The approximate formulae are not essentially different from the classical system which basically assumes the freezing point to be a linear function of fractional salt content. The agreement between the two approaches is excellent and the approximate system is good enough for most applications.

1. INTRODUCTION

The brine and gas content are essential parameters for determining the physical properties of sea ice such as the dielectric constant, strength and thermal conductivity. These parameters are usually obtained from measurements of bulk density, temperature and salinity by using the phase diagram of sea ice (a salt-water-ice system).

A presently widely used system of equations for determining the gas and brine volumes in sea ice has been developed by Cox and Weeks (1982). Their equations are valid for temperatures below -2°C . However, the temperature of low salinity ice, e.g. the brackish-water ice in the Baltic Sea, becomes higher than -2°C in spring, and then the variability of brine content becomes very high. This is also true for summer multi-year ice in the polar regions.

In this report the brine and gas content equations are extended up to the temperature where all the ice has melted. In addition, particular attention is paid to low salinities, so that the equations are forced to converge correctly towards the case of fresh-water ice.

2. SYSTEM OF EQUATIONS

A sample of sea ice is composed of pure ice, brine, solid salt crystals and gas. The brine consists of liquid water and ionized salts. The sample has the following measurable bulk properties: mass, volume, temperature and salinity.

In the mathematical formulae below the following notations are used:

Symbol	Quantity	Subscript	For
m	mass	i	pure ice
V	volume	b	brine
T	temperature	a	gas
S	salinity	s	salts
ρ	density	w	liquid water
		none	sample of sea ice

At temperatures higher than -4°C the amount of solid salt crystals is negligible (Cox and Weeks, 1982). Since we consider only this region, it is assumed that all the salts are dissolved in the brine.

Using these notations the following definitions can be written:

$$V = V_i + V_b + V_a, \quad (1a)$$

$$m = m_i + m_b + m_a, \quad (1b)$$

$$m_b = m_s + m_w, \quad (1c)$$

$$V_b = V_s + V_w. \quad (1d)$$

The mass of gas m_a is ignored. The gas and brine contents ν_a and ν_b , respectively, are:

$$\nu_a = V_a/V, \quad (2a)$$

$$\nu_b = V_b/V. \quad (2b)$$

In the following, equations will be derived for determining ν_a and ν_b from the measurements of density, salinity and temperature of a sea ice sample.

The salinity of the brine is, by definition,

$$S_b = \frac{m_s}{m_b} . \quad (3)$$

Using simply the relationship between volume, mass and density, the brine content can be expressed as (e.g., Cox and Weeks, 1982)

$$\nu_b = \frac{V_b}{V} = \frac{\rho S}{\rho_b S_b} . \quad (4)$$

The density of a sea ice sample depends on the amount of pure ice, brine and gas through

$$\rho = (1 - \nu_a - \nu_b) \rho_i + \nu_b \rho_b . \quad (5)$$

For given ρ , S , T , ρ_b and S_b , the brine and gas contents ν_b and ν_a are calculated from Eqs. (4)-(5).

The triple (ρ, S, T) is measured; S_b and ρ_b are obtained from empirical equations:

$$S_b = S_b(T) , \quad (6)$$

$$\rho_b = \rho_b(S_b, T) . \quad (7)$$

Note that S_b is actually the inverse function of $T_f = T_f(S_b)$, the freezing point as a function of salinity, i.e.

$$S_b = \text{Inv}(T_f) \quad (8)$$

It is convenient to combine Eqs. (4) and (5):

$$\nu_b = (1 - \nu_a) \frac{\rho_i S}{\rho_b (S_b - S) + \rho_i S} . \quad (9)$$

This equation behaves correctly also at the melting point of sea ice. This is easily understood by noting that as the ice is in thermal equilibrium and approaches the melting temperature, $S_b \rightarrow S$ and hence $\nu_a + \nu_b \rightarrow 1$. Note that the limiting behaviour is purely mathematical and has nothing to do with the physical behaviour of ice during the melting period

3. FORMULAE FOR BRINE CONTENT CALCULATIONS

In order to be able to use the gas and brine volume equations it is necessary to have first formulae for the salinity and density of brine. For low salinity ice it is natural to require that

$$S_b \rightarrow 0 \text{ as } T \rightarrow 0. \quad (10)$$

3.1 Accurate formulae

"Accurate" formulae can be derived on the basis of the UNESCO standard density and freezing point equations for normal sea water. Their applicability for the brine, however, depends on how close the salt composition of brine is to that of normal sea water. It is known that they are not exactly similar (Weeks and Ackley, 1982).

The relation between the freezing point temperature and sea water salinity at zero pressure is obtained from (UNESCO, 1978)

$$T_f(^{\circ}\text{C}) = -0.0575 \cdot S_b(^{\circ}/\text{‰}) + 1.710523 \cdot 10^{-3} \cdot [S_b(^{\circ}/\text{‰})]^{3/2} - 2.154996 \cdot 10^{-4} [S_b(^{\circ}/\text{‰})]^2 \quad (11)$$

This form satisfies the requirement (10). Now the brine salinity function (6) is obtained through inverting Eq. (11). This is easily done iteratively. The density of sea water at temperatures above -2°C is calculated from The One Atmosphere International Equation of State of Seawater (UNESCO, 1981), which describes the temperature dependence of density with powers from 1 to 5 and the salinity dependence with powers 1, 3/2 and 2. At low salinities and temperatures below zero only the linear terms are essential.

For pure ice density the following temperature dependence is used (Pounder, 1965):

$$\rho_i(\text{g/cm}^3) = 0.917 - 1.403 \cdot 10^{-4} T(^{\circ}\text{C}) \quad (12)$$

As an example, Figs. 1-2 show the results for some selected sea ice salinities. In the calculations it has been assumed that the gas content is zero and hence the brine content approaches unity as the temperature increases (cf. Eq. 9).

3.2 Approximate system

A general law for the freezing point of weak water-salts solutions is expressed as

$$T_f = 1.86 \cdot m, \quad (13)$$

where m is the molality of the solution. For a fixed relative composition of salts, this equation states that the freezing point is proportional to the fractional salt content σ ,

$$T_f \propto \sigma = \frac{S_b}{1-S_b}, \quad (14)$$

The brine salinity is easily obtained by inverting this:

$$S_b = \frac{T_f}{T_1 + T_f}, \quad (15)$$

where T_1 is a constant. This form also satisfies the requirement (10). In the classical work of Assur (1958) on the sea ice phase diagram, based on the normal sea water assumption for the brine, Eq. (15) was used for the brine content. Through linear regression the value of -54.11 °C was obtained for T_1 . The same equation was taken also by Schwerdtfeger (1963) in his widely cited paper but his value for T_1 was -55 °C. Here we choose the value of Assur's.

For the density of brine in the temperature range 0 to -2 °C it is quite reasonable to use a temperature independent linear approximation as Cox and Weeks (1982):

$$\rho_b \text{ (g/cm}^3\text{)} = 1 + 0.0008 \cdot S_b \text{ (‰)}. \quad (16)$$

This equation is an appropriate approximation of the UNESCO equation.

4. COMPARISON WITH COX AND WEEKS FORMULAE

The present UNESCO based equations for the brine volume can be formulated similarly to Cox and Weeks (1982). This makes it easier to use our expression as an extension of the Cox and Weeks formula to temperatures above -2 °C. Consequently, functions $F_1 = F_1(T)$ and $F_2 = F_2(T)$ are introduced corresponding to those of Cox and Weeks (1982):

$$F_1 = \rho_b S_b \quad , \quad (17)$$

$$F_2 = \rho_b / \rho_1 - 1 \quad . \quad (18)$$

The brine content equation (9) becomes now

$$v_b = (1 - v_a) \frac{\rho_1 S}{F_1(T) - \rho_1 S F_2(T)} \quad . \quad (19)$$

Coefficients for the third-degree polynomial fittings for $F_1(T)$ and $F_2(T)$ (Table 1) are computed from least-squares regression using the above mentioned UNESCO equations.

Table 1. Coefficients for the third-degree polynomials, $F_1(T)$ and $F_2(T)$ at the temperature interval 0° to -2° C based on UNESCO equations for $S_b(T)$ and $\rho_b(S_b, T)$.

	T^0	T^1	T^2	T^3
$F_1(T)$	$-4.1221 \cdot 10^{-2}$	$-1.8407 \cdot 10^1$	$-5.8402 \cdot 10^{-1}$	$2.1454 \cdot 10^{-1}$
$F_2(T)$	$9.0312 \cdot 10^{-2}$	$-1.6111 \cdot 10^{-2}$	$1.2291 \cdot 10^{-4}$	$1.3603 \cdot 10^{-4}$

Values for F_1 and F_2 (and corresponding densities when $v_a = 0$) at different temperatures are given in Table 2. At -2° C the value of F_1 calculated using the coefficients of Table 1 is 37.393, whereas it is 37.695 if the coefficients of Cox and Weeks are used. Corresponding values for F_2 are 0.12194 and 0.12223. To remove the discontinuity of F_1 at -2° C caused by the use of UNESCO equations above -2° C and the equations of Cox and Weeks below -2° C, another F_1 was calculated. It was based on the (T_f, S_b) -relationship of equation 11 and the required continuity of V_b/V at -2° C. Unfortunately this caused a density minimum at about -0.4° C, and therefore this approach was discarded.

Table 2. Values for S_b , F_1 , F_2 and ρ_b at different temperature based on UNESCO equations for $S_b(T)$ and $\rho_b(S_b, T)$.

S_b (‰)	T (°C)	ρ_b (g/cm ³)	F_1	F_2
0	0	0.9998	0	0.0903
2.0000	-0.1110	1.0015	2.0029	0.0921
4.0000	-0.2198	1.0031	4.0124	0.0938
6.0000	-0.3276	1.0047	6.0282	0.0956
8.0000	-0.4351	1.0063	8.0505	0.0973
10.0000	-0.5425	1.0079	10.0793	0.0991
12.0000	-0.6499	1.0095	12.1144	0.1008
14.0000	-0.7576	1.0111	14.1560	0.1025
16.0000	-0.8657	1.0128	16.2040	0.1043
18.0000	-0.9742	1.0144	18.2584	0.1060
20.0000	-1.0832	1.0160	20.3193	0.1077
22.0000	-1.1928	1.0176	22.3866	0.1095
24.0000	-1.3030	1.0192	24.4604	0.1112
26.0000	-1.4139	1.0208	26.5406	0.1129
28.0000	-1.5255	1.0224	28.6273	0.1147
30.0000	-1.6379	1.0240	30.7205	0.1164
32.0000	-1.7510	1.0256	32.8201	0.1182
34.0000	-1.8650	1.0272	34.9263	0.1199
36.0000	-1.9798	1.0289	37.9389	0.1216
36.3501	-2.0000	1.0291	37.4093	0.1219

A comparison between the present formulae and Cox and Weeks (1982) is given in Fig. 3. It is obvious that extrapolation of either the present accurate formula or Cox and Weeks leads to biased results. On the other hand, the approximate system performs very well through the range of 0 to -4 °C.

4. SENSITIVITY TO MEASUREMENT ERRORS

The relative error of the brine content according to Eqs. (4), (6) and (7) is

$$\frac{dv_b}{v_b} = \frac{d\rho}{\rho} + \frac{dS}{S} - \left(1 + 2 \cdot \frac{S_b}{\rho_b} \cdot \frac{\partial \rho_b}{\partial S_b}\right) \cdot \frac{1}{S_b} \frac{\partial S_b}{\partial T} dT \quad (20)$$

In this equation the first two terms are directly the relative errors of density and salinity, and the third term is nearly the same as the relative error of temperature. Using a linear approximation for S_b and noting that the brine density term is very small, we have

$$\frac{dv_b}{v_b} \cong \frac{d\rho}{\rho} + \frac{dS}{S} - \frac{dT}{T} \quad (21)$$

Obviously the brine volume error may become very large as $S \rightarrow 0$ or $T \rightarrow 0$. For $S \sim 1$ per mille and $T > -1$ °C it is the temperature measurement which usually causes difficulties. When instantaneous measurements are made in the field it is difficult to reach an accuracy better than about 0.1 °C (cf. Leppäranta et al., 1988). An illustration of the effect of ± 0.1 °C temperature error to the brine content estimate is presented in Fig. 4. For example, at a temperature of -0.2 °C or higher the accuracy of the brine volume calculations is worse than 50 %.

The error of the gas content estimates is obtained using Eq. 5. The total differential of v_a becomes

$$dv_a = \frac{d\rho}{\rho_i} + \left[\frac{\rho_b}{\rho_i} - 1 \right] dv_b + v_b \frac{d\rho_b}{\rho_i} \quad (22)$$

In the present high temperature regime the variation of the brine density is very small, the absolute value being approximately 1.01 g cm^{-3} . Thus we can write

$$dv_a \cong \frac{d\rho}{\rho_i} + 0.11 dv_b \quad (23)$$

Note that in the right-hand side the denominator of the first term is the density of pure ice and not the density of the sea ice sample. Field measurements of sea ice density are accurate to maybe 1-2 per cent, and so the brine content error causes a significant gas content error only at very high (≥ -0.5 C)° temperatures.

5. CONCLUSIONS

The UNESCO equations for the seawater density and freezing temperature are international standards, and on the other hand the Cox and Weeks equations for calculating brine volume content and density of sea ice have become well-established in use. The former system is valid for temperatures higher than -2 °C and the latter for temperatures lower than -2 °C. The difference in the calculated brine content at -2 °C between the two systems is very small. Therefore it seems best to combine them using the coefficients of Table 1 above -2 °C and the coefficients of Cox and Weeks below -2 °C. The discontinuity may cause problems in theoretical calculations but hardly in

experimental work.

It is true that the relative composition of salts is not exactly the same in brine and in sea water (e.g., Weeks and Ackley, 1982). This may raise the question of using the UNESCO equations which are calibrated for sea water. Thus using a relatively simple and general brine salinity formula may become advantageous, although it is based on the same assumption of salt composition in brines. In the temperature range 0 to -4°C the assumption of freezing point being directly proportional to the fractional salt content yields excellent agreement with the combined UNESCO - Cox and Weeks system. This simplified system is accurate enough for most practical purposes.

For mathematical modeling purposes it would be highly desirable to present the brine content as a continuous function of temperature and salinity. Moreover, at $T = -2^{\circ}\text{C}$ this function should also have all derivatives with respect to temperature since at -2°C nothing physically special occurs in the brine. In the light of the present knowledge the best thing to do might be to revise the Cox and Weeks (1982) work by extending their equations up to zero temperature using (10) as a boundary condition. They cut their analysis at $T = -2^{\circ}\text{C}$ for an unknown but likely unnecessary reason. Such revision, based on Assur's (1958) work, is presently in progress.

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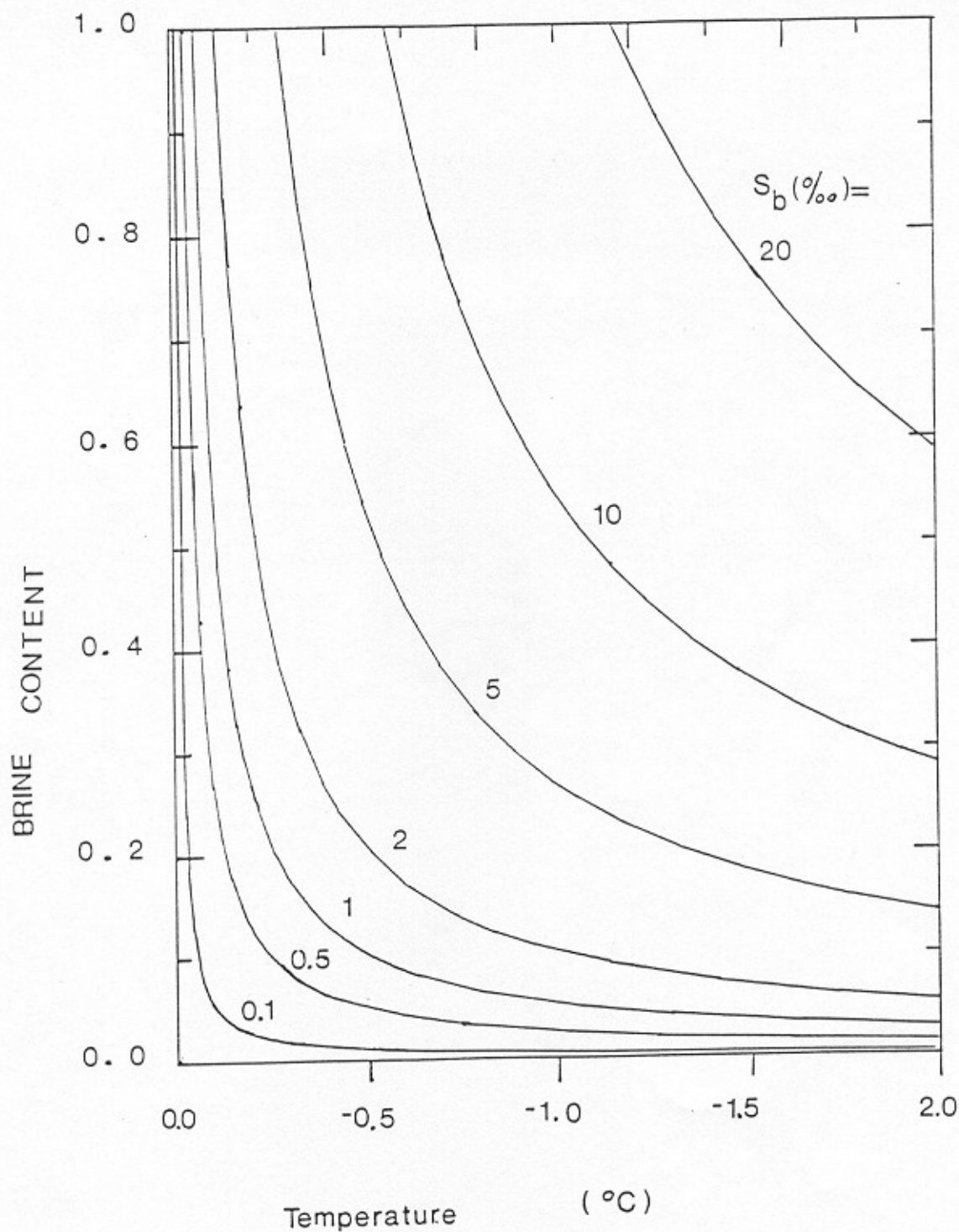


Fig. 1. Brine content as a function of temperature above -4°C for various sea ice salinities. The calculations are based on the UNESCO normal sea water freezing point and density equations. The formulae have been fitted to the range 0 to -2°C , and the lower temperature regime is an extrapolation.

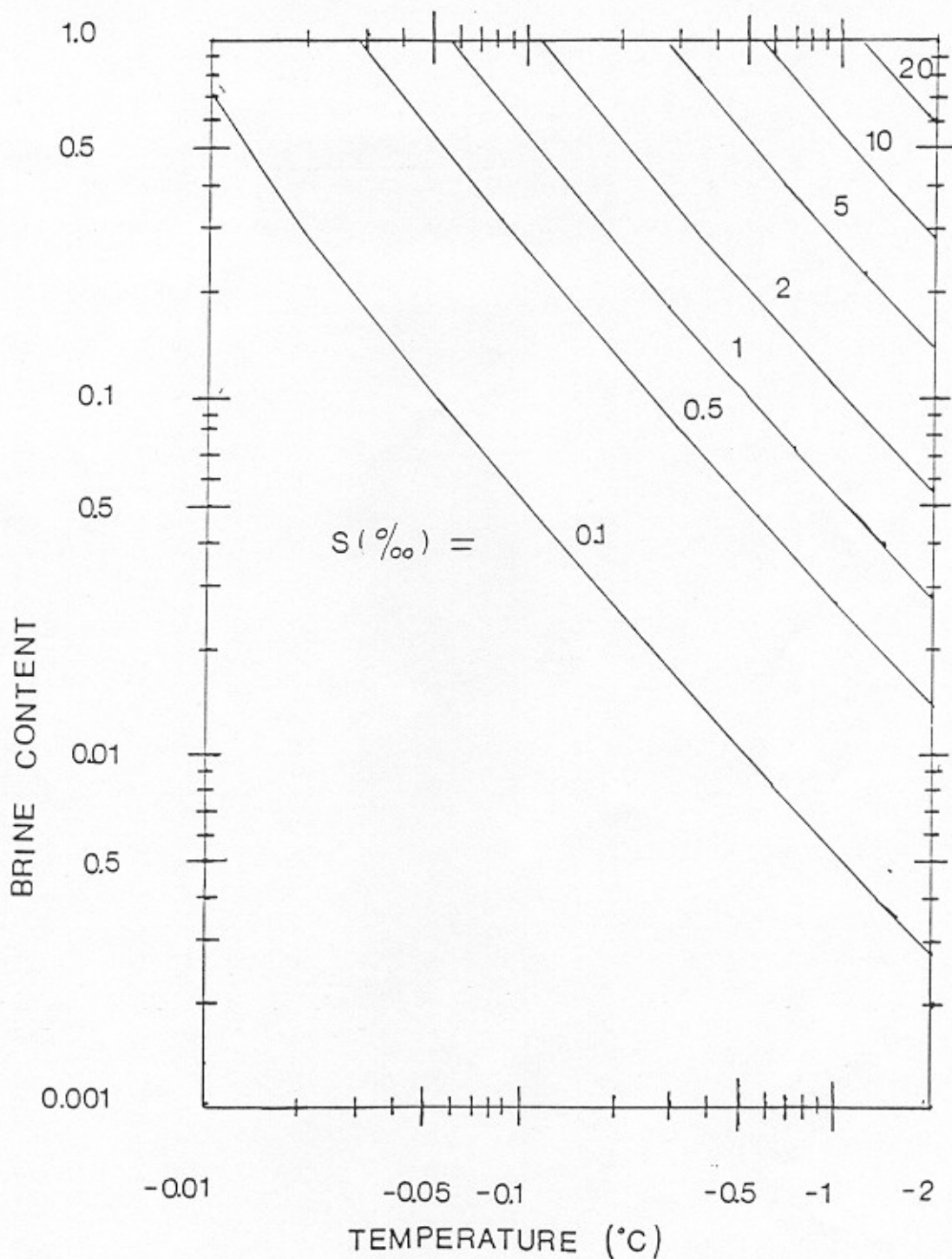
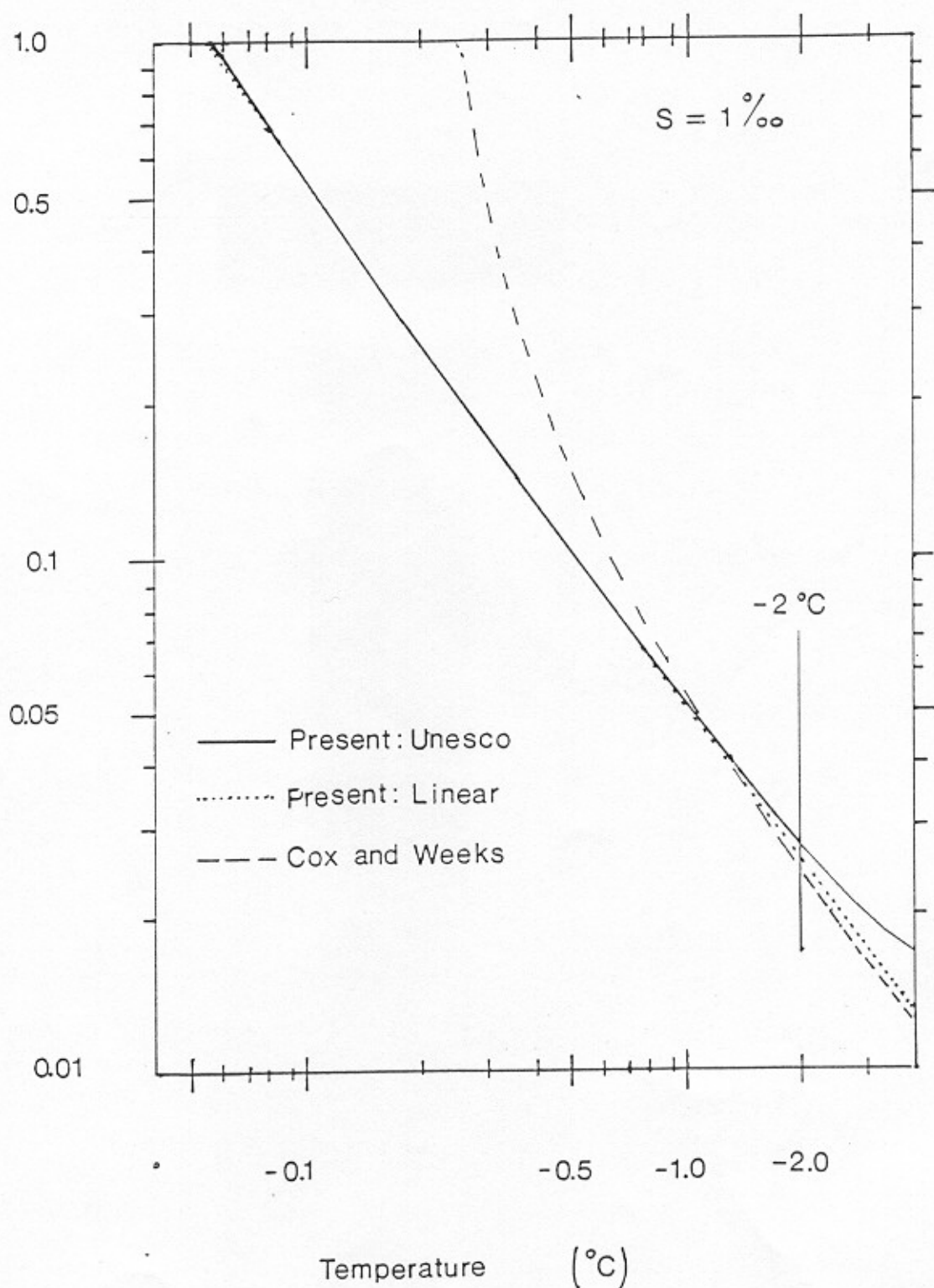


Fig. 2. The logarithmic temperature dependence of the brine content above -4°C for various sea ice salinities. The calculations are based on the UNESCO normal sea water freezing point and density equations. The formulae have been fitted to the range 0 to -2°C , and the lower temperature regime is an extrapolation.



Comparison between the present brine content equations and that of Cox and Weeks (1982). Ice salinity is 1.0 per mille. Note that the UNESCO based system is claimed to be valid for temperatures 0 to -2 °C and the Cox and Weeks system for temperatures below -2 °C .

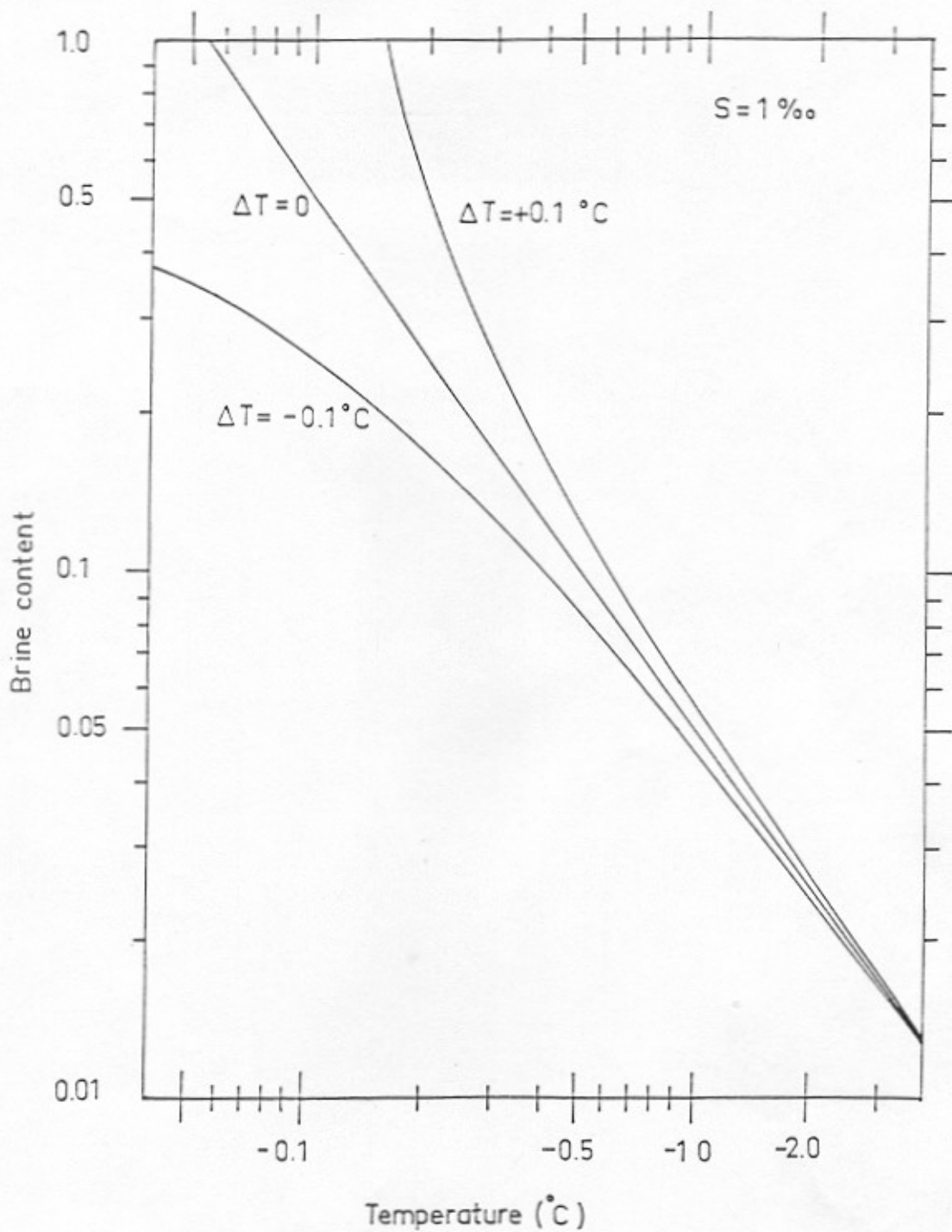


Fig. 4. Brine content for one per mille salinity ice in the temperature range 0 to $-4\text{ }^{\circ}\text{C}$: the correct temperature (mid-line) and temperature biased by $+0.1$ and $-0.1\text{ }^{\circ}\text{C}$.