

## The system NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O: I. The ice liquidus at 1 atm total pressure\*

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(Received April 11, 1989; accepted in revised form December 15, 1989)

**Abstract**—Phase relations in the ice-stable field of the system NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O have been determined under 1 atm total pressure along the NaCl-H<sub>2</sub>O and CaCl<sub>2</sub>-H<sub>2</sub>O binaries and along five pseudobinaries with constant NaCl/(NaCl+CaCl<sub>2</sub>) weight ratios. The results are in excellent agreement with published data along the NaCl-H<sub>2</sub>O binary but show large discrepancies when compared to previous determinations of the ice liquidus along the CaCl<sub>2</sub>-H<sub>2</sub>O binary and in the NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O ternary. Eutectic temperatures and compositions are -21.20°C (±0.01°) and 23.2 wt% for the NaCl-H<sub>2</sub>O binary and -49.95°C (±0.15°) and 30.33 wt% for the CaCl<sub>2</sub>-H<sub>2</sub>O binary. The minimum temperature reached during our experiments in the ternary system was -34°C; therefore, we do not report isotherms below -35°C or the ternary eutectic temperature.

At moderate to high salinities, isotherms cross the ice sub-field at lower total salt concentrations than previously reported. Fluid inclusion salinities determined from previously published freezing-point data may be in error by as much as 2 wt% total salt. In addition, NaCl/(NaCl+CaCl<sub>2</sub>) weight ratios estimated from hydrohalite- and ice-melting temperatures may be in error by as much as 0.15.

### INTRODUCTION

FLUID INCLUSIONS ARE a primary means of determining the PTX conditions of formation or alteration of minerals. In order to do so, compositions of fluid inclusions must be known and phase equilibria and volumetric (PVTX) data for the applicable fluid system must be available. Our ability to determine compositions of inclusions has advanced significantly in recent years, owing to the development of new analytical techniques and improvements in existing techniques which allow smaller samples to be analyzed. Similarly, there has recently been a renewed effort to obtain PVTX data on geologically important fluid systems over wide ranges of temperature and pressure.

Fluids from a variety of geologic environments may be adequately represented by the simple NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O ternary system. Fluids approximated by this system are important in geothermal reservoirs, oceanic hydrothermal systems, metamorphic environments, petroleum reservoirs, and ore deposits of gold, copper, tin, tungsten, uranium, lead, and zinc (WHITE, 1968, 1981; CRAWFORD et al., 1979a,b; KWAK and TAN, 1981; KELLY et al., 1986; ROBERT and KELLY, 1987; VANKO et al., 1988; WITT, 1988). However, the paucity of freezing-point depression data for this and other ternary or higher order aqueous salt systems has limited our ability to interpret microthermometric and analytical data obtained from fluid inclusions formed in these environments. In this paper we describe results of an experimental study to determine the ice liquidus in the NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O system at 1 atm total pressure and the application of these data for determining compositions of vapor-saturated, low-to-moderate salinity (<30 wt%) fluid inclusions approximated by this system.

### EXPERIMENTAL PROCEDURE

The procedure used in this study is a modification of the one used by HALL et al. (1988) to determine the ice liquidus in the system NaCl-KCl-H<sub>2</sub>O. Simply stated, as a low salinity water-salt solution of known cationic ratio is cooled below its freezing point, pure H<sub>2</sub>O ice will precipitate from the solution. With continued cooling additional ice will precipitate, causing the total salinity of the liquid phase in equilibrium with the ice to increase while the cationic ratio remains constant. The composition of the liquid thus moves directly away from the H<sub>2</sub>O apex along a pseudobinary that passes through the bulk composition of the initial liquid. Isotherms within the ice field are determined by sampling the liquid in equilibrium with ice over a range of temperatures for several different NaCl/(NaCl + CaCl<sub>2</sub>) anhydrous weight ratios ( $X_{\text{NaCl}}$ ).

HALL et al. (1988) determined the liquid composition by weighing a sample of liquid, evaporating it to dryness, and weighing the remaining salt residue. The hygroscopicity of CaCl<sub>2</sub>, however, makes routine determination of the salt concentration by this method impractical. We did find, however, that the CaCl<sub>2</sub>(aq) stock solution concentration could be determined to a high degree of precision by drying; therefore, this method was used to determine the stock solution compositions while the salinities of solution in equilibrium with ice were determined by comparing densities of salt solutions of known concentration and  $X_{\text{NaCl}}$  ratio with densities of solutions sampled during the freezing-point depression experiment. That is, the density of our sample solution of known  $X_{\text{NaCl}}$  but unknown total salinity was compared to the standard solution having the same  $X_{\text{NaCl}}$  to locate the total salinity corresponding to that density.

The freezing-point measurements were conducted in a sealed 1500 ml reaction vessel equipped with ports for a 15 ml sampling pipet, a platinum resistance thermometer (PRT), and an electric stirrer (Fig. 1). Aliquots of concentrated salt solution were diluted with distilled, deionized H<sub>2</sub>O to produce approximately 1 liter volumes containing about 3 wt% salt. The dilute solution was poured into the reaction vessel, which was then sealed and suspended in a mechanically refrigerated bath (FIS Systems MC-8-80) containing ethyl alcohol (Fig. 1). The volume of salt solution in the reaction vessel and alcohol in the bath were adjusted so that the tip of the PRT was at least 13 cm below the air/solution interface while the air/solution interface was about 4 cm below the air/alcohol interface.

A magnetic stirrer fixed in the bottom of the bath continuously stirred the alcohol. The salt solution was stirred, except during sampling, by a teflon-coated electric stirrer. The pipet was continuously immersed during intervals between sampling, and solution was flushed through the pipet before extraction of each sample.

\* Presented at PACROFI II, Second Biennial Pan-American Conference on Research on Fluid Inclusions, held in Blacksburg, VA, January 4-7, 1989.

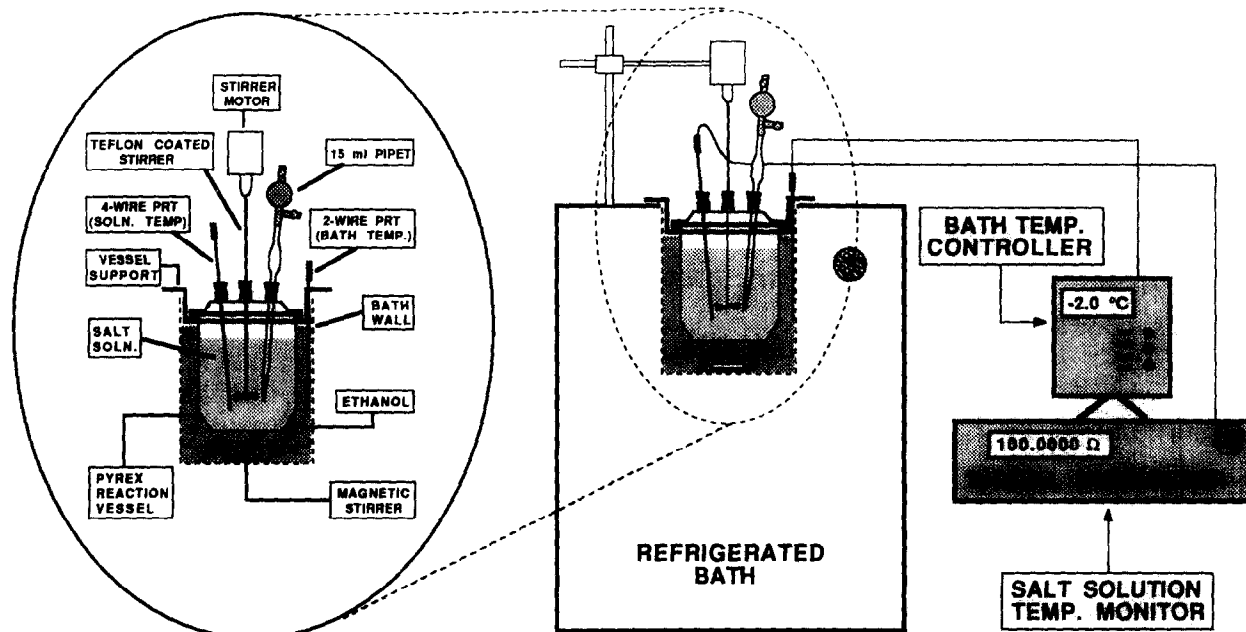


FIG. 1. Schematic drawing of the freezing-point depression apparatus used in this study.

The temperature of the liquid was measured with a four-wire, 100 ohm PRT (OMEGA PR11, temperature coefficient of 0.00385) and a digital multimeter (DMM; Keithley 193A) (Fig. 1). The DMM and PRT were calibrated together at the freezing points of  $\text{H}_2\text{O}$  ( $0.000^\circ\text{C}$ ) and triply distilled  $\text{Hg}$  ( $-38.842^\circ\text{C}$ ) several times during the course of the experiments. Sampling temperatures were recorded as ohms and converted to temperature through a second-order polynomial regression of the resistance versus temperature data from  $-60^\circ$  to  $+30^\circ\text{C}$  (Table XVIII, OMEGA Temperature Measurement Handbook). Resistance could be read to four decimal places corresponding to temperature readings precise to  $\pm 0.0015^\circ\text{C}$ . The precision of the temperature measurements (generally better than  $\pm 0.02^\circ\text{C}$ ) was limited by changes in solution temperature during sampling.

The dilute solution was initially undercooled to approximately  $3^\circ\text{C}$  below its expected freezing temperature. Ice was nucleated by inoculating the supercooled solution with a wire chilled in liquid nitrogen. Upon formation of ice, the solution temperature immediately rose to the equilibrium temperature corresponding to the bulk composition and the quantity of ice generated. After the solution temperature stabilized the stirring motor was stopped and a sample taken from near the PRT tip. Each pipet of solution was visually checked for included ice and emptied into a 15 ml high-density polyethylene bottle which was immediately capped. Though it is possible that very fine ice crystals could have been entrained in the samples the precision of the data from this study and the agreement of it with the most precise of the published  $\text{NaCl-H}_2\text{O}$  and  $\text{CaCl}_2\text{-H}_2\text{O}$  freezing point data indicate that contamination of the samples with ice was negligible.

The alcohol bath was cooled at a rate of about  $0.02^\circ\text{C}/\text{min}$  in steps of  $1^\circ\text{C}$ . Solution temperature lagged  $1^\circ$  to  $3^\circ\text{C}$  behind bath temperature; therefore, solution temperature was not strictly static during sampling. The temperature controller (FTS Systems 41P) was set such that the rate of temperature change of the solution was very slow as the sampling temperature was approached. Temperature gradients, which inevitably occurred when the stirrer in the reaction vessel was shut off, are irrelevant as long as the temperature of the solution in equilibrium with ice is known for the region from which the sample was taken. Samples were always taken very close to the sensitive portion of the RTD and with the exception of the most dilute (highest freezing temperature) samples the reaction vessel always contained substantial quantities of ice (usually  $\frac{2}{3}$  or more of the vessel's volume). Comparisons with the very precise data of SCATCHARD and PRENTISS (1933), GIBBARD and GOSSMANN (1974), and

GIBBARD and FONG (1975) (discussed below) show that the accuracy of the higher temperature portions of the experiment does not appear to have suffered from the lower quantities of ice in the vessel.

During cooling the ice/solution ratio increased as the salinity of the solution increased and more ice precipitated. This ratio was controlled by replacing solution lost to sampling with aliquots of concentrated parent solution. During some experiments the mass of ice in the reaction vessel became so large that ice-free samples could not be extracted. When this occurred large quantities (75–150 ml) of solution (generally including ice) were extracted and discarded and replaced with proportional quantities of parent solution. Bailing and replenishing continued until the ice/solution ratio permitted contin-

Table 1. Coefficients of Equation 1

$a_0$	= -252.80766161
$a_1$	= -4.46838599
$a_2$	= 0.00000000
$a_3$	= -3.11224433
$b_1$	= 433.18270190
$b_2$	= -232.86374780
$b_3$	= 51.80774407
$c$	= 0.39937513
$d$	= 37.89983342
$e$	= 4.51383486
$f$	= 3.00567613
$g_1$	= -111.52366055
$g_2$	= 108.45638078
$g_3$	= -34.82557222
$h$	= 0.05251418

uation of the experiment. If this procedure failed to produce an ice/solution ratio that would permit sampling of solution uncontaminated by ice, the experiment was abandoned and a new solution of moderate concentration (e.g., 15 wt%) was prepared from the reserve of parent solution and the experiment was restarted where the initial experiment was abandoned. Each experiment ended when the solution was believed to be saturated in hydrohalite (NaCl·2H<sub>2</sub>O) or antarcticite (CaCl<sub>2</sub>·6H<sub>2</sub>O). After evaluation of the data, however, it became apparent that this had occurred only during the two binary experiments.

With the exception of the  $X_{\text{NaCl}} = 0.8$  pseudobinary, parent so-

lutions were prepared from stocks of concentrated CaCl<sub>2</sub>-H<sub>2</sub>O and NaCl-H<sub>2</sub>O solution. Stock solution compositions were determined by mass difference between aliquots of solution and the masses of anhydrous salt residue after drying. The  $X_{\text{NaCl}} = 0.8$  parent solution was prepared by adding anhydrous NaCl and water to CaCl<sub>2</sub>-H<sub>2</sub>O stock solution. All solution compositions were corrected to masses under vacuum. Two splits were drawn from each parent solution—one was used for the freezing-point depression experiment and the other for preparing the density standards.

Densities of both the calibration standards and the solutions of

Table 2. Experimentally Determined Freezing Point Depressions ( $\theta$ , °C) and Total Salinities (wt%) for Various NaCl/(NaCl+CaCl<sub>2</sub>) Wt Ratios Shown in Parentheses at the Head of Each Pair of Data Columns

(1.000)		(0.593)		(0.195)		(0.000)	
$\theta$	wt%	$\theta$	wt%	$\theta$	wt%	$\theta$	wt%
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.84	3.08	1.70	3.13	1.55	3.18	1.42	3.13
2.03	3.40	2.06	3.77	2.03	4.09	2.08	4.42
5.42	8.45	3.01	5.32	3.37	6.34	3.68	7.09
6.98	10.48	4.05	6.92	4.40	7.87	4.06	7.64
9.22	13.11	5.19	8.50	5.05	8.75	5.21	9.16
10.27	14.25	5.21	8.54	6.00	9.95	6.02	10.15
12.49	16.46	6.02	9.58	7.02	11.13	6.03	10.20
12.86	16.78	7.08	10.88	8.09	12.27	7.06	11.35
14.91	18.57	8.10	12.05	9.02	13.18	8.08	12.39
16.91	20.18	9.10	13.10	10.04	14.12	8.42	12.64*
19.17	21.80	10.03	14.03	11.13	15.06	9.08	13.34
20.64	22.80	11.02	14.96	11.97	15.75	10.98	14.83*
21.48	23.34	12.19	16.00	13.96	17.22	11.62	15.46
		13.24	16.89	16.09	18.65	12.03	15.72
		14.08	17.55	18.07	19.82	13.50	16.77
		15.14	18.36	20.36	21.08	14.21	17.31
		17.04	19.69	22.01	21.94	15.30	18.04*
		19.06	21.02			16.02	18.42
		21.02	22.19			17.80	19.46
		23.23	23.41			19.32	20.19
		23.28	23.43			19.64	20.40
						20.78	20.97
						21.12	21.16
						21.97	21.56
						23.08	22.04
						24.02	22.41
						25.23	23.01
						25.25	22.95
						26.08	23.37
						27.06	23.73
						27.08	23.73
						27.21	23.78
						27.22	23.82
						28.08	24.16
						28.98	24.44
						30.16	24.89
						32.09	25.52
						32.13	25.56
						34.07	26.17
						35.72	26.69
						36.03	26.78
						37.07	27.08
						38.08	27.39
						39.03	27.66
						39.83	27.88
						40.80	28.14
						42.16	28.50
						42.89	28.68
						43.15	28.71
						44.00	28.97
						44.77	29.16
						45.64	29.37
						46.55	29.58
						46.66	29.61
						48.28	29.94
						49.37	30.23
						50.14	30.39
						50.51	30.46
						51.20	30.59*

(0.796)		(0.393)		(0.169)	
$\theta$	wt%	$\theta$	wt%	$\theta$	wt%
0.00	0.00	0.00	0.00	19.99	20.86
1.71	3.03	1.59	3.12	22.11	21.94
2.01	3.54	2.04	3.88	24.05	22.85
3.05	5.20	2.10	4.02	25.98	23.70
4.01	6.68	3.18	5.84	28.02	24.54
4.55	7.43	4.22	7.40	30.08	25.34
4.94	7.97	5.46	9.08	30.21	25.39
4.98	8.09	6.94	10.88	32.11	26.09
6.12	9.57	8.06	12.10	34.03	26.75
6.13	9.56	9.16	13.24		
7.03	10.69	10.06	14.09		
8.84	12.78	11.11	15.04		
10.12	14.12	12.06	15.84		
11.00	14.98	13.00	16.60		
11.91	15.81	14.02	17.37		
13.32	17.05	15.32	18.30		
14.19	17.79	16.95	19.39		
15.19	18.58	17.03	19.41		
16.05	19.25	19.36	20.85		
17.03	19.96	21.22	21.87		
18.01	20.65	23.21	22.96		
18.99	21.30	25.07	23.85		
19.00	21.31	26.93	24.71		
20.05	21.99				
20.96	22.56				
22.13	23.25				
22.48	23.63*				

\*These data were excluded from the regression routine.

Table 3. Coefficients of Equation 2

$a_0 =$	0.00079300
$a_1 =$	-23.60559803
$a_2 =$	-14.28248382
$a_3 =$	-6.28485097
$a_4 =$	-1.63493939
$a_5 =$	-0.22344814
$a_6 =$	-0.01233080
$b_1 =$	5.93722121
$b_2 =$	8.52707977
$b_3 =$	3.58341351
$b_4 =$	0.50474224
$c_2 =$	1.46447853
$c_3 =$	1.42997903
$c_4 =$	0.00000000
$c_5 =$	-0.34061248
$c_6 =$	-0.08075286

Table 4. Total salinity (Wt%) corresponding to various freezing-point depressions( $\theta$ ) and weight fractions ( $X_{NaCl}$ ) calculated from Equation 2.

$\theta$ (°C)	$X_{NaCl}$	Wt%
1.0	1.0	1.73
5.0	1.0	7.87
10.0	1.0	13.99
15.0	1.0	18.64
20.0	1.0	22.35
1.0	0.8	1.82
5.0	0.8	8.05
10.0	0.8	13.98
15.0	0.8	18.44
20.0	0.8	21.97
1.0	0.6	1.92
5.0	0.6	8.24
10.0	0.6	14.00
15.0	0.6	18.26
20.0	0.6	21.60
25.0	0.6	24.33
1.0	0.4	2.02
5.0	0.4	8.45
10.0	0.4	14.04
20.0	0.4	21.24
30.0	0.4	25.83
1.0	0.2	2.12
5.0	0.2	8.68
10.0	0.2	14.10
20.0	0.2	20.90
30.0	0.2	25.40
1.0	0.0	2.22
5.0	0.0	8.92
10.0	0.0	14.18
20.0	0.0	20.56
30.0	0.0	24.84
40.0	0.0	27.89

unknown concentration were measured with a vibrating U-tube densimeter (Paar DMA60 and 602HP remote cell with a borosilicate glass tube). All densities were measured at nominal temperatures of 25° and 35°C. The U-tube temperature varied from 25.003° to 25.092°C and from 34.970° to 35.004°C for the calibration solutions (OAKES et al., 1990) and from 25.007° to 25.097°C for the solutions of unknown concentration. The densimeter was maintained at temperature with a Neslab RTE-220 circulating bath while the sample bottles were stored in the bath for several hours prior to each density measurement to ensure thermal equilibrium between the tube and the solutions. The temperatures of the circulating bath and U-tube

were monitored by two separate resistance bridges and four-wire PRT's. A more detailed description of the density measurements and the measured densities are presented in OAKES et al. (1990).

Densities of both the calibration and experimental solutions were evaluated using a stepwise linear least squares regression technique to generate an equation describing wt% total salt ( $W$ ) as a function of  $T_u$  (U-tube temperature in °C divided by 10.0),  $X_{NaCl}$ , and density ( $R$ ). The coefficients  $a_i, b_j, c,$  etc. are listed in Table 1.

$$W = \sum_{i=0}^3 a_i X_{NaCl}^i + \sum_{j=1}^3 b_j R^j + c T_u R + d T_u X_{NaCl} + e R^3 X_{NaCl} + f R X_{NaCl}^3 + \sum_{k=1}^3 g_k T_u R^k X_{NaCl} + h T_u R^3 X_{NaCl}^2 \quad (1)$$

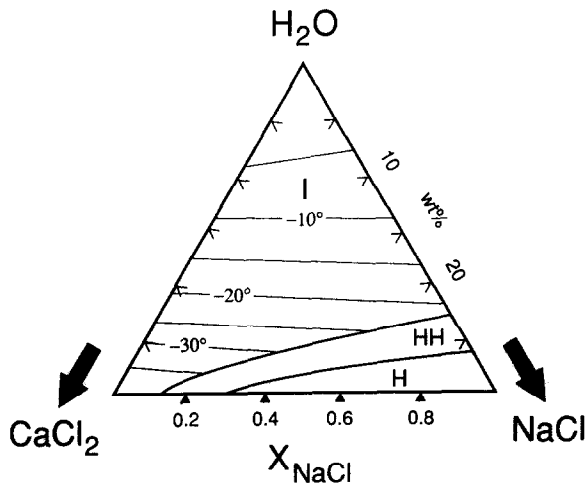


FIG. 2. Isotherms of the ice liquidus at 1 atm total pressure in the system NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O calculated from Eqn. (2) are shown in 5°C intervals. The ice-hydrohalite and hydrohalite-halite cotectics were constructed using data from YANATIEVA (1946). HH = Hydrohalite (NaCl · 2H<sub>2</sub>O), H = Halite (NaCl), I = Ice (H<sub>2</sub>O).

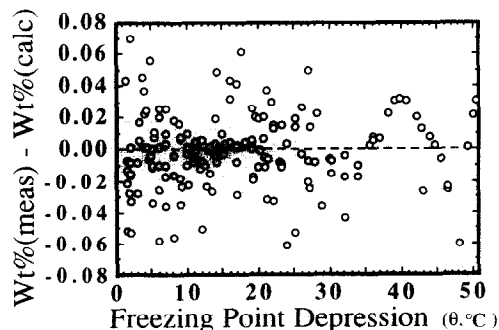


FIG. 3. Comparison of measured salinities [Wt% (meas)] from this study with salinities predicted by Eqn. (2) [Wt% (calc)].

The calibration equation for wt% total salt is expressed as a function of temperature as well as  $R$  and  $X_{\text{NaCl}}$  because the U-tube temperature was not easily maintained at 25.00°C (drift was generally less than 0.004°C/h). Because the calibration data are essentially limited to 25° and 35°C the regressions were restricted to linear functions of  $T_u$ .

## RESULTS

Experimental data for the two binaries (NaCl-H<sub>2</sub>O and CaCl<sub>2</sub>-H<sub>2</sub>O) and five pseudobinaries are presented in Table 2. Salinities generated from Eqn. (1) were regressed as a function of freezing-point and  $X_{\text{NaCl}}$  resulting in the equation

$$W = \sum_{i=0}^6 a_i T_f^i + \sum_{j=1}^4 b_j T_f^j X_{\text{NaCl}} + \sum_{k=2}^6 c_k T_f^k X_{\text{NaCl}}^2 \quad (2)$$

where  $W$  is the total salinity in weight percent;  $T_f$  is the freezing temperature (°C) divided by 10.0; and  $a_i$ ,  $b_j$ , and  $c_k$  are the regression coefficients. Values of the regression coefficients for Eqn. (2) are listed in Table 3.

Isotherms of the ice liquidus at 1 atm total pressure calculated from Eqn. (2) are shown on Fig. 2. Representative values calculated from Eqn. (2) are listed in Table 4 and differences between experimental salinity values and values predicted from Eqn. (2) are shown on Fig. 3. The residuals plotted on Fig. 3 reveal that all experimental values are represented within 0.07 wt% by Eqn. (2). The standard deviation ( $\sigma$ ) of residual wt% values for the fit of Eqn. (1) is 0.025 wt% while the  $\sigma$  value for wt% values determined from Eqn. (2) is 0.013 wt%. Therefore, the total error ( $1\sigma$ ) of salinities estimated from Eqn. (2) is  $\pm 0.038$  wt%.

Because our results are more plentiful at high salinities, we included low-salinity data of GIBBARD and FONG (1975) in our regression. Note that GIBBARD and FONG (1975) did not use the three most concentrated solutions from their  $X_{\text{NaCl}} = 0.51$  pseudobinary in their determination of osmotic coefficients. When combined with our data these three points and their next three most concentrated solutions along this pseudobinary were not fitted to within  $3\sigma$  values. Thus, the six most concentrated solutions of GIBBARD and FONG (1975) along the  $X_{\text{NaCl}} = 0.51$  pseudobinary were excluded from the derivation of Eqn. (2). It will be shown below, however, that Eqn. (2) reproduces GIBBARD and FONG's (1975) binary and ternary data extremely well over the entire range of their data.

## COMPARISON WITH PREVIOUS STUDIES

Several determinations of freezing-point depression have been made for the binary systems NaCl-H<sub>2</sub>O and CaCl<sub>2</sub>-H<sub>2</sub>O. Agreement among different data sets, however, is much better for the NaCl-H<sub>2</sub>O binary than for the CaCl<sub>2</sub>-H<sub>2</sub>O binary. As shown on Fig. 4 our results along the NaCl-H<sub>2</sub>O binary are in excellent agreement with previous freezing-point measurements made by SCATCHARD and PRENTISS (1933), GIBBARD and GOSSMANN (1974), and HALL et al. (1988). The data of RODEBUSH (1918) differs significantly from the results of this study and the three studies mentioned above over the entire temperature range. The fit by POTTER et al. (1978) deviates to higher temperatures at freezing points lower than -11°C because it is based entirely on RODEBUSH's (1918) data at temperatures less than -14°C.

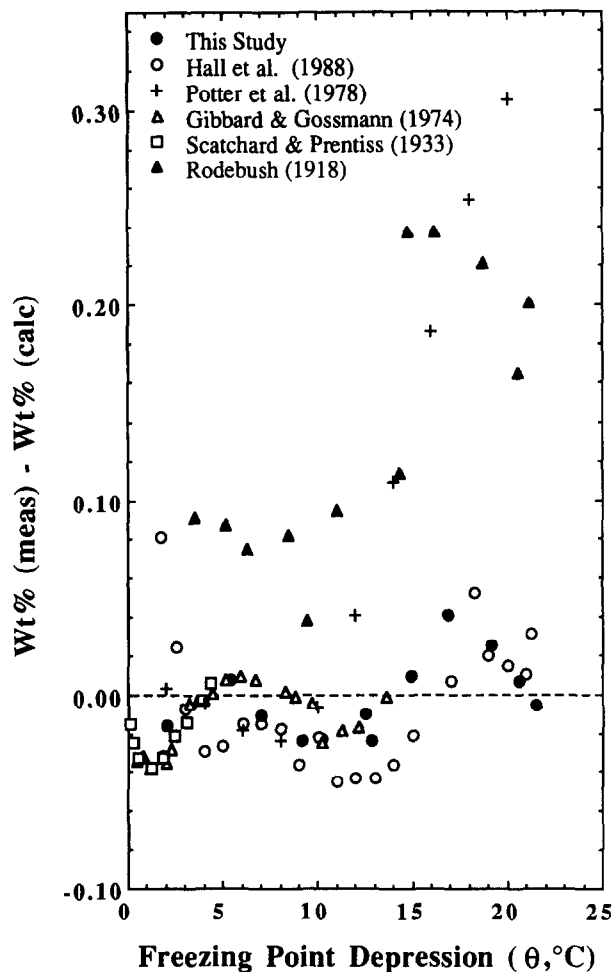


FIG. 4. Comparison of experimental salinities determined along the NaCl-H<sub>2</sub>O binary with salinities predicted by Eqn. (2). For clarity not all the data of SCATCHARD and PRENTISS (1933) and GIBBARD and GOSSMANN (1974) are shown.

The most recent previous determination of freezing-point depression along the CaCl<sub>2</sub>-H<sub>2</sub>O binary was made by GIBBARD and FONG (1975); however, their data extend to only -3.95°C (7.5 wt% CaCl<sub>2</sub>). Several investigations of freezing-point depression of concentrated solutions were made prior to 1950, with variable results. The data of these investigators are plotted as residuals versus temperature on Fig. 5.

Freezing-point depression measurements of ternary NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O solutions have been made by YANATIEVA (1946), GIBBARD and FONG (1975), and LUK'YANOVA and SHOIKHET (referenced in YANATIEVA (1946) as having determined the -10°C isotherm; data unavailable). Prior to our study YANATIEVA's (1946) data along the  $X_{\text{NaCl}} = 0.04, 0.08, 0.15,$  and  $0.51$  pseudobinaries from -6.5°C to the antarctice-ice and hydrohalite-ice cotectics were the most extensive compilation for this system. The ternary data of GIBBARD and FONG (1975) are limited to the  $X_{\text{NaCl}} = 0.51$  pseudobinary from -0.3° to -6.3°C.

Yanatieva's isotherms differ significantly from those determined by us and by Gibbard and Fong. Fig. 6a shows that the  $X_{\text{NaCl}} = 0.51$  pseudobinary data of Gibbard and Fong are in excellent agreement with our fit over their entire temper-

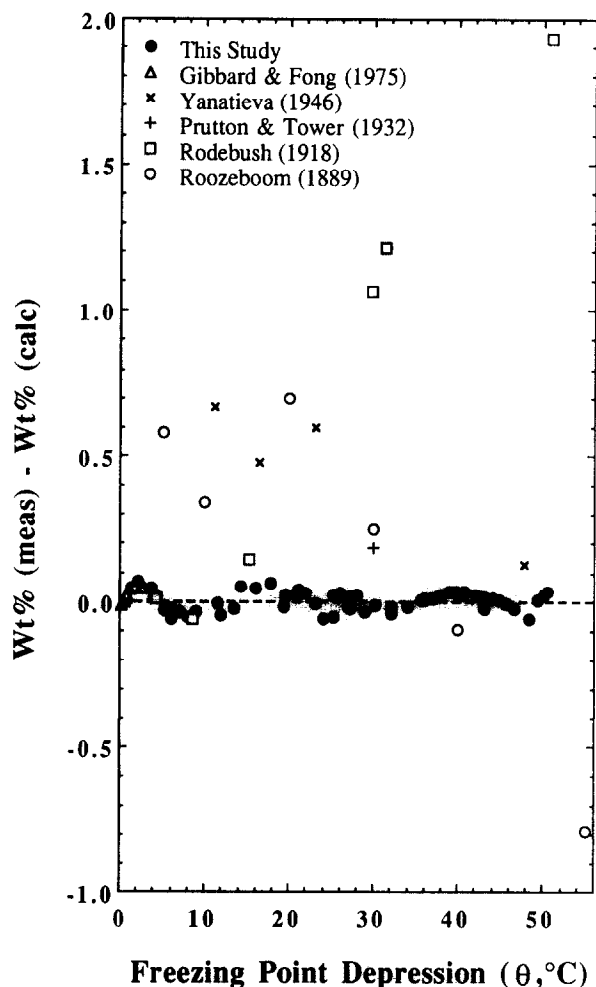


FIG. 5. Comparison of experimental salinities determined along the  $\text{CaCl}_2\text{-H}_2\text{O}$  binary with salinities predicted by Eqn. (2).

ature range even though only their five most dilute samples along this pseudobinary were incorporated in the derivation of Eqn. (2). The  $X_{\text{NaCl}} = 0.51$  pseudobinary data of Yanatieva, however, show large positive deviations of as much as 1.8 wt% from our fit (Fig. 6b). When plotted on a triangular diagram on a wt% basis our isotherms and those determined by GIBBARD and GOSSMANN (1974) and GIBBARD and FONG (1975) are nearly straight (Fig. 2). Yanatieva's isotherms, however, have substantial curvature concave toward the  $\text{H}_2\text{O}$  apex (cf. Fig. 4.6, p. 89 in CRAWFORD, 1981). The maximum deviation of Yanatieva's data from our fit occurs roughly along the  $X_{\text{NaCl}} = 0.5$  pseudobinary.

#### DISCUSSION

Fluid inclusions thought to contain aqueous solutions of NaCl and  $\text{CaCl}_2$ , as evidenced by low initial melting temperatures during microthermometric analysis of the inclusions, have generally been modeled using the freezing-point depression data of YANATIEVA (1946). This study, however, implies that Yanatieva's reported salinities are too high by as much as 2 wt%. For many geologic applications this salinity difference is relatively unimportant and is often within the

range of measured ice-melting temperatures for a population of natural fluid inclusions. However, a potentially significant consequence of the difference between her data and ours is in the determination of  $X_{\text{NaCl}}$  values of fluid inclusions. Because of the concave curvature of her isotherms compared to the slight convex curvature of our isotherms, our isotherms intersect the ice-hydrohalite cotectic at substantially higher  $X_{\text{NaCl}}$  values and somewhat lower salinities than Yanatieva's. For example, a fluid inclusion in which hydrohalite melts at about  $-25^\circ\text{C}$  in the presence of ice, solution, and vapor has an  $X_{\text{NaCl}}$  ratio of 0.70 according to our data, compared to 0.53 according to Yanatieva (Fig. 7a).

We assume in the above comparison that any inaccuracies in Yanatieva's compositional data for the position of the ice-hydrohalite cotectic are insignificant. Fluid inclusion and geothermal brine composition data from the Salton Sea Geothermal System (SSGS), California (HELGESON, 1968; WHITE, 1968; SAN DIEGO GAS AND ELECTRIC, 1980; WILLIAMS, 1986; MCKIBBEN et al., 1987, 1988; OAKES, 1988; THOMPSON and FOURNIER, 1988) support this assumption and favor our ice liquidus data over Yanatieva's. The compositions of brines sampled from several SSGS geothermal wells are plotted on Fig. 7b. These data define a linear trend roughly parallel to the  $X_{\text{NaCl}} = 0.66$  pseudobinary. Fluid inclusion compositions determined from Yanatieva's ice liquidus and ice-hydrohalite cotectic data also define a linear trend on Fig. 7b; however

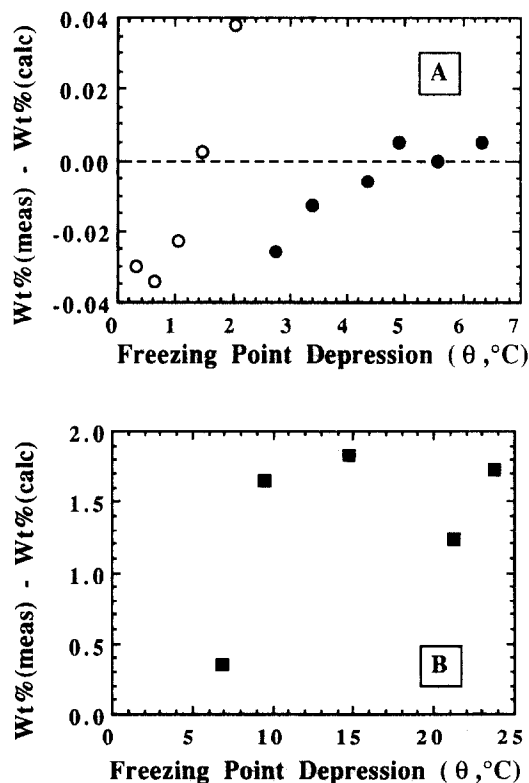


FIG. 6. (a) Comparison of experimental salinities and freezing-point depression data of GIBBARD and FONG (1975) along the  $X_{\text{NaCl}} = 0.51$  pseudobinary with salinities predicted by Eqn. (2). The five unshaded points were incorporated in the derivation of Eqn. (2). (b) Comparison of experimental salinities and freezing-point depression data of YANATIEVA (1946) along the  $X_{\text{NaCl}} = 0.51$  pseudobinary with salinities predicted by Eqn. (2).

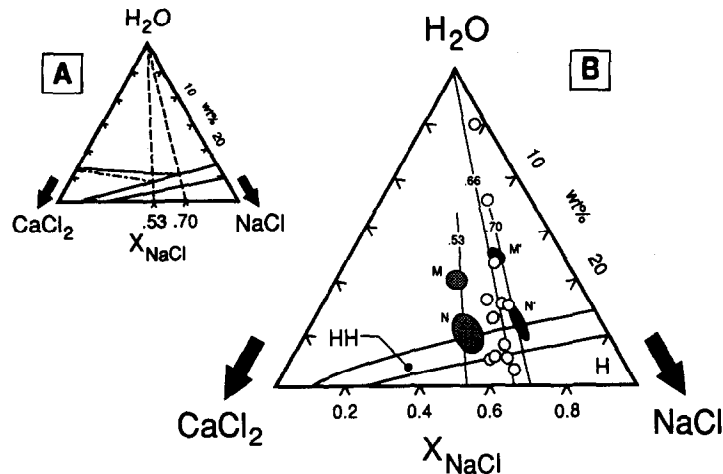


FIG. 7. (a) An example of the difference in  $X_{\text{NaCl}}$  that results from modelling hydrohalite- and ice-melting temperatures from YANATIEVA's (1946) data and ours. For an inclusion in which hydrohalite melts at  $-25^{\circ}\text{C}$  in the presence of ice, solution, and vapor,  $X_{\text{NaCl}} = 0.53$  from Yanatieva's data versus  $0.70$  from our data. Dash-dot curve is Yanatieva's  $-25^{\circ}\text{C}$  isotherm and light solid curve is our  $-25^{\circ}\text{C}$  isotherm. Dashed lines are the pseudobinaries corresponding to the respective  $X_{\text{NaCl}}$ . The ice (I), hydrohalite (HH), and halite (H) fields are labeled in Fig. 7b. (b) Geothermal brine (open circles) and fluid inclusion (stippled ovoid regions) compositions from the Salton Sea Geothermal System, California. The lightly stippled regions M and N represent fluid inclusion compositions modelled using Yanatieva's data. The dark stippled regions M' and N' represent reinterpretation of the data in M and N using Eqn. (2) and Yanatieva's compositional results for the ice-hydrohalite cotectic. Because the geothermal brine compositions have been plotted with KCl combined with NaCl on a wt% equivalent basis, their total salinities have been exaggerated.

these data fall along the  $X_{\text{NaCl}} = 0.53$  pseudobinary. If the ice- and hydrohalite-melting temperatures are reinterpreted using our Eqn. (2) and the cotectic determined by Yanatieva the fluid inclusion compositions are shifted to higher  $X_{\text{NaCl}}$  and cluster more tightly along the  $X_{\text{NaCl}} = 0.70$  pseudobinary, thereby eliminating most of the discrepancy. The fields M' and N' are smaller and narrower than fields M and N because of the smaller change in  $X_{\text{NaCl}}$  between  $-21.2^{\circ}$  and  $-30^{\circ}\text{C}$  along the ice-hydrohalite cotectic implied from our data versus Yanatieva's. Though these arguments supporting the superiority of our data are not conclusive it does seem more plausible that the ice-liquidus data of Yanatieva are inaccurate rather than the alternative that brine in the SSGS has undergone a large change in the relative concentrations of NaCl and CaCl<sub>2</sub>. The small difference between the  $X_{\text{NaCl}}$  ratios ( $\Delta X_{\text{NaCl}} = 0.04$ ) implied by the reinterpreted fluid inclusion data and that implied by the geothermal brine data may be a result of our modelling of the geothermal brine compositions using the quaternary system NaCl-KCl-CaCl<sub>2</sub>-H<sub>2</sub>O versus representation of the fluid inclusion data by the ternary NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O. That is, in Fig. 7b the KCl concentration in the brines was combined with NaCl on a wt% equivalent basis while the fluid inclusion compositions were plotted only as NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O solutions. It is also possible that small compositional errors in Yanatieva's ice-hydrohalite cotectic data contribute to the difference.

Contemporary occurrences of brines containing CaCl<sub>2</sub> as the predominant salt are rare (HARDIE, 1983) while the only evidence for CaCl<sub>2</sub> as the *most abundant salt* in fluid inclusions is based on the freezing-point depression data of Yanatieva. In most of these cases, if the ice- and hydrohalite-melting point data are reanalyzed using our results,  $X_{\text{NaCl}}$  ratios will be significantly increased to values more consistent with

brine compositions sampled from contemporary geologic environments. Owing to the good agreement between calculated fluid inclusion salinities and  $X_{\text{NaCl}}$  and compositions of natural fluids, we recommend that  $X_{\text{NaCl}}$  and salinities of NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O inclusions be determined using our ice liquidus data in conjunction with Yanatieva's ice-hydrohalite cotectic data, pending verification of the location of the ice-hydrohalite cotectic by future studies.

*Acknowledgments*—We thank Don Hall and Mike Sterner for their helpful suggestions on experimental design and procedure and I-Ming Chou and Scott Wood for their expeditious reviews.

Funding for work conducted at V.P.I. & S.U. was provided by NSF Grant No. EAR-865778 from the Earth Sciences Division of NSF and DOE Grant No. DE-FG05-89ER14065 from the Office of Basic Energy Sciences (both to RJB). The density measurements, carried out at Oak Ridge National Laboratory, were supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, under Contract No. DE-AC05-84OR21400 (to JMS) with Martin Marietta Energy Systems, Inc.

*Editorial handling:* S. A. Wood

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