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The densities of halite-saturated WIPP-A and NBT-6 brines and their NaCl contents in weight percent, molal, and molar units from 20° to 100°C

by

I-Ming Chou, B. Huizinga, M.A. Clynne, and R.W. Potter II

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ABSTRACT

A series of density measurements has been performed at 30°, 50°, 70°, and 90°C for halite-undersaturated WIPP-A and NBT-6 brines with various NaCl contents approaching saturation. The densities of halite-saturated WIPP-A and NBT-6 brines were obtained by extrapolating these measured densities to halite saturation points. The maximum difference between the densities obtained in this fashion and those calculated from the model of Potter and Haas is 0.015 g/cm^3.

The NaCl contents in halite-saturated WIPP-A and NBT-6 brines are reported in wt %, molal, and molar units from 20° to 100°C.

INTRODUCTION

The migration of brine inclusions in natural salt deposits due to an imposed temperature gradient must be evaluated in designing radioactive waste repositories to see if significant quantities of brines will reach the storage canisters and what the consequences will be. In order to quantify this problem, a quantitative model for the migration rate of brines in salt as a function of the pertinent environmental parameters is needed. Several theoretical models for predicting the migration rates of brines have been reviewed by Cheung (1980). However, these models are difficult to apply because of an insufficient data base. The solubility data for halite in brines expressed in molar (moles/liter) units are needed for the application of these models, but most solubility data available are in molal (moles/1000g H_2O) units or in wt. %. In order to make the unit conversion, density data for halite-saturated brines are needed.

The halite solubility data in wt. % for WIPP-A[1)] and NBT-6[1)] brines between 0° and 100°C were obtained by Clynne and Potter (unpub. data). This report presents the measured density data for the halite-saturated WIPP-A and NBT-6 brines between 20° and 100°C, and compares them with those calculated from the model of Potter and Haas (1978). From these data, the halite solubility in molar units is obtained for WIPP-A and NBT-6 brines from 20° to 100°C.

EXPERIMENTAL METHOD

The densities of saturated solutions of NaCl and KCl from 10° to 105° have been determined by Thurmond et al. (unpub. data) using calibrated hygrometers. However, their experimental method cannot be applied in the present study because the composition of the halite-saturated complex brines will change through evaporation.

The experimental apparatus is illustrated in Fig. 1, and the procedures are as follows:

1. Put a teflon-coated magnetic stirring bar in the Pt-lined pressure vessel and seal by using a torque wrench to press a teflon disk against the stem seat.

2. Connect the pressure vessel with a capillary line to the valve assembly.

[1)]Their compositions are given in table 1.

3. Put the pressure vessel in a glycol bath maintained at the desired temperature.

4. Evacuate the pressure vessel, using a vacuum pump.

5. Using a syringe, fill up the pressure vessel with distilled water by maintaining the pressure of the system near one atm. After the system reaches thermal equilibrium (~ 1 hour) disconnect the syringe and calculate the total amount of water added from the weight difference of the syringe before and after loading.

6. Calculate the volume of the pressure vessel at the set temperature using the density data given in the steam tables (Keenan et al., 1969) and the weight of water added.

7. Repeat steps 4 to 6 three or more times and obtain an average value for the volume of the pressure vessel at the set temperature.

8. Open the pressure vessel and dry it.

9. Load the pressure vessel with a weighed amount of reagent-grade NaCl (but less than that needed for saturation) and the same magnetic stirring bar used in step 1. The pressure vessel is then sealed by pressing a new teflon disk with the same torque setting on the wrench as in step 1.

10. Repeat steps 2 to 4.

11. Load the pressure vessel with the brine under study using a syringe. Fill up the vessel by maintaining the pressure of the system near one atm. while stirring the solution with a submersible magnetic stirrer. After the system reaches thermal equilibrium (~ 1 hour) disconnect the syringe and calculate the total amount of brine loaded from the weight difference of the syringe before and after loading.

12. Calculate the density of the brine using the weights of NaCl and brine loaded and the average volume of the pressure vessel obtained in step 7.

13. Repeat steps 8 to 12 four or more times and approach halite saturation by loading the pressure vessel with an increased amount of NaCl.

14. Change the temperature setting of the glycol bath and repeat steps 1 to 13.

The pressure vessel is immersed in a bath filled with ethylene glycol. The temperature of the bath is regulated to ± 0.01°C, and that of the pressure vessel is measured by a platinum resistance thermometer accurate to ± 0.02°C and precise to ± 0.005°C. The volume of the pressure vessel is about 34 cm^3

and its measurements are precise to 0.08 cm^3. The weights of NaCl loaded are measured to ± 0.01g and that of solution are measured to ± 0.0001g. The obtained density data are precise to ± 0.0033 g/cm^3.

EXPERIMENTAL RESULTS

The experimental densities obtained for halite-undersaturated WIPP-A and NBT-6 brines are given in table 2 and 3 respectively.

For each temperature, these density data were fit to an equation of the following form:

$$\rho = \sum_{i=0}^{i} a_i w^i \qquad (1)$$

where ρ is the density in g/cm^3, w is the wt % of NaCl added to the brines (see tables 2 and 3), and a_i are empirical coefficients derived from least squares regression. These coefficients are given in table 4. Densities of halite-saturated WIPP-A and NBT-6 brines were calculated from these equations using the solubility data given by Clynne and Potter (unpub. data). Results are given in table 5. These "measured" densities were fit to equations of the following form:

$$\rho = \sum_{i=0}^{2} a_i t^i \qquad (2)$$

where ρ is the density in g/cm^3, t is the temperature in °C, and a_i are empirical coefficients derived from least-squares regression. These coefficients are given in table 6. The maximum differences between the densities calculated from these equations and those reported in table 5 are ± 0.0005 and ± 0.0008 g/cm^3 for WIPP-A and NBT-6 respectively.

CALCULATED DENSITIES OF THE HALITE-SATURATED WIPP-A AND NBT-6 BRINES

Densities of the halite-saturated WIPP-A and NBT-6 brines have also been calculated by using the model of Potter and Haas (1978). These calculated densities and the sources of the density data for the binary solutions used in the calculations are given in tables 7a and 7b respectively. No density data are available for Na_2SO_4-H_2O solution in the temperature-concentration region of the present calculation. We assumed that ρ = 1.2777 for Na_2SO_4 solution at all temperatures. Since NBT-6 does not contain Na_2SO_4 and WIPP-A contains only 0.439 wt. % of Na_2SO_4, the above assumption will not significantly affect the calculated densities. These calculated densities are compared with the measured densities in Figs. 2a and 2b for halite-saturated WIPP-A and NBT-6 brines respectively. The dashed lines are the least-squares regression of the calculated densities (triangles), and the solid curves are those for measured densities (circles). The maximum difference between the calculated and measured densities is 0.015 g/cm^3 which will in turn give a difference of only 0.02 in calculated NaCl molar content of the halite-saturated brines. From here on, only the measured densities reported in table 6 will be used for molar concentration calculations.

THE NaCl CONTENTS IN HALITE-SATURATED WIPP-A AND NBT-6 BRINES IN WT %, MOLAL AND MOLAR UNITS

The solubilities of NaCl in wt % for WIPP-A and NBT-6 brines between 0° and 100°C were measured by Clynne and Potter (unpub. data) and were represented by the equation

$$S = \sum_{i=0}^{3} a_i t^i \qquad (3)$$

where t is the temperature in °C, S is the solubility of NaCl, in addition to the original NaCl content of the brine, in grams per 100g of saturated solution, and a_i are empirical coefficients derived from least-squares regression. These coefficients are given in table 8.

The molal contents of NaCl in halite-saturated WIPP-A and NBT-6 brines ($m^{sat.}_{NaCl}$) were calculated from

$$m^{sat.}_{NaCl} = m^{orig.}_{NaCl} + m^{added}_{NaCl}$$

where m^{added}_{NaCl} is the additional number of moles of NaCl per 1000g of H_2O required for the brine to reach halite saturation, and $m^{orig.}_{NaCl}$ are the original molal contents of brines (1.9252 for WIPP-A and 1.2222 for NBT-6). Values for m^{added}_{NaCl} were calculated from the equation

$$m^{added}_{NaCl} = (W^{added}_{NaCl} \times 1000)/58.443 \cdot {}^{W}H_2O$$

where W^{added}_{NaCl} is the additional weight of NaCl in grams required to saturate 100g of brines with respect to halite, ${}^{W}H_2O$ is the weight of H_2O in grams in 100g of the original brines (74.887g for WIPP-A and 70.0g for NBT-6), and 58.443 is the formular weight of NaCl. Values of W^{added}_{NaCl} were calculated from

$$S = W^{added}_{NaCl} \times 100/(W^{added}_{NaCl} + 100)$$

where S was defined in eq. (3) and its values were calculated from eq. (3) and the data given in table 8.

The molar contents of NaCl in halite-saturated WIPP-A and NBT-6 brines ($M^{sat.}_{NaCl}$) were calculated from

$$M^{sat.}_{NaCl} = (W^{orig.}_{NaCl} + W^{added}_{NaCl}) \times \rho \times 1000/[58.443 \times (100 + W^{added}_{NaCl})]$$

where $W^{orig.}_{NaCl}$ is the weight of NaCl in grams in 100g of the original brines (8.426g for WIPP-A and 5.0g for NBT-6).

The calculated values for $m^{sat.}_{NaCl}$, $M^{sat.}_{NaCl}$, S, W^{added}_{NaCl}, M^{added}_{NaCl} and ρ are listed in table 9 for halite-saturated WIPP-A and NBT-6 brines between 20° and 100°C. Coefficients of the least squares regression equations for $m^{sat.}_{NaCl}$ and $M^{sat.}_{NaCl}$ listed in table 9 are given in table 10. The maximum differences between the concentrations calculated from these equations and those listed in table 5 are ± 6.5×10^{-5} except that for $m^{sat.}_{NaCl}$ of WIPP-A, which is ± 0.012.

EQUATIONS FOR $\partial M^{sat.}_{NaCl} / \partial t$

Most of the theoretical models for predicting the migration rates of brine inclusions in salt require $\partial M^{sat.}_{NaCl} / \partial t$ data. These data for WIPP-A and NBT-6 brines between 20° and 100°C can be calculated from equations given in table 11. These equations were obtained by differentiating $M^{sat.}_{NaCl}$ equations given in table 10 with respect to t, where t is the temperature in °C.

Applying the data given in tables 10 and 11 in various theoretical models, migration rates of WIPP-A and NBT-6 brine inclusions in single crystals of NaCl have been calculated at 50° and 100°C by Chou (1981, 1982, and unpub. data).

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Table 1. Compositions of synthetic brines.

	WIPP-A[1)]		NBT-6
Component	g/liter of solution[2)]	wt %[3)]	wt %
NaCl	101.55	8.426	5
KCl	57.20	4.746	5
Na_2SO_4	5.175	0.429	0
$MgCl_2$	137.08	11.374	10
$CaCl_2$	1.665	0.138	10
H_2O	-	74.887	70

1)Similar to WIPP brine A reported by Molecke described in Jenks (1979)
2)This is the way the solution was prepared.
3)Density at 20°C = 1.2052 (g/cm3) (Clynne and Potter, unpub. data)) was used in converting g/liter values to wt %.

Table 2. Densities of halite-undersaturated WIPP-A

T(°C)	Wt % NaCl[1)]	Density (g/cm^3)
30.00	0.00	1.2005
30.03	1.90	1.2150
30.13	2.83	1.2185
30.02	3.36	1.2223
30.06	3.68	1.2226
49.70	0.00	1.1909
50.01	2.45	1.2058
49.96	3.41	1.2101
50.05	3.89	1.2115
50.05	4.25	1.2128
50.13	4.49	1.2140
70.00	0.00	1.1802
70.07	2.60	1.1973
70.09	4.63	1.2072
70.15	4.96	1.2088
90.00	0.00	1.1679
90.09	2.64	1.1902
90.24	4.08	1.2019
90.11	5.43	1.2056
90.06	5.72	1.2078

1) In final solution, in addition to NaCl already in WIPP-A

Table 3. Densities of halite-undersaturated NBT-6

T(°C)	Wt % NaCl[1)]	Densities (g/cm^3)
30.09	0.00	1.2549
30.10	0.49	1.2575
30.09	0.67	1.2584
30.13	0.94	1.2595
49.91	0.00	1.2458
50.10	0.76	1.2528
50.13	1.06	1.2558
50.12	1.44	1.2567
50.06	1.53	1.2572
70.00	0.00	1.2351
70.15	1.19	1.2453
70.11	1.83	1.2478
70.03	2.26	1.2492
90.00	0.00	1.2226
90.07	1.72	1.2406
90.02	2.59	1.2477
90.04	3.01	1.2499
90.00	3.25	1.2503

1)In final solution,in addition to NaCl already in NBT-6.

Table 4. Coefficients of the least-squares regression equations for the experimentally measured densities of halite-undersaturated WIPP-A and NBT-6 brines

Brine	T(°C)	a_0	$a_1 x 10^3$	$a_2 x 10^4$
WIPP-A	30.0	1.20056	8.799	-7.532
	50.0	1.19092	7.202	-4.729
	70.0	1.18021	7.463	-3.467
	90.0	1.16771	10.611	-6.382
NBT-6	30.0	1.25490	5.865	-10.196
	50.0	1.24574	12.246	-31.170
	70.0	1.23513	10.902	-20.940
	90.0	1.22254	12.996	-13.306

Table 5. Densities of halite-saturated WIPP-A and NBT-6 brines

Brine	T(°C)	Wt % NaCl[1)]	Density (g/cm^3)[2)]
WIPP-A	30.0	3.84	1.2232
	50.0	4.56	1.2139
	70.0	5.33	1.2101
	90.0	6.10	1.2087
NBT-6	30.0	0.94	1.2595
	50.0	1.54	1.2572
	70.0	2.42	1.2492
	90.0	3.41	1.2514

1)In final solution, in addition to NaCl already in brines; Data from Clynne and Potter (unpub. data).
2)Calculated from equations, the coefficients of which are given in table 4.

Table 6. Coefficients of the least-squares regression equations for the "experimental" densities of halite-saturated WIPP-A and NBT-6 brines between 20° and 100°C.

Brine	a_0	$a_1 \times 10^4$	$a_2 \times 10^6$
WIPP-A	1.24347	-8.29	4.938
NBT-6	1.27273	-4.99	2.813

Table 7a. Densities of the halite-saturated WIPP-A and NBT-6 brines calculated from the model of Potter and Haas (1978)

	Density (g/cm^3)	
T(°C)	WIPP-A	NBT-6
0	1.2254	1.2623
25	1.2186	1.2561
40	-	1.2524
50	1.2125	1.2476
60	-	1.2466
75	1.2075	1.2425
100	1.1997	1.2382

Table 7b. Sources of the density data for the binary solutions used in the Potter-Haas model calculations given in table 7a.

Solution	Data Source
$NaCl-H_2O$	Potter and Brown (1977)
$KCl-H_2O$	Potter and Brown (1976)
$CaCl_2-H_2O$	extrapolated from Potter and Clynne (1976)
$MgCl_2-H_2O$	extrapolated from International Critical Tables (National Research Council, 1928)
$Na_2SO_4-H_2O$	No data available, ρ =1.2777 g/cm^3 was used for all calculations.

Table 8. Coefficients of the least-squares regression equations for NaCl solubilities in WIPP-A and NBT-6 brines between 0° and 100°C (Clynne and Potter (unpub. data)).

Brine	a_0	a_1	$a_2 x 10^5$	$a_3 x 10^6$
WIPP-A	2.8188	0.03346	3.4244	0
NBT-6	-0.42311	0.05829	-54.636	4.079

Table 9. The NaCl contents in halite-saturated brines in wt %, molal (m) and molar (M) units

T(°C)	S	W_{NaCl}^{added}	m_{NaCl}^{added}	$m_{NaCl}^{sat.}$	ρ (g/cm^3)	$M_{NaCl}^{sat.}$
		(a) WIPP-A				
20	3.4946	3.6211	0.8274	2.7526	1.2289	2.4447
30	3.8464	4.0003	0.9140	2.8393	1.2230	2.5004
40	4.2049	4.3895	1.0029	2.9282	1.2182	2.5590
50	4.5704	4.7893	1.0943	3.0195	1.2144	2.6205
60	4.9426	5.1996	1.1880	3.1133	1.2115	2.6849
70	5.3217	5.6208	1.2843	3.2095	1.2096	2.7526
80	5.7077	6.0532	1.3831	3.3083	1.2087	2.8236
90	6.1005	6.4968	1.4844	3.4097	1.2089	2.8985
100	6.5002	6.9521	1.5885	3.5137	1.2099	2.9767
		(b) NBT-6				
20	0.5568	0.5599	0.1369	1.3591	1.2639	1.1957
30	0.9440	0.9530	0.2330	1.4552	1.2603	1.2716
40	1.2954	1.3124	0.3208	1.5430	1.2573	1.3404
50	1.6353	1.6625	0.4064	1.6286	1.2548	1.4071
60	1.9884	2.0287	0.4959	1.7181	1.2529	1.4769
70	2.3789	2.4369	0.5957	1.8179	1.2516	1.5548
80	2.8315	2.9140	0.7123	1.9345	1.2508	1.6458
90	3.3705	3.4881	0.8526	2.0748	1.2506	1.7551
100	4.0205	4.1889	1.0242	2.2464	1.2510	1.8879

Table 10. Coefficient of the least-squares regression equations[1)] for $m^{sat.}_{NaCl}$ and $M^{sat.}_{NaCl}$ given in table 8.

Brine	concentration unit	a_0	$a_1 x 10^3$	$a_2 x 10^5$	$a_3 x 10^7$
WIPP-A	$m^{sat.}_{NaCl}$	2.587	8.02	1.24	0
	$M^{sat.}_{NaCl}$	2.345	4.70	1.61	0
NBT-6	$m^{sat.}_{NaCl}$	1.112	14.74	-14.28	10.87
	$M^{sat.}_{NaCl}$	1.002	11.58	-11.20	8.48

1) $m^{sat.}_{NaCl}$ or $M^{sat.}_{NaCl} = \sum_{i=0}^{3} a_i t^i$

where t is the temperature in °C.

Table 11. Coefficients for the equations of $\partial M^{sat.}_{NaCl}/\partial t$ for WIPP-A and NBT-6 brines between 20° and 100°C[1)].

Brine	$a_0 x 10^3$	$a_1 x 10^5$	$a_2 x 10^6$
WIPP-A	4.70	3.23	0
NBT-6	11.58	-22.40	2.54

1) $\partial M^{sat.}_{NaCl}/\partial t = \sum_{i=0}^{2} a_i t^i$, where t is the temperature in °C.

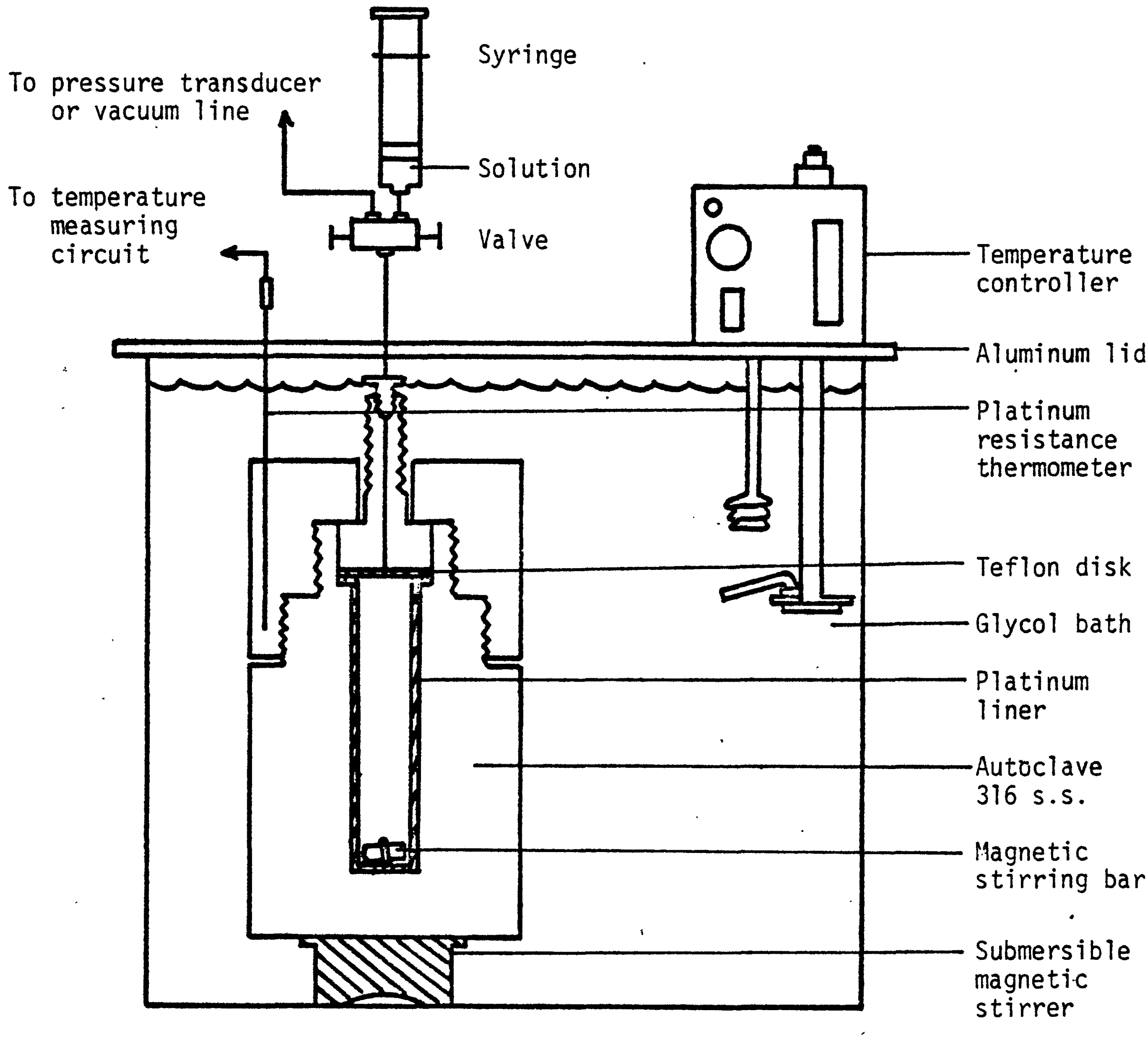

Figure 1. Schematic diagram of the experimental apparatus used in this investigation.

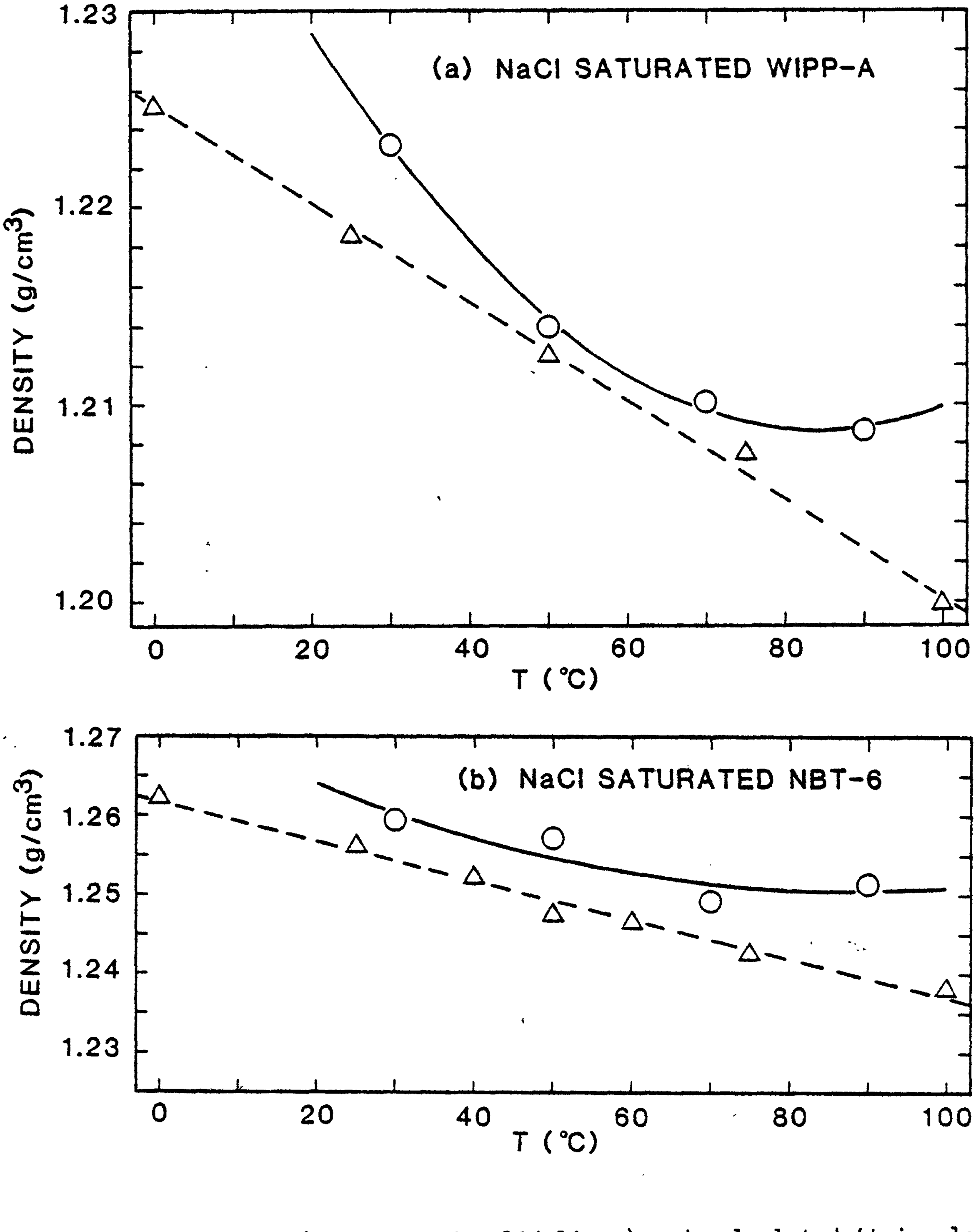

Figure 2. Measured (circles and solid lines) and calculated (triangles and dashed lines) densities of the halite-saturated WIPP-A and NBT-6 brines. For detail, see text.