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Solubility Relations in the Ternary System NaCl–CsCl–H_2O at 1 atm. 1. Solubilities of Halite from 20 to 100 °C

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Solubilities of halite in the ternary system NaCl–CsCl–H_2O have been determined by the visual polythermal method at 1 atm from 20 to 100 °C along five constant CsCl/(CsCl + H_2O) weight ratio lines. These five constant weight ratios are 0.1, 0.2, 0.3, 0.4, and 0.5. The maximum uncertainties in these measurements are ±0.02 wt % NaCl and ±0.15 °C. The data along each constant CsCl/(CsCl + H_2O) weight ratio line were regressed to a smooth curve. The maximum deviation of the measured solubilities from the smooth curves is 0.06 wt % NaCl. Isothermal solubilities of halite were calculated from these smoothed curves at 25, 50, and 75 °C.

Introduction

^{137}Cs is a significant producer of both heat and radioactivity for about 100 years in high-level radioactive waste (*1*). Since a committee of geologists in The National Academy of Sciences–National Research Council studied the problem (*2*) in 1955, natural salt deposits, either in bedded or domal forms, have been considered as promising candidates for the terminal storage sites for high-level wastes. Knowledge of solubility relations in the system NaCl–CsCl–H_2O is essential for the assessment and eventual solution of problems related to the leaching and the subsequent migration of the ^{137}Cs radionuclide in salt repositories.

Plyushchev et al. (*3*) determined the solubility relations in the system NaCl–CsCl–H_2O at 25, 50, and 75 °C, using the isothermal method. Na^+ and Cl^- concentrations in the equilibrated solutions were determined gravimetrically while the concentration of Cs^+ was calculated by difference. Since the bulk composition and the final solution composition were known, the composition of the solid phases was determined by using the Schreinemaker residue method.

The solubility data of Plyushchev et al. (*3*) at 25, 50, and 75 °C are shown in Figure 1 with the coexisting solid phases omitted for clarity. The crossover of the isotherms indicates the poor quality of the data. The present paper reports the solubilities of halite in the ternary system NaCl–CsCl–H_2O from 20 to 100 °C at 1 atm. Solubility relations in the CsCl-rich region of this system at 25, 50, and 75 °C will be presented in subsequent papers in this series.

Experimental Section

The visual polythermal method used in this study has been discussed in detail previously (*4*, *5*). Solubilities of halite have been determined between 20 and 100 °C along the five constant CsCl/(CsCl + H_2O) weight ratio lines, BD, BE, BF, BG, and BH shown in Figure 2. The solid phase involved in these solubility measurements is halite as indicated by the data of Plyushchev et al. (*3*), Chou et al. (*6*), and Chou and Romankiw (*7*). As an example for the composition line BF, a sample (~ 12 g) was prepared by mixing weighed amounts of NaCl and a stock solution of 30 wt % CsCl (point F in Figure 2) in a Pyrex tube containing a magnetic stirring bar. A layer of silicone oil (~ 1 cm) was added to seal the tube and prevent water gain or loss. The assembly was mounted in a glycol bath, as shown in Figure 3, and incrementally heated and vigorously agitated until the last crystal was dissolved. Heating increments were made progressively smaller as the amount of salt decreases. The temperature (read to ±0.1 °C with a calibrated platinum resistance thermometer) at which the last salt crystal disappeared was taken as the equilibrium temperature for the bulk composition in the tube. Experiments showed that 1 mg of salt could easily be seen with the unaided eye. Once the last crystal dissolved, the solution had to be significantly supercooled to induce crystallization. This precludes the possibility of reversing the solubility data by simple cooling. However, the equilibrium between crystals and solution in the heating experiments has been sufficiently demonstrated (*4*).

Results and Discussion

The measured halite solubilities along the five constant CsCl/(CsCl + H_2O) weight ratio lines are listed in Table I together with smoothed values and the deviation of the measured values from the smoothed results. The maximum uncertainties in these measurements are ±0.15 °C. The smoothed values were obtained from a least-squares regression of the experimental values to an equation of the form

$$S = \sum_{0}^{i} a_i t^i \qquad (1)$$

where S is the solubility in grams of NaCl per 100 g of saturated solution (g/100 g), and t is the temperature in degrees Celsius. The coefficients, a_i, for the regression equation are listed in

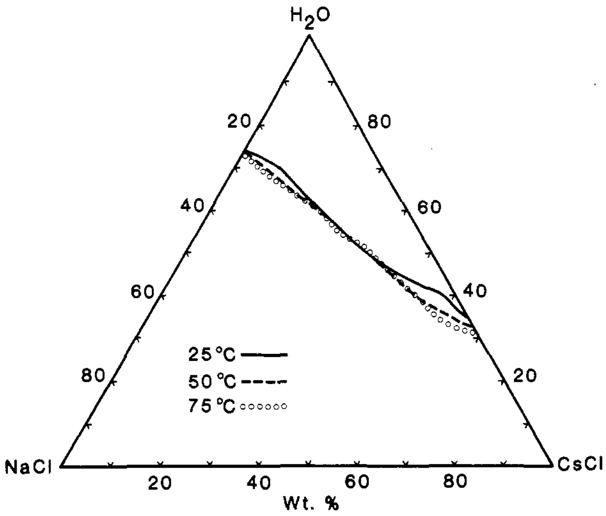

Figure 1. Solubility isotherms based on the data of Plyushchev et al. (3). Note isotherm crossovers.

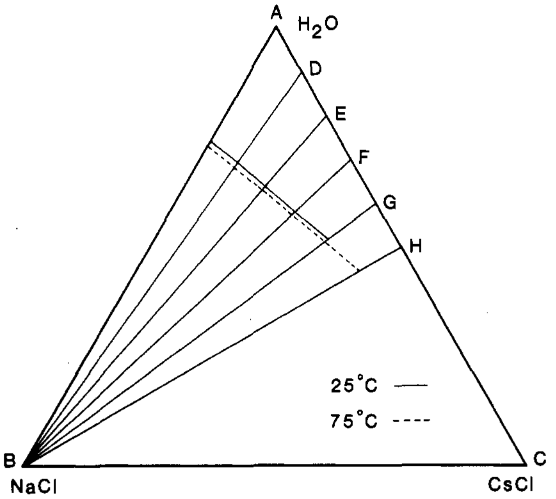

Figure 2. Solubilities of halite were determined between 20 and 100 °C along five constant CsCl/(CsCl + H_2O) weight ratio lines, BD, BE, BF, BG, and BH. These five lines correspond respectively to 0.1, 0.2, 0.3, 0.4, and 0.5 weight ratios in CsCl/(CsCl + H_2O). The solubility isotherms at 25 and 75 °C determined in this study (see Table III) are also shown. Data at 50 °C are omitted for clarity. No crossovers among these three isotherms.

Table II. The experimental results were also fitted by least squares to a single equation

$$S = 25.939 + (1.2695 \times 10^{-2})t + (7.9434 \times 10^{-5})t^2 - (3.54268 \times 10^{-1})Z + (4.29974 \times 10^{-4})Z^2 - (2.78538 \times 10^{-4})Zt \quad (2)$$

where Z is weight percent of CsCl in the halite-saturated solution. The first three coefficients of this equation are consistent with a_0, a_1, and a_2 of Clynne et al. (8). Equation 2 is easier to apply than eq 1. However, the maximum difference between the observed values and the calculated values derived from eq 2 is −0.14 (Figure 4), which compares with 0.06 derived from eq 1 (Table I).

The halite solubility data along the line defined by CsCl/(CsCl + H_2O) weight ratio = 0.5 listed in Table I are limited to $t \geq 48.2$ °C. In a plot of solubility vs. temperature, the data at lower temperatures along this composition line do not follow the trend indicated by the high-temperature data. The reason for this is that at lower temperatures halite is metastable with respect to a new hydrous compound, CsCl·2NaCl·$2H_2O$ (6), and hence the experimental technique used in this study is not applicable. The exact temperature at which halite becomes metastable along this composition line has not been determined.

Table I. Experimentally Determined Halite Solubilities along Five Constant CsCl/(CsCl + H_2O) Weight Ratio Lines Compared to Those Calculated from Eq 1

	NaCl, wt %		
T, °C	exptl	calcd	difference
(a) CsCl/(CsCl + H_2O) Weight Ratio = 0.1 (Line BD in Figure 2)			
23.3	23.40	23.40	0.00
32.1	23.61	23.64	−0.03
38.3	23.82	23.78	0.04
44.2	23.91	23.91	0.00
50.3	24.05	24.04	0.01
57.4	24.15	24.17	−0.02
63.7	24.27	24.30	−0.03
71.4	24.45	24.45	0.00
73.7	24.53	24.50	0.03
84.9	24.78	24.76	0.02
92.3	24.92	24.96	−0.04
93.7	25.02	25.00	0.02
(b) CsCl/(CsCl + H_2O) Weight Ratio = 0.2 (Line BE in Figure 2)			
29.0	20.85	20.83	0.02
38.1	20.91	20.93	−0.02
42.1	20.96	20.98	−0.02
49.9	21.07	21.09	−0.02
51.2	21.11	21.11	0.00
58.2	21.22	21.22	0.00
62.3	21.31	21.30	0.01
65.0	21.38	21.35	0.03
68.9	21.45	21.43	0.02
74.4	21.53	21.54	−0.01
81.8	21.67	21.71	−0.04
85.1	21.81	21.79	0.02
88.8	21.90	21.89	0.01
(c) CsCl/(CsCl + H_2O) Weight Ratio = 0.3 (Line BF in Figure 2)			
22.0	17.70	17.70	0.00
28.1	17.74	17.76	−0.02
30.8	17.78	17.78	0.00
33.8	17.83	17.81	0.02
35.3	17.84	17.82	0.02
43.6	17.89	17.90	−0.01
43.9	17.87	17.90	−0.03
49.9	17.97	17.97	0.00
55.6	18.05	18.04	0.01
62.3	18.13	18.13	0.00
66.9	18.21	18.20	0.01
72.0	18.30	18.30	0.00
78.2	18.41	18.42	−0.01
81.2	18.50	18.49	0.01
(d) CsCl/(CsCl + H_2O) Weight Ratio = 0.4 (Line BG in Figure 2)			
25.1	14.31	14.33	−0.02
30.6	14.50	14.46	0.04
34.0	14.50	14.52	−0.02
43.9	14.65	14.65	0.00
49.0	14.70	14.71	−0.01
56.1	14.79	14.79	0.00
59.6	14.80	14.83	−0.03
61.8	14.85	14.86	−0.01
65.8	14.93	14.92	0.01
67.8	15.01	14.95	0.06
75.7	15.06	15.09	−0.03
78.0	15.11	15.13	−0.02
85.4	15.29	15.28	0.01
(e) CsCl/(CsCl + H_2O) Weight Ratio = 0.5 (Line BH in Figure 2)			
48.2	11.25	11.25	0.00
59.3	11.41	11.40	0.01
68.1	11.51	11.52	−0.01
68.9	11.51	11.53	−0.02
78.9	11.70	11.68	0.02
88.6	11.83	11.84	−0.01

Table II. Regression Coefficients for Halite Solubility Equations along Five Constant $CsCl/(CsCl + H_2O)$ Weight Ratio Lines

$CsCl/(CsCl + H_2O)$, wt ratio	a_0	a_1	a_2	a_3	a_4
0.1	22.539	0.046 19	-4.590×10^{-4}	2.628×10^{-6}	
0.2	20.668	0.001 58	1.370×10^{-4}		
0.3	17.473	0.012 62	-1.391×10^{-4}	1.704×10^{-6}	
0.4	12.683	0.117 55	-2.768×10^{-3}	3.048×10^{-5}	-1.73×10^{-7}
0.5	10.790	0.006 96	5.469×10^{-5}		

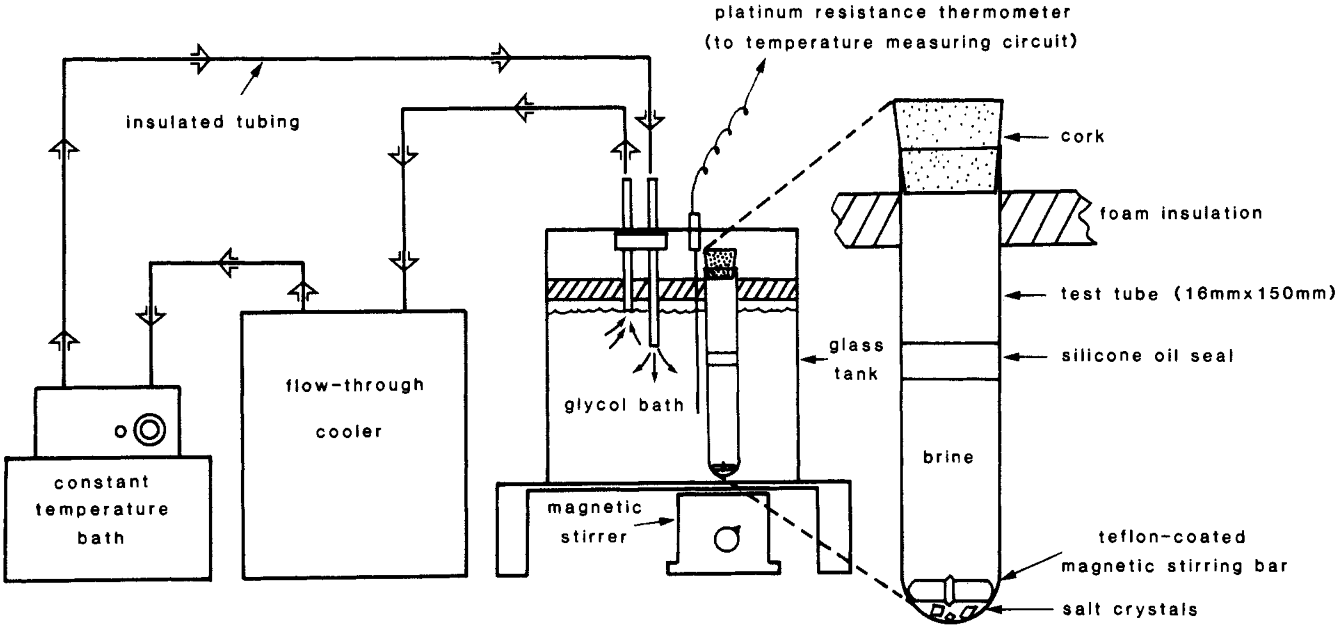

Figure 3. Schematic diagram of the experimental setup used in this study. The flow-through cooler was used only for experiments below 40 °C.

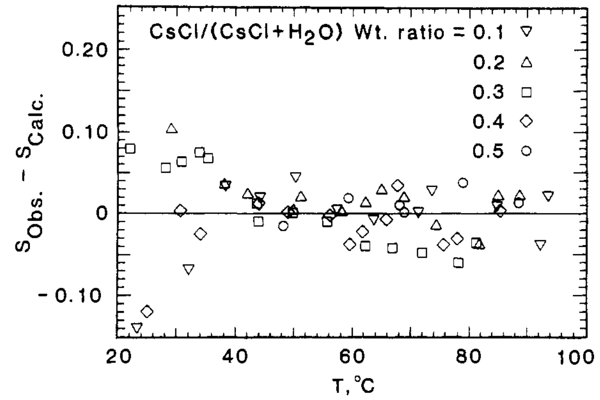

Figure 4. Differences between the observed and calculated (from eq 2) halite solubilities (in wt %).

Table III. Isothermal Solubilities of Halite Calculated from Eq 1

$CsCl/(CsCl + H_2O)$, wt ratio	isothermal solubilities (wt % NaCl) 25 °C	50 °C	75 °C
0.0[a]	26.31	26.77	27.33
0.1	23.45	24.03	24.53
0.2	20.79	21.09	21.56
0.3	17.73	17.97	18.36
0.4	14.32	14.72	15.08
0.5	b	11.27	11.62

[a] Data from Potter and Clynne (4). [b] Halite metastable (6).

Isothermal solubilities of halite at 25, 50, and 75 °C in the ternary system $NaCl-CsCl-H_2O$ were calculated from eq 1 by using the data listed in Table II. The results are given in Table III and plotted in Figure 2. The solubility data in the binary system $NaCl-H_2O$ are from Potter and Clynne (4). The solubility isotherm at 50 °C is omitted in Figure 2 for clarity.

Conclusions

The data presented here represent a more internally consistent and precise set of halite solubility measurements in the ternary system $NaCl-CsCl-H_2O$ than those reported by Plyushchev et al. (3). The present data also show that halite is slightly more soluble. The range of the deviations of the measured solubilities from the smooth curves is 0.00-0.06 in wt % of NaCl. The precision of the method used in this study is 0.03-0.05 wt % NaCl at one standard deviation (4).

Acknowledgment

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Registry No. NaCl, 7647-14-5; CsCl, 7647-17-8.

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Solubility Relations in the Ternary System NaCl–CsCl–H_2O at 1 atm. 2. Solubility Relations at 25 °C

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Solubility relations in the CsCl-rich region of the ternary system NaCl–CsCl–H_2O have been determined at 25 °C by using the isothermal method. These data together with the halite solubility data reported in part 1 of this series complete the solubility relations for the entire ternary system at 25 °C. A new compound, $CsCl\cdot 2NaCl\cdot 2H_2O$, and a new solid-solution series, $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$ with x ranging from 0 to 0.427, were found in this study. The new compound is monoclinic, belongs to space group $I2/c$, and has $a = 13.620$ (2), $b = 5.831$ (1), $c = 10.709$ (2) Å, $\beta = 91.27$ (1)°, $Z = 4$, $V = 850.3$ (1) Å^3; refractive indices are $n_\alpha = 1.520$, $n_\beta = 1.540$, $n_\gamma = 1.552$; density $D_x = 2.509$ g/cm^3. The solid solution is cubic with the cell edge slightly larger than that of CsCl and the refractive index $n^{25}{}_D = -0.14638x + 1.6405$.

Introduction

Solubilities of halite in the ternary system NaCl–CsCl–H_2O between 20 and 100 °C, measured by means of the visual polythermal method, have been reported in part 1 of this series (*1*). That experimental technique, however, is not applicable in the Cs-rich region of the ternary system, because more complicated phase relations are involved.

The solubility relations at 25 °C as determined by Plyushchev et al. (*2*) are summarized in Figure 1. In their experiment, Na^+ and Cl^- concentrations in the equilibrated solutions were determined gravimetrically with the concentration of Cs^+ being calculated by difference. The composition of solid phases was determined by using the Schreinemaker residue method along with the data on bulk composition and final solution composition. The existence of solid solutions between NaCl and CsCl was suggested and refractive indices were reported for three solid-solution samples. However, their compositions and crystal structure were not determined.

This paper presents the results of solubility measurements in the Cs-rich region of the ternary system at 25 °C. This report also includes chemical compositions, crystal structures, and optical properties of a new compound and a new solid-solution series found in this study. Solubility relations at 50 and 75 °C will be reported in the subsequent paper in this series. The preliminary results of this study have been presented earlier (*3*, *4*).

Experimental Section

The isothermal method was used in this study. Samples (12–15 g) of known composition were loaded into Pyrex tubes containing a Teflon-coated magnetic stirring bar. A layer of silicone oil (~1 cm) was added to seal the tube. The assembly was mounted in a constant-temperature glycol bath regulated at 25 ± 0.1 °C. The assemblage was well agitated and allowed to equilibrate for at least 2 weeks. The detailed experimental setup has been reported previously (ref *1*, Figure 3). It was found experimentally that equilibrium in the system could be reached within 12 days at 25 °C (*2*). At the end of a run, solids were separated from the solution, washed with alcohol in a vacuum-filtration system, and then dried in air for less than 30 min. Extreme care was taken to preserve the solids as prolonged drying may dehydrate the solids. The solids and the solution were then analyzed according to the following procedures:

(a) H_2O content for both the solution and the coexisting solid were determined by the weight loss of the sample dried to constant weight at 400 °C.

(b) A weighed amount of dried solid (W_{total} g) from the residue in step a was dissolved in distilled water to form a 25-mL solution, in which

$$M_{NA^+} + M_{Cs^+} = M_{Cl^-(total)} \tag{1}$$

$$(M_{Na^+})(W_{NaCl}) + (M_{Cs^+})(W_{CsCl}) = W_{total}(1000/25) \tag{2}$$

where M_i and W_i are molar (mol/L) concentration and molecular weight of i, respectively. $M_{Cl^-(total)}$ was measured coulometrically with a Buchler digital chloridometer, and the two unknowns, M_{Na^+} and M_{Cs^+}, were calculated from the two equations given above.

(c) The sample composition (in wt %) was calculated from M_{Na^+}, M_{Cs^+}, and H_2O content data according to the following relations:

$$x = \text{wt \% of } H_2O \text{ as determined in step a} \tag{3}$$

$$y = \text{wt \% of NaCl} = (100 - x)(M_{Na^+}W_{NaCl})/[(M_{Na^+}W_{NaCl}) + (M_{Cs^+}W_{CsCl})] \tag{4}$$

$$z = \text{wt \% of CsCl} = 100 - x - y \tag{5}$$

Results and Discussion

Solubility Data. Solubility relations determined at 25 °C in the CsCl-rich region of the ternary system are summarized in Table I and shown in Figure 2. These data and the previous halite solubility data (*1*) are used in Figure 3 to show the solubility relations for the entire ternary system.

The bulk compositions given in Table I are accurate to within ±0.03 wt %. The final solution compositions given in Table I are the average values of analyses of three aliquots. For each aliquot, one determination was made for H_2O content, and at least four were made for chloride. The precision of the H_2O content measurements (in wt %) ranges from ±0.02 to ±0.18 with an average of ±0.07. The accuracies are within ±0.38