a relatively weak solute-solvent interaction in this system. In more concentrated solutions above 10 mol %, the simple Debye equation (eq 6) may no longer be valid and much more hindered rotational and translational motion of the solvated Li^+ ion is expected with decreasing the number of solvent molecules (*9*).

Registry No. ^7Li, 13982-05-3; NH_3, 7664-41-7; $LiNO_3$, 7790-69-4.

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Solubility Relations in the System Sodium Chloride-Ferrous Chloride-Water between 25 and 70 °C at 1 atm

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Solubility relations in the ternary system $NaCl-FeCl_2-H_2O$ have been determined by the visual polythermal method at 1 atm from 20 to 85 °C along six composition lines. These six composition lines are defined by mixing $FeCl_2 \cdot 4H_2O$ with six aqueous NaCl solutions containing 5, 10, 11, 15, 20, and 25 wt % of NaCl, respectively. The solid phases encountered in these experiments were NaCl and $FeCl_2 \cdot 4H_2O$. The maximum uncertainties in these measurements are ±0.02 wt % NaCl and ±0.15 °C. The data along each composition line were regressed to a smooth curve when only one solid phase was stable. When two solids were stable along a composition line, the data were regressed to two smooth curves, the intersection of which indicated the point where the two solids coexisted. The maximum deviation of the measured solubilities from the smoothed curves is 0.14 wt % $FeCl_2$. Isothermal solubilities of halite and $FeCl_2 \cdot 4H_2O$ were calculated from these smoothed curves at 25, 50, and 70 °C.

Introduction

Hydrated ferrous chloride is an occasional phase found together with halite and/or sylvite in fluid inclusions in quartz in pegmatites (e.g., Naumov and Shapenko (*1*)) and in porphyry systems (e.g., Grant et al. (*2*)). However, data on the solubility of ferrous chloride in geothermal brines do not exist. In this study, the solubility relations in the system $NaCl-FeCl_2-H_2O$ were determined at 1 atm and between 25 and 70 °C.

Experimental Section

The visual polythermal method used in this study has been discussed in detail previously (*3-5*). Solubilities of $FeCl_2 \cdot 4H_2O$ have been determined between 20 and 75 °C along the two composition lines AL and BL shown in Figure 1, and between 40 and 75 °C along the line CL. Solubilities of halite have been determined between 20 and 85 °C along the lines DL, EL, FL, and GL, and between 20 and 40 °C along the line CL. As an example for the composition line EL, a sample (~12 g) was prepared by mixing weighed amounts of $FeCl_2 \cdot 4H_2O$ (Fisher, Lot No. 742298) and a stock solution of 15 wt % NaCl (point E in Figure 1) 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. To minimize oxidation of the sample solution during the experiment, the test tube was sealed by a rubber stopper and a stream of H_2 (at ~1 atm) was kept flowing continuously through the cavity above the silicone seal. The assembly was first heated to dissolve most of the solids and then allowed to cool slowly to nucleate a small number of relatively large crystals. The assembly was then mounted in a glycol bath and incrementally heated and vigorously agitated until the last crystal was dissolved. Heating increments were made progressively smaller as the amount of salt decreased. The temperature (read to ±0.1 °C with a calibrated platinum resistance thermometer) at which the last crystal disappeared was taken as the equilibrium temperature for the bulk composition in the tube. Once the last crystal dissolved, the solution had to be significantly supercooled to induce crystallization. This phenomenon 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 (*3*).

Results and Discussion

Weighing $FeCl_2 \cdot 4H_2O$ directly out of the bottle, although convenient, might introduce extra uncertainties into the experiment. The magnitude of these uncertainties was estimated by coulometrically titrating Cl^- in a 10.00 wt % $FeCl_2$ solution prepared in the same fashion. Duplicate analyses gave 9.89 ± 0.04 wt % $FeCl_2$. The system used for solubility measurements was also calibrated by determining the solubility of $FeCl_2 \cdot 4H_2O$ in the binary system $FeCl_2-H_2O$ and comparing the results (Table I) with those reported by Schimmel (*6*) (Figure 2). It is clear from Figure 2 that our data agree very well with those of Schimmel at temperatures above 40 °C. Below 40 °C, however, our data show that $FeCl_2 \cdot 4H_2O$ is slightly less soluble. The discrepencies at lower temperatures can be attributed to the scattering of Schimmel's data but not to the uncertainties involved in weighing $FeCl_2 \cdot 4H_2O$ in this study, since

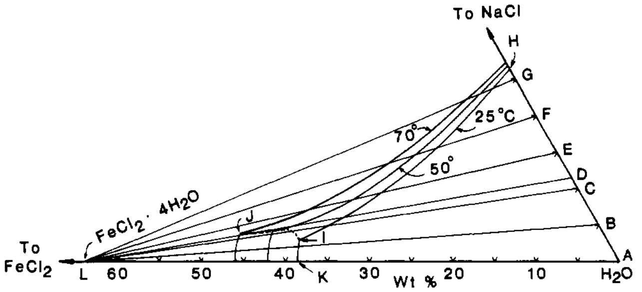

Figure 1. Solubilities of $FeCl_2·4H_2O$ and halite were determined between 20 and 85 °C along seven composition lines, AL, BL, CL, DL, EL, FL, and GL. These seven composition lines are defined by mixing $FeCl_2·4H_2O$ with seven aqueous NaCl solutions containing 0, 5, 10, 11, 15, 20, and 25 wt % of NaCl, respectively. The solubility isotherms at 25, 50, and 70 °C determined in this study (see Table IV) are also shown. At 25 °C, solutions saturated with respect to halite and $FeCl_2·4H_2O$ lie on curves HI and IK, respectively. The dashed curve IJ is the trace of the isothermal invariant points between 25 and 70 °C where solutions coexist with two solids.

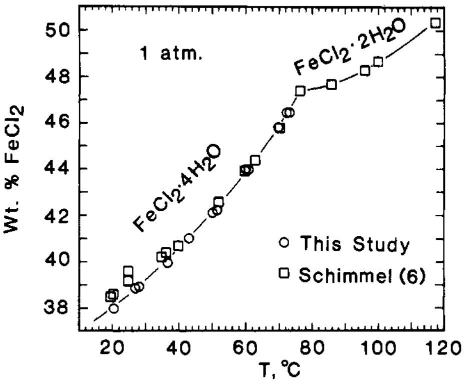

Figure 2. Solubility of hydrated ferrous chlorides in the binary system $FeCl_2–H_2O$ at 1 atm and between 20 and 120 °C. The solid curves are least-squares regression lines using our data for $FeCl_2·4H_2O$ and Schimmel's (6) data for $FeCl_2·2H_2O$. Solubilities of $FeCl_2·2H_2O$ were not determined in this study.

Table I. Experimentally Determined $FeCl_2 • 4H_2O$ Solubilities along Three Composition Lines Compared to Those Calculated from Eq 1

	[$FeCl_2$], wt %		
T, °C	exptl	calcd	diff, wt %
(a) Composition Line AL in Figure 1			
20.50	37.99	38.06	−0.08
26.65	38.87	38.76	0.11
27.98	38.94	38.92	0.02
36.57	39.97	40.04	−0.07
42.87	41.03	40.96	0.07
50.15	42.14	42.13	0.01
51.49	42.22	42.36	−0.14
60.02	43.99	43.89	0.10
60.88	44.01	44.05	−0.04
69.77	45.82	45.83	−0.01
72.26	46.46	46.36	0.10
73.07	46.46	46.54	−0.08
(b) Composition Line BL in Figure 1			
19.16	36.71	36.76	−0.05
28.89	37.99	37.92	0.07
43.05	39.99	39.96	0.03
58.17	42.49	42.61	−0.12
67.11	44.49	44.41	0.08
(c) Composition Line CL in Figure 1			
42.51	38.48	38.48	0.00
60.67	41.97	41.97	0.00
73.50	44.98	44.98	0.00

Table II. Experimentally Determined Halite Solubilities along Five Composition Lines Compared to Those Calculated from Eq 1

	[$FeCl_2$], wt %		
T, °C	exptl	calcd	diff, wt %
(a) Composition Line CL in Figure 1			
21.71	32.50	32.50	0.00
30.55	35.00	35.00	0.00
33.60	36.86	36.86	0.00
(b) Composition Line DL in Figure 1			
24.93	30.00	29.99	0.01
33.38	32.00	32.03	−0.03
41.28	33.91	33.82	0.09
46.40	34.99	35.09	−0.10
51.32	36.54	36.52	0.02
55.57	38.01	37.98	0.03
62.56	40.98	41.01	−0.03
66.16	42.95	42.94	0.01
(c) Composition Line EL in Figure 1			
34.81	25.06	25.06	0.00
51.99	28.05	28.07	−0.02
60.12	29.97	29.93	0.04
70.90	33.48	33.51	−0.03
77.90	36.79	36.78	0.01
(d) Composition Line FL in Figure 1			
25.60	14.45	14.43	0.02
47.65	16.95	17.02	−0.07
61.69	19.51	19.45	0.06
73.47	21.99	21.96	0.03
81.84	23.97	24.01	−0.04
(e) Composition Line GL in Figure 1			
28.17	3.80	3.80	0.00
44.47	4.88	4.89	−0.01
62.61	6.49	6.48	0.01
74.14	8.01	7.94	0.07
75.50	8.07	8.15	−0.08
83.44	9.51	9.50	0.01

Table III. Regression Coefficients for Solubility Equations along Seven Composition Lines for (a) $FeCl_2 • 4H_2O$ and (b) Halite

comp line[a]	a_0	a_1	a_2	a_3
(a) Solubility of $FeCl_2·4H_2O$				
AL	36.335	0.062 85	1.050×10^{-3}	
BL	35.079	0.067 45	1.067×10^{-3}	
CL	33.853	0.050 39	1.375×10^{-3}	
(b) Solubility of Halite				
CL	44.702	−1.161 96	2.763×10^{-2}	
DL	18.789	0.711 44	-1.369×10^{-2}	1.278×10^{-4}
EL	13.156	0.615 39	-1.096×10^{-2}	8.930×10^{-5}
FL	13.322	0.003 81	1.549×10^{-3}	
GL	1.488	0.110 97	-1.458×10^{-3}	1.533×10^{-5}

[a] Composition lines shown in Figure 1.

the latter can only result in higher solubilities. The $FeCl_2·4H_2O–FeCl_2·2H_2O$ transition temperature was reported by Schimmel to be 76.5 °C. Solubilities of $FeCl_2·2H_2O$ were not determined in this study because the powdery nature of the solids made the visual polythermal method difficult to apply.

The measured $FeCl_2·4H_2O$ solubilities along the three composition lines AL, BL, and CL shown in Figure 1 are listed in Table I together with smoothed values and the deviation of the measured values from the smoothed values. Results for halite solubilities are given in Table II. 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 $FeCl_2$ per 100 g of saturated solution (g/100 g), and *T* is the temperature in degrees

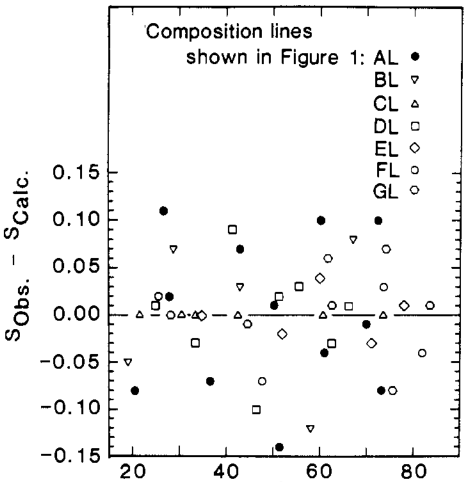

Figure 3. Differences between the observed and calculated (from eq 1 using the regression coefficients given in Table III) solubilities of $FeCl_2 \cdot 4H_2O$ and halite (in weight percent of $FeCl_2$).

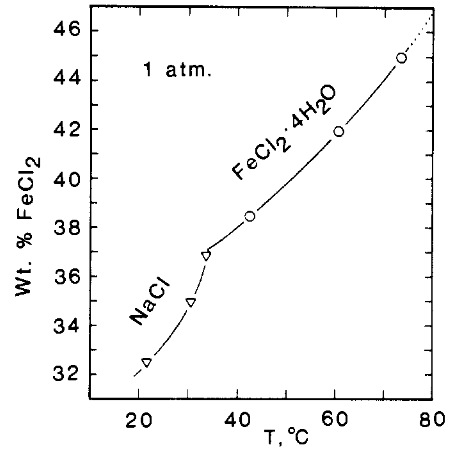

Figure 4. Solubilities of halite (triangles) and $FeCl_2 \cdot 4H_2O$ (circles) determined along the composition line CL shown in Figure 1. The solid curves are least-squares regression lines. $FeCl_2 \cdot 4H_2O$ is metastable with respect to $FeCl_2 \cdot 2H_2O$ at temperatures above 74.6 °C.

Table IV. Isothermal Solubilities Calculated from Eq 1 for (a) $FeCl_2 \bullet 4H_2O$ and (b) Halite along Seven Composition Lines

comp line[a]	isothermal solubility, wt % $FeCl_2$ 25 °C	50 °C	70 °C
	(a) $FeCl_2 \cdot 4H_2O$		
AL	38.56	42.15	45.80
BL	37.43	41.10	45.30
CL		39.78	44.12
	(b) Halite		
CL	33.25		
DL	30.00	36.15	
EL	23.70	27.60	33.10
FL	14.35	17.50	21.20
GL	3.67	5.35	7.48

[a] Composition lines shown in Figure 1.

Celsius. The coefficients, a_i, for the regression equation are listed in Table III. The differences between the observed and calculated solubilities (in weight percent) are summarized in Figure 3; the maximum difference is 0.14.

Of the seven composition lines studied, line CL is the only one involving two solids. The results are shown in Figure 4. Halite and $FeCl_2 \cdot 4H_2O$ coexist at 33.8 °C with halite being stable at lower temperatures and $FeCl_2 \cdot 4H_2O$ at higher temperatures.

Isothermal solubilities of halite and $FeCl_2 \cdot 4H_2O$ at 25, 50, and 70 °C in the ternary system $NaCl-FeCl_2-H_2O$ were calculated from eq 1 by using the data listed in Table III. The results are given in Table IV and plotted in Figure 1. The solubility data in the binary system $NaCl-H_2O$ are from Potter and Clynne (*3*). The dashed curve IJ shown in Figure 1 is the trace of the isothermal invariant points between 25 and 70 °C where solutions coexist with two solids.

Conclusions

The solubility relations in the ternary system $NaCl-FeCl_2-H_2O$ are presented between 25 and 70 °C at 1 atm. The range of deviation of the measured solubilities from the smoothed curves is 0.00–0.14 in weight percent of $FeCl_2$.

Registry No. NaCl, 7647-14-5; $FeCl_2$, 7758-94-3.

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Excess Volumes of the Water/Methanol, *n*-Heptane/Ethyl Acetate, *n*-Heptane/*n*-Butyraldehyde, and *n*-Heptane/Isobutyraldehyde Systems

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Excess volumes at 298.15 K have been measured by means of a vibrating tube densimeter for the binary mixtures of water with methanol, and *n*-heptane separately with ethyl acetate, *n*-butyraldehyde, and isobutyraldehyde. Partial molar volumes have also been calculated.

Introduction

Few thermodynamic data have been published for systems containing hydrocarbons with either aldehydes or esters. This may be attributed to the difficulty involved in working with these compounds. Aldehydes are oxidized rapidly in the presence of air while esters are hygroscopic.

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