K for various mixtures obtained by replacing H in H_2O + AN by successive *n*-alkyl groups. It can be seen that the curve has curvature upto $n = 2$ and is a line thereafter. Therefore, the $V^E(x=0.5)$ for C_2–C_5 1-alkanol mixtures with AN can be represented by eq 3 with a standard deviation $\sigma = 0.015$ cm^3 mol^{-1}.

$$V^E(x=0.5)/(\text{cm}^3\ \text{mol}^{-1}) = 0.06 + 0.011n \qquad (3)$$

The V^E of mixing of $-OH$ and $-CH_2$ groups with acetonitrile are 0.06 and 0.011 cm^3 mol^{-1}, respectively. Obviously, eq 3 can be used to predict $V^E(x=0.5)$ values for mixtures of higher *n*-alkanols with AN.

The observed V^E can be considered as arising from two types of interactions between the components: (1) physical interaction consisting mainly of dispersion forces and making a positive contribution, and (2) chemical or specific interaction resulting in a volume decrease. The latter includes charge-transfer forces, forming and/or breaking of H bonds and other complex forming interactions. It is well-known that both acetonitrile and 1-alkanols are associated in liquid state. Acetonitrile contains molecules with strong parallel and antiparallel orientations and this strongly ordered structure is stabilized by dipole–dipole interactions (*8*), whereas 1-alkanols are associated through the hydrogen bonding of their hydroxyl groups. Association decreases with increase in molar mass of 1-alkanol (*9*–*12*). The increase in V^E with the increase in molar mass of 1-alkanol implies that acetonitrile–1-alkanol interaction is relatively weaker. Therefore, the negative V^E in the case of MeOH + AN results because the decrease in volume due to the fitting in of acetonitrile molecules in the H-bonded network of MeOH overweighs the total increase in volume due to physical interactions and to the breaking up of MeOH structure by acetonitrile. Assuming the positive contribution due to H-bond breaking to be constant, the observed increase in V^E with increase in molar mass of 1-alkanol can be rationalized.

The skewness of V^E–x curves for these mixtures is due to the difference in component molar volumes and to the presence of specific interactions, the position of the extremum exhibiting the net effect. It is interesting to compare 1-alkanol + AN with H_2O + AN (*13*) for which V^E (298.15 K) is minimum (−0.56 cm^3 mol^{-1}) at $x = 0.33$. Our mixtures are H_2O + AN in which one H of H_2O is replaced by CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, or n-C_5H_{11}. The extremum occurs at $x = 0.44$, 0.77, 0.60, 0.61, and 0.55, respectively. It is clear that an increase in hydrophobicity of 1-alkanol results in the shift of extremum toward higher mole fraction of acetonitrile. The maximum at $x \simeq 0.6$ in the case of PrOH, BuOH, and AmOH indicates that if H bonding is assumed to be constant in these alkanols, then even an increase in the difference in molecular size of the two components does not change the position of the maximum.

Registry No. MeCN, 75-05-8; MeOH, 67-56-1; EtOH, 64-17-5; PrOH, 71-23-8; BuOH, 71-36-3; 1-pentanol, 71-41-0.

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Solubility Relations in the System Potassium Chloride–Ferrous Chloride–Water between 25 and 75 °C at 1 atm

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Solubility relations in the ternary system KCl–$FeCl_2$–H_2O have been determined by means of the visual polythermal method at 1 atm from 18 to 75 °C along 10 composition lines. Solubilities of sylvite were measured along five composition lines defined by mixing KCl with five aqueous $FeCl_2$ solutions containing 10, 20, 30, 38, and 45 wt % of $FeCl_2$, respectively. Solubilities of $FeCl_2 \cdot 4H_2O$ were also determined along five composition lines defined by mixing $FeCl_2 \cdot 4H_2O$ with five aqueous KCl solutions containing 5, 10, 14.98, 19.97, and 24.99 wt % KCl, respectively. The maximum uncertainties in these measurements are ±0.02 wt % in KCl, ±0.15 wt % in $FeCl_2$, and ±0.15 °C. The data along each composition line were regressed to a smooth curve. The maximum deviations of the measured solubilities from the smoothed curves are 0.22 wt % in KCl and 0.12 wt % in $FeCl_2$. Isothermal solubilities of sylvite and $FeCl_2 \cdot 4H_2O$ were calculated from these smoothed curves at 25, 40, 50, 60, 70, and 75 °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*)). Two potassium iron chloride phases, which have possible compositions of $KFeCl_{3-4} \cdot nH_2O$ and $KFe_2Cl_{5-7} \cdot mH_2O$ determined by means of SEM/energy dispersive analyses on opened high salinity fluid inclusions from a porphyry copper deposit, were reported by Quan et al. (*3*). The oxidation state of iron in these phases has not been determined. Also, the data on solubility of iron chloride in hydrothermal brines are lacking. Solubility relations in the system $NaCl$–$FeCl_2$–H_2O between 25 and 70 °C at 1 atm were recently reported by Chou and Phan (*4*). In this study, the solubility relations in the system KCl–$FeCl_2$–H_2O were determined at 1 atm and between 25 and 75 °C.

Experimental Section

The visual polythermal method used in this study has been

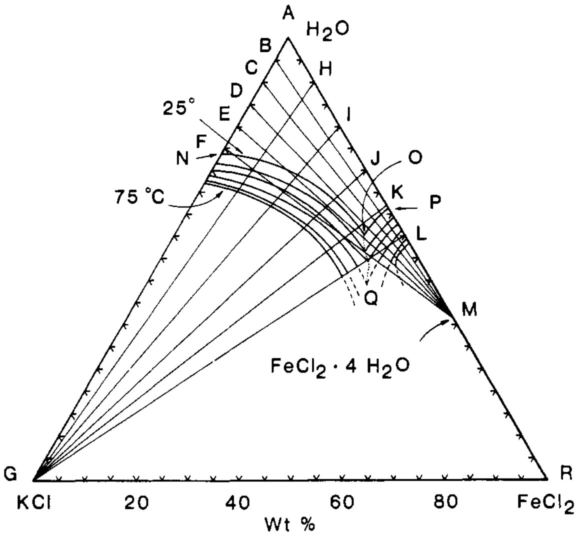

Figure 1. Solubilities of sylvite were determined between 20 and 80 °C along five composition lines, HG, IG, JG, KG, and LG, defined by mixing KCl with five $FeCl_2$ solutions containing 10, 20, 30, 38, and 45 wt % of $FeCl_2$, respectively. Solubilities of $FeCl_2 \cdot 4H_2O$ were measured between 18 and 70 °C along five composition lines, BM, CM, DM, EM, and FM, defined by mixing $FeCl_2 \cdot 4H_2O$ with five KCl solutions containing 5, 10, 14.98, 19.97, and 24.99 wt % of KCl, respectively. The solubility isotherms at 25, 40, 50, 60, 70, and 75 °C determined in this study (see Table IV) are also shown. At 25 °C, solutions saturated with sylvite and $FeCl_2 \cdot 4H_2O$ lie on curves NO and OP, respectively. The dotted curve OQ is the trace of the isothermal invariant points between 25 and 60 °C where solutions coexist with both sylvite and $FeCl_2 \cdot 4H_2O$.

previously discussed in detail (*4–7*). The procedures for sample preparations and for solubility measurements are the same as those given by Chou and Phan (*4*). Reagents used were $FeCl_2 \cdot 4H_2O$ (Fisher, Lot No. 742298) and KCl (Fisher, Lot No. 792168). Solubilities of sylvite have been determined between 20 and 80 °C along the four composition lines HG, IG, JG, and KG shown in Figure 1, and between 50 and 75 °C along the line LG. Solubilities of $FeCl_2 \cdot 4H_2O$ have been determined between 18 and 70 °C along the lines BM, CM, DM, EM, and FM. The temperature at which the last crystal disappeared for a known bulk composition in a polythermal run was read to ±0.1 °C on a calibrated platinum resistance thermometer and was taken as the equilibrium temperature.

Results and Discussion

The measured sylvite solubilities along the five composition lines HG, IG, JG, KG, and LG 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 $FeCl_2 \cdot 4H_2O$ solubilities are given in Table II. The maximum uncertainties in these measurements are ±0.15 °C. The experimental values were fitted, by using the method of least squares, to an equation of the form

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

where S is the solubility in grams of KCl and $FeCl_2$ per 100 g of, respectively, sylvite and $FeCl_2 \cdot 4H_2O$ saturated solutions (g/100 g), and T is the temperature in degrees Celsius. The coefficients, a_i, for the regression equation are listed in Table III. The smoothed values listed in Table I were calculated from eq 1. The differences between the observed and calculated solubilities (in weight percent) are summarized in Figure 2. The maximum differences are 0.12 for $FeCl_2$ (open symbols) and 0.22 for KCl (solid symbols); however, all differences in KCl, except one, are less than 0.11.

Table I. Experimentally Determined Sylvite Solubilities along Five Composition Lines Compared with Those Calculated from Eq 1

T, °C	KCl, wt % exptl	KCl, wt % calcd	diff, wt %
(a) Composition Line HG in Figure 1			
26.36	20.04	20.09	−0.05
34.10	21.40	21.32	0.08
51.06	23.99	24.02	−0.03
75.96	27.99	27.98	0.01
(b) Composition Line IG in Figure 1			
24.29	13.51	13.58	−0.07
42.57	17.02	16.91	0.11
54.06	19.01	19.00	0.01
64.95	20.96	20.99	−0.03
78.75	23.48	23.50	−0.02
(c) Composition Line JG in Figure 1			
24.63	9.48	9.49	−0.01
33.64	10.96	10.93	0.03
46.02	13.01	13.06	−0.05
60.91	15.91	15.88	0.03
75.98	19.00	19.01	−0.01
(d) Composition Line KG in Figure 1			
23.19	8.01	8.01	0.00
29.82	9.03	8.92	0.11
38.54	10.00	10.22	−0.22
51.64	12.49	12.42	0.07
67.27	15.48	15.40	0.08
79.74	18.01	18.06	−0.05
(e) Composition Line LG in Figure 1			
49.84	9.99	10.03	−0.04
60.06	12.83	12.76	0.07
74.21	16.52	16.54	−0.02

Table II. Experimentally Determined $FeCl_2 \cdot 4H_2O$ Solubilities along Five Composition Lines Compared with Those Calculated from Eq 1

T, °C	$FeCl_2$, wt % exptl	$FeCl_2$, wt % calcd	diff, wt %
(a) Composition Line BM in Figure 1			
18.87	37.10	37.11	−0.01
40.58	40.30	40.24	0.06
54.08	42.37	42.45	−0.08
70.81	45.49	45.47	0.02
(b) Composition Line CM in Figure 1			
28.61	37.96	38.06	−0.10
31.87	38.72	38.60	0.12
32.56	38.72	38.71	0.01
39.89	39.97	39.94	0.03
49.99	41.57	41.64	−0.07
57.20	42.89	42.87	−0.02
69.54	45.00	44.99	0.01
(c) Composition Line DM in Figure 1			
21.98	36.60	36.61	−0.01
42.46	39.88	39.83	0.05
57.27	42.34	42.41	−0.07
70.87	45.00	44.97	0.03
(d) Composition Line EM in Figure 1			
27.01	37.17	37.17	0.00
46.97	40.05	40.06	−0.01
58.67	42.51	42.49	0.02
68.51	44.96	44.96	0.00
(e) Composition Line FM in Figure 1			
35.05	38.00	38.02	−0.02
39.92	38.95	38.93	0.02
56.18	41.96	41.97	−0.01

Data listed in Table III were used in eq 1 to calculate isothermal solubilities of sylvite and $FeCl_2 \cdot 4H_2O$ at 25, 40, 50, 60, 70, and 75 °C in the ternary system $KCl–FeCl_2–H_2O$. The

Table III. Regression Coefficients for Solubility Equations along Five Composition Lines Each for (a) Sylvite and (b) $FeCl_2 \bullet 4H_2O$

comp line[a]	a_0	a_1	a_2
	(a) Solubility of Sylvite		
HG	15.896	0.159 14	
IG	9.155	0.182 20	
JG	6.077	0.123 55	6.135×10^{-4}
KG	5.384	0.094 29	8.110×10^{-4}
LG	−3.280	0.267 13	
	(b) Solubility of $FeCl_2{\cdot}4H_2O$		
BM	34.830	0.110 33	5.635×10^{-4}
CM	33.396	0.160 33	9.324×10^{-5}
DM	33.632	0.124 76	4.976×10^{-4}
EM	35.776	−0.002 06	1.987×10^{-3}
FM	31.459	0.187 07	

[a] Composition lines shown in Figure 1.

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

comp line[a]	isothermal solubilities					
	25 °C	40 °C	50 °C	60 °C	70 °C	75 °C
	(a) Sylvite (in wt % of KCl)					
HG	19.87	22.26	23.85	25.44	27.04	27.83
IG	13.71	16.44	18.27	20.09	21.91	22.82
JG	9.55	12.00	13.79	15.70	17.73	18.79
KG	8.25	10.45	12.13	13.96	15.96	17.02
LG	*b*	*b*	10.08	12.75	15.42	16.75
	(b) $FeCl_2{\cdot}4H_2O$ (in wt % of $FeCl_2$)					
AM	38.56	40.53	42.10	43.89	45.88	46.96
BM	37.94	40.14	41.76	43.48	45.31	46.27
CM	37.46	39.96	41.65	43.35	45.08	45.95
DM	37.06	39.42	41.11	42.91	44.80	45.79
EM	36.97	38.87	40.64	42.81	45.37	46.80
FM	*c*	*c*	40.81	42.68	*c*	*c*

[a] Composition lines shown in Figure 1. [b] Sylvite not stable. [c] $FeCl_2{\cdot}4H_2O$ not stable.

results are given in Table IV and plotted in Figure 1. The solubility data in the binary systems $KCl–H_2O$ and $FeCl_2–H_2O$ are, respectively, from Potter and Clynne (*5*) and Chou and Phan (*4*). The dotted curve OQ shown in Figure 1 is the trace of the isothermal invariant points between 25 and 60 °C where solutions coexist with sylvite and $FeCl_2{\cdot}4H_2O$. Each isothermal invariant point locates at the intersection of two smooth isothermal solubility curves, one for sylvite and the other for $FeCl_2{\cdot}4H_2O$. Sometimes, it is difficult to identify the solid phases visually in the composition range near the isothermal invariant point. However, the change in solid phase in polythermal experiments along a specific composition line is indicated by the abrupt change in slope of solubility curves in a wt %-*T* plot as demonstrated by Figure 4 of Chou and Phan (*4*). The $FeCl_2{\cdot}4H_2O–FeCl_2{\cdot}2H_2O$ transition occurs at 76.5 °C along the composition line AM (Schimmel (*8*)) and at about 64 °C along FM as indicated by the appearance of powdery crystals of the dihydrate; the exact transition temperatures in the ternary system were not located in this study.

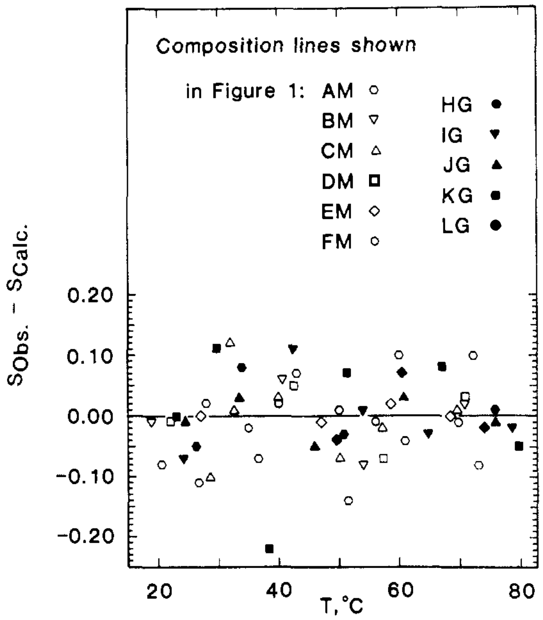

Figure 2. Differences between the observed and calculated (from eq 1 in which the regression coefficients given in Table III are used) solubilities of sylvite (in weight percent of KCl, solid symbols) and $FeCl_2{\cdot}4H_2O$ (in weight percent of $FeCl_2$, open symbols).

The two possible potassium iron chloride phases found in fluid inclusions (*3*) were not observed in these experiments. It is likely that these phases are metastable or that at least part of the iron in these phases is in the ferric state and, therefore, the compounds are not stable under the reducing conditions of this study.

Conclusion

The solubility relations in the ternary system $KCl–FeCl_2–H_2O$ are presented between 25 and 75 °C at 1 atm. The ranges of deviation of the measured solubilities from the smoothed curves are 0.00–0.22 and 0.00–0.12 in weight percent of KCl and $FeCl_2$, respectively.

Registry No. KCl, 7447-40-7; $FeCl_2$, 7758-94-3.

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