Modeling of Heavy Metal Salt Solubility Using the Extended UNIQUAC Model

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Solid–liquid equilibria in complex aqueous systems involving a heavy metal cation (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}) and one or more ions for which Extended UNIQUAC parameters have been published previously are modeled using the Extended UNIQUAC model. Model parameters are determined on the basis of a data bank with more than 4,000 experimental data points for binary and ternary aqueous systems. The parameters are generally valid in the temperature range from the freezing point to the boiling point of the respective solutions.

Introduction

Knowledge of the thermodynamic properties of aqueous solutions of the transition-metal salts is necessary in order to develop better methods for their extraction and separation from ores and polluted soil.

Solid–liquid equilibrium (SLE) calculations are important for the design and operation of industrial crystallizers and also for processes where precipitation is to be avoided. SLE calculations for aqueous electrolyte solutions are also applied in geochemistry and metallurgy. Generally, the study of solubility in these systems is motivated by the search for better procedures to obtain pure salts based on various raw materials poor in metal ions. The study of SLE in aqueous salt solutions is interesting in connection with the production of complex fertilizers (for example, the production of fertilizers containing potassium, nitrogen, and traces of cobalt). Manganese and cobalt salts are also widely used in agriculture. In treating zinc pyrites by the chlorinated roast method it is important to know the conditions for the separation of zinc salts from solutions containing sodium salts.

Because of this, much experimental work has been done, but to our knowledge no previous work concerning the modeling of the solubility of heavy metal salts has been published. A thermodynamic model able to represent the complex behavior of these systems is greatly needed in order to design, optimize, and simulate processes where they are involved.

The model used in this work is the Extended UNIQUAC model described by Thomsen et al. (1996), Thomsen and Rasmussen (1999), Pereda et al. (2000), and Iliuta et al. (2000). The model has been applied for describing SLE, vapor–liquid equilibrium (VLE), and thermal properties of aqueous electrolyte systems. The model consists of a UNIQUAC term, a Debye-Hückel term, and the Soave–Redlich–Kwong (SRK) cubic equation of state for calculating vapor-phase fugacities in systems with a vapor phase. Only pure-component and binary interaction parameters are used in the model. The evaluation of model parameters is based on binary and ternary experimental data. The interaction parameters are temperature dependent.

The extended UNIQUAC model has been used previously to describe the excess properties of aqueous and mixed-solvent electrolyte mixtures containing several ions like H^+, Na^+, K^+, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, OH^-, CO_3^{2-}, HCO_3^-, SO_3^{2-}, HSO_3^-. The aim of this work is to determine model parameters for heavy metal ions like Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. With these parameters it will be possible to make SLE calculations for these strongly nonideal systems. The main difficulty in the parameter estimation was the very scattered character of the data for many of the systems included in the database. An important step in the modeling of the phase behavior of these systems was therefore a careful analysis of the experimental data.

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Table 1. Parameters for Calculating Equilibrium Constants for the Solid–Liquid Equilibrium of Heavy Metal Salts According to Eq. (7)

	A	B	C	D	E
$Co(NO_3)_2$	642.97	−33,880	−81.497	164.34	−11.731
$Co(NO_3)_2 \cdot 3H_2O$	600.18	−29,841	−84.323	171.37	−10.786
$Co(NO_3)_2 \cdot 6H_2O$	618.72	−30,377	−87.782	178.40	−9.8408
$Co(NO_3)_2 \cdot 9H_2O$	583.96	−29,783	−82.080	185.43	−8.8956
$CoCl_2$	−138.63	10,074	23.848	13.710	−22.341
$CoCl_2 \cdot 2H_2O$	535.56	−22,322	−76.652	18.396	−21.711
$CoCl_2 \cdot 4H_2O$	−1,347.7	65,626	201.88	23.082	−21.081
$CoCl_2 \cdot 6H_2O$	−5.4820	−2,084.2	5.6150	27.769	−20.450
$CoSO_4$	−21.092	3,914.4	3.9851	43.900	−22.795
$CoSO_4 \cdot H_2O$	31.605	−1,855.3	−3.3572	46.243	−22.480
$CoSO_4 \cdot 6H_2O$	−321.67	12,059	50.097	57.959	−20.904
$CoSO_4 \cdot 7H_2O$	83.115	−8,669.0	−8.8584	60.302	−20.589
$CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	−1,574.1	65,720	239.04	−205.04	−50.376
$CoSO_4 \cdot K_2SO_4 \cdot 4H_2O$	−1,358.1	77,371	199.18	−150.53	−63.954
$CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$	−1,522.5	48,469	240.00	−145.85	−63.324
$CoSO_4 \cdot Na_2SO_4 \cdot 4H_2O$	−1,721.0	60,847	268.51	−184.98	−72.272
$Cu(NO_3)_2$	61.814	−15,731	2.9043	14.567	−11.731
$Cu(NO_3)_2 \cdot 3H_2O$	97.025	−7,587.9	−8.8787	21.597	−10.786
$Cu(NO_3)_2 \cdot 6H_2O$	15.239	−6,036.0	4.0604	28.626	−9.8408
$Cu(NO_3)_2 \cdot 9H_2O$	−53.156	−3,862.1	14.752	35.655	−8.8956
$CuCl_2$	−711.41	32,012	109.76	−136.06	−22.341
$CuCl_2 \cdot 2H_2O$	−676.66	28,885	104.68	−131.38	−21.711
$CuCl_2 \cdot 2KCl \cdot 2H_2O$	−1,899.7	67,696	299.60	−365.37	−63.676
$CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$	−2,195.3	84,008	341.37	−424.57	−50.728
$CuCl_2 \cdot KCl$	−1,389.4	55,828	215.83	−253.06	−43.323
$CuCl_2 \cdot KCl \cdot 2H_2O$	−1,496.6	57,786	233.13	−248.37	−42.693
$CuSO_4$	−568.66	28,209	87.902	−105.87	−22.795
$CuSO_4 \cdot 3H_2O$	−596.12	24,523	91.360	−98.844	−21.849
$CuSO_4 \cdot 5H_2O$	−571.92	19,463	89.523	−94.158	−21.219
$CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	−2,056.2	75,714	318.23	−354.82	−50.376
$CuSO_4 \cdot K_2SO_4 \cdot 2H_2O$	−1,854.8	62,846	289.73	−304.99	−64.584
$CuSO_4 \cdot Na_2SO_4 \cdot 2H_2O$	−2,133.3	77,815	330.76	−339.44	−72.902
$Fe(NO_3)_2$	475.43	−8,535.3	−70.544	146.98	−11.731
$Fe(NO_3)_2 \cdot 6H_2O$	501.60	−25,183	−70.543	161.03	−9.8408
$Fe(NO_3)_2 \cdot 9H_2O$	−154.46	1,006.0	29.167	168.06	−8.8956
$FeCl_2$	−226.28	13,997	36.356	−3.6543	−22.341
$FeCl_2 \cdot 2H_2O$	−265.13	11,720	43.449	1.0319	−21.711
$FeCl_2 \cdot 4H_2O$	−187.93	5,597.3	33.035	5.7181	−21.081
$FeCl_2 \cdot 6H_2O$	−892.20	32,736	140.60	10.404	−20.450
$FeSO_4$	−93.574	5,948.2	14.518	26.536	−22.795
$FeSO_4 \cdot H_2O$	56.432	−5,122.7	−5.9667	28.879	−22.480
$FeSO_4 \cdot 7H_2O$	−24.255	−5,383.5	7.9490	42.937	−20.589
$FeSO_4 \cdot 3Na_2SO_4$	−5,109.7	193,000	790.28	−688.23	−175.01
$FeSO_4 \cdot K_2SO_4 \cdot 6H_2O$	−1,512.2	48,704	238.39	−163.21	−63.324
$FeSO_4 \cdot Na_2SO_4 \cdot 4H_2O$	−1,946.3	70,816	302.18	−202.35	−72.272
$Mn(NO_3)_2$	257.09	−7,115.3	−36.020	106.12	−11.731
$Mn(NO_3)_2 \cdot H_2O$	675.00	−34,752	−95.508	108.46	−11.416
$Mn(NO_3)_2 \cdot 2H_2O$	310.47	−17,914	−41.562	110.81	−11.101
$Mn(NO_3)_2 \cdot 4H_2O$	297.20	−16,992	−40.002	115.49	−10.471
$Mn(NO_3)_2 \cdot 6H_2O$	346.73	−19,551	−47.330	120.18	−9.8408
$MnCl_2$	−449.61	23,333	70.835	−44.511	−22.341
$MnCl_2 \cdot 2H_2O$	−400.47	15,136	65.143	−39.825	−21.711
$MnCl_2 \cdot 4H_2O$	−296.50	7,358.5	50.987	−35.138	−21.081
$MnCl_2 \cdot 6H_2O$	−69.594	−2,474.5	16.809	−30.452	−20.450
$MnCl_2 \cdot 4KCl$	−3,216.1	127,450	501.57	−507.81	−105.64
$MnCl_2 \cdot 2KCl \cdot 2H_2O$	−1,816.9	72,727	284.00	−273.82	−63.676
$MnCl_2 \cdot KCl \cdot 2H_2O$	−546.19	13,124	93.522	−156.82	−42.693
$MnSO_4$	−317.60	15,616	49.041	−14.321	−22.795
$MnSO_2 \cdot H_2O$	−123.67	2,658.5	21.014	−11.978	−22.480
$MnSO_4 \cdot 5H_2O$	−406.55	13,468	64.195	−2.6054	−21.219
$MnSO_4 \cdot 7H_2O$	−312.07	8,355.7	50.609	2.0808	−20.589
$MnSO_4 \cdot 3Na_2SO_4$	−5,402.1	205,460	833.43	−729.09	−175.01
$MnSO_4 \cdot K_2SO_4 \cdot 2H_2O$	−1,722.5	65,539	265.65	−213.44	−64.584
$MnSO_4 \cdot K_2SO_4 \cdot 4H_2O$	−1,588.0	54,477	248.38	−208.75	−63.954
$MnSO_4 \cdot Na_2SO_4 \cdot 2H_2O$	−1,817.7	65,552	282.79	−247.89	−72.902
$2MnSO_4 \cdot K_2SO_4$	−1,944.3	77,154	298.60	−232.45	−88.009

SLE Calculation

The criterion for SLE in aqueous solutions is that the chemical potential of the solid is identical to the sum of the chemical potentials of the aqueous components of the solid. The chemical potential of a component is the sum of a standard state chemical potential and a term that describes the concentration dependence, the latter being calculated using the Extended UNIQUAC model.

The equilibrium between an aqueous solution and the solid salt $K_\kappa A_\alpha \cdot n\mathrm{H_2O(s)}$, consisting of κ cations K, α anions A, and n water molecules, can be described by the equation

$$K_\kappa A_\alpha \cdot n\mathrm{H_2O(s)} \Leftrightarrow \kappa K(\mathrm{aq}) + \alpha A(\mathrm{aq}) + n\mathrm{H_2O(L)}. \quad (1)$$

The criterion for SLE is that the chemical potential of the crystalline salt is equal to the sum of the chemical potentials of the constituent parts of the salt in the aqueous solution

$$\mu_{K_\kappa A_\alpha \cdot n\mathrm{H_2O(s)}} = \kappa\mu_{K(\mathrm{aq})} + \alpha\mu_{A(\mathrm{aq})} + n\mu_{w(\mathrm{L})}, \quad (2)$$

The symmetrical convention was adopted for water and the asymmetrical convention based on mole fraction for all other species.

The chemical potential for water can be written as

$$\mu_{w(L)} = \mu_w^0 + RT \ln a_w = \mu_w^0 + RT \ln(\gamma_w x_w), \quad (3)$$

where μ_w^0 is the standard state chemical potential for pure liquid water at system temperature and pressure, a_w is the water activity, and γ_w is the symmetrical water activity coefficient. According to the symmetrical convention, the activity coefficient of water is unity in the pure-component state at all temperatures, $\gamma_w = 1$ for $x_w = 1$.

The chemical potential for solutes can be written as

$$\mu_{i(\mathrm{aq})} = \mu_i^{*,x} + RT \ln(\gamma_i^{*,x} x_i), \quad (4)$$

where $\gamma_i^{*,x}$ is the asymmetrical rational activity coefficient for solute i, and $\mu_i^{*,x}$ is the standard state chemical potential for solute i based on the asymmetrical convention and mole fraction scale. This is the hypothetical ideal state of pure solute i defined by the constraint that the activity coefficient of solute i is 1 at infinite dilution at all temperatures.

Based on the expressions for the chemical potential (Eqs. 3 and 4), the equilibrium condition (Eq. 2) can be expressed as

$$-\frac{\Delta G^0}{RT} = \ln[K(T)] = \kappa \ln(\gamma_K^{*,x} x_K) + \alpha \ln(\gamma_A^{*,x} x_A) + n \ln(\gamma_w x_w), \quad (5)$$

Table 1. Parameters for Calculating Equilibrium Constants for the Solid–Liquid Equilibrium of Heavy Metal Salts According to Eq. 7 (Continued)

	A	B	C	D	E
$Ni(NO_3)_2$	435.00	−22,745	−58.615	132.00	−11.731
$Ni(NO_3)_2 \cdot 2H_2O$	1,634.4	−70,212	−241.76	136.69	−11.101
$Ni(NO_3)_2 \cdot 4H_2O$	1,484.1	−65,405	−218.74	141.37	−10.471
$Ni(NO_3)_2 \cdot 6H_2O$	950.70	−42,105	−139.15	146.06	−9.8408
$Ni(NO_3)_2 \cdot 9H_2O$	441.02	−21,488	−61.933	153.09	−8.8956
$NiCl_2$	−303.42	17,749	48.392	−18.630	−22.341
$NiCl_2 \cdot 2H_2O$	−387.22	24,288	57.936	−13.944	−21.711
$NiCl_2 \cdot 4H_2O$	−380.44	18,952	59.251	−9.2576	−21.081
$NiCl_2 \cdot 6H_2O$	−539.59	22,370	84.898	−4.5714	−20.450
$NiCl_2 \cdot 7H_2O$	−266.91	8,270.7	45.704	−2.2283	−20.135
$NiSO_4$	−139.09	6,678.5	21.935	11.560	−22.795
$NiSO_4 \cdot H_2O$	−76.563	1,344.9	13.736	13.903	−22.480
$NiSO_4 \cdot 6H_2O$	135.35	−10,556	−16.814	25.619	−20.904
$NiSO_4 \cdot 7H_2O$	39.608	−6,552.1	−2.3903	27.962	−20.589
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	−1,712.3	66,154	262.76	−237.38	−50.376
$NiSO_4 \cdot K_2SO_4 \cdot 6H_2O$	−1,589.2	51,866	249.46	−178.19	−63.324
$NiSO_4 \cdot Na_2SO_4 \cdot 4H_2O$	−1,723.8	59,961	269.59	−217.32	−72.272
$Zn(NO_3)_2$	355.96	−12,657	−49.762	127.73	−11.731
$Zn(NO_3)_2 \cdot H_2O$	442.36	−15,519	−63.864	130.07	−11.416
$Zn(NO_3)_2 \cdot 2H_2O$	423.23	−18,635	−59.510	132.41	−11.101
$Zn(NO_3)_2 \cdot 4H_2O$	379.65	−18,156	−52.917	137.10	−10.471
$Zn(NO_3)_2 \cdot 6H_2O$	372.15	−19,800	−51.070	141.79	−9.8408
$Zn(NO_3)_2 \cdot 9H_2O$	292.84	−18,300	−38.012	148.81	−8.8956
$ZnCl_2$	154.74	−13,161	−14.742	−22.904	−22.341
$ZnCl_2 \cdot 1.5H_2O$	−538.56	10,469	96.690	−38.778	−43.736
$ZnCl_2 \cdot 2.5H_2O$	−708.96	17,220	122.07	−34.092	−43.106
$ZnCl_2 \cdot 3H_2O$	−201.23	1,216.9	38.418	−15.875	−21.396
$ZnCl_2 \cdot 4H_2O$	−284.83	2,647.2	52.418	−13.531	−21.081
$ZnSO_4$	−232.26	13,714	35.455	7.2860	−22.795
$ZnSO_4 \cdot H_2O$	−185.45	7,625.9	29.145	9.6291	−22.480
$ZnSO_4 \cdot 6H_2O$	−280.43	8,991.8	44.662	21.345	−20.904
$ZnSO_4 \cdot 7H_2O$	−297.62	7,913.3	48.234	23.688	−20.589
$ZnSO_4 \cdot K_2SO_4 \cdot 6H_2O$	−1,633.4	51,262	257.43	−182.46	−63.324
$ZnSO_4 \cdot Na_2SO_4 \cdot 4H_2O$	−2,103.1	77,896	325.48	−221.60	−72.272
$ZnSO_4 \cdot (NH_4)2SO_4 \cdot 6H_2O$	−1,545.1	52,106	241.74	−241.66	−50.376
$ZnSO_4 \cdot 3Na_2SO_4$	−5,195.8	191,270	805.67	−707.48	−175.01

where

$$\Delta G^0 = -RT\ln[K(T)] = \kappa\mu_K^{*,x} + \alpha\mu_A^{*,x} + n\mu_w^0 - \mu_{K_\kappa A_\alpha n\mathrm{H_2O}} \quad (6)$$

represents the increment in standard state chemical potential by equilibrium (Eq. 1) at the temperature T. The chemical potential of the salt is equal to its standard state chemical potential because the solid salt is in its standard state. The standard state of solid salts is here defined as the pure crystalline component at system temperature and pressure.

SLE calculation therefore reduces to the solution of Eq. 5 in order to obtain the composition of the liquid phase in equilibrium with the solid phase. In Eq. 5 $K(T)$ is the equilibrium constant at the temperature T for the solid–liquid equilibrium (Eq. 1). If values of the chemical potentials of all ions and salts are known, it is possible to calculate the value of the equilibrium constants from Eq. 6. Further, if the enthalpies of formation and the heat capacities of ions and salts are known, it is possible to evaluate the temperature dependency of the equilibrium constants. For heavy metal salts, however, only a few of these thermodynamic properties are available.

The equilibrium constant for solid–liquid equilibrium was therefore calculated from the expression

$$\ln[K(T)] = A + \frac{B}{T} + C\ln T + D\frac{(T-298.15)^2}{1{,}000T} + E\frac{T-200}{T}\ln\frac{T-200}{98.15}. \quad (7)$$

This expression has the same form as the expression that would be obtained if the value of $K(T)$ was derived from the thermodynamic properties of the ions and salts. The last two terms in Eq. 7 reflect the correlation being used for the temperature dependency of the standard state heat capacity of the ions [Thomsen and Rasmussen (1999)]. The parameters A, B, C, D, and E for the pertinent salts were fitted to experimental solubility data. These parameters are listed in Table 1.

Extended UNIQUAC model

The activity coefficients are determined by the Extended UNIQUAC model. This thermodynamic model was described earlier by Thomsen et al. (1996).

According to Eqs. 3 and 4, the total molar Gibbs energy of an aqueous electrolyte solution consists of a contribution from water and a contribution from the ions:

$$G = x_w[\mu_w^0 + RT\ln(\gamma_w x_w)] + \sum_{\text{ions}} x_i[\mu_i^{*,x} + RT\ln(\gamma_i^{*,x} x_i)]. \quad (8)$$

This expression can be divided into a term for the ideal part (I) and the excess part (E) of the total molar Gibbs energy:

$$G = G^I + G^E = \underbrace{x_w(\mu_w^0 + RT\ln x_w) + \sum_{\text{ions}} x_i(\mu_i^{*,x} + RT\ln x_i)}_{G^I} + \underbrace{RT\left(x_w\ln\gamma_w + \sum_{\text{ions}} x_i\ln\gamma_i^{*,x}\right)}_{G^E}. \quad (9)$$

The Extended UNIQUAC expression for the molar excess Gibbs energy is represented by the sum of three terms: a combinatorial or entropic term, a residual or enthalpic term, and an electrostatic term. The first two terms constitute the short-range contributions, while the latter constitutes the long-range contribution. The first two terms constitute the UNIQUAC model derived by Abrams and Prausnitz (1975) and Maurer and Prausnitz (1978):

$$G^E = G^E_{SR} + G^E_{LR} = G^E_{\text{Combinatorial}} + G^E_{\text{Residual}} + G^E_{\text{Debye-Hückel}}.$$

The combinatorial, entropic term is

$$\frac{G^E_{\text{Combinatorial}}}{RT} = \sum_i x_i\ln\left(\frac{\phi_i}{x_i}\right) - \frac{z}{2}\sum_i q_i x_i\ln\left(\frac{\phi_i}{\theta_i}\right),$$

where $z = 10$ is the coordination number; x_i is the mole fraction, ϕ_i is the volume fraction, and θ_i is the surface area fraction of component i

$$\phi_i = \frac{x_i r_i}{\sum_l x_l r_l}; \qquad \theta_i = \frac{x_i q_i}{\sum_l x_l q_l}, \quad (10)$$

where r_i and q_i are volume and surface area parameters for component i. The residual, enthalpic term is

$$\frac{G^E_{\text{Residual}}}{RT} = -\sum_i x_i q_i\ln\left(\sum_k \theta_k\psi_{kl}\right), \quad (11)$$

where the parameter ψ_{kl} is given by

$$\psi_{kl} = \exp\left(-\frac{u_{kl}-u_{ll}}{T}\right), \quad (12)$$

where u_{kl} and u_{ll} are interaction energy parameters. The interaction energy parameters are considered temperature dependent: $u_{kl} = u_{kl}^{(0)} + u_{kl}^{(t)}\,(T-298.15)$.

The combinatorial and the residual terms of the UNIQUAC excess Gibbs energy function are based on the rational, symmetrical activity coefficient convention. The ionic activity coefficients needed in Eq. 5 are the rational asymmetric activity coefficients. The rational asymmetrical activity coefficient for ion i is obtained from the rational symmetrical activity coefficient by the relation $\gamma_i^{*,x} = \gamma_i/\gamma_i^{\infty}$. The infinite

dilution activity coefficient γ_i^∞ is calculated from the UNIQUAC equation by setting the mole fraction of water equal to one.

The Debye–Hückel electrostatic term is expressed in terms of the rational, symmetrical convention for water and the rational, asymmetrical convention for the solutes. The following expression for the Debye–Hückel contribution to the excess Gibbs energy was used:

$$\frac{G^E_{\text{Debye-Hückel}}}{RT} = -x_w M_w \frac{4A}{b^3}\left[\ln(1+bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2}\right]. \quad (13)$$

This expression is a simplification of the excess Gibbs energy term given by Debye and Hückel (1923), as suggested by Fowler and Guggenheim (1949).

Based on table values of the density and the dielectric constant of pure water, the Debye-Hückel parameter A can be approximated in the temperature range 273.15 K $< T <$ 383.15 K by

$$A = \left[1.131 + 1.335\times10^{-3}\cdot(T-273.15) + 1.164\times10^{-5}\cdot(T-273.15)^2\right](\text{kg}\cdot\text{mol}^{-1})^{1/2}. \quad (14)$$

The parameter b is dependent on the size of the involved ions, but is usually considered constant. The value used in this work is 1.50 $(\text{kg}\cdot\text{mol}^{-1})^{1/2}$.

Table 2. Experimental Mean Molal Activity Coefficient (γ) and Osmotic Coefficient (Φ) Data Used for Parameter Estimation*

System	Reference	Data Type	No. of Data Points	Conc. (molality)	Temp. (K)	Avg. Rel. Dev. (%)
$MnSO_4$	Plake (1935)	Φ	8	0–0.3	373.15	11
	Robinson and Jones (1936)	Φ	22	0.1–4.2	298.15	4.5
	Rard (1984)	Φ	22	0.1–5.0	298.15	5.9
$MnCl_2$	Rard (1984)	Φ	28	0.1–7.7	298.15	3.2
	Guggenheim and Stokes (1958)	γ	1	0.1	298.15	4.1
	Robinson and Stokes (1940)	γ	16	0.1–2.2	298.15	4.7
$FeSO_4$	Nikolaev et al. (1989)	Φ	14	0.1–1.8	298.15	14
$FeCl_2$	Kangro and Groeneveld (1962)	Φ	5	1.0–5.0	298.15	4.7
	Stokes and Robinson (1941)	γ	15	0.1–2.6	298.15	5.4
	Susarev et al. (1976)	γ	9	0.5–4.8	298.15	11
	Guggenheim and Stokes (1958)	γ	1	0.1	298.15	2.8
$CoCl_2$	Guggenheim and Stokes (1958)	γ	1	0.1	298.15	0.25
	Robinson and Stokes (1940)	γ	15	0.1–2.0	298.15	28
$Co(NO_3)_2$	Robinson et al. (1942)	Φ	16	0.1–2.2	298.15	7.8
	Guggenheim and Stokes (1958)	γ	1	0.1	298.15	5.5
$NiSO_4$	Plake (1935)	Φ	9	0–0.3	373.15	8.2
	Robinson and Jones (1936)	Φ	15	0.1–2.6	298.15	17
$NiCl_2$	Robinson and Stokes (1940)	Φ	15	0.1–2.0	298.15	7.5
	Pearce and Eckstrom (1937)	a_w	12	0.1–4.9	298.15	1.6
	Plake (1935)	Φ	9	0–0.3	373.15	3.6
$CuSO_4$	Robinson and Jones (1936)	Φ	9	0.1–1.4	298.15	25
	Plake (1935)	Φ	9	0–0.3	373.15	8.2
	Downes and Pitzer (1976)	Φ	6	0.5–1.4	298.15	31
$CuCl_2$	Brown (1948)	Φ	9	0.1–6.0	298.15	4.1
	Downes and Pitzer (1976)	Φ	18	0.4–1.7	298.15	2.0
	Guggenheim and Stokes (1958)	γ	1	0.1	298.15	2.4
$Cu(NO_3)_2$	Robinson et al. (1942)	Φ	16	0.1–2.2	298.15	1.1
	Brown (1948)	Φ	27	0.1–8.0	298.15	3.8
	Guggenheim and Stokes (1958)	γ	1	0.1	298.15	1.0
$ZnSO_4$	Robinson and Stokes (1949)	Φ	18	0.1–3.5	298.15	14
	Kangro and Groeneveld (1962)	Φ	4	1.0–4.0	298.15	11
	Robinson and Jones (1936)	Φ	20	0.1–3.6	298.15	12
	Apelblat (1992)	Φ	7	2.9–4.2	283.15–313.15	33
$ZnCl_2$	Pan (1966)	Φ	19	0.2–2.4	298.15	40

*The average relative deviation between experimental and calculated data are given in the last column.

Table 3. Experimental SLE Data Used for Parameter Estimation*

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$MnSO_4$	Jones and Getman (1904a)	9	0.1
	Dzhabarov et al. (1970b)	23	0.3
	Caven and Johnston (1927)	2	0.2
	Dzhabarov et al. (1970a)	1	0.2
	Zhelnin (1977)	3	1.0
	Zhelnin and Gorshtein (1971b)	1	0.2
	Lemets and Nenno (1973)	3	1.3
	Dzyuba and Kovalenko (1985)	3	0.5
	Rohmer (1939a)	9	2.2
	Petlicka (1970)	8	1.2
	Schreinemakers (1909a)	2	0.4
	Shevchuk et al. (1993)	1	2.6
	Benrath (1930)	3	1.6
	Soroka et al. (1986)	1	3.7
	Benrath and Benrath (1929)	1	1.6
	Flöttmann (1928)	3	0.6
	Caven and Johnston (1928)	2	1.4
	Nguyen et al. (1972)	2	3.5
	Dzyuba and Kovalenko (1985)	3	0.5
	Maksimenko and Shevchuk (1974)	1	0.2
	Zhelnin and Gorshtein (1971b)	2	0.5
	Karnaukhov and Runov (1967)	1	0.2
	Krepelka and Bejha (1933)	3	0.04
	Benrath (1929)	1	2.1
	Schreinemakers and van Prooje (1913)	1	2.3
	Druzhinin (1961)	1	0.5
	Gorokhova and Druzhinin (1968)	1	0.5
$MnCl_2$	Biltz (1902)	5	0.08
	Jones and Getman (1904a)	9	0.1
	Benrath (1941)	3	0.0
	Süss (1913)	4	0.4
	Tereshchenko et al. (1975)	2	0.4
	Benrath (1934b)	8	0.3
	Zhelnin and Gorshtein (1972)	1	0.2
	L'Haridon and Lang (1968)	1	0.4
	Balarev and Spassov (1979)	2	0.6
	Il'chenko et al. (1975)	1	0.2
	Shevchuk and Pavlenko (1971b)	1	0.5
	Balarev and Spassow (1980a)	1	0.2
	Filippov et al. (1983)	1	0.2
	Balarev et al. (1979)	3	0.4
	Petrov and Shevchuk (1979a)	4	0.7
	Petrov and Shevchuk (1979b)	4	2.1
	Putivl'skii et al. (1987)	1	0.5
	Parilova (1968)	3	0.6
	Druzhinin and Parilova (1968)	2	0.3
	Zhelnin and Gorshtein (1971a)	1	0.2
	Pavlenko (1971)	1	0.5
	Zul'fugarly and Aliev (1983)	1	0.2
	Lomtva and Kydynov (1985)	1	1.3
	Parilova and Druzhinin (1968)	3	0.8
	Grekova et al. (1961)	2	0.3
	Grekova et al. (1973a)	2	0.3
	Shyityeva et al. (1982)	1	0.6
	Murzubraimov (1978)	1	1.2
	Grekova et al. (1973b)	1	0.9
	Rysmendeev (1968)	1	0.4
	Druzhinin (1961)	1	0.2

I is the ionic strength based on molality:

$$I = \frac{1}{2}\sum_i m_i z_i^2. \tag{15}$$

Because the UNIQUAC model is in the Lewis–Randall thermodynamic framework while the Debye–Hückel theory is in the McMillan–Mayer framework, there is an inherent inconsistency in simply adding G^E (UNIQUAC) to G^E (Debye–Hückel). The nature of this inconsistency is obscure. While it is possible to include corrections, they are usually not important (except for large solute molecules) according to Haynes and Newman (1998).

Model Parameter Estimation

Model parameter estimation was based on an extended database. The existing databank (IVC-SEP) for aqueous elec-

trolyte systems was extended by the addition of a considerable amount of SLE data, activity coefficients and osmotic coefficients for systems containing the cations (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}). A list of sources containing the experimental data is presented in Tables 2 and 3.

The experimental data were found directly from the original articles. This allows us to avoid misprints noticed in data compilations of Linke and Seidell (1965) and Stephen et al. (1979) and gives more information concerning the data. More than 4,000 experimental data points were included in the databank. Unfortunately, a relatively large amount of experimental data existing in the literature is incomplete, for example, SLE data with the concentrations expressed as molarity or gram/liter without reporting the mixture density. Such data have not been used. The estimation of model parameters was performed as a least-square minimization (Thomsen et al., 1996).

The weighted sum of squared residuals

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$Mn(NO_3)_2$	Jones and Getman (1904a)	9	0.6
	Funk (1899)	11	3.3
	Tereshchenko et al. (1975)	1	3.1
	Strizhneva et al. (1975)	1	3.1
	Ewing and Rasmussen (1942)	30	1.1
	Runov (1966)	1	0.4
$MnSO_4 + Na_2SO_4$	Caven and Johnston (1928)	29	1.2
	Benrath (1929)	21	1.3
	Benrath and Benrath (1929)	19	1.2
	Schreinemakers and van Prooje (1913)	7	1.1
$MnSO_4 + K_2SO_4$	Caven and Johnston (1927)	13	1.0
	Karnaukhov and Runov (1967)	15	3.5
	Caven and Johnston (1926)	7	1.0
	Benrath (1930)	49	1.9
	Nadgafova et al. (1988)	11	2.7
$MnSO_4 + (NH_4)_2SO_4$	Caven and Johnston (1927)	2	0.5
	Benrath (1931a)	1	0.9
	Schreinemakers (1909a)	1	1.3
$MnCl_2 + NaCl$	Petrov et al. (1984b)	2	1.1
	Filippov et al. (1983)	24	0.6
	Petrov and Shevchuk (1979a)	4	1.5
	Druzhinin (1961)	13	0.8
	Gorokhova and Druzhinin (1968)	1	1.0
$MnCl_2 + KCl$	Tereshchenko et al. (1975)	18	2.2
	Süss (1913)	3	6.1
	Parilova and Druzhinin (1968)	58	4.0
$MnSO_4 + MnCl_2$	Druzhinin (1961)	14	2.9
	Gorokhova and Druzhinin (1968)	1	2.1
$Mn(NO_3)_2 + KNO_3$	Strizhneva et al. (1975)	17	10
	Runov (1966)	19	12
$MnCl_2 + Mn(NO_3)_2$	Tereshchenko et al. (1975)	10	10
	Il'chenko et al. (1975)	6	5.3
$FeSO_4$	Fraenckel (1907)	36	0.3
	Bielopolskij and Szpunt (1941)	35	0.4
	Legrand (1967)	4	0.6
	Bielopolskij and Urusow (1948)	2	0.7
	Agde and Barkholt (1926)	8	0.5
	Etard (1894)	5	0.9
	Bursa et al. (1977)	3	0.4
	Bursa and Stanisz-Lewicka (1980)	2	0.5
	Legrand and Pâris (1966)	1	0.006
	Bursa and Przepiera (1975)	2	0.5
	Occleshaw (1925)	1	0.3
	Bursa et al. (1982a)	3	0.3
	Bursa et al. (1982b)	4	0.04
	Benrath and Benrath (1929)	1	10
	Soroka et al. (1986)	1	0.6
	Girich et al. (1987)	1	0.6
	Bruhn et al. (1965)	1	12

$$S = \sum_{\gamma\text{-data}} \left[\frac{\left(\gamma^{\text{calc}} - \gamma^{\text{exp}}\right)}{0.25\gamma^{\text{exp}}} \right]^2 + \sum_{\substack{\text{SLE-data} \\ \text{(saturated salts)}}} \left[\frac{\Delta G^0 + RT\sum_i \nu_i \ln a_i}{0.25\,RT} \right]^2 + \sum_{\substack{\text{SLE data} \\ \text{(nonsaturated salts)}}} \left[\max\left(\frac{\Delta G^0 + RT\sum_i \nu_i \ln a_i}{0.25\,RT}, 0 \right) \right]^2 \quad (16)$$

was minimized. In this expression, γ-data and SLE-data are experimental activity coefficients (osmotic coefficients, water activities, and mean ionic activities) and solid–liquid equilibrium data, respectively. The superscripts "calc" and "exp" signify values calculated by the model and experimental values. The number 0.25 is a weighting factor.

The weighting factor for the activity coefficient data was chosen so that a 25% deviation between calculated and experimental data would give a squared residual of 1.

The term for SLE data consists of two parts. The first part pertains to the solid phase(s) that, according to experimental data, is in equilibrium with liquid. This term is zero for saturated solutions and nonzero for unsaturated and supersaturated solutions. The second part pertains to all other salts (nonsaturated salts) that potentially can be formed in the solution. If the value of the activity product of one such salt exceeds that of the equilibrium constant of the corresponding solid–liquid equilibrium, this salt is supersaturated and a positive contribution is added to the object function. The SLE data were weighted so that a solubility index of 1.28 and 0.78 give a squared residual of 1. The solubility index of a salt is a measurement of the degree of saturation of the salt and is calculated as the ratio between the activity product and the solubility product of the salt.

Extended UNIQUAC parameters for a number of species, including the Na^+, K^+, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-} ions,

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$FeCl_2$	Goldschmidt and Syngros (1894)	4	0.05
	Biltz (1902)	6	0.05
	Schimmel (1928)	37	0.4
	Legrand (1967)	21	0.6
	Atbir et al. (1996)	2	0.3
	Schimmel (1952)	6	0.4
	Shchedrina et al. (1964)	1	0.8
	Shchedrina and Ozerova (1965)	1	0.8
	Bursa et al. (1977)	55	0.7
	Bursa and Przepiera (1975)	2	0.4
	Legrand and Pâris (1966)	14	0.8
	Chou and Phan (1985)	12	0.5
	Boeke (1911)	2	1.3
	Belov et al. (1985)	1	0.1
	Balarev and Spassow (1980b)	2	0.6
	Boeke (1909)	1	1.5
	Bursa et al. (1982b)	26	0.5
	Shchedrina and Krasnova (1972)	1	0.03
	Shchedrina and Mel'nichenko (1974)	1	0.6
	Balarew and Spassov (1979)	1	0.5
	Belarew et al. (1979)	1	0.1
	Atbir et al. (2000)	5	0.5
$Fe(NO_3)_2$	Funk (1899)	13	0.6
$FeSO_4 + Na_2SO_4$	Bursa and Przepiera (1975)	41	0.6
	Benrath and Benrath (1929)	9	5.0
	Koppel (1905)	20	4.3
$FeSO_4 + K_2SO_4$	Legrand (1967)	17	1.0
	Legrand and Pâris (1966)	12	1.2
$FeCl_2 + NaCl$	Bursa and Przepiera (1975)	25	0.5
	Chou and Phan (1985)	35	3.3
$FeCl_2 + KCl$	Legrand (1967)	20	0.9
	Legrand and Pâris (1966)	15	0.6
	Atbir et al. (1996)	20	0.8
	Chou and Phan (1986)	38	1.1
	Atbir et al. (2000)	41	1.1
$FeSO_4 + FeCl_2$	Legrand (1967)	17	0.8
	Bursa et al. (1977)	51	0.8
	Legrand and Pâris (1966)	12	0.9
	Bursa et al. (1982b)	23	0.5

were determined by Thomsen and Rasmussen (1999). These parameters were maintained unchanged in this work. UNIQUAC volume and surface-area parameters for the heavy metal ions and parameters for the interaction of heavy metal ions with water and with the ions Na^+, K^+, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-} were evaluated using experimental values of activity coefficients and salt solubility.

Solid–liquid equilibrium calculations in aqueous solutions containing only a heavy metal ion Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+} and one or more of the ions Na^+, K^+, NH_4^+, Cl^-, NO_3^- or SO_4^{2-} could be performed satisfactorily without considering the formation of complex ions.

Results and Discussions

UNIQUAC interaction parameters for the interaction of heavy metal ions with water, and with three different anions and three different cations are reported in Table 4. UNIQUAC volume and surface-area parameters for the heavy metal ions are reported in Table 5. All these parameters were

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$CoSO_4$	Jones and Getman (1904a)	7	0.2
	Rohmer (1939b)	22	0.8
	Koppel (1905)	10	1.7
	Ganz et al. (1974)	1	0
	Crockford (1932)	2	0.5
	Zhang et al. (1989)	3	1.7
	Bursa and Stanish-Levitska (1980)	3	2.0
	Bakaev and Margulis (1978)	1	0.6
	Caven and Gardner (1933)	2	1.1
	Caven and Johnston (1928)	1	1.0
	Filippov et al. (1985)	1	0.5
	Filippov and Nokhrin (1985a)	1	0.5
	Längauer (1933)	1	0.2
	Shevchuk and Pavlenko (1970)	1	1.8
	Druzhinin and Kondrat'eva (1966)	1	0.4
	Filippov and Yakovleva (1979a)	1	0.6
	Shevchuk et al. (1979)	3	2.3
	Basset and Henshall (1950)	1	0.9
	Druzhinin (1967)	1	0.4
	Sieprawski and Cohen-Adad (1973)	1	2.1
	Zavitskaya (1970)	1	1.4
	Zavitskaya (1974a)	4	1.3
	Zavitskaya (1974b)	2	1.1
	Kondrat'eva and Druzhinin (1968)	1	0.9
	Filippov and Yakovleva (1979b)	1	0.6
	Shevchuk and Pavlenko (1971a)	1	1.8
	Kondrat'eva and Beskov (1970)	1	0.3
	Oikova and Barkov (1979)	1	2.1
	Kuchkarov (1983)	1	1.5
	Kondrat'eva et al. (1971)	1	0.5
$CoCl_2$	Jones and Pearce (1907)	11	0.8
	Biltz (1902)	5	0.1
	Jones and Getman (1904a)	7	0.2
	Cohen-Adad and Said (1967)	7	0.8
	Cohen-Adad et al. (1968)	2	2.6
	Foote (1923)	1	1.6
	Benrath (1934a)	10	0.7
	Bassett et al. (1939)	1	0.2
	Filippov et al. (1991)	1	0.07
	Filippov et al. (1985)	1	0.08
	Shevchuk and Pavlenko (1971b)	1	0.5
	Pavlenko (1971)	1	0.5
	Bassett and Sanderson (1932)	4	0.7
	Filippov et al. (1983)	1	0.2
	Grekova et al. (1961)	2	0.6
	Grekova et al. (1973a)	2	0.6
	Shyityeva et al. (1982)	1	1.0
	Oikova (1979)	1	0.3
	Grekova et al. (1973b)	1	0.4
	Sanfeliz Prieto et al. (1996)	1	0.5
	Stoev and Zlateva (1993)	2	0.4
	Foote (1927)	2	0.2
	Mazetti (1926)	1	0.7

obtained by minimizing the sum of squared residuals S. Parameters describing the interactions between heavy metal cations were not estimated due to insufficient data.

In Table 2 the sources of the experimental activity coefficient data used for the parameter estimation are listed. The relative deviations between experimental and calculated data reflect the low weight this type of data were given in the parameter estimation. The focus of this work is on solubility calculations, which means that we mainly deal with saturated solutions. Many of the activity and osmotic coefficient data pertain to dilute, unsaturated solutions. As a result, the model represents some of these data with a poor accuracy.

Table 3 lists the sources of experimental SLE data used for the parameter estimation. The number of data points quoted in Table 3 reflects the number of data points from a given source that we chose to use for the parameter estimation. The sources may contain more data that were not used in this work. The absolute deviations quoted in Table 3 are the average absolute deviations between calculated and experimental solubilities from a given source. In Table 3 the data are sorted according to the binary and ternary system they belong to. In many cases, the same source appears twice or more, because each article with ternary data usually also contains binary data.

For many systems the model is able to reproduce binary and ternary SLE data within one mass percent from the experimental values. Unfortunately, for several systems the data coming from various references did not agree well, and the deviation between calculated and experimental values therefore is more than one percent. Also, in several systems the components form solid solutions in some temperature ranges. We did not attempt to model solid solutions. For some systems it was not possible to determine whether the solid phase was a solution or a double salt. More experimental work needs to be done in order to determine that.

The SLE results for binary and ternary systems are summarized in the following paragraphs. In all figures, the salt solubility is expressed as wt. %. The experimental solubility

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$Co(NO_3)_2$	Jones and Pearce (1907)	11	0.6
	Jones and Getman (1904a)	8	0.3
	Funk (1899)	17	0.7
	Wilcox and Bailey (1927)	3	1.3
	Druzhinin and Kondrat'eva (1966)	1	0.4
	Druzhinin (1967)	1	0.4
	Kondrat'eva and Druzhinin (1968)	1	0.4
	Kondrat'eva and Beskov (1970)	1	1.0
$CoSO_4 + Na_2SO_4$	Zhang et al. (1989)	14	0.9
	Caven and Gardner (1933)	11	1.1
	Filippov and Yakovleva (1979a)	19	0.6
	Basset and Henshall (1950)	13	0.3
	Benrath (1931b)	10	1.3
	Benrath and Benrath (1929)	12	1.6
	Koppel (1905)	19	1.8
$CoSO_4 + K_2SO_4$	Benrath and Ritter (1939)	63	1.2
	Kucharov et al. (1977)	13	2.0
	Shevchuk and Pavlenko (1970)	1	0.4
	Caven and Johnston (1928)	9	0.4
	Filippov and Rumyantsev (1988)	15	0.4
	Basikhina and Druzhinin (1974)	7	2.4
	Kucharov (1978)	2	0.7
	Shevchuk and Pavlenko (1971a)	3	1.2
	Shevchuk et al. (1979)	6	2.0
	Tukhtaev et al. (1984)	2	0.9
$CoSO_4 + (NH_4)_2SO_4$	Shevchuk and Pavlenko (1970)	11	1.1
	Caven and Gardner (1933)	13	0.3
	Shevchuk et al. (1980)	2	0.9
$CoCl_2 + NaCl$	Filippov et al. (1983)	24	0.3
	Sanfeliz Prieto et al. (1996)	11	0.6
	Mazetti (1926)	9	0.7
	Foote (1927)	9	0.2
$CoCl_2 + KCl$	Cohen-Adad and Said (1967)	34	2.4
	Lesnykh et al. (1970)	1	1.7
	Filippov et al. (1991)	15	1.0
	Benrath and Ritter (1939)	41	4.4
$CoSO_4 + CoCl_2$	Bursa and Stanish-Levitska (1980)	63	1.1
	Filippov et al. (1985)	16	1.8
	Längauer (1933)	11	1.3
	Benrath and Ritter (1939)	52	3.3

data are marked with symbols, while the curves are calculated using the parameters presented in this work.

The model parameters are generally valid in the temperature range 0–110°C, as this is the validity range of the parameters taken from the previous work (Thomsen and Rasmussen, 1999). In this work, however, experimental data from a wider temperature range, down to −60°C and up to +160°C, have been used to determine the model parameters. The results are shown to be accurate in this wider temperature range, which shows the very good predictive capability of this model.

Binary systems

Sulphates. The solubility curves for the sulphates of the cations considered here display a common trend. The salt solubility first increases with increasing temperature. At

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$NiSO_4$	Rohmer (1939b)	34	0.3
	Hausrath (1902)	24	0.1
	Chrétien and Rohmer (1934)	3	0.2
	Jones and Getman (1904a)	9	0.2
	Bruhn et al. (1965)	1	1.5
	Koppel (1905)	14	0.8
	Girich et al. (1986b)	2	0.6
	Zhang et al. (1989)	7	0.2
	Kudryashov and Lebedev (1989)	3	1.7
	Druzhinin (1969)	2	0.4
	Bakaev and Margulis (1978)	1	0.7
	Usmanova (1969)	1	0.5
	Caven and Gardner (1933)	2	0.8
	Hill and Taylor (1938)	1	0.2
	Filippov and Rumyantsev (1988)	1	0.5
	Filippov et al. (1988)	1	0.5
	Filippov et al. (1985)	1	0.3
	Caven and Johnston (1926)	1	1.2
	Baichalova and Imanakunov (1970)	1	1.0
	Girich et al. (1986a)	3	0.7
	Shkodina et al. (1991)	3	1.3
	Benrath (1931b)	2	1.6
	Surin (1971)	2	0.5
	Shevchuk et al. (1993)	1	1.8
	Onishchenko et al. (1979)	1	1.1
	Karnaukhov et al. (1974)	1	0.6
	Tembotov and Druzhinin (1973)	1	0.1
	Bruhn et al. (1965)	1	1.5
$NiCl_2$	Biltz (1902)	5	0.09
	Jones and Getman (1904a)	9	0.06
	Ozerov (1959)	26	3.6
	Foote (1923)	1	0.04
	Benrath (1932)	8	0.6
	Balej (1989)	3	1.3
	Filippov et al. (1985)	1	1.0
	Petrov and Shevchuk (1979c)	4	0.4
	Belarew and Spassov (1979)	2	1.3
	Troitskii (1972)	1	0.2
	Foote (1912)	1	3.2
	Balarev et al. (1979)	1	2.1
	Petrov and Shevchuk (1979b)	4	0.4
	Stoev and Zlateva (1993)	1	0.3
	Oikova (1979)	1	0.2
	Vidyakina and Druzhinin (1968)	4	1.8
	Parilova et al. (1968)	3	0.8
	Grekova et al. (1961)	2	3.0
	Druzhinin et al. (1967)	1	0.5
	Murzubraimov et al. (1978)	2	2.0
	Grekova et al. (1973b)	1	0.5
$Ni(NO_3)_2$	Jones and Pearce (1907)	11	0.2
	Jones and Getman (1904a)	8	0.2
	Sieverts and Schreiner (1934)	45	1.2
	Funk (1899)	14	2.4

higher temperatures the salt solubility decreases with increases of temperature. The intersection of two different branches of a solubility curve represents a point where two solids are precipitating simultaneously, a two-solids saturation point. A two-solids saturation point can be either an eutectic or a peritectic point. The temperatures at which these changes take place vary rather strongly from system to system. In the aqueous $ZnSO_4$, $NiSO_4$, and $CoSO_4$ systems the solubility curves consist of three branches corresponding to the three hydrates that precipitate in the solution: heptahydrate, hexahydrate, and monohydrate.

The solubility curve for $MnSO_4$ consists of four branches corresponding to ice, heptahydrate, pentahydrate, and monohydrate. The cryohydratic point of $MnSO_4$ (eutectic point involving ice) is the lowest among these sulfates, -11.4°C because of the large solubility of this salt in water (32.3 wt. % at the eutectic temperature). The calculated solubility curve and the experimental data are shown in Figure 1. It can be seen

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$NiSO_4 + Na_2SO_4$	Zhang et al. (1989)	23	1.3
	Filippov et al. (1988)	27	0.6
	Filippov et al. (1989)	2	0.9
	Druzhinin et al. (1961)	8	1.6
	Benrath (1931b)	13	1.0
	Caven and Gardner (1933)	14	4.6
	Benrath and Benrath (1929)	15	2.6
	Koppel (1905)	19	3.2
$NiSO_4 + K_2SO_4$	Druzhinin and Usmanova (1971)	3	0.7
	Druzhinin (1969)	37	0.4
	Filippov and Rumyantsev (1988)	28	0.2
$NiSO_4 + (NH_4)_2SO_4$	Caven and Gardner (1933)	11	0.8
	Hill and Taylor (1938)	13	0.4
$NiCl_2 + NaCl$	Filippov et al. (1986)	15	0.3
	Petrov et al. (1984b)	2	3.2
	Petrov and Shevchuk (1979c)	4	2.1
$NiCl_2 + KCl$	Ozerov (1959)	19	1.0
	Filippov et al. (1991)	10	1.2
	Petrov et al. (1984a)	1	0.07
	Vidyakina and Druzhinin (1968)	16	1.9
$NiCl_2 + NH_4Cl$	Troitskii (1972)	1	2.0
	Foote (1912)	2	3.1
$NiSO_4 + NiCl_2$	Filippov et al. (1985)	21	2.8
$CuSO_4$	Rivett (1912)	14	0.4
	Jones and Getman (1904a)	6	0.6
	Chambers and Frazer (1900)	4	0.9
	Miles and Menzies (1937)	25	0.5
	Hausrath (1902)	22	0.08
	Caven and Johnston (1927)	3	0.3
	Crockford (1932)	2	0.3
	Schreinemakers (1911)	3	0.2
	Massink (1918)	2	0.1
	Agde and Barkholt (1926)	14	2.4
	Flöttmann (1928)	3	0.06
	Bakaev and Margulis (1975)	2	0.3
	Averina and Shevchuk (1968)	1	0.2
	Occleshaw (1925)	2	0.04
	Schreinemakers (1910–11)	3	0.2
	Filippov et al. (1998)	1	0.06
	Caven and Mitchell (1924)	6	0.5
	Druzhinin and Kosyakina (1961)	2	0.2
	Babayan et al. (1973)	1	0.4
	Karchevskii et al. (1989)	1	0.4
	Filippov and Nokhrin (1985b)	1	0.03
	Averina and Shevchuk (1967)	1	0.2
	Filippov and Nokhrin (1985a)	1	0.03
	Schreinemakers (1909b)	1	0.7
	Akbaev et al. (1971)	1	0.1
	Averina and Shevchuk (1969)	1	0.6
	Bakeev et al. (1992)	3	1.3
	Bruhn et al. (1965)	2	1.3

that metastable hydrates can also be formed in the solution. Metastable saturation points were not used for the parameter estimation.

In the $CuSO_4$ system, only two hydrates can be formed in the solution, the pentahydrate and the trihydrate. In the case of $FeSO_4$, three hydrates are reported: heptahydrate, tetrahydrate, and monohydrate. The temperature range in which the tetrahydrate might exist though is very narrow, and this could be the reason why the experimental data coming from different investigators do not agree. We therefore chose to ignore the tetrahydrate, and thus our calculated solubility curve for $FeSO_4$ has only two branches, corresponding to the heptahydrate and the monohydrate, respectively.

For $NiSO_4$ the solubility curve also includes a branch corresponding to the anhydrous salt that starts precipitating at about 107°C. For all the other sulphates the anhydrous salts

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$CuCl_2$	Jones and Pearce (1907)	10	0.2
	Biltz (1902)	5	0.04
	Isaachsen (1891)	9	0.7
	Jones and Getman (1904a)	10	0.4
	Foote (1923)	2	0.6
	Benrath (1932)	4	0.8
	Novikov et al. (1979)	4	1.2
	Schreinemakers (1911)	4	0.3
	Schreinemakers (1910–11)	3	0.3
	Balarev and Spasov (1980b)	1	0.2
	Bassett et al. (1939)	1	1.0
	Stepin (1976)	1	0.4
	Filippov et al. (1998)	1	0.2
	Chrétien and Weil (1935)	4	1.2
	Balarew and Spassov (1979)	1	0.2
	Druzhinin and Kosyakina (1961)	1	0.2
	Balarev and Spassow (1980a)	1	0.2
	Blidin (1956)	1	2.1
	Druzhinin et al. (1979)	1	0.06
	Schreinemakers and de Baat (1909)	1	0.1
	Schreinemakers (1909b)	1	0.1
	Akbaev (1971)	1	0.06
	Akbaev and Ezhova (1974)	1	0.2
	Schreinemakers (1914)	2	0.5
$Cu(NO_3)_2$	Jones and Pearce (1907)	10	0.2
	Jones and Getman (1904a)	9	1.3
	Funk (1899)	19	1.4
	Wilcox and Bailey (1927)	5	1.4
	Massink (1918)	3	1.0
	Kazantzev (1923)	20	1.3
$CuSO_4 + Na_2SO_4$	Caven and Johnston (1927)	22	1.7
	Schreinemakers (1911)	5	1.4
	Benrath and Benrath (1929)	15	3.3
	Schreinemakers (1910–11)	5	1.4
	Massink (1918)	6	1.1
	Druzhinin and Kosyakina (1961)	11	1.0
	Filippov and Nokhrin (1985b)	18	0.8
$CuSO_4 + K_2SO_4$	Caven and Mitchell (1924)	21	1.1
	Nabiev et al. (1984a)	2	1.5
$CuSO_4 + (NH_4)_2SO_4$	Ugai (1985)	10	1.0
	Averina and Shevchuk (1968)	9	1.0
	Caven and Mitchell (1924)	23	1.2
	Bakeev et al. (1992)	81	4.7
	Akbaev et al. (1971)	7	6.5
	Averina and Shevchuk (1969)	2	0.2
$CuCl_2 + NaCl$	Schreinemakers (1911)	4	2.6
	Schreinemakers (1910–11)	3	3.9
	Druzhinin and Kosyakina (1961)	18	2.2
	Filippov et al. (1986)	17	0.1
	Schreinemakers and de Baat (1909)	10	0.6
$CuCl_2 + KCl$	Chrétien and Weil (1935)	73	2.8
	Schreinemakers (1914)	5	2.2
$CuCl_2 + NH_4Cl$	Akbaev and Ezhova (1974)	12	8.5

start precipitating at higher temperatures (120–140°C the sulphates of Co, Fe, and Mn).

The experimental solubility data at 97°C of Benrath (1929) for all six salts show large deviations from model calculations and from other experimental data. These data were therefore not used for the parameter estimation.

Chlorides. The solubility of the heavy metal chlorides considered in this work increases with increases of temperature, up to about 110–140°C, depending on the salt. The model describes all these systems very accurately, as shown in Figure 2 for $NiCl_2$. In this system, four hydrates can be formed: heptahydrate, hexahydrate, tetrahydrate, and dihydrate.

The solubility curve for $ZnCl_2$ consists of six branches, corresponding to ice, four different hydrates: $ZnCl_2 \cdot 4H_2O$, $ZnCl_2 \cdot 3H_2O$, $ZnCl_2 \cdot 2.5H_2O$, $ZnCl_2 \cdot 1.5H_2O$, and anhy-

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
$CuSO_4 + CuCl_2$	Schreinemakers (1911)	3	0.6
	Schreinemakers (1910–11)	3	0.6
	Saleeva (1972)	1	0.5
	Druzhinin and Kosyakina (1961)	10	0.3
	Filippov et al. (1998)	13	0.4
	Schreinemakers (1909b)	7	1.1
$CuSO_4 + Cu(NO_3)_2$	Massink (1918)	10	0.7
$Cu(NO_3)_2 + NaNO_3$	Massink (1918)	6	4.9
$Cu(NO_3)_2 + NH_4NO_3$	Schreinemakers et al. (1924)	9	24
	Meijer (1924)	6	26
$ZnSO_4$	Rohmer (1940)	19	2.0
	Bursa and Stanisz-Lewicka (1981)	10	0.8
	Shevchuk and Druzhinin (1958)	2	0.2
	Callendar and Barnes (1897)	13	0.3
	Schröder (1936)	11	0.5
	Benrath (1930)	3	1.1
	Girich et al. (1987)	1	3.6
	Nabiev et al. (1978)	2	0
	Bury (1924)	18	3.5
	Cohen and Hetterschij (1925)	13	0.5
	Caven and Johnston (1928)	2	0.3
	Cohen (1900)	15	3.1
	Pieniazek et al. (1982)	3	1.8
	D'Ans and Kaufmann (1957)	6	0.4
	Shevchuk and Moshinskii (1969)	1	0.3
	Caven and Gardner (1933)	1	0.5
	Hill and Taylor (1938)	1	0.7
	Karchevskii et al. (1989)	1	0.6
	Shevchuk and Kost' (1967)	1	0.5
	Caven and Johnston (1926)	1	0.5
	Nguyen Quy Nga (1972)	1	0.6
	Karnaukhov et al. (1974)	1	0.5
	Bouchacourt et al. (1977)	2	0.07
	Duishenalieva et al. (1961)	1	1.4
	Shevchuk and Pilipchenko (1966)	1	0.02
	Jones and Getman (1904b)	10	0.4
$ZnCl_2$	Bursa and Stanisz-Lewicka (1981)	10	1.4
	Meerburg (1903)	1	1.3
	Usubalieva et al. (1974)	1	0.9
	D'Ans and Kaufmann (1957)	2	0.7
	Dietz (1899)	10	3.3
	Balkunova and Kydynov (1982)	1	3.7
	Tschischinoff and Schachoff (1936)	2	1.9
	Chizhikov and Shakov (1936)	1	0.4
	Shchedrina and Ozerova (1965)	1	0.6
	Shevchuk and Moshinskii (1969)	2	2.2
	Balarev and Spassow (1980a)	1	0.6
	Druzhinin et al. (1982)	1	0.4
	Burlakova (1992)	2	3.2
	Jones (1893)	10	0.08
	Biltz (1902)	5	0.1
	Chambers and Frazer (1900)	6	0.2
$Zn(NO_3)_2$	Jones and Getman (1904b)	9	2.8

Table 3. Experimental SLE Data Used for Parameter Estimation* (Continued)

System	Reference	No. of Data Points	Avg. Abs. Dev. Mass %
	Funk (1899)	19	1.8
	Ewing et al. (1933)	49	2.0
$ZnSO_4 + Na_2SO_4$	Caven and Johnston (1928)	17	0.3
	Koppel (1905)	21	0.9
	Benrath and Benrath (1929)	22	1.1
	Levi (1924)	15	1.1
	Bouchacourt et al. (1977)	9	0.6
	Benrath (1930)	26	1.1
$ZnSO_4 + K_2SO_4$	Benrath (1930)	36	1.4
	Nabiev et al. (1978)	9	1.4
	D'Ans and Kaufmann (1957)	10	1.0
	Caven and Johnston (1926)	10	0.8
	Tukhtaev et al. (1978)	2	1.0
	Shevchuk and Pilipchenko (1966)	10	1.8
	Nabiev et al. (1984b)	2	3.5
	Pilipchenko et al. (1972)	1	2.9
$ZnSO_4 + (NH_4)_2SO_4$	Benrath (1931b)	28	1.6
	Caven and Gardner (1933)	11	0.2
	Hill and Taylor (1938)	11	0.6
	Shevchuk and Kost' (1967)	7	1.0
	Shevchuk and Druzhinin (1958)	35	1.9
	Pilipchenko et al. (1972)	1	4.7
$ZnSO_4 + ZnCl_2$	Bursa and Stanisz-Lewicka (1981)	126	2.9
	D'Ans and Kaufmann (1957)	16	2.0
	Shevchuk and Moshinskii (1969)	3	28
	Bouchacourt et al. (1977)	13	11

*The average absolute deviation is the average difference between experimental and calculated salt solubility measured in mass %.

drous $ZnCl_2$. The experimental data were very scattered between about -10 and 50°C. Different investigators do not even agree on the type of solid phase.

In the system $FeCl_2$–water, three different hydrates can be formed: hexahydrate, tetrahydrate, and dihydrate. Above 140°C, the model predicts the precipitation of the anhydrous salt, and its solubility decreases with increasing temperature, but supplementary experimental data are needed in order to confirm that. Systems containing $MnCl_2$ and $CoCl_2$ also form hexahydrates, tetrahydrates, and dihydrates, and the shapes of the solubility curves are almost identical to each other. In the case of $CoCl_2$, however, the temperature range where the tetrahydrate precipitates is very narrow. $CuCl_2$ has only one hydrate ($CuCl_2 \cdot 2H_2O$) in the whole temperature range from -40°C to 100°C.

Nitrates. The solubility curves for $Fe(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, and $Cu(NO_3)_2$ have a common shape. The solubility increases with increasing temperature like the solubility of the chlorides. Three hydrates can be formed in the systems containing cobalt or copper nitrates: nonahydrate, hexahydrate, and trihydrate. In both cases, the temperature range where the nonahydrate exists is very narrow. In the case of

Table 4. Parameters $u_{ij}^{(0)} = u_{ji}^{(0)}$ and $u_{ij}^{(t)} = u_{ji}^{(t)}$ for Calculating UNIQUAC Interaction Parameters $u_{ij} = u_{ij}^{(0)} + u_{ij}^{(t)}$ $(T - 298.15)$, Valid at 273.15–383.15 K

	H_2O	Na^+	K^+	NH_4^+	Cl^-	SO_4^{2-}	NO_3^-
				$u_{ij}^{(0)}$ (K)			
Mn^{2+}	704.62	−97.541	−108.526	90.186	1,598.11	1,111.67	941.95
Fe^{2+}	765.58	−86.698	−107.393	2,500.0*	1,623.74	1,116.97	1,538.76
Co^{2+}	696.98	−76.939	−132.445	−14.869	1,825.10	1,116.68	1,663.40
Ni^{2+}	613.817	−22.403	−160.415	−42.437	1,646.37	1,032.19	1,254.23
Cu^{2+}	543.836	−132.551	−182.704	50.680	1,473.93	1,305.42	1,765.29
Zn^{2+}	792.116	−114.828	−189.220	−27.345	1,646.75	1,490.25	1,554.13
				$u_{ij}^{(t)}$			
Mn^{2+}	2.461	−1.060	−1.591	−1.656	16.213	12.274	10.064
Fe^{2+}	2.350	0.751	−0.723	0.00*	14.095	10.049	7.041
Co^{2+}	3.636	0.497	0.565	0.00*	10.955	12.156	16.739
Ni^{2+}	4.181	2.067	0.719	0.00*	10.785	11.975	3.213
Cu^{2+}	1.638	1.026	−0.610	0.202	13.344	8.531	12.973
Zn^{2+}	2.172	0.217	0.775	−0.071	17.102	6.019	7.064

*No experimental data were available to fit this parameter.

Table 5. UNIQUAC Volume and Surface Area Parameters for Heavy Metal Ions

	r	*q*
Mn^{2+}	3.4943	4.2932
Fe^{2+}	2.2651	4.3810
Co^{2+}	3.1219	4.2345
Ni^{2+}	3.3799	2.5409
Cu^{2+}	4.5685	5.0114
Zn^{2+}	2.5718	4.9911

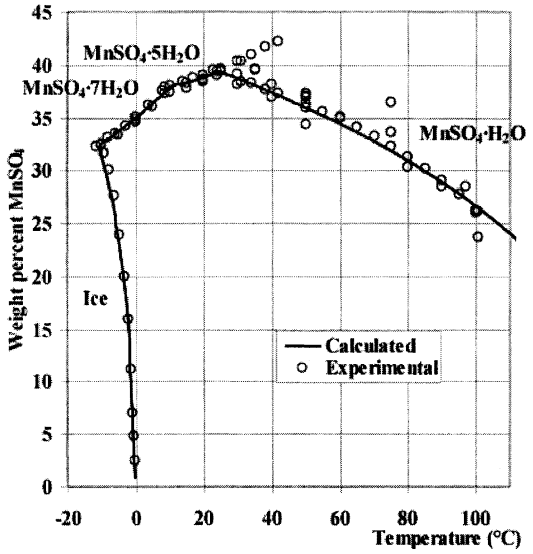

Figure 1. Solubility of $MnSO_4$ in water as a function of temperature.

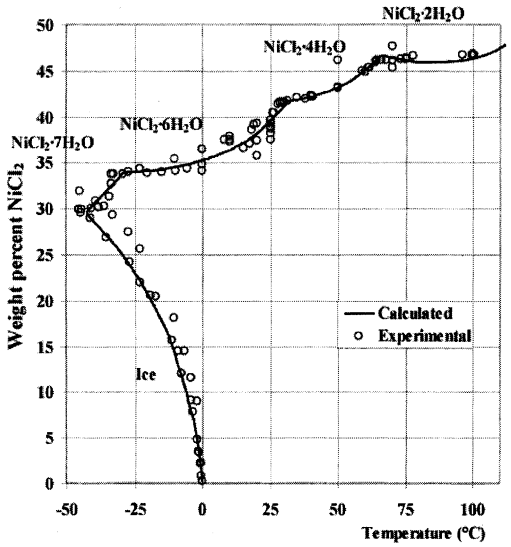

Figure 2. Solubility of $NiCl_2$ in water as a function of temperature.

$Ni(NO_3)_2$, four different hydrates are formed in the solution: nonahydrate, hexahydrate, tetrahydrate, and dihydrate. For $Fe(NO_3)_2$, only experimental data up to 60°C were found in the literature. Two hydrates are formed in the solution: nonahydrate and hexahydrate.

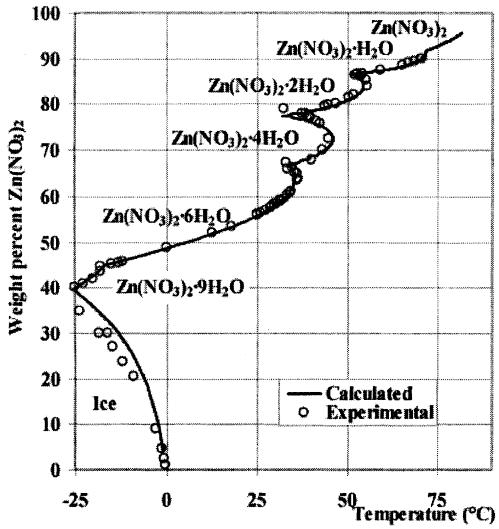

Figure 3. Solubility of $Zn(NO_3)_2$ in water as a function of temperature.

The behavior of the systems containing $Zn(NO_3)_2$ or $Mn(NO_3)_2$ is very different from the other nitrates, as is illustrated in Figure 3 for zinc nitrate. Five hydrates are formed in the solution containing zinc nitrate: nonahydrate, hexahydrate, tetrahydrate, dihydrate, and monohydrate. The corresponding hydrates, except for the nonahydrate, are also formed in aqueous manganese solutions. The aqueous $Zn(NO_3)_2$ system has five eutectic points and one peritectic point. The peritectic point is the transition point between the nonahydrate and the hexahydrate. The model is able to represent this complex behavior very accurately, as appears from Figure 3.

Ternary systems

It can be seen from Table 3 that most of the ternary experimental data belong to the systems $MSO_4 + (Na, K, or NH_4)_2SO_4 + H_2O$, $MCl_2 + (Na, K, or NH_4)Cl + H_2O$, and $MSO_4 + MCl_2 + H_2O$ (M represents the heavy metal ion). The experimental data are generally very scattered; the values of the salt solubility and the type of the solid phase precipitating in the solution differ. Reliable experimental data are lacking. Therefore, the modeling of the behavior of some of these systems was very difficult.

$MSO_4 + (Na, K, or NH_4)_2SO_4 + H_2O$. In the ternary systems $MSO_4 + Na_2SO_4 + H_2O$, at low temperatures (up to about 10–20°C) the solubility diagrams have two branches, one corresponding to $Na_2SO_4 \cdot 10H_2O$ and the other to the hydrate of the heavy metal sulphate corresponding to that temperature range (the heptahydrate for all systems except for the $CuSO_4$ system where the pentahydrate is precipitating). At higher temperatures double salts are formed in these systems. In all systems, a double salt of the type $MSO_4 \cdot Na_2SO_4 \cdot nH_2O$ is formed up to about 110°C, where $n = 2$ for

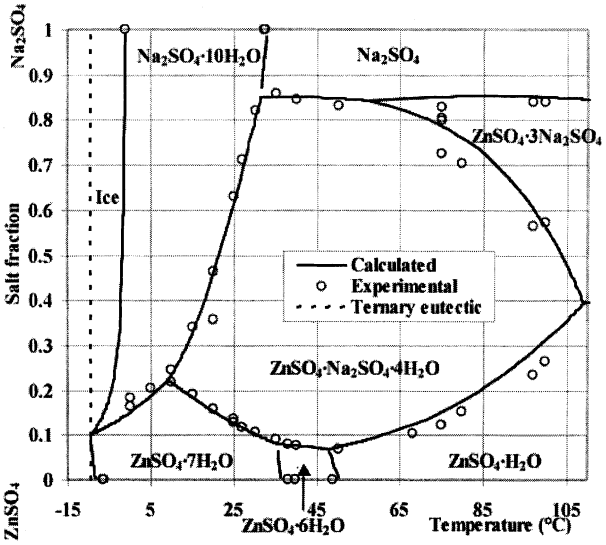

Figure 4. $ZnSO_4 + Na_2SO_4 + H_2O$ System at −10°C to 110°C.

The dashed line marks the temperature of the (calculated) ternary eutectic point (−9.6°C).

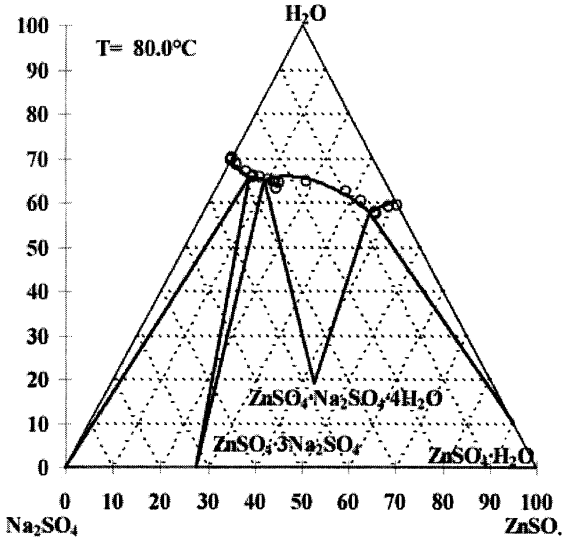

Figure 5. Solubility isotherm at 80°C for the system $ZnSO_4 + Na_2SO_4 + H_2O$.

The experimental data are from Benrath (1930); The unit is in wt. %.

the systems with M = Cu and M = Mn, and $n = 4$ for all the others. For M = Zn, M = Fe, and M = Mn a second double salt is formed, $MSO_4 \cdot 3Na_2SO_4$. The concentration and temperature range of this anhydrous double salt is much larger for M = Mn than for M = Zn and M = Fe. An example of a phase diagram showing this phase behavior in the temperature range from −20°C to 120°C is illustrated in Figure 4 for the system $ZnSO_4 + Na_2SO_4 + H_2O$. Each point on a line in the diagram marks the composition of a liquid in equilibrium with two salts. Each salt has its own field, showing the temperature and the concentration range where the salt can precipitate. Figure 5 represents a solubility isotherm for this system. The tie lines indicate the compositions of the solid phases and the concentration range within which they precipitate.

In the ternary systems $MSO_4 + K_2SO_4 + H_2O$, a double salt can form at temperatures from just below 0°C. The temperature and concentration ranges within which the double salt precipitates can be very large, as is illustrated in Figure 6 for the $NiSO_4 + K_2SO_4 + H_2O$ system. The chemical formula of the double salt is $MSO_4 \cdot K_2SO_4 \cdot nH_2O$, $n = 6$ for M = Fe, M = Co, M = Ni, and M = Zn, and $n = 2$ for M = Cu. For M = Co, it seems that a second double salt with $n = 4$ starts precipitating at about 100°C (Figure 7), but supplementary experimental data at higher temperatures are needed in order to verify this. Figures 6 and 7 and the isotherms presented in Figures 8 and 9 illustrate the behavior of two different kinds of systems. The diagram for the $NiSO_4 + K_2SO_4 + H_2O$ system at 25°C is shown in Figure 8. This diagram maintains almost the same shape at temperatures up to 110°C. The isotherm for the $CoSO_4 + K_2SO_4 + H_2O$ system at 25°C has a shape similar to this, but at 99.5°C a double salt precipitates (Figure 9). As can be seen in Figure 8, there is a strong discrepancy between data from different sources.

In the aqueous $MnSO_4 + K_2SO_4 + H_2O$ system, it seems that three different double salts can be formed. However, the experimental data coming from different sources do not agree well and they are not sufficient for a complete description of the phase diagram in the whole temperature range.

For the ternary systems $MSO_4 + (NH_4)_2SO_4 + H_2O$, experimental data covering the temperature range of interest were found only for M = Zn and M = Cu. For M = Co and M = Ni, only data at 25°C are available, and for M = Fe and M = Mn data were insufficient for a parameter estimation. For M = Zn and M = Cu, double salts with the chemical formula $MSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ precipitate in a wide temperature and concentration range. This behavior is similar to that of the corresponding systems containing K_2SO_4

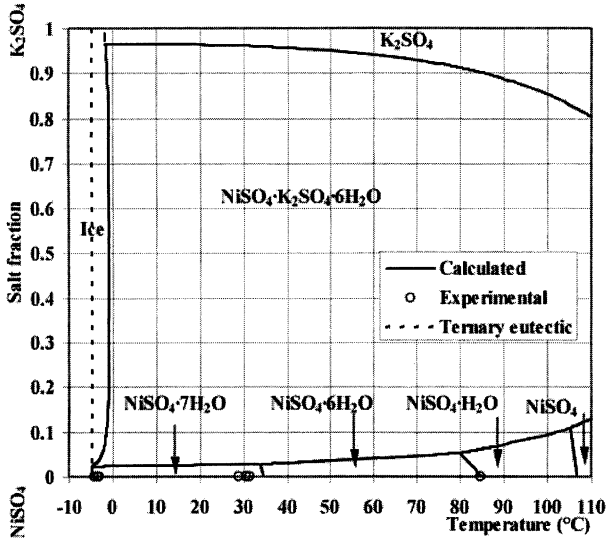

Figure 6. $NiSO_4 + K_2SO_4 + H_2O$ System at −10°C to 110°C.

The dashed line marks the temperature of the (calculated) ternary eutectic point (−4.8°C).

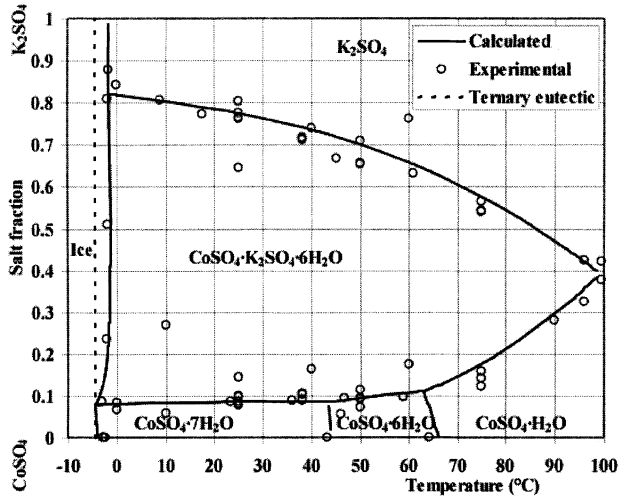

Figure 7. $CoSO_4 + K_2SO_4 + H_2O$ System at -10°C to 100°C.

The dashed line marks the temperature of the (calculated) ternary eutectic point (-4.4°C).

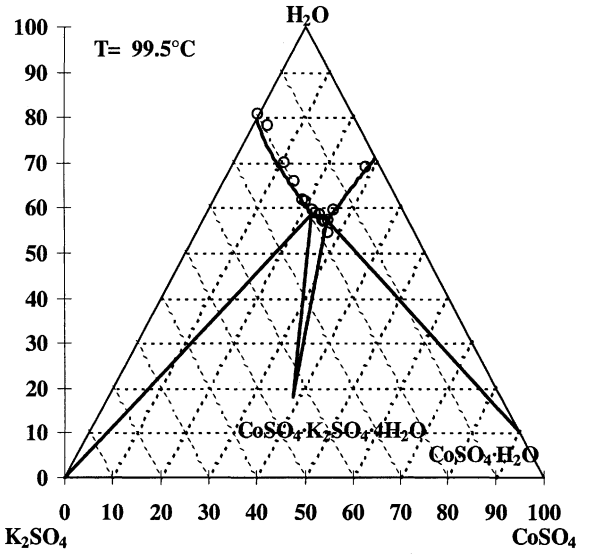

Figure 9. Solubility isotherm for the system $CoSO_4 + K_2SO_4 + H_2O$.

The experimental data are from Benrath and Ritter (1939) (in wt. %).

instead of $(NH_4)_2SO_4$. A large amount of experimental data are available for the system with M = Zn. The diagram for this system at temperatures between -20°C and 110°C is shown in Figure 10. The 35°C isotherm for the same system is presented in Figure 11.

The many experimental data for the system with M = Cu, from different sources, do not agree satisfactorily, making the parameter estimation difficult.

At 25°C, a double salt with the formula $[MSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$ is precipitating in the systems with M = Co and M = Ni and the behavior is very similar to the one observed for the zinc and copper systems.

MCl_2 + (Na, K, or NH_4)Cl + H_2O. In the ternary systems containing NaCl and a heavy metal chloride (M = Mn, Fe, or Ni) no double salt is formed at temperatures below 110°C. The phase behavior in these three systems follows a common pattern. Figure 12 shows the diagram for the $MnCl_2 + NaCl + H_2O$ system in the temperature range from -40°C to 110°C. In Figure 13 the 75°C isotherm for the same system is presented. Experimental data for the systems with M = Co and M = Cu are only available up to about 35°C, and no double salt was reported in this temperature range. Based on the available data, the present model predicts a behavior for these systems similar to the one observed for M = Mn, M = Fe, and M = Ni. However, supplementary reliable data in a wider temperature range are needed in order to check the predicted results.

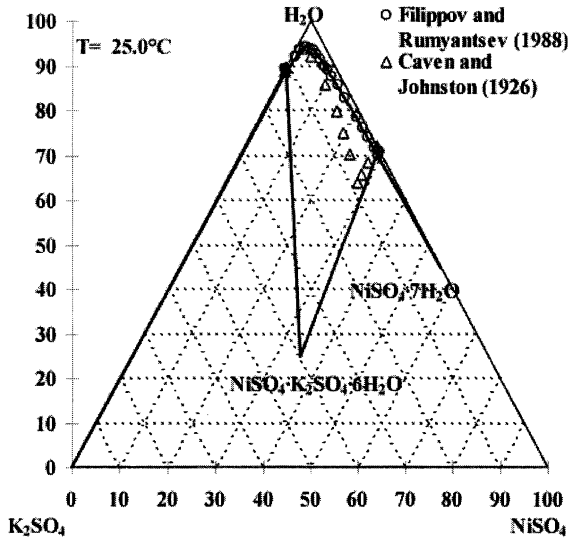

Figure 8. Solubility isotherm for the system $NiSO_4 + K_2SO_4 + H_2O$ at 25°C (in wt. %).

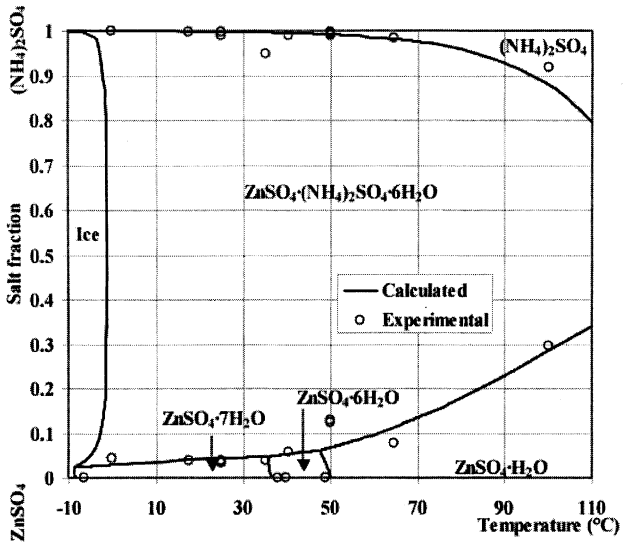

Figure 10. $ZnSO_4 + (NH_4)_2SO_4 + H_2O$ System in the temperature range from -20°C to 110°C.

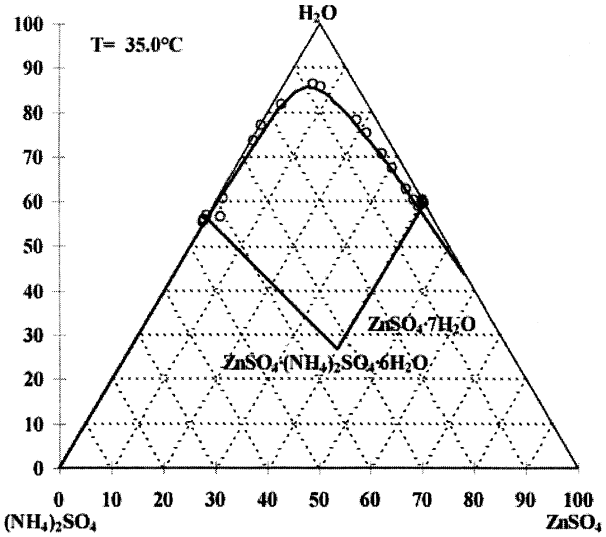

Figure 11. Solubility isotherm for $ZnSO_4 + (NH_4)_2SO_4 + H_2O$ system at 35°C.

The experimental data are from Shevchuk and Druzhinin (1958) (in wt. %).

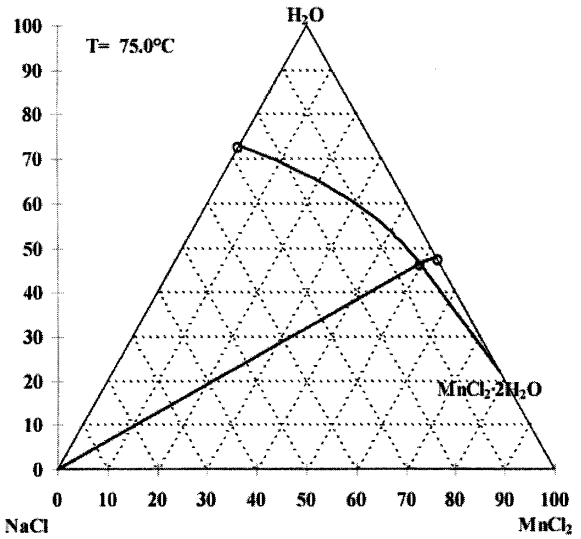

Figure 13. Solubility isotherm for $MnCl_2 + NaCl + H_2O$ system at 75°C.

The experimental data are from Petrov and Shevchuk (1979a); the unit is in wt. %.

For the system with M = Cu, Druzhinin and Kosyakina (1961) reported the formation of a double salt at 25°C, but other investigators do not report the existence of this double salt at temperatures below 35°C.

In the system with M = Zn, both double salts and solid solutions are reported in the literature. These data were not sufficient for a proper description of this system.

The behavior of the ternary systems $MCl_2 + KCl + H_2O$ was found to be very difficult to represent accurately because the data are contradictory. Various double salts and solid solutions are reported in the literature and the data are generally insufficient for a proper characterization of these salts. We therefore neglected the formation of solid solutions and some double salts that cannot be characterized. Good results were obtained for the systems with M = Fe, M = Co, and M = Cu. As an example, Figure 14 shows the phase diagram for the system $FeCl_2 + KCl + H_2O$ from −40°C to 110°C. For this system, ternary data are available between 0 and 75°C. The formation of a double salt only at 70°C by Atbir et al. (2000) was ignored, as more information is needed in order to evaluate the properties of this salt.

Only very few data were found for the systems $MCl_2 + NH_4Cl + H_2O$. For M = Ni the formation of solid solutions is

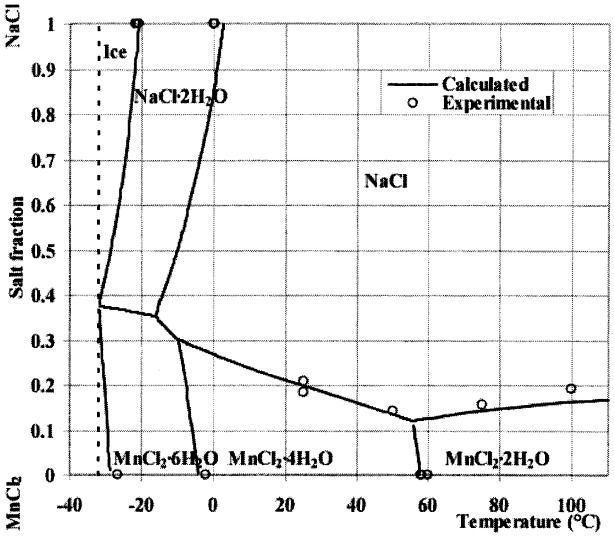

Figure 12. $MnCl_2 + NaCl + H_2O$ System at −40°C to 110°C.

The dashed line marks the temperature of the (calculated) ternary eutectic point (−31.7°C).

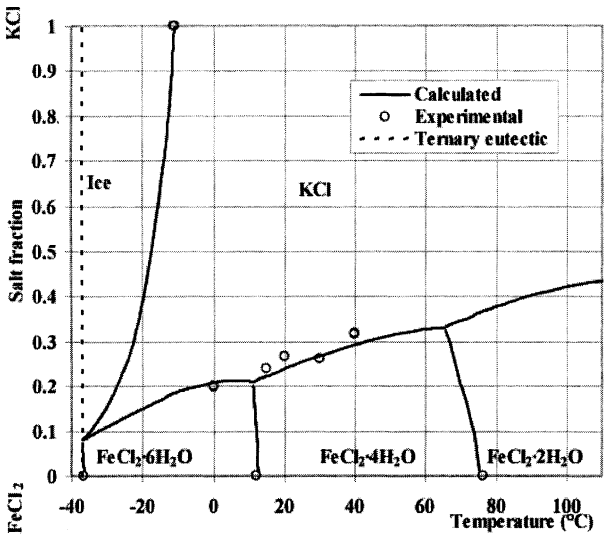

Figure 14. $FeCl_2 + KCl + H_2O$ System at −40°C to 110°C.

The dashed line marks the temperature of the (calculated) ternary eutectic point (−37.0°C).

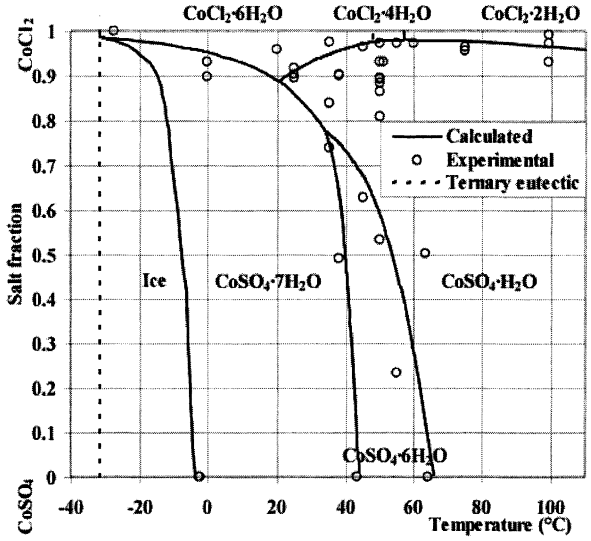

Figure 15. $CoSO_4 + CoCl_2 + H_2O$ System at −40°C to 110°C.

The dashed line marks the temperature of the (calculated) ternary eutectic point (−31.6°C).

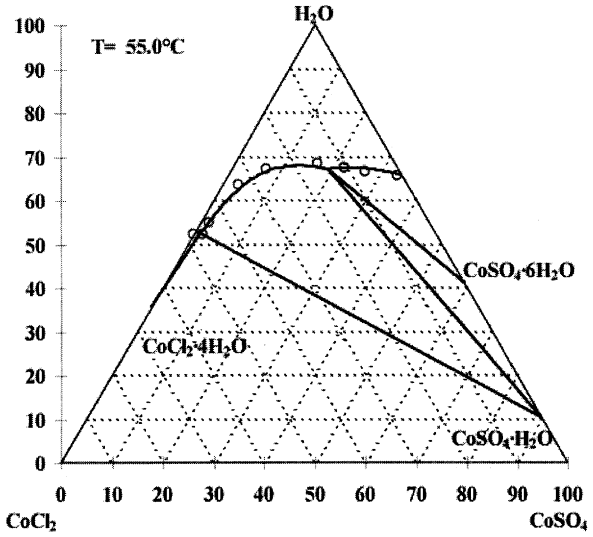

Figure 16. Solubility isotherm for the $CoSO_4 + CoCl_2 + H_2O$ system at 55°C.

The experimental data are from Bursa and Stanish-Levitska (1980); the unit is in wt. %.

reported, but we did not attempt to model solid solutions in this work. Concerning the systems with M = Mn, M = Co, and M = Fe, no data were available in the literature. For M = Cu, experimental data were only found for 30 and 40°C. This was not sufficient for a proper characterization of the two different double salts that might form at these temperatures. The same problem was encountered for M = Zn. It is possible that solid solutions form at higher temperatures in these systems, as in the system with M = Ni.

$M(NO_3)_2 + (Na,\ K,\ or\ NH_4)NO_3 + H_2O$. Only very few data for this type of system were found. It was therefore not possible to determine whether or not double salts or solid solutions form in these systems.

$MSO_4 + MCl_2 + H_2O$. Apparently no double salt is formed in ternary systems of heavy metal chlorides and sulphates. Generally, the model is able to represent the phase behavior accurately in the whole temperature range. For the $NiSO_4 + NiCl_2 + H_2O$ and $MnSO_4 + MnCl_2 + H_2O$ systems, experimental data are only available at 25°C. For the system $CuSO_4 + CuCl_2$, experimental data are available at 25 and 35°C. Figure 15 presents the phase diagram for the $CoSO_4 + CoCl_2 + H_2O$ system in the temperature range from −40°C to 110°C, and in Figure 16, the 55°C isotherm for this system is shown. It can be seen that the experimental data are rather scattered, but the model is able to represent the phase behavior with a fair accuracy.

$MSO_4 + M(NO_3)_2 + H_2O$ and $MCl_2 + M(NO_3)_2 + H_2O$. Figure 17 shows a solubility isotherm for the $CuSO_4 + Cu(NO_3)_2 + H_2O$ system at 35°C. No data were found for other systems of this type. As the model parameters for all the species present in these ternary systems are known, it can be assumed that the activities are calculated correctly for these systems. Still, information about the solid phases formed in these systems is necessary in order to perform solid–liquid-equilibrium calculations.

M_1, M_2 (SO_4, Cl, or NO_3) + H_2O. Data for ternary systems with two different heavy metal ions and either sulfate, chloride, or nitrate are scarce and vary in quality. In the $MnCl_2 + CoCl_2 + H_2O$ system, a solid solution apparently precipitates from all mixtures of the two salts at 25°C (Shevchuk and Pavlenko, 1971b). No UNIQUAC parameters for the interactions between heavy metal ions have been estimated.

Conclusion

A databank for aqueous systems containing heavy metal chlorides, nitrates, and sulphates was compiled. Many data

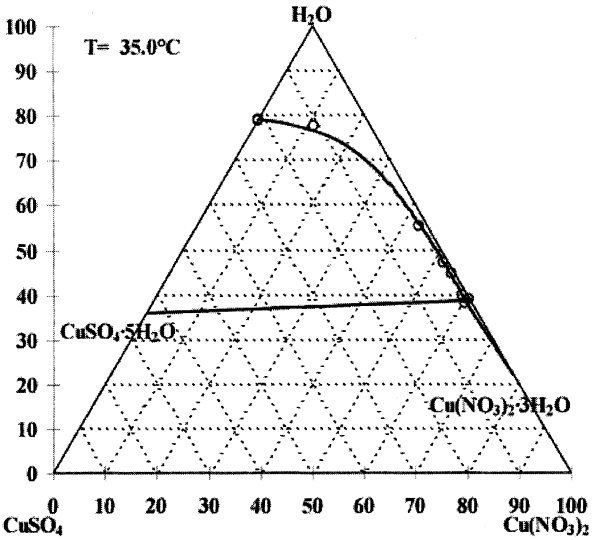

Figure 17. Solubility isotherm for the $CuSO_4 + Cu(NO_3)_2 + H_2O$ system at 35°C.

The experimental data are from Massink (1918); the unit is in wt. %.

for these systems are scattered. For many of these systems, further experimental work is necessary in order to describe their phase behavior properly.

The complex phase behavior of systems containing heavy metal sulphates, chlorides, and nitrates has been treated. The extended UNIQUAC model for electrolytes has been shown to be an adequate thermodynamic model for these systems. The model is able to represent SLE data in binary and ternary systems with a good accuracy. In some of these systems the solid phase formed is not pure, but a solid solution. We did not attempt to model solid solutions.

The model only requires binary interaction parameters. These parameters have a linear temperature dependency. Only model parameters specific to the heavy metal cations or the interaction of heavy metal cations with other species were determined.

Notation

A = Debye–Hückel parameter, $(\text{kg}\cdot\text{mol}^{-1})^{1/2}$
a_i = the activity of component i
b = Debye–Hückel parameter, $(\text{kg}\cdot\text{mol}^{-1})^{1/2}$
G^E = excess Gibbs energy, $\text{J}\cdot\text{mol}^{-1}$
ΔG^0 = increment in standard state Gibbs energy of formation, $\text{J}\cdot\text{mol}^{-1}$
I = ionic strength, $\text{mol}\cdot(\text{kg H}_2\text{O})^{-1}$
M_w = molar mass of water, $\text{kg}\cdot\text{mol}^{-1}$
q = surface-area parameter
r = volume parameter
R = gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
S = objective function
T = temperature, K
x = mole fraction
u, $u^{(0)}$ = UNIQUAC interaction parameters, K
$u^{(t)}$ = UNIQUAC interaction parameters, dimensionless

Greek letters

α = stoichiometric coefficient of anion
A = anion
γ_w = symmetrical water activity coefficient
$\gamma_i^{*,x}$ = asymmetrical rational activity coefficient for solute i
κ = stoichiometric coefficient for cation
K = cation
ν_i = stoichiometric coefficient of component i
μ_i = chemical potential of species i

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