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Solubility of Gypsum in MSO_4 Solutions (M = Mg, Mn, Co, Ni, Cu, Zn) at 298.15 K and 313.15 K

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The search for literature data in the ternary systems M^{2+}, $Ca^{2+} + SO_4^{2-} + H_2O$ (M = Mg, Mn, Co, Ni, Cu, Zn) revealed a lack of data. A reason might be the difficulties of Ca analysis at high concentrated bivalent metal solutions. The solubility of gypsum was determined in MSO_4 solutions (M = Mg, Mn, Co, Ni, Cu, Zn) over a broad concentration range at $T = 298.15$ K and $T = 313.15$ K. With increasing magnesium and heavy metal sulfate, respectively, the gypsum solubility decreases to a minimum and rises afterward to a maximum at about 1.2 mol MSO_4/kg. Above that concentration, the solubility of gypsum decreases again until saturation with MSO_4. At both temperatures and in the whole concentration range, no double salt formation was noticed. With increasing temperature, the solubility of gypsum increases also.

Introduction

Polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, a triple salt of calcium sulfate, is a common mineral in rock salt formations. In the past century, some effort has been undertaken to determine the stability field of the salt in the temperature range between $T = 298.15$ K and $T= 373.15$ K. At $T = 298.15$ K, polyhalite has only a small crystallization field, which expands with increasing temperature. Harvie et al.[1] published parameters for the Pitzer model to calculate the stability field of polyhalite in the oceanic system.

D'Ans[2] reported the existence of heavy metal substituted polyhalites $A_2SO_4 \cdot MSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ (A = K, NH_4; M = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd).

We have published recently the characterization by thermal analysis, Raman spectroscopy, and powder X-ray diffraction as well as details for the preparation of these polyhalite analogues.[3] In a next step, the fields of crystallization from aqueous solutions at ambient temperatures shall be investigated. Because crystallization of polyhalite proceeds very slowly, the experimental data will be combined with a thermodynamic model based on Pitzer's equations. For the parametrization of the model activity, data of $CaSO_4$ in solutions of the metal sulfates MSO_4 (M = Mg, Mn, Co, Ni, Cu, Zn) are needed. Solubility studies can provide such data if the thermodynamic solubility constant of the solid phase is known with sufficient accuracy, equilibration is fast enough, and formation of solid solutions can be excluded. Crystallization of gypsum $CaSO_4 \cdot 2H_2O$ fulfils these requirements in the solutions of interest.

However, few studies with scattered data exist concerning the solubility of gypsum in $MSO_4 + H_2O$ (M = Mg, Mn, Co, Ni, Cu, Zn) systems from dilute solutions until the saturation of the metal sulfate.

Umetsu et al.[4] examined the solubility of $CaSO_4$ in solutions of zinc, magnesium, copper, and cobalt sulfate over a temperature range of T = (298.15 to 473.15) K. The data consists of not more than five different metal sulfate concentrations per temperature.

For the system $Mg^{2+} + Ca^{2+} + SO_4^{2-} + H_2O$, several authors[4–12] published data in the temperature range from T = (298.15 to 328.15) K, though the majority of the data deal with dilute solutions. Cameron et al.[5] and Kolosov[9] are the only two that determined the solubility of gypsum in magnesium sulfate solutions until the saturation with $MgSO_4 \cdot 7H_2O$ at $T = 298.15$ K. Data above $T = 298.15$ K were provided by Novikova[8] at $T = 308.15$ K up to the saturation of $MgSO_4 \cdot 7H_2O$ and by Bodaleva et al.[7] at $T = 328.15$ K for gypsum and anhydrite until 2.5 mol $MgSO_4$/kg.

Table 1 summarizes the available data sources on the solubility of gypsum in heavy metal sulfate solutions. To improve the data situation, we performed solubility determinations of gypsum in solutions of $MgSO_4$, $MnSO_4$, $CoSO_4$, $NiSO_4$, $CuSO_4$, and $ZnSO_4$ at $T = 298.15$ K and $T = 313.15$ K.

Experimental Section

Materials and Solutions. All salt hydrates employed in the study ($MgSO_4 \cdot 7H_2O$ p.a. RdH; $MnSO_4 \cdot 4H_2O$ p.a. Merck; $CoSO_4 \cdot 7H_2O$ purr. ABCR; $NiSO_4 \cdot 6H_2O$ p.a. Merck; $CuSO_4 \cdot 5H_2O$ p.a. Fluka; $ZnSO_4 \cdot 7H_2O$ p.a. Fluka) were analyzed by powder X-ray diffraction and thermal analysis. The exact metal sulfate molality of the solutions used were calculated from the mass of the salt hydrate and deionized water (Seralpur Pro 90 CN) used for preparation. Calcium sulfate hemihydrate was obtained by dehydration of gypsum ($CaSO_4 \cdot 2H_2O$ p.a. Fluka) at $T = 373.15$ K for 48 h. Afterward, it was analyzed with Raman spectroscopy and DTA/TG.

Equilibration and Phase Separation. Solutions were prepared by weighing deionized water and appropriate amounts of the metal sulfate hydrates into waterproof tightly sealed bottles so that at least three-quarters of the bottle was filled with solution. Then, they were lowered into a water thermostat (type ED, Julabo Labortechnik GmbH with a stirring drive of 15, H + P Labortechnik AG) until the water covered the bottles. The metal sulfate solution was kept at least 12 h at $T = 298.15$ K and $T = 313.15$ K, respectively, before adding calcium sulfate

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Table 1. Literature Sources on Solubility of Gypsum in $MSO_4 + H_2O$ (M = Mn, Ni, Cu, Zn)

M	*T*/K	molal concentration range	data points	reference
Mn	273 to 453	dilute solutions until saturation of $MnSO_4$	89	Zhelnin et al.[13]
	298, 348	dilute solutions until saturation of $MnSO_4$	23	Korf et al.[14]
	303, 378	at 0.73 and 1.64 mol $MnSO_4$/kg	20	Farrah et al[15]
Co	298 to 473	from 0.5 until 0.7 mol $CoSO_4$/kg	40	Umetsu et al.[4]
Ni	318, 348, 363	from 0.4 until saturation of $NiSO_4$	43	Campbell et al.[16]
Cu	298 to 473	from 0.8 until 1 mol $CuSO_4$/kg	43	Umetsu et al.[4]
	298	dilute solutions until 1.0 mol $CuSO_4$/kg	5	Harkins et al.[5]
	298, 318, 333	dilute solutions until 1.0 mol $CuSO_4$/kg	18	Mutalala et al.[17]
Zn	298 to 473	from 0.15 until 1.3 mol $ZnSO_4$/kg	53	Umetsu et al.[4]
	298	dilute solutions until saturation of $ZnSO_4$	11	Hagemann[18]
	298, 318, 333	dilute solutions until 1.7 mol $ZnSO_4$/kg	21	Mutalala et al.[19]

hemihydrate, $CaSO_4 \cdot 1/2H_2O$. During equilibration the solution was stirred thoroughly with a Teflon-covered magnetic stirrer for a varying duration depending on the temperature. Samples at $T = 298.15$ K were equilibrated up to 28 days but at least 11 days. The $T = 313.15$ K samples were stirred up to 50 days but at least 28 days to ensure that gypsum and not anhydrite was the stable phase, especially in concentrated MSO_4 solutions. The temperature uncertainty was ± 0.1 K.

After equilibration stirring was stopped, the solid settled down for at least 12 h and the solution became clear. The bottles were placed on a platform inside the thermostat, so they could be opened and still be kept at the equilibrium temperature. A frit of glass fiber membrane with 0.6 μm pore size (MN 85/70, Macherey & Nagel) was lowered into the solution and then a certain mass of clear solution was separated from the solid for chemical analyses.

The solid from each sample was isolated by suction filtration, washed with (4 to 5) mL of ethanol, and air-dried. Afterward, solid phases were identified by Raman spectroscopy and powder X-ray diffraction.

Analytics. The concentrations of metal sulfate at the points where two solid phases were present (gypsum and metal sulfate hydrate) were analyzed by titration with EDTA and ErioT as indicator for all bivalent ions except nickel. The latter was determined gravimetrically as bis-[dimethylglyoximato]-nickel-(II) with dimethylglyoxim.

Calcium was determined by ICP-OES with an Optima 3000 (Perkin-Elmer), using the emission line 396.847 nm. The calcium analysis was performed by the standard addition method with inductively coupled plasma−optical emission spectroscopy (ICP-OES) to deal with every sample separately. This assures the lowest influence of nonspectral interferences, especially because the densities of the samples are very different due to the high concentration differences of the MSO_4 (M = Mg, Mn, Co, Ni, Cu, Zn). This leads to noticeable differences in the viscosity even for the relatively dilute solutions. With increasing metal sulfate concentration, the solutions have to be diluted more and more. Therefore, the amount of calcium for analysis in the diluted solutions decreases with increasing metal sulfate concentration, which is amplified by the decrease of gypsum solubility at high metal sulfate concentrations.

The measurements required dilution ratios in the range of 1:100 until 1:1000. For each data point, a blank, the sample, and two addition steps were measured. These four solutions were prepared by mass. The blank consisted of a MSO_4 (M = Mg, Mn, Co, Ni, Cu, Zn) stock solution diluted to the appropriate concentration as in the diluted sample. For the addition steps, the same weight of sample was used as for the pure diluted sample. Addition of an appropriate amount of calcium sulfate from a stock solution requires a rough estimation of the $CaSO_4$ concentration in the sample solution. For these estimations, solubility data of the $T = 298.15$ K and $T = 323.15$ K isotherm of the $Ca^{2+} + Mn^{2+} + SO_4^{2-} + H_2O$ system published by Zhelnin[13] were used.

In the first addition step, the same amount of calcium sulfate as assumed in the sample was added. In the second addition step, twice as much was added. The sample, the first addition step, and the second addition step were diluted in the same amount of water, taking into account the water added by the calcium sulfate addition.

The ICP-OES measurements were carried out at an RF power of 1300 W with a nebulizer gas flow of 0.8 L/min, an auxiliary gas flow of 0.5 L/min, and a coolant gas flow of 15 L/min.

The molality of calcium in the sample was calculated by linear regression of the measured intensities versus added calcium molality. For it, the intensity of the blank was subtracted from the sample and the two addition steps. The linear regression was completed with uncertainty estimation at 95 % probability.

Raman spectra were recorded with a FT-spectrometer RFS 100/S (Bruker). The samples were filled into holders of aluminum and measured from 1200 cm^{-1} to 350 cm^{-1} with a 1064 nm laser and a power of 75 mW at 200 accumulation cycles. The powder X-ray diffraction analysis was conducted on a D5000 (Siemens) using Cu Kα radiation in the (10 to 50)° range 2θ and a collection time of 1 s/0.02° step. The recorded patterns were matched against the PDF2-file of the International Centre for Diffraction Data and our own database. Thermal analysis was performed with a DTA/TG 22 (Seiko) using (10 to 20) mg of sample in a crucible of platinum at a heating rate of 5 K/min up to 773.15 K under nitrogen flow.

Results and Discussion

The solubility data obtained are listed in the Supporting Information and plotted in Figure 1. The error bars indicate uncertainty at 95 % probability of the Ca-analysis by the standard addition method.

As can be seen for all ternary systems the solubility of gypsum decreases at low concentrations of bivalent metal sulfate until it reaches a minimum. It then rises with increasing amount of magnesium or heavy metal sulfate to a maximum. With a further increase of metal sulfate concentration, the gypsum solubility decreases again until saturation of the added bivalent metal sulfate is reached. In the whole concentration range, no double salt formation was observed. The form of the solubility curves is the same at $T = 298.15$ K and at $T = 313.15$ K. From the diagrams, it also can be noticed that the $CaSO_4 \cdot 2H_2O$ solubility rises with temperature. In Figure 2, the effect of the various sulfates on the solubility of gypsum is compared at $T = 298.15$ K.

Systematic trends within the series of MSO_4 (M = Mn, Co, Ni, Cu, Zn) are difficult to recognize (Figure 2). The nearly coincident curves for $MnSO_4$ and $ZnSO_4$ are remarkable. The results show that gypsum solubility in $MgSO_4$ solutions is lowest and well distinguished from the other solutions. Systematic

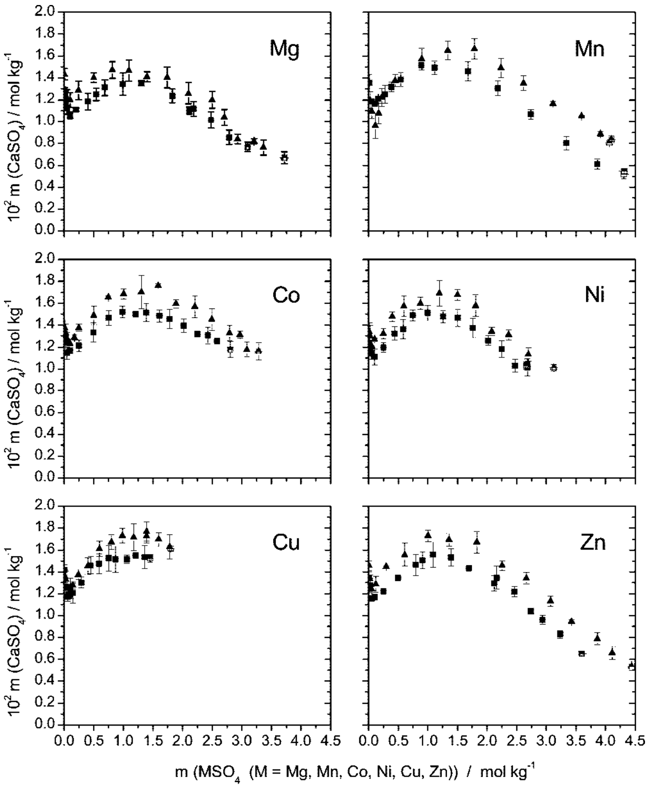

Figure 1. Molal solubility m of gypsum in $MSO_4 + H_2O$ (M = Mg, Mn, Co, Ni, Cu, Zn). Square, $T = 298.15$ K; triangle, $T = 313.15$ K; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

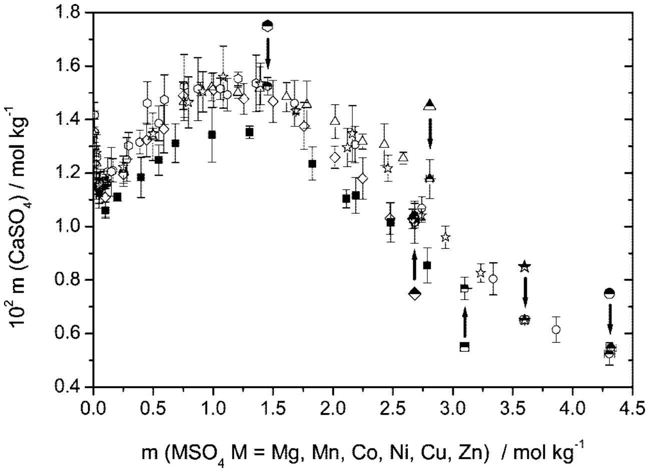

Figure 2. Molal solubility m of gypsum in $MSO_4 + H_2O$ (M = Mg, Mn, Co, Ni, Cu, Zn) at $T = 298.15$ K. Filled square, Mg; circle, Mn; triangle, Co; diamond, Ni; hexagon, Cu; star, Zn; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

errors can be excluded. The method chosen for the ICP-OES calcium analyses minimizes nonspectral and spectral interferences as much as possible. Also, the calcium wavelength applied for measurements shows no spectral interferences with any of the elements present in the samples, although the wavelength is slightly less sensitive.

Attempts to correlate the effect of different sulfates on gypsum solubility with other properties of these sulfate solutions such as the water activity yield no simple picture. Main factors influencing the $\gamma_{\pm}$ ($CaSO_4$) and a_w are the hydration abilities of the cations M^{2+} and the competing formation of the ion pairs ($CaSO_4°$) and ($MSO_4°$) (M = Mg, Mn, Co, Ni, Cu, Zn). The interplay of these factors is quite complex so that no simple variation scheme for the solubility can be figured out.

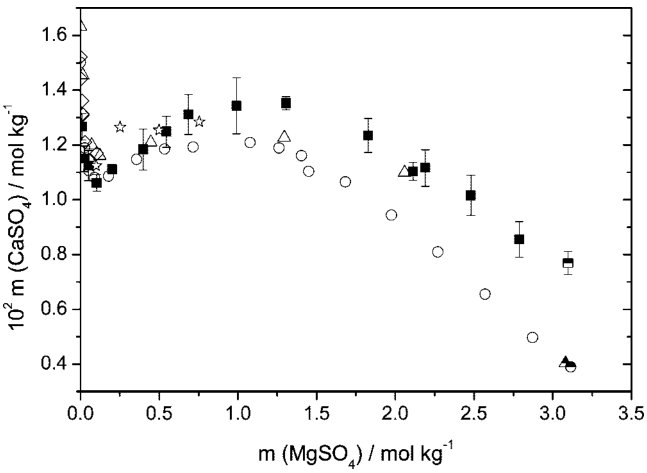

Figure 3. Molal solubility m of $CaSO_4 \cdot 2H_2O$ in magnesium sulfate solution at $T = 298.15$ K. Filled square, data this study; star, Umetsu et al.;[4] circle, Cameron et al.;[5] diamond, Harkins et al.;[6] triangle, Kolosov;[9] half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

System $Mg^{2+} + Ca^{2+} + SO_4^{2-} + H_2O$. From the literature (Cameron et al.,[5] Novikova,[8] Harkins et al.[6]), it is known that difficulties of the analysis of calcium in concentrated bivalent metal sulfate solution appear. Therefore, most of the literature data on the ternary system $Mg^{2+} + Ca^{2+} + SO_4^{2-} + H_2O$ at $T = 298.15$ K were done at dilute solutions of magnesium sulfate. In dilute solutions, the solubility curve of gypsum of all authors coincide. For higher concentrations, only Cameron et al.[5] and Kolosov[9] published data. Both differ slightly in the $CaSO_4$ concentration at the minimum of the curve and at magnesium concentrations above 1.6 mol/kg (Figure 3). Our experimental data resembles the results of Cameron et al.[5] until a $MgSO_4$ concentration of 0.4 mol/kg; above this concentration, our data points are systematically higher (Figure 3).

Cameron et al.[5] described the difficulties of Ca analysis in his paper and suggested overcoming this problem by hanging a selenite crystal into magnesium sulfate solutions and weighing the mass loss of the crystal after equilibration. Harkins et al.[6] stated some years later that the technique proposed by Cameron et al.[5] "leaves much to be desired from the standpoint of accuracy". His determinations by dissolving a selenite crystal yielded lower $CaSO_4$ concentrations in water compared with the oxalate method.

For a direct comparison of our data at $T = 313.15$ K no data are available in the literature. Novikova[8] published the gypsum solubility in the $Mg^{2+} + Ca^{2+} + SO_4^{2-} + H_2O$ system at $T = 308.15$ K, Umetsu et al.[4] at $T = 318.15$ K, and Bodaleva et al.[7] at 318.15 K. Up to 1.0 mol/kg, all data nearly coincide (Figure 4).

The data of Bodaleva et al.[7] at $T = 318.15$ K rise steeply up to 0.016 mol $CaSO_4$/kg at the maximum point and then decrease sharply. In the paper concerning the data at $T = 318.15$ K, the authors did not give any information of how the experiments were performed. They mentioned difficulties with the Ca analysis at higher $MgSO_4$ concentrations, but there is no statement about how the Ca was analyzed for the data given. Umetsu et al.[4] published molarities. Conversion of the values into molality was done with the densities given by Söhnel et al.[20]

System $Ca^{2+} + Mn^{2+} + SO_4^{2-} + H_2O$. The system $Ca^{2+} + Mn^{2+} + SO_4^{2-} + H_2O$ is the one best described in the literature of the systems investigated by us. This is due to the

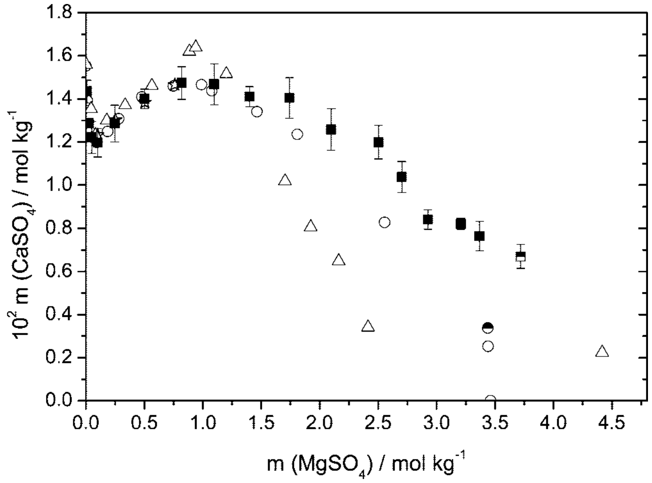

Figure 4. Molal solubility *m* of gypsum in magnesium sulfate solution at T = 313.15 K. Filled square, data this study; circle, Novikova[8] at T = 308.15 K; star, Umetsu[4] et al. at T = 318.15 K; triangle, Bodaleva et al.[7] at T = 328.15 K; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

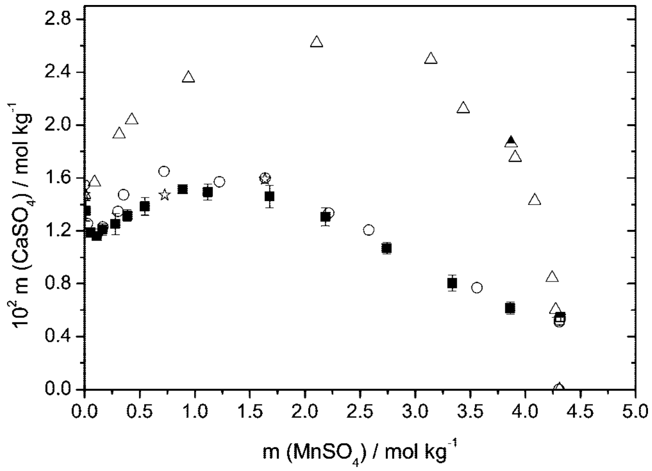

Figure 5. Molal gypsum solubility *m* in $MnSO_4$ solution at T = 298.15 K. Filled square, this study; circle, Zhelnin et at.;[13] triangle, Korf et al.;[14] star, Farrah et al.[15] at T = 303.15 K; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

extensive work of Zhelnin et al.[13] In the temperature range from T = (273.15 to 373.15) K, he studied the solubility of gypsum until saturation with manganese sulfate. Further data published by Korf et al.[14] seem not to represent equilibrium data. They are much higher than those of Zhelnin et al.[13] and no minimum can be depicted (Figure 5).

Our data are in good agreement with Zhelnin's[13] data at T = 298.15 K. The maximum appears at a higher calcium sulfate concentration in Zhelnin's data, but this is within the experimental error. Another difference occurs in the concentration range of 0.3−0.9 mol $MnSO_4$/kg. Here, the new data does not rise as steep to the maximum as the literature data. With the data of Farrah et al.[15] at T = 303.15 K, it becomes obvious that Zhelnin's data are slightly too high for this concentration range. Also, at T = 313.15 K the two data points given by Farrah et al.[15] for that temperature fall onto our solubility curve (Figure 6).

System Ca^{2+}, Co^{2+} + SO_4^{2-} + H_2O. Investigations in the Ca^{2+} + Co^{2+} + SO_4^{2-} + H_2O system have been performed only by Umetsu et al.,[4] although he determined not more than five points per temperature and not above 0.75 mol $CoSO_4$/kg. The data given by Umetsu et al.[4] are published in mol/L solution. With the $CoSO_4$ densities of Söhnel et al.,[20] the values were converted to molality.

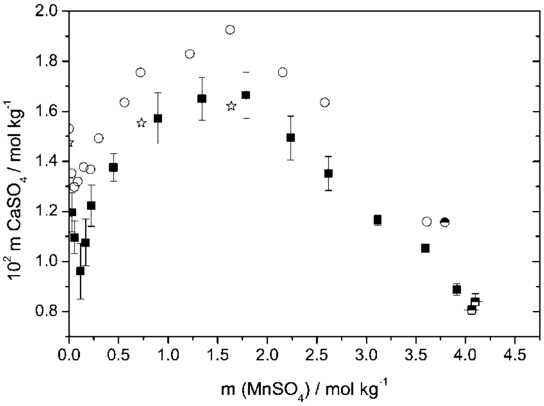

Figure 6. Molal gypsum solubility *m* in $MnSO_4$ solution at T = 313.15 K. Filled square, this study; circle, Zhelnin et at.[13] at T = 323.15 K; star, Farrah et al.[15] at T = 313.15 K; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

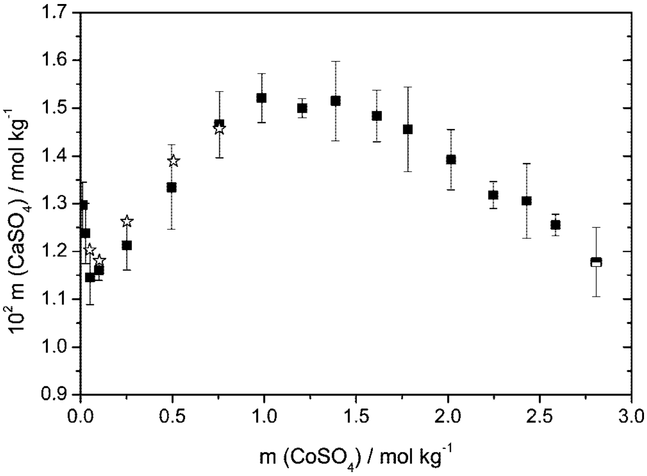

Figure 7. Molal gypsum solubility *m* in $CoSO_4$ solution at T = 298.15 K. Filled square, this study; star, Umetsu et al.;[4] half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

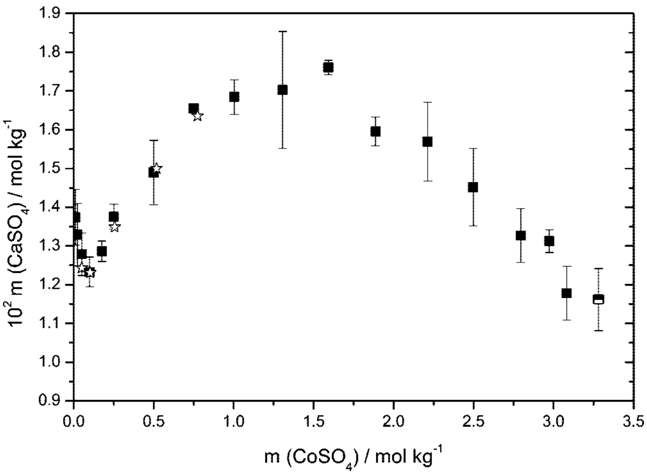

Figure 8. Molal gypsum solubility *m* in $CoSO_4$ solution at T = 313.15 K. Filled square, this study; star, Umetsu et al.[4] at T = 318.15 K; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

Figures 7 and 8 show the gypsum solubility in cobalt sulfate solution at T = 298.15 K and T = 313.15 K, respectively. Our data agree with the values of Umetsu et al.[4] within the error limits.

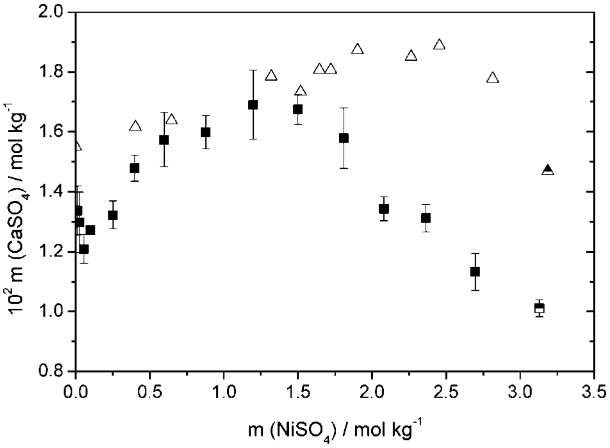

Figure 9. Molal solubility *m* of gypsum in nickel sulfate solution at T = 313.15 K. Filled square, this study; triangle, Campbell et al.[16] at T = 318.15 K; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

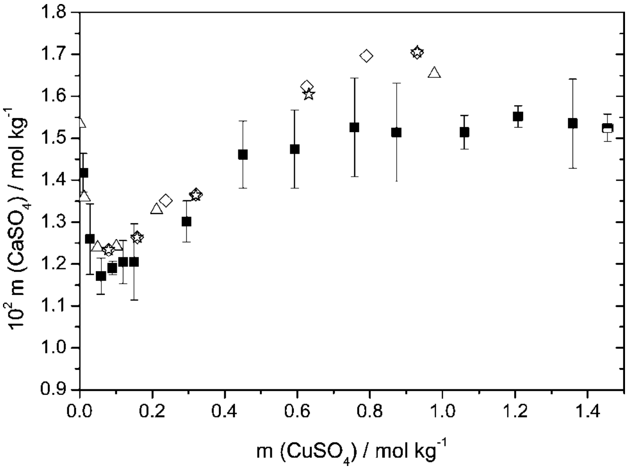

Figure 10. Molal solubility *m* of $CaSO_4 \cdot 2H_2O$ in $CuSO_4 + H_2O$ at T = 298.15 K. Filled square, this study; star, Umetsu et al.;[4] triangle, Harkins et al.;[6] diamond, Mutalala et al.;[17] half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

System $Ca^{2+} + Ni^{2+} + SO_4^{2-} + H_2O$. No data were found in the literature for T = 298.15 K. Campbell et al.[16] published data for T = 318.15 K, 348.15 K, and 363.15 K. His lowest $NiSO_4$ concentration was 0.4 mol/kg, and thus he missed the solubility minimum of gypsum (Figure 9).

Until 1.5 mol $NiSO_4$/kg, Campbell's results agree with our data. However, at higher concentrations his solubility is much too high. This is due to the method of calcium analysis used by Campbell et al.[16] Ca was analyzed gravimetrically as calcium oxalate monohydrate. It is known the bivalent metal oxalate dihydrate has a similar solubility as the calcium oxalate, and therefore the $Ni(C_2O_4) \cdot 2H_2O$ falsifies the result to higher calcium sulfate concentrations.

System $Ca^{2+} + Cu^{2+} + SO_4^{2-} + H_2O$. In the literature, three data sets are published for the solubility of gypsum in copper sulfate solutions until 1.0 mol/kg. At T = 298.15 K, Umetsu et al.,[4] Harkins et al.,[6] and Mutalala et al.[17] are in good agreement with one another (Figure 10).

The experimental results of this study differ by about 10 % from the literature data at high copper sulfate concentrations, although this might be within the uncertainty limits.

For T = 313.15 K, our data agree nearly within the experimental error with literature data at T = 318.15 K (Figure 11).

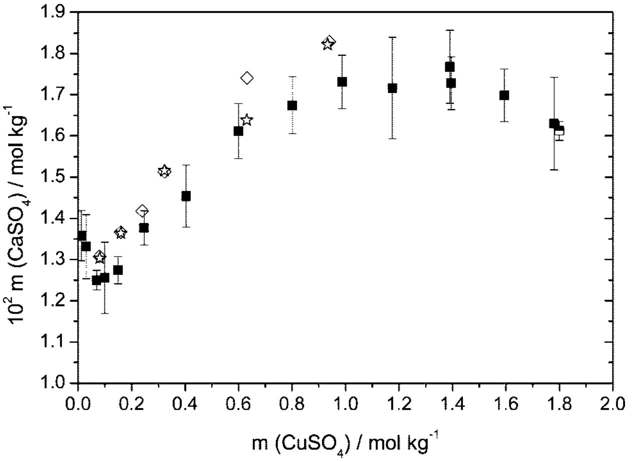

Figure 11. Molal solubility *m* of $CaSO_4 \cdot 2H_2O$ in $CuSO_4 + H_2O$ at T = 313.15 K. Filled square, this study; star, Umetsu[4] et al. at T = 318.15 K; diamond, Mutalala et al.[17] at T = 318.15 K; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

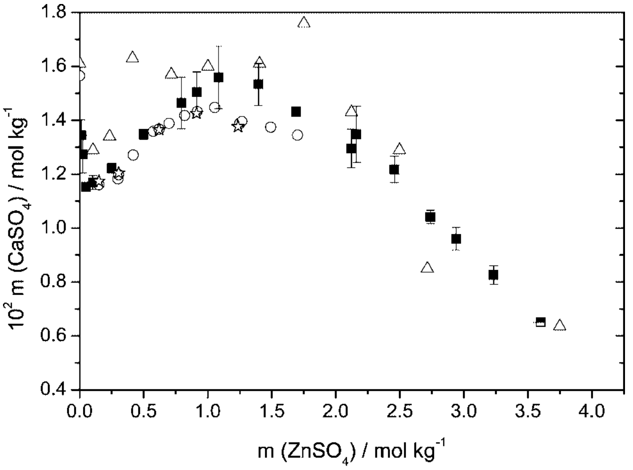

Figure 12. Molal gypsum solubility *m* in zinc sulfate solution at T = 298.15 K. Filled square, this study; star, Umetsu et al.;[4] triangle, Hagemann;[18] circle, Mutalala et al.;[19] half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

The data points given by Umetsu et al.[4] are molarities, which were converted to molalities by us using the densities of copper sulfate solutions.[20]

System $Ca^{2+} + Zn^{2+} + SO_4^{2-} + H_2O$. The system $Ca^{2+} + Zn^{2+} + SO_4^{2-} + H_2O$ was examined by Umetsu et al.,[4] Mutalala et al.,[19] and Hagemann[18] at T = 298.15 K. For higher temperatures, data are published by Umetsu et al.[4] and by Mutalala et al.[19] The data of Hagemann span until high zinc sulfate concentrations without reaching the saturation point of zinc sulfate (Figure 12).

There is considerable scatter in the data. The upper limit of Umetsu's and Mutalala's measurements is 1.7 mol $ZnSO_4$/kg. There is rough agreement between these three data sets.

Our data are in between Hageman's and Mutalala's solubility curves. For zinc sulfate solutions, up to 0.5 mol/kg good agreement with Mutalala et al.[19] can be stated.

At T = 313.15 K, no direct comparison with literature data can be done. Umetsu et al.[4] and Mutalala et al.[19] determined the gypsum solubility for T = 318.15 K.

Figure 13 shows that our data resembles the values of Umetsu et al.[4] and Mutalala et al.[19] within the error except for the last data point given in the literature.

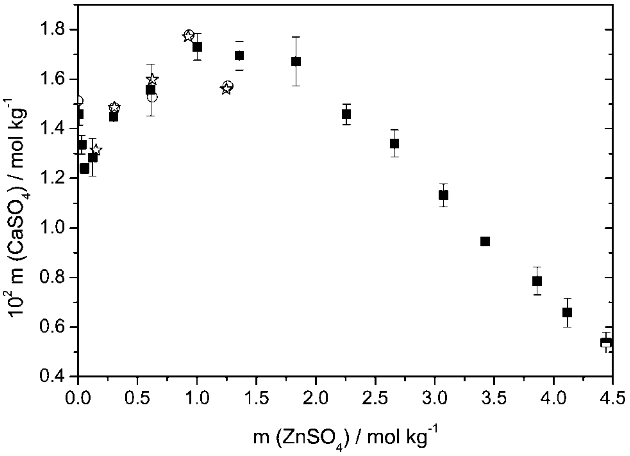

Figure 13. Molal gypsum solubility *m* in zinc sulfate solution at $T = 313.15$ K. Filled square, this study; star, Umetsu et al.[4] at $T = 318.15$ K; circle, Mutalala et al.[19] at $T = 318.15$ K; half-filled symbol, invariant point. Vertical lines indicate uncertainty at 95 % confidence limit.

Umetsu et al. published his investigations in mol/L solution. With densities by Söhnel et al.,[20] the values were converted to molalities.

Comparison of the Investigated Systems. Gypsum solubility at $T = 298.15$ K is plotted in Figure 10 for all examined systems. As can be noticed, the solubility of gypsum in the different metal sulfate systems show the same curve progression within the error bars. Only the magnesium sulfate solubility is significantly lower.

The minimum and the maximum point of the curve appear for all systems at almost the same bivalent metal sulfate concentration. At higher concentrations, a differentiation in the concentration dependence of gypsum solubility can be observed. In nickel sulfate, the gypsum solubility falls off much steeper than in the other sulfate solutions. Finally, it reaches the values for $MgSO_4$ solution. Gypsum solubility in the $MnSO_4$ and $ZnSO_4$ solutions is equal within experimental error until the highest concentrations. A systematic comparison of the solubility behavior of gypsum at high metal sulfate concentration is complicated due to very different solubility of the MSO_4 hydrates, where the curves end. Solubility behavior of gypsum at $T = 313.15$ K is essentially the same as for $T = 298.15$ K only the absolute values are higher (see also Figure 1).

Conclusions

Gypsum solubility in MSO_4 (M = Mg, Mn, Co, Ni, Cu, Zn) was determined at $T = 298.15$ K and $T = 313.15$ K. The data were obtained by isothermal saturation starting with calcium sulfate hemihydrate. Ca analysis was performed with ICP-OES using the standard addition method. The new data allow for the first time a systematic comparison of the influence of a series of bivalent metal sulfates on the solubility of gypsum. The general graph of solubility variation on MSO_4 concentration is the same for all investigated systems and at both temperatures studied. The solubility decreases first at low metal sulfate concentration until it reaches a minimum. Further increase of the bivalent metal sulfate leads to an increase of the gypsum solubility up to a maximum. Then the calcium sulfate concentration decreases with rising MSO_4 until it reaches the saturation point of magnesium sulfate and the heavy metal sulfate, respectively. No double salt formation was observed in the whole concentration range. In the solutions of $MgSO_4$ gypsum, solubility is significant lower than in all other MSO_4 solutions. The solubility of gypsum in solutions of MSO_4 (M = Mn, Co, Cu, Zn) is the same within the experimental error. For $NiSO_4$ solutions at molalities $m_{NiSO4} \geq 1.5$ mol/kg, the solubility decreases steeper and the data approach the curve in the system with $MgSO_4$. The very similar solubility curves are obviously a result of compensating effects of cation hydration and ion association on gypsum solubility.

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Supporting Information Available:

Solubility data of the determined systems $M^{2+} + Ca^{2+} + SO_4^{2-} + H_2O$ (M = Mg, Mn, Co, Ni, Cu, Zn) at $T = 298.15$ K and $T = 313.15$ K are included. This material is available free of charge via Internet at http://pubs.acs.org.

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