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Modeling of the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ ternary phase diagram between 283.15 K and 348.15 K

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ABSTRACT

A new set of ternary interaction parameters is proposed to describe the excess properties of aqueous solutions in the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ chemical system between 283.15 K and 348.15 K at $P = 101.3$ kPa, using the Pitzer formalism. The parameters were determined using a combination of (i) experimental solubility values between 283.15 K and 323.15 K coming from the literature and a new set of experimental osmotic coefficients at 298.15 K and 308.15 K, (ii) reliable solid-liquid equilibrium models based on Pitzer equations for the $\text{CoSO}_4\text{-H}_2\text{O}$ and $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ binary systems, from literature. The new interaction parameters defined in this study allow to reproduce correctly the change in the hydration state of salts with temperature ($\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{CoSO}_4\text{-nH}_2\text{O}$ with $n = 1, 6, 7$) as well as their solubility products. They also allow to accurately represent the experimental phase diagram of the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ system according to temperature.

1. Introduction

Lithium and cobalt play a crucial role in the transition to greener energy. They are among the most important metals necessary for manufacturing electric vehicle batteries, which are the largest consumers of cobalt—right after portable electronics [1,2]—and lithium. Both cobalt sulfate and lithium sulfate are salts involved in the manufacturing and recycling of lithium-ion batteries. In the recycling process, these two salts can be obtained by leaching the cathodes of batteries made of LiCoO_2 [3] with sulfuric acid. Lithium sulfate can also be extracted during the leaching of lithium ores, which contain minerals like spodumene, using the same technique [4,5]. Lithium salt is employed to obtain lithium hydroxide monohydrate [6]. Similarly, cobalt sulfate is produced as a precursor for obtaining cobalt oxide; these two (hydr-)oxides are used to produce LiCoO_2 cathodes for Li-ion batteries [7–9]. With the growing demand for lithium and cobalt driven by the development of electric vehicles and the need for better energy storage solutions, battery recycling is becoming increasingly—financially and environmentally—appealing [10–12]. Despite the fact that numerous recycling techniques already exist [8,13], there is limited data available on solid-liquid equilibria in multi-component aqueous systems containing Li- or Co-sulfates. However, investigating

such multicomponent systems is crucial for identifying the putative formation of double salts or solid solutions and designing optimized recycling processes for greener lithium-ion battery production. Part of this investigation can rely on the development of comprehensive thermodynamic models that predict the behavior of lithium and cobalt in concentrated aqueous solutions.

Most of the literature data about aqueous Li- and Co-sulfates concerns the binary systems $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{CoSO}_4\text{-H}_2\text{O}$. Sohr et al. [14] collected all the published solubility data that have been measured to describe the phase diagram of the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ system, between 250.15 and 543.15 K. Experimental osmotic coefficient data have been obtained at 298.15 K by El Guendouzi et al. [15] and Rard et al. [16], and at 323.15 K by Rard et al. [16] Holmes and Mesmer [17] also measured osmotic coefficient values at 383.14, 413.23, 443.16, 473.17 and 498.19 K.

Based on their results, Holmes and Mesmer [17] optimized values for the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{b} to model the binary interactions between Li^+ and SO_4^{2-} up to 498.19 K. The extended application of these temperature-variable parameters down to 298.15 K shows that they correctly describe the experimental osmotic coefficient measured by El Guendouzi et al. [15] and Rard et al. [16] However, the Holmes and Mesmer [17] model does not include the solubility product of the solid

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Table 1
Reagent Description Table.

Chemical name	CAS no.	Source	Purity (% mass)	Purification
Lithium sulfate monohydrate (Li ₂ SO ₄ ·H ₂ O)	10,102-25-7	Thermo Scientific	≥ 99% (supplier)	None
Cobalt sulfate heptahydrate (CoSO ₄ ·7H ₂ O)	10,026-24-1	Thermo Scientific	≥ 99% (supplier)	None
Water	7732-18-5	This laboratory	16 μS·cm ⁻²	Double reverse osmosis

Table 2

Pitzer's binary interaction parameters for CoSO₄-H₂O and Li₂SO₄-H₂O systems after Vielma's [18] model and literature on the Li₂SO₄-H₂O binary system [14–17], respectively, and the ternary interaction parameter $\theta_{Li^+,Co^{2+}}$ defined in this study. a₁-a₆ were converted from [18] to be consistent with Eq. (7).

Parameters	a ₁	a ₂	a ₃	a ₄	a ₅	a ₆
Li ₂ SO ₄ -H ₂ O system						
β ⁽⁰⁾	0.1726	0	-2.2313E-07	0	-3.5772	0
β ⁽¹⁾	73.6045	-0.2038	1.9473E-04	0	-8630.6888	0
C ^ϕ	-0.0710	0	1.0500E-07	0	16.9609	0
CoSO ₄ -H ₂ O system						
β ⁽⁰⁾	0.4534	0	0	0	-78.21	0
β ⁽¹⁾	12.3673	0	-2.2288E-05	0	-2260.9	0
β ⁽²⁾	-2588.760	-2.0540	0	0	0	552.140
C ^ϕ	-0.1086	0	0	0	40.11	0
CoSO ₄ -Li ₂ SO ₄ -H ₂ O system						
θ	3.2997	-0.0048	0	0	-545.7865	0
ψ	0	0	0	0	0	0

Table 3

Standard enthalpies of formation ΔH_f^o and standard entropies S^o of the solid hydrates and aqueous CoSO₄ at 298.15 K obtained by Vielma [18].

	CoSO ₄ ·7H ₂ O _(s)	CoSO ₄ ·6H ₂ O _(s)	CoSO ₄ ·H ₂ O _(s)	CoSO _{4(aq)}
ΔH _f ^o / kJ·Mol ⁻¹	-2979.26	-2683.79	-1214.05	-967.47
S ^o / J·Mol ⁻¹ ·K ⁻¹	403.51	363.00	127.40	-94.2

salt Li₂SO₄·H₂O, which makes it impossible to describe the solid-liquid equilibria of the Li₂SO₄-H₂O system.

Regarding the CoSO₄-H₂O binary system, Vielma [18] published a complete review gathering all the solubility data [19–21], enthalpy of dilution, enthalpy of dissolution, and experimental osmotic coefficient values [22–24] for temperatures between 270.15 and 373.15 K. Based on this exhaustive collection of experimental data, he developed a set of Pitzer binary interaction parameters for the CoSO_{4(aq)} ion pair, allowing for an accurate modeling of the solution properties. Vielma [18] also proposed standard enthalpy of formation and standard entropy for the solid salts CoSO₄·nH₂O (n = 1, 6, 7) as well as for CoSO_{4(aq)}, to describe solid-solution equilibria according to temperature.

Although the two binary phase diagrams are well documented, the temperature-dependent phase diagram of the CoSO₄-Li₂SO₄-H₂O ternary system was not thoroughly studied. Indeed, until recently, the

only data available for this ternary system were solubility values at T = 298.15 K proposed by Blidin et al. [25], Filippov et al. [26], and Shevchuk et al. [27]. The latter authors also determined two polysaturated points (i.e., the composition of the solution saturated with respect to both cobalt sulfate and lithium sulfate salts) at T = 323.15 and 348.15 K. In our previous work [28], this system was completed by measurements of the solid-liquid equilibria at 283.15, 298.15, 308.15 and 323.15 K. To our knowledge, no model has been developed to describe the phase diagram and the solution properties for this ternary system, and even less so as a function of temperature.

This work aims to model phase diagrams and solution properties of the CoSO₄-Li₂SO₄-H₂O ternary system. To do this, the model development was done in three distinct steps. i) Harmonization of the model of Vielma [18] for the CoSO₄-H₂O binary system and revision of the model of Holmes and Mesmer [17] for the Li₂SO₄-H₂O binary system. ii)

Table 4

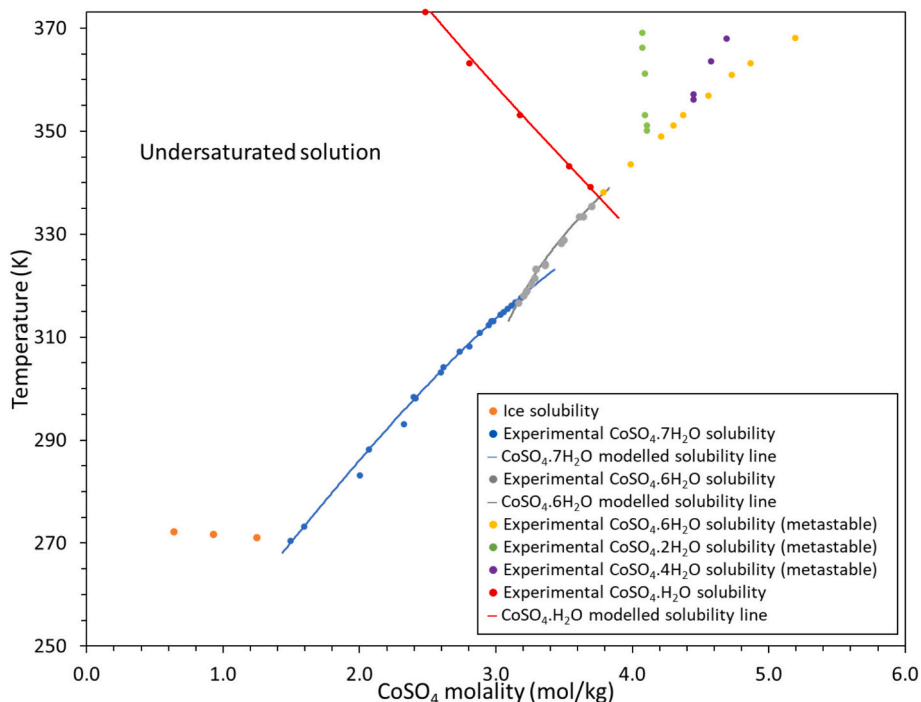
Standard properties of cobalt sulfate hydrate [18], water [35] and dissociated ions [37–39].

Species	ΔH ^o [kJ/Mol]	S ^o [J/(Mol.K)]	C _p = a + bT + c/T ² [J.(Mol.K) ⁻¹]			Ref.
			a	b	c.1e-5	
CoSO ₄ ·7H ₂ O	-2978.73	408.81	87.523	1.0187	0	18,*
CoSO ₄ ·6H ₂ O	-2683.26	368.30	64.737	1.15	0	18,*
CoSO ₄ ·H ₂ O	-1213.52	132.70	42.954	0.6619	0	18,*
Li ₂ SO ₄ ·H ₂ O	-1731.51	171.14	-342.1870	1.4180	0	*
Co ²⁺	-57.6	-107.4	1008.641	-2.104	-363.878	37,38
Li ⁺	-278.46	11.22	180.900	-0.2988	-26.769	37,41
SO ₄ ²⁻	-909.34	18.5	3273.536	-6.8171	-1335.192	37,39
H ₂ O	-285.83	69.95	74.992	0.0017	0	35

* : this work.

Table 5Log K parameters of Eq. (4) defined in this work for every stable phase encountered in $\text{CoSO}_4\text{-H}_2\text{O}$ and $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ binary system between 250.15 K and 373.15 K.

Parameters	A	B	C	D	E	Stability domain (K)
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	-1546.8283	-0.2593	79,644.3804	567.6366	-4,437,423.21	268.15–316.45
$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	-1528.0310	-0.2628	79,026.1108	561.3577	-4,437,423.21	316.45–337.35
$\text{CoSO}_4 \cdot \text{H}_2\text{O}$	-1417.9073	-0.2502	76,759.5392	518.8803	-4,437,423.21	337.35–373.15
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	-1324.1475	-0.2307	68,010.4	487.4050	-3,626,914.6655	250.15–373.15

**Fig. 1.** Zoom on the water-rich domain of the $\text{CoSO}_4\text{-H}_2\text{O}$ binary phase diagram with modeled solid-liquid equilibrium (lines) (obtained from this work) and literature solubility data [19–21] (circles).

Measurement of osmotic coefficient in the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ ternary system at 298.15 and 308.15 K. iii) Optimization of ternary interaction parameters for the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ based on the two previous steps and available experimental data [25–28]. The new model allows the plotting of the solid-liquid ternary phase diagram of the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ system at temperatures of $T = 283.15, 298.15, 308.15,$ and 323.15 K, under constant pressure $P = 101.3$ kPa.

2. Theoretical background

2.1. Excess gibbs free energy

The excess Gibbs free energy of an aqueous solution (G^{ex}) represents the difference between the Gibbs free energy of the real solution and that of the ideal solution of same composition. The derivation of this G^{ex} with respect to the water mass (w_w) or the species mole number allows obtaining the osmotic coefficient of the solution (ϕ), and the activity

coefficients of the dissolved species (γ), respectively. The Pitzer model [29] expresses G^{ex} according to a sum of terms that represent specific interactions, either binary or ternary, between aqueous species. In the present case, the chemical system is composed of two cations (Li^+ and

Table 7Calculated deviation between experimental and modeled osmotic coefficients using the Pitzer interaction parameters determined in this work for the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ binary system.

Temperature	σ_ϕ (this work)	N*
298.15	0.0047	76
325.15	0.0056	48
383.15	0.0067	30
413.15	0.0042	18
443.15	0.0031	13
473.15	0.0062	20
498.15	0.0076	16
Total	0.0054	224

* Number of experimental data used for deviation calculations (σ_ϕ).**Table 6**Calculated deviation (σ_{SI}) between measured and modeled solubilities based on the log K functions defined in this study.

Species	σ_{SI} (This work)	N*	T range (K)
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}_{(s)}$	0.0129	28	268.15–316.45
$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}_{(s)}$	0.0015	11	316.45–337.35
$\text{CoSO}_4 \cdot \text{H}_2\text{O}_{(s)}$	0.0985	5	337.35–373.15
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}_{(s)}$	0.0357	132	250.15–373.15

* Number of experimental data used for deviation calculations (σ_{SI}).

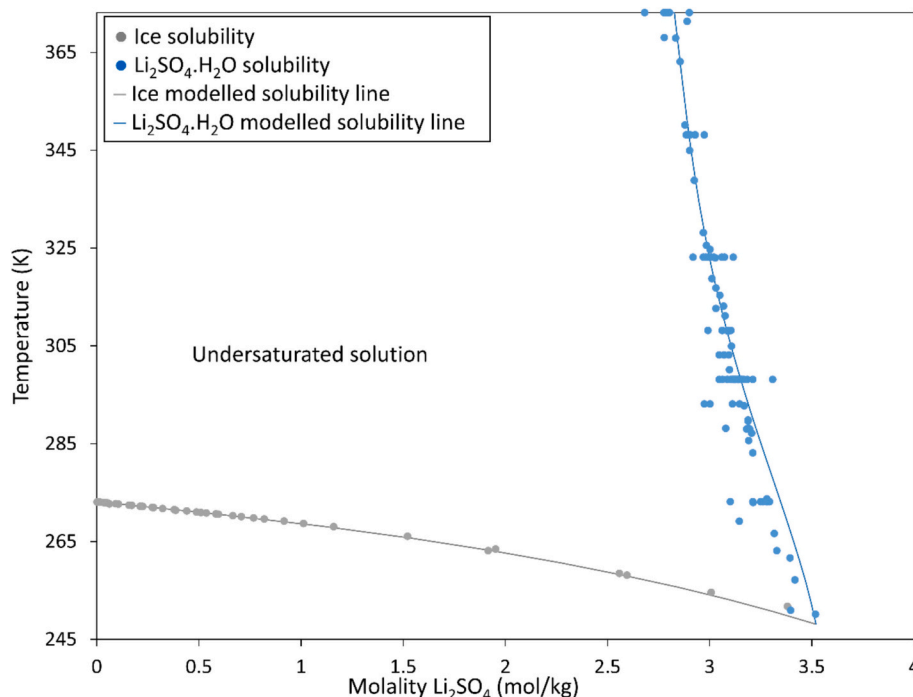


Fig. 2. Zoom on the water-rich domain of the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ binary phase diagram with modeled solid-liquid equilibrium (blue line) (obtained from this work) and literature solubility data (Sohr et al. [14] (circles)). The calculated stability line of ice (see text) is also drawn (grey line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 8

Chemical composition of the initial solutions used to measure osmotic coefficient in the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ ternary system at 298.15 and 308.15 K at $P = 101.3 \text{ kPa}^a$.

Experiment name	T (K) ^a	Molality of CoSO_4 (mol. kg^{-1}) ^b	Molality of Li_2SO_4 (mol. kg^{-1}) ^b
ISO-1	298.15	0.3189(0.0002)	1.3858(0.0008)
ISO-2		0.717(0.0003)	1.1534(0.0004)
ISO-3		0.9207(0.0004)	0.9966(0.0005)
ISO-4		1.2956(0.0008)	0.7129(0.0010)
ISO-1	308.15	0.3131(0.0003)	1.2902(0.0008)
ISO-2		0.7548(0.0003)	1.1874(0.0005)
ISO-3		1.0015(0.0005)	1.0466(0.0005)
ISO-4		1.4476(0.0009)	0.8074(0.0005)

^a : Standard uncertainties for temperature and pressure are $u(T) = 0.5 \text{ K}$ and $u(P) = 0.2 \text{ kPa}$. ^b: Absolute standard uncertainties for the molalities are indicated by 0.

Co^{2+}) and one anion (SO_4^{2-}), and G^{ex} can be expressed as follows in eq. (1):

$$\frac{G^{\text{ex}}}{w_w \times RT} = \frac{4IA_\phi}{b} \ln\left(1 + bI^{\frac{1}{2}}\right) + 2m_{\text{SO}_4^{2-}} \left[m_{\text{Li}^+} \left(B_{\text{Li}^+, \text{SO}_4^{2-}} + (m_{\text{Li}^+} + 2m_{\text{Co}^{2+}}) C_{\text{Li}^+, \text{SO}_4^{2-}} \right) + m_{\text{Co}^{2+}} \left(B_{\text{Co}^{2+}, \text{SO}_4^{2-}} + (m_{\text{Li}^+} + 2m_{\text{Co}^{2+}}) C_{\text{Co}^{2+}, \text{SO}_4^{2-}} \right) \right] + m_{\text{Li}^+} m_{\text{Co}^{2+}} \left(2\phi_{\text{Li}^+, \text{Co}^{2+}} + m_{\text{SO}_4^{2-}} \Psi_{\text{Li}^+, \text{Co}^{2+}, \text{SO}_4^{2-}} \right) \quad (1)$$

Where R is the ideal gas constant ($8.3145 \text{ J.K}^{-1}.\text{mol}^{-1}$), T is the temperature (K), A_ϕ the Debye-Hückel parameter ($\text{kg}^{\frac{1}{2}}.\text{mol}^{-\frac{1}{2}}$), I is the ionic strength ($\text{mol}.\text{kg}^{-1}$), b is a universal parameter set by Pitzer at $1.2 \text{ kg}^{\frac{1}{2}}.\text{mol}^{-\frac{1}{2}}$ [30], m_i is the molality of species i , $B_{M,\text{SO}_4^{2-}} = \beta_{M,\text{SO}_4^{2-}}^{(0)} + \beta_{M,\text{SO}_4^{2-}}^{(1)} g(\alpha_1 \sqrt{I}) + \beta_{M,\text{SO}_4^{2-}}^{(2)} g(\alpha_2 \sqrt{I})$ with $M = \text{Li}^+$ or Co^{2+} and $g(x) = \frac{2[1-(1+x)e^{-x}]}{x^2}$, $C_{M,\text{SO}_4^{2-}} = \frac{C_{M,\text{SO}_4^{2-}}^\phi}{2\sqrt{2z_M}}$ and $\phi_{\text{Li}^+, \text{Co}^{2+}} = \theta_{\text{Li}^+, \text{Co}^{2+}} + {}^E\theta_{\text{Li}^+, \text{Co}^{2+}}(I)$.

In the above equations, fixed parameters are $\alpha_1 = 2.0 \text{ kg}^{\frac{1}{2}}.\text{mol}^{-\frac{1}{2}}$ and $\alpha_2 = 0 \text{ kg}^{\frac{1}{2}}.\text{mol}^{-\frac{1}{2}}$ for 1:2 electrolytes, like Li_2SO_4 , and $\alpha_1 = 1.4 \text{ kg}^{\frac{1}{2}}.\text{mol}^{-\frac{1}{2}}$ and $\alpha_2 = 12 \text{ kg}^{\frac{1}{2}}.\text{mol}^{-\frac{1}{2}}$ for 2:2 electrolytes, like CoSO_4 .

Adjustable parameters are $\beta_{M,\text{SO}_4^{2-}}^{(0)}$, $\beta_{M,\text{SO}_4^{2-}}^{(1)}$, $\beta_{M,\text{SO}_4^{2-}}^{(2)}$, $C_{M,\text{SO}_4^{2-}}^\phi$, $\theta_{\text{Li}^+, \text{Co}^{2+}}$, and $\Psi_{\text{Li}^+, \text{Co}^{2+}, \text{SO}_4^{2-}}$.

${}^E\theta_{\text{Li}^+, \text{Co}^{2+}}$ accounts for unsymmetrical mixing effects and depends on the charges of the ions, on the ionic strength and on the solvent properties. The theory and equations for calculating this parameter are described elsewhere in the literature [29].

Solid-Liquid equilibria

The saturation index (SI) is widely used to assess the deviation from equilibrium between a given mineral and an aqueous solution. For a given reaction of mineral dissolution, it is defined by the eq. (2) below:

$$\text{SI} = \log_{10}\left(\frac{Q}{K}\right) \quad (2)$$

$Q = \prod_i a_i^{\nu_i}$ is the ion activity product (IAP), calculated from the activity of dissolved species (a_i) and their stoichiometric coefficient (ν_i). K is the equilibrium constant of the reaction, and it varies with temperature. A negative SI means that the solution is undersaturated with respect to the mineral, whereas a positive SI indicates that the solution is oversaturated. When equilibrium is reached, the activity product (IAP) is equal to the equilibrium constant (K), meaning that the saturation index is 0. For optimization purpose, the saturation index is relevant for two cases: i) to determine the equilibrium constant of a mineral when its solubility is known and the activity coefficients of the solutes are correctly calculated (the ion activity product, calculated for the chemical composition of the solution at equilibrium with the mineral, directly provides the value of the equilibrium constant) and ii) to optimize interaction parameters when the equilibrium constant is known: the target ion activity product calculated on a solid-liquid equilibrium line must match the equilibrium constant of the dissolution/precipitation reaction.

Table 9

Osmotic coefficient measured in the CoSO₄-Li₂SO₄-H₂O ternary system from DVS experiments at $T = 298.15$ K and $P = 101.3$ kPa^a.

Sample name	Relative humidity (%) RH) ^b	Li ₂ SO ₄ molality (mol.kg ⁻¹) ^c	CoSO ₄ molality (mol.kg ⁻¹) ^c	SO ₄ ²⁻ molality (mol.kg ⁻¹) ^c	ϕ ^d
ISO-1	91.8	1.6309 (0.0010)	0.3753 (0.0002)	2.0063 (0.0012)	0.84 (0.11)
ISO-1	90	1.9093 (0.0015)	0.4394 (0.0003)	2.3487 (0.0018)	0.89 (0.09)
ISO-1	88.2	2.1866 (0.0021)	0.5032 (0.0005)	2.6898 (0.0026)	0.92 (0.08)
ISO-1	85.5	2.5160 (0.0030)	0.5790 (0.0007)	3.0950 (0.0037)	1.00 (0.07)
ISO-1	83.3	2.7861 (0.0039)	0.6412 (0.0009)	3.4274 (0.0048)	1.05 (0.07)
ISO-1	81.2	3.0419 (0.0048)	0.7001 (0.0011)	3.7420 (0.0059)	1.10 (0.06)
ISO-1	79.5	3.2401 (0.0055)	0.7457 (0.0013)	3.9858 (0.0068)	1.14 (0.06)
ISO-1	80.9	3.0876 (0.0049)	0.7106 (0.0011)	3.7982 (0.0060)	1.10 (0.06)
ISO-1	82.6	2.8836 (0.0042)	0.6637 (0.0010)	3.5473 (0.0052)	1.06 (0.07)
ISO-1	84.1	2.6918 (0.0036)	0.6195 (0.0008)	3.3114 (0.0044)	1.03 (0.07)
ISO-1	85.8	2.4709 (0.0029)	0.5687 (0.0007)	3.0396 (0.0036)	0.99 (0.08)
ISO-1	87.4	2.2602 (0.0023)	0.5202 (0.0005)	2.7803 (0.0028)	0.96 (0.09)
ISO-1	89.4	2.0146 (0.0017)	0.4637 (0.0004)	2.4783 (0.0021)	0.89 (0.09)
ISO-2	89.5	1.6283 (0.0012)	1.0125 (0.0007)	2.6408 (0.0019)	0.89 (0.09)
ISO-2	87.7	1.8071 (0.0015)	1.1237 (0.0009)	2.9308 (0.0024)	0.95 (0.08)
ISO-2	86	1.9740 (0.0018)	1.2275 (0.0011)	3.2015 (0.0029)	1.00 (0.08)
ISO-2	84.2	2.1404 (0.0022)	1.3310 (0.0014)	3.4714 (0.0036)	1.05 (0.07)
ISO-2	82.5	2.2876 (0.0026)	1.4225 (0.0016)	3.7101 (0.0042)	1.10 (0.07)
ISO-2	80.9	2.4189 (0.0030)	1.5041 (0.0019)	3.9229 (0.0049)	1.15 (0.07)
ISO-2	79.1	2.5746 (0.0035)	1.6009 (0.0022)	4.1755 (0.0057)	1.19 (0.06)
ISO-2	80.7	2.4442 (0.0031)	1.5199 (0.0019)	3.9641 (0.0050)	1.15 (0.07)
ISO-2	82.4	2.3012 (0.0027)	1.4309 (0.0017)	3.7321 (0.0044)	1.10 (0.07)
ISO-2	84.1	2.1488 (0.0023)	1.3362 (0.0014)	3.4850 (0.0037)	1.05 (0.07)
ISO-2	85.7	1.9960 (0.0019)	1.2411 (0.0012)	3.2372 (0.0031)	1.01 (0.08)
ISO-2	87.4	1.8359 (0.0015)	1.1416 (0.0010)	2.9775 (0.0025)	0.96 (0.08)
ISO-2	89.1	1.6488 (0.0012)	1.0252 (0.0007)	2.6740 (0.0019)	0.92 (0.09)
ISO-3	87.9	1.5476 (0.0013)	1.4298 (0.0012)	2.9773 (0.0025)	0.95 (0.08)
ISO-3	86.2	1.6902 (0.0016)	1.5616 (0.0015)	3.2518 (0.0031)	1.01 (0.08)
ISO-3	84.5	1.8147 (0.0019)	1.6766 (0.0017)	3.4913 (0.0036)	1.06 (0.07)
ISO-3	82.8	1.9380 (0.0022)	1.7905 (0.0020)	3.7285 (0.0042)	1.12 (0.07)
ISO-3	80.9	2.0733 (0.0026)	1.9155 (0.0024)	3.9888 (0.0050)	1.17 (0.07)
ISO-3	79.2	2.1861 (0.0029)	2.0197 (0.0027)	4.2057 (0.0056)	1.22 (0.07)
ISO-3	80.8	2.0787 (0.0026)	1.9205 (0.0024)	3.9992 (0.0050)	1.17 (0.07)
ISO-3	82.3	1.9697 (0.0023)	1.8197 (0.0021)	3.7894 (0.0044)	1.13 (0.07)
ISO-3	84	1.8497 (0.0020)	1.7089 (0.0018)	3.5586 (0.0038)	1.08 (0.07)

Table 9 (continued)

Sample name	Relative humidity (%) RH) ^b	Li ₂ SO ₄ molality (mol.kg ⁻¹) ^c	CoSO ₄ molality (mol.kg ⁻¹) ^c	SO ₄ ²⁻ molality (mol.kg ⁻¹) ^c	ϕ ^d
ISO-3	85.6	1.7243 (0.0017)	1.5930 (0.0015)	3.3173 (0.0032)	1.03 (0.08)
ISO-3	89.5	1.4000 (0.0010)	1.2934 (0.0009)	2.6935 (0.0019)	0.91 (0.09)
ISO-3	91.5	1.2188 (0.0007)	1.1261 (0.0007)	2.3449 (0.0014)	0.83 (0.10)
ISO-4	91.6	0.8775 (0.0005)	1.5947 (0.0010)	2.4721 (0.0015)	0.84 (0.10)
ISO-4	90.1	0.9870 (0.0007)	1.7938 (0.0013)	2.7808 (0.0020)	0.88 (0.09)
ISO-4	87.6	1.1253 (0.0010)	2.0452 (0.0018)	3.1705 (0.0028)	0.98 (0.08)
ISO-4	85.8	1.2245 (0.0012)	2.2254 (0.0022)	3.4498 (0.0034)	1.05 (0.08)
ISO-4	83.7	1.3271 (0.0014)	2.4119 (0.0026)	3.7390 (0.0040)	1.12 (0.07)
ISO-4	81.7	1.4183 (0.0017)	2.5776 (0.0030)	3.9959 (0.0047)	1.19 (0.07)
ISO-4	79.9	1.4968 (0.0019)	2.7202 (0.0034)	4.2170 (0.0053)	1.25 (0.07)
ISO-4	81.4	1.4270 (0.0017)	2.5935 (0.0031)	4.0205 (0.0048)	1.21 (0.07)
ISO-4	83.2	1.3451 (0.0015)	2.4445 (0.0027)	3.7895 (0.0042)	1.14 (0.07)
ISO-4	85	1.2608 (0.0013)	2.2913 (0.0023)	3.5521 (0.0036)	1.08 (0.08)
ISO-4	86.8	1.1700 (0.0011)	2.1263 (0.0019)	3.2963 (0.0030)	1.01 (0.08)
ISO-4	88.6	1.0704 (0.0009)	1.9454 (0.0016)	3.0158 (0.0025)	0.95 (0.09)
ISO-4	90.6	0.9531 (0.0006)	1.7321 (0.0012)	2.6852 (0.0018)	0.87 (0.10)

^a : Standard uncertainties for temperature and pressure are $u(T) = 0.5$ K and $u(P) = 0.2$ k Pa. ^b: Standard uncertainty for RH is $u(RH) = 0.5\%$. ^c: Absolute standard uncertainties for the molalities are indicated by (). ^d: Absolute standard uncertainties for the osmotic coefficient are indicated by () and are rounded to two significant digits to ensure a meaningful level of precision.

In order to estimate the difference between calculated and measured solubility data, we computed the deviation from saturation indices for salt-solution equilibria using Eq. (3).

$$\sigma_{SI} = \sqrt{\frac{\sum (\log IAP - \log K)^2}{N}} = \sqrt{\frac{\sum (SI_{exp})^2}{N}} \quad (3)$$

In cases where the standard properties of the compounds involved in the reaction are already known, the equilibrium constant can be calculated independently from the activity model.

The reaction properties (e.g. $\log K$) depend on temperature according to Eq. (4) [31] below:

$$\log K = A + BT + \frac{C}{T} + D \log(T) + \frac{E}{T^2} \quad (4)$$

A, B, C, D and E are adjustable parameters, with T in Kelvin. More details about the form of Eq. (4) are given in supplementary information 1.

Solubility data

The model defined in this work aims at describing properties like mineral solubility in the chemical systems of interest. The corresponding experimental data used as references have been measured in previous works for the CoSO₄-H₂O binary system [19–21], for the Li₂SO₄-H₂O binary system [14] and for the Li₂SO₄-CoSO₄-H₂O ternary system [25–28]. More details about the experimental procedures, including the time required to reach equilibrium when given, are reported in Table 2a

Table 10Osmotic coefficient measured in the CoSO₄-Li₂SO₄-H₂O ternary system from DVS experiments at T = 308.15 K and P = 101.3 kPa^a.

Sample name	Relative humidity (%) RH) ^b	Li ₂ SO ₄ molality (mol.kg ⁻¹) ^c	CoSO ₄ molality (mol.kg ⁻¹) ^c	SO ₄ ²⁻ molality (mol.kg ⁻¹) ^c	Φ ^d
ISO-1	85.1	2.4725 (0.0031)	0.6001 (0.0008)	3.0726 (0.0039)	1.04 (0.08)
ISO-1	83.7	2.6810 (0.0038)	0.6507 (0.0009)	3.3317 (0.0047)	1.06 (0.07)
ISO-1	79.9	3.1346 (0.0055)	0.7608 (0.0013)	3.8954 (0.0068)	1.14 (0.06)
ISO-1	81.8	2.9249 (0.0047)	0.7099 (0.0011)	3.6347 (0.0058)	1.09 (0.07)
ISO-1	83.6	2.6957 (0.0039)	0.6542 (0.0009)	3.3500 (0.0048)	1.06 (0.07)
ISO-1	85.5	2.4512 (0.0031)	0.5949 (0.0007)	3.0462 (0.0038)	1.02 (0.08)
ISO-1	88.4	2.0761 (0.0020)	0.5039 (0.0005)	2.5800 (0.0025)	0.95 (0.09)
ISO-1	90.9	1.7631 (0.0013)	0.4279 (0.0003)	2.1910 (0.0016)	0.86 (0.10)
ISO-2	90.7	1.4202 (0.0005)	0.9031 (0.0003)	2.3233 (0.0008)	0.89 (0.10)
ISO-2	88.5	1.6678 (0.0008)	1.0605 (0.0005)	2.7283 (0.0013)	0.95 (0.09)
ISO-2	86.9	1.8294 (0.0010)	1.1632 (0.0006)	2.9925 (0.0016)	1.00 (0.08)
ISO-2	84.8	2.0342 (0.0013)	1.2935 (0.0008)	3.3277 (0.0021)	1.05 (0.07)
ISO-2	83.1	2.1962 (0.0016)	1.3964 (0.0010)	3.5926 (0.0026)	1.10 (0.07)
ISO-2	81	2.3772 (0.0019)	1.5115 (0.0012)	3.8887 (0.0031)	1.15 (0.07)
ISO-2	82.8	2.2130 (0.0016)	1.4072 (0.0010)	3.6202 (0.0026)	1.11 (0.07)
ISO-2	84.6	2.0496 (0.0013)	1.3032 (0.0008)	3.3528 (0.0021)	1.06 (0.07)
ISO-2	86.3	1.8818 (0.0011)	1.1965 (0.0007)	3.0783 (0.0018)	1.02 (0.08)
ISO-2	88.1	1.6939 (0.0008)	1.0771 (0.0005)	2.7710 (0.0013)	0.97 (0.09)
ISO-2	89.8	1.5195 (0.0006)	0.9662 (0.0004)	2.4856 (0.0010)	0.92 (0.09)
ISO-3	86	1.6640 (0.0014)	1.5923 (0.0013)	3.2563 (0.0027)	1.02 (0.08)
ISO-3	84.4	1.7921 (0.0017)	1.7149 (0.0016)	3.5070 (0.0033)	1.07 (0.07)
ISO-3	82.7	1.9339 (0.0020)	1.8506 (0.0019)	3.7845 (0.0039)	1.11 (0.07)
ISO-3	81.1	2.0514 (0.0023)	1.9630 (0.0022)	4.0144 (0.0045)	1.15 (0.07)
ISO-3	79.5	2.1737 (0.0026)	2.0800 (0.0025)	4.2537 (0.0051)	1.19 (0.06)
ISO-3	81.4	2.0327 (0.0022)	1.9451 (0.0021)	3.9777 (0.0043)	1.14 (0.07)
ISO-3	83.2	1.8996 (0.0019)	1.8177 (0.0018)	3.7173 (0.0037)	1.09 (0.07)
ISO-3	85.1	1.7547 (0.0016)	1.6791 (0.0015)	3.4338 (0.0031)	1.04 (0.08)
ISO-3	87.1	1.5792 (0.0012)	1.5111 (0.0012)	3.0903 (0.0024)	0.99 (0.08)
ISO-3	89.4	1.3791 (0.0009)	1.3196 (0.0008)	2.6987 (0.0017)	0.92 (0.09)
ISO-4	91.5	0.8616 (0.0004)	1.5448 (0.0007)	2.4064 (0.0011)	0.87 (0.11)
ISO-4	89.5	1.0079 (0.0006)	1.8071 (0.0010)	2.8150 (0.0016)	0.93 (0.09)
ISO-4	85.4	1.2239 (0.0009)	2.1944 (0.0016)	3.4184 (0.0025)	1.09 (0.08)
ISO-4	83.8	1.3300 (0.0011)	2.3847 (0.0020)	3.7147 (0.0031)	1.12 (0.08)
ISO-4	82	1.4163 (0.0013)	2.5393 (0.0023)	3.9556 (0.0036)	1.18 (0.07)
ISO-4	80.1	1.5063 (0.0015)	2.7007 (0.0027)	4.2070 (0.0042)	1.24 (0.07)

Table 10 (continued)

Sample name	Relative humidity (%) RH) ^b	Li ₂ SO ₄ molality (mol.kg ⁻¹) ^c	CoSO ₄ molality (mol.kg ⁻¹) ^c	SO ₄ ²⁻ molality (mol.kg ⁻¹) ^c	Φ ^d
ISO-4	81.9	1.4211 (0.0013)	2.5479 (0.0023)	3.9690 (0.0036)	1.18 (0.07)
ISO-4	83.4	1.3414 (0.0011)	2.4050 (0.0020)	3.7464 (0.0031)	1.14 (0.07)
ISO-4	85	1.2631 (0.0010)	2.2647 (0.0018)	3.5278 (0.0028)	1.08 (0.08)
ISO-4	86	1.2085 (0.0009)	2.1668 (0.0016)	3.3753 (0.0025)	1.05 (0.08)
ISO-4	87.7	1.1158 (0.0007)	2.0005 (0.0013)	3.1163 (0.0020)	0.99 (0.09)

^a : Standard uncertainties for temperature and pressure are u(T) = 0.5 K and u(P) = 0.2 k Pa. ^b: Standard uncertainty for RH is u(RH) = 0.5%. ^c: Absolute standard uncertainties for the molalities are indicated by (). ^d: Absolute standard uncertainties for the osmotic coefficient are indicated by () and are rounded to two significant digits to ensure a meaningful level of precision.

Table 11Osmotic coefficient measured in the CoSO₄-Li₂SO₄-H₂O ternary system from climatic chamber experiments at T = 298.15 K and P = 101.3 kPa^a.

Sample name	Relative humidity (%) RH) ^b	Li ₂ SO ₄ molality (mol.kg ⁻¹) ^c	CoSO ₄ molality (mol.kg ⁻¹) ^c	SO ₄ ²⁻ molality (mol.kg ⁻¹) ^c	Φ ^d
ISO-1	91.0	1.6896 (0.0034)	0.3999 (0.0008)	2.0895 (0.0042)	0.89 (0.16)
ISO-1	89.0	2.0429 (0.0041)	0.4835 (0.0010)	2.5264 (0.0051)	0.91 (0.13)
ISO-1	88.0	2.1553 (0.0044)	0.5101 (0.0010)	2.6654 (0.0053)	0.95 (0.13)
ISO-1	87.0	2.2737 (0.0046)	0.5382 (0.0011)	2.8119 (0.0056)	0.98 (0.12)
ISO-1	85.0	2.5393 (0.0051)	0.6010 (0.0012)	3.1403 (0.0063)	1.02 (0.11)
ISO-1	83.0	2.7978 (0.0057)	0.6622 (0.0013)	3.4600 (0.0069)	1.06 (0.11)

^a : Standard uncertainties for temperature and pressure are u(T) = 0.5 K and u(P) = 0.2 k Pa. ^b: Standard uncertainty for RH is u(RH) = 1.5%. ^c: Absolute standard uncertainties for the molalities are indicated by (). ^d: Absolute standard uncertainties for the osmotic coefficient are indicated by () and are rounded to two significant digits to ensure a meaningful level of precision.

of supplementary information 2.

Osmotic coefficients

The osmotic coefficient is a thermodynamic property used to evaluate deviations from the ideality of electrolyte solutions. It quantifies the non-ideal behavior of a solution due to the interactions between aqueous species and is particularly important to optimize interaction parameters of electrolyte solutions in geochemistry. It is related to the activity of water and the molality of solutes according to Eq. (5).

$$\Phi = -\frac{1000 \ln a_w}{M_w \sum_i \nu_i m_i} \quad (5)$$

Where a_w is the water activity, M_w is the molar mass of water (g.mol⁻¹), m_i is the molality of electrolyte i (mol.kg⁻¹), and ν_i is the number of ions resulting from the dissociation of a molecule of solute i . The uncertainties of the osmotic coefficients were calculated based on the uncertainties associated with the measurement apparatus, specifically the water activity (a_w) and the molality of the compound (m_i). However, the uncertainty in m_i was found to be negligible compared to that of a_w , and was therefore not included in the final calculation. All the experiments of this work were performed at the atmospheric pressure and therefore the water fugacity is supposed equal to the vapor partial pressure, the gases behaving as ideal gases. The detail of the relation

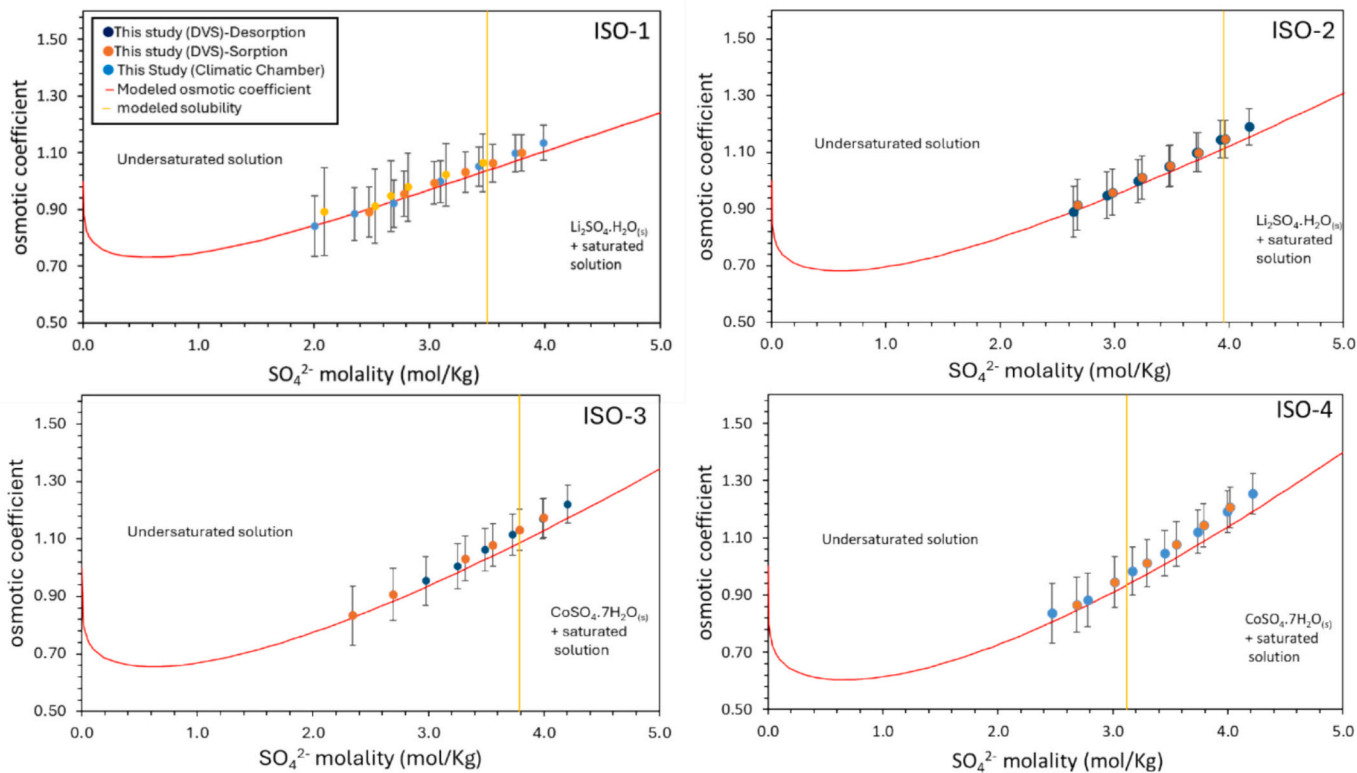


Fig. 3. Experimental (symbols) and modeled (lines) osmotic coefficient obtained in this study as a function of the sulfate molality in the ternary system $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ at $T = 298.15\text{ K}$. The vertical yellow lines show the calculated solubility limits set by equilibrium with either $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ or $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ salts (see Fig. 6). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

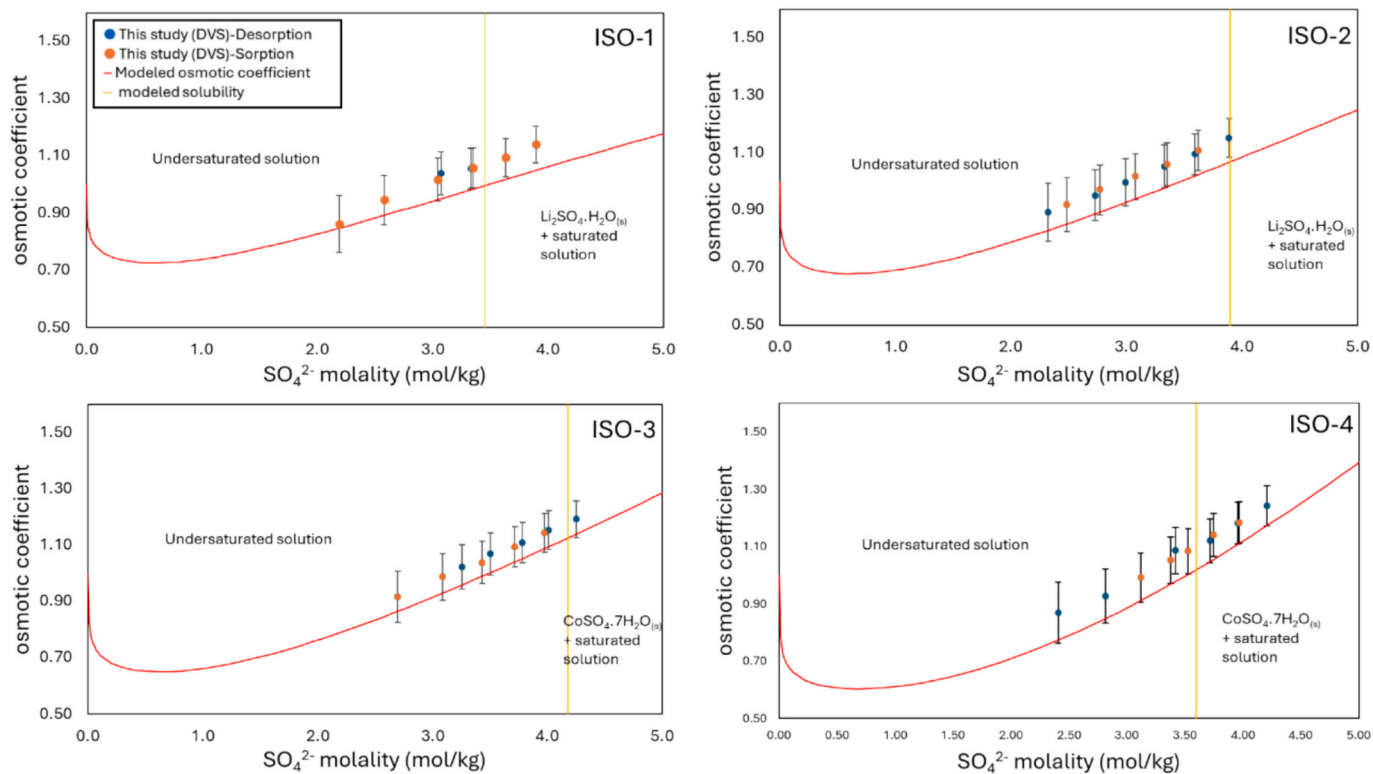


Fig. 4. Experimental (symbols) and modeled (lines) osmotic coefficient obtained in this study as a function of the sulfate molality in the ternary system $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ at $T = 308.15\text{ K}$. The vertical yellow lines show the calculated solubility limits set by equilibrium with either $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ or $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ salts (see Fig. 7). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

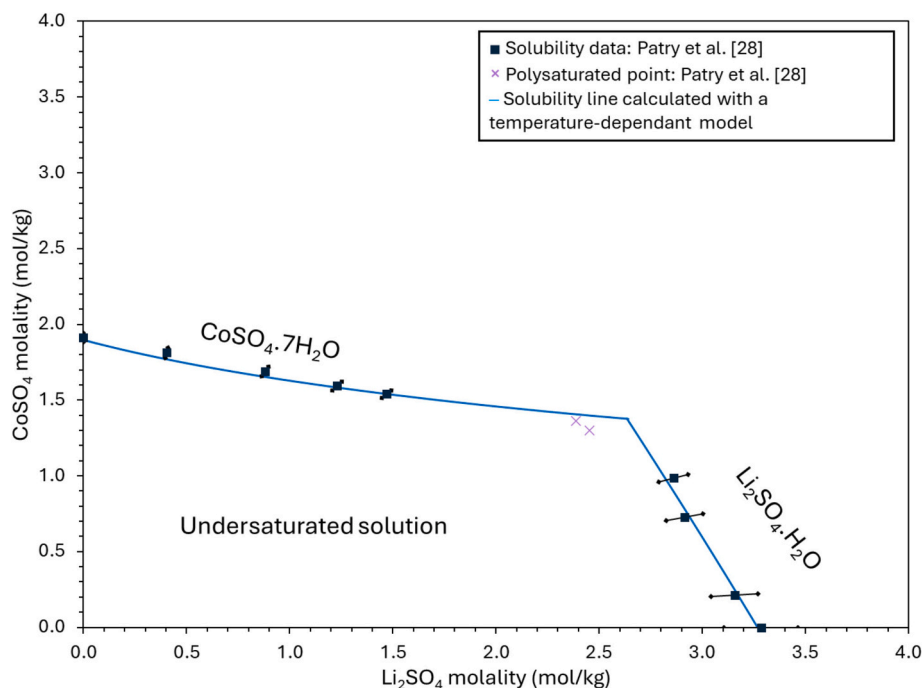


Fig. 5. Zoom on the water-rich domain of the isothermal section of the ternary phase diagram of $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ at $T = 283.15$ K.

Table 12

Calculated deviation between experimental and modeled values of solubilities (σ_{SI}) and osmotic coefficients (σ_ϕ) for the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ ternary system. Into brackets, number of experimental data used for deviation calculations. Deviation for solubility is calculated for each salt in the ternary system.

T (K)	σ_{SI} $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$	σ_{SI} $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$	σ_{SI} $\text{CoSO}_4\cdot 6\text{H}_2\text{O}$	σ_ϕ
283.15	0.1139(5)	0.0257(6)	/	/
298.15	0.0478(6)	0.0437(8)	/	0.0094(61)
308.15	0.0902(6)	0.0653(7)	/	0.0742(40)
323.15	0.0939(5)	/	0.1809(4)	/

between a_w and relative humidity (RH) can be found in supplementary information 3.

When available, experimental osmotic coefficients are used for model calibration and parameter optimization. They can serve as targets to refine model parameters, such as interaction parameters of the Pitzer model, ensuring the model reproduces the experimental osmotic behavior over concentration ranges. To quantify the agreement between calculated and experimental osmotic coefficients, the deviation is computed using Eq. (6):

$$\sigma_\phi = \sqrt{\frac{\sum (\phi_{calc} - \phi_{exp})^2}{N}} \quad (6)$$

where ϕ_{calc} and ϕ_{exp} are the calculated and experimental osmotic coefficients, respectively, and N is the number of data points.

2.2. Parameterization

The Pitzer approach, summarized in Eq. (1) uses binary and ternary interactions parameters that must be defined for each chemical system. For this, a parameterization methodology was developed based on the coupling of the geochemical calculation code PhreeSCALE [32] and the optimization software PEST [33]. This iterative method allows for quick access to the interaction parameters that will enable fitting the modeled values to experimental data.

The binary interaction parameters for the $\text{CoSO}_4\text{-H}_2\text{O}$ system are

taken from Vielma [18]. Therefore, the optimization procedure focuses on the binary system $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ and on the ternary interaction parameters θ and ψ in the ternary system. The revision of the activity model of Holmes and Mesmer [17] for $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ is justified by the fact that it was built based on osmotic coefficient data measured above 383.15 K and did not consider solubility.

The model development for the ternary system relies on solubility data coming from the literature [25–28], and on osmotic coefficient data obtained experimentally in this work. Ternary interaction parameters were first determined at a single temperature (e.g., $T = 283.15, 298.15, 308.15,$ and 323.15 K). Then, the $a_1\text{-}a_6$ coefficients of eq. (7) implemented in PhreeSCALE [32] have been regressed to describe θ and ψ , according to temperature:

$$Y(T) = a_1 + a_2T + a_3T^2 + a_4T^3 + \frac{a_5}{T} + a_6\ln(T) \quad (7)$$

This eq. (7) also applies for the binary interaction parameters $\beta_{M,\text{SO}_4}^{(0)}, \beta_{M,\text{SO}_4}^{(1)}, C_{M,\text{SO}_4}^\phi$ but differs from the temperature functions used by Vielma [18]. Thus, the corresponding coefficients needed to be converted for harmonization purposes. The relationships used to convert these temperature functions are detailed in supplementary information 4.

3. Materials and method

All concentrations in this work are given in molality units, namely moles per kilogram of water, and are noted mol.kg^{-1} .

3.1. Materials

For all experiments, $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ salt (purity $\geq 99\%$) and $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ salt (purity $\geq 99\%$), both from Thermo Scientific, were used. $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ was stored under high relative humidity (RH = 98%) to avoid partial dehydration of the compound before its use. Table 1 summarizes the chemical samples used in this work.

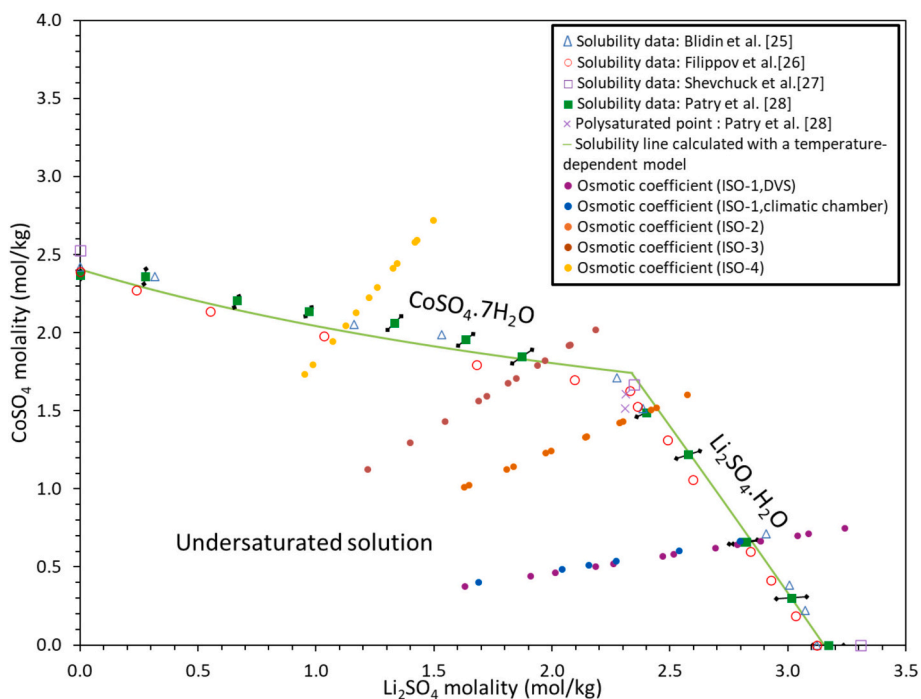


Fig. 6. Zoom on the water-rich corner of the isothermal section of the ternary phase diagram of $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ at $T = 298.15\text{ K}$.

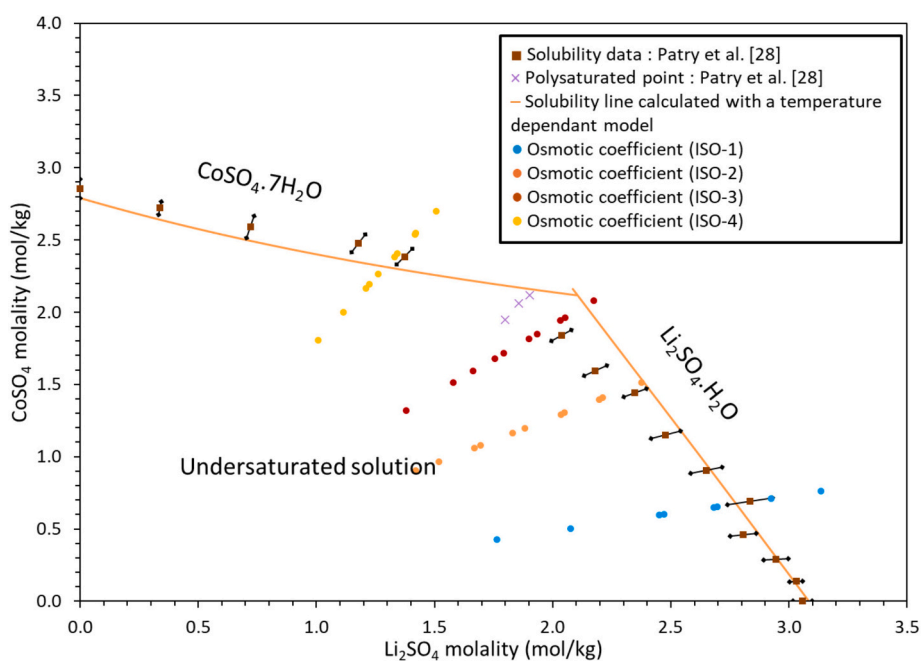


Fig. 7. Zoom on the water-rich domain of the isothermal section of the ternary phase diagram of $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ at $T = 308.15\text{ K}$.

3.2. Experimental procedure

Osmotic coefficients were determined using two complementary gravimetric sorption procedures. The first one uses a Dynamic Vapor Sorption (DVS) apparatus [34] (DVS-1, Surface Measurement Systems, UK). This instrument consists of a high-precision microbalance, with an uncertainty of $\pm 0.0005\text{ mg}$, housed within a climatic chamber that allows precise temperature control from 283.15 to 313.15 K with a ± 0.1

K uncertainty. The apparatus also includes humidity probes for real-time monitoring and regulation of the sample's humidity, and a humidity generation system capable of maintaining relative humidity (RH) between 0% and 95% , with a stated stability of $\pm 1\%$.

Prior to any experiment, water stoichiometry was checked for every hydrated solid sample using XRPD to confirm its purity. Solids and solvent used to prepare the solutions were weighed accurately, and the aqueous solutions were conditioned in a thermostated jacket at the

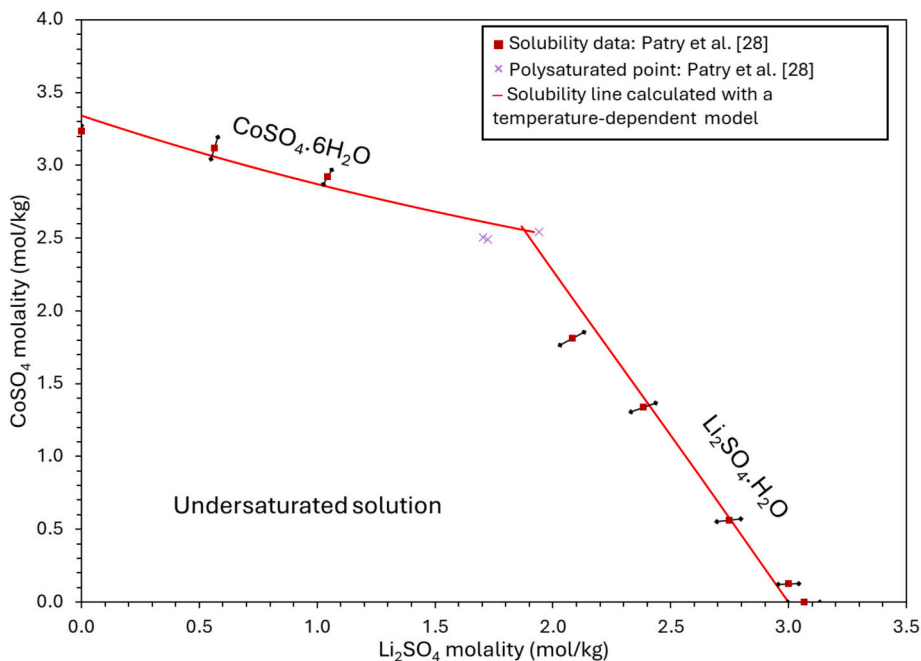


Fig. 8. Zoom on the water-rich domain of the isothermal section of the ternary phase diagram of $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ at $T = 323.15$ K.

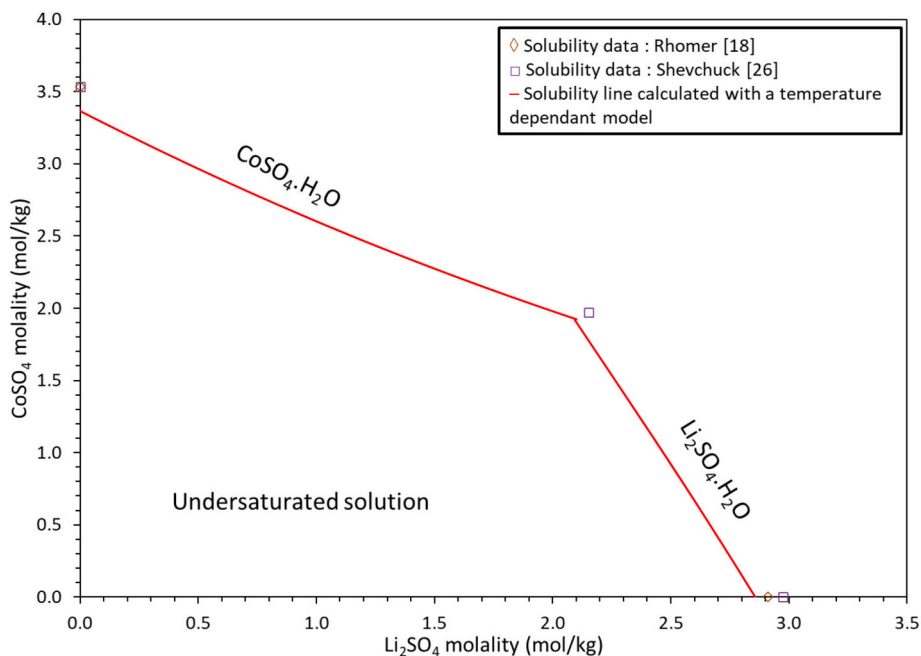


Fig. 9. Zoom on the water-rich domain of the isothermal section of the ternary phase diagram of $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ at $T = 348.15$ K.

working temperature for 24 h to ensure thermal equilibration. For each measurement, 20 to 30 mg of the aqueous solution was placed in the sample pan. A relative humidity program, consisting of both sorption (condensation) and desorption (evaporation) steps with 2% RH increments, was then applied. The specific program varied depending on the sample and temperature; however, the studied range was maintained between 77% and 93% RH. Equilibrium was considered reached when the sample mass exhibited a variation of less than $0.0005\% \cdot \text{min}^{-1}$ over a minimum period of 10 min.

In this study, and as a preliminary validation before investigating the ternary isothermal sections at various temperatures, osmotic coefficient

data have been measured on the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ binary system at 298.15 and 313.15 K. The comparison of our results with experimental and modeled data from literature (Table 5a and b, Fig. 5a and b – Supplementary information 5) shows the good consistency of the DVS measurements and the relevance of this technique for the determination of osmotic coefficient of inorganic salt solutions. These measurements could not be conducted on the binary $\text{CoSO}_4\text{-H}_2\text{O}$ system because the minimum RH required to access an equilibrium (i.e., 98%) is out of the RH stability range of the apparatus. The second gravimetric vapor sorption procedure used to get osmotic coefficient on ternary aqueous solutions consists in using a climatic chamber (C-20-350 from CTS

GmbH, Germany), whose internal volume is 350 L, and where temperature and relative humidity can be varied in the ranges 253 to 453 K, and 10 to 98%, respectively. The measured temperature and relative humidity precision are 0.3 K and 1.5%, respectively. This material allows working with volumes of solution (up to 0.5 Liter) bigger than with DVS (20 to 30 μL), but the principle of the measurement remains the same. In the climatic chamber, relative humidity and temperature are imposed above the solution, and the mass evolution is monitored with a high-precision balance (Combics 3 from Sartorius Weighing Technology GmbH, with a precision of 0.01 g) until equilibrium is reached (no more mass variation for 48 h). The samples are continuously stirred to guarantee the homogeneity of the aqueous solutions.

4. Results and discussion

4.1. Binary systems

Binary interaction parameters for the two systems ($\text{CoSO}_4\text{-H}_2\text{O}$ and $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$) are taken from literature [17,18]. Vielma [18] considered the different $\text{CoSO}_4\cdot n\text{H}_2\text{O}$ salts dissolved as $\text{CoSO}_4(\text{aq})$ ion pairs, while Holmes and Mesmer [17] considered Li_2SO_4 and $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ as completely dissociated, with no existence of chemical complexes (neither neutral nor charged) in the brines. This second assumption is maintained in the present work. Both authors proposed different expressions for the temperature-dependent equation, but as said above, Pitzer's interaction parameters for the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ binary system were re-estimated. It was thus decided to only homogenize Vielma's writing using the Eq. (7) [31], and determine our own parameters for the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ binary system. Results are displayed in Table 2.

For the $\text{CoSO}_4\text{-H}_2\text{O}$ binary system Vielma [18] proposed standard state properties for the three hydrated salts, as well as for the $\text{CoSO}_4(\text{aq})$, as detailed in Table 3.

Based on these data (Table 3), the proposed heat capacity, C_p , of $\text{CoSO}_4(\text{aq})$ ($-305 \text{ J}(\text{mol}\cdot\text{K})^{-1}$), and using the water heat capacity proposed by IAPWS [35], a first attempt was made to convert Vielma's data into a log K function that satisfies Eq. (4). This procedure is further detailed in Supplementary Information 1. The resulting log K values, as well as the corresponding phase diagram, and the solubility deviations (σ_{SI}) are presented in Supplementary Information 6 (respectively designated as Table 6a, Fig. 6a, and Table 6b).

As said above, Vielma's work was based on the hypothesis that only $\text{CoSO}_4(\text{aq})$ exists in solution, without considering the presence of the individual species Co^{2+} and SO_4^{2-} . Our approach assumes complete dissociation of the salt, meaning both ions are explicitly considered. Nevertheless, Vielma's study still provides an accurate description of the binary $\text{CoSO}_4\text{-H}_2\text{O}$ phase diagram, and it was therefore decided to adapt Vielma's log K data to a model accounting for the complete dissociation of the solid.

To achieve this, standard entropies and enthalpies of formation for Co^{2+} and SO_4^{2-} were taken from the Thermoddem database [37–39]. With these values, we recalculated the standard entropies and enthalpies of dissolution for the various hydrates, as well as the temperature-dependent equations describing their heat capacities, again based on the Maier–Kelley equation. All these data are provided in Table 4. Further details on the procedure can be seen in the supplementary information 7.

These equations impose different constraints on the temperature dependence of the log K functions in comparison to those proposed by Vielma. Taking these constraints into account required adjusting the C_p of formation of the hydrates to achieve the best fit of the model parameters.

The temperature-dependent heat capacity equations for both $\text{CoSO}_4\cdot\text{H}_2\text{O}$ and $\text{CoSO}_4\cdot 6\text{H}_2\text{O}$ have been modified. The b parameter for the C_p of the monohydrate increased from 0.4184 to 0.6619, corresponding to a

45% rise. This difference likely results from the estimation made in DeKock [40], since no experimental data were reported for this hydrate. Similarly, the b parameter for the C_p of the hexahydrate increased from 0.9656 to 1.1500 (15% rise). This may also be due to the data used in DeKock [40], as the fit was limited to the 15–330 K range, while the stability range of this phase extends from 320 to 340 K (and up to 368 K when considering metastable solubilities). This leaves a narrow temperature interval uncovered, although the extrapolation remains acceptable.

The recalculated log K values obtained in this study, based on calculations using Table 4, can be found in Table 5. These values were used to model the phase diagram shown in Fig. 1 and the solubility deviations (σ_{SI}) summarized in Table 6.

These parameters do provide a comparable fit as the one proposed by Vielma, while being assessed under the hypothesis of a complete dissociation of the dissolved salts.

This new set of temperature-dependent log K functions was used in the following to maintain consistency with previous parameterizations.

Holmes and Mesmer [17] did not consider the solubility of the hydrated lithium-sulfate salt $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ and, therefore, did not determine any log K consistent with their activity model. A first set of log K was thus determined using the selected solubility data from Sohr et al. [14] to calculate the ionic activity product and finally fit the temperature-dependent log K function of $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ over the range 230.15–373.15 K. The resulting A-E adjustable parameters of Eq. (4) gave the solubility curve representation found in supplementary information 8. One can observe that the modeled solubility data using Holmes and Mesmer's interaction parameters does not match the experimental data below 285 K. This is due, as said earlier, to the lack of use of experimental osmotic coefficients data at low temperatures for the optimization of the interaction parameters, and the lack of consideration of experimental solubility data in their fit at low temperatures. Therefore, it was decided to propose a new optimization for the interaction parameters and log K based on these parameters to propose an optimized model between 250.15 K and 373.15 K.

First, a new optimization was done using both osmotic coefficients from literature [15–17] and selected solubilities from Sohr et al. [14], which were used to add constraints on the general model but also to fill the lack of osmotic coefficients at low temperature. Using the iterative method detailed earlier, new Pitzer interaction parameters were determined (Table 2). Modeled osmotic coefficients were then compared to the experimental data (see supplementary information 9). Deviation between experimental and modeled osmotic coefficients are given in Table 7 below.

One can note that the parameters provide accurate reproducibility of the experimental osmotic coefficient data between 298.15 K and 498.15 K. The model does not lose accuracy with increasing temperature, as the errors above 373.15 K do not increase significantly.

Then, we determined log K parameters following the same methodology as the one used for Vielma's model. Standard entropies and enthalpies of formation for Li^+ and SO_4^{2-} were obtained from the Thermoddem database [37,39,41]. Based on these values, we recalculated the standard entropies and enthalpies of dissolution for the monohydrate, along with the temperature-dependent equations describing their heat capacities, again based on the Maier–Kelley equation. The complete set of data is provided in Table 4.

We calculated the heat capacities for the aqueous species Li^+ and SO_4^{2-} using the previously detailed standard entropies and enthalpies of formation from Thermoddem, and for water from IAPWS [35], all described according to the Maier–Kelley [36] expression. The recalculated log K values obtained in this study, based on calculation using Table 4, can be found in Table 5. These values were used to model the phase diagram shown in Fig. 2 and the solubility deviations (σ_{SI}) summarized in Table 6.

These parameters do provide a better fit for both osmotic coefficient and solubility data, while being assessed under the hypothesis of a complete dissociation of the dissolved salts. This new set of temperature-dependent log K is used in the following of this work.

An additional evaluation of the model was done by calculating the equilibrium line between ice and the aqueous solution at sub-zero temperatures. The temperature function of the equilibrium constant for ice was taken from the FrezChem database [42,43]. Results are in excellent agreement with experimental data (Fig. 2).

4.2. Ternary system

4.2.1. Measurement of osmotic coefficients at 298.15 and 308.15 K

For both temperatures, a set of four different chemical compositions of the initial solutions have been prepared (Table 8) (the quantity of water contained in the hydrates was accounted for calculating the salt concentrations in the stock solutions). The experimental osmotic coefficient is reported according to the equilibrium relative humidity and the corresponding sulfate molality in Table 9 and Table 10. Experimental data obtained using the climatic chamber are detailed in Table 11.

The graphical representation of these data, as well as their uncertainties, are shown in Fig. 3 at 298.15 and Fig. 4 at 308.15 K.

One can note that (i) in Fig. 3 and for ISO-1 solution, Table 11 experimental results from climatic chamber and DVS agree with each other, showing the robustness of the measurements for both techniques. (ii) Sorption and desorption processes give the same results, which demonstrates that the measurements do represent thermodynamic equilibrium, and that the technique allows access to the repeatability of the data during one experiment.

At a given temperature, we can observe that the osmotic coefficient of a mixture tends to decrease when the Co/Li concentration ratio increases. This behavior is observed at both 298 and 308 K, when moving from ISO-1 (low Co/Li ratio) to ISO-4 (high Co/Li ratio). The higher the initial concentration of CoSO_4 , the lower the osmotic coefficient. The osmotic coefficients values of the mixtures range between the osmotic coefficients measured in the binary Li_2SO_4 and CoSO_4 solutions (end-members), which is fully consistent. Furthermore, Fig. 3 and Fig. 4 show that DVS experiments made it possible to extend the measurement of osmotic coefficient in solutions that are metastable with respect to the salt solubility, which is indicated by the vertical yellow lines in the figures.

These osmotic coefficients in metastable solutions are relevant to describe osmotic coefficient evolution as they can extend the work domain for a solution that would be supposed to recrystallize at high relative humidity, such as CoSO_4 , allowing to obtain more data. (i.e. Fig. 3).

Finally, when the same experiments are performed at different temperatures, a decrease of the osmotic coefficient values can be observed as temperature increases.

4.3. Modeling solubility in the ternary system

At this stage, the binary interaction parameters and the Log K of single salts in the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{CoSO}_4\text{-H}_2\text{O}$ binary systems are known. Besides, experimental measurements of solid-liquid equilibria showed that no double salts can form in this chemical system [28]. Therefore, the remaining parameters that must be determined to complete the description of the phase diagram of the ternary system $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ are the Pitzer parameter $\theta_{\text{Li}^+, \text{Co}^{2+}}$, and $\psi_{\text{Li}^+, \text{Co}^{2+}, \text{SO}_4^{2-}}$. For this, we implemented osmotic coefficients obtained in this work, as well as solubility data already obtained [25–28], in the optimization procedure. As a result, it was found that only the $\theta_{\text{Li}^+, \text{Co}^{2+}}$ parameter was necessary to describe the solubility limits and the osmotic coefficient in the ternary system, with overall $\sigma_{SI} = 0.0869$ and $\sigma_\phi = 0.0540$. Introducing the parameter $\psi_{\text{Li}^+, \text{Co}^{2+}, \text{SO}_4^{2-}}$ did not improve the optimization results and

could therefore be set equal to 0. It was also found that $\theta_{\text{Li}^+, \text{Co}^{2+}}$ varies with temperature. Calculated osmotic coefficients are plotted in Fig. 3 at 298.15 K and in Fig. 4 at 308.15 K, where they can be compared to the experimental data points. Calculated solid-liquid equilibria are plotted in Fig. 5 ($T = 283.15$ K), Fig. 7 ($T = 298.15$ K), Fig. 8 (308.15 K), and Fig. 9 (323.15 K), where they can be compared graphically to the experimental solubility data. The detailed deviation criteria (σ_{SI} and σ_ϕ) according to temperature and nature of stable salt are summarized Table 12.

The modeled osmotic coefficients proposed at 298.15 and 308.15 K closely align with those obtained experimentally in this study, as shown in Table 12, Fig. 3 and Fig. 4. By close looking at the solubility of salts in the ternary system (Figs. 6–9), the model fits well with the experimental data. Table 12 also confirms the good accuracy with $\sigma_\phi < 0.075$. Although the fitting at 323.15 K is less accurate and increases the general σ_{SI} of the modeled ternary phase diagram, it remains within the experimental uncertainty range.

One polysaturated point was also reported at 348.15 K in the literature by Shevchuk et al. [27] Although there is not as many data points as in the other isothermal cuts, the polysaturated point proposed in the literature is pertinent enough to model both solubility lines in this isothermal cut. Fig. 9 shows the solubility model and the existing experimental data for comparison.

As seen in Fig. 9, the experimental data obtained from the literature are enough to build an extrapolated phase diagram. Here, with the help of Pitzer's equation, the proposed model seems to be consistent, at least with the only point we have at our disposal, but acquiring new data to validate it would confirm our approach.

5. Conclusion

An experimental determination of the osmotic coefficients in the $\text{CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ ternary system was successfully performed at 298.15 K and 308.15 K using gravimetric vapor sorption methods. Combined with literature binary parameters and solubility data, these new measurements enabled the optimization of ternary Pitzer interaction parameters $\theta_{\text{Li}^+, \text{Co}^{2+}}$ and $\psi_{\text{Li}^+, \text{Co}^{2+}, \text{SO}_4^{2-}}$ providing accurate predictions of solubilities and osmotic coefficients from 283.15 K to 323.15 K. The model also reproduces polysaturated equilibria at 348.15 K, confirming its robustness across a wide temperature range.

Further refinement using complementary thermodynamic data (e.g., heat capacities, enthalpies of dilution and of dissolution) could enhance parameter reliability. Extending the approach to acidic systems such as $\text{H}_2\text{SO}_4\text{-CoSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ would also improve the modeling of sulfuric acid leaching conditions relevant to lithium-ion battery recycling.

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CRedit authorship contribution statement

Nino Patry: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Arnault Lassin:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization. **Laurent André:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization. **Nicolas Couvrat:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization. **Yohann Cartigny:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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