Experimental and numerical study of the chemical behavior of the ternary $CoSO_4$-Li_2SO_4-H_2O system

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Cobalt sulfate and lithium sulfate are two of the main compounds obtained from the recycling of Lithium-ion batteries (LiB). Leaching is used to extract metals from the used batteries, but these methods require: i) high quantity of solvent and ii) expensive costs for neutralizing the acid. Multiple alternative recycling methods have already been proposed [1], but the cost is still too high compared to extracting raw materials [2].

The improvement of previous methods or the development of new alternative methods for recycling LiB after leaching require an improved knowledge of the physico-chemical properties of these solutions and a better understanding of their chemical behavior. The approach adopted in this study combines thermodynamic modelling, based on the Pitzer model [3], and experimental data acquisition. Thus, new experimental thermodynamic data, such as solubilities, solution and dilution enthalpies, heat capacities and osmotic coefficient have been measured to help developing a reliable thermodynamic model for the $CoSO_4$-Li_2SO_4-H_2O system.

During this study, solubilities have been determined by Discontinuous Isoperibolic Thermal Analysis (DITA) [4] and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Dynamic Vapor Sorption (DVS) experiments were carried out to characterize hydrated solid forms and to obtain osmotic coefficients. Calorimetric measurements have been performed to obtain solution and dilution enthalpies as well as heat capacities of $CoSO_4$ and Li_2SO_4 aqueous solutions. In parallel, InSitu-X-Ray Diffraction measurements (InSituX®) [5] were used to describe and characterize the rich landscape of hydrates of the binary phase diagram $CoSO_4$–H_2O.

All these experimental data contribute to the calibration of the Pitzer model, i.e. the determination of the specific interaction parameters between solutes. In a first step, the binary cation-anion parameters are determined allowing description of the osmotic coefficient of both binary systems. In a second step, ternary interaction parameters are optimized to calculate the salt-solution equilibria in the ternary phase diagram $CoSO_4$-Li_2SO_4-H_2O. The temperatures we investigated so far range between 25 and 35°C and should be extended to higher values.

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