

Solubility and related properties in hydrometallurgy^{*,**}

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Abstract: Thermodynamically consistent models based on accurately measured data are required for reliable predictions of equilibria and thermodynamic properties for a wide variety of multicomponent, multiphase systems and reactions relevant to hydrometallurgy. Recent developments in our laboratory concerning the measurement and modeling of physicochemical properties of electrolyte solutions over wide ranges of conditions are reviewed. Particular emphasis is on applications to the refining of alumina via the Bayer process, in which various solubility phenomena involving solid, aqueous, and gaseous phases are of critical importance to product yield and purity as well as to economical and environmental sustainability. Appropriately designed models and software allow these aspects to be tackled by thermodynamic process simulations of alumina refinery circuits.

Keywords: aqueous solutions; density; heat capacity; high pressure; high temperature; modeling; solubility; thermodynamics.

INTRODUCTION

In the industrial context, the modeling of physicochemical properties of systems involving electrolyte solutions, including solubilities, is worryingly unsatisfactory. This is mainly because the models employed by industry are often purely empirical in nature, requiring that their parameters be determined by regression of data which have in general been measured on multicomponent solutions. Such models show a high degree of parameter correlation, leading to error propagation and consequent failures when attempts are made to extrapolate to smaller subsystems or beyond the ranges of parameterization. This behavior complicates process simulations that depend critically on solution properties.

Solubility is a key thermodynamic property for numerous hydrometallurgical processes, many of which contribute significantly to the world economy. In Australia, for example, the alumina industry is a major contributor to export income, earning in excess of A\$7 billion per annum. The refining of alumina from bauxite ores, which are found in abundant deposits in Australia and elsewhere, occurs via the Bayer process. This hydrometallurgical process is employed worldwide and, in brief, involves a circuit of hot, concentrated, alkaline sodium aluminate solutions (“Bayer liquors”) for the selective extraction (“digestion”) of alumina and, on cooling, the subsequent precipitation of purified gibbsite, Al(OH)₃. The Bayer process is often referred to as the largest recrystallization process in the world (in modern Bayer plants, ~500 million liters of caustic aluminate solution are in the circuit at any time). Some of the world’s largest Bayer plants are located in Australia, the world’s largest alumina producer

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(~30 % of the global annual production of ~60 Mt). However, major productivity gains are required for Australian producers to remain globally competitive. Although the Bayer process is mature, it still requires improved models of thermodynamic properties of process liquors to increase productivity and reduce energy consumption.

Our laboratory is equipped with facilities for the measurement of chemical speciation, solubilities, water activities, as well as heat capacities, c_p , and densities, ρ (up to 300 °C). Results of recent measurements and new modeling approaches for systems of hydrometallurgical interest are reviewed here.

INDUSTRY NEEDS

The design of new plants and equipment requires knowledge of process liquor properties beyond current plant operating conditions, which in turn demands hitherto unavailable modeling capabilities. These goals can hardly be achieved with the existing, purely empirical property models, owing to the following serious problems. In particular, empirical models

- are based on “independent” property functions (e.g., for c_p , ρ , solubility) characterized in a way that they are not related to each other by thermodynamics;
- have been parameterized for multicomponent electrolyte systems (frequently the process liquor itself);
- fail when extrapolated outside the parameterization ranges or to smaller subsystems;
- exhibit appreciable parameter correlation and consequent error propagation;
- inevitably result in plant-specific models, requiring a particular model for each plant and even for different parameterization ranges within each plant;
- cannot be used to establish standards within and between companies with regard to the incorporation of property functions into process simulators.

To overcome these problems, it is necessary to develop improved models that are thermodynamically consistent and can therefore be based on accurate measurements of only a few properties, such as heat capacities and densities. Then, the thermodynamic consistency of the model ensures that other properties, such as enthalpies and solubilities, can be predicted for wide ranges of conditions, even those outside of current plant operating ranges. The incorporation of such robust models into process simulators allows better process control and permits the exploration of process modifications to increase yields and cut greenhouse gas emissions.

THERMODYNAMIC CONSISTENCY

Recently, a Pitzer model that describes the thermodynamic properties of Bayer liquor solutions, consisting of the components $\text{NaOH} + \text{NaAl}(\text{OH})_4 + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{NaCl} + \text{NaF} + \text{Na}_2\text{C}_2\text{O}_4$ (sodium oxalate) + NaHCOO (sodium formate) + NaCH_3COO (sodium acetate) + H_2O , has been developed [1]. The model is primarily based on experimentally determined densities and heat capacities [2–6], which are integrated to give Gibbs energies. From these, a Gibbs energy minimization algorithm calculates, in a thermodynamically consistent manner, enthalpies, and the activity and osmotic coefficients of these solutions as well as the solubilities of relevant solid phases, including gibbsite ($\text{Al}(\text{OH})_3$), boehmite (AlOOH), and the “impurities” sodium oxalate and kogarkoite (Na_3FSO_4) [7], in Bayer liquors over concentration and temperature ranges of industrial interest. The modeling software developed in our laboratory is known as BAYER.EXE [1].

The Pitzer model’s thermodynamic consistency (Fig. 1) is its key advantage over purely empirical models: for instance, by basing the model on heat capacity data, it permits the prediction of solubilities for ranges of temperature and composition in which no solubilities have been measured [8]. In

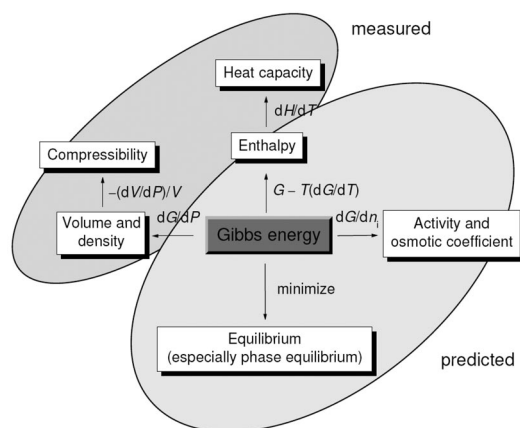


Fig. 1 Thermodynamic consistency indicated by thermodynamic relationships among measurable quantities. The shaded areas relate to the experimental and modeling strategy applied in this work.

contrast, an empirical correlation of heat capacities cannot be employed to predict solubilities at all; nor can an empirical solubility model be used to predict heat capacities.

MEASUREMENT OF THERMODYNAMIC PROPERTIES

Densities

A purpose-built vibrating-tube densimeter has been established in our laboratory, which has a platinum-rhodium vibrating tube with inlet/outlet tubes of platinum and an optical detection system, and is capable of measuring densities of corrosive fluids at temperatures up to 300 °C and pressures up to 30 MPa [3]. Densities of sodium hydroxide solutions at concentrations $0.1 < m/\text{mol kg}^{-1} < 8$ have been measured using this instrument over the temperature range from (50 to 300) °C at a pressure of 10 MPa [3]. Figure 2a compares measured densities with values calculated from the volumetric Pitzer model incorporated in BAYER.EXE.

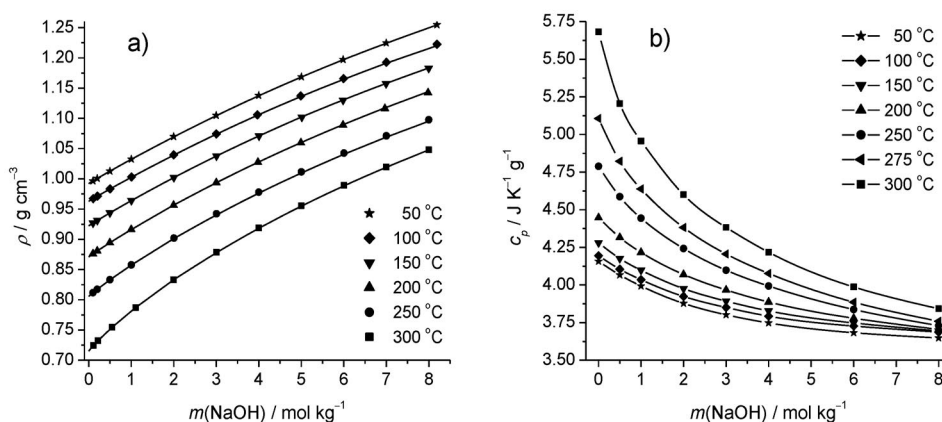


Fig. 2 (a) Densities [3] and (b) heat capacities [6] of NaOH(aq) up to 8 mol kg⁻¹ at temperatures from (50 to 300) °C and a pressure of 10 MPa.

The apparent molar volumes, V_ϕ , of ternary, aqueous NaOH + “NaAl(OH)₄” mixtures obey a linear pro-rata additivity rule as a function of aluminate substitution, also known as Young’s rule (Figs. 3a and 3b). This slope, which is the same for all investigated ionic strengths at a given temperature, depends linearly on temperature. This allows a reliable extrapolation to V_ϕ of pure, hypothetical “NaAl(OH)₄”(aq) using only two parameters in addition to those for V_ϕ of NaOH(aq).

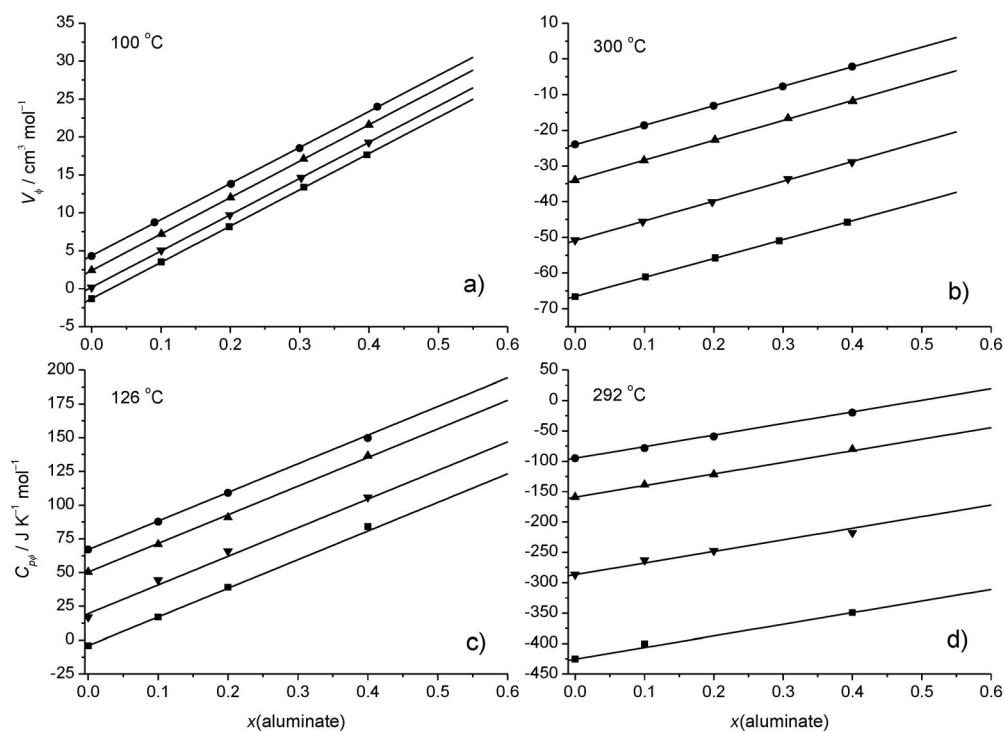


Fig. 3 Apparent molar volumes (a, b) and heat capacities (c, d) of aqueous NaOH + “NaAl(OH)₄” mixtures as a function of aluminate substitution at constant ionic strengths $I/\text{mol kg}^{-1}$ of 1 (■), 2 (▼), 4 (▲) and 6 (●) at various temperatures and a pressure of 10 MPa.

Heat capacities

A commercial Setaram C-80 calorimeter has been modified to allow accurate determinations of the isobaric volumetric heat capacities of chemically aggressive liquids at high temperatures [6]. Heat capacities of aqueous solutions of sodium hydroxide at concentrations from (0.5 to 8) mol kg⁻¹ were measured at temperatures from (50 to 300) °C and a pressure of 10 MPa (Fig. 2b). Apparent molar isobaric heat capacities of NaOH(aq) were calculated using densities determined for the same solutions by vibrating-tube densimetry (see above). Standard state (infinite dilution) partial molar isobaric heat capacities of NaOH(aq) were obtained by extrapolation using an extended Redlich–Meyer equation. In addition, values of the standard heat capacity change for the ionization of water up to 300 °C could be derived by combining the new NaOH(aq) results with literature data for HCl(aq) and NaCl(aq) [6].

A new comprehensive set of heat capacities of aqueous NaOH + “NaAl(OH)₄” mixtures was measured at $1 < I/(\text{mol kg}^{-1}) < 6$, up to 40 % aluminate substitution and up to 300 °C. As for 25 °C [5], apparent molar heat capacities of ternary mixtures were found to depend linearly on aluminate substitution at all temperatures (Figs. 3c and 3d). This slope was the same for all investigated ionic strengths at a given temperature and depended linearly on temperature. Therefore, similar to V_ϕ (see above), only

two parameters (in addition to those for NaOH(aq) heat capacities) are required to model c_p of aqueous NaOH + “NaAl(OH)₄” mixtures. This allows a reliable extrapolation to derive apparent molar heat capacities of pure, hypothetical “NaAl(OH)₄(aq)”.

In addition, heat capacities of mixtures of NaOH(aq) with major Bayer liquor “impurities”: Na₂CO₃(aq), Na₂SO₄(aq), NaCl(aq) were measured under industrially relevant conditions of ionic strength and temperature. Taken collectively, these heat capacity data provide a knowledge base for describing Bayer liquor properties required for the modeling of high-temperature digestion of bauxite.

Water activities

An extensive series of isopiestic measurements was carried out on ternary electrolyte mixtures of relevance to the Bayer process. The experimental protocol was such that a complete series of ternary mixtures, whose compositions cover the whole range from one binary end member to the other, could be investigated simultaneously [9]. Our results for many systems (with the notable exception of NaOH + NaCl + H₂O) studied at temperatures from (25 to 100) °C confirmed a venerable experimental observation, known as “Zdanovskii’s rule” [10], which holds that the molal concentrations of ternary mixed solutions *at constant solvent activity* vary in a linear manner (Fig. 4). Zdanovskii’s rule provides a fundamentally sound criterion for ideal mixing, i.e., the apparent constancy of interaction (other than through changes in solvation) between the component electrolytes (without in any way implying small or negligible interactions between the ions) [11]. Zdanovskii’s rule also provides a theoretical basis for understanding the mixing rules for many thermodynamic properties, such as activity coefficients, enthalpies of mixing, heat capacities, densities, and solubilities. This has important consequences for the thermodynamically consistent modeling of multicomponent electrolyte solutions [9,11].

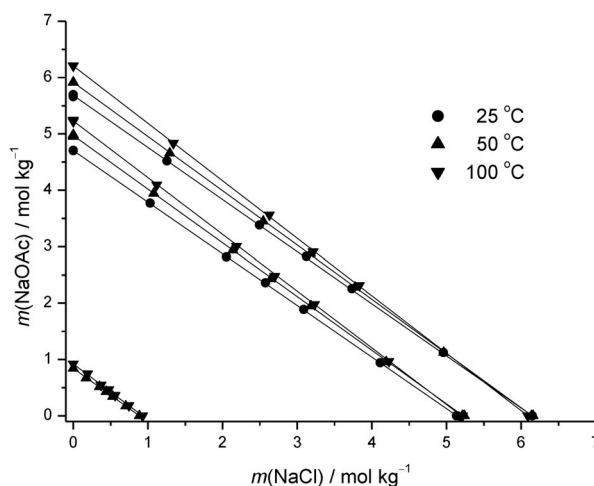


Fig. 4 Isopiestic molalities in the ternary NaOAc + NaCl + H₂O system measured at (25 to 100) °C. Each series corresponds to a constant water activity; the lines indicate Zdanovskii’s rule.

Viscosities

Despite being a transport property, the viscosities of mixed electrolyte solutions were successfully predicted on the basis of Zdanovskii’s rule applied to the Gibbs energy of activation of viscous flow [12]. This assumption results in a linear mixing rule for the logarithm of viscosity and consequently a negative deviation of viscosity from linearity (“Young’s rule”). Such behavior was indeed observed in our laboratory for mixtures of various electrolytes occurring in Bayer liquors [13], including the NaOH +

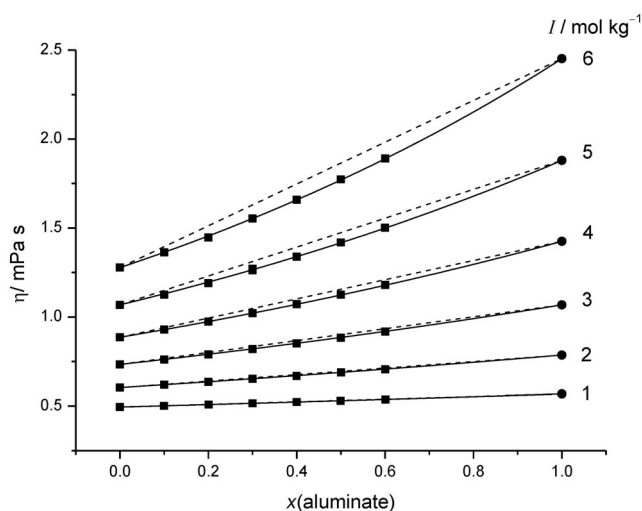


Fig. 5 Viscosities in the ternary $\text{NaOH} + \text{NaAl}(\text{OH})_4 + \text{H}_2\text{O}$ system as a function of aluminate substitution at constant ionic strengths I at 70°C (squares). Solid lines, Zdanovskii's rule; dashed lines, "Young's rule"; dots, extrapolated viscosities of hypothetical, pure " $\text{NaAl}(\text{OH})_4(\text{aq})$ ".

$\text{NaAl}(\text{OH})_4 + \text{H}_2\text{O}$ system (Fig. 5). Zdanovskii's (rather than Young's) rule permits extrapolation to viscosities of hypothetical, pure " $\text{NaAl}(\text{OH})_4(\text{aq})$ ".

IMPURITY CONTROL

Organic compounds in the Bayer process

The chemistry of "organics" in Bayer liquors is extremely complex. Organic compounds enter the process through the bauxite ore, which contains woody material (lignin, cellulose, hemicellulose) and humic substances. The latter originate from plant and animal material transformed by oxidative (decomposition) and reductive (resynthesis) humification processes [14] during geochemical ore formation. The harsh conditions prevailing during bauxite digestion result in degradation of the organic material contained in the ore. Different types of ore and different conditions during the digestion stage of the Bayer process thus lead to different distributions of organics in Bayer liquors [15,16]. While many organics are detrimental to product quality and yield (e.g., by retarding gibbsite crystallization or reducing crystal size), positive effects of humic substances (complexation of iron, stabilization of aluminate and oxalate supersaturation) have also been reported [17,18].

The redox potential E_{H} of the liquor during digestion is negative enough to form hydrogen, methane, ammonia, metallic mercury, and various volatile organic compounds (VOCs) [19]. While many VOCs are short-lived due to their high reactivity, a number of volatiles (including Hg) are released during flash cooling and/or dissolve in the so-called digestion condensate. This leads to certain environmental issues, which can be compounded because the condensate is used for washing or dilution throughout the refinery. The partitioning of various classes of volatile substances among liquor, steam, and condensate has been successfully modeled within the framework of our existing Bayer liquor model [20].

As mentioned above, the organic macromolecules extracted from the two main carbon sources in bauxite (partly) decompose in hot Bayer liquors. The primary low-molecular-weight products are benzenecarboxylates, phenolates, and aliphatic carboxylates; however, polymeric carbon backbones enriched in aromatic groups have also been reported to persist [17]. Although the carbonate ion is the thermodynamically stable form of carbon under (aerobic) Bayer process conditions, benzoate, succi-

nate, acetate, formate, and particularly oxalate are found to be (meta-)stable in 6 mol kg⁻¹ NaOH solution for up to five weeks at temperatures up to 180 °C [21]. The last three of these sodium carboxylates are currently incorporated in our Bayer liquor model [1]. Organic impurities are known to affect the physicochemical properties of the liquor, including density, heat capacity, and gibbsite solubility. In particular, due to its very low solubility in Bayer liquors [7], sodium oxalate interferes with gibbsite precipitation, since it promotes heterogeneous nucleation of gibbsite and affects the agglomeration of gibbsite crystals through coprecipitation [18].

Thermodynamic simulation of impurity transport through an alumina refinery

Due to the cyclic nature of the Bayer process, any impurity entering the process stream will tend to build up in the circuit unless there are appropriate control strategies. Unfortunately, some of these impurities form sparingly soluble solids that precipitate, form scale, contaminate the product, or change its morphology. To avoid these and other problems at various stages of the process, it is desirable in Bayer plant operations to achieve a steady state of impurity concentrations by focusing on process inputs and outputs.

In a recent thermodynamic process simulation of the Bayer circuit [22], a library of subroutines for thermochemical calculations, ChemApp [23], was combined with our Bayer liquor model [1]. A FORTRAN code was specifically developed to simulate the liquor cycle of the Bayer process from digestion, clarification, precipitation, evaporation, and back to digestion, including flash cooling and heating steps. This code is particularly suitable for investigating the fate of impurities since it calculates iteratively a steady state determined by the compositions of the input and output streams to each stage, including the associated energy balances.

Being a major decomposition product of organics due to its high (meta-)stability, oxalate will accumulate in the liquor unless controlled. A simulation [22] of oxalate build-up showed that the liquor first became supersaturated with respect to sodium oxalate when cooled to gibbsite precipitation temperature (Fig. 6). This result accords with industrial experience [18]. To avoid coprecipitation with gibbsite, sodium oxalate crystallization inhibitors have been developed [18]. It is thus better to control the concentration of organics by crystallizing sodium oxalate *after* gibbsite precipitation [18] or by applying other removal methods such as wet oxidation [24] (which in turn may result in decomposition products that act as gibbsite seed poisons or “yield inhibitors” and are difficult to destroy [25]).

Fluoride is another significant impurity in some bauxites and may thus build up in Bayer liquors. Since sulfate is a common liquor impurity, sparingly soluble kogarkoite [7], Na₃FSO₄, can then become supersaturated and form scale, particularly in heat exchangers, which requires costly clean-up operations [26]. The simulation of fluoride accumulation in Bayer liquors [22] showed that kogarkoite first becomes supersaturated in the evaporators after the gibbsite precipitation stage. On further fluoride build-up, kogarkoite was predicted to co-crystallize with gibbsite (Fig. 6). This scenario has indeed been encountered by the industry, leading to a major incident in a large Bayer plant [26].

Finally, our thermodynamically consistent Bayer liquor model [1] covers temperature and concentration ranges from boehmite digestion to gibbsite precipitation in this Bayer process simulation [22]. The potential energy savings of modifying the process to precipitate boehmite could also be explored, and possible reductions in the overall energy consumption of the Bayer process were identified [22]. These simulations have demonstrated that our Bayer liquor model is suitable for use by commercial process simulators.

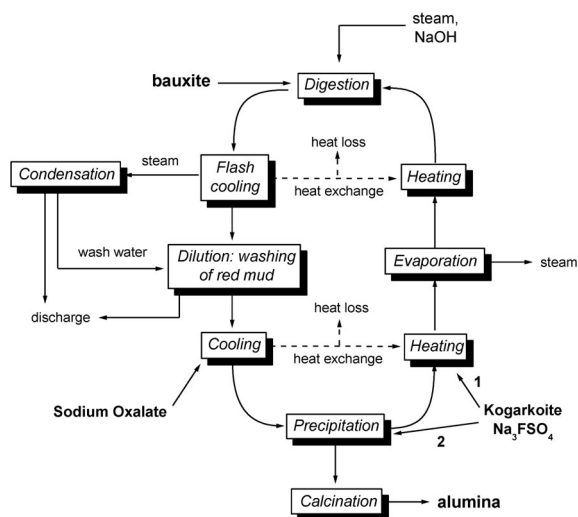


Fig. 6 Simulation of the accumulation of oxalate and fluoride in a Bayer process circuit [22]. The process stages in which liquors first become supersaturated with respect to sodium oxalate and kogarkoite, respectively, are indicated by arrows. Boxes indicate equilibrium calculations.

CONCLUSIONS

Solubility phenomena in hydrometallurgy include not only the solid-solute phase transitions commonly encountered in leaching and precipitation processes but also gas-solute equilibria of volatile compounds. Some of these volatile compounds are highly relevant to problems of environmental pollution and occupational safety and health. Examples include volatile organics in the Bayer process and hydrochloric acid in concentrated chloride leach solutions [27]. A prerequisite for the successful modeling of solubilities and related physicochemical properties, such as densities and heat capacities, in hydrometallurgical systems is a thermodynamically consistent description of the aqueous phase. In our studies, water activity has been identified as the key quantity governing the thermodynamic behavior of concentrated process solutions. The associated “Zdanovskii’s rule” [9–12] and other mixing rules such as Young’s rule [2,5,28,29] are pivotal for the prediction of physicochemical properties of multicomponent systems from those determined experimentally for simpler subsystems. The resulting models can then be used for meaningful thermodynamic simulations of hydrometallurgical processes, including impurity cycles, which may lead to higher product quality and quantity as well as to reductions in emissions and energy consumption.

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