

A COMPREHENSIVE PHYSICOCHEMICAL MODEL OF SYNTHETIC BAYER LIQUORS

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Abstract

A physicochemical model based on the Pitzer equations has been developed to represent the thermodynamic properties of synthetic Bayer liquor solutions, consisting of the components NaOH – NaAl(OH)₄ – Na₂CO₃ – Na₂SO₄ – NaCl – NaF – Na₂C₂O₄ (sodium oxalate) – NaHCOO (sodium formate) – NaCH₃COO (sodium acetate) – H₂O. The model calculates, in a thermodynamically consistent manner, heat capacities, enthalpies, activity and osmotic coefficients, vapour pressures, boiling point elevations and densities of these solutions as well as the solubilities of gibbsite, Al(OH)₃, boehmite, AlOOH, sodium oxalate, and other relevant solid phases in synthetic Bayer liquors over the concentration and temperature ranges of industrial interest. Possible extensions of the model to predict the properties of actual plant liquors and applications to Bayer process simulation will be presented.

1 Introduction

As there are currently no fundamental theories that permit the reliable prediction of the thermodynamic properties of concentrated binary (single salt plus solvent water) and multi-component electrolyte solutions from first principles, it is necessary to use semi-empirical models parameterised with respect to experimental data to correlate such properties. An important issue is the thermodynamic consistency of these models, which means that the various properties and functions are related to each other via the standard thermodynamic relationships such as partial differentiations or the Gibbs-Duhem equation (McGlashan 1979). Within the thermodynamics of chemical systems, the Gibbs energy function, G , is an especially useful quantity, as other measurable properties of interest such as enthalpy, heat capacity, volume (density) and chemical potentials (activities) can be derived by appropriate differentiations to ensure thermodynamic consistency. Moreover, at chemical or phase equilibrium in homogeneous (single-phase) or heterogeneous (multi-phase) systems respectively, the Gibbs energy assumes a minimum with respect to the compositional variables at constant temperature and pressure. Therefore, knowledge of the Gibbs energy of the system permits all thermodynamic properties of the liquor, together with solubilities, vapour pressures, etc. to be calculated.

Thermodynamically consistent electrolyte models, based on various kinds of data measured over wide ranges of temperatures (from ca. –60°C to 300°C), pressures and concentrations up to saturation, have been reported for several binary and multicomponent systems (Pabalan & Pitzer 1991). The semi-empirical ion-interaction model developed by Pitzer (1973, 1991) is particularly useful as it is able to correlate, in a thermodynamically consistent way, the properties of electrolyte solutions within the experimental uncertainty of high-precision measurements over wide ranges of conditions. Parameterisation is performed on the binary and ternary subsystems and the model equations are then used to predict the properties of the multicomponent system.

Until recently (Königsberger, Eriksson et al. 2005), no comprehensive, thermodynamically consistent model for Bayer liquors appears to have been reported in the literature. The purely empirical property functions almost invariably used industrially to describe the properties of multicomponent mixtures are generally thermodynamically inconsistent. In other words, independently derived functions, not related to each other by thermodynamics, are used to describe properties like densities, heat capacities or solubilities. Furthermore, empirical property functions are often valid only over limited concentration and temperature ranges and frequently fail to extrapolate correctly to the known properties of their binary solution subsystems or even to those of pure water. In such circumstances it is difficult to perform process simulations in a coherent way. When the conditions fall outside the parameterisation range of the

empirical model, process simulations become virtually impossible. An important issue here is the tendency of protagonists of various models to represent “good fits” to limited sets of data as evidence of their preferred models’ fundamental validity (Loehe & Donohue 1997): an approach which is scientifically unjustified and which will ultimately fail. Real progress in this area cannot occur without a more thermodynamically rigorous approach.

In ARC Projects SPIRT 29940103 (AMIRA P507A) and LP0349107 (AMIRA P507B), we have developed the first thermodynamically consistent model of synthetic Bayer liquors consisting of the components NaOH – (hypothetical, pure) NaAl(OH)₄ – Na₂CO₃ – Na₂SO₄ – NaCl – NaF – Na₂C₂O₄ (sodium oxalate) – NaHCOO (sodium formate) – NaCH₃COO (sodium acetate) – H₂O. With this Pitzer model, it is possible to generate, in good agreement with available experimental data, thermodynamic properties such as heat capacities, enthalpies, volumes (densities) and activities of the electrolyte components and the solvent (water) over wide ranges of industrially relevant conditions. The model also predicts solubilities of gibbsite, Al(OH)₃, boehmite, AlOOH, and the sodium salts of oxalate, fluoride, sulphate, carbonate, along with other relevant solid phases in synthetic Bayer liquors. It reproduces the thermodynamic, particularly (unpublished) isopiestic, data measured in the earlier AMIRA Projects P380A and P380B. In the form of a software product, the synthetic liquor model has been delivered to, and has been well received by, our sponsors in the alumina refining industry. Our most recent ARC Linkage Project LP0560477 will extend this knowledge to plant liquors.

2 Pitzer Model

The Pitzer model has been reviewed many times, so only the essential points are given here. The set of equations developed by Pitzer (1973, 1991) can precisely represent the excess properties of even concentrated electrolyte solutions as a function of composition, temperature and pressure. The total excess Gibbs energy, G^E , of a binary solution is given by

$$G^E = w_w \nu m RT (1 - \phi + \ln \gamma_{\pm}),$$

where R and T have their usual meaning, w_w is the mass of the solvent, $\nu = \nu_M + \nu_X$ and ν_M , ν_X are the stoichiometric coefficients of cations and anions respectively, m is the molality of the salt (solute), ϕ is the osmotic coefficient of the solvent (water) and γ_{\pm} is the mean activity coefficient of the solute. In the Pitzer model, G^E contains a Debye-Hückel term, a representation of the ionic-strength-dependent

second virial coefficient B_{MX} as well as a third virial coefficient C_{MX} that is taken independent of ionic strength,

$$G^E/(w_w RT) = -A_\phi (4I b^{-1}) \ln(1 + bI^{1/2}) + 2v_M v_X [m^2 B_{MX} + m^3 v_M z_M C$$

$$B_{MX} = \beta_{MX}^{(0)} + 2\beta_{MX}^{(1)} [1 - (1 + \alpha_1 I^{1/2}) \exp(-\alpha_1 I^{1/2})] (\alpha_1^2 I)^{-1} \\ + 2\beta_{MX}^{(2)} [1 - (1 + \alpha_2 I^{1/2}) \exp(-\alpha_2 I^{1/2})] (\alpha_2^2 I)^{-1}.$$

In (2) and (3), I is the molality-based stoichiometric ionic strength, A_ϕ is the Debye-Hückel coefficient for the osmotic function (at 25°C, $A_\phi = 0.3915 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ (Bradley & Pitzer 1979)) and z_i is the formal charge of the ion i . The constant b equals 1.2 for all solutes, $\alpha_1 = 2$ and $\alpha_2 = 0$ (i.e. $\beta_{MX}^{(2)}$ is not needed) unless $z_i \geq 2$ for both ions, in which case $\alpha_1 = 1.4$ and $\alpha_2 = 12$ and $\beta_{MX}^{(2)}$ must be included. For 3–2 and 4–2 electrolytes, $\alpha_1 = 2$ and $\alpha_2 = 50$ have been used (Pitzer 1991). It should be noted that b , α_1 and α_2 are taken as temperature independent. Thus at fixed pressure and temperature, G^E is expressed in terms of up to four adjustable parameters $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$ and C_{MX} per electrolyte, which are generally determined by fitting the equations to osmotic and/or activity coefficient data. Values of $\beta_{MX}^{(2)}$ are relatively large and negative for solutes which are significantly ion-paired (associated). However, if the value of the ion-association constant exceeds some critical value, the resulting complexes are better taken into account as individual species (Harvie et al. 1984).

Equations for ϕ and $\ln \gamma_\pm$, which are related to the partial molar excess Gibbs energies of solvent and solute, are obtained by appropriate differentiation (Pitzer 1991). There are also general equations for G^E , ϕ and $\ln \gamma_\pm$ that are valid for multicomponent solutions (Pitzer 1991). For the latter, so-called higher-order electrostatic terms, ${}^E\theta(I)$, are usually taken into account. These can be derived from a theoretical treatment (Pitzer 1975) of the effect of electrostatic forces arising from the unsymmetrical mixing of ions of the same charge type, e.g. between HCO_3^- and CO_3^{2-} , and are functions of ionic strength. In addition, the parameters ${}^S\theta_{M,M'}$, ${}^S\theta_{X,X'}$, $\Psi_{M,X,X'}$ and $\Psi_{M,M',X}$ are used to describe specific interactions in ternary systems. Pitzer (1991) presents a convenient method to calculate ${}^E\theta(I)$ and reviews extensive tables of binary and ternary interaction parameters. As the Pitzer model assumes that quaternary and higher-order interactions are negligible, predictions of thermodynamic properties can be made for multicomponent electrolyte solutions once all relevant binary and ternary parameters are known.

Equations for apparent molar volumes, enthalpies and heat capacities can be derived from the excess Gibbs energy by appropriate differentiation with respect to pressure or temperature. The respective equations and a discussion of the strengths and limitations of the Pitzer model are given in our recent paper (Königsberger, Eriksson et al. 2005).

3 Comprehensive Pitzer model for synthetic Bayer liquors

It should be emphasized that in the present Pitzer model for synthetic Bayer liquors all solutes are treated as strong electrolytes, i.e. the model does not contain any species other than Na^+ , OH^- , $\text{Al}(\text{OH})_4^-$, CO_3^{2-} , SO_4^{2-} , Cl^- , F^- , $\text{C}_2\text{O}_4^{2-}$, CH_3COO^- and HCOO^- . All activity coefficients are calculated from interactions among these species rather than, for instance, via formation of ion pairs or complexes.

When available in the literature, critically evaluated Pitzer models for binary electrolyte solutions, which are capable of calculating thermal (e.g. heat capacities) and volumetric (e.g. densities) properties over wide ranges of conditions, were employed: NaOH (Simonson et al. 1989), NaCl (Pitzer et al. 1984), Na_2SO_4 (Holmes & Mesmer 1986) and Na_2CO_3 (Königsberger 2002). For hypothetical pure $\text{NaAl}(\text{OH})_4$ solutions, two literature models were combined (Wesolowski 1992, Simonson et al. 1989) and a volumetric Pitzer model was derived (Königsberger, Bevis et al. 2005). To incorporate fluoride into the model, thermodynamic data for aqueous and solid phases, including kogarkoite, Na_3FSO_4 , were taken from various sources and adjusted with respect to experimental data. For NaCH_3COO , a literature model (Beyer & Steiger 2002) has been tentatively adopted. Thermodynamic measurements for NaHCOO

and $\text{Na}_2\text{C}_2\text{O}_4$ are sparse. For sodium formate, various approximations have been made, including the plausible assumption that the heat capacities of $\text{NaHCOO}(\text{aq})$ are temperature independent (Königsberger 2001, 2002). Sodium oxalate is modelled assuming that its Pitzer parameters are equal to those of Na_2SO_4 (Holmes & Mesmer 1986). The model includes a few ternary interaction parameters selected from the literature (Pabalan & Pitzer 1991, Wesolowski 1992, Königsberger 2001). Gibbs energies of solid phases, which are required for solubility calculations, were either adopted (occasionally slightly adjusted) from the literature (gibbsite, boehmite, sodium sulphate, carbonate, fluoride, kogarkoite) or optimised with respect to solubility data (e.g. sodium oxalate solubilities in water) using the ChemSage optimiser (Königsberger & Eriksson 1995).

The model outlined above has been incorporated into a ‘stand-alone’ code that calculates the thermodynamic properties of aqueous solutions and two-phase equilibria between the aqueous phase and stoichiometric solid phases (or the water vapour phase). This code is based on the condition of equal chemical potentials of the components in the two phases at equilibrium, which is mathematically equivalent to the condition of minimal Gibbs energy.

After specifying the temperature, the concentrations of the synthetic Bayer liquor components are entered. Amongst other options this allows specification of concentrations, including ‘industrial’ units, that have been determined at room temperature for prediction of properties at other temperatures. All unit conversions are performed internally, using densities calculated from the various volumetric Pitzer models. The calculations can be performed either at ‘saturation’ pressure (vapour pressure of steam-saturated water at $t \geq 100^\circ\text{C}$, 1 bar at $t \leq 100^\circ\text{C}$) or at a pressure specified by the user.

As a result of the calculation, temperature, pressure as well as ionic strength and concentrations of the components (in various units) are displayed. Furthermore, boiling point elevations, vapour pressure, heat capacities, densities (and their associated apparent molar quantities), water activity and osmotic coefficient as well as conventional single-ion and mean ionic activity coefficients of solutes are shown. Also, saturation indices ($SI = a/a_{\text{sat}}$, which means that the solution is saturated when $SI = 1$, undersaturated when $SI < 1$ and supersaturated when $SI > 1$) and solubilities of selected solid phases are given.

The model has been validated for all binary and ternary subsystems over wide temperature and concentration ranges using experimental data (heat capacities, water activities, solubilities, densities) available in the literature or measured in our laboratories. It also performs well for more complicated solutions, e.g. the model calculations agree with experimental densities of twelve 7-component synthetic Bayer liquors to better than 0.1% (Königsberger, Bevis et al. 2005). However, it should be emphasized here that no Bayer plant liquor data have been used for parameterisation of the model.

Rosenberg and Healy (1996) have carefully measured gibbsite solubilities in Worsley plant liquors and developed a gibbsite solubility model based on Debye-Hückel-type activity coefficient functions, whose parameters were fitted to the experimental data. Agreement with a series of measurements of alumina solubility, with temperature and liquor concentrations both within and outside the range used in the correlation, was excellent, except at low and high caustic concentrations (Figure 1, open symbols). Recently, Bennett et al. (2004) have reported significant deviations of Rosenberg-Healy (R-H) model predictions from experimental gibbsite solubilities when the model was applied to process liquors from a different refinery (Gove). This is not surprising given that the R-H model had been calibrated with respect to specific refinery conditions. Bennett et al. (2004) discuss possible reasons for these deviations (e.g. contrasting impurity composition due to different raw materials, considerable variation in impurity treatment from plant to plant) and conclude that this ‘variability ... renders the development of a universally applicable, phenomenological solubility model practically impossible’.

To overcome this problem, Bennett et al. (2004) have proposed a ‘Group Method of Data Handling (GMDH) polynomial neural network’ for developing a gibbsite solubility model. The GMDH algorithm has been able to automatically create the solubility model with virtually no user intervention. The performance of this model compares favourably

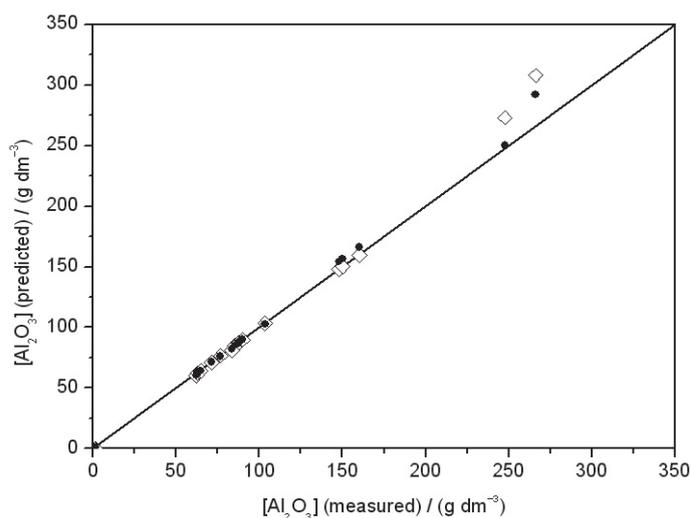


Figure 1: Predicted vs. experimental (Rosenberg and Healy 1996) gibbsite solubilities in plant liquors. Open symbols, model of Rosenberg and Healy (1996); solid symbols, present Pitzer model for synthetic liquors.

with the R-H model. However, using algorithms like GMDH for model development might be dangerous when the calibration data set contains erroneous values, which could lead to biased model predictions.

The present Pitzer model for *synthetic* liquors was compared to the Worsley gibbsite solubility equilibrium data given in Table 6 of Rosenberg and Healy (1996). Bennett et al. (2004, Table 2) used these data for their GMDH predictions. Input data to our model were liquor compositions as given in both tables. When total organic carbon (TOC) is represented by the low molecular weight 'organics' of our model so as to reflect the experimentally determined TOS/TOC ratio (Rosenberg and Healy 1996), there is an excellent agreement between our model predictions and experimental gibbsite solubility data (Figure 1, solid symbols). This is despite the fact that our model for synthetic Bayer liquors has not been calibrated for any plant liquors.

Our model deviates from measured solubilities at (i) high caustic concentrations and (ii) high temperatures. Rosenberg and Healy (1996) suggest that the departure at the highest caustic concentrations may be a consequence of analytical errors, or of their activity coefficient equations not being appropriate at this extreme. The ionic strengths of these solutions are indeed very high ($I > 16 \text{ mol dm}^{-3}$), which is likely to cause problems with our Pitzer model as well. To overcome possible model inaccuracies at high temperatures, heat capacity and density data are being measured in our current ARC Linkage Project LP0349107 (AMIRA P507B) so as to describe thermodynamic properties of Bayer liquors in a consistent way to 300°C.

At very low caustic concentrations, predictions of the R-H and GMDH models are too low ($< 0.1 \text{ g/L Al}_2\text{O}_3$) and too high (1.1 to 4.5 g/L Al_2O_3) respectively, while our model gives realistic results (0.7 to 1.1 g/L Al_2O_3 ; measured: 1.0 to 1.6 g/L). This good performance is certainly due to the fact that Pitzer models extrapolate correctly to binary (e.g. NaOH – H_2O) and ternary (e.g. NaOH – $\text{NaAl}(\text{OH})_4$ – H_2O) subsystems and to pure water.

Bennett et al. (2004) report that the GMDH network failed to identify fluoride concentration as a significant variable of the system. They consider this “a bit of a curiosity”, as fluoride binds strongly to Al^{3+} , but offer the formation of $\text{AlF}(\text{OH})_3^-$ as a likely explanation. Similarly, our model predicts insignificant ($< 1\%$) changes in gibbsite solubilities within the NaF range considered by Bennett et al. (up to 7 g/L), although neither $\text{AlF}(\text{OH})_3^-$ nor other fluoride complexes are included in our model. However, at higher NaF levels our model predicts the liquors to be highly supersaturated with respect to kogarkoite.

Rosenberg and Healy (1996) report that their attempts to include the effect of temperature on the activity coefficient had virtually no impact on the quality of fit. Our model predicts that the ratio of hydroxide to ‘aluminate’ activity coefficients is indeed virtually temperature independent.

As the present model is based on various, thermodynamically consistent sets of data rather than on fits to solubility data only, these results follow from our model in a fundamental way. For instance, heat capacity data of NaOH – $\text{NaAl}(\text{OH})_4$ solutions (Magalhães et al. 2002) imply that the activity coefficients of sodium hydroxide and ‘sodium aluminate’ have the same temperature dependence. Fundamental models are frequently capable of describing various, including new, scenarios which they do not ‘know’ about, although they might not give predictions as accurate as those of phenomenological models that have been ‘trained’ or fitted with respect to a limited set of data.

Further evidence for this is provided by simulations regarding an obviously erroneously reported liquor composition (Bennett et al. 2004, Table 2, third-last data point), which gives a TOC of 0.17 g/L, while the original source (Rosenberg & Healy 1996, Table 6) reports 17 g/L TOC. The measured gibbsite solubility was 83.6 g/L Al_2O_3 (Rosenberg & Healy 1996), while the GMDH model and our model predicted 79.9 and 77.4 g/L respectively. This means that the GMDH model agrees reasonably well with experiment even though the TOC input was incorrect, while our model (with the incorrect TOC value) shows a larger deviation although it agrees very well with other experimental data in these temperature and concentration ranges. Therefore, it was immediately obvious from our model that this data point is likely to be erroneous. Repeating the calculation with the correct value of 17 g/L TOC from the original source (Rosenberg & Healy 1996), the calculated solubility was found to be 82.0 g/L Al_2O_3 in much better agreement with the measured value.

It should be noted that a certain assumption about TOC partitioning between sodium formate and acetate (whose thermodynamic properties are rather dissimilar) resulted in an excellent agreement between predicted and measured gibbsite solubilities in the precipitation temperature range. We are certainly aware that this model of Bayer ‘organics’ is oversimplified and needs improvement. One of the key answers to this challenge might be to develop refinery-specific blends of ‘organics’, each of which is modelled in a fundamental manner.

4 Extension to plant liquors

In terms of number of components and ranges of temperature and concentration that cover all aspects of the Bayer process from (gibbsitic) bauxite digestion to gibbsite (or boehmite) precipitation, the existing Pitzer model of *synthetic* Bayer liquors described above is one of the largest thermodynamically consistent electrolyte models that has ever been developed for an industrial process. However, the Australian alumina industry has a specific need for the development of sound and robust models of *plant* Bayer liquors that not only describe the thermo-

dynamic and transport properties well but can also be incorporated in process simulators.

This will only be achieved by researching a number of important issues that could not be addressed before a good description of synthetic liquor behaviour had been developed. Such issues include models for (i) humic substances that originate from the natural organic matter found in typical Australian bauxite ores, (ii) kinetic effects, e.g. the effect of surface tension on liquid–vapour phase transitions, (iii) viscosity and (iv) the effects of additional inorganic and low-molecular-weight organic components (which arise from the decomposition of humic materials under Bayer plant conditions). The developed model should also incorporate the heat capacity and density data that are currently being measured in our ARC Linkage Project LP0349107 (AMIRA P507B) to 300°C. Moreover, since the concentrations of some of the liquor components are often not determined by routine analysis, they must be estimated where necessary. This approach should allow us to exploit much of the experimental data previously determined ‘in-house’ by the alumina companies. It will hence lead to a robust thermodynamic model with predictive capabilities that will make it suitable for realistic simulations of new Bayer process variants as all thermodynamic properties are calculated in a consistent way over wide ranges of conditions far beyond current industrial limits.

Since the model will be able, after some subsequent interface development, to be incorporated into commercial process simulators, these innovative features can then be applied to refinery conditions. For this purpose, we intend to develop, in direct collaboration with the industry, an entirely flexible software product that allows equilibrium calculations representing the various stages of the process to be coupled with material streams and kinetic equations. It may then even become computationally possible to optimise process parameters with a view to maximising product yield and minimising refinery releases and energy consumption. With such software products the Australian alumina industry should be better positioned to improve various aspects of alumina production as addressed in the recently published Alumina Technology Roadmap (Amira 2001).

5 Conclusion

The present Pitzer model of synthetic Bayer liquors is capable of calculating both the thermodynamic properties (e.g. C_p , ϕ , ρ) of, and solubilities in, these mixed electrolyte solutions in a satisfactory manner. Under certain assumptions regarding Bayer ‘organics’, the model predicts gibbsite solubilities even for plant liquors very well. Future research will focus on extensions that make the model generally applicable to wide ranges of refinery conditions.

To a large extent, the good performance of the model can be attributed to its thermodynamic consistency and proper parameterisation of the binary systems up to saturation, using high quality data or appropriate guesses when the latter are either unavailable or even unmeasurable (see sodium oxalate). Ternary interaction parameters describe second-order effects: they are not required for density and heat capacity modelling, although they can improve solubility calculations somewhat.

The modelling software developed in this work is a powerful facility for the analysis of chemical thermodynamics of synthetic Bayer liquors. It is capable of calculating thermodynamic properties of phases and solubilities in these complex solutions quickly and conveniently and has proven invaluable for studying the interrelations and correlations among the various model parameters and experimental data, which helps to identify the conditions for which new thermodynamic measurements should be performed.

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References

- Amira International 2001, Alumina Technology Roadmap, 39 pp., <http://www.amira.com.au/documents/Alumina/index.htm>
- Bennett, FR, Crew, P & Muller JK 2004, ‘A GMDH Approach to Modelling Gibbsite Solubility in Bayer Process Liquors’, *Int. J. Mol. Sci.*, vol. 5, pp. 101–109.
- Beyer, R & Steiger, M 2002, ‘Vapour Pressure Measurements and Thermodynamic Properties of Aqueous Solutions of Sodium Acetate’, *J. Chem. Thermodynamics*, vol. 34, pp. 1057–1071.
- Bradley, DJ & Pitzer, KS 1979, ‘Thermodynamics of Electrolytes. 12. Dielectric Properties of Water and Debye–Hückel Parameters to 350 °C and 1 kbar’, *J. Phys. Chem.*, vol. 83, pp. 1599–1603.
- Harvie, CE, Møller, N & Weare, JH 1984, ‘The Prediction of Mineral Solubilities in Natural Waters: The Na–K–Mg–Ca–H–Cl–SO₄–OH–HCO₃–CO₃–CO₂–H₂O System to High Ionic Strengths at 25°C’, *Geochim. Cosmochim. Acta*, vol. 48, pp. 723–751.
- Holmes, HF & Mesmer, RE 1986, ‘Thermodynamics of Aqueous Solutions of the Alkali Metal Sulfates’, *J. Solution Chem.*, vol. 15, pp. 495–518.
- Königsberger, E 2001, ‘Prediction of Electrolyte Solubilities from Minimal Thermodynamic Information’, *Monatsh. Chem.*, vol. 132, pp. 1363–1386.
- Königsberger, E 2002, ‘Solubility Equilibria. From Data Optimization to Process Simulation’, *Pure Appl. Chem.*, vol. 74, pp. 1831–1841.
- Königsberger, E & Eriksson, G 1995, ‘A New Optimization Routine for ChemSage’, *CALPHAD*, vol. 19, pp. 207–214.
- Königsberger, E, Bevis, S, Hefter, G & May PM 2005, ‘Comprehensive Model of Synthetic Bayer Liquors. Part 2. Densities of Alkaline Aluminate Solutions to 90 °C’, *J. Chem. Eng. Data*, in press.
- Königsberger, E, Eriksson, G, May, PM & Hefter, G 2005, ‘Comprehensive Model of Synthetic Bayer Liquors. Part 1. Overview’, *Ind. Eng. Chem. Res.*, accepted.
- Loche, JR & Donohue, MD 1997, ‘Recent Advances in Modeling Thermodynamic Properties of Aqueous Strong Electrolyte Systems’, *AIChE Journal*, vol. 43, pp. 180–195.
- Magalhães, MCF, Königsberger E, May, PM & Hefter, G 2002, ‘Heat Capacities of Concentrated Alkaline Aluminate Solutions at 25 °C’, *J. Chem. Eng. Data*, vol. 47, pp. 960–963.
- McGlashan, ML 1979, *Chemical Thermodynamics*, Academic Press, London.
- Pabalan, RT & Pitzer, KS 1991, ‘Mineral Solubilities in Electrolyte Solutions’, *Activity Coefficients in Electrolyte Solutions*, 2nd. Edn., Pitzer, KS, Ed., CRC Press, Boca Raton, Florida, USA, pp. 435–490.
- Pitzer, KS 1973, ‘Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations’, *J. Phys. Chem.*, vol. 77, pp. 268–277.
- Pitzer, KS 1975, ‘Thermodynamics of Electrolytes. V. Effects of Higher Order Electrostatic Terms’, *J. Solution Chem.*, vol. 4, pp. 249–265.
- Pitzer, KS 1991, ‘Ion Interaction Approach: Theory and Data Correlation’, *Activity Coefficients in Electrolyte Solutions*, 2nd. Edn., Pitzer, KS, Ed., CRC Press, Boca Raton, Florida, USA, pp. 75–153.
- Pitzer, KS, Peiper, JC & Busey, RH 1984 ‘Thermodynamic Properties of Aqueous Sodium Chloride Solutions’, *J. Phys. Chem. Ref. Data*, vpl. 13, pp. 1–102.
- Rosenberg, SP & Healy, SJ 1996, ‘A Thermodynamic Model for Gibbsite Solubility in Bayer Liquors’, *Fourth International Alumina Quality Workshop*, Darwin, Australia, pp. 301–310.
- Simonson, JM, Mesmer, RE & Rogers PSZ 1989, ‘The Enthalpy of Dilution and Apparent Molar Heat Capacity of Sodium Hydroxide(aq) to 523 K and 40 Mpa’, *J. Chem. Thermodynamics*, vol. 21, pp. 561–584.
- Wesolowski, DJ 1992, ‘Aluminum Speciation and Equilibria in Aqueous Solution: I. The Solubility of Gibbsite in the System Na–K–Cl–OH–Al(OH)₃ from 0 to 100°C’, *Geochim. Cosmochim. Acta*, vol. 56, pp. 1065–1091.