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Thermodynamics of impurities in hydrometallurgical processes*

Erich Königsberger‡, Sebastian Bochmann, Peter M. May, and Glenn Hefter

School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, WA 6150, Australia

Abstract: Impurities in hydrometallurgical process liquors frequently impact on product quality and yield, change physicochemical properties of the liquor, and form hard scale on heat exchangers and condensers. Organic compounds are of particular concern especially in the Bayer process, where impurities build up in the recycled liquor if not controlled. Depending on the redox state of the liquor, such compounds can undergo a variety of complex chemical reactions, including the formation of volatiles that can potentially cause environmental, health, and safety concerns. To aid in the development of appropriate control strategies, robust thermodynamic models for multicomponent aqueous systems containing large numbers of electrolytes and nonelectrolytes are required. Applications of thermodynamic models are discussed that range from the partitioning of volatile compounds in flash trains to the prediction of mixing properties of organic impurities with major Bayer liquor components.

Keywords: aqueous solutions; electrolytes; high temperature; modeling; thermodynamics.

INTRODUCTION

Thermodynamic modeling of hydrometallurgical processes is usually focused on optimizing product yield. However, large numbers of inorganic and organic impurities enter process streams during the acidic or alkaline leaching of the ore. Since impurities tend to build up, especially when plant liquors are recycled, control strategies usually aim to achieve a steady state of impurity concentrations by balancing process inputs and outputs. However, the problems arising from impurities are often compounded because the impurities may be transformed by a variety of chemical and redox reactions, form precipitates or volatile compounds. Impurities frequently affect the physicochemical properties of the liquor, including important process parameters such as densities, heat capacities, and viscosities. They often interfere with process performance: for instance, precipitates may form scale or co-crystallize with the product. Improved thermodynamic modeling capabilities that allow robust predictions for multicomponent aqueous systems containing numerous electrolytes and nonelectrolytes at small to medium concentrations are therefore required. A number of applications and case studies will be explored in this brief review. These include the partitioning of volatile compounds among process liquors, steam and condensates in a train of flash vessels, the development of thermodynamically consistent models for organic impurities in Bayer liquors, and the prediction of their mixing properties with major liquor components.

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‡Corresponding author

ORGANIC IMPURITES IN THE BAYER PROCESS

The Bayer process is employed worldwide to extract alumina from bauxite ores. In outline, it is a gigantic recrystallization process, with a leaching ("digestion") step at high temperatures (up to 300 °C for ores consisting primarily of diaspore and boehmite, α- and γ-AlOOH(cr), respectively). At lower temperatures, a precipitation stage involves the seeded crystallization of purified gibbsite, $Al(OH)_3$(cr). The process liquor, an alkaline sodium aluminate solution, is recycled continuously and is thus prone to the accumulation of impurities, which have to be removed by appropriate control procedures. Figure 1 shows a schematic representation of the Bayer process, which also indicates possible problems caused by the formation of volatile organic compounds (VOCs).

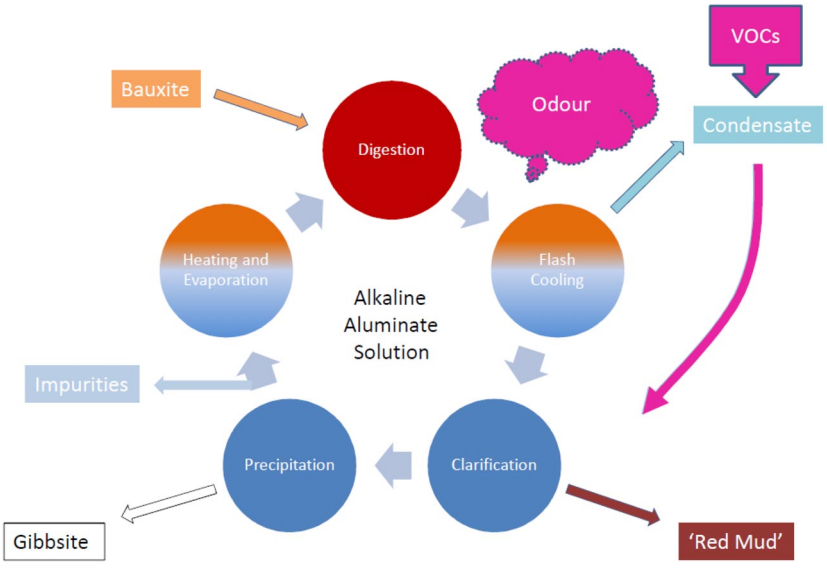

Fig. 1 Schematic of the Bayer process. Impurities entering at the high-*T* digestion stage are partly removed from the liquor stream as solids leaving with "red mud" (essentially iron hydroxides and other solid phases precipitated from the alkaline process liquor). Soluble impurities are controlled by appropriate treatment of side streams, which are discharged, e.g., after the precipitation stage. Typically, VOCs are formed during digestion. They may lead to odor problems, but can also be transported to other parts of the refinery since they partly dissolve in digestion condensates which are often used for washing solid waste ("red mud") and product (gibbsite).

Volatile organic compounds

Organic compounds in Bayer liquors [1] originate from plant (lignin, cellulose, hemicellulose) and animal material that has partly been transformed by oxidative (decomposition) and reductive (resynthesis) humification processes [2] during the geochemical formation of bauxite ores. During digestion, reducing conditions prevail which result in degradation of the organic material extracted from the ore. As a result, hydrogen, methane, ammonia, elemental mercury, and various VOCs are formed [3]. Due to their high reactivity, many VOCs are short-lived, whereas other volatiles (including Hg) are released during flash cooling and partly dissolve in the so-called digestion condensate (Fig. 1). This leads to certain environmental issues, including odor problems, which can be compounded when 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 [4] within the framework of our existing Bayer liquor (Pitzer) model [5].

In brief, Gibbs energies of some 40 aqueous organic species have been added to our Bayer liquor model. These were calculated from so-called Gibbs energies of hydration (i.e., differences in Gibbs energies of infinitely dilute aqueous and ideal gaseous species) using a model originally developed for geochemical applications [6]. In this model, the thermodynamic quantities of hydration were calculated by correlating a linear temperature dependence of the standard heat capacity of hydration with the standard Gibbs energy of hydration at 298.15 K. The standard enthalpy, entropy, heat capacity, and volume of hydration, which are required to calculate the temperature and pressure dependencies of the standard Gibbs energy of hydration, of numerous (mainly organic) solutes are collected in an electronic database [7]. To describe the non-ideality of the vapor phase, a virial equation of state truncated after the second virial coefficient was used. Since VOCs occur in the vapor phase at very low concentrations, only the second cross virial coefficients B_{12} had to be calculated (besides B_{11} for $H_2O(g)$) through appropriate correlations [6,8,9]. These models and approximations were shown to be reliable at temperatures up to about 280–300 °C and saturation pressure [6], which covers the conditions of interest in most hydrometallurgical processes, including the high-temperature digestion stage in Bayer plants.

The actual thermodynamic simulation comprised the calculation of the partitioning of volatile compounds among Bayer process liquors, steam and condensates in a high-temperature Bayer digester and a subsequent train of eight flash vessels [4]. The latter were simulated by calculating adiabatic (isenthalpic) boiling temperatures at successively lower pressures. Condenser temperatures were obtained by imposing the condition of 99.5 % condensation of the steam produced in the corresponding flash vessel. Liquid-vapor partitioning of volatiles was calculated for the temperatures and pressures prevailing at the two-phase equilibria in the flash vessels and condensers (Fig. 2). These equilibrium calculations were performed using ChemApp, a library of subroutines for thermodynamic calculations [10]. A FORTRAN code was written to define the material flows between the various stages, call the appropriate ChemApp routines, and collect the results [4].

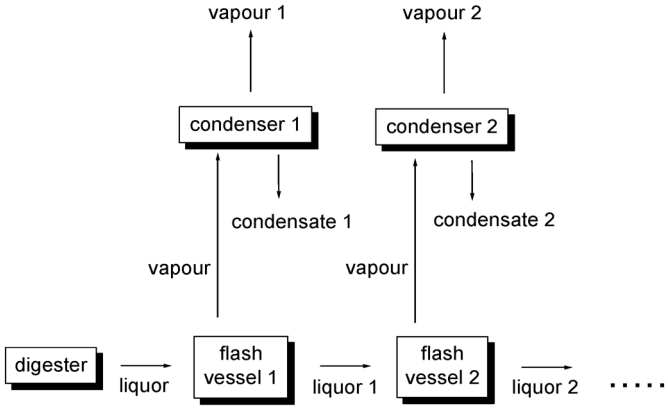

Fig. 2 Thermodynamic simulation of a train of 8 flash vessels and condensers in a Bayer plant. The liquor enters the first flash vessel from the high-temperature digester, passes the subsequent flash vessels operating at successively lower pressures, and is eventually cooled down to boiling temperature at atmospheric pressure.

Figure 3 presents the distribution of selected volatiles among the various phases. Since absolute concentrations of volatile compounds are in general unavailable, relative values (percentages) are given. These refer to a trace amount of each volatile leaving the digester as species dissolved in the liquor, which is taken as 100 %. In general, the distribution of trace amounts of volatiles between aqueous and vapor phases depends on the relative amounts of the two phases. For the flash tanks, these amounts are calculated assuming adiabatic expansion. The resulting relative liquor compositions shown in Fig. 3

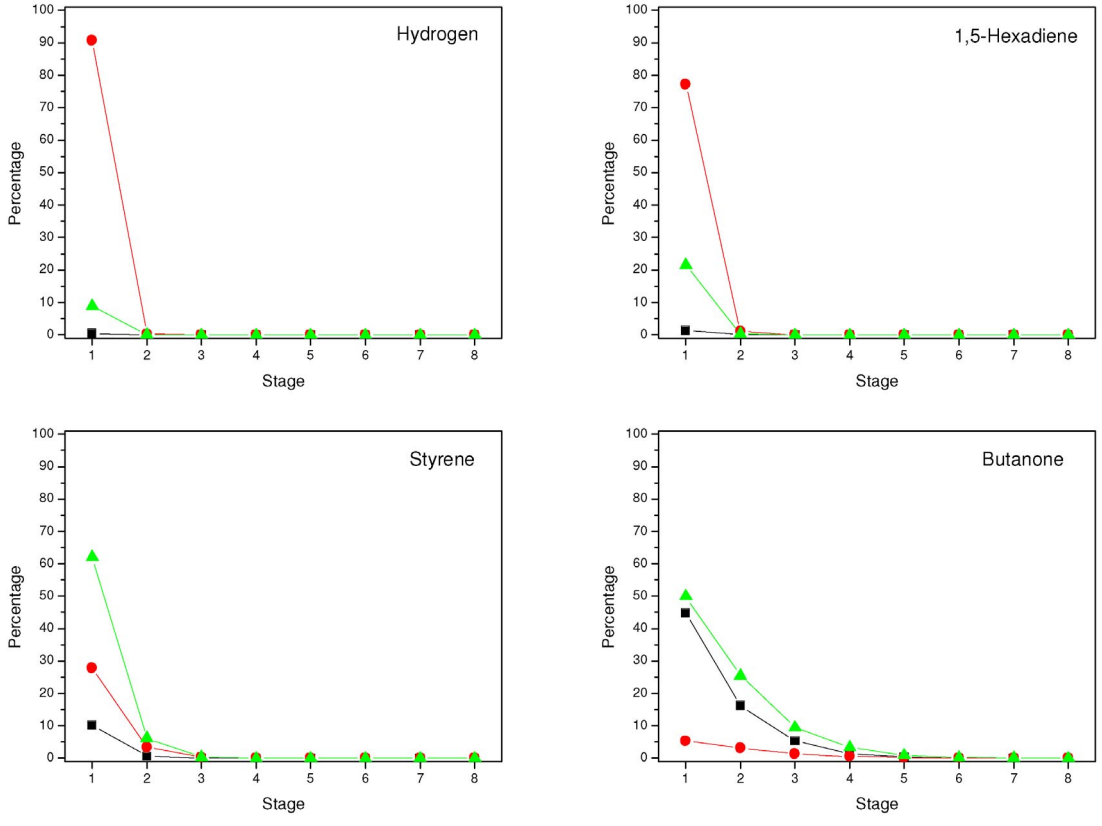

Fig. 3 Relative amounts of selected volatiles in liquor (■), steam (●), and condensate (▲) from thermodynamic simulations of a train of flash vessels in a Bayer plant. Hydrophobic solutes like H_2 and aliphatic hydrocarbons are virtually completely removed from the liquor in the first flash vessel, where they can be destroyed by thermal oxidation. Aromatic compounds, such as styrene, dissolve significantly in the first condensate and will be partly released on cooling and reducing the pressure. On the other hand, more hydrophilic substances like aldehydes, ketones, alcohols, and amines dissolve in the aqueous phases to much higher extents, and are consequently being transported down the train of flash vessels. They may be released in other parts of the refinery where digestion condensate is being used for washing or dilution purposes.

were then taken as input to the next flash vessel. The relative vapor compositions obtained from flashing were the inputs to the corresponding condensers (Fig. 2).

THERMODYNAMICALLY CONSISTENT PROPERTY MODELS

The apparatus, measurements, and modeling capabilities employed in our laboratory to describe the thermodynamic properties of Bayer liquor solutions have been reviewed recently [11]. In brief, the Murdoch Bayer liquor model is a Pitzer model with the components NaOH + $NaAl(OH)_4$ + Na_2CO_3 + Na_2SO_4 + NaCl + NaF + $Na_2C_2O_4$ (sodium oxalate) + NaHCOO (sodium formate) + $NaCH_3COO$ (sodium acetate, NaOAc) + H_2O [5]. The model is primarily based on experimentally determined densities and heat capacities of binary and ternary aqueous solutions [12–19], which are integrated to give Gibbs energies. From these, all integral and partial molar properties of the multicomponent liquor are calculated in a thermodynamically consistent manner. Together with the thermodynamic properties of relevant solid phases, the solubilities of gibbsite, boehmite, and the "impurities" sodium oxalate and

kogarkoite (Na_3FSO_4) [20] in Bayer liquors can be calculated over concentration and temperature ranges of industrial interest. The modeling software developed at Murdoch University, known as BAYER.EXE [5], has been coded as a DLL module for incorporation into commercial process simulators.

Models for metastable but persistent organic compounds

The primary low-molecular-weight (LMW) degradation products of organic macromolecules extracted in hot Bayer liquors from bauxite ores are benzenecarboxylates, phenolates, and aliphatic carboxylates [1]. Although the carbonate ion is the thermodynamically stable form of carbon under aerobic Bayer process conditions, benzoate, succinate, acetate, formate, and particularly the sparingly soluble oxalate are known to persist at metastable equilibrium with a 6 mol L^{-1} NaOH solution at temperatures up to 180 °C for up to five weeks [21]. In addition to the last three of these sodium carboxylates, sodium benzoate has recently been incorporated into our Bayer liquor model [5]. Due to their persistence, these compounds are treated as nonreactive components that have an impact on the thermodynamic properties of the liquor. Sodium benzoate permits coverage of a wider, more realistic, organic sodium-to-organic carbon range and also provides aromatic groups required for the modeling of high-molecular-weight organics (e.g., humic substances) by LMW compounds. The present thermodynamically consistent model of aqueous sodium benzoate has been derived from our own measurements [22,23] and from literature data (Fig. 4). In our laboratory, heat capacities and densities of sodium benzoate

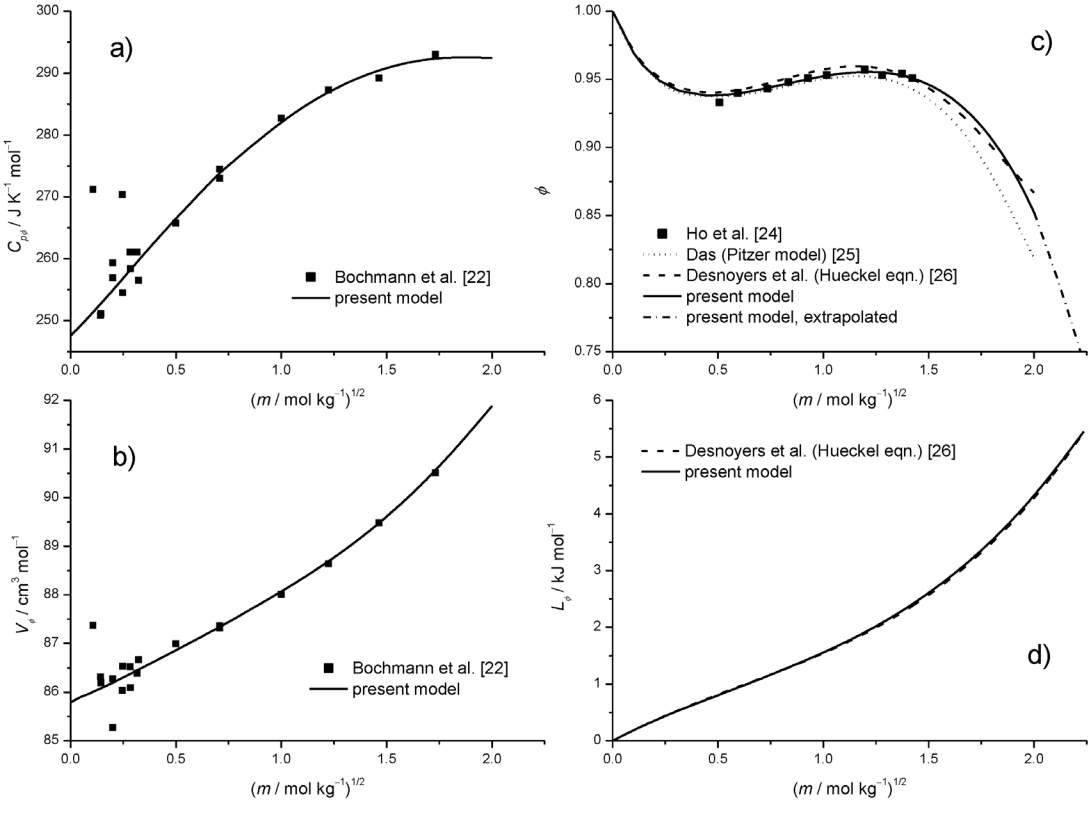

Fig. 4 The present model of aqueous sodium benzoate describes experimental data available at 25 °C [22,24–26] in a thermodynamically consistent manner: (a) heat capacities, (b) volumes, (c) osmotic coefficients, (d) enthalpies.

solutions were measured at 25 °C using a Picker calorimeter [22] and at 100 bar and temperatures up to 300 °C [23] using the equipment described earlier [11]. No decomposition was apparent even at these high temperatures.

PREDICTION OF THERMODYNAMIC PROPERTIES FOR MULTICOMPONENT ELECTROLYTE SOLUTIONS

A prerequisite for the successful modeling of physicochemical properties (such as densities and heat capacities) in hydrometallurgical systems is a thermodynamically consistent description of the mixing properties of multicomponent solutions. Because of the dimensional explosion involved in the experimental characterization of multicomponent systems, it is essential to employ reliable mixing rules such as Young's rule [15–18,27,28] or Zdanovskii's rule [29–31]. Such rules can then be used for the prediction of physicochemical properties of multicomponent systems from those determined experimentally for a manageable number of simpler (usually binary) subsystems.

Ternary mixtures of NaOH(aq) + NaOAc(aq) at 25 °C

Experimental data for the apparent molar volumes and heat capacities of ternary mixtures of NaOH(aq) + NaOAc(aq) at 25 °C [22] are plotted in Fig. 5 as a function of the stoichiometric "molar fraction" r ($\equiv m_{\mathrm{NaOAc}}/m_{\mathrm{NaOH}} + m_{\mathrm{NaOAc}}$) at stoichiometric ionic strengths of 1 and 4 mol kg^{-1}.

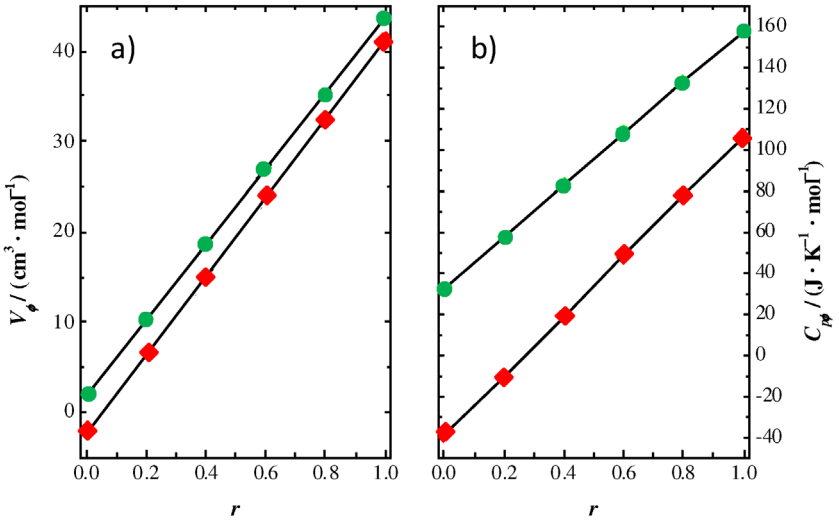

Fig. 5 Apparent molar volumes (a) and heat capacities (b) of NaOH(aq) + NaOAc(aq) mixtures at I = 1 mol kg^{-1}, ◆ and I = 4 mol kg^{-1}, ●, as function of the "molar fraction", r, at T = 298.15 K and p = 0.1 MPa. The lines represent the data calculated from Young's rule.

As has been found previously for other electrolyte mixtures [32], the present data show that both V_ϕ and $C_{p\phi}$ closely obey Young's rule [33], which posits linear relationships between the binary end-member quantities for ternary mixtures.

The magnitudes of the deviations from ideal (Young's rule) behavior of apparent molar volumes and heat capacities of the mixtures, $V_{\phi,\mathrm{mix}}$ and $C_{p\phi,\mathrm{mix}}$, are better seen in Fig. 6, which plots the excess quantities, Y_ϕ^{xs} ($Y = V$ or C_p), as a function of r, where Y_ϕ^{xs} is defined as

$$Y_{\phi}^{xs} \equiv Y_{\phi,mix} - Y_{\phi,mix}^{id}$$

with $Y_{\phi,mix}$ being the measured property of the mixture and $Y_{\phi,mix}^{id}$ the ideal property of the mixture calculated using Young's rule:

$$Y_{\phi,mix}^{id} = rY_{\phi,1} + (1 - r)Y_{\phi,2}$$

where $Y_{\phi,i}$ are the apparent molar quantities for the *binary* solutions of the two electrolytes (i = 1 or 2) measured at the total (stoichiometric) ionic strength of the *ternary* mixture.

As can be seen from Fig. 6, the deviations from ideal (Young's rule) mixing, while systematic, are extremely small: $V_{\phi}^{xs} < 0.3$ cm^3 mol^{-1} and $C_{p\phi}^{xs} < 1$ J K^{-1} mol^{-1} (the scatter is a realistic reflection of the likely experimental uncertainties). This is a critical insight of our strategy to deal with multicomponent solution mixtures given the inevitably limited experimental data available. Interestingly, the deviations from Young's rule appear to be negative at I = 1 mol kg^{-1} but positive at I = 4 mol kg^{-1}, although they are so small that they are barely detectable even with state-of-the-art instrumentation.

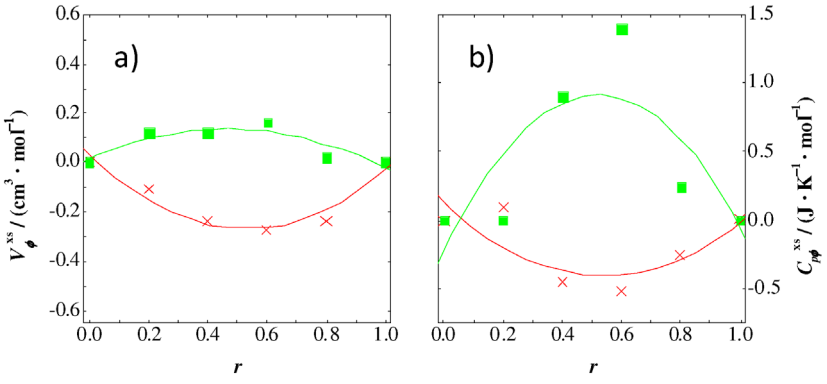

Fig. 6 Deviations from Young's rule of apparent molar volumes, V_{ϕ}^{xs} (a), and heat capacities, $C_{p\phi}^{xs}$ (b), of NaOH(aq) + NaOAc(aq) mixtures as function of the "molar fraction", r, at T = 298.15 K, p = 0.1 MPa and I = 1 mol kg^{-1}, × and I = 4 mol kg^{-1}, ■.

Ternary mixtures of NaOH(aq) + NaOAc(aq) at high temperatures

Apparent molar volumes for ternary electrolyte solutions NaOH(aq) + NaOAc(aq) at I/mol kg^{-1} = 3 and 4 over the temperature range 323 $\lesssim$ T/K $\lesssim$ 573 are plotted in Figs. 7 and 8 [23]. They conform very closely to linear (Young's rule) mixing behavior at all temperatures up to and including 573 K at both I. Again, even though the departures are extremely small ($V_{\phi}^{xs} < 1.6$ cm^3 mol^{-1}) they are systematic, increasing regularly with increasing T. This systematic behavior means that the effects of the non-ideal mixing, small as they are, can be accurately modeled.

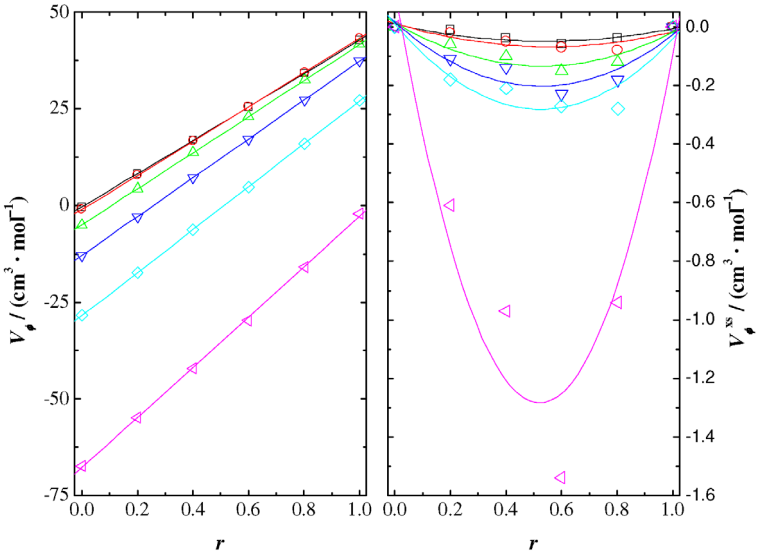

Fig. 7 Apparent molar volumes, V_ϕ, of mixtures of NaOH(aq) + NaOAc(aq) at I = 3 mol kg^{-1} and their deviation from ideal behavior, V_ϕ^{xs}, as a function of the molar fraction r at T/K = 323.15 (□), 373.15 (○), 423.15 (△), 473.15 (▽), 523.15 (◇), and 573.15 (◁) at pressure p = 10 MPa.

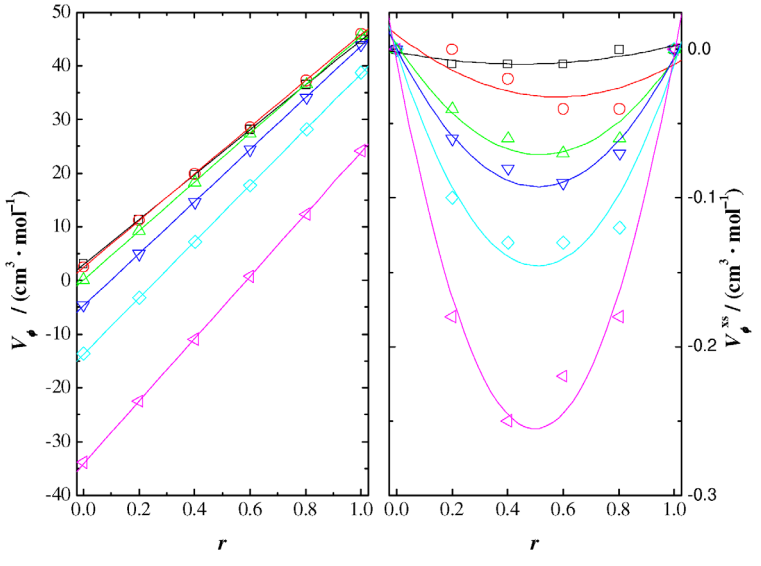

Fig. 8 Apparent molar volumes, V_ϕ, of mixtures of NaOH(aq) + NaOAc(aq) at I = 4 mol kg^{-1} and their deviation from ideal behaviour, V_ϕ^{xs}, as a function of the molar fraction r at T / K = 323.15 (□), 373.15 (○), 423.15 (△), 473.15 (▽), 523.15 (◇) and 573.15 (◁) at pressure p = 10 MPa.

CONCLUDING REMARKS

Robust thermodynamic models for industrially relevant organic substances have been incorporated in a consistent manner into our existing Bayer liquor model. Some of these compounds are volatile and therefore highly relevant to environmental pollution and OSH problems. The Murdoch models allow the prediction of the partitioning of volatile compounds between aqueous and vapor phases over tempera-

ture ranges of interest to Bayer-process alumina refining. Transport of these organic impurities through refineries can be simulated and possible origins of environmental problems can be identified.

Mixing rules for the prediction of physicochemical properties of multicomponent systems from those determined experimentally for simpler subsystems are crucial for hydrometallurgical simulations aiming at higher product quality and quantity as well as reductions in emissions and energy consumption. Thermodynamic properties, such as densities and heat capacities, of mixtures involving metastable but persistent organic compounds were found to follow Young's rule to a good approximation even at temperatures up to 300 °C. The resulting models do not require additional mixing parameters and can therefore be used for robust thermodynamic simulations of multicomponent systems.

However, predictions of partial molar quantities, such as activity coefficients, of mixture components are much more intricate and will be dealt with elsewhere [34].

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