Fluid Phase Equilibria 279 (2009) 141–148

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Modeling aqueous electrolyte solutions. Part 2. Weak electrolytes

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ARTICLE INFO

Article history:
Received 6 October 2008
Received in revised form 20 February 2009
Accepted 23 February 2009
Available online 9 March 2009

Keywords:
Mean ionic activity coefficient
Equation of state
PC-SAFT
Debye–Hückel
Aqueous solutions
Primitive model
Ion pairing
Ion association
Acids
Weak electrolytes

ABSTRACT

In this work the ePC-SAFT model is applied to weak electrolytes, such as weak acids or salts that do form ion pairs. Considering an association/dissociation equilibrium accounts for the fact that the electrolytes are not fully dissociated. Applying this approach, modeling the mean ionic activity coefficients (MIAC) as well as the water activity coefficients (WAC) is in very good agreement with experimental data for the aqueous HF system as well as for solutions of cadmium halides or alkali acetates. Experimental MIACs of $ZnBr_2$ and ZnI_2 reveal the formation of more than one complex in aqueous solutions. Implementing a simultaneous two-step ion-pairing mechanism also allows the modeling of the MIAC of these zinc salts in water.

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1. Introduction

The present paper is the continuation of our previous work [1]. It was already shown that the ePC-SAFT model proposed by Cameretti et al. [2] can be applied to aqueous solutions of strong electrolytes. The solution densities (pvT) and mean ionic activity coefficients (MIAC) of 115 systems were modeled with reasonable accuracy.

A solution of a strong electrolyte is considered a three-component system. The use of ion-specific instead of salt-specific parameters drastically reduces the total set of parameters. An additional advantage of this approach is the ability to directly apply the model to systems containing various electrolytes even when a common ion is present. In addition, the two parameters determined for each ion possess a physical meaning and are sequenced in a reasonable order.

In this work, we concentrate on the thermodynamic properties of weak acids and partially associated salts in water.

Strong acids like aqueous solutions of HCl, HBr, and HI (acid constants $K_a \gg 10^6$ mol/l at 25 °C) almost fully dissociate into their respective ions. In contrast, hydrogen fluoride (HF) in water behaves completely different ($K_a = 7 \times 10^{-4}$ mol/l). Odde et al. [3–5] studied the structure of HF in water as function of the number of water molecules surrounding one HF pair. Based on density functional theory, they concluded that HF – in contrast to the other hydrogen halides – does not dissociate in water at concentrations higher than 1 mol/l. They ascribe this behavior to the very strong HF–H bond compared to the OH–H bond as well as to the different stabilities (energies) of the dissociated and the undissociated species. In addition to that, the presence of the dominating species HF is accompanied by HF_2^- and even higher aggregates for which equilibrium constants have been determined [6]. Moreover, pH measurements by Warren [7] revealed that HF forms $(HF)_2$ dimers in water. This view is supported by Braddy et al. [6] who also assume the association of HF molecules even at low concentrations. Thus, a physically meaningful model of HF solutions needs to account for this specific behavior of HF in solution. Although other authors (e.g. Ref. [8]) have calculated the MIACs of strong acids in water, the simultaneous modeling of densities, water activities, and MIAC (especially for the weak acid HF) has not yet been reported. The approach we use in this work is implementing an association/dissociation mechanism using the acid constant K_a in combination with the classical ePC-SAFT model.

Whereas in [1] all salts were approximated to be fully dissociated, conductance and potentiometric studies [9,10] reveal that there is an ion-pair formation (association) for some salts even under moderate conditions. In general, the nature of the ion pairs formed in water can be subdivided into contact ion pairs (CIP)

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doi:10.1016/j.fluid.2009.02.015

and solvent-separated ion pairs (SSIP). In the CIP, the species are in direct contact with each other whereas in the SSIP, the ions either share one water molecule or are completely separated by water molecules. SSIPs are experimentally found in aqueous sulfate solutions, e.g. of $MgSO_4$ and $CdSO_4$ [11] or of $CoSO_4$, $NiSO_4$, $ZnSO_4$, and $CuSO_4$ [12]. As the hydration sheath is still intact within the SSIP species, we do not apply an ion-pairing theory to these systems. Here, classical ePC-SAFT modeling leads to reasonable results even without consideration of any ion pairing (compare Table 3 of this work). However, in highly concentrated salt solutions (e.g. $x_{\mathrm{salt}} > 0.25$ in an aqueous $NaClO_4$ solution), there are not enough water molecules available to maintain the hydration sheath [13]. Consequently, at those concentrations the ions are in direct contact and the formation of CIPs is preferred. Moreover, the formation of CIPs is also found in aqueous $CdCl_2$ solutions [11,14] even at low concentrations. In general, ion pairing is assumed to occur to a greater extent in asymmetric electrolytes than in 1:1 electrolytes.

Finally, the effect of so-called "local hydrolysis" [15], which is expected to occur for systems containing derivatives of weak acids can also result in a formation of ion pairs [16]. Derivatives of weak acids are strong proton acceptors, which might explain the unusual behavior of acetate salts in water [1]. Significant ion-pair formation was observed in aqueous solutions of lithium acetate whereas in aqueous solutions of potassium acetate, the electrolyte is almost completely dissociated [17]. Other strong proton acceptors are the anions of hydroxides, fluorides, and formiates. Thus, the effect of localized hydrolysis and ion pairing is also expected to be dominant in solutions containing these anions, and this is supported by experimental evidence [18–20].

To account for the association of ions (ion pairing) in the modeling, we apply the approach of an association/dissociation equilibrium, as e.g. proposed by Robinson and Stokes [21] (see Section 2 of this work). They applied the law of mass action for the ion-pair formation where the ion pair is in equilibrium with its respective free ions.

A similar approach has been successfully pursued by Tikanen et al. [22–24], who also determined an ion-pairing constant K_{ip} by evaluating all activities a_j of the ionic species. Simonin et al. [25] included the effect of the ion pairing in the MSA screening parameter Γ, which describes an inverse distance of shielding evoked by ions. They allowed for a change of Γ as a function of K_{ip}, which they adjusted to experimental MIAC data. Their approach provided excellent results for about 80 aqueous electrolyte systems including alkali acetates with ARDs for MIAC being lower than 1%. However, they apply their approach to any electrolyte system, including those where ion pairing is neither probable nor proven experimentally. They could not accurately describe aqueous rubidium or cesium solutions without assuming ion pairing. However, to the best of our knowledge, there is no experimental evidence for ion pairing in these systems and they could already be accurately described by the classical ePC-SAFT model [1].

In this work, only those electrolytes for which ion pairing has been proven experimentally are modeled as ion pairs, such as the alkali acetates or cadmium halides.

2. Theory

2.1. Implementation of ion pairing into ePC-SAFT

One possible description of electrolytes in solution is treating them as if they would not form ion pairs at all. In our previous work [1], we followed this approach, yielding good results for pvT, VLE, and MIAC data for many single-salt solutions. Although a slightly higher ARD was found for electrolytes containing fluorides or hydroxides for which ion pairing is expected ("localized hydrolysis"), the thermodynamic properties could already be modeled in good agreement with experimental data by the classical ePC-SAFT model. In contrast to the fluorides or hydroxides, using the universal parameter set of [1] did not allow for an even qualitative modeling of aqueous alkali acetate systems. For this reason, in the present work, we use a chemical model of ion pairing to account for the fraction of ionic species which are not dissociated.

As in [14,22–24], we consider ion pairing as a reaction where the completely dissociated electrolyte is in equilibrium with the ion pair formed:

$$\nu_-\mathrm{An}^{z-} + \nu_+\mathrm{Cat}^{z+} \overset{K_{\mathrm{ip}}}{\longleftrightarrow} [\mathrm{An}_{\nu_-} - \mathrm{Cat}_{\nu_+}]_{\mathrm{ip}}^{z_+\nu_+ + z_-\nu_-} \tag{1}$$

Here, z and ν denote the valence and the stoichiometric factor of the ions, respectively. ν_+ and ν_- add up to ν. K_{ip} is given by the law of mass action as:

$$K_{\mathrm{ip}} = \prod_j a_j^{*,\nu_j} = \frac{a_{\mathrm{ip}}^*}{a_-^{*,\nu_-}\cdot a_+^{*,\nu_+}} \tag{2}$$

where the a_j^* are the activities of the ions and of the ion pair related to the reference state of infinite dilution, respectively. The mean ionic activity of any electrolyte can be expressed with the well-known definition of the molality-based MIAC in Eq. (5) yielding [21]:

$$a_\pm^{*,m} = \left((a_+^{*,m})^{\nu_+}\cdot(a_-^{*,m})^{\nu_-}\right)^{1/\nu} = \left(\alpha(\nu-2+\alpha)^{(\nu-1)}\right)^{1/\nu}\cdot m_s\cdot\gamma_\pm^{*,m} \tag{3}$$

where α and m_s are the fraction of the electrolyte species that do not form ion pairs and the total salt molality, respectively.

In the case of a 1:1 electrolyte, the activity $a_\pm^{*,m}$ is obtained by $a_\pm^{*,m} = \alpha m_s \gamma_\pm^{*,m}$ whereas the activity of the ion pair in solution is determined as follows:

$$a_{\mathrm{ip}}^{*,m} = (1-\alpha)\cdot m_s\cdot\gamma_{\mathrm{ip}}^{*,m} \tag{4}$$

The molality-based MIAC can be converted from the one based on mole fractions $\gamma_\pm^{*,x}$ using:

$$\gamma_\pm^{*,m} = \left((\gamma_+^{*,x})^{\nu_+}\cdot(\gamma_-^{*,x})^{\nu_-}\right)^{1/\nu}\cdot\left(\frac{1}{1+\nu\cdot 0.001\cdot M_w}\right) \tag{5}$$

The mole-fraction-based asymmetrical single-ionic activity coefficients $\gamma_{+,-}^{*,x}$ in Eq. (5) are directly obtained by ePC-SAFT.

The combination of Eqs. (3) and (4) with Eq. (2) finally yields the equilibrium constant for ion pairing K_{ip} as a function of the fraction $(1-\alpha)$ of ion pairs formed. For 2:1 or 1:2 electrolytes this results in:

$$K_{\mathrm{ip}}^m = \frac{\gamma_{\mathrm{ip}}^{*,m}\cdot(1-\alpha)}{m_s^2\cdot(\gamma_\pm^{*,m})^3\cdot\alpha(1+\alpha)^2} \tag{6}$$

whereas for symmetrical electrolytes one obtains:

$$K_{\mathrm{ip}}^m = \frac{\gamma_{\mathrm{ip}}^{*,m}\cdot(1-\alpha)}{m_s\cdot(\gamma_\pm^{*,m})^2\cdot\alpha^2} \tag{7}$$

2.2. Parameter estimation for ion pairs

In systems without ion pairing, two ion-specific ePC-SAFT parameters are used for each of the ions: the diameter of the hydrated ion σ_j and the dispersive-energy parameter u_j/k_{B}. However, systems with ion pairing do not contain only water, the anion, and the cation, but also the ion pair. This means that three more parameters need to be specified: segment diameter σ_{ip}, dispersive-energy parameter $u_{\mathrm{ip}}/k_{\mathrm{B}}$, and segment number $m_{\mathrm{seg,ip}}$ of the ion

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