Estimation of Pitzer interaction parameters from heat capacity, osmotic coefficient and density data: Application to the BaCl 2 -H 2 O system (0

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Estimation of Pitzer interaction parameters from heat capacity, osmotic coefficient and density data: Application to the $BaCl_2$-H_2O system (0<T<90°C and 0<m $BaCl_2$<2 mol.kgw^{-1})

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INTRODUCTION

The Pitzer formalism [1] uses the derivatives of the excess Gibbs free energy (G^{ex}) of brines to describe their properties like *(i)* the osmotic coefficient (ϕ), *(ii)* the apparent relative molar enthalpy (L_ϕ), *(iii)* the apparent molar heat capacity ($C_{p,\phi}$) and *(iv)* the apparent molar volume (V_ϕ). From the last three properties, we can calculate the measurable dilution enthalpy (ΔH^D), heat capacity (C_p) and density (d) of an electrolyte solution, respectively.
The expression for the excess Gibbs free energy and its links with the different apparent properties of a brine are given in Figure 1.

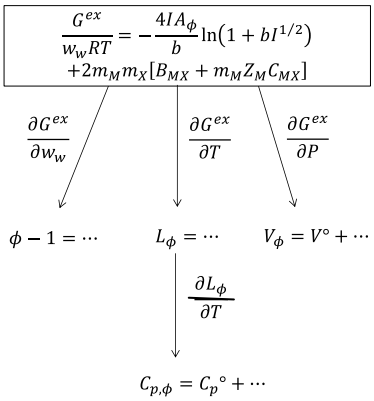

Fig. 1: Links between the three derivatives of the Gibbs excess energy (G^{ex}).

The equations for calculating such brine properties were implemented in the recent version (V3) of the geochemical code Phreeqc [2].
We present here an application of the software functions to the $BaCl_2$-H_2O binary system between 0 to 90°C up to 2 mol.kgw^{-1}.

DESCRIPTION OF THE WORK

The description of the $BaCl_2$-H_2O binary system needs the use of the Pitzer interaction parameters (β^0, β^1 and C^Φ) to compute B_{MX} and C_{MX}. These three interaction parameters depend on temperature according to the following equation [3]:

$$Y(T)=a_1 + a_2T + a_3T^2 + a_4/T + a_5\ln T + a_6/(T-263) + a_7/(680-T) + a_8/(T-227) \quad \textbf{(Eq. 1)}$$

We coupled an optimization software with Phreeqc V3 in order to estimate simultaneously the a_i parameters. Both Heat capacity and osmotic coefficient data are used as calibration data. Indeed, $C_{p,\phi}$ expression is a combination of the first and second derivatives of *Eq. 1* with respect to temperature sensitivity. So, the heat capacity data help determining a_2, a_3, a_5, a_6, a_7 and a_8 while the osmotic coefficient data help determining a_1 and a_4. V_ϕ expression depends on the volumetric parameters (β^{0V}, β^{1V} and $C^{\Phi V}$), which are the pressure derivatives of β^0, β^1 and C^Φ, respectively. In this study, we determined a value of β^{0V} which allows modelling the density. The partial molar heat capacity and volume of the solute at infinite dilution ($C_p°$ and $V°$, respectively) are computed with the HKF equation of state for aqueous species given in Johnson et al. [4], and using the parameters given in the Thermoddem database [5]. One of the originality of this work is to calculate the partial molar volume from the HKF parameters and not to consider it as an adjustable parameter.

RESULTS

The experimental data are provided by several previous studies [6-12]. We used the data at 0, 20, 25, 40, 60 and 90°C for the heat capacities and at 25 and 80°C for the osmotic coefficient to determine the interaction parameters.

Results are plotted on figures 2 to 4 as a function of $BaCl_2$ concentration. They represent, for different temperatures, the osmotic coefficient, the heat capacity and the density of the aqueous solution, respectively. For the density, a good match with experimental data at various temperatures could be obtained using a constant β^{0V} value. All the results presented in Fig. 2, 3 and 4 are obtained at 1 bar.

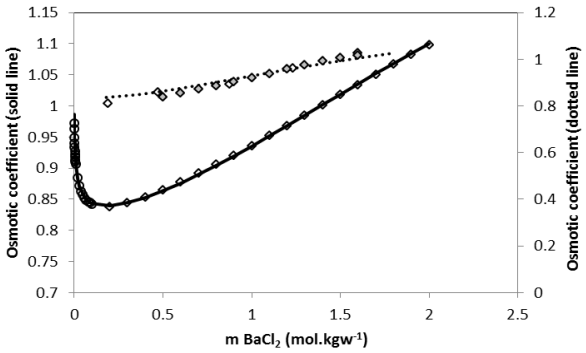

Fig. 2: Osmotic coefficient, ϕ, for the $BaCl_2$-H_2O binary system as a function of $BaCl_2$ molality at 25°C (solid line) and at 45°C (dotted line). The symbols correspond to the experimental data.

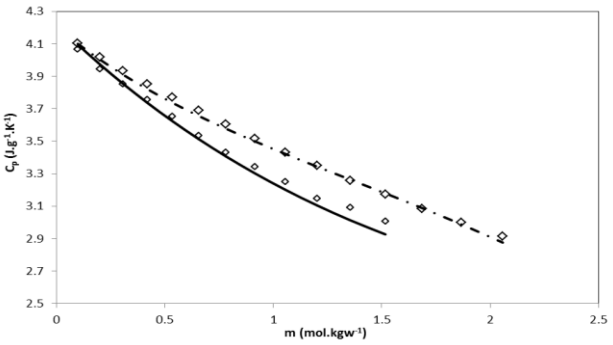

Fig. 3: Calculated (lines) and experimental (open symbols) heat capacity, C_p, for the $BaCl_2$-H_2O binary system as a function of $BaCl_2$ molality at 0°C (solid line) and 90°C (dash-dot line).

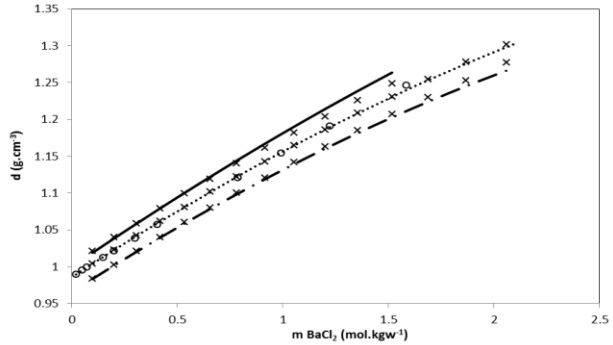

Fig. 4: Calculated (lines) and experimental (symbols) density as a function of $BaCl_2$ molality at 0°C (solid line), 55°C (dashed line) and 90°C (dash-dot line).

CONCLUSIONS

In this study we proposed a complete methodology to determine a full set of Pitzer interaction parameters for the $BaCl_2$-H_2O electrolyte system. The parameters are allow representing the osmotic coefficient, the solution heat capacity and the solution density for temperatures ranging from 0 to 90°C and concentrations up to 2 mol.kgw^{-1}. The work done on the binary $BaCl_2$ system can be extended to many other systems, if sufficient experimental data are available to fully parameterize the systems.

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