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## Estimation of Pitzer interaction parameters from heat capacity, osmotic coefficient and density data: Application to the BaCl<sub>2</sub>-H<sub>2</sub>O system (0<T<90°C and 0<m BaCl<sub>2</sub><2 mol.kgw<sup>-1</sup>)

Lach Adeline<sup>1,2</sup>, André Laurent<sup>1</sup>, Lassin Arnault<sup>1</sup>, Azaroual Mohamed<sup>1</sup>, Cézac Pierre<sup>2</sup>, Serin Jean-Paul<sup>2</sup>

<sup>1</sup>BRGM, D3E/BGE, 3 avenue Claude Guillemin, 45100 Orléans, France

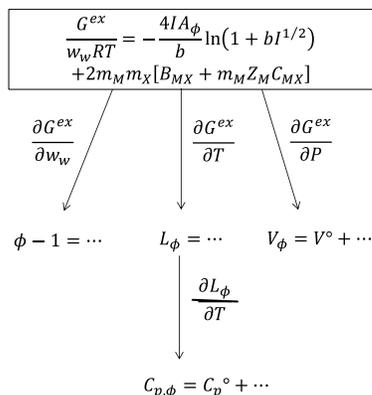
[A.Lach@brgm.fr](mailto:A.Lach@brgm.fr)

<sup>2</sup>LaTEP, UPPA, Rue Jules Ferry, 64075 Pau Cedex

### 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 ( $\phi$ ), (ii) the apparent relative molar enthalpy ( $L_\phi$ ), (iii) the apparent molar heat capacity ( $C_{p,\phi}$ ) and (iv) the apparent molar volume ( $V_\phi$ ). From the last three properties, we can calculate the measurable dilution enthalpy ( $\Delta H^D$ ), 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<sub>2</sub>-H<sub>2</sub>O binary system between 0 to 90°C up to 2 mol.kgw<sup>-1</sup>.

### DESCRIPTION OF THE WORK

The description of the BaCl<sub>2</sub>-H<sub>2</sub>O binary system needs the use of the Pitzer interaction parameters ( $\beta^0$ ,  $\beta^I$  and  $C^\phi$ ) to compute  $B_{MX}$  and  $C_{MX}$ . These three interaction parameters depend on temperature according to the following equation [3]:

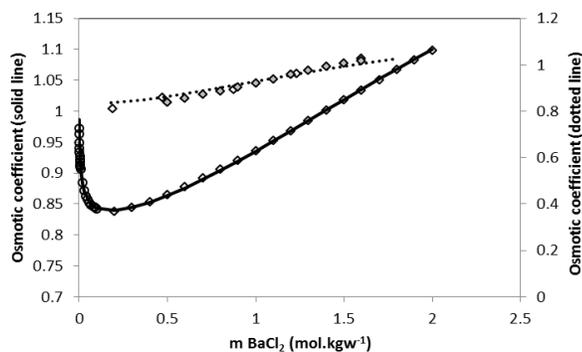
$$Y(T) = a_1 + a_2 T + a_3 T^2 + a_4/T + a_5 \ln T + a_6/(T-263) + a_7/(680-T) + a_8/(T-227) \quad (\text{Eq. 1})$$

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  $a_4$ .  $V_\phi$  expression depends on the volumetric parameters ( $\beta^{0V}$ ,  $\beta^{1V}$  and  $C^{\phi V}$ ), which are the pressure derivatives of  $\beta^0$ ,  $\beta^I$  and  $C^\phi$ , respectively. In this study, we determined a value of  $\beta^{0V}$  which allows modelling the density. The partial molar heat capacity and volume of the solute at infinite dilution ( $C_p^o$  and  $V^o$ , 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.

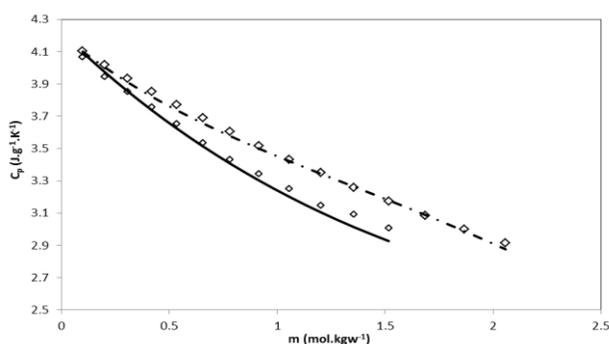
### RESULTS

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.

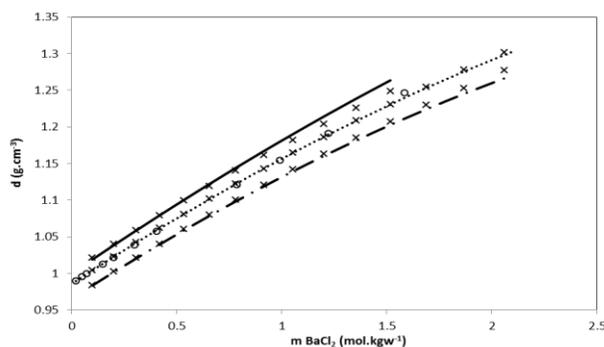
Results are plotted on figures 2 to 4 as a function of BaCl<sub>2</sub> concentration. They represent, for different temperatures, the osmotic coefficient, the heat capacity and the density of the aqueous solution, respectively. For the density, a good match with experimental data at various temperatures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



**Fig. 2:** Osmotic coefficient,  $\phi$ , for the  $\text{BaCl}_2\text{-H}_2\text{O}$  binary system as a function of  $\text{BaCl}_2$  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  $\text{BaCl}_2\text{-H}_2\text{O}$  binary system as a function of  $\text{BaCl}_2$  molality at 0°C (solid line) and 90°C (dash-dot line).



**Fig. 4:** Calculated (lines) and experimental (symbols) density as a function of  $\text{BaCl}_2$  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  $\text{BaCl}_2\text{-H}_2\text{O}$  electrolyte system. The parameters 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

$\text{mol.kgw}^{-1}$ . The work done on the binary  $\text{BaCl}_2$  system can be extended to many other systems, if sufficient experimental data are available to fully parameterize the systems.

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