



**HAL**  
open science

**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**

Adeline Lach, Laurent André, Arnault Lassin, Mohamed Azaroual, Pierre Cézac, Jean-Paul Serin

► **To cite this version:**

Adeline Lach, Laurent André, Arnault Lassin, Mohamed Azaroual, Pierre Cézac, et al.. 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

**HAL Id: hal-01135995**

**<https://brgm.hal.science/hal-01135995>**

Submitted on 26 Mar 2015

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## 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

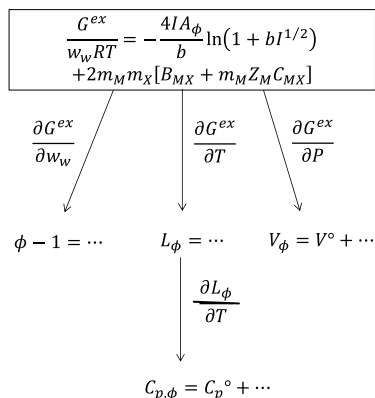
[A.Lach@brgm.fr](mailto:A.Lach@brgm.fr)

<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]:

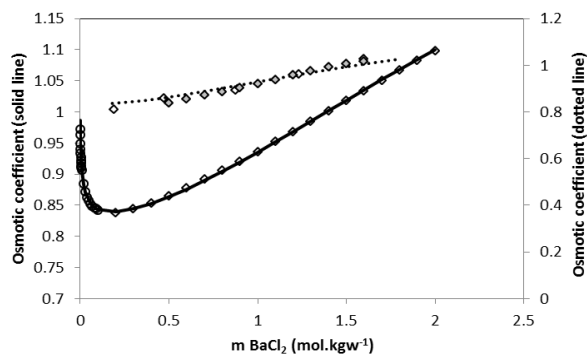
$$Y(T) = a_1 + a_2 T + a_3 T^2 + a_4/T + a_5 \ln T + a_6/(T-263) + a_7/(680-T) + a_8/(T-227) \quad (\text{Eq. 1})$$

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.

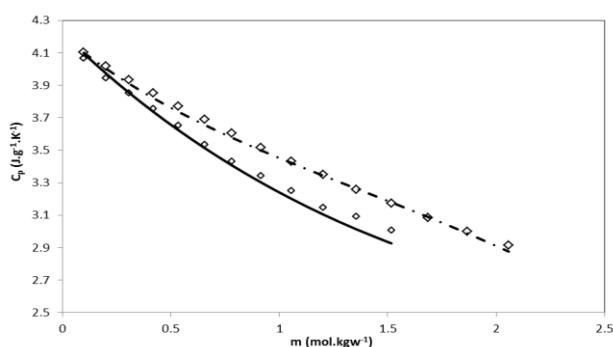
### RESULTS

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.

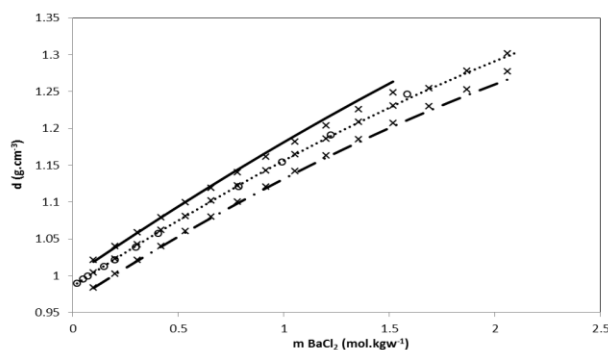
Results are plotted on figures 2 to 4 as a function of BaCl<sub>2</sub> concentration. They represent, for different temperatures, the osmotic coefficient, the heat capacity and the density of the aqueous solution, respectively. For the density, a good match with experimental data at various temperatures 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.

## REFERENCES

1. PITZER, "Activity coefficients in electrolyte solutions.", *CRC Press, Boca Raton* (1991).
2. PARKHURST et al., "Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations." (2013).
3. MØLLER, "The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system, to high temperature and concentration.", *Geochim. Cosmochim. Acta*, **52**, Page 821-837 (1988).
4. JOHNSON et al., "SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar." *Comput. Geosci.*, **18**, Page 899-947 (1992).
5. BLANC et al., "Thermoddem a database devoted to waste minerals" <http://thermoddem.brgm.fr>.
6. BECHTOLD et al., "The Vapor Pressures of Salt Solutions." *J. Am. Chem. Soc.*, **62**, Page 1390-1393 (1940).
7. ROBINSON et al., "Thermodynamics of the ternary system: water-sodium chloride-barium chloride at 25°C" *J. Res. Natl. Bur. Stand. A*, **69A**, Page 19-27 (1965).
8. HELAMS et al., "Osmotic Properties of Some Aqueous Solutions at 45°C." *J. Chem. Eng. Data.*, **10**, Page 323-325 (1965).
9. MOORE et al., "Isopiestic studies of some aqueous electrolyte solutions at 80°C" *J. Chem. Eng. Data.*, **17**, Page 180-182 (1972).
10. PERRON et al., "Apparent molal volumes and heat capacities of alkaline earth chlorides in water at 25 C." *Can. J. Chem.*, **52**, Page 3738-3741 (1974).
11. PUCHALSKA et al., "Densities and apparent molal volumes of aqueous  $\text{BaCl}_2$  solutions from 15 to 140°C and from 1 to 200 bar." *J. Chem. Eng. Data.*, **36**, Page 449-452 (1991).
12. ZAYTSEV et al., "Properties of Aqueous Solutions of Electrolytes.", *CRC Press* (1992).