



**HAL**  
open science

# Estimation of Pitzer interaction parameters from heat capacity and osmotic coefficient for the NaOH-H<sub>2</sub>O system at temperatures from 0 to 150°C and concentrations up to NaOH(s) saturation

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 and osmotic coefficient for the NaOH-H<sub>2</sub>O system at temperatures from 0 to 150°C and concentrations up to NaOH(s) saturation. *Thermodynamics*2015, Sep 2015, Copenhague, Denmark. hal-01315430

**HAL Id: hal-01315430**

**<https://hal.science/hal-01315430v1>**

Submitted on 17 May 2016

**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 and osmotic coefficient for the NaOH-H<sub>2</sub>O system at temperatures from 0 to 150°C and concentrations up to NaOH(s) saturation

*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, Water Environment and Ecotechnologies Direction (Orléans, France),

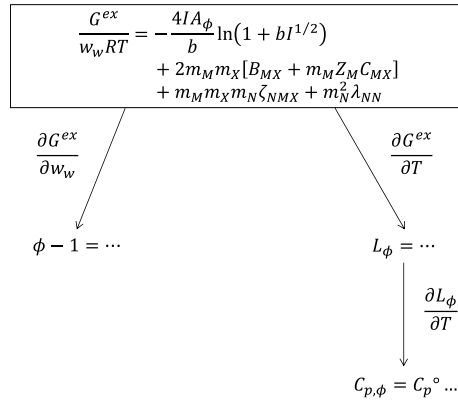
<sup>2</sup>LaTEP, UPPA (Pau, France)

A.Lach@brgm.fr

Keywords: Pitzer interaction model, NaOH electrolyte system, heat capacity, high saline solutions

## 1. Introduction

The aim of this study is to determine new Pitzer interaction parameters for the NaOH-H<sub>2</sub>O binary system from heat capacity and osmotic coefficient data between 0 and 150°C and up to NaOH solid salt saturation. As shown in Fig.1, from the excess Gibbs free energy ( $G^{ex}$ ) we can access to several properties [1]: the osmotic coefficient ( $\phi$ ), the apparent relative molar enthalpy ( $L_\phi$ ) and the apparent molar heat capacity ( $C_{p,\phi}$ ). With the last property, we can calculate heat capacity ( $C_p$ ) of an electrolyte solution.



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

As shown in our previous work [2] the interpretation of osmotic coefficient data needs taking into account the partial dissociation of NaOH. In this case, the interaction parameters used are  $\beta_{Na^+/OH^-}^0$ ,  $\beta_{Na^+/OH^-}^1$ ,  $C_{Na^+/OH^-}^\phi$ ,  $\zeta_{Na^+/OH^-/NaOH}$  and  $\lambda_{NaOH/NaOH}$  with the following temperature dependence [3]:

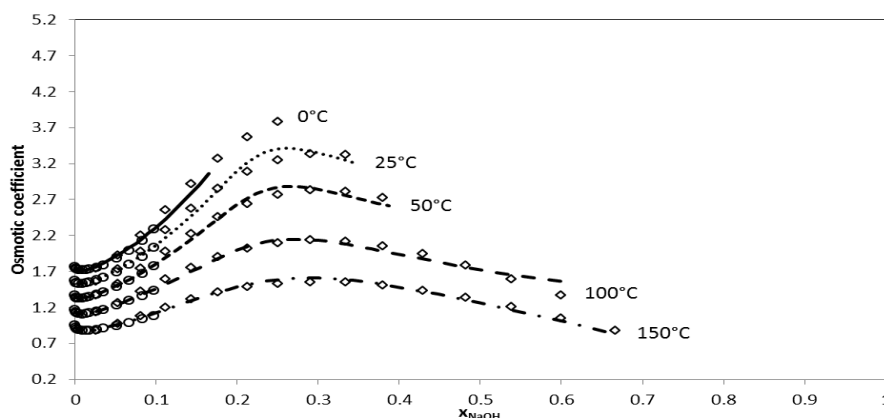
$$Y(T) = a_1 + a_2 T + a_3 T^2 + a_4/T + a_5 \ln T + a_6/(T-263) + a_7/(680-T) + a_8/(T-227) \quad (Eq. 1)$$

The  $C_{p,\phi}$  expression depends on the  $Y^j$  parameters which are a combination of the first and second temperature derivatives of Eq. 1. The partial molar heat capacity of the solute at infinite dilution ( $C_p^\circ$ ) is determined from the HKF equation of state for aqueous species given in Johnson et al. [4].

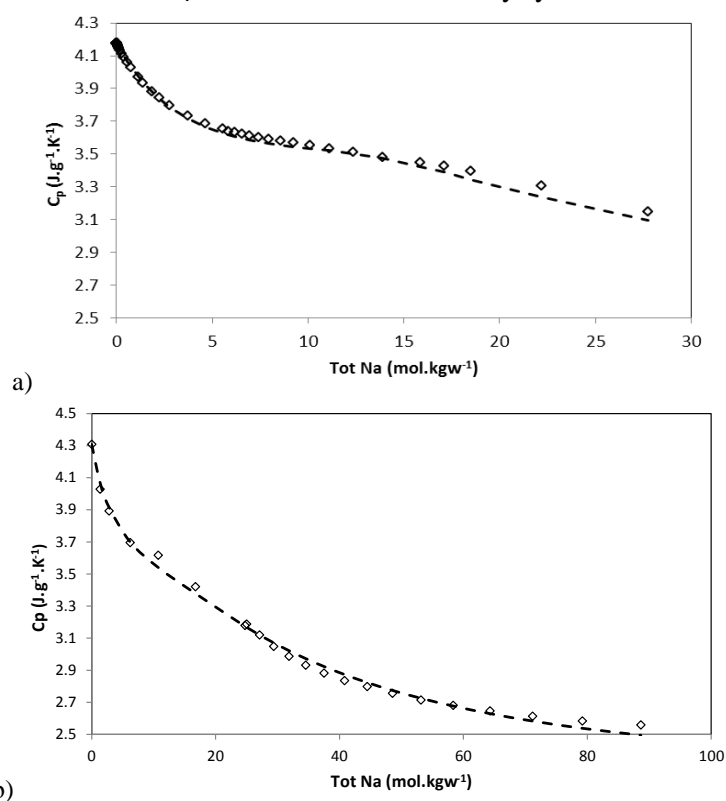
These equations were implemented in the geochemical code Phreeqc V3 [5]. Coupling with optimization software (PEST), new interaction parameters have been determined using simultaneously the heat capacity and osmotic coefficient data.

## 2. Results

In Fig. 2 we plotted the calculated (dotted lines) and experimental (open symbols) osmotic coefficient as a function of the molar fraction of total NaOH molality. For convenience of representation, the curves were shifted 1.2 for 0°C, 1 for 25°C and so on. In Fig. 3, we plotted the calculated (dotted lines) and experimental (open symbols) heat capacity as a function of NaOH molality. The results are obtained at saturated water vapour pressure.



**Fig. 2:** Osmotic coefficient,  $\phi$ , for the NaOH-H<sub>2</sub>O binary system at several temperatures.



**Fig. 3:** Heat capacity,  $C_p$ , for the NaOH-H<sub>2</sub>O binary system at a) 25°C and b) 148.89°C.

### 3. Conclusion

In this study, we proposed a new Pitzer parameterization able to reproduce the osmotic coefficient and the heat capacity data of NaOH-H<sub>2</sub>O complex solutions up to solid salt (NaOH(s)) saturation from 0 and 150°C. The developed methodology can be applied to many other electrolyte systems, if sufficient experimental data are available to fully parameterize the systems.

### References

- [1] K.S. Pitzer, “*Activity coefficients in electrolyte solutions*” (1991)
- [2] A. Lach, L. André, A. Lassin, M. Azaroual, J.-P. Serin and P. Cézac, *J. Solut. Chem.*, Accepted (2015)
- [3] N. Møller, *Geochim. Cosmochim. Acta*, 52, 821-837 (1988).
- [4] J. Johnson, E. Oelkers and H. Helgeson, *Comput. Geosci.*, 18, 899-947 (1992)
- [5] D.L. Parkhurst and C.A.J. Appelo, <http://pubs.usgs.gov/tm/06/a43/>, (2013)