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# 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

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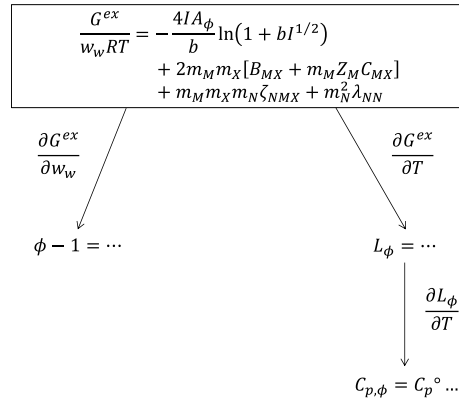
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## 1. Introduction

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  $\beta^0_{Na+/OH-}$ ,  $\beta^1_{Na+/OH-}$ ,  $C^{\phi}_{Na+/OH-}$ ,  $\zeta_{Na+/OH-/NaOH}$  and  $\lambda_{NaOH/NaOH}$  with the following temperature dependence [3]:

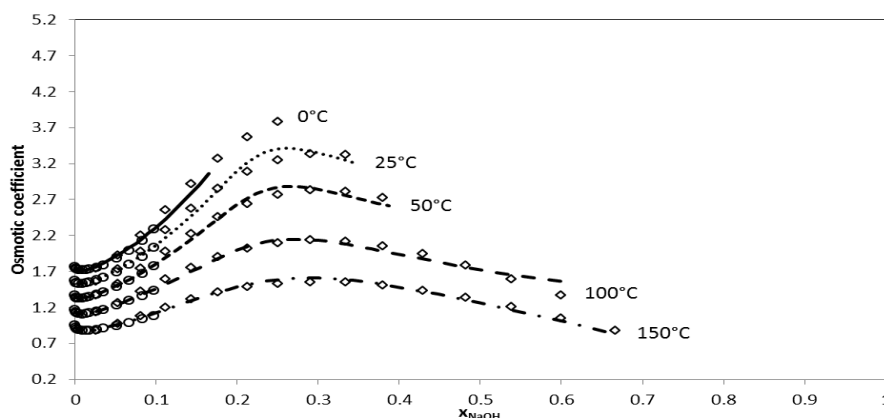
$$Y(T) = a_1 + a_2 T + a_3 T^2 + a_4 / T + a_5 \ln T + a_6 / (T - 263) + a_7 / (680 - T) + a_8 / (T - 227) \quad (\text{Eq. 1})$$

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].

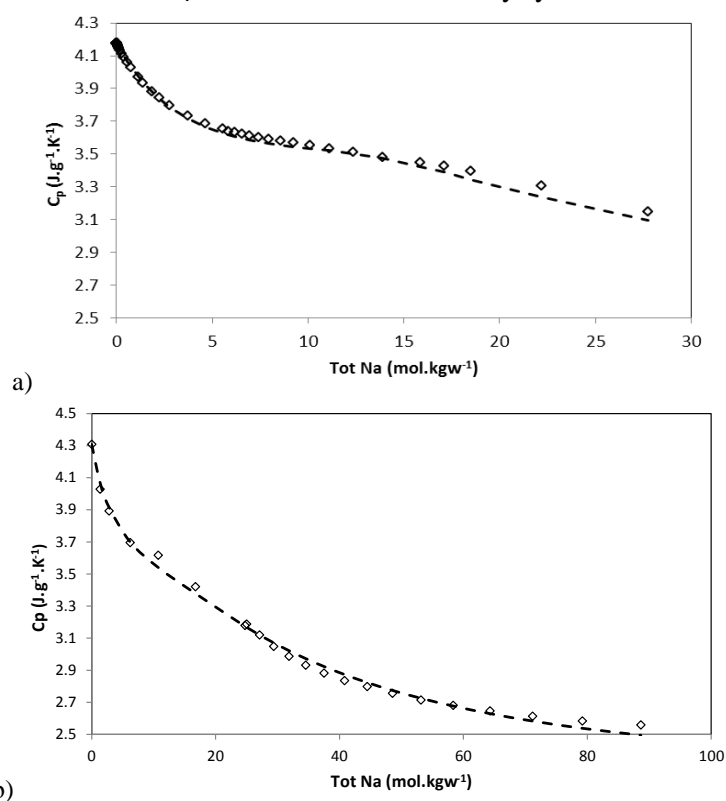
These equations were implemented in the geochemical code Phreeqc V3 [5]. Coupling with optimization software (PEST), new interaction parameters have been determined using simultaneously the heat capacity and osmotic coefficient data.

## 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)