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Estimation of Pitzer interaction parameters from heat capacity and osmotic coefficient for the NaOH-H₂O system at temperatures from 0 to 150°C and concentrations up to NaOH(s) saturation

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1. Introduction

The aim of this study is to determine new Pitzer interaction parameters for the NaOH-H₂O 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 (ϕ), the apparent relative molar enthalpy (L_ϕ) and the apparent molar heat capacity ($C_{p,\phi}$). With the last property, we can calculate heat capacity (C_p) of an electrolyte solution.

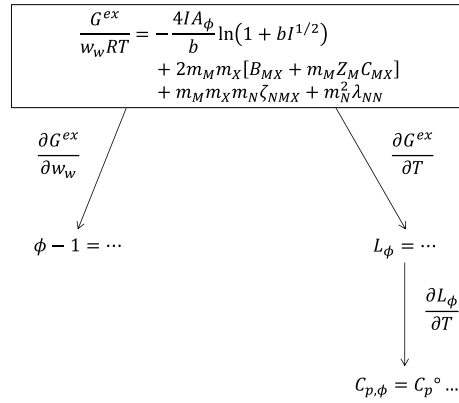


Fig. 1: Links between the three derivatives of the Gibbs excess energy (G^{ex}).

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

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

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^0) 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.

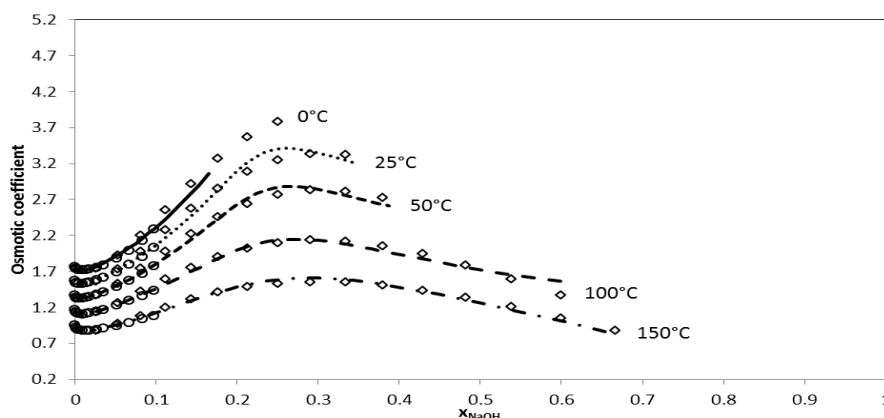


Fig. 2: Osmotic coefficient, ϕ , for the NaOH-H₂O binary system at several temperatures.

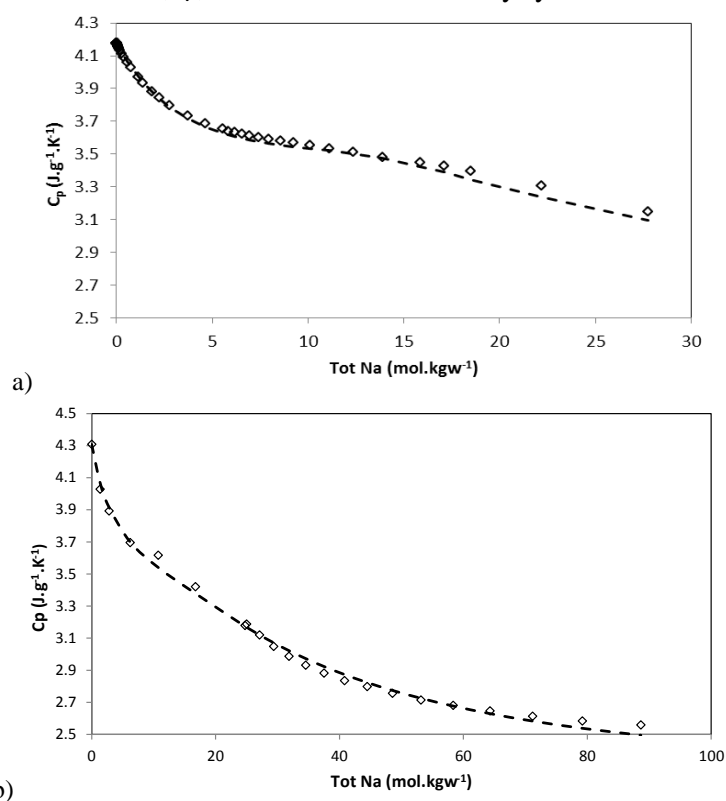


Fig. 3: Heat capacity, C_p , for the NaOH-H₂O binary system at a) 25°C and b) 148.89°C.

3. Conclusion

In this study, we proposed a new Pitzer parameterization able to reproduce the osmotic coefficient and the heat capacity data of NaOH-H₂O 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.

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