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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\textsubscript{2}-H\textsubscript{2}O system (0)

HAL Id: hal-01135995
https://hal-brgm.archives-ouvertes.fr/hal-01135995
Submitted on 26 Mar 2015

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Estimation of Pitzer interaction parameters from heat capacity, osmotic coefficient and density data: Application to the BaCl₂-H₂O system (0<T<90°C and 0<m BaCl₂<2 mol.kg⁻¹)

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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 (\( \Delta H^p \)), 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.

\[
\frac{G^{ex}}{R T} = -\frac{41}{b} \ln(1 + b t^{1/2}) + 2m_u m_x (b_{MX} + m_u Z_u C_{MX})
\]

\[\phi - 1 = ... \quad L_\phi = ... \quad V_\phi = V^o + ... \]

\[C_p,\phi = C_p^o + ... \]

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 BaCl₂-H₂O binary system between 0 to 90°C up to 2 mol.kg⁻¹.

DESCRIPTION OF THE WORK

The description of the BaCl₂-H₂O binary system needs the use of the Pitzer interaction parameters (\( \beta^o, \beta^t \) and \( \xi^o \)) to compute \( B_{MX} \) and \( C_{MX} \). These three interaction parameters depend on temperature according to the following equation [3]:

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

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 \( a_2, a_3, a_6, a_7 \) and \( a_8 \) while the osmotic coefficient data help determining \( a_1 \) and \( a_5 \). \( V_\phi \) expression depends on the volumetric parameters (\( \beta^o, \beta^t \) and \( C^o,\phi \)), which are the pressure derivatives of \( \beta^o, \beta^t \) and \( C^o,\phi \), respectively. In this study, we determined a value of \( \beta^o \) 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 Thermodem 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 BaCl₂ 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 \( \beta^o \) value. All the results presented in Fig. 2, 3 and 4 are obtained at 1 bar.
CONCLUSIONS

In this study we proposed a complete methodology to determine a full set of Pitzer interaction parameters for the BaCl₂-H₂O electrolyte system. The parameters are 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 mol.kgw⁻¹. The work done on the binary BaCl₂ system can be extended to many other systems, if sufficient experimental data are available to fully parameterize the systems.

REFERENCES


