

On the linear dependence on the water density at high temperatures of the cation-anion binary interaction parameters for the simple model (SIT) of the activity coefficients

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The analysis of the theoretical model for the activity coefficients predicts that the parameter of the binary cation-anion interaction is constant at isochoric conditions and decreases with the decrease of the density of water. The regression of experimental values of the activity coefficients of a number of 1-1 electrolytes indicates that the agreement between experiment and theory is observed at $T > 370$ K or at the density of water less than 950 kg m^{-3} .

Key words: activity coefficients; correlation

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1. The theoretical analysis

In thermodynamic modeling of geochemical processes it is necessary to know the activity coefficients of the ions, γ . It is known that at low electrolyte concentrations the forces of electrostatic attraction dominate, causing a decrease in the activity coefficients, whereas at high concentrations the repulsive forces appear and γ increase with increasing concentrations of the electrolyte.

The most accurate method to describe the activity coefficients is the Pitzer method [Pitzer, 1973], which includes both the electrostatic contribution and the repulsive contributions, given as a virial series in the concentration of particles. The Pitzer method uses a large number of parameters, which depend on T and P and have to be determined by regression of experimental data.

For modeling of geochemical systems it would be useful to have a less accurate method, if it can be used to predict the magnitude of the activity coefficients at high T and P. The SIT model [Grenthe et al., 1997] may be regarded as such a model. The SIT model can be viewed as a simplified Pitzer model, since SIT considers, in addition to electrostatic contributions, only binary cation-anion interactions. The following statement is accepted in the SIT model for γ_i , the activity coefficient of an ion i :

$$\ln \gamma_i = DH + \sum_j b_\gamma(i, j)m_j \quad (1),$$

where DH designates an electrostatic term (which is based on the Debye-Hückel theory), b_γ is the cation-anion binary interaction parameter, j is the counter-ion for i (i.e. if i is a cation, then j is an anion, and vice versa). For mean ionic activity coefficients of an 1-1 electrolyte, γ_\pm , SIT gives the following expression:

$$\ln \gamma_\pm = DH + b_\gamma m \quad (2),$$

where m is the molality of the electrolyte. Is it possible to predict values of the binary parameter b_γ at high T and P?

Pitzer [Pitzer, 1973, 1977] showed that for the combination of the "primitive model" for the interionic mean force potential and the simplest approximation for the cation-anion radial distribution function, the theory gives the following expression for the activity coefficients of 1-1 electrolyte in the molar concentration scale (C):

$$\ln \gamma_{\pm} = DH + 2 \cdot \frac{2\pi a^3}{3} C \quad (3),$$

where a stands for the hard-core diameter of ions.

Equation (3) is valid for the molar scale of concentrations, while equation (2) is written for the molal concentration scale. The ratio of the molar and molal concentrations depends on the molecular weight M of an electrolyte and the density ρ of the solution ρ , and in the limit of low concentrations this ratio is close to the density of pure water ρ_1^* :

$$\frac{C}{m} = \frac{1000\rho}{1000 + mM} \approx \rho_1^* \quad (4).$$

By comparing the constant of equation (3) with the parameter b_γ of equation (2) one obtains:

$$b_\gamma \approx \frac{4\pi a^3}{3} \cdot \frac{C}{m} = \text{const} \cdot \frac{C}{m} \approx \rho_1^* \cdot \text{const} \quad (5).$$

This analysis suggests that in isochoric conditions (at the constant density of water) b_γ is constant. If the water density changes, b_γ changes proportionally to ρ_1^* , i.e. it decreases with the decreasing density of water.

2. The analysis of experimental data

In order to verify the relation (5), we determined from the experimental values of activity coefficients of a number of 1:1 electrolytes (HCl, LiCl, NaCl, NaBr) the values of b_γ over a wide range of T and P (up to 598 K and 150 MPa). The data are presented graphically in Figures 1-4.

The analysis of results showed that at temperatures below 370 K (or the water density above 950 kg m⁻³) the parameter b_γ changes in a complicated way and in the general case does not follow the equation (5).

However, at T>370 K (or the water density less than 950 kg m⁻³) for all studied systems b_γ is roughly constant at isochoric conditions and decreases linearly with the decrease of the density of water.

We expect that equation (5) is useful for estimating the binary cation-anion interaction parameter at temperatures of 370 K and above.

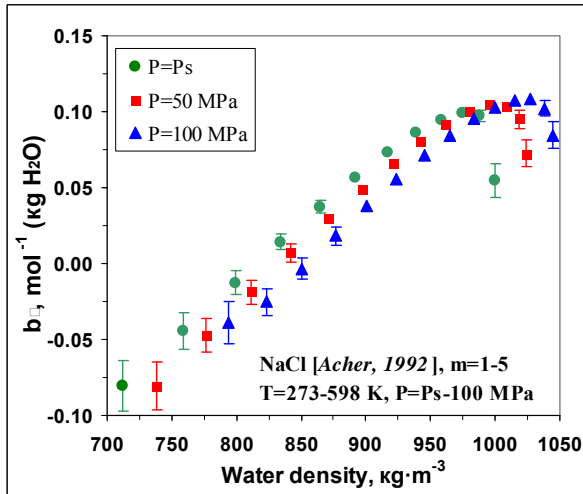


Fig. 1. Values of b_γ for NaCl

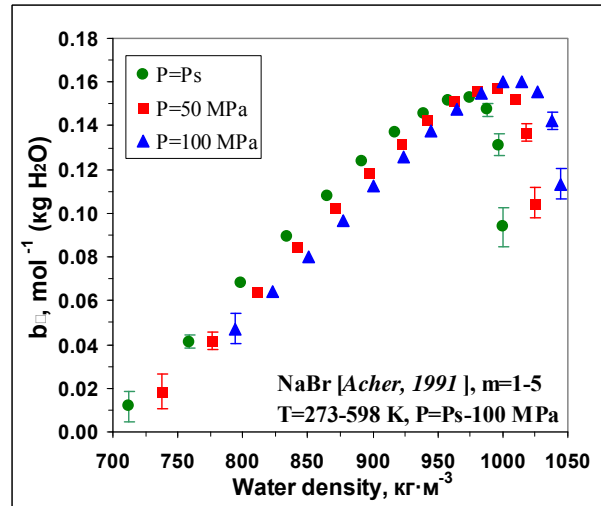


Fig. 2. Values of b_γ for NaBr

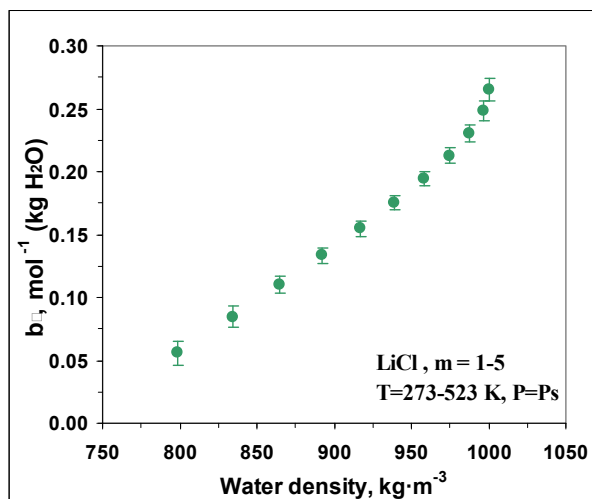


Fig. 3. Values of b_γ for LiCl. Experimental data for γ_\pm are taken from *Holmes and Mesmer*, [1983].

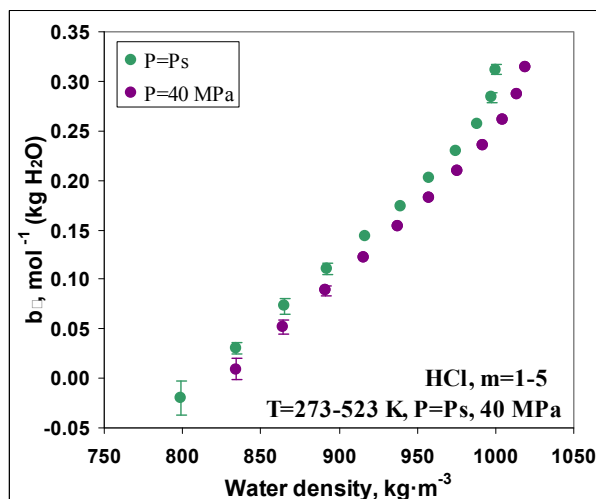


Fig.4. Values of b_γ for HCl. Experimental data for γ_\pm are taken from *Holmes et al.* [1987].

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