An equation for the critical pressures of aqueous calcium chloride solutions

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Critical properties of aqueous electrolyte solutions have been discussed by many workers (e.g., Shibue [1]; Liebscher [2]). Shibue [1] gave the equations of the critical temperatures and pressures of aqueous calcium chloride solutions. The present communication notes the typographic errors in the equation for the critical pressures and gives some complementary remarks on the equation.

The critical pressure was expressed as follows [1].

$$p_c = 22.064 + q_6 X/(X + q_5^2) + q_7 X^2 + q_8 X^4 \quad (1).$$

where p_c denotes the critical pressure in MPa, X the mole fraction of calcium chloride. Regression coefficients are designated as q_5, q_6, q_7, and q_8 in Equation (1). The equation was obtained from experimental data at $X \leq 0.0378$. The maximum concentration corresponds to 19.5 mass%.

Numerical values of q_5 and q_8 in Table 1 of Shibue [1] are incorrect. Correct coefficients of Equation (1) are as follows: $q_5 = -6.47588 \cdot 10^{-2}$, $q_6 = 8.58985$, $q_7 = 5.97149 \cdot 10^3$, $q_8 = 2.22618 \cdot 10^7$.

The second term on the right-hand side (RHS) of Equation (1) includes q_5 squared. If we use q_5 in stead of q_5 squared for the regression equation, we need to add an additional constraint; the value of $X + q_5$ does not become zero at any X values up to the maximum mole fraction. To eliminate the additional constraint, Shibue [1] squared q_5. The negative value of q_5 arises from the regression method. The Gauss–Newton method, which was applied to the nonlinear least-squares regression analysis, requires derivatives of RHS of Equation (1) with respect to q_5, q_6, q_7 and q_8. q_5^2The partial derivative with respect to q_5 contains the term $2q_5q_6X/(X +)^2$. This term includes q_5 as well as the square of q_5. Shibue [1] used q_5 as the variable for the least-squares regression analysis, which resulted in the negative value of q_5.

The critical temperature equation, which was given by a similar form to Equation (1), is shown again at the conference session.

[1] Shibue (2003) *Fluid Phase Equilibria* **213**, 39-51.
[2] Liebscher (2007) *Rev. Mineral. Geochem.* **65**, 15-47.