Thermodynamic modelling of Br partitioning in brines and marine evaporites

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Trace elements in brines and marine evaporites are often used as indicator for metamorphic processes. The behaviour of Br is particularly well investigated experimentally. The K_D (or b) value

$$b = \frac{\% \text{ trace element}_{solid\ solution}}{\% \text{ trace element}_{aqueous\ solution}}$$

depends on different parameters like temperature and composition of the aqueous solution. To calculate complex reactions like the evaporation of seawater, where the chemical composition is evolving rapidly, a large set of data for the distribution coefficients is necessary. In such reactions, $b_{Br\ in\ halite}$ is decreasing from 0.14 in halite saturated seawater to 0.073 at the beginning of the crystallisation of bischofite ($MgCl_2 \cdot 6H_2O$) (Braitsch and Herrmann 1963).

Thermodynamic modelling

A more general approach is the thermodynamic modelling of trace elements using Pitzer's equation for brines. Trace elements in solids can be treated as an extreme form of solid solutions and can thus be calculated by a set of different mathematical models (e. g. Saxena 1973). To obtain data for trace elements ($X_{trace} < 0.05$) two different methods are envisaged.

The usual way is to use thermodynamic data for the complete solid solution system and to extrapolate using mathematical models to trace element ranges of the mole fraction X_{trace}. Thermodynamical data for the complete solid solution system NaCl-NaBr were published by Kirgintsev and Trushnikova (1966).

Alternative formalisms

Due to the fact that no satisfying fit for the complete system was obtained by usual mathematical models, a new concept was developed. It is assumed that the Gibbs free energy of every solid solution system can be described correctly using a 5th order polynom

$$G^{ex} = p_1 + p_2X_1 + p_3X_1^2 + p_4X_1^3 + p_5X_1^4 + \ldots$$

where p_i denotes model parameters and X_1 the mole fraction of the major element in the solid solution. This general formalism was used to develop an equation for the activity coefficient

$$RT\ln\lambda_{trace} = p_1 - p_3X_1^2 - 2pX_1^3 - 3p_5X_1^4 - 4p_6X_1^5$$

Figure 1 presents our thermodynamic approach for very low contents of NaBr in NaCl in comparison to former medells. Hereby we used a fit of the Kirgintsev and Trushnikova (1966) data for the complete range of solid solutions. It can be seen that such an extrapolation is not suitable to obtain correct distribution coefficients.

Whereas no thermodynamic data are available from the literature for $X_{trace} < 0.05$, the distribution of Br between crystal and brine has been investigated (Braitsch and Herrmann 1963). To transform their results into thermodynamic data, a new formalism is developed:

$$\lambda_{NaBr} = \frac{a_{Br^-}^{aq} \cdot a_{Na^+}^{aq}}{K_{NaBr}^L} \cdot \frac{1}{b_{Br,halite}} \cdot \frac{1}{m_{Br^-}^{aq}} \cdot Q$$

with

$$Q = \frac{m_{Br^-}^{aq} \cdot M_{NaBr} + m_{Cl^-}^{aq} \cdot M_{NaCl} + 1000}{X_{Br} \cdot M_{NaBr} + X_{Clr} \cdot M_{NaCl}}$$

where m^{aq} = molality of the aqueous species; a^{aq} = activity of the species; M = molecular mass; X = mole fraction; $b_{Br,\ halite}$ = distribution coefficient of Br in halite; and K^L = solubility constant. This formalism was used to calculate the mole fraction of NaBr in NaCl from the original data of Braitsch and Herrmann (1963) using the program EQ3/6. The model parameter for the 5th order polynom were obtained by fitting the calculated data with the above formalism for λ_{NaBr}.

Results

Figure 1 clearly shows that using the 5th order

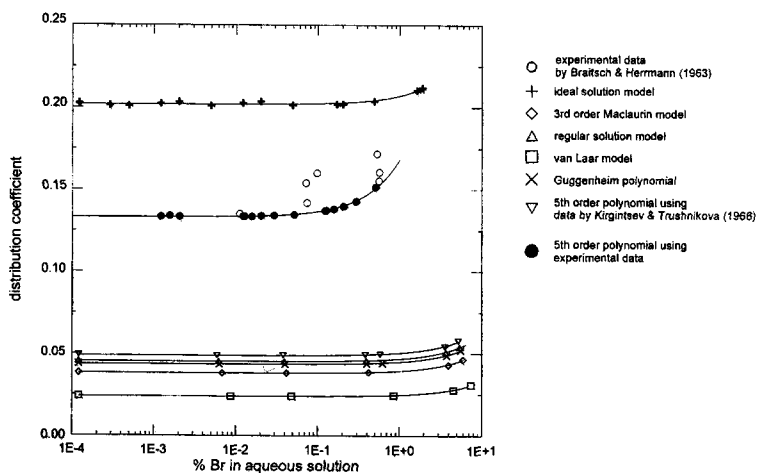FIG. 1. Experimental and thermodynamically calculated data of the distribution of Br in halite.

polynom and a fit for $X_{trace} < 0.05$ leads to more consistent data for the distribution coefficient relative to fits for the complete solid solution system. The described approach is suitable for the thermodynamic modelling of complex reactions like solution metamorphism in evaporite bodies, static and dynamical evaporation of seawater or mixing of highly concentrated brines.

References

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