Apparent dielectric constants of brines at 500-2000 bars and 200-550C

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Solubilities of quartz in mixed solvents have long been investigated experimentally over a wide range of P-T conditions. A number of equations for quartz solubilities in brines have also been proposed based on the experimental results. Although the equations are adequate for estimating temperatures of geothermal reservoirs with measured Si concentrations, they cannot be applied to calculate whole system equilibria of mixed solvents with other minerals.

On the other hand, SUPCRT92 (Johnson et al., 1992) provides thermodynamic data of numerous aqueous, gaseous and mineral species applicable for wide ranges of P-T conditions, although the data can be used only for systems with pure water solvents. Within the framework of electrostatic approach to predict thermodynamic properties of aqueous fluids taken in SUPCRT92, a chemical potential of a certain solute can be divided to the structural non solvation and solvation terms. The latter is expressed by the Born equation with the Born parameter of the solute and the dielectric constant of the solvent. Hence, if we can know the dielectric constants of brines, we may calculate the chemical potentials of solutes in the brines from the data given by SUPCRT92.

Since dissolved silica in an aqueous phase coexisting with quartz is mostly present as a neutral hydrated monomer (e.g., Walther and Helgeson, 1977), $SiO2(aq)$, the molality of $SiO2(aq)$ ($mSiO2(aq)$) can be expressed as (MacKenzie and Helgeson, 1984)

$\log mSiO2(aq) = \log aSiO2(aq) = \log K$, (1)

where $aSiO2(aq)$ stands for the activity of $SiO2(aq)$ and K refers to the equilibrium constant for the reaction in water,

$SiO2(quartz) = SiO2(aq)$. (2)
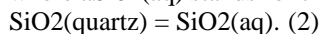
According to Akinfiev and Zotov (1999), a deviation of log K of the reaction ($D(\log K)$) in a mixture to that in water can be expressed as

$D(\log K) = -D(w) (1/e(mix) - 1/e(H2O)) / (2.303RT)$, (3)

where $D(w)$, $e(mix)$ and $e(H2O)$ represent the change in the Born parameter for the reaction, the dielectric constant of a mixture and of pure water, respectively. The Born parameter for $SiO2(aq)$ is assigned as 12910 (cal/mol) in SUPCRT92 for all P-T conditions, which is also in good agreement with experimental data of quartz solubilities in H2O-Ar and H2O-CO2 solutions at 1-5 kbar and 400-700C (Akinfiev and Zotov, 1999). Hence, by applying the equation (3) for the reaction (2) in brine, we obtain

$\log mSiO2(aq) = \log K - 2910 (1/e(brine) - 1/e(H2O)) / (2.303RT)$. (4)

We have reinvestigated about 300 data for quartz solubilities in brines of various salinities in previous experiments at a wide range of P-T conditions to estimate the dielectric constants of brines by using the equation (4). The all obtained constants were inter- or extrapolated for 1 molal NaCl solutions. The resultant constants at a temperature range of 200-550C for 500, 1000 and 2000 bars show slightly larger than those of pure water at high temperatures, while they abruptly increase with decreasing temperatures at around 350, 400 and 420C, respectively. It is quite interesting that NaCl changes its major dissolved species from NaCl(aq) to Na+ + Cl- almost at the above temperatures, implying the large effect of ionization of salt on the dielectric constants.

Experimental data of Saccocia and Seyfried Jr. (1990) for talc-quartz equilibria in brines were used for consistency check. By applying the equation (3) for all reactions concerned, the equilibria in brines were calculated by MIX99 (Hoshino et al., 2000) in which SUPCRT92 and the Debye-Huckel equation for activity coefficients of aqueous species are included. The resultant solubilities in the brines were well consistent with the experiments. Therefore, it can be said that the estimated dielectric constants are quite adequate as apparent ones to apply thermodynamic data of aqueous species in water solvents given by SUPCET92 to reactions in brines.