Estimation of the dielectric constant of geofluids from solubilities of quartz in brine

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The dielectric constant is a key parameter characterizing chemical properties of solvents. Geofluids are conceived commonly as mixtures of water, salt and gas species. The constant of a mixture of water and non-polar gas can be calculated easily by the modified Kirkwood equation (Akinfiev and Zotov, 1999), while there may be no simple equation to estimate that of water and salt.

Recent experimental results of solubilities of quartz in high temperature solvents of the H2O-NaCl system (e. g., Newton and Manning, 2000; Shmulovich et al., 2006) suggest that quartz solubility increases with increasing salinity (salt-in) at low to moderate NaCl concentrations, while it decreases with the salinity at high concentrations when the fluid densities are low (i.e., low-P and/or high-T). On the contrarily, when the fluid densities are high (high-P and/or low-T), the solubility decreases monotonically with increasing salinity (salt-out). It should be emphasized that the solubilities in only 3.2 wt% NaCl aqueous solutions measured by Foustoukos and Seyfried Jr. (2007) are about 10% higher than those in pure water calculated by SUPCRT92 (Johnson et al., 1992) at around P = 255 bars and T = 370C.

Based on those experimental data, the author has tried to estimate 'apparent' dielectric constants of the H2O-NaCl solvents, which are consistent with the data processing in SUPCRT92. Since activity coefficients of dissolved species are set as unity in all conditions in SUPCRT92, and dissolved silica in an aqueous phase coexisting with quartz is present as a neutral hydrated monomer (e. g., Walther and Helgeson, 1977), the measured concentrations (molalities) of silica (m(SiO2)) in quartz-saturated brines can be expressed as

logm(SiO2) = loga(SiO2) = logK,

where a(SiO2) stands for the activity of SiO2(aq) and K refers to the equilibrium constant for

SiO2(quartz) = SiO2(aq)
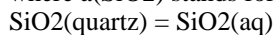
at P-T conditions of the experiments. According to Akinfiev and Zotov (1999), a deviation of logK of a reaction (D(logK)) in a mixture to that in pure water can be expressed as

D(logK) = -D(w) (1 / e(mix) - 1 / e(H2O)) / (2.303 R T),

where D(w), e(mix) and e(H2O) represent the difference in the Born coefficients for the reaction, the dielectric constant of a mixture and of pure water, respectively. The born parameters of neutral species are set as constant at any P and T in SUPCRT92. Hence, one may obtain the 'apparent' dielectric constants of brines from measured quartz solubilities in brines and those in pure water calculated by SUPCRT92.

The 'apparent' dielectric constant for 0.833 m NaCl solution calculated from the experimental data of Xie and Walther (1993) is 15.67 at P = 2 kb and T = 500 C where the constant for pure water derived from SUPCRT92 is 13.88. On the other hand, the constant for the solution estimated by them using the Looyenga (1965) mixing rule with an assumption of ideal mixing of H2O and uncharged NaCl is 14.32. In the presentation, consistencies of the resultant 'apparent' dielectric constants with the data processing of SUPCRT92 will be checked by comparing solubility calculations and their experimental data for quartz and wollastonite solubilities in brines.