

Complexing in calcium acetate and propanoate fluids at elevated temperatures and pressures

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The presence of saturated aliphatic carboxylic acids in low to medium temperature hydrothermal environments has been well documented. Experimental studies have demonstrated that acetic acid exists metastably to temperatures well above 300°C before undergoing decarboxylation (Palmer and Drummond, 1986). Similar expectations exist for propanoic and butanoic acids. Significant concentrations of acetic and propanoic acids have been measured in oil-field brines (Shock, 1994). Of particular interest has been the association of organic material with ore deposits such as the Mississippi Valley type. This has

stimulated investigation of stability relations of metallic-organic complexes at elevated temperatures and pressures as such complexes may serve as major agents for the dissolution, transport and precipitation of the metals. Spectroscopic investigations of sodium and calcium acetate and propanoate solutions have been undertaken in order to investigate their relative stabilities and complexing behaviour as a function of temperature and pressure.

Using a special hydrothermal pressure vessel fitted with conical diamond windows, Raman spectra of the acetate and propanoate solutions were measured at

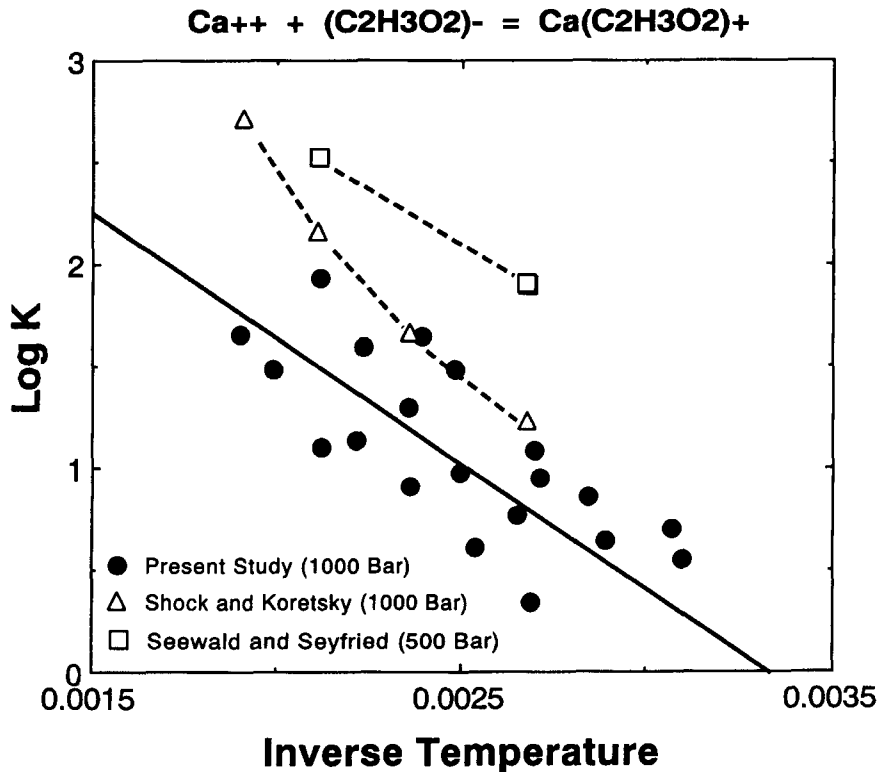


FIG. 1. Logarithm of the association constant of calcium acetate as a function of inverse temperature (K).

temperatures ranging from 25 to almost 500°C at 1000 and 2000 bars pressure. In the case of calcium acetate, measurements were made on 0.1, 0.5, and 1.0 molal solutions. The C-C symmetric stretch mode of the acetate complex was used to monitor the ion pairing of calcium with the acetate ligand. For the three concentrations, the spectral envelopes representing the C-C stretching mode were deconvoluted into two distinct bands: one representing unbound acetate; the other, acetate associated with calcium. The relative proportion of the band area representing the calcium acetate ion pair ($\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)^+$) increased relative to the band area representing unbound acetate with increasing temperature and decreasing pressure. Association constants based on these data were calculated for the three concentrations based on the assumption of equal Raman scattering coefficients (Fig. 1). These data are compared to those of Seewald and Seyfried (1991) and Shock and Koretsky (1993). At temperatures above 250°C, a third band begins to appear representing the neutral $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2^0$ species and increases with increasing temperature. Similar calculations have been

performed using the C-C-C symmetric stretch mode of the propanoate ligand for calcium propanoate solutions with the resultant association constant of $\text{Ca}(\text{C}_3\text{H}_5\text{O}_2)^+$ being weaker than that of calcium acetate. Over a brief period of the measurements, both the acetate and propanoate ligands existed metastably to 475°C. Decarboxylation occurred at higher temperatures with the acetate ligand reacting to form bicarbonate and methane. Both ligands were found to metastably persist over 24 hour periods at 400°C.

References

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