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Chlorargyrite (AgCl) solubility in low density hydrothermal fluids

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The goal of the study is to experimentally verify available experimental data and to modify equation of state proposed recently by *Akinfiev and Diamond* [*2003*] for thermodynamic description of neutral aqueous species in a wide range of thermal solvent densities expanding a low density region (ρ = 0.05–0.3 g·cm^{-3}). Solubility of chlorargyrite AgCl(s) was measured in aqueous solution at 400 °C vs. pressure (P = 100–400 bars), i.e. for the fluid densities from 0.04 to 0.5 g·cm^{-3}. Our previous data on the AgCl(s) solubility [*Voronin et al., 2005*] in a low density region of H_2O may be overestimated because of a methodological shortcoming (pressure was not under control during the experiment).

Key words: experiment, solubility of AgCl, low density fluid, equation of state

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Experimental technique

Experiments were carried out at 400 ± 1 °C in titanium alloy VT 8 autoclaves with the internal sampler [*Zakirov, Sretenskya, 1994*]. The pressure was measured by strain-gauge sensor D100 calibrated by the deadweight pressure system MP-2500 with an error less than 1%. Chemically pure (CP) AgCl pressed into tablets under a pressure of 30 kg·cm^{-2} was used as a solid phase reagent. The volume of titanium sampling ampoules was of 6.5 cm^3, the rest volume of the autoclave was 94 cm^3.

The experimental cycle was as following. At the bottom of autoclave the specified amount of distilled water was poured to produce required pressure at given temperature. In the medium part of the autoclave a titanium pan with 5–6 pieces of AgCl(s) (of 0.5–0.8 g) was located. The titanium sampling ampoule was located in the hood of the autoclave and was locked by a valve needle through Pt gasket. Graflex was used to seal the rod of the valve in the autoclave. The ampoule preliminary thoroughly washed by chloronitric acid was initially closed. After heating and 2–3 days staying at 400 °C ampoule has been opened for a few minutes. Herewith pressure lowered by ca 3–5 %. Then ampoule was closed again, the autoclave was removed from the oven and quenched in cold water while its top was aired by a fan.

Subsequently the ampoule was 2 times washed by a triple diluted hot aqua regia. The wash-outs were analyzed separately after addition of amount of water to get 4–5 times dilution of the aqua regia. Silver in the solution was determined by atomic emission spectrometer with inductively coupled plasma (ICP spectrometer by "JOBIN YVON HORIBA", France, the model "ULTIMA-2"). The detection limit of silver was 0.5 ppb. The content of silver in the blank samples was about 1 ppb. The content of silver in the 2nd washout was usually an order of magnitude smaller than in the 1st. In addition Ag-bearing solution of the autoclave without washing its walls was also analyzed. The concentration of Ag in these samples was typically an order of magnitude lower than the concentration in the fluid from the ampoule, probably due to precipitation of silver chloride on the walls of the autoclave during quenching. In dense fluids where AgCl (s) solubility is high the concentration of silver was determined by the weight loss method.

Experimental results

The experimental conditions and measured values of AgCl(s) solubilities are given in Table 1.

It's found out that in relatively dense fluids (0.3–0.5 g·cm^{-3}) solubility of chlorargyrite slightly increases with increasing pressure, whereas in low-density ones with decreasing pressure and the corresponding density from 0.3 to 0.05 g·cm^{-3} solubility shows sharp fall of about 3 orders of magnitude. In the coordinates of lg m_{Ag} – lg $P_{\mathrm{H_2O}}$ the dependence of the AgCl(s) solubility is expressed a straight line with a slope of about 7.5.

Table 1. Solubility of AgCl(s) in water at 400 ± 1 °C as a function of pressure

P, bar	ρ, g·cm^{-3}	m(Ag), mol·(kg H_2O)$^{-1}$	
		ICP	weight loss
108	0.0413	-5.89	
142	0.0592	-5.69	
152	0.0651	-5.35	
198	0.0996	-4.87	
246	0.1615	-3.96	
265	0.2036	-3.61	
284	0.2964		-2.78
296	0.3542	-3.00	-2.81
335	0.4558	-2.62	-2.7
357	0.4780	-2.55	
380	0.5073		-2.59
400	0.5240		-2.47

Evaluation of experimental data

Initially to identify the stoichiometry of silver species in hydrothermal low-density fluid the thermochemical properties of AgCl, AgCl(H_2O), AgCl(H_2O)$_2$, AgCl(H_2O)$_3$ molecules in the state of perfect gas for temperature range 298–1000 K by means of quantum chemistry (DFT B3LYP, Cl, O, H – 6-311+G(d,p), Ag – core potential LANL2DZ) were evaluated. The optimized structures are shown in Figure 1.

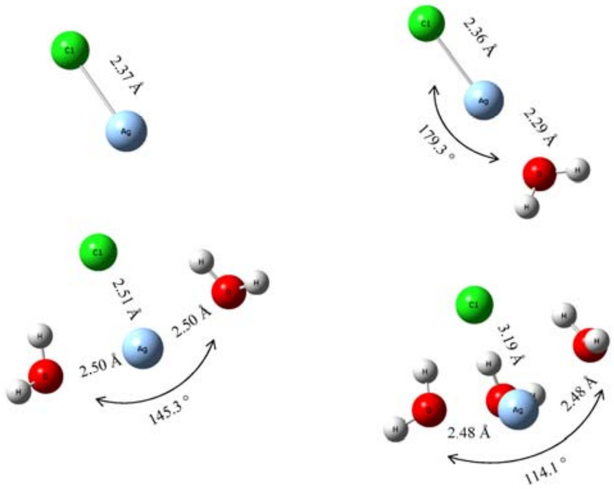

Fig. 1. Optimized by means of quantum chemistry computations structures of H_2O clathrates of AgCl ion pair in the state of a perfect gas. Numbers stand for bond distances in Å and angles in degrees

The thermochemical data obtained enable to compute equilibrium constants of the gaseous Ag-bearing species in the reaction of the type

$$\mathrm{AgCl} + n\mathrm{H_2O} = \mathrm{AgCl(H_2O)}_n$$

In this case equilibrium constant of the reaction should be expressed in the form:

$$\ln K_a = -\frac{\Delta_r G_T^o}{RT} = \ln \frac{f_{\mathrm{AgCl(H_2O)}_n}}{f_{\mathrm{AgCl}} \cdot f^n_{\mathrm{H_2O}}} = \ln \frac{p_{\mathrm{AgCl(H_2O)}_n} \cdot \gamma_{\mathrm{AgCl(H_2O)}_n}}{p_{\mathrm{AgCl}} \cdot \gamma_{\mathrm{AgCl}}} - n \cdot \ln f_{\mathrm{H_2O}}\,.$$

Assuming that fugacity coefficients of different Ag bearing species in the H_2O fluid are close to each other get the relation for ratio of their molalities in the fluid can be obtained

$$\ln \frac{p_{\mathrm{AgCl(H_2O)}_n} \cdot \gamma_{\mathrm{AgCl(H_2O)}_n}}{p_{\mathrm{AgCl}} \cdot \gamma_{\mathrm{AgCl}}} \approx \ln \frac{p_{\mathrm{AgCl(H_2O)}_n}}{p_{\mathrm{AgCl}}} = \ln \frac{m_{\mathrm{AgCl(H_2O)}_n}}{m_{\mathrm{AgCl}}} = \ln K_a + n \ln f_{\mathrm{H_2O}}\,.$$

The calculation results shown in Fig. 2 indicate that the linear associate, AgCl(H_2O) (sp-hybridization of Ag), is prevalent in the whole temperature range 0 - 600 ºC. Only at temperatures > 700 ºC and vapour pressures < 100 bar the anhydrous AgCl becomes a prevalent form. According to the computations concentrations of AgCl$(H_2O)_2$ and *a fortiori* AgCl$(H_2O)_3$ are void for the entire range of temperatures and pressures. Therefore, further fit of model parameters has been carried out solely for the monohydrate, AgCl (H_2O).

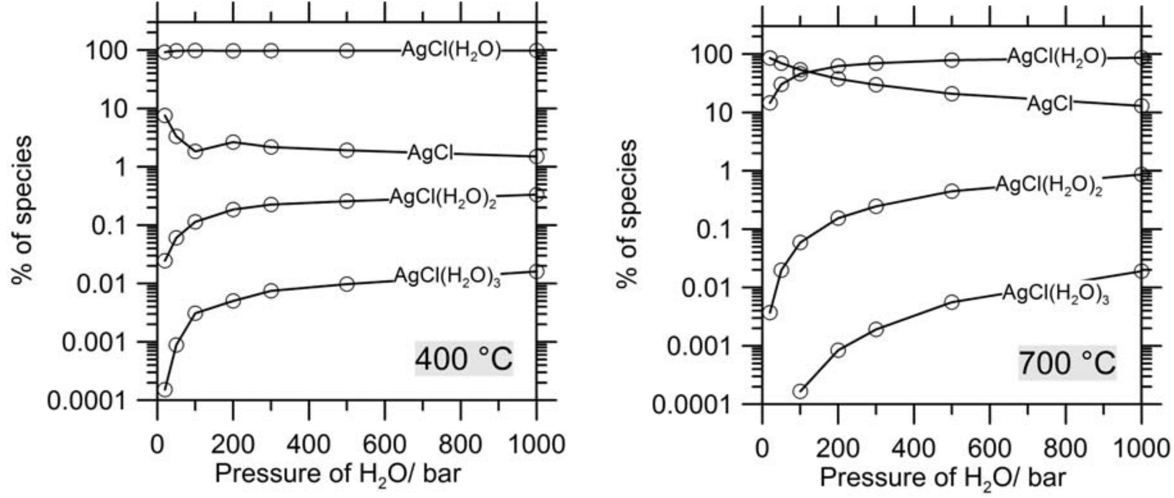

Fig. 2. Computed distribution of various Ag-bearing species (in mol %) in aqueous fluid as a function of H_2O pressure at 400 ºC (left) and 700 ºC (right)

The equation of state (EoS) (Akinfiev, Diamond, 2003) was employed to describe the experiment data. Because the prevailing form of Ag species has a high dipole moment the additional term, namely $\omega\left(\frac{1}{\varepsilon}-1\right)\cdot 10^5$, was introduced into the EoS. Here ω , the Born parameter [*Tanger, Helgeson, 1988*], reflects electrostatic interactions of the Ag species with the surrounding water molecules:

$$\mu^{o}_{aq}(P,T)=\omega\left(\frac{1}{\varepsilon}-1\right)\cdot 10^5+\mu^{o}_{g}(T)-RT\ln N_w+(1-\xi)RT\ln f^{o}_{1}+$$

$$+RT\xi\ln\left(\frac{\tilde{R}T}{M_w}\rho^{o}_{1}\right)+RT\rho^{o}_{1}\left[a+b\left(\frac{10^3}{T}\right)^{0.5}\right].$$

Thus, the basis of the resultant description are quantum-chemical calculations of $\mu^{\circ}_{g}(T)$ for gaseous hydrate water associates at standard pressure (1 bar) and the experimental data on chlorargyrite solubility: a) in a dense fluid at 25–300 °C and saturation water pressure [*Zotov et al., 1995*], and b) at 400 °C as a function of H_2O pressure (present study). As a result following values for standard state thermodynamic functions for gaseous hydrate AgCl(H_2O) $\mu^{o}_{298,g}$ = -50300 cal·mol^{-1}, $S^{\circ}_{g,298}$ = 77.281 cal·mol^{-1}·K^{-1}, $C^{\circ}_{p,g}$ (T) = 18.588 + 2.996·10^{-3}·T – 0.95·10^{5}·T^{2} as well as empirical parameters of the EoS: ξ= -0.38, a = 8.7015, b = -7.3785, ω = 0.143 cal·mol^{-1} were estimated.

Finally, the proposed EoS provides correct AgCl(s) solubility behaviour both vs pressure for supercritical aqueous fluid at 400 °C (solid line in Fig. 3) and vs temperature at 25 – 300 °C in dense fluid at the saturation pressure of H_2O [*Zotov et al., 1995*].

Conclusion

To describe the solubility of AgCl (s) over a wide range of temperatures and pressures, which includes the low-density region of aqueous fluids, the equation of state [*Akinfiev, Diamond, 2003*] has been modified. This modification provides correct solubility description both at supercritical conditions (400 ° C, 100–500 bar), and the corresponding experimental data at 25–300 °C in dense fluid at the saturation pressure of H_2O. The available experimental data of *Migdisov et al.* [*1999*] for water vapour at 300–360 ° C are in worse accordance. In order to match the experimental data as well as adjust the parameters of the EoS some additional experiments to determine the solubility of chlorargyrite in subcritical water vapour are desirable.

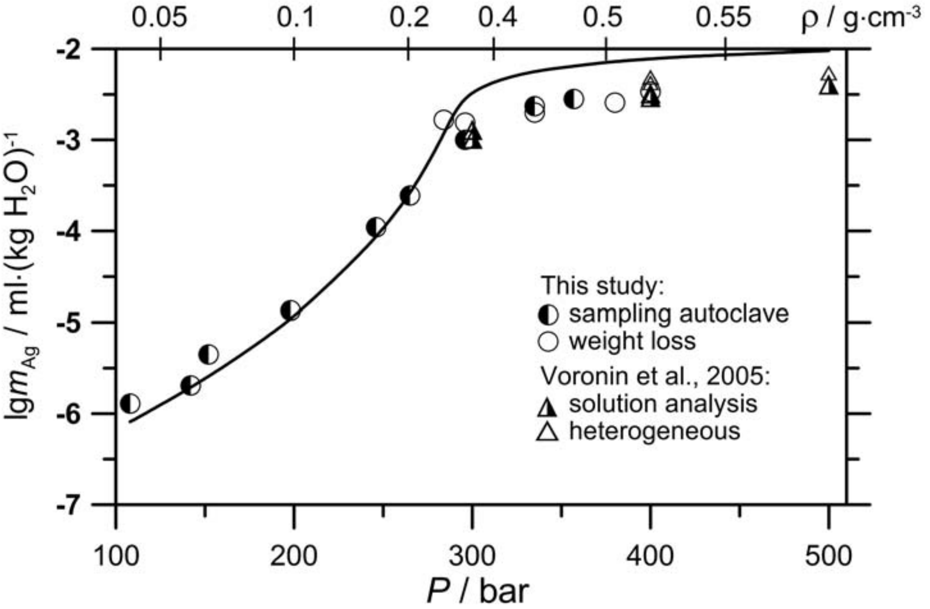

Fig. 3. Comparison of the experimental AgCl(s) solubility with calculated one as a function of H_2O vapour pressure at 400 ºC. Points stand for experiment, line depicts– calculated values after the model adopted in this study

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