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ORIGINAL ARTICLE

Molecular simulation study on K^+–Cl^- ion pair in geological fluids

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Abstract This paper reports a classical molecular dynamics study of the potential of mean forces (PMFs), association constants, microstructures K^+–Cl^- ion pair in supercritical fluids. The constrained MD method is used to derive the PMFs of K^+–Cl^- ion pair from 673 to 1273 K in low-density water (0.10–0.60 g/cm^3). The PMF results show that the contact ion-pair (CIP) state is the one most energetically favored for a K^+–Cl^- ion pair. The association constants of the K^+–Cl^- ion pair are calculated from the PMFs, indicating that the K^+–Cl^- ion pair is thermodynamically stable. It gets more stable as T increases or water density decreases. The microstructures of the K^+–Cl^- ion pair in the CIP and solvent-shared ion-pair states are characterized in detail. Moreover, we explore the structures and stabilities of the KCl–Au(I)/Cu(I) complexes by using quantum mechanical calculations. The results reveal that these complexes can remain stable for T up to 1273 K, which indicates that KCl may act as a ligand complexing ore-forming metals in hydrothermal fluids.

Keywords Molecular dynamics · KCl · Potential of mean force · Association constant · Geometry optimization

1 Introduction

Molecular-level knowledge of ion-pair associations is essential to understanding the kinetics and thermodynamic behaviors of ions in aqueous environments. An ion pair, consisting of a cation and an anion, simultaneously bonds together as an ion pair association. Generally, ions associate through the following stepwise mechanism (Marcus and Hefter 2006):

$$C^+ + A^- \rightleftharpoons C^+\|A^- \rightleftharpoons C^+|A^- \rightleftharpoons C^+A^- \qquad (1)$$

where C^+ and A^- in the initial state are two free ions. The bar | stands for a water molecule. $C^+\|A^-$ is the solvent separated ion-pair (SSIP), $C^+|A^-$ is the solvent-shared ion-pair (SShIP), and C^+A^- is the contact ion-pair (CIP). The free energy of C^+ and A^- along the pathway as a function of ionic separation is known as the potential of mean force (PMF) (Kirkwood 1935). The association constant (K_A) can be predicted from the PMF, which is especially important for understanding geochemical transformations such as mineral solubility, transport, and deposition (Liu et al. 2003).

Na^+ and K^+ are the dominant cations, and Cl^- is the major ion when the felsic mineral assemblages interact with chloride brines in hydrothermal ore deposits systems (Tutolo et al. 2014, 2015). Therefore, KCl and NaCl are very important in geo-fluids. Furthermore, the knowledge of the common chloride salt in supercritical conditions is also badly required by many processes in industrial production, such as supercritical fluid technology (Hu et al. 2007; Keshri et al. 2016; Stubbs 2016; Yui et al. 2010).

During the past decades, the properties of ion pair for common chloride complexes have been intensively studied experimentally using conductance measurements (Chiu and Fuoss 1968; Gujt et al. 2014; Ho and Palmer 1997; Ibuki et al. 2000; Zimmerman et al. 2012) as well as computationally employing molecular dynamics (MDs) methods (Chowdhuri and Chandra 2001; Fennell et al. 2009; Gallo et al. 2011; Keshri et al. 2016; Pluhařová et al. 2013; Yui et al. 2010; Zhang and Duan 2004) or Monte Carlo (MC)

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simulations (Gujt et al. 2014). The PMF of Na$^+$–Cl$^-$ ion pairs was first studied at ambient conditions using the constrained MD technique (Smith and Dang 1994). Later, there were several studies on the free energies of the ion-pair association of Na$^+$–Cl$^-$ ion pair in supercritical water (SCW) (Balbuena et al. 1996; Chialvo and Simonson 2003; Liu et al. 2003; Yui et al. 2010). Recently, the ab initio MD simulations are applied for computation of the PMF of Na$^+$–Cl$^-$ ion pairs at 300 K (Timko et al. 2010), which agrees with the classical MD simulations.

In the past few years, several studies on the microstructure of K$^+$–Cl$^-$ ion pairs at ambient conditions have been carried out using computer simulation (Cavallari et al. 2004; Chowdhuri and Chandra 2001). The PMF of K$^+$–Cl$^-$ ion pairs has been derived at ambient conditions (Chiu and Fuoss 1968; Gujt et al. 2014; Hefter and Salomon 1996), whereas there is a dearth of data for SCW conditions. Thus, the PMF data of an K$^+$–Cl$^-$ ion pair under high-T conditions are badly needed for better understanding the chemical behaviors of KCl in geological fluids.

Recently, the ion pair of metal complexes with salt chloride complexes (e.g., KCl) has been considered greatly important at near-magmatic supercritical conditions (Zajacz et al. 2010, 2011). They may play a crucial role in enhancing metal solubility at high T–P conditions and partitioning into a magmatic volatile-rich phase (Seward et al. 2014). Nevertheless, there are no data pertaining to the thermodynamic properties and the molecular structures of mixed KCl-metal species.

To investigate the microscopic properties of the ion pair states for K$^+$–Cl$^-$ ion pairs in hydrothermal fluids, we calculate the PMFs of the K$^+$–Cl$^-$ ion pair from 673 to 1273 K in low-density water (0.10–0.60 g/cm^3) by using the constrained MD method. The association constants for KCl are computed from PMF data, and the microstructures in CIP and SShIP states for K$^+$–Cl$^-$ ion pair are presented in detail. The radial distribution functions (RDFs) and coordination numbers (CNs) of KCl at high-T conditions are also analyzed using free MD simulations. Moreover, the geometry optimizations of the mixed KCl-metal complexes are performed using the static quantum–mechanical method. These fundamental properties of K$^+$–Cl$^-$ ion pair can significantly contribute to understanding of the behaviors of KCl in ore-forming fluids.

2 Computational methods

2.1 Classical MD Models

The box of classical MD simulations for the K$^+$–Cl$^-$ ion pair was a periodically repeated cubic cell with a side length of 19.65 Å. The simulations were performed at 653,

873, and 1273 K, and each of them was divided into three subsets with different water densities (ρ_w = 0.60, 0.30, and 0.10 g/cm^3). The simulation at ambient conditions (T = 298 K, P = 1 bar, and ρ_w = 1.0 g/cm^3) was also carried out to test our method by comparison with the experimental results. The numbers of water molecules were calculated from the equation of state of water (Wagner and Pruß 2002). The initial configurations of the KCl/NaCl aqueous systems were built with K$^+$/Na$^+$ and Cl$^-$ ions placed at the center of the box and the water molecules inserted with random orientations.

2.2 Classical MD details

Both constrained and free MD simulations were carried out using the package DLPOLY2.20 (Todorov et al. 2011). We used the SPC/E model to describe water molecules (Berendsen et al. 1987). The parameters of the K$^+$–Cl$^-$ ion pair were from Koneshan et al. (1998). We used the leapfrog MD algorithm with a time step of 0.5 fs. Each simulation was run for 500 ps before collecting data for 1500 ps.

2.3 Potential of mean forces and association constants

The PMFs, W(r), between the anion and the cation were calculated as a function integrating the total anion–cation mean force F(r), in Eq. (2). In each constrained MD simulation, the distance between the two ions was retained at a fixed constant, changing from 8.00 to 2.00 Å by a step of 0.20 Å.

$$W(r) = W_0(r) - \int_{r_0}^r F(r)dr \qquad (2)$$

where $W_0(r) = -e^2/4\pi\varepsilon r_0 + 4\varepsilon_{LJ}\left((\sigma_{LJ}/r_0)^{12}-(\sigma_{LJ}/r_0)^6\right)$ (ε_{LJ} and σ_{LJ} are the molecular parameters of K$^+$ and Cl$^-$ ions, which are mentioned in Sect. 2.2), $r_0 = 8.0$ Å, and ε is the dielectric constant of the SPC/E water (Plugatyr and Svishchev 2009).

The ion-pair association constants were calculated from the PMFs (Justice and Justice 1976) as follows:

$$K_A = 4\pi N_A 10^{-27} \int_0^{r_c} \exp\left(-\frac{W(r)}{kT}\right)r^2 dr \qquad (3)$$

where r_c is the interionic distance of criterion dividing the "associated ion-pair" and "free ions". The values of r_c are variable according to different definitions of the associated ion-pair: the associated ion-pair with both CIP and SShIP into consideration or the associated ion-pair only as CIP. In this work, r_c was calculated using both definitions (i.e., CIP + SShIP and CIP). The association constant, K$_A$

(L/mol), was converted into the molal concentration based association constant, K_A(m) (kg/mol), by multiplying the fluid density, ρ_w (g/cm^3) (K_A(m) = $\rho_w K_A$).

2.4 Geometry optimizations of the mixed KCl-metal complexes

To investigate the mixed KCl-metal complexes, geometry optimizations were applied to calculate the structures and binding energies of $KAuCl_2$ and $KCuCl_2$ complexes using static quantum–mechanical techniques. The initial configurations of investigated clusters (i.e., KCl, AuCl/CuCl, $KAuCl_2$, and $KCuCl_2$) were placed in a cubic box with a side length of 20 Å. Geometry optimizations were carried out using CP2K/QUICKSTEP package (VandeVondele et al. 2005). The electronic structures were calculated using hybrid Gaussian plane wave (GPW) implementation of density functional theory. PBE functional was utilized for the exchange–correlation (Perdew et al. 1996), and Goedecker–Teter–Hutter pseudopotentials were employed to describe the interaction between the valence electrons and the core states (Goedecker et al. 1996). The cutoff for electronic density was set to be 360 Ry. Binding energies of $KAuCl_2$ and $KCuCl_2$ were derived from the energy changes in the association reactions (i.e., $KCl + AuCl = KAuCl_2$ and $KCl + CuCl = KAuCl_2$).

3 Results and discussions

3.1 The potential of mean forces

Temperature and density dependence of the PMFs for the K^+–Cl^- ion pair are displayed in Fig. 1a, b. Because the variation of PMF values with density were similar at the three temperatures, here only the results at 873 K are shown. Only the PMF curves at 0.3 g/cm^3 are presented for the same reason. As the distance between ions increases,

the states of ion pair also change, which can be identified from the PMF shapes. The two minima found at $\sim$3.2 and $\sim$5.4 Å correspond to CIP and SShIP states, respectively, with a maximum at $\sim$4.5 Å called transition state (TS) between them (Fig. 1a, b). These positions of minima and maximum do not shift with temperature or density. The minima in CIP state tend to be deeper with increasing temperature (Fig. 1a) and decreasing density (Fig. 1b), indicating that CIP state becomes more associative in higher temperatures and in lower density conditions. It is noteworthy that the CIP state has a lower minimum than that of the SShIP state for the conditions investigated (Fig. 1a, b), which can be attributed to the more associative behaviors of ion pairs under CIP state than SShIP state in high-T or low-density solutions. The energy differences between CIP and TS state are much larger than the thermal energy ($\frac{3}{2}$RT), indicating that CIP state dominates at these conditions. The SShIP state is less favored due to the shallow energy barriers from SShIP to TS state and from SShIP to free ion state.

Comparing with Na^+–Cl^- and Li^+–Cl^- ion pairs in supercritical conditions (Yui et al. 2010; Zhang and Duan 2004), we found similar shapes of PMFs curves with K^+–Cl^- ion pair in supercritical fluids, with two minima and a saddle maximum. Overall, their first minimums are all deeper than the second minimums in supercritical fluids, indicating that CIP states are more stable in supercritical fluids. The distances between ions in CIP states (i.e., $\sim$2.2 Å for Li^+, $\sim$2.8 for Na^+, and $\sim$3.2 Å for K^+) will increase with larger size of cations under supercritical conditions.

3.2 Association constants for K^+–Cl^- ion pair

The calculated $\log K_A$ value of KCl under the ambient conditions is 0.48 for "CIP + SShIP" and 0.44 for "CIP", respectively, in excellent agreement with the experiment data of 0.53 (Fuoss 1980) and 0.41 (Hefter and Salomon

Fig. 1 The PMFs for the K^+–Cl^- ion pair in supercritical water from 0.10 to 0.60 g/cm^3 at T = 873 K (**a**) and from 653 to 1273 K at ρ = 0.30 g/cm^3 (**b**)
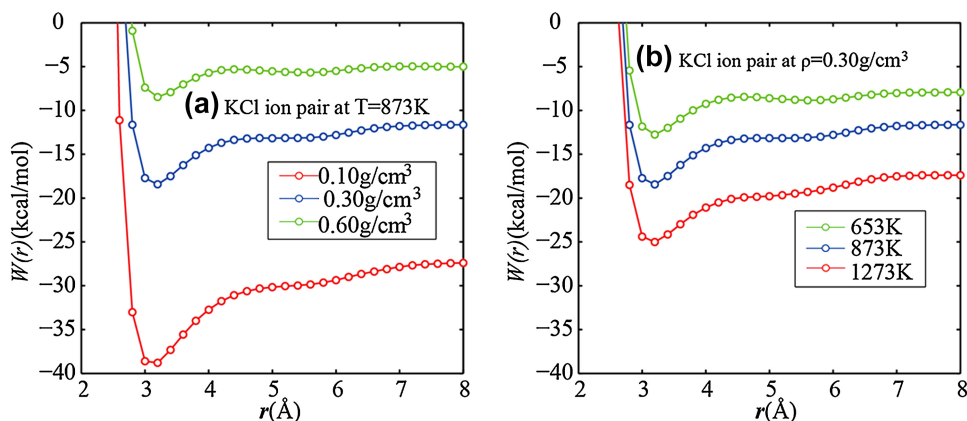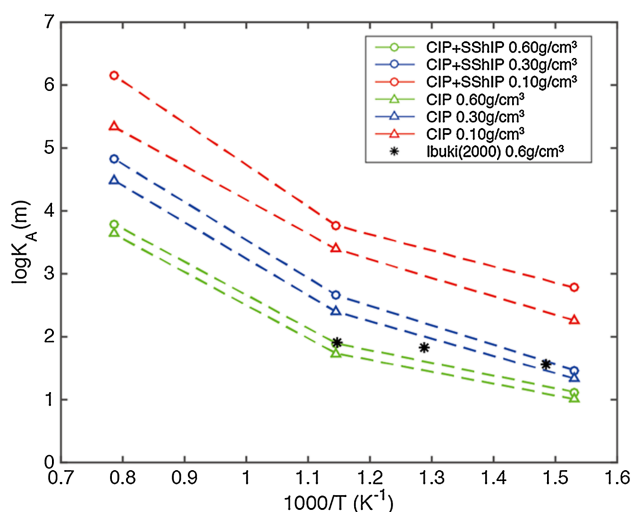
Fig. 2 $\log(K_A(m))$ values at different conditions for "CIP + SShIP" and "CIP". ρ_w and T are in g/cm^3 and K, respectively

1996) within 0.1 logK units. In SCW, our results are in good agreement with the experimental data by Ibuki et al. (2000) at 0.6 g/cm^3 within 0.5 logK units (in Fig. 2), which further validates the computational setup in this work.

The association constants of KCl versus temperature are plotted in different densities (Fig. 2). All the data of $\log K_A$ in Fig. 2 are >1 (i.e., the association constants >10), indicating that the ion pair of KCl holds stably in high-T low-density solutions. At the same temperature, the $\log K_A$ value increases for both "CIP + SShIP" and "CIP" methods from 0.6 to 0.1 g/cm^3, and at the same density, the $\log K_A$ value increases from 653 up to 1273 K (Fig. 2). The same trend with temperature and density is observed from LiCl and NaCl (Ibuki et al. 2000; Yui et al. 2010). Together with the data in this work, Yui et al. (2010), and Ibuki et al. (2000), it is observed that the $\log K_A$ values for LiCl, NaCl, and KCl are at the same order of magnitude in supercritical fluids.
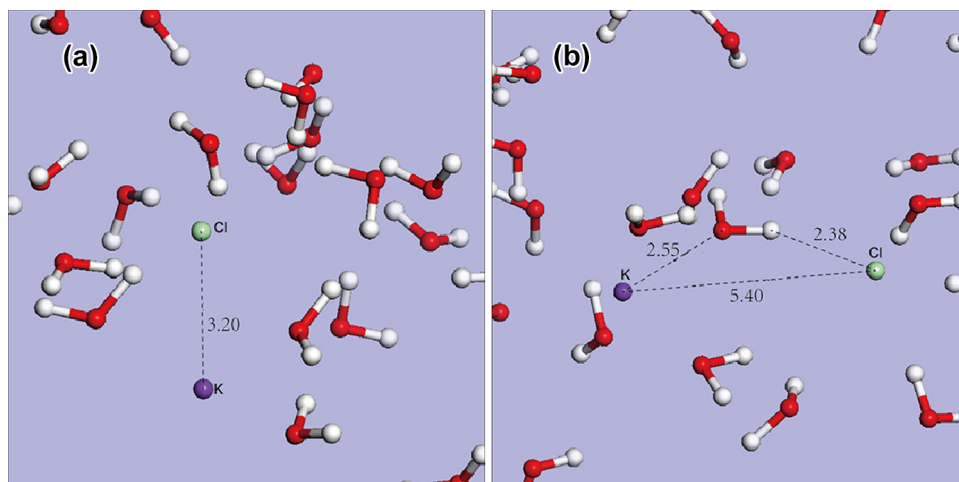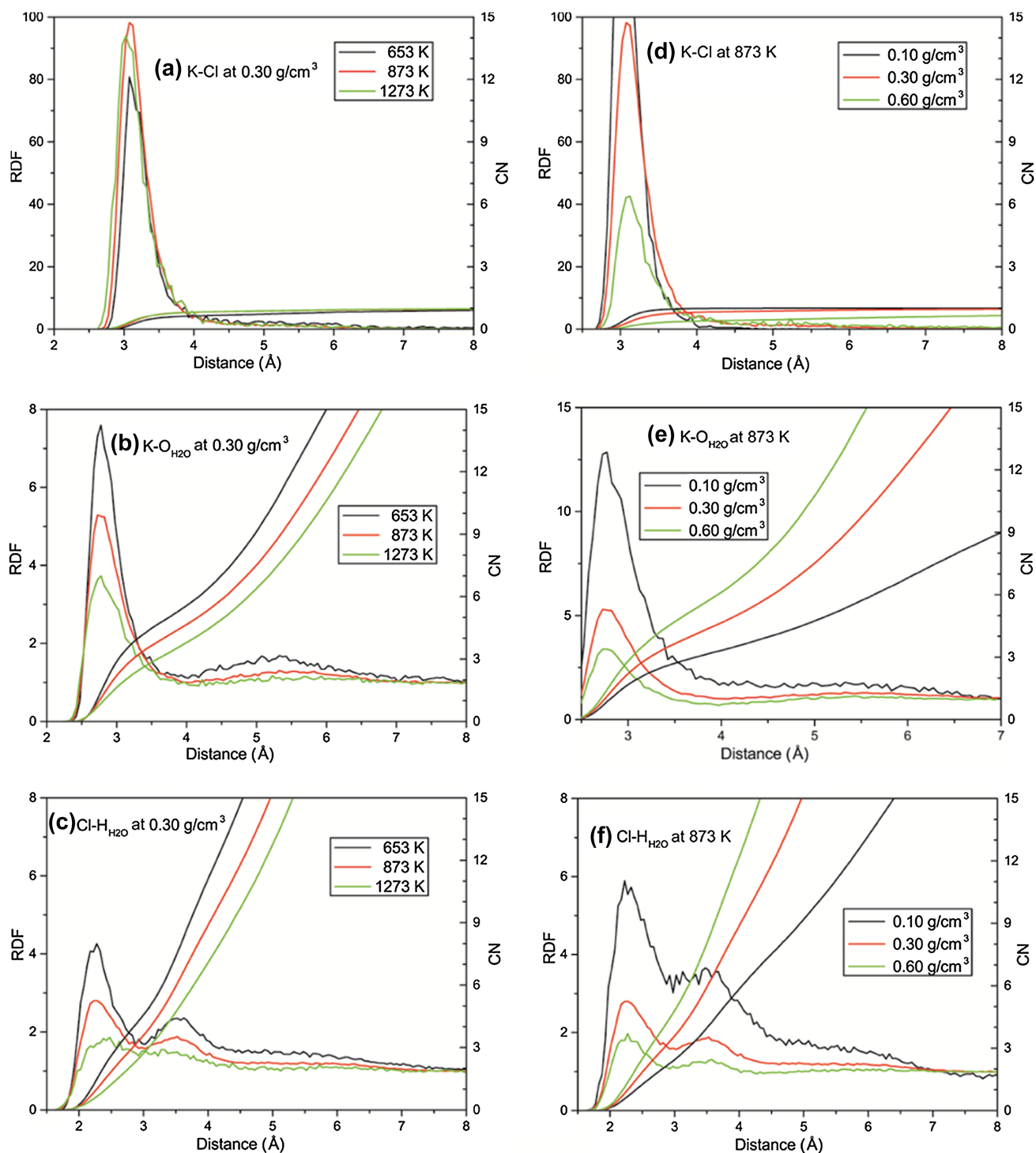
Comparing "CIP + SShIP" method with "CIP" method, it was found that the association constants of "CIP + S-ShIP" method were always larger than those of the "CIP" method. Their differences of $\log K_A$ values were less than 1 logK unit, indicating that the effects of SShIP hardly influenced the association constants. The difference of association constants became smaller with increasing density. When the water density increased to 0.6 g/cm^3, the differences between two data sets were less than 0.2 logK units.

3.3 Ion pair structures and hydration structures

The configurations of the K$^+$–Cl$^-$ ion pair in CIP and SShIP states at T = 653 K and ρ = 0.6 g/cm^3 are gathered in Fig. 3, where the microscopic structures are derived from the constrained MD simulations at 3.2 and 5.4 Å. It was observed that K$^+$–Cl$^-$ ion pair redirected neighboring waters (Fennell et al. 2009): in CIP state, the ion pair (Fig. 3a) has no water between K$^+$ and Cl$^-$ ions, while the microstructure in SShIP state (Fig. 3b) has one molecular of water between ions, with the oxygen closer to K$^+$ and the hydrogen pointing to Cl$^-$.

Figure 4 depicts the RDFs and CNs derived from the trajectories of free MD simulations. The sharp RDF peaks of K–Cl are shown at ~3.15 Å in 0.30 g/cm^3 solutions at all temperatures (Fig. 4a) and at 873 K from 0.10 to 0.60 g/cm^3 (Fig. 4b). These results indicate the distance of ions is ~3.15 Å in high-T low-density solutions, where the ion pair is in CIP state. The RDF curves for K around Cl hold no obvious maximum at r ~ 5 Å for all conditions (Fig. 4a, d), showing that the SShIP structure is unfavorable at the investigated conditions. There are two hydration shells for K$^+$ ion and Cl$^-$ ion as shown in the RDF profiles of K–O and Cl–H (Fig. 4b, d, c, f). According to the CN curves of K–O and Cl–H (Fig. 4b, d, c, f), the hydrated water molecules around ions become more dense as temperature decreases or density increases.

Fig. 3 Snapshots in CIP state (**a**) and SShIP state (**b**) for the K$^+$–Cl$^-$ ion pair from simulations at T = 653 K and ρ_w = 0.6 g/cm^3

Fig. 4 RDFs and CNs for K around Cl, water O around K, and water H around Cl in the simulations of KCl solutions at 0.3 g/cm^3 (**a**, **b**, **c**) and at 873 K (**d**, **e**, **f**)

3.4 The KCl–Au(I)/Cu(I) complexes

The optimized structures of KCl, AuCl, CuCl, KAuCl$_2$, and KCuCl$_2$ are shown in Fig. 5. The structures of the KCl–Au(I)/Cu(I) complexes (shown in Fig. 5c, f) indicate that

ore-forming metals (i.e., Au and Cu) are two-fold coordinated, consistent with the previous studies (Liu et al. 2011; Mei et al. 2013; Zajacz et al. 2011). As displayed for KAuCl$_2$ complex in Fig. 5c, K atom is closer to one Cl atom (2.96 Å) than the other Cl (4.42 Å), while for
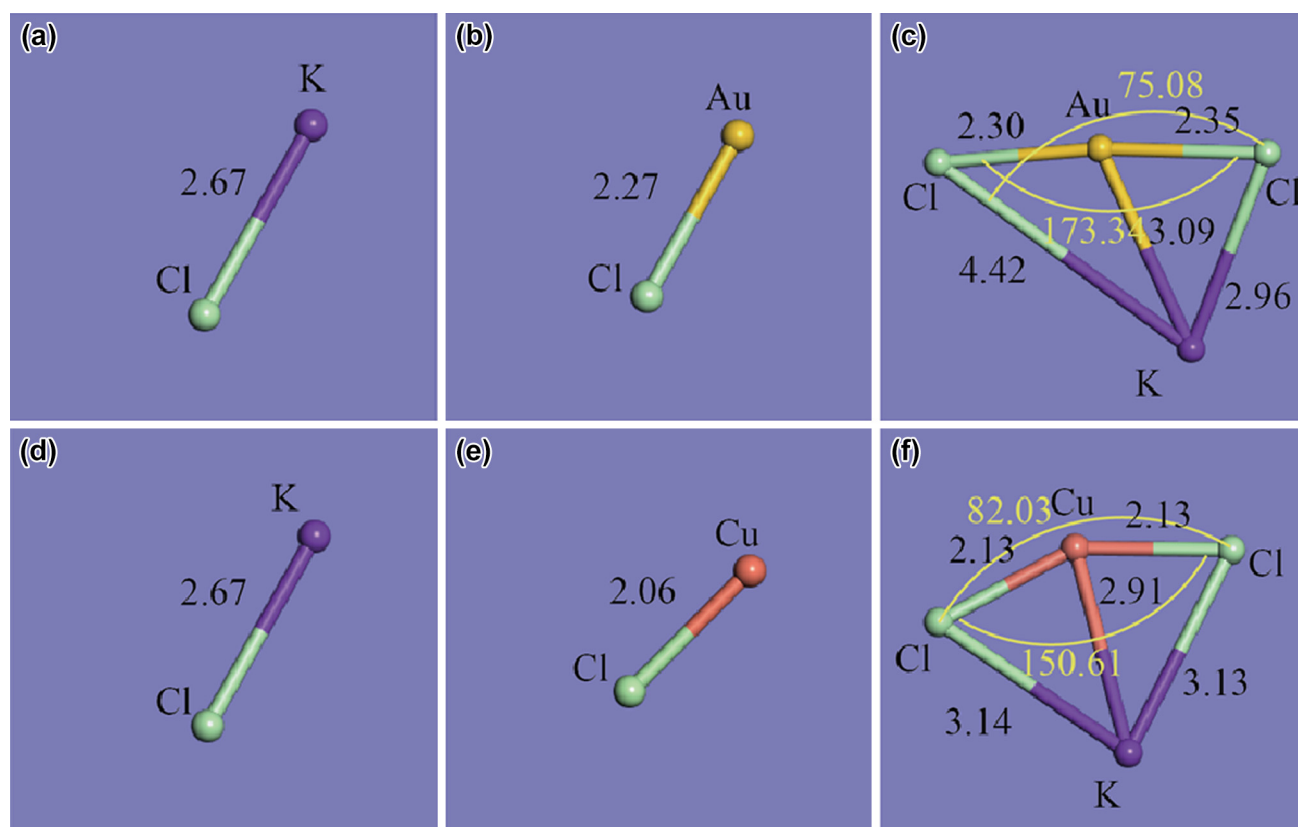
Fig. 5 Geometry optimizations of KCl, AuCl, CuCl, KAuCl$_2$, and KCuCl$_2$

Table 1 Binding energies of KAuCl$_2$ and KCuCl$_2$ in association reactions

Reaction	Binding energy (kcal/mol)
KCl + AuCl = KAuCl$_2$	−59.9
KCl + CuCl = KCuCl$_2$	−54.0

KCuCl$_2$ complex (Fig. 5f), the distances of K and two Cl are almost equal (3.13 and 3.14 Å). The geometry of KCuCl$_2$ is similar with that of NaCuCl$_2$ (Zajacz et al. 2011), where Na/K ions are on the midperpendicular of the linear CuCl$_2^-$ structures.

Table 1 collects the estimated energy changes of the mixed KCl-metal complexes during association reactions. The binding energies of two complexes are on a similar level (−59.9 and −54.0 kcal/mol for KAuCl$_2$ and KCuCl$_2$, respectively). Even at 1273 K, the thermal energy (2.5 kcal/mol) is significantly smaller than these binding energies, which indicates that the complexes hold stably at temperature up to 1273 K.

According to the above analyses, the K$^+$–Cl$^-$ ion pair can keep stable in CIP state under supercritical conditions, and the mixed KCl-metal complexes also hold stably even at 1273 K. Herein, we propose that these mixed KCl-metal complexes are stable in high-T low-density solutions and

KCl is likely to be a ligand to easily form complexes with ore-forming metal clusters, which is in agreement with the experiments (Zajacz et al. 2010, 2011). The results of geometry optimization thus provide fundamental understanding of the effect of K$^+$–Cl$^-$ ion pair in transport and deposition of metals in ore-forming hydrothermal fluids.

4 Conclusions

In summary, we investigated the PMFs, association constants, CIP and SShIP structures and hydration structures of K$^+$–Cl$^-$ ion pairs in supercritical fluids by using classical MD simulations. The PMFs of K$^+$–Cl$^-$ ion pairs are evaluated with the constrained MD method. The analyses indicate that CIP state is the most favorable for a K$^+$–Cl$^-$ ion pair. The association constants calculated from PMFs show an increasing trend with increasing temperature or decreasing water density. The static quantum–mechanical method is used to calculate the geometry optimizations and binding energies of KAuCl$_2$ and KCuCl$_2$. The energy data prove the thermodynamic stability of these complexes for T up to 1273 K.

This work provides the microscopic and quantitative properties of a K$^+$–Cl$^-$ ion pair in supercritical solutions.

In Au/Cu-rich fluids, KCl is likely to be a critical factor in controlling the release of ore-forming metals. In future studies, thermodynamics properties of KCl–Au(I)/Cu(I) complexes in ore-forming fluids will be further addressed by using first principle molecular dynamic simulations (FPMD) which takes account of the effects of solvent.

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