SOLVATION EFFECTS OF COMPLEX ANIONS IN CRYOLITE MELT

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Equilibrium constants of the main dissociation scheme of cryolite complex anions and corresponding solvation energies are calculated using both the Hartree–Fock and density-functional schemes with direct inclusion of the reaction field into the Hamiltonian in a self-consistent way. The results are compared with previous *a posteriori* static-reaction-field calculations.

Key words: Fluoroaluminates; Aluminum; Solvation; Ionic melts; Self-consistent reaction field; Cryolite; *Ab initio* calculations.

The extraordinary importance of cryolite for aluminum production motivated many scientific activities devoted to the study of the cryolite melt structure and energetics. Though being an object of steady interest, the structure of molten cryolite was not satisfactorily explained yet. In their monograph, Grjotheim *et al.*[1] list various possible dissociation schemes of cryolite. For a long time, the most frequently discussed ionic equilibrium in the melt has been $AlF_6^{3-} \rightarrow AlF_4^- + 2\ F^-$. Recently, based on the results of high-temperature *in situ* Raman spectroscopy studies, an alternative dissociation scheme $AlF_6^{3-} \rightarrow AlF_5^{2-} + F^- \rightarrow AlF_4^- + 2\ F^-$, with relatively high concentration of AlF_5^{2-} ion, was proposed[2,3]. The conclusions are based[2,3] on decomposition of measured bands in the region of totally symmetric valence vibrations of the anions considered. However, the way of decomposition of vibrational spectra could represent the critical point of the interpretation of experimental data in this case[4]. The discussion concerning the dissociation scheme of the cryolite melt has not yet led to results which are acceptable without critical comments.

There is no surprise that this topic is also a subject of theoretical studies. Both, classical mechanics simulations based either on the Monte Carlo (MC) or molecular dynamics (MD) scheme and quantum-chemical studies

are present in the literature. MC (ref.[5]) and MD (ref.[6]) simulated cryolite melt structures do not confirm the dissociation scheme according to the quoted papers[2,3]. In contrast to the MC results, the MD simulation agrees well with basic features of the equilibrium crystal structure of cryolite (six-fold Al coordination, Al–F distance).

Concerning quantum-chemical studies of halogenoaluminates, the paper of Bock *et al.*[7] is a post-Hartree–Fock study of halogenoaluminate systems. The molecules and ions in the ideal gas phase served as model clusters and the influence of the molten salt environment was simulated by presence of some alkali metal atoms in model clusters. The paper of Bouyer *et al.*[8] is a density functional (DFT) study of fluoroaluminate anions. The solvation was modelled using clusters containing sodium and calcium atoms in a way similar to Bock's paper[7]. Relative stabilities of individual complexes were compared and the concentrations of individual compounds of cryolite melt in dependence on cryolite ratio were calculated. The approximate way of obtaining the solvation energies used in that paper can lead to inaccuracy in values of equilibrium constants. Moreover, the set of ions considered in the melt is too much restricted to be able to clarify the structure of cryolite melt.

Evidently, for at least qualitative description of the structure and energetics of cryolite melts, a quantum-chemical method of Hartree–Fock quality is required, providing good results for a proper choice of a set of quasi-species (either real or hypothetical molecules or ions representing the cryolite melt) including, at the same time, the electrostatic effect of the melt environment. Our recent paper[9] is devoted to the statistical-thermodynamic analysis of such a scheme extended to the proposal of solvation energy evaluation based on the ideal conductor model of the melt. As a result qualitatively correct description of cryolite in the environment of "chemically indifferent" melt, NaCl, was obtained. The results were in good agreement with the experimental findings[10].

One of approximations used in ref.[9] was the computation of solvation energies in a pure *a posteriori* manner, using vacuum-optimized geometry. In the case of reactions with small energy differences of reactants, the errors caused using this approximation may influence the result.

The aim of this paper is to test how the direct inclusion of reaction field into the Hamiltonian in a self-consistent way influences the equilibrium constants of the main dissociation scheme of complex anions expected in the cryolite melt. The influence of reaction field on the geometry of the ions under study is considered as well. For the exhaustive solution of the problem of structure and equilibrium composition of the cryolite melt, the

set of considered quasi-species must be extended for complex anions containing two or more aluminum atoms, as it was concluded in ref.[9]. This is, however, beyond the scope of the present study. Our aim was rather to demonstrate the possibilities of methodological improvement, simplicity of its use and its influence on the results.

THEORETICAL

The effect of the molten salt environment can be modelled by enclosing the species in a cavity in a continuum with infinite relative electric permittivity. For the purpose of our calculations, we found the value of ε = 1 000 to be sufficient to represent the infinite permittivity. This allows to use the standard polarized continuum model of solvation[11] (PCM) which has been already routinely implemented in a number of quantum-chemical packages. We used the GAUSSIAN 94 package[12] for both vacuum and self-consistent reaction field (SCRF) determination of melt energy. Calculations were performed both at HF and DFT levels of theory. For DFT calculations, Perdew and Wang's 91 gradient-corrected functional[13] (PW91) was used. At both levels of theory, the vacuum-optimized geometry of fluoroaluminate anions was reoptimized in the molten salt environment. The 6-311+G(2d) basis set[14] for all atoms was used. For each species, a single spherical cavity, centered on the aluminum atom, was chosen. The radius of the cavity R_k was determined as

$$R_k = \sup\{R_{k,i}\}_{i=1}^{n_k} \ , \tag{1}$$

where n_k is the number of atoms in the respective anion of the k-th type, i runs over all the atoms of the anion and

$$R_{k,i} = \left| \mathbf{r}_{k,i} - \mathbf{r}_{k,0} \right| + \rho_i \ , \tag{2}$$
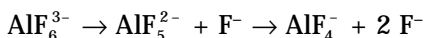
where $\left| \mathbf{r}_{k,i} - \mathbf{r}_{k,0} \right|$ is the distance of the i-th atom from the center of mass of the considered anion ($\mathbf{r}_{k,i}$ and $\mathbf{r}_{k,0}$ being the radiusvectors of the i-th atom and the center of mass, respectively) and ρ_i is the ionic radius of the i-th atom of the anion. The value of 1.33 Å was used as ionic radius of F$^-$ in accordance with our previous work[9]. To be consistent with the model[9], the cavity shape and size were not further refined beyond its definition by Eqs (*1*) and (*2*).

To compare our SCRF calculations with the previous *a posteriori* static model[9], the static field solvation energy was also evaluated (see ref.[9]),

$$\Delta E^{\text{static}} = -\frac{Q_k^2}{2R_k} , \tag{3}$$

where Q_k is the charge enclosed in the spherical cavity of the radius R_k.

The equilibrium constant, K, for the reaction scheme

$$\text{AlF}_6^{3-} \rightarrow \text{AlF}_5^{2-} + \text{F}^- \rightarrow \text{AlF}_4^- + 2\ \text{F}^-$$

or, in more general form,

$$\sum_i \nu_i A_i \rightarrow \sum_j \nu_j B_j , \tag{4}$$

where ν_j, ν_i are the stoichiometric coefficients of the respective quasi-species, A_i, B_j, is then, of a given temperature T (see ref.[9]),

$$K = \frac{\prod_j c_j^{\nu_j}}{\prod_i c_i^{\nu_i}} = \frac{\prod_j \Lambda_j^{\nu_j}}{\prod_i \Lambda_i^{\nu_i}} \exp\left[\frac{\sum_i \nu_i \mu_{i,\text{solv}} - \sum_j \nu_j \mu_{j,\text{solv}}}{kT}\right], \tag{5}$$

where c_i is the concentration of the species of i-th type, Λ_i are the translational parts of the statistical sum and μ_i are the respective chemical potentials. For the latter, in our case of highly ionic system where the electrostatic contributions are highly dominant, it is well justified to take the electrostatic Helmholtz free energy and to neglect all the other (dispersion, cavitation, *etc.*) contributions.

RESULTS AND DISCUSSION

Table I summarizes the geometries of fluoroaluminate anions optimized *in vacuo* and in the melt. From Table I one can see only minor influence of the melt environment on the bond lengths in all species considered. This can be attributed to high symmetry of the respective species and, consequently, to the high symmetry of the reaction field. The trend to reduce slightly the atomic distances in the melt is evident for all species both at HF and DFT

levels of theory. Note the symmetrizing effect of the melt environment on the two different bond lengths in the AlF_5^{2-} anion.

Table II contains the total *in vacuo* energies, compares solvation energies in the environment of the ionic melt for both SCRF and static reaction field and shows the radii of cavities used for static field calculations for all the anions considered. Despite obvious differences between the total *in vacuo* energies of the two different schemes used (HF *vs* DFT), the differences in energies of solvation are, as expected, much smaller since correlation effects

TABLE I
HF- and DFT-optimized bond lengths (Å) for quasi-species in gas phase and in solution

Quasi-species	HF		DFT	
	vacuum	melt	vacuum	melt
AlF_4^-	1.673	1.669	1.714	1.708
AlF_5^{2-} (ax.)	1.804	1.754	1.848	1.792
AlF_5^{2-} (eq.)	1.752	1.746	1.799	1.787
AlF_6^{3-}	1.869	1.812	1.919	1.848

TABLE II
HF- and DFT-calculated total energies without solvent, solvation energies (self-consistent reaction field), solvation energies (static reaction field) (a.u.) and radii of cavities (Å) of quasi-species in the melt

Quasi-species	Method	E(vacuum)	ΔE(SCRF)	ΔE(stat)	R(CAV)
F^-	HF	–99.4461	–0.1832	–0.1991	1.33
	DFT	–99.8784	–0.1777	–0.1991	1.33
AlF_4^-	HF	–640.2172	–0.0936	–0.0882	3.00
	DFT	–642.3232	–0.0900	–0.0870	3.04
AlF_5^{2-}	HF	–739.5681	–0.3481	–0.3380	3.13
	DFT	–742.1046	–0.3399	–0.3333	3.18
AlF_6^{3-}	HF	–838.7522	–0.7516	–0.7450	3.20
	DFT	–841.7244	–0.7331	–0.7335	3.25

play an extremely small role in solvation of anions in comparison with the electrostatic contribution. The self-consistent reaction field provides slightly higher stabilization of the fluoroaluminate anions than the static reaction field. On the other hand, the stabilization of the fluoride anion is slightly lower. This is caused by a contribution from higher multipoles in case of the complex fluoroaluminate particles, which is completely absent in case of the static solvation model.

Table III shows the values of respective equilibrium constants calculated for temperature of 1000 K. One can see only minor discrepancy between the two different reaction fields. A part of it is caused by different geometries in vacuum and in the melt environment and, consequently, by different cavity sizes of the respective reaction fields. (The static field solvation energy (Eq. (*3*)), being an *a posteriori* correction, is determined from the *in vacuo* cavity size.) Having the melt-optimized geometry available in our case, we also recalculated all the equilibrium constants for the static field using the melt cavity sizes. As expected, all the equilibrium constants were shifted towards the K(SCRF). However, as one can see from Table III, only a part of the discrepancy can be attributed to the cavity difference; for the rest, the way of determining the reaction field must be responsible. Comparing the respective equilibrium constants for the two levels of theory (where only very slight differences are expected), note that the HF and DFT numbers are closer for the SCRF case than for the static field model.

TABLE III
HF- and DFT-calculated equilibrium constants (mol/l) of some reactions at 1 000 K: not considering the solvent effect (vacuum) and in the melt considering the self-consistent reaction field (SCRF) or static reaction field using vacuum-(stat/vacuum) and melt-optimized (stat/melt) geometries

Reaction	Method	K(vacuum)	K(SCFR)	K(stat/vacuum)	K(stat/melt)
$AlF_5^{2-} \rightarrow F^- + AlF_4^-$	HF	$2.8 \cdot 10^{26}$	$4.6 \cdot 10^{16}$	$3.1 \cdot 10^{19}$	$5.6 \cdot 10^{18}$
	DFT	$4.1 \cdot 10^{26}$	$5.1 \cdot 10^{16}$	$1.3 \cdot 10^{20}$	$2.2 \cdot 10^{19}$
$AlF_6^{3-} \rightarrow 2\,F^- + AlF_4^-$	HF	$4.2 \cdot 10^{75}$	$4.2 \cdot 10^{35}$	$1.4 \cdot 10^{40}$	$2.1 \cdot 10^{38}$
	DFT	$2.5 \cdot 10^{75}$	$8.6 \cdot 10^{35}$	$2.1 \cdot 10^{41}$	$1.3 \cdot 10^{39}$
$AlF_6^{3-} \rightarrow F^- + AlF_5^{2-}$	HF	$1.5 \cdot 10^{49}$	$9.1 \cdot 10^{18}$	$4.6 \cdot 10^{20}$	$3.7 \cdot 10^{19}$
	DFT	$6.1 \cdot 10^{48}$	$1.7 \cdot 10^{19}$	$1.6 \cdot 10^{21}$	$6.0 \cdot 10^{19}$

From Table III it is evident that the use of self-consistent reaction field shifts the equilibrium constants towards the dissociation of complex particles in a way very similar to the static reaction field model. Therefore, the model of self-consistent reaction field also leads to the result that almost all aluminum atoms are coordinated with four fluorine atoms in AlF_4^- complex ions. However, this result can be affected by the fact that only a limited subset of possible quasi-species in the melt was used.

CONCLUSIONS

Generally, the *a posteriori* model of solvation is believed to give less satisfactory results than the self-consistent reaction field scheme. Our results indicate that in the case of solvation in the ionic melt the self-consistent reaction field and static reaction field models provide comparable equilibrium constants of the main dissociation scheme of cryolite complex anions. The equilibrium is slightly less shifted to the dissociation in comparison with the simple *a posteriori* static reaction field. The values of equilibrium constants are predominantly determined by stabilization energy of the fluoride anion. To obtain reliable values of the equilibrium constants, the cavity radius of the fluoride anion must be chosen in a more exact way. We see two ways how to accomplish this task. The first, phenomenological possibility is to parametrize the cavity radius of fluoride anion until the equilibrium gas pressure over melts of various compositions will be reproduced. The other, theoretically better justified approach, is based on the minimization of the solvation free energy with inclusion of dispersion-repulsion terms[15,16].

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