Structure and Binding of Ionic Clusters in Th and Zr Chloride Melts

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We discuss microscopic ionic models for the structure and the binding of small clusters which may exist as structural units in molten $ThCl_4$ and $ZrCl_4$ and in their mixtures with alkali halides according to Raman scattering studies of Photiadis and Papatheodorou. The models are adjusted to the two isolated tetrahedral molecules. Appreciably higher ionicity is found for $ThCl_4$ than for $ZrCl_4$, and this fact underlies the strikingly different behaviour of the two systems in the dense liquid state – in particular, a molecular-type structure for molten $ZrCl_4$ against a structure including charged oligomers in molten $ThCl_4$.

Key words: Ionic Clusters; Liquid Structure; Molten Salts.

1. Introduction

A number of polyvalent-metal halide melts behave as molecular liquids (see [1] for a review, mainly focused on trihalides). In comparison with more conventional molten salts, this behaviour is macroscopically characterised by a relatively low melting point, high fluidity and very low electrical conductivity of the melt. Among tetrahalides, molten $ZrCl_4$ in a Raman scattering study of Photiadis and Papatheodorou [2] has been proposed to consist of $ZrCl_4$ tetrahedral monomers in equilibrium with a neutral oligomeric species, possibly the Zr_2Cl_8 dimer. For molten $ThCl_4$, the same authors [3] have emphasized that the higher melting point (771 °C *vs.* 437 °C), the observed ionic conductivity (0.6 $\Omega^{-1}cm^{-1}$ at 810 °C), and the stability of a glassy state indicate an ionic-type binding. Using also their Raman scattering results on liquid mixtures of $ThCl_4$ with alkali chlorides, they have proposed for the pure melt coexistence of neutral monomers with charged oligomers preserving tetrahedral and octahedral coordinations for the Th(IV) ion. For both $ZrCl_4$ and $ThCl_4$ the monomer is the main species in the vapour and for the former compound it has been shown to coexist with Zr_2Cl_8 dimers.

In earlier work [4, 5] we evaluated the binding in the isolated tetrahedral monomers of $ThCl_4$ and $ZrCl_4$ within the general framework of an ionic model that we had originally developed for trivalent-metal chlorides [6]. The results were used to study the relative stability of charged oligomers of these two compounds. Although the details of the interionic forces and of the input data were quite different in [4] and in [5], as dicussed further below, the common conclusion was that the character of the bonding is considerably more ionic in $ThCl_4$ than in $ZrCl_4$. The present short review pays main attention to the ionic molecular model evaluated in [5], which allowed for the electronic polarizability of the metal ion and used basic input on bond lengths and molecular vibrational frequencies from the study of Konings and Hildebrand [7]. After discussing the binding in the isolated tetrahedral monomer, we discuss the stability of the neutral dimer against dissociation into two monomers and the ion-transfer reaction consisting of the exchange of one chlorine between two neutral dimers.We also examine the role of counterion compensation for charged clusters in the specific case of Cs counterions and report on a number of other ion-transfer reactions leading to various positively and negatively charged oligomeric species.

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2. Ionicity of the Tetrahedral Monomer

As in our earlier studies [4 - 6, 8 - 11] our model for Th and Zr halide clusters incorporates the Born model of cohesion and the shell model for vibrational motions and lattice defects. Overlap repulsions of exponential form are described by ionic radii and stiffness parameters. Electron-shell deformability is described through (i) effective valences subject to overall charge compensation and (ii) electrical and overlap polarizabilities of the halogens. The electrical polarizability of the metal ions is also included. We refer to our study of the Al-based chloride clusters for a detailed presentation of the model and for thorough tests of its usefulness in describing neutral and charged clusters [6]. This test study gave excellent agreement with the available experimental data as well as with first-principles results from refined Hartree-Fock and density-functional calculations.

A number of model parameters can be transferred to tetrachlorides from our earlier studies of other compounds. As a first step we redetermine the model parameters for $ZrCl_4$ by fitting measured properties of the gaseous monomer. The input data are the Zr-Cl bond length of 2.32 Å and the vibrational frequencies ν_1 = 375 cm^{-1} and ν_4 = 100 cm^{-1}. We find z_{Zr} = 3.27, R_{Zr} = 1.20 Å and α_{Zr} = 1.4 Å^3, the two former values being in excellent agreement with our earlier determination [11]. In a parallel approach to $ThCl_4$ we use the values 2.567 Å for the Th-Cl bond length and the values ν_1 = 325 cm^{-1} and ν_4 = 70 cm^{-1}. We then find z_{Th} = 3.25, R_{Th} = 1.41 Å and α_{Th} = 2.0 Å^3.

The above model parameters for $ThCl_4$ [5] are quite different from those of our earlier study [4] (z_{Th} = 3.25 against 3.68 and R_{Th} = 1.41 Å against 1.43 Å). These differences are due both to the somewhat different values of the input molecular data and to the present inclusion of the electronic polarizability of the metal ion. On comparing the model parameters for Th and Zr it is seen that, while the effective valence of the two ions is essentially the same, the Th ion has a sizably larger ionic radius and polarizability. We show immediately below that these differences suffice to stabilize the higher oligomers that were proposed by Photiadis and Papatheodorou [3] to form in acidic mixtures of molten $ThCl_4$ with CsCl and in the pure $ThCl_4$ melt.

3. The Neutral Dimer and its Ion-transfer Products

On account of thermal fluctuations, the equilibrium shape that we find for the M_2Cl_8 dimer (with M = Th or Zr) consists of two five-cornered prisms sharing an edge, and thus each metal ion is fivefold-coordinated. We estimate the binding energy of Zr_2Cl_8 relative to two monomers to be only 0.3 eV, consistently with the experimental fact that the dimer is a minority species in the gas phase. We instead find that binding is higher for Th_2Cl_8, about 0.9 eV. This result is consistent with a stronger ionic character of the binding, but conflicts with the fact that the main observed species in the gas phase is again the tetrahedral monomer. From our calculations the breathing mode lies at 406 cm^{-1} in Zr_2Cl_8 and 332 cm^{-1} in Th_2Cl_8, in fair agreement with the Raman scattering data showing a mode at 404 cm^{-1} for Zr_2Cl_8 in the vapour and a band at 341 cm^{-1} in the $ThCl_4$ melt [3].

With regard to the ionized states of the M_2Cl_8 dimer, we find that the M_2Cl_9 negative ion is formed by two distorted MCl_6 octahedra sharing a face, while the M_2Cl_7 positive ion is formed by two MCl_4 tetrahedra sharing a corner. For the ionization equilibrium

$$2\,MCl_4 \leftrightarrow \tfrac{1}{2}\,M_2Cl_9 + \tfrac{1}{2}\,M_2Cl_7 + E_{\mathrm{d}} \qquad (1)$$

we find $E_{\mathrm{d}} \cong -0.23$ eV for Th and $E_{\mathrm{d}} \cong -1.0$ eV for Zr. On account of the Coulomb interaction energy between the ionized species, it can be expected that the dissociation equilibrium should be more strongly shifted to the right for Th than for Zr.

4. Charged and Cesium-compensated Clusters

We discuss in this section the molecular clusters that according to the experiments of Photiadis and Papapheodorou [2, 3] seem to be relevant in the liquid $(CsCl)_{1-x}$-$(MCl_4)_x$ mixtures. We briefly recall their main findings. For M = Zr (i) in the CsCl-rich region ($0 < x < 0.33$) the spectra of the mixture are similar to those of molten Cs_2ZrCl_6 and suggest that the predominant species are the $(ZrCl_6)^{2-}$ octahedra; (ii) in the intermediate region ($0.33 < x < 0.66$) the structure of the melt evolves towards dominancy of the $(Zr_2Cl_9)^-$ species, passing through intermediate species that may be $(ZrCl_5)^-$, $(Zr_2Cl_{10})^{2-}$ and / or $(Zr_2Cl_{11})^{3-}$; and (iii) in the $ZrCl_4$-rich region

($0.66 < x \leq 1$) the spectrum of the $(Zr_2Cl_9)^-$ species is preserved while the spectrum of the pure $ZrCl_4$ liquid emerges.

For M = Th, on the other hand, (i) the spectra from molten Cs_2ThCl_6 and from the liquid mixture at x = 0.33 are interpreted as due to vibrations of the $ThCl_6$ octahedron; (ii) this spectrum persists at $x < 0.33$ but is enriched by other structures, which are interpreted as due to the presence of $ThCl_7$; (iii) in the composition range $0.33 < x < 0.5$ the Th_2Cl_9, Th_2Cl_{10} and Th_2Cl_{11} charged dimers are again proposed to be present; and (iv) higher negatively charged oligomers such as Th_3Cl_{14} are proposed to form in the composition range $x > 0.5$. Assuming that such oligomers remain stable in the mixtures with increasing concentration x of $ThCl_4$ up to the pure $ThCl_4$ melt, at $x = 1$ they must be compensated by positively charged clusters such as Th_2Cl_6 and Th_3Cl_{10}.

In our calculations we have constructed each of the above-mentioned molecular ions and considered also its Cs-compensated counterpart. The main general points that emerge are (i) charge compensation by alkali counterions is crucial in stabilizing the more highly charged species and therefore in determining the equilibrium between the various species, and (ii) each counterion has a multiplicity of equilibrium positions around the core of the complex anion, so that the counterions must be seen as executing correlated motions in the outer regions of the charge-compensated cluster. We report a number of examples below.

The MCl_6 molecular ion is a perfect octahedron and can bind two Cs ions on top of the centres of two opposite faces with a large energy gain of ≈ 7 eV. In the Cs-compensated molecule the breathing mode lies at 299 cm^{-1} for M = Zr and at 269 cm^{-1} for M = Th, to be compared with the measured values of 319 cm^{-1} and 295 cm^{-1} , respectively. Two MCl_6 octahedra can be joined via face-sharing, edge-sharing or corner-sharing to form the M_2Cl_9, M_2Cl_{10} and M_2Cl_{11} negatively charged dimers, respectively. The preferred positions of the compensating Cs ions are (i) facing a bonding chlorine in CsM_2Cl_9, (ii) at the opposite ends of the dimer in $Cs_2M_2Cl_{10}$, and (iii) in the outer parts of the central region of the cluster in $Cs_3M_2Cl_{11}$, with each Cs being first neighbour of the bonding chlorine and of four terminal chlorines. The energy gain on charge compensation is of order 2 eV, 6 eV and 12 eV in the three cases. Thus, while a highly charged polynuclear ion such as M_2Cl_{11} is uncommon, it may in some cases be stabilized by suitable alkali counterions.

Of course, the doubly-charged Zr_2Cl_{10} cluster is the dimer of $ZrCl_5$: this is a five-cornered prism in the shape of a trigonal bipyramid and can bind a Cs ion to three of its chlorines, with an energy gain of about 2 eV. Photiadis and Papatheodorou [2] attribute modes at about 338 and 148 cm^{-1} to either $ZrCl_5$ or Zr_2Cl_{10} in liquid CsCl-$ZrCl_4$ mixtures. We find that the breathing mode of these charged or Cs-compensated monomers and dimers lies at about 330 cm^{-1} in all cases. Therefore, the issue of the relative stability of the $ZrCl_5$ monomer and the Zr_2Cl_{10} dimer cannot be answered on the basis of the Raman scattering evidence alone. However, we find from our present calculations that charge compensation by Cs counterions stabilizes the dimer by about 1 eV relative to two separate, Cs-compensated $ZrCl_5$ monomers.

Turning to the $ThCl_7$ cluster, we find that it has the shape of a pentagonal bipyramid, a rare example of a sevenfold-coordinated metal ion. Compensation by three Cs ions creates a complex static structure in which each Cs atom is asymmetrically bound to three chlorines. Again, local charge compensation by counterions is crucial in stabilizing the highly-charged anionic species.

5. Charged Oligomers in Molten Thorium and Zirconium Chloride

Photiadis and Papatheodorou [3] observed continuous changes in the Raman spectrum of the liquid $(CsCl)_{1-x}$-$(ThCl_4)_x$ systems with increasing x above 0.33. They proposed that a possible way to account for such continuous changes is through an extended linkage of $ThCl_6$ octahedra being formed in the melt as its composition is changed towards pure $ThCl_4$. In [4] and [5] we reported results for the structure and energetics of the higher oligomorphic clusters that are proposed to be present in these liquid systems for $x \geq 0.5$. The relevant calculations concern, first of all, the incremental energy $\Delta E^{(n)}$ for binding of the doubly charged M_nCl_{4n+2} polyanions, for M = Th or Zr. $\Delta E^{(n)}$ is defined as

$$\Delta E^{(n)} = E_b^{(n)} - E_b^{(n-1)} - E_b(MCl_4), \qquad (2)$$

where $E_b^{(n)}$ is the binding energy of the n-th member of the series and $E_b(MCl_4)$ is the binding energy of

MCl_4. Our results for $\Delta E^{(n)}$ clearly confirm the higher stability of the Th polyanions.

A further question concerns the equilibria described by the formula

$$2\,MCl_4 \leftrightarrow \tfrac{2}{n+m}\left[(M_nCl_{4n-2})^{2+} + (M_mCl_{4m+2})^{2-}\right] + E_M(n,m) \quad (3)$$

for the coexistence of doubly charged polyanions and polycations in the pure melt. Our calculations of the activation energies $E_M(n,m)$ for M = Th or Zr show that all these activation energies are significantly larger for the Zr compound, signalling that ion transfer between neutral species is relatively unfavoured in this melt.

Thus, our results confirm the appreciably greater stability of charged oligomers of Th chloride than of Zr chloride.

6. Summary

In summary, we have developed a microscopic model for the ionic interactions in Th and Zr halides from an analysis of their gaseous monomers. We have found general agreement with the proposals and the quantitative results presented in the Raman scattering studies of Photiadis and Papatheodorou [2, 3]. At a given value of the ionic radius the main factors governing the relative stability of different local configurations are the metal-chlorine Coulomb attractions and the screening by counterions. The difference between the ionic radii and the polarizabilities of the metal ions are sufficient to explain the stability of the higher oligomers of $ThCl_4$ and $ZrCl_4$.

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