

Structure and Energetics of Clusters Relevant to Thorium Tetrachloride Melts

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We study within an ionic model the structure and energetics of neutral and charged molecular clusters which may be relevant to molten ThCl_4 and to its liquid mixtures with alkali chlorides, with reference to Raman scattering experiments by Photiadis and Papatheodorou. As stressed by these authors, the most striking facts for ThCl_4 in comparison to other tetrachloride compounds (and in particular to ZrCl_4) are the appreciable ionic conductivity of the pure melt and the continuous structural changes which occur in the melt mixtures with varying composition. After adjusting our model to data on the isolated ThCl_4 tetrahedral molecule, we evaluate (i) the Th_2Cl_8 dimer and the singly charged species obtained from it by chlorine-ion transfer between two such neutral dimers; (ii) the ThCl_6 and ThCl_7 clusters both as charged anions and as alkali-compensated species; and (iii) various oligomers carrying positive or negative double charges. Our study shows that the characteristic structural properties of the ThCl_4 compound and of the alkali-Th chloride systems are the consequence of the relatively high ionic character of the binding, which is already evident in the isolated ThCl_4 monomer.

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

1. Introduction

A great deal of evidence has been obtained over the last decade on the static and dynamic structure of molten trivalent-metal halides and of their liquid mixtures with alkali-metal halides (for a recent review see [1]). Systematic structural studies of similar systems involving tetravalent-metal halides are in comparison relatively few. A notable exception is the early study of the pure GeBr_4 molecular liquid, whose structure was determined at the level of partial structure factors from anomalous X-ray scattering experiments [2] and related to the crystal structure through a change in the short-range molecular packing [3]. More recent instances come from the Raman scattering studies carried out by Photiadis and Papatheodorou on ZrCl_4 [4] and on ThCl_4 [5] in various states of aggregation, both in the pure compound and in mixtures with alkali halides over a very broad range of composition. As these authors emphasize, the behaviour of these two systems is strikingly different under a number of aspects, as we proceed to briefly recall immediately below.

For both ZrCl_4 and ThCl_4 the main species in the gas phase is the tetrahedral monomer, and for the former compound the monomer has been shown to be in equilibrium with Zr_2Cl_8 dimers formed from two edge-sharing five-cornered prisms. However, for ZrCl_4 (i) the crystal structure contains zigzag chains of bridged ZrCl_6 octahedra, forming three distinct pairs of Zr-Cl bonds [6]; (ii) melting yields a high-fluidity, non-conducting liquid where ZrCl_4 monomers are in equilibrium with a small polymeric species, which could be the Zr_2Cl_8 dimer or possibly the $\text{Zr}_6\text{Cl}_{24}$ hexamer in a ring configuration; and (iii) chlorination through mixing with CsCl at various compositions favours the formation of the $(\text{ZrCl}_5)^-$ and $(\text{ZrCl}_6)^{2-}$ species, with all the possibilities that they have of aggregating into dimeric charged units (Zr_2Cl_9 , $\text{Zr}_2\text{Cl}_{10}$ and $\text{Zr}_2\text{Cl}_{11}$) via various forms of chlorine sharing as the mixture composition is changed.

In contrast, for ThCl_4 (i) two tetragonal crystal structures have been reported, in which each Th atom shares with its neighbours eight chlorine atoms on the corners of a dodecahedron [7, 8]; (ii) melting, oc-

curing at an appreciably higher temperature (771 °C against 437 °C), is apparently accompanied by a drop in the metal-ion coordination and yields a liquid with an appreciable ionic conductivity (0.6 $\Omega^{-1}\text{cm}^{-1}$ at 810 °C) [9, 10]; and (iii) continuous structural changes seem to occur in the liquid mixtures with varying composition. A possible way to account for such continuous changes is through an extended linkage of ThCl_6 octahedra in the melt. In addition, a glassy state is stable for the ThCl_4 compound.

Among trichlorides, molten AlCl_3 [11] and FeCl_3 [12] may be similarly contrasted in their electrical transport behaviour. In both compounds, melting occurs from a layered crystal structure with very large entropy and relative volume changes and with a drop in the coordination of the metal ion from sixfold to essentially fourfold. Molecular dimers formed from two edge-sharing tetrahedra are the main species in the gas phase and these units persist as structural components in the melt. Yet the ionic conductivities in the two melts near freezing are very different. The appreciable conductivity of molten FeCl_3 [13, 14] can be explained by assuming that neutral dimers and ionized species coexist in equilibrium. The relevant ionized species are in this case the Fe_2Cl_7 anion, formed by two corner-bridged FeCl_4 tetrahedra and the Fe_2Cl_5 cation, built from two face-sharing FeCl_4 tetrahedra [15] (see also [16]). Ionic conduction can then proceed *via* chlorine hops from Fe_2Cl_7 anions to neutral dimers.

In previous work an ionic model that we had earlier developed for trivalent-metal chlorides [17] has been used to study various Zirconium chloride clusters, with regard to the pure ZrCl_4 vapour and melt and to the liquid CsCl-ZrCl_4 mixtures [18]. For the latter we have shown a crucial role of the Cs counterions in stabilizing the complex anions and in determining the energetics of their equilibria. In the present work we apply the same model to the evaluation of small clusters which may be relevant to molten ThCl_4 and its liquid mixtures with alkali halides. In Sect. 2 we adjust the model to data on the isolated tetrahedral monomer and demonstrate that ThCl_4 is considerably more ionic than ZrCl_4 . This result immediately suggests that ion transfer between neutral molecular units is favoured in molten ThCl_4 as compared to molten ZrCl_4 . In Sect. 3 we examine the stability of the neutral dimer against dissociation into two neutral monomers and evaluate the ion-transfer reaction consisting of the exchange of one chlorine between two

neutral dimers. In Sect. 4 we evaluate the Th_2Cl_6 and Th_2Cl_7 clusters both as charged anions and as alkali-compensated species, while in Sect. 5 we evaluate a number of other ion-transfer reactions leading to positively and negatively charged oligomeric species. Finally, Sect. 6 presents a summary of our results and our main conclusions.

2. Interionic Force Model and Ionicity of the Tetrahedral Monomer

The microscopic model that we use for tetrachlorides incorporates the Born model of cohesion in the crystalline state [19] and the shell model for vibrational motions and crystal defects [20]. Electron-shell deformability is described through (i) effective valences z_i subject to overall charge compensation, and (ii) electrical and overlap polarizabilities of the halogens (denoted by α_{Cl} and α_s , respectively). Overlap repulsions of exponential form are described by ionic radii R_i and stiffness parameters ρ_i . We refer to our study of Al-based chloride clusters for a detailed presentation of the model and for thorough tests of its usefulness in describing neutral and charged clusters of polyvalent-metal halides [17]. 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 earlier studies of other ionic compounds. Thus, for each tetrachloride we need at most three disposable parameters. In our study of ZrCl_4 [18] these parameters (the ionic radius and the effective valence of the Zr ion, and the electrical polarizability of the Cl ion) have been determined by fitting measured properties of the isolated ZrCl_4 tetrahedral molecule. In a parallel approach to the ThCl_4 molecule we use the value 2.58 Å for the Th-Cl bond length [21] and the estimated values $\nu_3 = 350 \text{ cm}^{-1}$ and $\nu_1 = 330 \text{ cm}^{-1}$ for the vibrational mode frequencies of the tetrahedron [5]. We then find $\nu_2 = 95 \text{ cm}^{-1}$ and $\nu_4 = 70 \text{ cm}^{-1}$ for the other modes of the ThCl_4 tetrahedron, in fair agreement with the estimated values $\nu_2 = 110 \text{ cm}^{-1}$ and $\nu_4 = 85 \text{ cm}^{-1}$ [5]. We have included van der Waals interactions between the chlorines through a strength parameter $C_{\text{Cl}} = 5.5 \text{ e}\text{\AA}^{5/2}$ [17].

Table 1 collects the values of the model parameters for ThCl_4 and ZrCl_4 . The main result of such a

Table 1. Interionic force parameters for Zr and Th chlorides.

M	z_M	R_M Å	ρ_M Å	R_{Cl} Å	ρ_{Cl} Å	α_{Cl} Å ³	α_s Å ³
Th	3.67 ₆	1.43	0.077	1.71	0.238	1.36	0.94
Zr	3.26 ₈	1.20	0.065	1.71	0.238	1.36	0.46

Table 2. Interionic force parameters for alkali ions.

A	R_A (Å)	ρ_A (Å)	α_A (Å ³)
Li	0.816	0.104	0.029
Na	1.17	0.079	0.285
K	1.46	0.099	1.15
Cs	1.72	0.067	2.79

comparative study of these two molecules is that the former is considerably more ionic than the latter. The effective valence of Th is 3.68 against 3.27 for Zr and the ionic radius is 1.43 Å for Th against 1.20 Å for Zr (given their meaning as overlap parameters, only the difference in magnitude of these ionic radii is significant [22]). Reductions of the effective valence by about 20% relative to the nominal valence are already common in trichlorides [17], so that the ThCl_4 molecule is evidently quite close to the ideal ionic model. It also turns out that, if we assume the same value for the electric polarizability of the chlorine ions in the two molecules, then the counterbalancing effect of overlap polarizability is appreciably larger in ThCl_4 , thus reducing the role of electron-shell polarization. These results suggest at once that ion transfer between neutral units is favoured in the condensed phases of ThCl_4 as compared to those of ZrCl_4 . The quantitatively different character of the binding in the two isolated monomers already anticipates the different physical behaviour of the two melts.

We conclude this section by reporting in Table 2 for completeness the model parameters for alkali ions that we shall use in our calculations on alkali compensated clusters. The overlap parameters are from work on alkali halides [22]. We also allow for the polarizability α_A of the alkali ions, with values taken from the tabulation by Jaswal and Sharma [23].

3. The Neutral Dimer and its Ion-transfer Products

The equilibrium shape that we find from our calculations for the isolated Th_2Cl_8 dimer in its static

ground state at zero temperature is best described as built from two ThCl_4 tetrahedra which form a bound state by asymmetric sharing of two corners. More precisely, each of the two Th ions is in a slightly distorted fivefold coordination having three terminal chlorines at a distance of 2.58 Å as in the isolated tetrahedral monomer, one bonding chlorine at a distance of 2.74 Å and a further bonding chlorine at a distance of 2.80 Å. Of course, such a minute distortion will be averaged out by fluctuations, yielding for the Th_2Cl_8 dimer a symmetric shape formed by two five-cornered prisms sharing an edge.

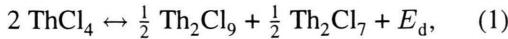
Our estimated value for the binding energy of the Th_2Cl_8 dimer is quite appreciable, about 1.6 eV relative to two isolated monomers. This result conflicts with the fact that the main observed species in the gas phase is the tetrahedral monomer. It is consistent, however, with the stronger ionic character of the binding in ThCl_4 . In their work on molten ThCl_4 Photiadis and Papatheodorou [5] exclude a monomer-dimer equilibrium on the basis that the negligible thermal expansion of the melt rules out drastic structural changes with increasing temperature. They note that the partial presence of ThCl_4 molecules in the melt cannot be excluded, from the fact that the predicted ν_1 -mode frequency of the isolated monomer at $\approx 330 \text{ cm}^{-1}$ is close to the observed Raman-scattering band in the melt at 341 cm^{-1} . However, after fitting this monomer frequency as described in Sect. 2 we find from our calculations that the breathing mode of the two triplets of terminal chlorines in the isolated dimer is at a frequency of 335 cm^{-1} , even closer to the 341 cm^{-1} Raman band of the melt. Therefore, we feel that the nature of the neutral species (if any) in the pure ThCl_4 melt should be the object of further study. The dimer is characterized by a fivefold coordination of the Th atoms, as already noted.

We go on to present our results for the ionized states of the Th_2Cl_8 dimer. We find that the Th_2Cl_9 negative ion is formed by two distorted ThCl_6 octahedra sharing a face, with two triplets of terminal chlorines (Cl^T) at bond lengths of 2.61 Å and the triplet of bonding chlorines (Cl^B) at bond lengths of 2.81 Å. The values of the main molecular bond angles are $\angle \text{Th}-\text{Cl}^B-\text{Th} = 99.6^\circ$ and $\angle \text{Cl}^T-\text{Th}-\text{Cl}^T = 100.1^\circ$.

The Th_2Cl_7 positive ion is instead formed from two ThCl_4 tetrahedra sharing a corner, with $\text{Th}-\text{Cl}^T$ bond lengths of 2.56 Å and $\text{Th}-\text{Cl}^B$ bond lengths of 2.70 Å. The molecular bond is essentially straight (in contrast

to the case of the Zr_2Cl_7 positive ion, where we find $\angle \text{Zr}-\text{Cl}^{\text{B}}-\text{Zr} = 126.3 \text{ \AA}$ and the other molecular bond angles are $\angle \text{Cl}^{\text{T}}-\text{Th}-\text{Cl}^{\text{T}} = 117.8^\circ$ and $\angle \text{Cl}^{\text{T}}-\text{Th}-\text{Cl}^{\text{B}} = 98.5^\circ$.

Finally, we report our result for the ionization equilibrium



all clusters being in the isolated state *in vacuo*. Here and in the following sections we choose the initial state as consisting of two isolated monomers, in order to obtain significant comparisons between the energetics of different ionization equilibria. We find $E_d \approx 0.16 \text{ eV}$, with the convention that (here and in the following) a positive sign means a release of energy if the reaction goes from left to right. Since the above estimate does not include the gain in Coulomb attractive energy between the two ionized products in a dense phase, we may expect that the ionization equilibrium (1) should be shifted to the left in calculations referring to the dense ThCl_4 melt. In contrast, we find $E_d \approx -1.1 \text{ eV}$ for the same ionization equilibrium if Th is replaced by Zr.

4. The Charged and Alkali-compensated ThCl_6 and ThCl_7 Clusters

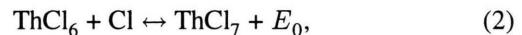
In their Raman scattering study Photiadis and Papatheodorou [5] have recorded a large number of spectra for solid compounds in the phase diagrams of the $(\text{ACl})_{1-x}-(\text{ThCl}_4)_x$ systems (with A = Li, Na, K or Cs) and for liquid mixtures at various compositions x . Taking as examples the Cs_2ThCl_6 and Cs_3ThCl_7 compounds, these can be viewed as containing negatively charged and Cs-compensated clusters of ThCl_6 and ThCl_7 , respectively. The observed spectra from molten Cs_2ThCl_6 and from the liquid mixture at $x = 0.33$ are interpreted as due to the vibrations of the ThCl_6 octahedron. This spectrum persists at $x < 0.33$ but is enriched by other structures, which are interpreted as due to the presence of ThCl_7 .

From our calculations the isolated ThCl_6 cluster is indeed an octahedron, with a Th-Cl bond length of 2.69 \AA . On adding two compensating alkalis, these find their static equilibrium positions above the centers of two opposite faces of the octahedron: the Th-Cl bond length is slightly reduced to 2.68 \AA and the $\text{Cl}_1-\text{Th}-\text{Cl}_2$ bond angle (Cl_1 being bound to the first alkali atom and Cl_2 to the second) opens up somewhat, from 90° to 101.1° for A = Li and to 95.3° for A = Cs. The

A-Cl bond length is 2.68 , 3.08 , 3.43 and 3.68 \AA for A = Li, Na, K and Cs, respectively. Of course, all pairs of faces are equivalent in the octahedron and therefore the two alkali atoms in an isolated cluster must be seen as executing correlated motions around the ThCl_6 octahedron. The breathing mode of the alkali-compensated cluster lies at $281 - 284 \text{ cm}^{-1}$ depending on the alkali, in fair agreement with the measured value [5] $\nu_1(A_{1g}) \approx 295 \text{ cm}^{-1}$ which is not affected by the alkali counterion.

Turning to the ThCl_7 cluster, we find that in the isolated state it has the shape of a pentagonal bipyramid – a rare example of a sevenfold-coordinated metal ion. The Th-Cl bond lengths are 2.80 \AA in the planar pentagon and 2.73 \AA out of the plane. Compensation by three Cs atoms creates a complex static structure in which each Cs atom is asymmetrically bound to three chlorines. Again, correlated motions of the counterions around the octahedral core of the cluster are indicated.

Finally, the activation energies entering the ionization equilibria



and



are $E_0 = -4.1 \text{ eV}$ and $E'_0 = 1.7 \text{ eV}$. Local charge compensation by counterions is evidently crucial in stabilizing the highly-charged anionic species. We also estimate the binding energy of Cs_2ThCl_6 as 7.1 eV relative to the isolated component molecules (ThCl_4 and two CsCl).

5. Charged and Cs-compensated Oligomers

As already recalled in Sect. 1, Photiadis and Papatheodorou [5] observe continuous changes in the Raman spectrum of the liquid $(\text{ACl})_{1-x}-(\text{ThCl}_4)_x$ systems with increasing x above 0.33. They propose that a possible way to account for such continuous changes is through an extended linkage of ThCl_6 octahedra in the melt. Here we examine the structure and energetics of the relevant oligomeric clusters.

5.1. Negatively Charged and Cs-compensated Dimers

Considering first the composition range $0.33 < x < 0.5$, two ThCl_6 octahedra can be joined *via* face-sharing, edge-sharing or corner-sharing to form the

Th_2Cl_9 , $\text{Th}_2\text{Cl}_{10}$ and $\text{Th}_2\text{Cl}_{11}$ charged dimers, respectively. We have already presented our results for the Th_2Cl_9 negative ion in Sect. 3 above. Cesium compensation of this charged cluster places a Cs atom in the outer region of the bond, with an energy gain of 2.3 eV.

We find the stable static structure of the doubly charged $\text{Th}_2\text{Cl}_{10}$ anion as formed from two edge-sharing octahedra, with a $\text{Th}-\text{Cl}^T$ bond length of 2.64 Å and a $\text{Th}-\text{Cl}^B$ bond length of 2.81 Å. There also are some distortions in the bond angles relative to the ideal octahedral value of 90°, and in particular the $\text{Th}-\text{Cl}^B-\text{Th}$ bond angle is 112.9°. Cesium compensation is effected by bonding each of two Cs atoms to three terminal chlorines at the opposite ends of the dimer and is accompanied by an energy gain of about 7 eV.

Similarly, the stable static structure of $\text{Th}_2\text{Cl}_{11}$ is obtained from two octahedra sharing a chlorine corner. The $\text{Th}-\text{Cl}^B$ bond length is 2.77 Å and there are two slightly different values of the $\text{Th}-\text{Cl}^T$ bond length, at 2.67 - 2.68 Å. The $\text{Th}-\text{Cl}^B-\text{Th}$ bond is straight and all bond angles are very close to 90°. Compensation by Cesium yields complex static structures, with the most stable one containing three Cs atoms in the outer parts of the central region of the dimer. The energy gain is as large as 14.8 eV. Thus, while a highly charged polynuclear ion such as $(\text{Th}_2\text{Cl}_{11})^{3-}$ is uncommon, it may in some cases be stabilized by suitable alkali counterions.

5.2. Negatively Charged Trimers and Positively Charged Dimers and Trimers

Higher oligomers are proposed by Photiadis and Papatheodorou [5] to form in the composition range $x > 0.5$. We find the static shape of the doubly charged $\text{Th}_3\text{Cl}_{14}$ anion to be a chain-like structure formed from three ThCl_6 octahedra bonded to each other by sharing an edge. Table 3 reports the increments $\Delta E^{(n)}$ in binding energy of the doubly charged $\text{Th}_n\text{Cl}_{4n+2}$ polyanions on increasing n by unity in the range $1 \leq n \leq 3$. We have defined the incremental binding energy as

$$\Delta E^{(n)} = E_b^{(n)} - E_b^{(n-1)} - E_b(\text{ThCl}_4), \quad (4)$$

with $E_b^{(n)}$ the binding energy of the n -th member of the series and $E_b(\text{ThCl}_4)$ the binding energy of ThCl_4 . By comparison with our earlier results on oligomeric chains of single-bonded tetrahedral anions for triva-

Table 3. Incremental binding energy $\Delta E^{(n)}$ of the $(\text{Th}_n\text{Cl}_{4n+2})^{2-}$ series as a function of n (in eV).

	$n = 1$	$n = 2$	$n = 3$
$(\text{Th}_n\text{Cl}_{4n+2})^{2-}$	4.20	3.44	2.38

Table 4. Activation energies $E_M(n, m)$ for the reactions (5) *in vacuo* (in eV).

M	$E_M(2, 2)$	$E_M(2, 3)$	$E_M(3, 2)$	$E_M(3, 3)$
Th	-4.2	-2.4	-2.3	-1.1
Zr	-5.1	-3.7	-3.6	-2.7

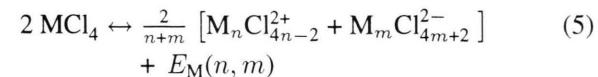
lent metal halides [24], we see that the double bond between adjacent units in a short chain of octahedra yields values of $\Delta E^{(n)}$ larger by roughly a factor of 3 and that convergence is not yet reached at $n = 3$. In the large- n limit we may expect a value of $\Delta E^{(n)}$ for doubly-bonded octahedra approximately twice as large as for singly-bonded tetrahedra, *i. e.* of the order 1 eV.

Assuming that such negatively charged oligomers remain stable in the liquid Th-alkali halide mixtures with increasing concentration x of ThCl_4 up to the pure ThCl_4 melt, then at $x = 1$ they must be compensated by positively charged clusters. We have evaluated the clusters Th_2Cl_6 and $\text{Th}_3\text{Cl}_{10}$. The former cluster is formed from two edge-sharing tetrahedra, with a $\text{Th}-\text{Cl}^B$ bond length of 2.76 Å and a $\text{Th}-\text{Cl}^T$ bond length of 2.54 Å. Insertion of an edge-sharing octahedron between the two tetrahedra yields a chain-like static structure for $\text{Th}_3\text{Cl}_{10}$. Another possible polymeric series is evidently emerging, again formed from octahedra bonded to each other by sharing an edge but terminating at the opposite ends with two tetrahedra and carrying a double positive charge.

5.3. Equilibria of Charged Oligomers

The coexistence of doubly charged oligomeric anions and cations in the pure ThCl_4 melt, as discussed just above in Sect. 5.2, is evidently alternative to the equilibrium between the neutral Th_2Cl_8 dimer and its singly charged ionization products that we have examined in Sect. 3. We proceed to evaluate the relevant ionization equilibria, for comparison with (1).

We consider the equilibria described by



in vacuo, for the cases $n, m = 2$ and 3 and taking $\text{M} = \text{Th}$ or Zr . The corresponding values of the energy $E_{\text{M}}(n, m)$ are reported in Table 4.

A number of general points are immediately evident from Table 4. Firstly, all the ionization reactions of the type (5) that we have evaluated *in vacuo* are endothermic: this is not surprising, as the activation energies $E_{\text{M}}(n, m)$ do not include the gain in attractive energy from the Coulomb interactions between the reaction products in a dense phase. Secondly, all activation energies are appreciably larger for the Zr compounds, signalling again that ion transfer is unfavoured in these less ionic systems. Thirdly, the activation energies for the Th compounds decrease as the sizes (n, m) of the oligomers increase: this trend evidently reflects the fact that with increasing (n, m) the same amount of excess charge is being spread over larger molecular volumes. The stability of long chain-like structures in the pure ThCl_4 melt is consistent with the formation of a glassy state.

We should at this point contrast the value $E_{\text{Th}}(3,3) = -1.1$ eV for the endothermic reaction $2 \text{ThCl}_4 \leftrightarrow [(\text{Th}_3\text{Cl}_{10})^{2+} + (\text{Th}_3\text{Cl}_{14})^{2-}]/3$ *in vacuo* with the value $E_{\text{d}} = 0.16$ eV for the exothermic reaction $2 \text{ThCl}_4 \leftrightarrow [(\text{Th}_2\text{Cl}_7)^+ + (\text{Th}_2\text{Cl}_9)^-]/2$ that we have evaluated in Sect. 3. Bearing again in mind that the Coulombic attractions between the charged clusters in the dense melt have not been included in our calculations, it seems to us difficult to decide on the basis of this comparison between these two alternative pictures of the state of ionization in the pure ThCl_4 melt.

6. Concluding Remarks

The possibility of fourfold, fivefold, sixfold and even sevenfold coordination for a tetravalent metal ion by halogens and the various connectivities that may be formed by joining these basic structural units by single, double or triple halogen bonds gives great structural richness to a tetrahalide liquid and to its mixtures with alkali halides.

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We have in this work successfully extended a microscopic ionic model first proposed for trihalide systems [17] to deal with a number of neutral and charged clusters which are relevant to the condensed phases of thorium tetrachloride and to its liquid mixtures with alkali halides. From our calculations, at given values of the ionic radii the main factor governing the relative stability of different local configurations is the Coulomb energy associated with the $\text{Th}-\text{Cl}$ interactions and with screening by counterions.

Starting from the basic fact that the binding in the ThCl_4 tetrahedral molecule is very close to the ideal ionic picture, we have found general agreement with the suggestions and quantitative results presented in the Raman scattering study of Photiadis and Papatheodorou [5]. However, on the basis of our calculations we have been unable to discriminate between two alternative pictures of the state of ionization of the pure ThCl_4 melt. We have considered first an ionization equilibrium between the neutral dimer and its singly charged ionization products, which would parallel the state of ionization which is believed to be present in molten FeCl_3 [15]. We have also studied the ionization equilibria between doubly charged oligomers, which has been proposed for the ThCl_4 melt [5] and may explain the stability of a glassy state for this compound. We believe that this question should be re-examined in future studies of the pure melt, both by diffraction studies and by computer simulation.

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