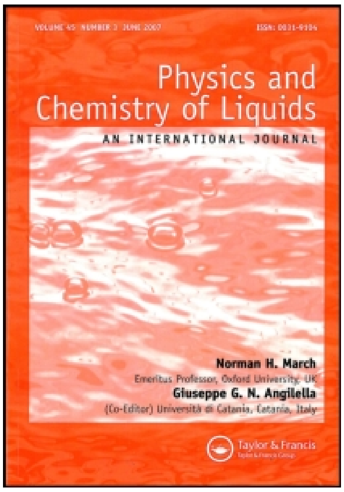

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An Ionic Model for $FECL_3$-Based Melts from a Study of the Molecular Dimer and Other Molecular Structures

Z. Akdeniz[a]; G. Pastore[b]; M. P. Tosi[c]
[a] Physics Department, University of Istanbul, Istanbul, Turkey and International Centre for Theoretical Physics, Trieste, Italy [b] Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica Teorica, Università di Trieste, Trieste, Italy [c] Istituto Nazionale di Fisica della Materia and Classe di Scienze, Scuola Normale Superiore, Pisa, Italy

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AN IONIC MODEL FOR FECL$_3$-BASED MELTS FROM A STUDY OF THE MOLECULAR DIMER AND OTHER MOLECULAR STRUCTURES

Z. AKDENIZ,[a] G. PASTORE[b] and M. P. TOSI[c]

[a]*Physics Department, University of Istanbul, Istanbul, Turkey and International Centre for Theoretical Physics, I-34014 Trieste, Italy;*
[b]*Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica Teorica, Università di Trieste, I-34014 Trieste, Italy;*
[c]*Istituto Nazionale di Fisica della Materia and Classe di Scienze, Scuola Normale Superiore, I-56126 Pisa, Italy*

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A model of ionic interactions accounting for ionic polarizability through electrostatic and shell deformation dipoles is developed for applications to molten iron trichloride and its mixtures with alkali chlorides in the acidic range of composition. The main focus is on (i) bond lengths and bond angles in molecular clusters as possible precursors of local structures in melts, and (ii) stability of local structures against fluctuations into ionized states. The determination of the ionic interactions is based on structural properties of the neutral monomer and dimer in the vapour phase, in parallel with, and using some input from, our earlier study of aluminium trichloride. The model is used to study the structure of charge-carrying clusters obtained from the monomer ($(FeCl_4)^-$ and $(FeCl_2)^+$) and from the dimer ($(Fe_2Cl_7)^-$ and $(Fe_2Cl_5)^+$); it is also tested through calculations of the vibrational frequencies of the various clusters. The role of the metal ion polarizability is discussed with regard to $FeCl_3$ and Fe_2Cl_6. Comparisons with data from experiment and from molecular orbital calculations are presented.

Keywords: Molten salts; molecular structures

1. INTRODUCTION

Work on trivalent metal halides has revealed a rich variety of melting behaviours [1]. A striking example is presented by YCl_3, $AlCl_3$ and $InCl_3$. These salts have the same layer-type structure in the crystal, which is formed from a slightly distorted cubic close packing of chlorines accomodating the trivalent metal ions inside every second (111) plane of octahedral sites [2]. On melting YCl_3 retains a closely packed structure with octahedral-type coordination for the metal ions [3, 4], while $AlCl_3$ transforms into a liquid of correlated Al_2Cl_6 dimers offering tetrahedral coordination for the Al^{3+} ions [5, 6]. On the other hand $InCl_3$ melts with a very large relative change in volume as found for $AlCl_3$, but the melting temperature and the ionic conductivity of the melt near freezing are similar to those of YCl_3 [1]. Preliminary neutron diffraction data on molten $InCl_3$ indicate a metal-ion coordination between five and six [7].

Considerable progress has been made in semiquantitatively understanding the liquid structure of systems such as YCl_3 and other closely packed trivalent chlorides on the basis of simple rigid-ion models for the ionic interactions [8]. On the contrary the stability of strong local structures in a melt such as $AlCl_3$ has to be modelled, at a level suitable for classical methods in the computer simulation of disordered systems, through the use of a fairly sophisticated polarizable-ion model [6]. In addition to accounting for the basic Al_2Cl_6 local structure in the pure $AlCl_3$ melt, one needs to examine charge-carrying units such as $(AlCl_4)^-$ and $(Al_2Cl_7)^-$, with the aims of (i) assessing the stability of local structures in the pure melt against fluctuations into ionized states, and (ii) extending the usefulness of the model into the highly interesting area of liquid mixtures with alkali halides.

The focus of the present work is on $FeCl_3$. The $FeCl_3$ crystal structure differs from the $AlCl_3$ structure primarily in the interlayer correlations, being based on an almost perfect hexagonal (rather than cubic) close packing of chlorines with each metal ion at the centre of an almost perfect octahedron [2]. The entropy and relative volume changes on melting are very large and close in magnitude to those of $AlCl_3$ [1]. An average first-neighbour coordination number of 3.6 chlorines around a metal ion has been reported from a neutron diffraction study of the melt [9]. As for YCl_3 [4] and $AlCl_3$ [10], the measured neutron structure factor of molten $FeCl_3$ shows coexistence of intermediate range order with chemical and topological short-range order [9].

In view of its remarkable melting mechanism and of the experimental interest in the structural properties of the melt, we extend below to iron trichloride our earlier study [6] of the ionic interactions in aluminium trichloride. The main attention is on bond lengths and bond angles in neutral and ionized molecular units as possible precursors of local structures in melts. Ionic polarizability is included by supplementing the dipoles resulting from a linear electrostatic treatment with counterbalancing dipoles arising from the overlap deformability of the electronic shells of the ions. In this respect our treatment may be viewed as an extension of the shell model in the lattice dynamics of ionic crystals [11, 12]. As emphasized in our work on $AlCl_3$ [6], this aspect is crucial in allowing the formation of a dimeric local structure with a correct description of halogen bridging and of the first-neighbour distance between metal ions.

2. THE MODEL

The potential energy U of an ionic cluster, as a function of the interionic vector distances $\mathbf{r}_{ij}$ and of the electric dipole moments $\mathbf{p}_i$ carried by the ions, is written as the sum of the charge–charge interaction energy U_{cc}, the interionic overlap repulsive energy U_r, the chlorine–chlorine van der Waals energy U_W and the chlorine polarization terms associated with charge-dipole interactions (U_{cd}), dipole–dipole interactions (U_{dd}) and overlap-deformability (U_{sm}).

The specific expressions for these various terms are as follows:

$$U_{cc} = \frac{1}{2}e^2 \sum_{i \neq j} \frac{Z_i Z_j}{r_{ij}} \tag{2.1}$$

with Z_i the conventional integral ionic valences;

$$U_r = \sum_{i \neq j} \Phi_{ij}(r_{ij}) \tag{2.2}$$

with the function $\Phi_{ij}(r)$ written in the form proposed by Busing [13]

$$\Phi_{ij}(r) = f(\rho_i + \rho_j) \exp\left[(R_i + R_j - r)/(\rho_i + \rho_j)\right] \tag{2.3}$$

in terms of ionic radii R_i and ionic shell-stiffness parameters ρ_i, with $f = 0.05\ e^2/\text{Å}^2$;

$$U_W = -\frac{1}{2}\sum_{i \neq j} \frac{C_i C_j}{r_{ij}^6}, \tag{2.4}$$

with the double sum running over the chlorines only;

$$U_{cd} = -\sum_{i \neq j} Z_i e \frac{\mathbf{p}_j \cdot \mathbf{r}_{ij}}{r_{ij}^3} \tag{2.5}$$

with the sum over j running over the chlorines only;

$$U_{dd} = \frac{1}{2}\sum_{i \neq j} \left[\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}^3} - 3\frac{(\mathbf{p}_i \cdot \mathbf{r}_{ij})(\mathbf{p}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right] + \frac{1}{2\alpha}\sum_j p_j^2, \tag{2.6}$$

with α the polarizability of Cl^- and all sums running over the chlorines only; and

$$U_{sm} = \frac{Y}{\alpha K}\sum_{i,j} \frac{\mathbf{p}_j \cdot \mathbf{r}_{ij}}{r_{ij}} \left| \frac{d\Phi_{ij}(r_{ij})}{dr_{ij}} \right|, \tag{2.7}$$

the sum over i being restricted to the metal ions and that over j to the chlorines. The quantities Y and K in eqn (2.7) are shell-model parameters. The inclusion of point-ion polarizability for the trivalent metal ion will be briefly discussed in section 3.1 below.

Minimization of U with respect to each dipole yields its equilibrium value in an arbitrary configuration of the cluster as the sum of a point-ion term proportional to the local electric field and to a counteracting dipole due to the overlap of the valence electron shell of the chlorine with the neighbouring metal ions. Each contribution to the overlap dipole on a chlorine is directed along a Fe-Cl bond and points towards the metal ion.

The potential energy function of a cluster is handled by a computer programme which is designed to perform two basic functions, namely (i) the optimization of a given starting configuration of the cluster by minimization of its energy towards states of static (stable or unstable) equilibrium and (ii) the study of static and dynamic deformations of the cluster for the evaluation of its vibrational frequencies and of its dynamical evolution at constant total energy. A description of the static and dynamic algorithms used in the programme can be found in ref. [6].

3. MODEL PARAMETERS AND STRUCTURE OF THE MONOMER AND DIMER

The expressions for the energy terms reported in eqns (2.1)–(2.7) involve seven parameters. For a first assessment we may use the approximate transferability of their values between similarly bonded salts to adopt for the five parameters involving the chlorine ion in $FeCl_3$ (R_{Cl}, ρ_{Cl}, C_{Cl}, α and Y/K) the values determined in the study of Wang Li and Tosi [14] on $(AlCl_4)^-$, thus keeping R_{Fe} and ρ_{Fe} as the only disposable parameters for iron trichloride. In fact, the fitting of a single relevant bond length suffices for an assessment of both these parameters, owing to the approximate proportionality between the radius and the stiffness parameter for polyvalent metal ions in the Busing potential which was demonstrated by Wang Li and Tosi [14].

The first row in Table I, marked model M_1, shows the values of the parameters that we have obtained in the above way for iron trichloride by fitting the measured value of the Fe-Cl bond length in the $FeCl_3$ monomer, $r_{Fe\text{-}Cl} = 2.14$ Å [15]. The equilibrium shape of the monomer is correctly found to be an equilateral triangle of chlorines with the iron at its centre (D_{3h} symmetry).

The results obtained with model M_1 for the bond lengths and bond angles of the Fe_2Cl_6 dimer in the D_{2h} configuration (two tetrahedra sharing an edge formed by two bridging chlorines, as in the aluminium trihalide dimers) are reported in the first row of Table II. Comparison with the measured values of these structural quantities, as obtained by

TABLE I Interionic force parameters (M denotes Fe^{3+} and X denotes Cl^-)

	f $(e^2/Å^2)$	R_M (Å)	ρ_M (Å)	R_X (Å)	ρ_X (Å)	C_X $(eÅ^{5/2})$	α $(Å^3)$	Y/K $(Å^3/e)$
M_1	0.05	1.1	0.048	1.71	0.238	5.5	3.0	0.83
M_2	0.05	1.10	0.0476	1.71	0.238	5.5	2.82	0.66

electron diffraction on the vapour phase [16] and reported in the third row of Table II, shows quite good agreement with the data, even though no parameter of the model has as yet been adjusted to properties of the dimer.

Relatively minor adjustments of the model parameters are therefore sufficient to reproduce with very good accuracy the structural data on the Fe_2Cl_6 dimer. We have put main attention on the details of the chlorine bridge and the iron – iron distance, which are very sensitive to the details of the chlorine polarization. These adjustments lead to model M_2, with values of the parameters as shown in the second row of Table I and structural predictions on the dimer in the D_{2h} configuration as shown in the second row of Table II.

Within the M_2 model the value of the energy needed to break the dimer into its atomic constituents in the ionized state is found to be 103.0 eV. Correspondingly the binding energy of the monomer (still in the D_{3h} symmetry at equilibrium, with a Fe-Cl bond length of 2.14 Å) is 50.6 eV. The dissociation of the dimer into two neutral monomers is thus estimated to require about 1.8 eV. This estimate appears to be consistent with the fact that in the vapour at thermal equilibrium the dominant species shifts from dimeric below 600 K to monomeric above 600 K.

An *ab initio* molecular orbital study of the Fe_2Cl_6 molecule at the Hartree-Fock level, carried out by Scholz and Curtiss [17], has yielded the D_{2h} symmetry for the equilibrium structure with a $^{11}B_{3u}$ electronic ground state, which is a high-spin state with five unpaired *d*-electrons on each iron atom. The effective charge on the iron, as obtained from Mulliken's population analysis, ranges from about +2 to about +1 depending on the choice of the basis set of wave functions. The fourth row in Table II reports the optimized structural parameters of the

TABLE II Equilibrium structural parameters of Fe_2Cl_6 in the D_{2h} configuration (bond lengths in Å, bond angles in degrees). The notations Cl^B and Cl^T denote bridging and terminal chlorines, respectively

	$Fe\text{-}Cl^B$	$Fe\text{-}Cl^T$	Fe-Fe	$Cl^B\text{-}Cl^B$	$Cl^T\text{-}Cl^T$	$Cl^B\text{-}\widehat{Fe}\text{-}Cl^B$	$Cl^T\text{-}\widehat{Fe}\text{-}Cl^T$
M_1	2.35	2.18	3.23	3.40	3.77	92.9	120.0
M_2	2.32	2.15	3.20	3.37	3.72	93.0	120.1
Expt[16]	2.326	2.127	3.20	3.372	3.723	92.9	122.1
QCC[17]	2.397	2.207	3.226	3.224	3.880	84.6	123.1

Fe_2Cl_6 molecule as obtained in these calculations with the STO-3G basis set.

In parallel with other *ab initio* calculations of Scholz and Curtiss [17] we have evaluated other structures for the Fe_2Cl_6 molecule within the M_2 model. These are a D_{2h} planar structure with two bridging chlorines and two C_s structures with either one or three bridging chlorines. We have found that all these structures correspond to extrema in the potential energy function, but are mechanically unstable against deformation since some of their vibrational modes have imaginary frequency. These results are in accord with those of the quantum chemical calculations.

All the calculations to be reported below will be based on the M_2 model, except where explicitly noted. We stress again that this model is adjusted to the structural data on the neutral monomer and dimer of iron trichloride.

3.1. The role of the metal ion polarizability

As noted above, the $FeCl_3$ monomer is a planar molecule in the shape of an equilateral triangle of chlorines with the iron at its centre. However, for other trihalides such as, for example $SbCl_3$ the equilibrium shape of the monomer is a trigonal pyramid with the metal ion at its apex.

Within the present model such a distortion of the monomer is stabilized if the polarizability of the metal ion is sufficiently large, from the gain in polarization energy which ensues from a finite electric field acting on the metal ion in an out-of-plane position. We have tested this possibility by attributing to Fe^{3+} a finite polarizability as a variable parameter while keeping constant all the other parameters of the model. We find in this case that the trivalent metal ion starts taking an out-of-plane equilibrium position as its polarizability approaches a value of about 1 Å^3.

While the polarizability of Fe^{3+} does not seem to be precisely known, a value of order 0.1 – 0.2 Å^3 would seem reasonable by analogy with other trivalent positive ions. For such values the planar shape of the monomer is definitely stable. We have also checked that with this choice the structural parameters of the dimer are almost unchanged relative to the values shown for model M_2 in Table II above.

4. STRUCTURE OF CHARGED CLUSTERS

In view of the structural similarities between iron and aluminium trichloride that emerge from the above discussion of the neutral monomer and dimer, it is not surprising that similarities are also found for charge-carrying clusters in these two systems. Thus, a number of the results reported in this section on the structure of charged clusters for the former system closely parallel our earlier findings on the latter [6].

4.1. Structure and binding energy of $(FeCl_4)^-$ and $(FeCl_2)^+$

The $(FeCl_4)^-$ cluster is found to have tetrahedral shape with a Fe-Cl bond length of 2.22 Å. We also find that $(FeCl_2)^+$ has linear shape with a Fe-Cl bond length of 2.065 Å. From the binding energies of these two clusters we estimate an activation energy of 9.2 eV for the dissociation reaction $FeCl_3 \rightarrow (FeCl_2)^+ + Cl^-$ and an activation energy of 7.6 eV for the dissociation reaction $Fe_2Cl_6 \rightarrow (FeCl_4)^- + (FeCl_2)^+$. Thus, both the monomer and the dimer are strongly stable against dissociation into charge-carrying species.

4.2. Structure and binding energy of $(Fe_2Cl_7)^-$

As for the $(Al_2Cl_7)^-$ anion, we find a very complex potential-energy landscape for the $(Fe_2Cl_7)^-$ cluster. Its low-energy structures are formed by two $FeCl_4$ tetrahedra sharing a chlorine in a bent configuration. Four such corner-bridged structures, which essentially differ only for internal rotations giving different relative orientations to the two triplets of terminal chlorines, are reported in Table III. The C_s and C_{2v} configurations have a 'staggered' and an 'eclipsed' arrangement of the two $FeCl_3$ groups, respectively. The C_2 and C'_{2v}

TABLE III Theoretical results for corner-bridged structures of $(Fe_2Cl_7)^-$ (bond lengths in Å, bond angles in degrees). The ranges of values shown for bond lengths and bond angles span those appropriate to inequivalent terminal chlorines

	$Fe\text{-}Cl^B$	$Fe\text{-}Cl^T$	$Fe\text{-}Fe$	$Fe\text{-}\widehat{Cl^B}\text{-}Fe$	$Cl^T\text{-}\widehat{Fe}\text{-}Cl^B$
C_2	2.37	2.18–2.20	3.76	105	97–109
C_s	2.35–2.38	2.17–2.19	3.78	106	94–110
C_{2v}	2.37	2.18–2.20	3.87	109	96–110
C'_{2v}	2.38	2.17–2.19	4.03	116	100–117

configurations are obtained from the C_{2v} one by rotations of the two $FeCl_3$ groups around the Fe-Cl^B bonds in opposite directions, by 30° and by 180° respectively.

The C_2 configuration is found in our calculations to lie at the lowest energy (−106.19 eV relative to separated ions) and to be mechanically stable. The C_s configuration is almost degenerate in energy with the C_2 one, but one of its vibrational modes has imaginary frequency. The C_{2v} and C'_{2v} structures lie at still higher energies and are both mechanically unstable against small deformations leading them into the C_2 structure. Therefore, all the other corner-bridged structures correspond to a multiplicity of saddle points separating several equivalent energy minima for the molecular ion in the equilibrium C_2 structure. These results for the $(Fe_2Cl_7)^-$ cluster agree with our earlier results [6] for the $(Al_2Cl_7)^-$ one, which were in turn consistent with those obtained from *ab initio* [18] and semiempirical [19] molecular orbital calculations.

4.3. Structure and binding energy of $(Fe_2Cl_5)^+$ and $(Al_2Cl_5)^+$

We have found two mechanically stable configurations for the $(Fe_2Cl_5)^+$ cluster, corresponding to two separate minima in the potential-energy landscape for this molecular ion. A symmetric configuration with three bridging chlorines, formed by two $FeCl_4$ tetrahedra sharing a face, has lowest energy (−95.4 eV relative to separated ions). Its structural parameters are given in Table IV. An asymmetric double-bridged configuration, as already reported in our earlier calculations on the $(Al_2Cl_5)^+$ cluster, lies higher in energy by 0.8 eV.

The triple-bridged configuration is also more stable for $(Al_2Cl_5)^+$, at an energy of −94.6 eV relative to separated ions. Its calculated structure is also reported in Table IV. The double-bridged configuration is higher in energy by 0.6 eV.

From the above results we find that the energy required for the ionization reaction $2(Fe_2Cl_6) \rightarrow (Fe_2Cl_7)^- + (Fe_2Cl_5)^+$ is 4.4 eV *in vacuo*, when both ionized species are in their equilibrium lowest-energy configuration. The activation energy required by the same ionization reaction for the Al_2Cl_6 dimer *in vacuo* is is 4.7 eV. The doubly-bridged configuration of the $(M_2Cl_5)^+$ cluster should nevertheless be expected

TABLE IV Equilibrium bond lengths in $(Fe_2Cl_5)^+$ and $(Al_2Cl_5)^+$ (in Å)

	M-Cl^B	M-Cl^T	M-M
M = Fe	2.31	2.10	2.76
M = Al	2.25	2.01	2.78

to be the relevant one for ionic fluctuations associated with anion transfer between neighbouring dimers in the molten state. Our earlier conclusion that such a fluctuation is a rare event is therefore confirmed for $AlCl_3$ and extended to $FeCl_3$.

5. VIBRATIONAL FREQUENCIES OF IONIC CLUSTERS

Model M_2 has been used to evaluate the vibrational frequencies for all the ionic clusters treated in the preceding sections. Following our earlier discussion of the vibrational spectra of the Al-based clusters [6] and that given by Manteghetti and Potier [20] for the $(Al_2Cl_7)^-$ cluster, the vibrational modes can be classified under the two main types of bond stretching and bond bending. This allows one to correlate the mode frequencies across the whole series of clusters starting from the bond stretching (v_3 and v_1) and bond bending (v_2 and v_4) modes of the basic $(FeCl_4)^-$tetrahedron.

At the quantitative level our results for the vibrational frequencies of the neutral monomer and dimer can be tested against experimental data from infrared and Raman spectroscopy on these molecules in the vapour phase or when trapped inside an inert matrix [21–24]. These comparisons show that (as was also the case for the Al-based clusters [6]) the present model tends to overestimate somewhat the stiffness of the Fe-based clusters under stretching, but yields very reasonable agreement with the available evidence on the bond-bending modes. Since the latter lie generally in the low frequency region below 200 cm^{-1}, one may expect that all relevant structural fluctuations in $FeCl_3$-based melts would be well accounted for.

6. CONCLUDING REMARKS

In this work we have determined a classical model of ionic interactions for $FeCl_3$-based ionic clusters. A number of structural similarities have emerged between these clusters and the $AlCl_3$-based ones. A dilation of the metal-chlorine bond length in the basic MCl_4 tetrahedral group by about 0.07 Å in going from Al to Fe seems to be the primary structural difference between the two classes of systems. On these grounds we expect the $FeCl_3$-based melts to be similar in their structural behaviour to the $AlCl_3$-based melts. Structural fluctuations in the pure $FeCl_3$ melt may nevertheless be more conspicuous, in view of the somewhat higher melting temperature.

The present model should find useful applications in classical simulation studies of the iron trichloride melt and of its mixtures with molten chlorides. The ionic interactions in these dense phases will have to be constructed from the pair potentials that we have proposed and from the electric fields generated by the individual ions. Hence, the model should be sufficiently flexible to allow for structural fluctuations and rearrangements of local structures up to their dissolution when energetically favourable.

To test this flexibility away from the state of tetrahedral coordination for the trivalent iron ion which has been the common feature of all the structures evaluated in the present work, we have extended our analysis to states of sixfold coordination by studying $(FeCl_6)^{3-}$ clusters within the M_2 model. We find a mechanically stable equilibrium configuration having octahedral symmetry for this cluster, with a Fe-Cl bond length of 2.47 Å and six distinct vibrational frequencies ranging from 90 to 280 cm^{-1}. The other relevant sixfold coordination for trivalent metal ions in their chloride compounds is that exemplified by the UCl_3-type crystal structure, in which the metal ion is surrounded by six chlorines lying at the corners of a trigonal prism [2]. Such a type of configuration we find to be mechanically unstable for the isolated $(FeCl_6)^{3-}$ cluster, but will presumably be stabilized in dense phases by charge compensation due to other metal ions and possibly by secondary metal-chlorine bonds between neighbouring clusters.

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