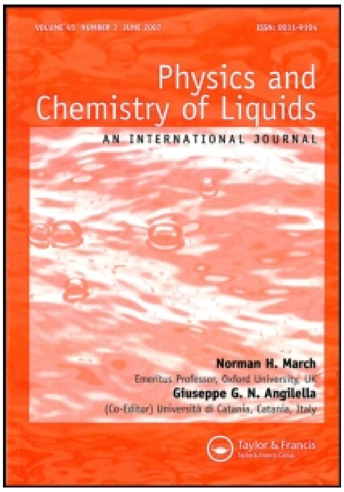
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Molecular clusters in gaseous and liquid $AlCl_3$

Z. Akdeniz[a]; Z. Çiçek Önem[a]; R. Ruberto[b]; G. Pastore[cd]; M. P. Tosi[e]
[a] Physics Department, Istanbul University, Turkey [b] CNISM and Dipartimento di Fisica dell'Università, Italy [c] CNR-INFM DEMOCRITOS National Simulation Center, I-34100 Trieste, Italy [d] Dipartimento di Fisica Teorica dell'Università, I-34100 Trieste, Italy [e] NEST-CNR-INFM, Scuola Normale Superiore, I-56126 Pisa, Italy

To cite this Article Akdeniz, Z. , Önem, Z. Çiçek , Ruberto, R. , Pastore, G. and Tosi, M. P.(2008) 'Molecular clusters in gaseous and liquid $AlCl_3$', Physics and Chemistry of Liquids, 46: 1, 1 — 8
To link to this Article: DOI: 10.1080/00319100701658332
URL: http://dx.doi.org/10.1080/00319100701658332

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Physics and Chemistry of Liquids
Vol. 46, No. 1, February 2008, 1–8

Molecular clusters in gaseous and liquid $AlCl_3$

Z. AKDENIZ†, Z. ÇIÇEK ÖNEM†, R. RUBERTO‡,
G. PASTORE*§¶ and M.P. TOSI⊥

†Physics Department, Istanbul University, 34118 Vezneciler-Istanbul, Turkey
‡CNISM and Dipartimento di Fisica dell'Università, I-98166 Messina, Italy
§CNR-INFM DEMOCRITOS National Simulation Center, I-34100 Trieste, Italy
¶Dipartimento di Fisica Teorica dell'Università, I-34100 Trieste, Italy
⊥NEST-CNR-INFM, Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy

(*Received 5 June 2007; in final form 1 September 2007*)

Motivated by results on molecular clusters formed from octahedral connectivity in NbF_5 and by simulation and neutron diffraction studies of liquid $AlCl_3$ and related materials, we discuss the gaseous n-mers of $AlCl_3$ built from corner-sharing or edge-sharing tetrahedra. We use an interionic force-law model to evaluate the energetics of these clusters and examine their relevance to liquid structure near freezing and at higher temperatures as determined by means of classical molecular-dynamics simulation.

Keywords: Molecular clusters; Liquid structure from model simulations; Molten salts

1. Introduction

It is well established experimentally [1,2] that polymerization equilibria involving monomers, dimers and trimers operate in vapours of NbF_5 and other pentafluorides to make the structure of these vapours strongly dependent on thermodynamic conditions. The $(NbF_5)_2$ dimer is formed from two edge-sharing octahedra, while the $(NbF_5)_3$ trimer as reported in the literature from electron diffraction studies [1] is a ring formed by three corner-sharing octahedra (see left panel in figure 1). A recent calculation [3] based on an interionic force-law model adapted to some measured properties of MF_5 monomers (with $M = Nb$, Ta, V. Sb and Mo) has reproduced these isolated n-mer states and has also found a chain trimer consisting of two terminal octahedra that are connected by edge sharing to a 7-fold-co-ordinated unit (see right panel in figure 1). Seven-fold co-ordination of a pentavalent atom may be unfavourable on quantum chemistry grounds, but the two double-halogen bonds replacing three single-halogen bonds contribute to enhance the binding energy of the chain trimer. As a result, the ring and chain forms of the $(MF_5)_3$ cluster shown in figure 1 appear from these calculations to have approximately similar binding energies, within a few tenths of an eV.

---

*Corresponding author. Email: pastore@ts.infn.it

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100701658332

The present work aims at examining the stability of dimers and higher clusters arising from the connectivity of tetrahedral units. The specific compound that we focus upon is $AlCl_3$, a material that has drawn much attention in the literature from its most unusual melting behaviour. It was first proposed in an X-ray diffraction study [4] that $AlCl_3$ melts from an ionic layer structure into a molecular liquid of dimers. The $(AlCl_3)_2$ dimer has the shape of two edge-sharing tetrahedra. Thus crystalline $AlCl_3$ at melting undergoes a collective structural transition in which the co-ordination of each Al atom changes from 6-fold to 4-fold [5,6]. Neutron diffraction studies of liquid $AlCl_3$ and related materials near freezing ($AlBr_3$, $GaBr_3$ and GaI_3) have confirmed the 4-fold co-ordination of the trivalent metal ions [7,8]. Recent theoretical studies using both *ab-initio* methods [9,10] and interionic force-law models [11,12] have yielded results in broad agreement with the observed structure of these liquids near freezing as observed in the diffraction experiments. Some further observations should be mentioned at this point: (i) a temperature-dependent equilibrium between dimers and monomers has been reported from both Raman scattering and electron diffraction experiments in dilute vapours of $AlCl_3$ [13,14]; and (ii) polymeric complex anions from corner-sharing tetrahedra are well known in liquid chloro- and bromo-aluminates [15].

The plan of this article is briefly as follows. In section 2 we evaluate the structure and the energetics of the two series of ring and chain clusters built, respectively from corner sharing and from edge sharing tetrahedra, using an interionic force-law model. In section 3 we report results on the average distribution of clusters from classical molecular-dynamics simulations of liquid $AlCl_3$, showing how the equilibrium populations of dimers, monomers and chain trimers depend on some important details of the model and on temperature. Section 4 concludes the article with a summary and some discussion of further perspectives.

2. Isolated ring and chain clusters in $AlCl_3$

The calculations that we report in this section are based on an interionic force model proposed by two of us [16] for neutral and ionized clusters that are relevant to molten chloroaluminates. The model accounts for the deformability of the ions through the use of effective ionic valences and of electrical and overlap polarizabilities, and its parameters are adjusted to the bond length in the $(AlCl_4)^-$ molecular ion and to an

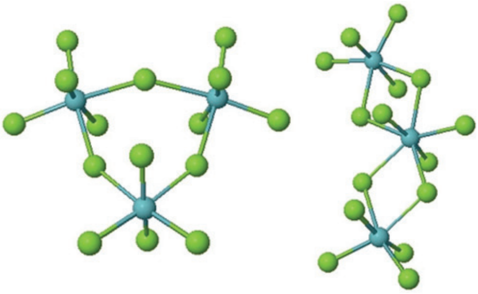


Figure 1. The ring trimer (left) and chain trimer (right) in gaseous NbF_5 and other fluorides of pentavalent elements.

Al–Cl bond length and a vibrational frequency of the $(AlCl_3)_2$ dimer. The results of the model for various other bond lengths and for the relative energies of various clusters are in close agreement with those obtained by means of first-principles calculations carried out in a density-functional approach involving a local-density approximation supplemented by gradient corrections [16].

The ground state of the dimer in the model has the well-known shape formed by two edge-sharing tetrahedra (see left panel in figure 2), with values of 228 and 206 pm for the Al–bonding-Cl and the Al–terminal-Cl bond length respectively, and its energy will be taken as the zero of reference for the following discussion of the energetics of other clusters. Breakage of one chlorine bond yields a cluster formed by a tetrahedron and a trigonal monomer sharing a corner (see right panel in figure 2). This structure is, however, mechanically unstable: i.e., the net force on each nucleus vanishes but the cluster lies at a saddle point in the potential energy landscape where one of its vibrational modes has an imaginary frequency. This saddle point lies at $75\,\mathrm{kJ\,mol^{-1}}$ above the double-bonded ground state. This result is in excellent agreement with first-principles calculations by East and Hafner [10], who report the same saddle-point structure at $73\,\mathrm{kJ\,mol^{-1}}$ above the ground state of the dimer. Also, there is very good quantitative agreement between the internal Al–Cl bond lengths in the saddle-point structure (214 and 254 pm in our model calculations, against 216 and 275 pm in the first-principles calculations of East and Hafner [10]).

The higher $(AlCl_3)_n$ polymers form two series depending on whether the Al-centered units are connected *via* double-chlorine bonds or single chlorine bonds (mixtures of these bond types are also conceivable, of course). Their structures are illustrated for n up to six in figures 3 and 4, respectively. Starting with the chain trimer in the top-left panel of figure 3, it consists of two terminal tetrahedra bound *via* edge sharing to a 5-fold-co-ordinated unit. The higher polymers in this series merely involve an increasing number of such 5-fold internal units. The ring trimer in the top-left panel of figure 4, on the other hand, consists of three corner-sharing tetrahedra and the higher members of this series merely involve an increasing number of such tetrahedral units. Each of these structures lies at a minimum in the potential energy landscape of each cluster, i.e. all their vibrational-mode frequencies are real. In our exploration of the potential energy landscapes we have also met various mechanically unstable structures, which often differ from the corresponding stable structures merely by rotations of terminal chlorine groups.

Turning to the energetics of the clusters shown in figures 3 and 4, we find that the chain trimer lies at a deeper minimum that the ring trimer by some $36\,\mathrm{kJ\,mol^{-1}}$ (i.e. 0.38 eV). The excess binding of the chain trimer is evidently associated with the presence of two double-chlorine bonds *in lieu* of three single chlorine bonds: however, bearing in mind that the excess binding is only 0.36% of the total binding energy of the trimer relative to separated ions, and that the central 5-fold structure that may be

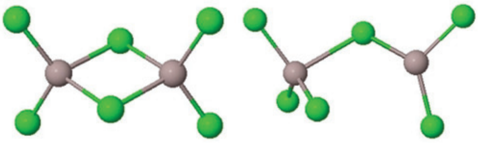


Figure 2. Illustrating the ground-state (left) and a saddle-point state (right) of the Al_2Cl_6 cluster.

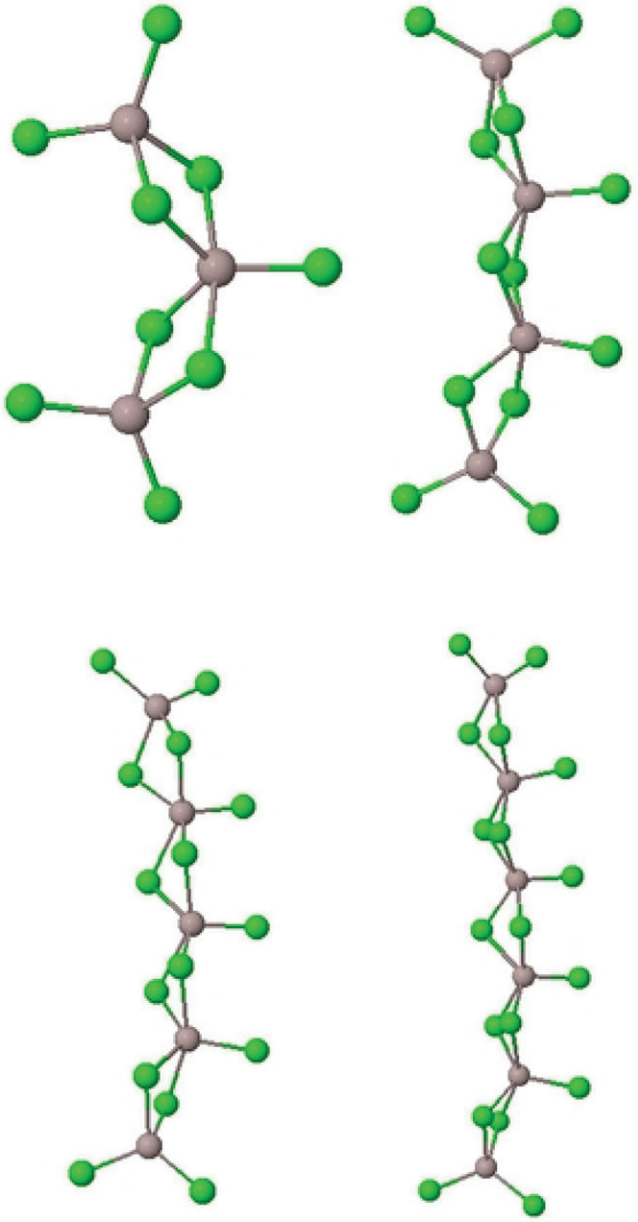


Figure 3. Illustrating the series of chain polymers for the $(AlCl_3)_n$ clusters, with n in the range from 3 to 6 (top left to bottom right).

unfavoured by quantum-chemical effects only approximately accounted for the model; the above value for the energy difference between the two forms of the isolated trimer should be regarded as being only an estimate. If we take the calculated binding energies of all clusters at their face value, then we find that the difference in binding energy between the two forms of each n-mer decreases with increasing n and indeed the ring n-mer becomes more strongly bound at $n = 6$.

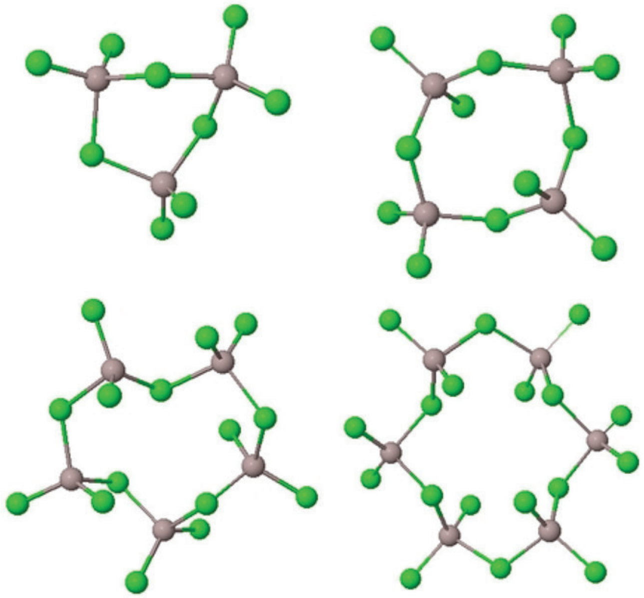


Figure 4. Illustrating the series of ring polymers for the $(AlCl_3)_n$ clusters, with n in the range from 3 to 6 (top left to bottom right).

It remains for us to compare these binding energies with those of separated monomers and dimers. Our calculations indicate that there is a preference for each isolated n-mer (with $n \geq 3$) to break into isolated dimers. For instance, for the chain clusters the decomposition reactions *in vacuo* read as follows:

$$\left\{ \begin{array}{l} (AlCl_3)_3 \rightarrow \frac{3}{2}(AlCl_3)_2 + 0.02\,\mathrm{eV} \\ (AlCl_3)_3 \rightarrow (AlCl_3)_2 + AlCl_3 - 0.40\,\mathrm{eV} \\ (AlCl_3)_4 \rightarrow 2(AlCl_3)_2 + 0.23\,\mathrm{eV} \\ (AlCl_3)_5 \rightarrow \frac{5}{2}(AlCl_3)_2 + 0.50\,\mathrm{eV} \\ (AlCl_3)_6 \rightarrow 3(AlCl_3)_2 + 0.98\,\mathrm{eV} \end{array} \right. . \tag{1}$$

A positive sign in front of the energy term in the right-hand side of these equations denotes that energy is released in breaking the higher cluster. Indeed, to our knowledge no report has been given in the literature of n-mers higher than dimers in $AlCl_3$ vapours. The chain trimer is found to be energetically almost stable against breakage into dimers, but in this case entropy terms will favour the dissociated state at finite temperature. We again see from equation (1) that the dimer is energetically quite stable against breakage into monomers.

3. Clusters in liquid $AlCl_3$

We turn to discuss the population of clusters in liquid $AlCl_3$ as a function of temperature, on the basis of data from microcanonical simulation runs using the classical molecular-dynamics method previously developed and described in detail in the work of Goat *et al.* [11]. In these runs, we allow for thermal expansion by means of the temperature-dependent density reported by Janz [17], extrapolating it beyond its reported range of validity ($462\,\mathrm{K} < T < 569\,\mathrm{K}$) up to 673 K. The data take the form of histograms reporting the relative number of various ion groups as a function of the number of ions composing them, as collected during the evolution of the sample after equilibration and averaged over the whole run.

We give first in figure 5 the results that we obtain by means of the same effective-charge interionic-force model that we have used in the calculations reported in section 2, except that we have introduced a saturation factor in the van der Waals interactions between the halogens in order to prevent system collapse arising in close ion-ion collisions from an imbalance between sixth-inverse-power attractions and exponential overlap repulsions [12]. It is evident from figure 5 that within this model there is an absolute predominance of dimers in the liquid near freezing (bottom panel) and that these dimers progressively break up into recognizably single monomers as the temperature of the liquid is raised. The message from these results thus parallels the observed behaviour of the vapours of $AlCl_3$ that we have recalled in section 1, except that in figure 5 some trimers also appear with increasing temperature in the relatively dense liquid. These trimers are of the chain type, and should be viewed as formed by the attachment of a monomer to a dimer (see again the top-left panel in figure 3).

The cluster population, however, is also strongly dependent on the details of the interionic force model. We have repeated the simulation runs with an interionic-force

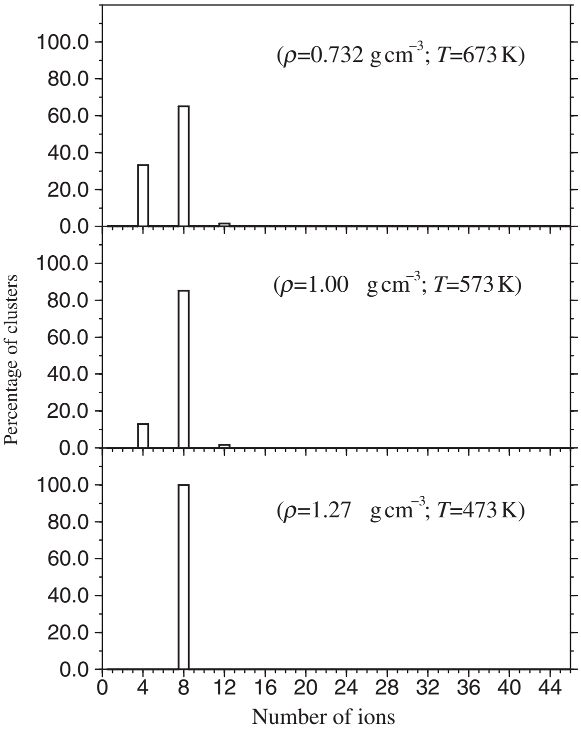


Figure 5. Histograms giving the population of various ion groups in liquid $AlCl_3$ at the indicated temperature and density, from classical simulations using the effective-charge model leading to figures 2–4.

model that adopts nominal rather than effective ionic charges, as again adjusted to properties of monomer and dimer [18], and the results for the cluster population are shown in figure 6. This model, which was shown elsewhere [12] to yield good quantitative agreement with the results of neutron and X-ray diffraction experiments on the liquid structure of $AlCl_3$ and related materials near freezing, generally enhances the cohesion of the clusters. It predicts that higher clusters can be present in the structure of the liquid near freezing (bottom panel in figure 6), these clusters being again of the chain type and thus to be envisaged as dimer–dimer or dimer–monomer structures. Increases in temperature lead to progressive dissolution of the higher clusters in favour of dimers and chain trimers and ultimately establish an equilibrium between dimers and monomers.

4. Summary and future perspectives

In summary, we have evaluated the structure and the energetics of the isolated clusters that may be of interest in relation to gaseous and liquid $AlCl_3$ and we have found that the most relevant ones in practice, besides the Al_2Cl_6 dimer, are the $AlCl_3$ monomer and the Al_3Cl_9 chain trimer. Breakage of the dimer into monomers may require an activation energy E approaching a value of 1 eV, and a monomer–dimer equilibrium may start being established at temperatures of order $T \approx 600\,K$ corresponding to

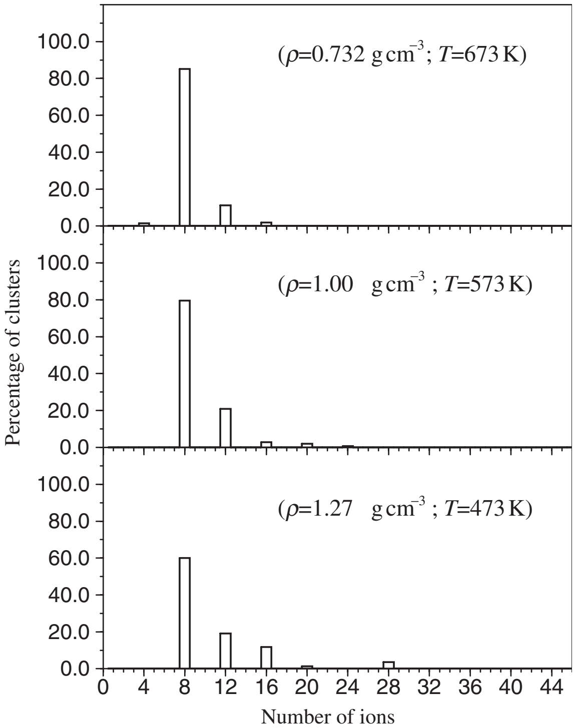


Figure 6. Histograms giving the population of various ion groups in liquid $AlCl_3$ at the indicated temperature and density, from classical simulations using a nominal-charge model.

$k_BT \approx E/20$. A ratio of order 20 between a characteristic binding energy and a characteristic thermal energy is typical of thermally activated defect excitation processes in classical systems [5]. The chain trimer, which can be viewed as formed by attaching a monomer to a dimer in a linear (bent) configuration, may be energetically competitive with the dimer and may be present in the relatively dense liquid phase in suitable thermodynamic conditions. Although these conclusions follow from our calculations on models of $AlCl_3$, we have evidence that they also apply to related materials such as $AlBr_3$, $GaBr_3$ and GaI_3, with the onset of the monomer–dimer equilibrium being shifted downwards towards the standard freezing point in the latter liquid material.

As already discussed elsewhere [11,12], the main fault of the present pseudoclassical models is their inaccuracy in the prediction of the pressure of the system at given temperature and density. This fault implies errors of order 1 GPa and may have relevant consequences in determining the difference in the scenarios that we have found with different models for the cluster population in the liquid. Work is in progress to obtain control of the equation of state of these materials and to extend our studies to other thermodynamic states in which the breakage of dimers may be followed by further breakage into fully ionized states.

Acknowledgements

Z.A. and M.P.T. thank Professor V. E. Kratsov and the Condensed Matter and Statistical Physics Section of the Abdus Salam International Center for Theoretical Physics in Trieste for their hospitality. Z.A. acknowledges support from the Research Fund of Istanbul University under Project Number UDP-1220/13062007. Z.A. and Z.Ö.Ç. also acknowledge support from the Turkish Scientific and Technological Research Council (TUBITAK).

References

[1] M. Hargittai. *Chem. Rev.*, **100**, 2233 (2000).
[2] S. Boghosian, E.A. Pavlatou, G. Papatheodorou. *Vibr. Spectr.*, **37**, 133 (2005).
[3] Z. Çiçek Önem, Z. Akdeniz, M.P. Tosi. *Z. Naturforsch. A*, In press.
[4] R.L. Harris, R.E. Wood, H.L. Ritter. *J. Amer. Chem. Soc.*, **73**, 3150 (1951).
[5] N.H. March, M.P. Tosi. *Phys. Chem. Liq.*, **10**, 39 (1980).
[6] M.P. Tosi, D.L. Price, M.-L. Saboungi. *Ann. Rev. Phys. Chem.*, **44**, 173 (1998).
[7] Y.S. Badyal, D.A. Allen, R.A. Howe. *J. Phys. Condens. Matter.*, **6**, 10193 (1994).
[8] M.-L. Saboungi, M.A. Howe, D.L. Price. *Molec. Phys.*, **79**, 847 (1993).
[9] B. Kirchner, A.P. Seitsonen, J. Hutter. *J. Phys. Chem., B*, **110**, 11475 (2006).
[10] A.L.L. East, J. Hafner. *J. Phys. Chem. B*, **111**, 5316 (2007).
[11] E. Goat, R. Ruberto, G. Pastore, Z. Akdeniz, M.P. Tosi. *Phys. Chem. Liq.*, **45**, 487 (2007).
[12] R. Ruberto, G. Pastore, Z. Akdeniz, M.P. Tosi. *Molec. Phys.*, In press.
[13] M. Blander. *Molten Salt Chemistry*, p. 664, Interscience, New York (1964).
[14] K. Aarset, Q. Shen, H. Thomassen, A.D. Richardson, K. Hedberg. *J. Phys. Chem., A*, **103**, 1644 (1999).
[15] Z. Akdeniz, M. Çaliskan, Z. Çiçek, M.P. Tosi. *Z. Naturforsch.*, **55a**, 575, and references therein (2000).
[16] Z. Akdeniz, M.P. Tosi. *Z. Naturforsch.*, **54a**, 180 (1999).
[17] G.J. Janz. *J. Phys. Chem. Ref. Data*, **17**, Suppl. No. 2 (1988).
[18] Z. Akdeniz, G. Pastore, M.P. Tosi. *N. Cimento*, **20D**, 595 (1998).