LIQUID DICHLORIDES AND DICHLORIDE-MONOCHLORIDE MIXTURES

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ABSTRACT

We give a short review of the progress done recently in the interpretation of the structure of molten divalent cation chlorides and of the stability of chloro complexes in molten salt mixtures.

INTRODUCTION

In recent years neutron scattering experiments from isotropically enriched samples have yielded a large amount of structural information on molten divalent cation chlorides, namely BaCl$_2$ (1), SrCl$_2$ (2), ZnCl$_2$ (3), CaCl$_2$ (4), MgCl$_2$, and MnCl$_2$ (5).

The experimental results show a close connection between the structural properties in the melt and the behavior of these systems in the hot solid phase, where a variety of interesting phenomena, like fast ionic conduction or glass transition are observed. Similar liquid structures are found for BaCl$_2$ and SrCl$_2$, both crystallizing in a fluorite type structure at high temperature. Like other fluorite type materials, they undergo a transition to a high conductivity phase (superionic) before melting. The increase of conductivity is related to the high concentration of anionic defects (6). The disorder of the anionic component and the crystalline order of the cations are reflected in the liquid in the high degree of short range order for the metal ions in comparison with the chlorine ions.

A very different structure is observed in liquid ZnCl$_2$, whose glass forming tendencies are well-known (7,8). MgCl$_2$ and MnCl$_2$ have some similarities with the ZnCl$_2$ structure. In the liquid phase one observes a very well defined local structure of chlorines arranged in a tetrahedral coordination around the zinc ion with a close similarity to the local structure of the glass. The existence of these tetrahedral units is confirmed by spectroscopic data (9). Moreover, the addition of excess chlorine breaks the bridging of the tetrahedral units and modes are observed related to the [ZnCl$_4$]$^{2-}$ complexes (10).

Complexes are also found in some of the molten mixtures of polyvalent cation halides and alkali halides upon addition of alkali
halide. The experiments (11) and computer simulation (12) show for instance for mixtures of AlCl₃ and alkali halides the existence of complexes in which halogen ions are coordinated in a tetrahedral configuration around the polyvalent cation. There are, however, a number of systems like CaCl₂-2LiCl, where complexes are not revealed at all. In CaCl₂-2KCl coexistence of sixfold and fourfold coordinated configurations around the calcium ions is observed (13).

For a liquid dichloride a first interpretation of the difference of the structural properties can be obtained just looking at the classification scheme of crystalline structures and molecular shapes for sp bonded AB₂ compounds (14-16). The increasing ionicity corresponds in the crystal to an increase in the coordination number and in the molecules to a transition from a linear to a bent molecule.

In this scheme SrCl₂ and BaCl₂ lie in the high ionicity limit, and ZnCl₂, MgCl₂ and MnCl₂ in the low ionicity limit. It is interesting to note that the low ionicity limit seems to favor the formation of complexes.

A more accurate analysis of the liquid structure could be attempted of course by using the statistical mechanical theories and computer simulation. We give now a short review of the progress done for some of the compounds and mixtures just mentioned.

**STRUCTURAL PROPERTIES OF MOLTEN SrCl₂**

Detailed simulation work on molten SrCl₂ has been done by de Leeuw (17) assuming a rigid ion potential. McGreevy and Mitchell (2) found a significant disagreement with their neutron scattering data. A refined liquid theory has been applied by Pastore et al. (18), and a careful analysis has been performed.

The indications, which come out, are that the rigid ionic model gives reasonable agreement with the thermodynamics of the liquid, but large discrepancies are found in the Sr-Sr pair distribution function. The main conclusions of the work of Pastore et al. can be summarized as follows:

1. The Sr-Sr correlations, which are most sensitive to the model of interionic forces, are dominant. They determine the main features of the liquid structure. Moreover, the cation short range order drives the transition to the crystal in the superionic phase (19).

2. A simple classical jellium model works in reproducing the Sr-Sr structure when the cation-cation Coulomb repulsion is screened by the electronic dielectric constant of the material. This suggests an important role of the distortions of the electronic shells in determining the correlations.
Simulation of liquid ZnCl$_2$ with a rigid ionic model has been done by Woodcock et al. (20) and most recently by Gardner and Heyes (21). This model gives a reasonable agreement with the gross features of the Zn-Cl and Cl-Cl pair correlations, but it fails completely in the prediction of the Zn-Zn structure. This means that the model is not able to reproduce one of the most important conclusions of the experimental work; the close similarity between the local structure of the liquid and the glass (3, 7, 8). As proposed by Desa et al. (8), this structure can be seen as a distorted random close packing of chlorine ions with a Cl-Cl coordination number of the order of 8-10. The Zn ions are occupying the tetrahedral holes in such a way as to maximize corner sharing of the resulting ZnCl$_4$ tetrahedra at the expense of edge or face sharing.

Theoretical work has been done by Ballone et al. (22). They examined a number of different models, starting from the simple charged hard sphere model, and then introducing non-additive excluded volume effects and an effective screening. Now the anion-anion correlations are the dominant ones, and by choosing suitable values of the non-additive ionic radii the authors are able to reproduce the local tetrahedral coordination. Finally, with the introduction of a distance dependent dielectric screening they get very reasonable results. They conclude that the Zn-Zn correlations reflect mostly the real binding forces, even if a combination of non-additivity of ionic radii and an effective $r$-dependent dielectric screening can give a reasonable account of the correlations.

STABILITY OF CHLORO COMPLEXES IN MOLTEN SALT MIXTURES

A number of experiments on molten mixtures of polyvalent cation halides and alkali halides, as said in the introduction, indicate the existence of units of halogen ions coordinated in a fourfold configuration around the polyvalent cation. For instance the existence of [AlCl$_4$]$^-$ units in molten LiCl-AlCl$_3$ has been directly established by Biggin et al. (11) by neutron scattering experiments. On the other hand in recent work with Raman spectroscopy, Sakai et al. (13) did not reveal complexes in systems like CaCl$_2$-2LiCl, CaCl$_2$-2NaCl, SrCl$_2$-2KCl and SrCl$_2$-2RbCl. As mentioned above, in CaCl$_2$-2KCl there is a coexistence of sixfold and fourfold coordination for the calcium ions.

Saboungi et al. (12) showed by computer simulation on an AlCl$_3$-NaCl mixture that an ionic model can reproduce structural features of a complexing liquid. A similar kind of approach has been developed by Akdeniz et al. (23). They applied a simple ionic model to the solutions of divalent cation chlorides (MC$_2$) in molten alkali chlorides. They evaluated the complex stability as a function of
the alkali chloride solvent and of the solute concentration. The complexes are dissociated when the solute concentration exceeds the "stoichiometric" composition 1/3, but it is also found that the stability is determined by the ionic screening length of the solution. A stability criterion is established in terms of a "critical" ratio between the screening length and the M-Cl distance. The dissociation of the complexes takes place when this ratio is less than 1.60. In the table below the values of the ratio for different MCl-alkali chloride mixtures are given. The prediction of complex forming (above the line) and non forming (below the line) are in agreement with the experiments.

|      | Li  | Na  | K   | Rb  | Cs |
|------|-----|-----|-----|-----|----|
| Be   | 1.93| 1.96| 1.99| 2.01| 2.03|
| Mg   | 1.69| 1.71| 1.74| 1.75| 1.77|
| Ca   | 1.58| 1.60| 1.62| 1.63| 1.64|
| Sr   | 1.53| 1.55| 1.57| 1.58| 1.60|
| Ba   | 1.49| 1.51| 1.53| 1.54| 1.55|

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