ORDERED IONIC LIQUIDS:
CHLOROALUMINATES AND SILICATES

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ABSTRACT
Ordering in NaCl-AlCl₃ melts leads to sharp minima in the solubility of
divalent chlorides MCl₂ (e.g., CoCl₂, FeCl₂, and NiCl₂) near the 50-50
mole % composition. The composition dependence of these solubilities
in acid melts can be described by using either the coordination cluster
theory or the solubility product principle. The magnitudes of the sol­
ubility products are largely related to the fact that the standard free
energy of formation of 2NaAlCl₄ from 2NaCl and 2AlCl₃ is consider­
ably more negative than the corresponding free energy for M(ACl₄)₂.
In basic melts, solubilities are largely related to the formation of the
associated species MCl⁺, MCl₂, MCl₃⁻, and MCl₄²⁻, which appear to
have very large formation constants.

INTRODUCTION
Molten chloroaluminates and silicates belong to a class of ordered ionic solu­
tions that have striking physicochemical properties. In this paper, we will examine
the influence of ordering on solubilities in molten chloroaluminates to explain the
very steep minima that have been observed near the most ordered composition.
These minima in solubilities (and maxima in activity coefficients in dilute solu­
tion) are predicted by physical solution theories¹-⁴ and concepts. Solubilities in
very highly ordered solutions can also be described in chemical terms⁵ that provide
clarifying insights into these phenomena.

The properties of molten chloroaluminates parallel those of silicates. For ex­
ample, addition of AlCl₃ to NaCl produces the tetrahedral AlCl₄⁻ anion in the melt.
Beyond the 50-50 (neutral) composition, the addition of AlCl₃ produces Al₂Cl₇⁻ and

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Al$_3$Cl$_{10}^-$ ions in which the aluminum pairs are connected by a bridging chloride ion to form a bent Al-Cl-Al triplet. Similar molecular ions (SiO$_{4}^{4-}$, Si$_2$O$_{6}^{6-}$, Si$_3$O$_{10}^{8-}$) are formed in silicates at silica mole fractions less than 0.43. The last two ions have bridging oxygens with Si-O-Si bridging angles analogous to those for the corresponding chloroaluminate ions. Because of the low temperatures of the liquids, there is a considerable body of very accurate data for the chloroaluminates. On the other hand, because of generally high liquidus temperatures, data for silicate melts are not as accurate. Thus, one can perform much more precise and detailed analyses of chloroaluminates than one can for the silicates, and studies of chloroaluminates, in addition to being significant in their own right, also can provide insights into the properties of silicates.

ORDERING

Because there are different types of ordering phenomena in different liquids, one needs to examine the particular liquids under study. In this section, we discuss ordering in NaCl-AlCl$_3$ mixtures to illustrate the phenomenon and its thermodynamic consequences. The most ordered composition in this binary melt is at 50-50 mole % where NaCl and AlCl$_3$ combine to form a low melting liquid, which largely contains Na$^+$ cations and AlCl$_4^-$ anions. Except for the structural complexity of the polyatomic anion, this liquid is a simple molten salt analogous to alkali halides exhibiting coulomb ordering represented in one dimension as $\ldots + - - - + - - - \ldots$. Since the tetrahedral AlCl$_4^-$ ions, which are the nearest neighbors of Na$^+$ cations, have their four chlorides on their periphery, the coulomb order leads to topological order of the next nearest neighbor sodiums and aluminums, which can be written in one dimension as $\ldots$Na-Al-Na-Al-Na-Al$\ldots$, where the order is defined in terms of repetitive Na-Al pairs in sequence. In addition, there is a chemical order related to the definitiveness of the structures of the molecular ions (AlCl$_4^-$ here and Al$_2$Cl$_7^-$ and/or Al$_3$Cl$_{10}^-$ at higher concentrations of AlCl$_3$). Addition of NaCl or AlCl$_3$ to the 50-50 mixture decreases the topological order by decreasing the range of repetition of the Na-Al pairs by the substitution of Cl$^-$ or Al$_2$Cl$_7^-$ ions for AlCl$_4^-$ ions in the ordered array.

Such solutions cannot be perfectly ordered and one must consider the degree of disorder. One measure of disorder is the extent of disproportionation of the AlCl$_4^-$ anions according to the reaction

$$2\text{AlCl}_4^- \rightleftharpoons \text{Cl}^- + \text{Al}_2\text{Cl}_7^- \quad (1)$$

with a disproportionation constant, $K_D$, of $1.06 \times 10^{-7}$ at 175°C. When one considers that a number of Na$^+$ cations are next nearest neighbors to any one Al
in $\text{AlCl}_4^{-}$ or $\text{Al}_2\text{Cl}_7^{-}$ and are nearest neighbors to $\text{Cl}^-$, disproportionation can be re-expressed in terms of the disordering reaction

$$2\text{Na} - \text{Al} \rightleftharpoons \text{Na} - \text{Na} + \text{Al} - \text{Al}$$

(2)

The very small value of $K_D$ indicates very little disorder (i.e., the melt is highly ordered). By this measure, the organic chloroaluminates (e.g., methylethylimidazolium tetrachloroaluminate) are considerably more ordered than NaAlCl$_4$. This order is dramatically reflected in the thermodynamic properties of the binary NaCl-AlCl$_3$ solutions shown in Figure 1, in which are plotted $\text{FE}/\text{RT}$, $\ln a_{\text{NaCl}}$, and $\ln a_{\text{AlCl}_3}$ versus the mole fraction of AlCl$_3$. The activities of the two components, $a_{\text{NaCl}}$ and $a_{\text{AlCl}_3}$, were deduced from the electromotive force measurements of Boxall and Osteryoung (plotted as $\text{FE}/\text{RT}$) for the concentration cell $\text{Al|NaCl-AlCl}_3||\text{NaCl(saturated)} - \text{AlCl}_3|\text{Al}$. The activities are plotted for the solids as the standard states. The salient feature of this plot is the extremely steep change in the activities at the 50-50 composition. This steepness is related to the disproportionation constant ($K_D$) and to the Darken excess stability function

$$E_S = \frac{RT}{1 - X_{\text{NaCl}}} \left( \frac{d \ln \gamma_{\text{NaCl}}}{d X_{\text{NaCl}}} \right)$$

(3)

which has been correlated with the degree of order. A plot of this function, directly calculated from the data by numerical differentiation, is shown in Figure 2 and shows an exceptionally high narrow peak. Because of the narrowness of the peak, the error in the peak height is relatively large. One can determine the peak height more accurately by calculation from the value of $K_D$, which, in effect, uses all the data near the 50-50 composition for the calculation; this leads to a value for the peak height of $1.1 \times 10^6$ cal mol$^{-1}$ ($4.7 \times 10^6$ joules mol$^{-1}$). This solution is indeed highly ordered.

**SOLUBILITIES OF SOLUTES**

How does ordering manifest itself in the thermodynamic properties of solutes? The coordination cluster theory$^{1,2}$ for the activity coefficients of a solute $C$ dissolved in the solvent $A-B$ can be used to illustrate these properties. The theory leads to the expression for the activity coefficient of $C$, $\gamma_C$, in terms of the coordination number $Z$ (for additive molten salt systems, this is for the coordination of next nearest neighbors), the mole fractions and activity coefficients of the solvent components, $X_A, X_B, \gamma_A, \gamma_B$, the activity coefficients of the solute in pure $A$ and pure $B$, $\gamma_{C(A)}, \gamma_{C(B)}$, a parameter $g_E^F$, which represents the excess free energy of mixing of $A$ and $B$ in the next nearest neighbor shell of solute ions (cations in the case we
containing \((Z-i)A^+\) cations and \(iB^+\) cations, and a parameter \(t\), which is \(1/Z\) for this case.

\[
\frac{1}{\gamma_C} = \sum_{i=0}^{Z} \frac{Z!}{(Z-i)!i!} \left( \frac{X_A\gamma_A}{\gamma_{C(A)}} \right)^{Z-i} \left( \frac{X_B\gamma_B}{\gamma_{C(B)}} \right)^i \exp \left( -\frac{g_i^E}{RT} \right)
\]  

(4)

Examination of the ratios of the activity coefficients of \(\text{NaCl}(A)\) and \(\text{AlCl}_3(B)\) (essentially the same as the activity ratios near \(X_{\text{AlCl}_3} = 0.5\)) in Figure 1 provides insights into the solute properties. At concentrations below \(X_{\text{AlCl}_3} = 0.5\), \(\gamma_{\text{NaCl}}/\gamma_{\text{AlCl}_3}\) is very large and, with a small change of concentration to \(X_{\text{AlCl}_3} > 0.5\), this ratio becomes very small. As a consequence, only two of the \(Z\) terms in the summation on the r.h.s. of Eq. (4) are important, with the term for \(i = 0\) being predominant in basic solutions \((X_{\text{AlCl}_3} < 0.5)\) and that for \(i = Z\) being predominant in acidic solutions \((X_{\text{AlCl}_3} > 0.5)\). For both these terms, the value of \(g_i^E = 0\). Calculations of the activity coefficients in the \(\text{NaCl-}\text{AlCl}_3\) solvent at 175°C for a hypothetical solute \(C\), for which \(\gamma_C(A)\) and \(\gamma_C(B)\) are both unity, and for \(Z = 4\) are illustrated in Figure 3. There is a steep maximum in the activity coefficients at about \(X_{\text{AlCl}_3} = 0.5\). For a relatively insoluble material, a sharp maximum in the activity coefficient denotes a sharp minimum in the solubility. This property should be common with strongly ordered solvents for a solute that interacts much more weakly with the two solvent components than the solvent components interact with each other. Recent measurements at 175°C of the solubilities of solid \(\text{CoCl}_2\) in \(\text{NaCl}-\text{AlCl}_3\) solutions at \(X_{\text{AlCl}_3} > 0.5\) have been well fitted by Eq. (4) for a value of the activity coefficient of solid \(\text{CoCl}_2\) in molten \(\text{AlCl}_3\) of 0.35.\(^5\) This derived value indicates that \(\text{CoCl}_2\) interacts relatively weakly with \(\text{AlCl}_3\).

Because ordering in this melt is very strong, one can also describe this solubility in chemical terms. In basic melts, the solvent can be considered to be primarily a binary mixture of \(\text{NaCl}\) with \(\text{NaAlCl}_4\) with very small concentrations of \(\text{NaAl}_2\text{Cl}_7\). On the acid side, not very far from the 50-50 composition, the melt can be considered to be an essentially binary mixture of \(\text{NaAlCl}_4\) with \(\text{NaAl}_2\text{Cl}_7\) with very small concentrations of \(\text{Cl}^-\). The solubility of \(\text{CoCl}_2\) in acidic melts can be described in terms of the solubility product, \(K_{SP}\)

\[
K_{SP} = X_{\text{Co}^{2+}}X_{\text{Cl}^-}^2 = X_{\text{Co}^{2+}} \left( K_D^2/X_{\text{Al}_2\text{Cl}_7}^2 \right)
\]  

(5)

where \(X_{\text{Co}^{2+}}\) and \(X_{\text{Al}_2\text{Cl}_7}\) are cation and anion fractions, respectively, in the reciprocal system \(\text{Na}^+, \text{Co}^{2+}/\text{AlCl}_7^-, \text{Al}_2\text{Cl}_7^-, \text{Cl}^-\). At 175°C, the solubility product was found to be \(4.66 \times 10^{-15}\).\(^5\) The values of the standard free energy of solution of \(\text{CoCl}_2\) at infinite dilution is given by \(-RT \ln K_{SP}\) (29.39 kcal mol\(^{-1}\)) and is exactly given by the sum of the standard free energies for the following reactions:\(^9,\(^10\)

\[
\text{CoCl}_2(s) + \text{NaAlCl}_4(\ell) \rightleftharpoons 2\text{NaCl}(\ell) + \text{Co(AlCl}_4)_2(\ell)
\]  

(6a)
A value of -5.2 kcal mol\(^{-1}\) has been deduced for the free energy of formation of \(\text{Co(AlCl}_4\text{)}_2(\ell)\) from \(\text{CoCl}_2(\ell)\) and \(\text{AlCl}_3(\ell)\).\(^5\) This small value again reflects the weak interactions of \(\text{CoCl}_2\) with \(\text{AlCl}_3\). In fact, the insolubility of solid \(\text{CoCl}_2\) in acid melts is directly related to the fact that the standard free energy of formation of \(\text{Co(AlCl}_4\text{)}_2(\ell)\) from solid \(\text{CoCl}_2\) and liquid \(\text{AlCl}_3\) (-5.2 kcal mol\(^{-1}\)) is much larger than the free energy of formation of \(2\text{NaAlCl}_4(\ell)\) from \(2\text{NaCl}(\ell) + 2\text{AlCl}_3(\ell)\). An analogous conclusion is deduced from the coordination cluster theory where \(\gamma_{\text{CoCl}_2(\text{AlCl}_4)}\) (0.35) is considerably larger than the very small values of the activity coefficients of \(2\text{NaCl}\) (based on liquid as the standard state) in the acid melts.

Both the coordination cluster theory and the chemical concept of \(K_{SP}\) lead to the conclusion that other insoluble divalent salts (such as solid \(\text{FeCl}_2\) and \(\text{NiCl}_2\), which are reactants in the “Zebra” batteries under development for automobile propulsion) will, in all likelihood, have the same dependence of their solubilities on concentration, but with a different magnitude. Thus, the general behavior of solubilities of divalent salts in somewhat acidic haloaluminate melts of any one basic halide is universal and requires knowledge of but a single constant for each salt at a given temperature. Differences between the solubility products for different divalent salts in any one solvent are largely related to differences in the standard free energies of formation of the tetrachloroaluminate from the pure divalent chloride and \(\text{AlCl}_3\).

Solubilities in basic compositions are not this simple unless one considers compositions where there is only one species, e.g., for \(\text{Co}^{++}\), the \(\text{CoCl}_2^{2-}\) species, which was spectroscopically observed by Oye and Gruen in \(\text{KCl-AlCl}_3\) solutions.\(^1\)\(^1\)

These authors observed another species at low chloride ion concentrations. At somewhat higher concentrations where the very large majority of cobalt ions are present as \(\text{CoCl}_4^{2-}\), one can represent the solubilities of \(\text{CoCl}_2(s)\) and their dependence on the solvent composition with but a single parameter. Using the coordination cluster theory, this parameter is the activity coefficient of \(\text{CoCl}_2\) at infinite dilution in molten \(\text{NaCl}\). For the chemical description, this is the formation constant of \(\text{CoCl}_2^{2-}\) from \(\text{Co}^{3+}\) and four \(\text{Cl}^{-}\) ions. However, at smaller concentrations of chloride one must consider all four of the constants for the reactions to form \(\text{CoCl}_n^{2-n}\), \(n = 1 - 4\).

\[
\begin{align*}
\text{Co}^{3+} + \text{Cl}^- & \rightleftharpoons \text{CoCl}^+ & K_{11} \\
\text{CoCl}^+ + \text{Cl}^- & \rightleftharpoons \text{CoCl}_2 & K_{12} \\
\text{CoCl}_2 + \text{Cl}^- & \rightleftharpoons \text{CoCl}_3^- & K_{13} \\
\text{CoCl}_3^- + \text{Cl}^- & \rightleftharpoons \text{CoCl}_4^{2-} & K_{14}
\end{align*}
\]
where the formation constants are related to bond free energies, $\Delta A_{1n}$, through the statistical mechanical relations\textsuperscript{12}:

\begin{align}
K_{11} &= Z(\beta_{11} - 1) \quad \text{(8a)} \\
K_{11}K_{12} &= \frac{Z(Z - 1)}{2!}(\beta_{11}\beta_{12} - 2\beta_{1} + 1) \quad \text{(8b)} \\
K_{11}K_{12}K_{13} &= \frac{Z(Z - 1)(Z - 2)}{3!}(\beta_{11}\beta_{12}\beta_{13} - 3\beta_{11}\beta_{12} + 3\beta_{11} - 1) \quad \text{(8c)} \\
K_{11}K_{12}K_{13}K_{14} &= \frac{Z(Z - 1)(Z - 2)(Z - 3)}{4!}(\beta_{11}\beta_{12}\beta_{13}\beta_{14} - 4\beta_{11}\beta_{12}\beta_{13} + 6\beta_{11}\beta_{12} - 4\beta_{11} + 1) \quad \text{(8d)}
\end{align}

where $\beta_{1n} = \exp(-\Delta A_{1n}/RT)$ and $Z$ is a coordination number for Co\textsuperscript{2+}.\textsuperscript{12} Values of the bond free energies for each of the four successive chloride additions to the coordination shell of Co\textsuperscript{2+} can all be different. In the coordination cluster theory, the analogous differences are contained in the term $g_i^E$ in Eq. 4. When we use the simple approximation for $g_i^E$

\begin{equation}
g_i^E = (Z - i)(i)h \quad (9)
\end{equation}

then values of the analogue to $\Delta A_{1n}$ differ by $Z^2h$ according to the relation $\Delta A_{1n}' = \Delta A_{1n} - (n - 1)Z^2h$. An approximation for values of $\Delta A_{1n}$ can be made crudely from the expression\textsuperscript{13} $\Delta A_{1n} \sim \frac{\Delta G^\circ}{Z}$ where $\Delta G^\circ$ is the standard free energy change for reaction (6a) and $Z$ is a coordination number. For a value of $K_{11}$ of the order of 50,000, Thus, even at the neutral composition (50-50 mole % NaCl-AlCl\textsubscript{3}), where the concentration of chloride in the solvent is $3.3 \times 10^{-4}$ at $175^\circ$C, one expects that a large fraction of the cobalt ions in solution would be present as CoCl\textsuperscript{+} and some of the other species. In fact, examination of the natural logarithm of the apparent solubility products at $175^\circ$C in Table II of Ref. 5 indicates a value that is 0.2–0.3 larger than those at higher acidity at $X_{AlCl_3} = 0.513$ and 3.0–3.1 larger at $X_{AlCl_3} = 0.502$. If $K_{11}$ is of the order of $5 \times 10^4$, the magnitude of the difference at 0.513 is correct for the presence of CoCl\textsuperscript{+} and at $X_{AlCl_3} = 0.502$, there would have to be more than one species. Thus, at $X_{AlCl_3} = 0.502$, about 95% of the solubilization of CoCl\textsubscript{2} is caused by the formation of chlorocobalt species, which are present at a much higher total concentration than Co\textsuperscript{2+} ions with no Cl\textsuperscript{-} as a near neighbor. Measurements are underway to investigate this point, and preliminary data confirm this phenomenon at $255^\circ$C.

CONCLUSIONS

Both a physical theory (coordination cluster theory) and chemical concepts (solubility product principle and the formation of associated species) lead to useful
descriptions of the concentration dependence of the solubilities of divalent chlorides in chloroaluminates. Both points of view provide insights into the strikingly sharp minima in the solubility of solutes in the highly ordered molten NaCl-AlCl₃ solutions. Further work is underway to investigate the formation constants for chlorocobalt species in basic melts in this system.

In addition, these results provide valuable insights into the properties of other ordered liquids, such as silicates. Largely because of the much higher temperatures of stabilities of molten silicates, the thermodynamic properties of silicates¹⁴,¹⁵ indicate that the relatively more ordered binary silicate systems, such as Na₂O-SiO₂ and CaO-SiO₂ are considerably less ordered than the NaCl-AlCl₃ system. This implies that the chemical description of the thermodynamic properties of silicates will not be as well defined and as simple as those in the NaCl-AlCl₃ system discussed here. Despite this, there is a clear maximum near 33 mole % SiO₂ in the activity coefficients of a solute, such as FeO, in either the Na₂O-SiO₂ or CaO-SiO₂ system and, for example, the phase diagram of the ternary FeO-CaO-SiO₂ system exhibits minima in the concentration of FeO for different FeO liquidus isotherms near a line connecting the FeO composition corner with the composition at the 33.3 mole % SiO₂ in the CaO-SiO₂ binary line. The thermodynamic data for, e.g., CaO-SiO₂, are consistent with a larger degree of disproportionation of the SiO₄²⁻ anion that are likely to be present at 33 mole % SiO₂, and there is probably a broader distribution of different species at all compositions where the nominal average composition of the species parallels those of chloroaluminates. For one of the least ordered binary silicate systems, FeO-SiO₂, the degree of disproportionation of SiO₄²⁻ is undoubtedly considerable.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences, under Contract W-31-109-ENG-38.

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Figure 1. Plots of the EMF (as $FE/RT$) of the measurements of Boxall et al. and of values of $\ln a_{NaCl}$ and $\ln a_{AlCl_3}$ deduced from these measurements. $a_{NaCl}$ and $a_{AlCl_3}$ are the activities based on solid as the standard state.
Figure 2. The Darken excess stability function calculated directly from the data of Boxall et al. The actual peak height calculated from the disproportionation constant is $1.1 \times 10^6$ cal mol$^{-1}$. 
Figure 3. Activity coefficients of a hypothetical solute C in a binary NaCl-AlCl$_3$ solvent calculated from the Coordination Cluster Theory, where the activity coefficient of C is unity in NaCl and AlCl$_3$.