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Solubility of AgCl in Molten NaCl-$AlCl_3$ and KCl-$AlCl_3$

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ABSTRACT

Measurements of AgCl solubility (in mol fraction units) in molten NaCl-$AlCl_3$ and KCl-$AlCl_3$ were determined by an electromotive force technique. For the NaCl-$AlCl_3$ experiments, the temperature was maintained at 448 K and the composition of the solvent varied from $X_{AlCl_3}^{solvent} = 0.500$ to $X_{AlCl_3}^{solvent} = 0.530$. There was a compositional dependence of the AgCl solubilities with a minimum near the equimolar solvent composition. The minimum solubility in mol fraction of AgCl was 5.75×10^{-3} at $X_{AlCl_3}^{solvent} = 0.505$. The true solubility produce for AgCl at 448 K was calculated to be 7.35×10^{-9}. The magnitude of the solubility product is primarily related to the fact that the standard free energy of formation of $NaAlCl_4$ from NaCl and $AlCl_3$ is about 67 kJ mol^{-1} more negative than the corresponding free energy for $AgAlCl_4$ (*i.e.*, $AgAlCl_4$ is unstable). In basic and in somewhat acidic melts, the solubility is related to the formation of the associated ionic species such as AgCl, $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$. From our measurements, the formation constant of AgCl at 448 K, K_{11}, was 1.36×10^6. Further, the specific bond free energy for the associated complex AgCl, ΔA_{11}, has been calculated as -47.5 kJ mol^{-1}. For the KCl-$AlCl_3$ experiments, the composition was maintained at the equimolar and the temperature varied in the range 518 to 583 K. The AgCl solubility increases from 4.32×10^{-3} at 518 K to 6.85×10^{-3} at 583 K. The apparent heat of solution was 17.68 kJ mol^{-1} for this temperature range.

Molten chloroaluminates are ordered ionic liquids with striking physicochemical properties.[1-6] For example, one interesting observation is the sharp minimum in solubility and maximum in activity coefficients of solutes in NaCl-$AlCl_3$ at the equimolar composition.[7] Activity coefficients are large and can change by more than one order of magnitude as the composition is increased from 50 to 60 mole percent (m/o) $AlCl_3$. Solutes which interact with NaCl and $AlCl_3$ more weakly than these two salt components interact with each other, are often insoluble at the equimolar composition because of a large maximum in the activity coefficients of the solute. The magnitude of the effect in chloroaluminates is larger the stronger the interaction between the monovalent chloride and $AlCl_3$ (*i.e.*, the more negative is the excess free energy of mixing of the solvent components). We present here a further contribution on the nature of ordered ionic liquids and the solubilities of metal chlorides in the NaCl-$AlCl_3$ melts.[7-10] Such melts are potential electrolytes in batteries under development for automobile propulsion. Theoretically, we can describe the influence of ordering on solute solubility in ordered ionic liquids with both chemical and physical models.

There is both topological and chemical order in the NaCl-$AlCl_3$ system. The liquid is most ordered at the equimolar composition where NaCl and $AlCl_3$ combine to form a low temperature melt containing mostly Na^+ cations and $AlCl_4^-$ anions. Except for the structural complexity of the polyatomic anion, the liquid is a simple molten salt analogous to the alkali halides exhibiting coulomb ordering represented in one dimension as $(\cdots + - + - + - \cdots)$. Since the tetrahedral $AlCl_4^-$ ions, which are the nearest neighbors of Na^+ cations, have their four chlorides on their periphery, the coulomb ordering leads to topological order of the next nearest neighbor sodium and aluminum ions, which can be written in one dimension as ($\cdots$ Na-Al-Na-Al-Na-Al $\cdots$), 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 polyions ($AlCl_4^-$ at the equimolar composition, and $Al_2Cl_7^-$ and/or $Al_3Cl_{10}^-$ at higher concentrations of $AlCl_3$). Addition of NaCl or $AlCl_3$ to the equimolar mixture decreases the topological order

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* Electrochemical Society Active Member.

by decreasing the range of repetition of the Na-Al pairs by the substitution of $\mathrm{Cl^-}$ or $\mathrm{Al_2Cl_7^-}$ ions for $\mathrm{AlCl_4^-}$ ions in the ordered array. Such solutions are not perfectly ordered.[4] One measure of disorder is the extent of disproportionation of the $\mathrm{AlCl_4^-}$ ion according to

$$2 \cdot \mathrm{AlCl_4^-} \leftrightarrow \mathrm{Cl^-} + \mathrm{Al_2Cl_7^-} \quad K_{\mathrm{D,448\,K}} = 1.06 \times 10^{-7} \qquad [1]$$

If one considers that a number of $\mathrm{Na^+}$ cations are next nearest neighbors to any one $\mathrm{Al^{3+}}$ in $\mathrm{AlCl_4^-}$ or $\mathrm{Al_2Cl_7^-}$ and are nearest neighbors to $\mathrm{Cl^-}$, then disproportionation Eq. 1 can be re-expressed in terms of the disordering reaction

$$2 \cdot \text{Na-Al} \leftrightarrow \text{Na-Na} + \text{Al-Al} \qquad [2]$$

The small value for the equilibrium constant of Eq. 1 indicates little disorder and the melt is highly ordered. Equation 2 is a physical way of expressing the chemical process described in Eq. 1. The advantage of the chemical approach is that the ordering phenomenon can be expressed in terms of an additive solution of NaCl, $\mathrm{NaAlCl_4}$, and $\mathrm{NaAl_2Cl_7}$. Because of the near ideal behavior of mixtures of three salts with a common cation and different anions such a description of ordering can be very precise.

As $\mathrm{AlCl_3}$ is added to equimolar NaCl-$\mathrm{AlCl_3}$, $\mathrm{AlCl_4^-}$ ions react to form $\mathrm{Al_2Cl_7^-}$ ions according to the reaction

$$\mathrm{AlCl_4^-} + \mathrm{AlCl_3} \leftrightarrow \mathrm{Al_2Cl_7^-} \qquad [3]$$

At 448 K, Eq. 3 has a formation constant of[4,5] 2.4×10^4. Therefore, over 99% of the $\mathrm{AlCl_3}$ added to $\mathrm{NaAlCl_4}$ is present as $\mathrm{Al_2Cl_7^-}$ ions at $X_{\mathrm{AlCl_3}} = 0.51$, well over 90% at $X_{\mathrm{AlCl_3}} = 0.63$, and about 80% at $X_{\mathrm{AlCl_3}} = 0.67$. This property greatly simplifies the chemical description of these melts, which can be described as additive ternary solutions of NaCl, $\mathrm{NaAlCl_4}$, and $\mathrm{NaAl_2Cl_7}$ with some $\mathrm{Al_2Cl_6}$ that is negligible below $X_{\mathrm{AlCl_3}} = 0.57$ and is about 4% at $X_{\mathrm{AlCl_3}} = 0.625$.

Experimental

Polarographic grade $\mathrm{NaAlCl_4}$, $\mathrm{AlCl_3}$, and AgCl were obtained from APL Engineered Materials (Urbana, IL). The salts were supplied in glass ampuls which were sealed under an argon atmosphere. The salts were used without any subsequent purification. The experiments were performed in an argon-filled glove box. The glove box atmosphere was circulated through a purifier continuously, and the oxygen and water content were always kept below 5 ppm and were usually below 1 ppm. The furnace employed for these measurements was a pot furnace (Glascol Model TM-572) fitted to a power proportional temperature controller (Omega Model CN-2011).

The solubility apparatus is shown in Fig. 1. The solubility apparatus consisted of a 1 liter Pyrex resin reaction jar. The ground glass cover had ports for an alumel-chromel thermocouple, the electrodes, a fused silica stirrer, and materials addition. The electrochemical cell was a simple AgCl concentration cell. It consisted of silver metal indicator electrodes dipping into solutions of AgCl-NaCl-$\mathrm{AlCl_3}$. The half-cell compartments were separated by an asbestos salt bridge made by tightly rolling a small strand of asbestos string, firing it to a white ash, and then collapsing a 6 mm Pyrex tubing around it with tweezers. As a result, fine capillaries were formed which allowed for electrical contact but minimal mass diffusion. In addition, the resistance of such salt bridges was large. Electrode potentials were stable and totally reproducible. A new asbestos salt bridge was used for each experiment. The cell can be described schematically as

$$\mathrm{Ag/AgCl}(X)\text{-NaCl-}\mathrm{AlCl_3}//$$
$$\text{asbestos salt bridge}//\mathrm{AgCl}(X_r) - \text{NaCl-}\mathrm{AlCl_3/Ag}$$

where X_r corresponds to the reference electrode compartment concentration. For dilute solutions of AgCl where Henry's law is obeyed, the AgCl activity coefficient, γ_{AgCl} is composition independent. Further, when the concentrations of AgCl in the reference and indicator electrodes are small, then junction potential effects can be neglected. For the above conditions, the Nernst expression is

$$E_{\mathrm{cell}} = -\frac{RT}{F} \ln \frac{X}{X_r} \qquad [4]$$

All measurements in the NaCl-$\mathrm{AlCl_3}$ and KCl-$\mathrm{AlCl_3}$ obeyed the Nernst equation at the concentrations studied. About 400 g of NaCl-$\mathrm{AlCl_3}$ were melted in the reaction jar. Then AgCl was added to the melt, and the solution was stirred. Voltages were recorded after each addition. Generally, electromotive forces were stable within 30 min of material addition. The solubility limit for AgCl was reached when the electromotive force did not change with AgCl addition.

The applicability of the electromotive force technique to determine metal chloride solubilities in chloroaluminate solvents has been confirmed in previous studies[11] by the agreement between the solubilities determined by electromotive force measurements with those determined by chemical analysis (*i.e.*, ICP) methods.

Results and Discussion

AgCl-NaCl-$AlCl_3$ system.—Figure 2 presents the experimental results, plotted following Eq. 4, for AgCl in an equimolar NaCl-$\mathrm{AlCl_3}$ melt at 448 K. For dilute solutions, the curve is linear which is consonant with our assumption that these solutions are Henrian. Further, the slope corresponds to a one-electron transfer, as expected. At the solubility limit, the electromotive force is independent of concentration. The solubility limits for a range of AgCl concentrations have been calculated in the manner indicated in Fig. 2. All other solvent compositions show the same form and behave in a similar fashion as Fig. 2. A

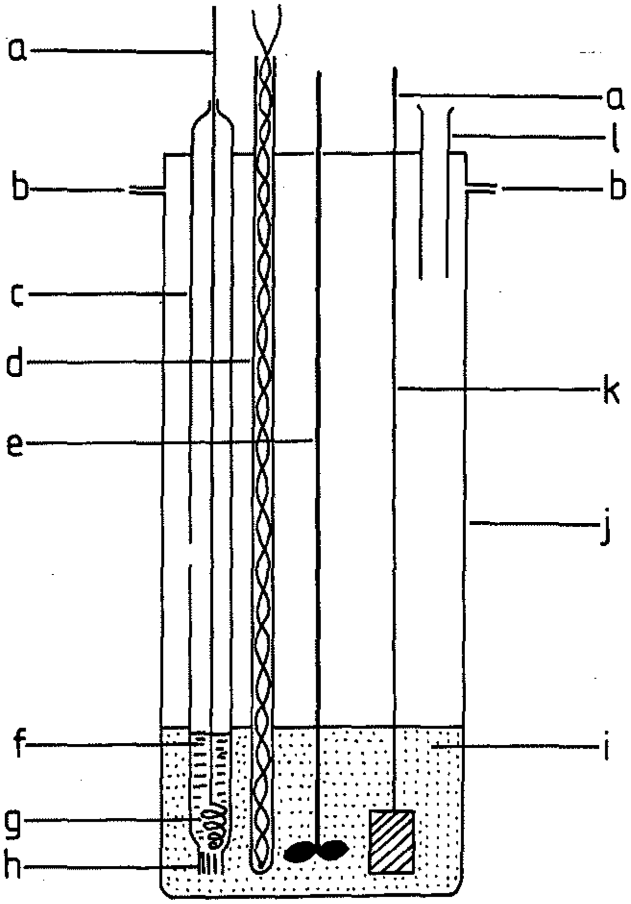

Fig. 1. Electrochemical cell for solubility experiments (a) silver wire electrodes, (b) ground glass joint, (c) reference electrode, (d) thermocouple well, (e) stirrer, (f) reference electrode solution, (g) silver wire spiral, (h) asbestos sealed into glass, (i) solution studied, (j) resin reaction jar, (k) silver indicator electrode, and (l) materials addition and sampling.

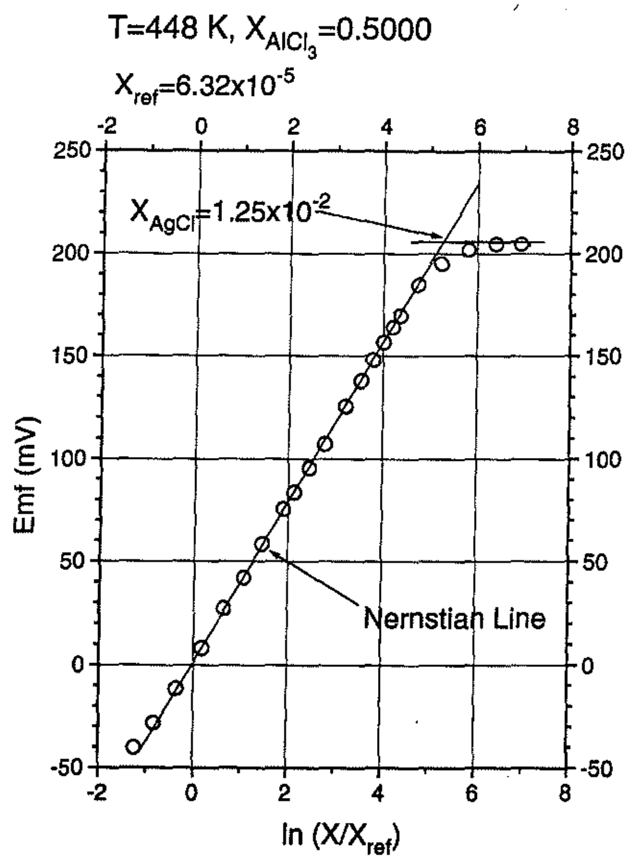

Fig. 2. Experimental electrochemical results for the equimolar NaCl-AlCl$_3$ system. Other compositions exhibited the same behavior.

summary of the mole fractions of NaCl, AlCl$_3$, and AgCl in the melts is given in Table I. The solubility of AgCl depends on composition. The minimum AgCl solubility is 5.75×10^{-3} at $X_{\text{AlCl}_3}^{\text{solvent}} = 0.5050$, and the solubility increases as the solvent becomes more basic (addition of NaCl) or acidic (addition of AlCl$_3$). The changes in the AgCl solubility with composition can be related to the bonding interactions between NaCl and AlCl$_3$. Both physical and chemical models have been used to describe and interpret such results.[8,9] However, the physical description is not adequate here.

The coordination cluster theory (CCT).—The dependence of the AgCl solubility on the solvent composition has been related to physicochemical concepts. The CCT is based on a physical model for the description of dilute solutions of a solute in a mixed solvent.[7,11-13] Consider a solute C, dissolved in the solvent A-B. The CCT leads to the expression for the activity coefficient of C, γ_{C}, in terms of the coordination number Z (for additive molten salt systems Z represents the coordination of the next-nearest neighbors), the mole fractions and activity coefficients of the solvent components, X_{A}, X_{B}, γ_{A}, γ_{B}, the activity coefficients of the solute in pure A and pure B, $\gamma_{\text{C(A)}}$, $\gamma_{\text{C(B)}}$, a parameter g_i^{E}, which represents the excess free energy of mixing of A and B in the next nearest neighbor shell of solute cations containing $(Z - i)\text{A}^+$ cations and $i\text{B}^+$ cations, and a parameter t, which is equal to Z^{-1} for an additive salt solution. The parameter g_i^{E} can be represented further by the expression $(Z - i)ih$, where h is a regular solution mixing parameter. Because of the highly ordered solution, this term is not important here. The final expression for the activity coefficient of C, γ_{C}, is

$$\frac{1}{\gamma_{\text{C}}} = \sum_{i=0}^{Z} \frac{Z!}{(Z-i)!\,i!} \left(\frac{X_{\text{A}}\gamma_{\text{A}}^{t}}{\gamma_{\text{C(A)}}^{1/z}}\right)^{(Z-i)} \left(\frac{X_{\text{B}}\gamma_{\text{B}}^{t}}{\gamma_{\text{C(B)}}^{1/z}}\right)^{i} \exp\left(\frac{-g_i^{\text{E}}}{RT}\right) \qquad [5]$$

Because the NaCl-AlCl$_3$ (or A-B) system is strongly complexed (*i.e.*, ordered), the compositional dependence of γ_{NaCl} and γ_{AlCl_3} near the equimolar composition is large.[14] Consequently, there is a composition dependence for the activity coefficients of AgCl. At concentrations below $X_{\text{AlCl}_3}^{\text{solvent}} = 0.50$, $\gamma_{\text{NaCl}}/\gamma_{\text{AlCl}_3}$ is large and, with a small change of concentration to $X_{\text{AlCl}_3} > 0.50$, this ratio becomes small. Consequently, Eq. 5 can be simplified. Only two of the $Z + 1$ terms in the summation on the right-hand side of Eq. 5 are important. The term for $i = 0$ is predominant in basic solutions, and the term for $i = Z$ is predominant in acid solutions. Since g_i^{E} is zero for $i = 0$ and $i = Z$, we can set the appropriate exponentials in Eq. 5 to unity. Calculations for the CCT are generally not sensitive to reasonable values of Z. Because the Ag$^+$ cation is relatively small, there is a large radius ratio between the AlCl$_4^-$ anion and the Ag$^+$ cation, and not many AlCl$_4^-$ units can be packed around an Ag$^+$ cation. Consequently, we chose a value of $Z = 4$ for our CCT calculations. The values for γ_{NaCl} and γ_{AlCl_3} with respect to the pure liquid standard state are known at 448 K.[14] In addition, there are no values for the AgCl activities in the pure solvent components at 448 K (*i.e.*, $\gamma_{\text{AgCl(NaCl)}}$ and $\gamma_{\text{AgCl(AlCl}_3)}$). Hence the absolute values of γ_{AgCl} in the NaCl-AlCl$_3$ solutions cannot be specifically calculated, but a ratio of these activity coefficients can be calculated. For acidic compositions, for $g_i^{\text{E}} = 0$, and with the appropriate substitutions Eq. 5 is simplified to

$$\frac{\gamma_{\text{AgCl(AlCl}_3)}}{\gamma_{\text{AgCl}}} = \left(\frac{X_{\text{NaCl}} \cdot \gamma_{\text{NaCl}}^{1/4}}{\gamma_{\text{AgCl(NaCl)}}^{1/4}/\gamma_{\text{AgCl(AlCl}_3)}^{1/4}} + X_{\text{AlCl}_3} \cdot \gamma_{\text{AlCl}_3}^{1/4}\right)^4 \qquad [6]$$

In Fig. 3, we have plotted calculations for the values of γ_{AgCl} from Eq. 6 for our acidic data at 448 K for the ratio $\gamma_{\text{AgCl(NaCl)}}/\gamma_{\text{AgCl(AlCl}_3)} = 0.10$. We have also calculated curves for values of the ratio of 1 and 0.001. The results differ little from the curve plotted in Fig. 3. The function is sensitive to the activity coefficient ratio only when it gets to be improbably large, suggesting that the data in acid melts depend mainly on $\gamma_{\text{AgCl(AlCl}_3)}$ and not on $\gamma_{\text{AgCl(NaCl)}}$. The only effect of the activity coefficient ratio in acid melts is near the equimolar solvent composition where the curve rises higher the lower the ratio. Figure 3 has been plotted for $g_i^{\text{E}} = 0$. We also have plotted the calculation for $g = (Z - i)ih$ with $h = -2000$ and $h = +2000$. The activity coefficients are weakly dependent on the value for h, and the indicated curve for $g_i^{\text{E}} = 0$ is shifted almost imperceptibly for changes in g_i^{E} values.

We also have plotted in Fig. 3, the experimental values of $(-\ln X_{\text{AgCl}} - k)$, where X_{AgCl} is equal to $1/\gamma_{\text{AgCl}}$ with the solid as the standard state. The constant, k, needed to shift the experimental data points to the calculated CCT curve is +2.2162. The concentration dependence of the measurements is not well represented at the lowest concentrations of AlCl$_3$. If the theory is an accurate representation of the properties of these solutions at higher AlCl$_3$ compositions, then the shift of 2.2162 is equal to $\ln \gamma_{\text{AgCl(AlCl}_3)}$. Hence, the value for $\gamma_{\text{AgCl(AlCl}_3)}$ is 9.2 with the solid as standard state. The partial excess free energy of solution for AgCl, $\Delta\bar{G}_{\text{AgCl(AlCl}_3)}^{xs}$, was calculated to be 8.26 kJ mol^{-1}. It is difficult to interpret fully the differences in the values for the partial excess free energies of solution, between different solutes in NaCl-AlCl$_3$. However, from our previous work on the CoCl$_2$, NiCl$_2$, FeCl$_2$ solutes, all these solutes react weakly with AlCl$_3$. Here, the excess free energy is positive indicating the possibility that AgAlCl$_4$ is unstable.

Chemical description.—For this chemical description, we consider all four of the formation constants for the associated species, AgCl$_n^{1-n}$. Consequently, a series of formation reactions (up to four chlorides) is generated

$$\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl} \quad K_{11} \qquad [7a]$$

$$\text{AgCl} + \text{Cl}^- \leftrightarrow \text{AgCl}_2^- \quad K_{12} \qquad [7b]$$

$$\text{AgCl}_2^- + \text{Cl}^- \leftrightarrow \text{AgCl}_3^{2-} \quad K_{13} \qquad [7c]$$

$$\text{AgCl}_3^{2-} + \text{Cl}^- \leftrightarrow \text{AgCl}_4^{3-} \quad K_{14} \qquad [7d]$$

The formation constants are related to the specific bond free energies, ΔA_{1n}, through the following statistical mechanical relations[15]

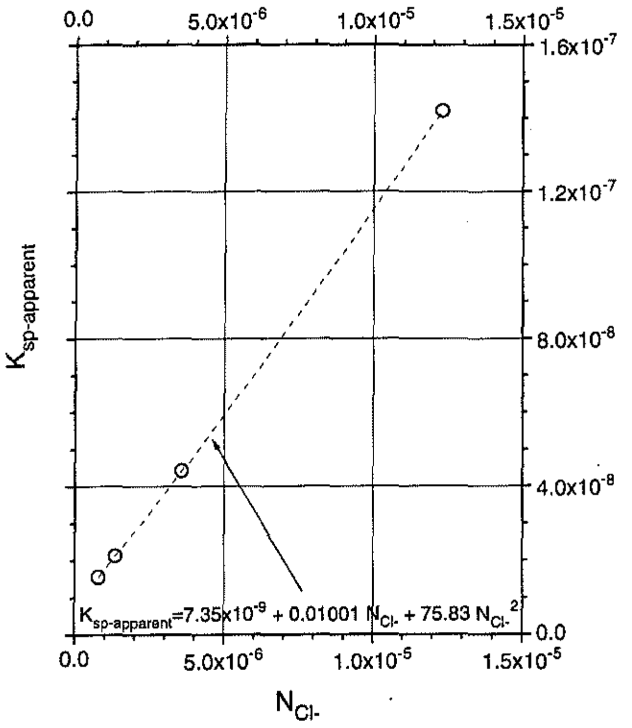

Fig. 4. Plot of $K_{sp}^{apparent}$ vs. ion fraction of free chlorine for the acidic compositions in the AgCl-NaCl-AlCl$_3$ system.

with Eq. 8. The β_{12} value of 5.07×10^3 is much smaller than the β_{11} value of 3.40×10^5. This difference has been ascribed to a coulomb effect for transition metal cations, an effect which also applies when the Ag$^+$ cations effectively have a relatively small radius in chloride melts.

If the solvent near the equimolar composition is NaAlCl$_4$, then the thermodynamics of AgCl dissolution can be described[16-18] in three steps

$$\mathrm{AgCl_{(s)} + NaAlCl_{4(l)} = NaCl_{(s)} + AgAlCl_{4(l)}} \quad \Delta G^\circ_{16} \qquad [16]$$

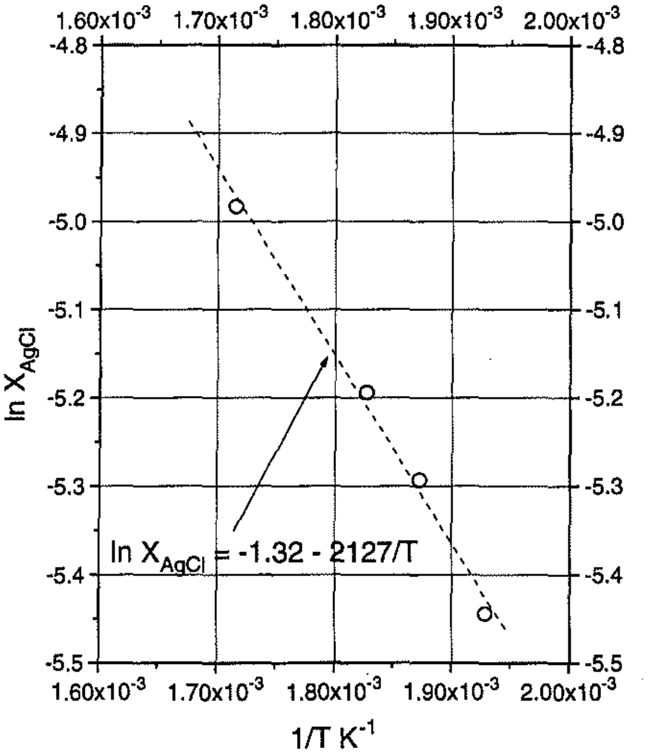

Fig. 5. Van't Hoff plot for the AgCl-KCl-AlCl$_3$ system.

Table III. Solubility of AgCl in equimolar KCl-AlCl$_3$ from 518.5 to 583.0 K.

T (K)	AgCl solubility
518.5	4.32×10^{-3}
534.0	5.02×10^{-3}
547.2	5.55×10^{-3}
583.0	6.85×10^{-3}

$$\mathrm{NaCl_{(s)} = NaCl_{(\propto\,dilution)}} \quad \Delta G^E_{17} \qquad [17]$$

$$\mathrm{AgAlCl_{4(l)} = AgAlCl_{4(\propto\,dilution)}} \quad \Delta G^E_{18} \qquad [18]$$

where, ΔG°_{16} is the standard free energy change for the metathetical reaction given by Eq. 16, and ΔG^E_{17} and ΔG^E_{18} are the excess free energies of solution of NaCl$_{(l)}$ and AgAlCl$_{4(l)}$ in the solvent at infinite dilution. The sum of $\Delta G^\circ_{16} + \Delta G^E_{17} + \Delta G^E_{18}$ is exactly related to the solubility product, K_{sp}, in ion fraction units, by the relation

$$\Delta G^\circ_{19} = \Delta G^\circ_{16} + \Delta G^E_{17} + \Delta G^E_{18} = -RT \ln (K_{sp}) \qquad [19]$$

At 448 K, the value for $-RT \ln K_{sp}$ is 69.76 kJ mol^{-1}. The value for ΔG^E_{17} is probably small, and the value for ΔG^E_{18} is probably similar to the measured enthalpies of mixing in the AgNO$_3$-NaNO$_3$ binary system,[19] which is approximately 2800 J mol^{-1}. Thus, the insolubility of AgCl in NaAlCl$_4$ is related to the fact that the standard free energy of formation of NaAlCl$_{4(l)}$ from the two constituent solid chlorides is much more negative than the corresponding free energy of formation of AgAlCl$_{4(\propto\,dilution)}$ by close to 67 kJ mol^{-1}. This result implies that AgAlCl$_4$ is an unstable compound with a standard free energy of formation of 23 kJ mol^{-1}.

AgCl-KCl-AlCl$_3$ system.—The solubility of AgCl in equimolar KCl-AlCl$_3$ as a function of temperature is given in Table III. The AgCl solubility increases as the temperature is raised, as expected. The results are given in Fig. 5 where ln X_{AgCl} is plotted against the reciprocal absolute temperature. In such instances, the Van't Hoff equation holds

$$\frac{\partial \ln X_{AgCl}}{\partial(1/T)} = -\frac{\Delta H^\circ_r}{R} \qquad [20]$$

The data in Fig. 5 are well represented by a linear relationship indicating that the heat capacities of the components are temperature independent for the temperature interval studied. The apparent enthalpy of solution for AgCl in equimolar KCl-AlCl$_3$ has been calculated with Eq. 20 to be -17.68 kJ mol^{-1}. Since the electromotive force of the electrochemical cell obeyed the Nernst equation, Eq. 4, below the solubility limit, this apparent enthalpy of solution is the true enthalpy of solution.

Conclusion

Chemical concepts (solubility product principle and the formation of associated species) lead to useful descriptions of the concentration dependence of the solubilities of AgCl in the chloroaluminate systems. Physical concepts do not appear to do as well. However, both viewpoints provide insights into the minima in the solute solubility in these highly ordered molten solutions. The solution properties in acid solutions can be described chemically in terms of a solubility product, the formation of AgCl species, and the disproportionation constant for Eq. 1. Although the AgCl$_2^-$ species is undoubtedly present in acid melts, its effect on the thermodynamic properties is small.

Manuscript submitted July 30, 1993.

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