Predicting the Composition of Acidic, Ionic Liquids in Contact with HCl Gas

Ernesto J. Angueira and Mark G. White
School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332

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*The acidic, chloroaluminate ionic liquid (IL) derived from the combination of 1-ethyl-3-methyl-1*H*-imidazolium chloride (EMIM-Cl) and aluminum chloride complex ($AlCl_3$) in contact with HCl gas was modeled using the principles of equilibrium thermodynamics of chemically reacting systems as a means to understand better the reactivity of arene formylations in these IL's. The concentration of an HCl-chloroaluminate species, $ClHAl_2Cl_7^-$ that has been characterized as a super acidic Brønsted species, increases with increasing HCl partial pressure. Another chloroaluminate species $Al_2Cl_7^-$, which has been characterized as a strong Lewis acid, showed concentrations that decreased with increasing HCl gas phase partial pressures. The ultimate conversion of toluene to tolualdehyde could be correlated with the sum of the predicted molar amounts of $ClHAl_2Cl_7^-$ and $Al_2Cl_7^-$, by assuming that each $ClHAl_2Cl_7^-$ combined with 1 tolualdehyde and each $Al_2Cl_7^-$ sequestered a single tolualdehyde molecule.*
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Introduction

The results of simulation studies can help to understand the properties of a complex mixture by examining the structures, thermodynamics and interactions at the molecular level. A recent text showed the results of such simulations studies for ionic liquids.[1] In this article, equilibrium thermodynamics were used to predict the composition of an EMIM-Cl/chloroaluminate IL as a function of HCl partial pressure above the mixture at room-temperature. Chandler and Johnson[2] modeled basic, neutral, and Lewis acidic chloroaluminate IL's using a collection of 22 elementary reactions to describe the species present in these materials. They predicted the free energies of formation for species appearing in the elementary reactions using semiempirical and higher-level quantum mechanical calculations. From these free energies of reaction they estimated the equilibrium constants for all 22 elementary reactions. The scope of this investigation was limited to Lewis and Brønsted acidic IL's and, thus, needed a maximum of six reactions to model the chemical equilibria over a range of $[AlCl_3/\mathbb{O}^+]^\circ$ ratios of 1 to 3 mol/mol where $\mathbb{O}^+ = EMIM^+$.

(1) $Cl^- + AlCl_3 \Leftrightarrow AlCl_4^-$, $K_1 = 6.7 \times 10^{51}$
(2) $AlCl_3 + AlCl_4^- \Leftrightarrow Al_2Cl_7^-$, $K_2 = 1.0 \times 10^{19}$
(3) $2\ AlCl_3 \Leftrightarrow Al_2Cl_6$, $K_3 = 3.0 \times 10^{15}$
(4) $HCl\ (g) + AlCl_3 \Leftrightarrow HAlCl_4$, $K_4 = 5.05$
(5) $HCl\ (g) + AlCl_4^- \Leftrightarrow ClHAlCl_4^-$, $K_5 = 0.133$
(6) $HCl\ (g) + Al_2Cl_7^- \Leftrightarrow ClHAl_2Cl_7^-$, $K_6 = 0.1$

Subsets were used of these six reactions and the corresponding equilibrium constants[2] to model the IL under the desired conditions. For example, when no HCl was added to the system, then only the first three reactions were used when $[AlCl_3/\mathbb{O}^+]^\circ$ ratio was >2, and only the first two reactions were needed for the case when $1 < [AlCl_3/\mathbb{O}^+]^\circ < 2$. For the case when $[AlCl_3/\mathbb{O}^+]^\circ < 1$, Chandler and Johnson established a set of equations to model the basic ionic liquid; whereas we used only Eq. 1. When HCl was added and when $1 < [AlCl_3/\mathbb{O}^+]^\circ < 2$, reactions 1, 2, 4, 5, & 6 were employed; whereas, when HC1

Correspondence concerning this article should be addressed to M. G. White at mark.white@che.gatech.edu.

was present, and when $[AlCl_3/\mathbb{O}^+]^\circ$ ratio >2, all six reactions were used.

A system of algebraic equations was developed to establish the equilibrium compositions from a consideration of the atom balances shown below and the equilibrium criteria.

Atom balances

$$[AlCl_3] = [AlCl_3]^\circ - [AlCl_4^-] - [HAlCl_4] - [ClHAlCl_4^-] - 2([Al_2Cl_6] + [Al_2Cl_7^-] + [ClHAl_2Cl_7^-])$$

$$[Cl^-] = [Cl^-]^\circ - [AlCl_4^-] - [Al_2Cl_7^-] - [ClHAlCl_4^-] - [ClHAl_2Cl_7^-]$$

Equilibrium criteria restraints

$$[AlCl_3][Cl^-]/[AlCl_4^-] - 1/K_1 = 0;$$

$$[AlCl_3][AlCl_4^-]/[Al_2Cl_7^-] - 1/K_2 = 0;$$

$$[AlCl_3]^2/[Al_2Cl_6] - 1/K_3 = 0;$$

$$[AlCl_3][HCl]/[HAlCl_4] - 1/K_4 = 0;$$

$$[AlCl_4^-][HCl]/[ClHAlCl_4^-] - 1/K_5 = 0;$$

$$[HCl][Al_2Cl_7^-]/[ClHAl_2Cl_7^-] - 1/K_6 = 0$$

These equations were committed to a spreadsheet environment, and the option "Solver" was used to establish mathematical solutions. It was found that uniform convergence was not possible in all cases and, therefore, it was necessary to appeal to our knowledge of the IL chemistry to choose the correct solution from among the possible mathematical solutions. As an example, it is known from the chemistry of the chloroaluminate IL's that the chloride anion appears in significant concentrations only in basic IL's, therefore, mathematical solutions in acidic IL's were discarded that showed significant concentrations of this anion. Also, it is known, that dimeric Al_2Cl_6 appears in significant concentrations only when $[AlCl_3/\mathbb{O}^+]^\circ > 2$. By these means, only those mathematical solutions that were consistent with the known phase diagram of the acidic IL's were accepted. Shown later are our efforts to model these systems and use the predictions to interpret results from reaction studies.

Experimental

Chemicals. The imidazolium compounds were obtained from Sigma Aldrich and used without further purification. Aluminum chloride (99.99%), obtained from Sigma Aldrich, was sublimed under a vacuum before use. Toluene (anhydrous, 99.8%) was obtained from Sigma Aldrich and used without further purification. HCl (anhydrous, 99+%) was obtained from Sigma Aldrich.

Preparation of IL's-chloroaluminates/EMIM-Cl. The weighing instrument, chemicals, and material transfers for $AlCl_3$, and EMIM-Cl were placed in a AtmosBag filled with dry Ar. $AlCl_3$ is weighed; and EMIM-Cl is added to it so as to obtain the desired $AlCl_3/\mathbb{O}^+$ molar ratio.

Titration studies. One equivalent of *p*-tolualdehyde per mol of Al in the sample was added to separate IL's which were prepared having the $Al/\mathbb{O}^+$ ratio of 1/2, 1/1, 1.5/1 and 2/1. The amount of base and Al was the same in each sample, whereas the amount of EMIM-Cl was varied to develop the desired $Al/\mathbb{O}^+$ ratio. The mixture of *p*-tolualdehyde and IL was slowly heated up to 413 K, and placed under a vacuum (200 milliT = 26.7 Pa) for 1/2 h so as to remove the weakly absorbed base. The vaporized base was condensed into a trap held at 77 K. The amount of base remaining in the IL was determined by weighing the amount of base found in the trap and subtracting this amount from the initial mass of base placed in the IL.

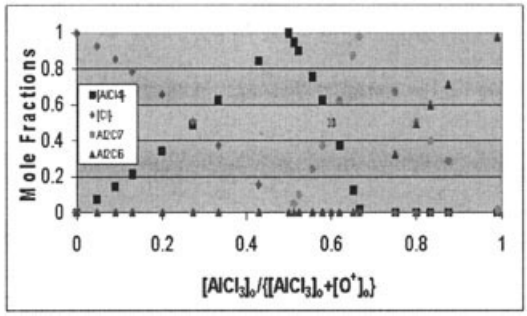

Figure 1. Modeling the EMIC IL speciation diagram.

Results

EMIM-Cl chloroaluminate IL without HCl added The first attempt at modeling was to reproduce Figure 13 in the publication by Chandler and Johnson[2]: the phase diagram for Al speciation over the range of $0 < [AlCl_3/\mathbb{O}^+]^\circ < \infty$ in the absence of HCl gas above the liquid. This result is shown in Figure 1 where only the first three reactions were used for the modeling. These predictions agree with those shown in the manuscript by Chandler and Johnson and, therefore, we believe that our mathematical routine is correct. That is, basic IL's ($0 < [AlCl_3/\mathbb{O}^+]^\circ < 1$) show Cl^- and $AlCl_4^-$ as the dominate species and no $AlCl_3$ or Al_2Cl_6 is present in these mixtures. The Cl^- concentration decreases to a value of 0 as $[AlCl_3/\mathbb{O}^+]^\circ$ approaches 1 that is, $[AlCl_3/(AlCl_3 + \mathbb{O}^+]^\circ = 1/2]$, where the concentration of $AlCl_4^-$ reaches a maximum value of unity. For $1 < [AlCl_3/\mathbb{O}^+]^\circ < 2$, the concentration of $AlCl_4^-$ decreases from its maximum value of unity to a value of 0 while the concentration of $Al_2Cl_7^-$ reaches a maximum value = 1. For values of $[AlCl_3/\mathbb{O}^+]^\circ > 2$, the concentration of $Al_2Cl_7^-$ decreases as the concentration of Al_2Cl_6 increases. The following shows a simulation on the effect of adding HCl gas to the Lewis acidic IL's.

Effect of adding HCl to an Acidic IL: $[AlCl_3/\mathbb{O}^+]^\circ = 2$. Thermodynamic calculations were completed for an IL at 298 K, where the value of $[AlCl_3/\mathbb{O}^+]^\circ$ was 2 mol/mol, and for HCl gas pressures from 0 to 500 psia (3.45 MPa) using reactions numbers 1 – 6 to simulate the formation of the IL. The goal of this modeling was to determine how HCl gas changed the equilibrium composition, if at all, and to determine what species were formed as HCl was introduced into the system. The results of the earlier modeling, Figure 1, show that the composition of the IL agrees with that predicted by Chandler and Johnson when no HCl was present in the IL: mole fraction of $Al_2Cl_7^- = 1$, all other species = 0. As the HCl partial pressure

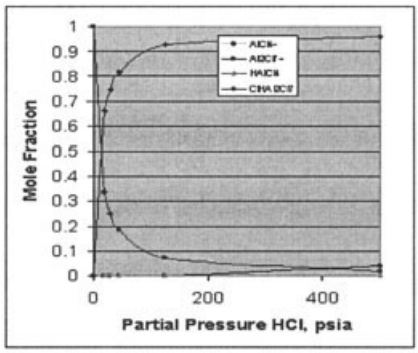

Figure 2. Equilibrium composition of IL as P_{HCl} changes for $[AlCl_3/\mathbb{O}^+]^\circ = 2$.

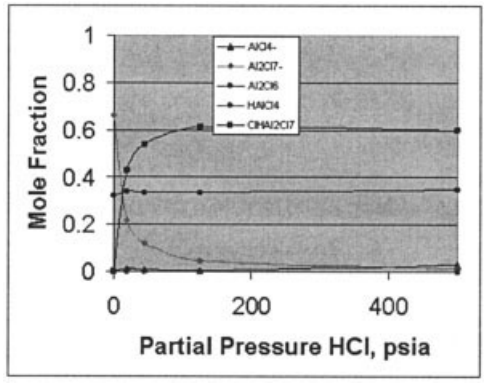

Figure 3. Equilibrium mixture composition for $[AlCl_3/\mathbb{O}^+]^\circ = 3$.

was increased, the mole fraction of the Brønsted super acidic, chloroaluminate anion, $ClHAl_2Cl_7^-$, increased rapidly at first and then its mole fraction appeared to approach an asymptote (Figure 2). The mole fraction of the Lewis acid, chloroaluminate anion ($Al_2Cl_7^-$) decreased monotonically for increasing partial pressure of HCl; whereas the mole fraction of the monomeric chloroaluminate anion, $AlCl_4^-$, remains constant at nearly 0 except at the highest HCl partial pressure where its mole fraction is 0.04. Finally, the mole fractions of the acidic chloroaluminate species, $HAlCl_4$ and $ClHAlCl_4^-$ (not shown), are small when the HCl pressure is less than 100 psia (0.69 MPa), and their mole fractions become significant (0.01) only when the HCl partial pressure is nearly 500 psia (3.45 MPa). No chloride anion (not shown) was formed in significant quantity which agrees with the fact that the melt was acidic. These results show that only the super acidic chloroaluminate anion ($ClHAl_2Cl_7^-$) was formed in significant amounts when HCl gas was added to this acidic IL. If this result is true, then this IL under HCl should catalyze the toluene carbonylation reaction which is known to proceed only in super acidic media.[3] Moreover, the strong Lewis acid, $Al_2Cl_7^-$, is also present and it should play a role in the arene carbonylation by forming an adduct with the weak Lewis base: tolualdehyde.[4]

We were also interested to learn the effect of adding HCl gas to a system where Al_2Cl_6 was also present. This condition was met when the $[AlCl_3/\mathbb{O}^+]^\circ > 2$, (for example, see Figure 1).

Acidic IL: $[AlCl_3/\mathbb{O}^+]^\circ = 3$. The IL phase diagram[5] shows that when $[AlCl_3/\mathbb{O}^+]^\circ$ equals 3, a precipitate of $AlCl_3$ forms in equilibrium with a liquid composed of a mixture having $[AlCl_3/\mathbb{O}^+]^\circ < 3$. This mixture was prepared to confirm the partial solubility of Al_2Cl_6 in the IL at room temperature when $[AlCl_3/\mathbb{O}^+]^\circ = 3$ (*vide infra*). When additional organic cation was placed in this mixture to the extent that the final mixture shows $[AlCl_3/\mathbb{O}^+]^\circ = 2$, then a single phase was formed. Calculations were repeated for the case where the value of $[AlCl_3/\mathbb{O}^+]^\circ = 3$ in an attempt to determine if HCl can be an agent to alter the solubility of Al_2Cl_6 in the IL at room-temperature, see Figure 3.

The predicted composition of this IL with $[AlCl_3/\mathbb{O}^+]^\circ = 3$ shows that the addition of HCl in the gas phase to the extent of 19.7 psia (135 kPa) does not cause the Al_2Cl_6 mole fraction to change much ($0.32 \rightarrow 0.34$) while the mole fraction of $Al_2Cl_7^-$ decreases from 0.67 to 0.22. At the same time, the mole fraction of super acidic chloroaluminate increased from zero to 0.61, while the mole fraction of the monomeric $AlCl_4^-$ increased from 0 to 0.01. The acidic $HAlCl_4$ and $ClHAlCl_4^-$ species appears only in very low mole fractions (<0.01) at all levels of HCl partial pressures < 500 psia (3.45 MPa). These simulations show that adding HCl gas to the system does not change the mole fraction of Al_2Cl_6 very much. Experimental verification of these predictions was sought by a visual inspection of an IL in a low pressure cell having $[AlCl_3/O^+]^\circ = 3$ was contacted with HCl gas at room-temperature for which the pressure was adjusted from 0 to 150 psia, 1.03 MPa, (Figures 4a and b). The single phase system (Figure 4a, $[AlCl_3/\mathbb{O}^+]^\circ = 2$) did not show any solid formation when HCl was added to the gas phase at 298 K.

No significant change was observed in the amount of precipitate in the IL ($[AlCl_3/\mathbb{O}^+]^\circ = 3$) upon application of increasing HCl partial pressures at 298 K. We shall seek confirmation of these predictions and visual observations using NMR[6] and Raman[7] spectroscopy's.

Summary of HCl effects. Shown in Figure 5 is a compilation of these calculations as a function of the HCl partial pressure ($0 < P_{HCl} < 44.7$ psia, 0.31 MPa) for a range of $[Al/\mathbb{O}^+]^\circ$ ratios of 1 to 100. The mole fractions of $AlCl_4^-$ and Al_2Cl_6 in these mixtures depend only upon the initial fraction of Al in the mixture and these mole fractions do not depend on the HCl partial pressure. Some recent literature citations[6] suggest that HCl interacts with the IL to alter the proportional of monomeric aluminum anion to dimeric aluminum anion by the following equilibrium

$$\mathbb{O}^+Al_2Cl_7^- + HCl \Leftrightarrow H^+\{\mathbb{O}^+[(AlCl_4)^-]_2\} \qquad (1)$$

The conclusion based on this report apparently is different from our predictions. We shall comment more on these findings.

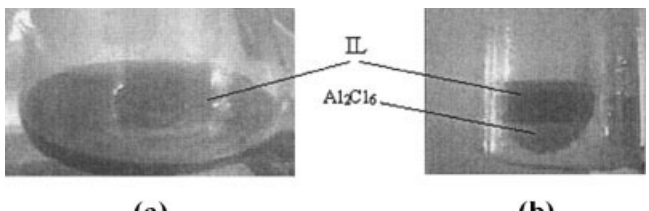

Figure 4. (a) EMIC/$AlCl_3$ = 1/2; (b) EMIC/$AlCl_3$ = 1/3.

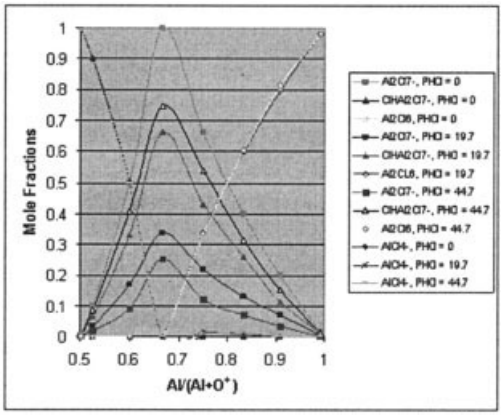

Figure 5. Summary of equilibrium calculations on acidic IL in contact with HCl.

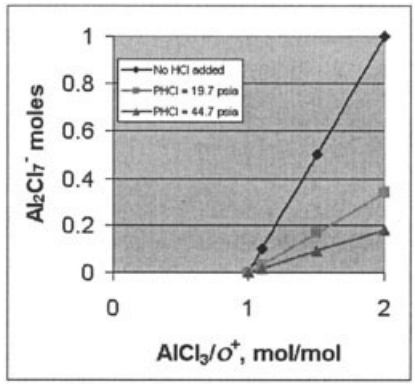

Figure 7. Estimates of Lewis acidic chloroaluminate anion $Al_2Cl_7^-$.

On the other hand, the mole fractions of the Lewis and Brønsted acids ($Al_2Cl_7^-$ and $ClHAl_2Cl_7^-$) depend on the composition of the initial mixture and the partial pressure of HCl above the IL. Notice how the mole fraction of the Brønsted acid increases with increasing partial pressure of HCl, and that the mole fraction of the Lewis acid decreases, proportionally, with increasing partial pressure of HCl over the range of $[AlCl_3/\mathbb{O}^+]°$ ratios from 1 to 100. Thus, the trend suggested for the cases where $[AlCl_3/\mathbb{O}^+]° = 2$ and 3 appears to describe also the behavior of the species found in the IL's having a wider range of $[AlCl_3/\mathbb{O}^+]°$ ratios.

Effect of HCl on Brønsted and Lewis acids. The simulations of the chemical equilibria that were used to summarize the effect of adding HCl gas to the acidic chloroaluminate IL's (Figure 5) can be examined in more detail to describe the effect upon the molar amounts of $ClHAl_2Cl_7^-$, Figure 6, when the partial pressure of HCl in the gas phase was 0, 19.7 (135 kPa) and 44.7 psia (0.31 MPa) and when $1 < [AlCl_3/\mathbb{O}^+]° < 2$. When no HCl was added, there was no super acidic chloroaluminate anion formed; however, when HCl was present at 19.7 (135 kPa) or 44.7 psia (0.31 MPa), super acidic anion was formed. Moreover, the molar amount of super acidic anion appears to increase linearly with increasing ratio of $[AlCl_3/\mathbb{O}^+]°$ when the partial pressure of HCl was either 19.7 (135 kPa) or 44.7 psia (0.31 MPa). Certainly, this species would be directly involved in the initiation of the toluene carbonylation reaction, and these results suggest that the conversion of toluene would be proportional to the ratio: $[AlCl_3/\mathbb{O}^+]°$.

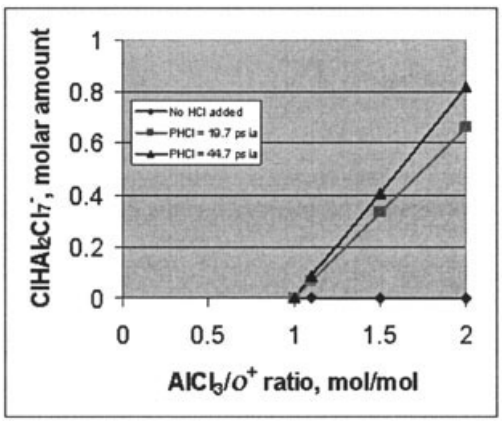

Figure 6. Effect of HCl upon super acidic chloroaluminate anion, $ClHAl_2Cl_7^-$.

Our predictions (Figure 7) show that the chloroaluminate anion has the highest molar amount for the case when no HCl was added to the gas phase, which is in keeping with the hypothesis that the acidic chloroaluminate anion arises from the chloroaluminate anion by reaction with dissolved HCl. Increasing the partial pressure of HCl above the IL causes a dramatic decrease in the chloroaluminate anion.

For all partial pressures of HCl, the chloroaluminate anion molar amount increases linearly with the ratio $[AlCl_3/\mathbb{O}^+]°$.

Correlation of Toluene Conversion Data. The next step is to properly use these equilibrium predictions to simulate our results from the formylation of toluene in acidic chloroaluminate IL's.[8,9] The *ultimate* conversion of toluene to form tolualdehyde increased linearly[8,9] with increasing ratio of $[AlCl_3/\mathbb{O}^+]°$ at a constant partial pressure of HCl at 44.7 psia (0.31 MPa) over the room temperature IL. The toluene formylation is equilibrium limited because of its slightly positive, free energy of reaction (~8 kcal/mol, 34 kJ/mol)[10] unless an agent is present to sequester the product so that the reverse reaction cannot occur. We observed this same effect with the triflic acid system so that the ultimate conversion of toluene to tolualdehyde depended on the formation of an adduct with the product aldehyde, so as to shift the chemical equilibrium to its product.[11] Thus, the final conversion of reactant was determined by the amount of acid present initially in the reaction mixture. The reaction becomes a stoichiometric reaction rather than a catalytic reaction because the "catalyst" cannot be regenerated *in situ*. Thus, it is possible to predict the ultimate toluene conversion knowing only the composition of the starting mixture.[11] We speculate that this same chemistry may be observed for the reaction completed in the acidic, chloroaluminate IL's. Thus, it is appropriate to examine species in the IL that may form an adduct with the product aldehyde. One such species is the super acidic chloroaluminate anion ($ClHAl_2Cl_7^-$) as it plays the same role in the IL system as triflic acid plays: (a) a catalyst to initiate the reaction mechanism, and (b) the same species becomes an agent to sequester the aldehyde against the back reaction by forming a carbocation and/or an oxonium ion. We believe that the strong Lewis acid, $Al_2Cl_7^-$, can also sequester

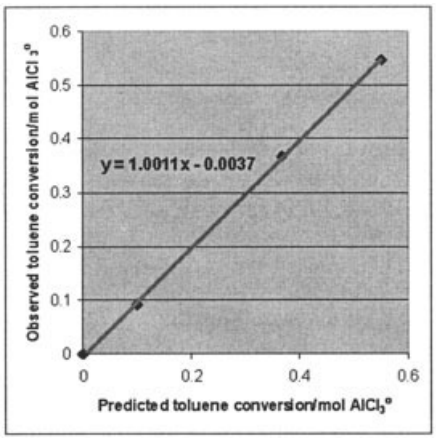

Figure 8. Correlation of toluene conversion with predicted amounts of Brønsted and Lewis Acids in IL.

the aldehyde by forming an adduct with the aldehyde. The stoichiometry for adduct formation will be discussed later.

The reaction can only be initiated by a superacidic species; therefore, no reaction will be observed if no superacidic species is present. This condition is met when the ratio $[AlCl_3/\mathbb{O}^+]^\circ = 1$ for *all values of the HCl partial pressure*. Therefore, we expect that no toluene carbonylation will be observed when $[AlCl_3/\mathbb{O}^+]^\circ = 1$, and that is what we observed.[8,9] When $[AlCl_3/\mathbb{O}^+]^\circ > 1$ and for HCl present in the gas phase, the thermodynamic predictions show that (a) the super acidic, chloroaluminate anion ($ClHAl_2Cl_7^-$) is present to initiate the reaction and to sequester part of the tolualdehyde, and (b) the Lewis acidic chloroaluminate anion ($Al_2Cl_7^-$) is also present to sequester the remaining amount of tolualdehyde. The ultimate conversion of toluene will be governed by the sum of the species that can sequester the aldehyde: $ClHAl_2Cl_7^- + Al_2Cl_7^-$. We may now speculate on the stoichiometry by which the tolualdehyde is sequestered by these two species. From the literature of triflic acid[12] and its hydrates, the water molecules can form adducts with triflic acid, CF_3SO_3H n H_2O, with n = 1/2, 1, 2, and 4. Water is a weak Lewis base in that it shows lone pairs of electrons on the oxygen that can be donated into a Lewis acid, and or can be protonated by a strong Brønsted acid. In this manner, water is similar to tolualdehyde in its interaction with strong Lewis and Brønsted acids and, thus, we expect that tolualdehyde may form an adduct with $ClHAl_2Cl_7^-$ with a stoichiometry of 1/2, 1, 2 or 4. We speculate that the Lewis acidic chloroaluminate anion can sequester at most 1 tolualdehyde molecule. The predicted toluene conversion is n x moles of $ClHAl_2Cl_7^-$ + 1 x moles of $Al_2Cl_7^-$ for values of n = 1/2, 1, 2, or 4. Accordingly, the observed toluene conversion per mole of $AlCl_3$ present initially in the system was plotted *vs.* the fraction of Al originally present as superacidic chloroaluminate anion, and the chloroaluminate anion weighted by the stoichiometry of n tolualdehyde molecules/super acid and 1 tolualdehyde molecule/Lewis acid (Figure 8). Only when n = 1, did the predicted toluene conversion agree with the observed toluene conversion for the cases $[AlCl_3/\mathbb{O}^+]^\circ = 1.0$, 1.1, 1.5, and 2. A slope of one suggests that the assumed stoichiometries for binding the tolualdehyde molecules were true and that the toluene conversion data were correlated with the predicted

Table 1. Correlation of Slope Data from Integrated Rate Plot[9]

HCl Partial Pressure, psia	$ClHAl_2Cl_7^-$, moles	$k[CO][ClHAl_2Cl_7^-]$
0	0	0.0000826
19.7 (135 kPa)	0.663	0.00151
29.7 (204 kPa)	0.748	0.00223
44.7 (308 kPa)	0.817	0.00331

species amounts. These results suggest that the toluene formylation reaction under added HCl gas can be correlated from the results of a simple chemical equilibrium theory. The ultimate conversion to the product aldehyde is predicted well from a consideration of the distribution of super acidic Brønsted ($ClHAl_2Cl_7^-$) and Lewis acid ($Al_2Cl_7^-$) chloroaluminate anions in the IL under HCl gas.

These thermodynamic estimates of the superacidic Brønsted chloroaluminate anion molar amounts can also be used to correlate data of toluene conversion vs. reaction time in a batch reactor for varying partial pressures of HCl. Data[8,9] at low conversion could be correlated with reaction time to produce initial slopes that were equal to the product: $k[CO][ClHAl_2Cl_7^-][AlCl_3]^\circ$ where [CO] is the concentration of CO dissolved in the IL. This dissolved CO concentration depends on the partial pressure of CO above the IL, P_{CO}, the temperature, and the Brønsted acidity of the liquid.[13] Since the slope data were extrapolated to zero conversion, the concentration of product aldehyde is zero and, therefore, the Lewis acidic chloroaluminate anion ($Al_2Cl_7^-$) was assumed to play no role in the chemistry under these "extrapolated" conditions. Accordingly, we seek to fit the slope data to the molar amount of super acidic Brønsted chloroaluminate anion (Table 1).

These data could be correlated on a semilog plot (Figure 9) with the equation shown below

$$\log_{10}\{k[CO][ClHAl_2Cl_7^-]\} = 1.94[ClHAl_2Cl_7^-] - 4.09;$$

$$\text{therefore} \quad k = 10^{(-4.09)} \text{ and } [CO] = \mathscr{H}P_{CO}$$

$$= 10^{\{1.94[ClHAl2Cl7-]\}}/[ClHAl_2Cl_7^-]. \quad (2)$$

From a consideration of these correlations, we suggest that the IL not in contact HCl shows a rate constant for this reaction equal to $10^{-4.09}$, and the effect of HCl on the reactivity of this

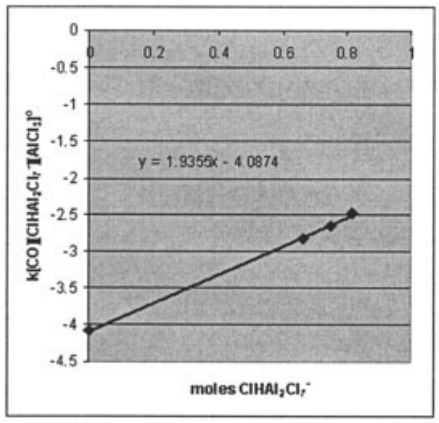

Figure 9. Correlation of integrated rate data.

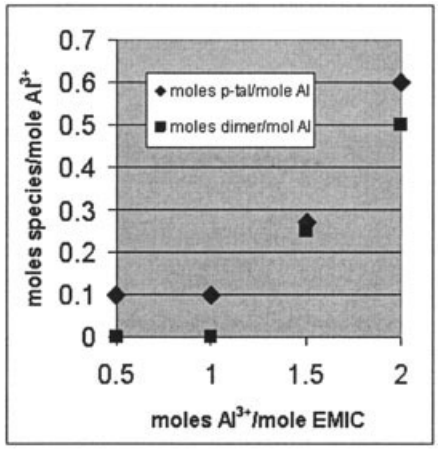

Figure 10. Titration of IL by a Lewis Base.

IL can be correlated directly with the superacidic Brønsted chloroaluminate anion molar amount, predicted from equilibrium thermodynamics, and indirectly through the effect of this super acid on the solubility of the CO in this IL through the effective Henry's law constant, $\mathcal{H}$, Eq. 2.

Data from the literature of arene carbonylation by trifluoromethane sulfonic acid shows that the CO solubility depends on the acid strength of the media.[13] That is, CO is much more soluble in triflic acid ($-H_o = 14.1$) than it is in concentrated sulfuric acid ($-H_o = 12$) at the same temperature and CO partial pressure. This observation is consistent with our correlation where the value of the Henry's Law constant depends on the molar amount of super acidic Brønsted chloroaluminate anion in the IL. The effect of the super acidic Brønsted chloroaluminate anion concentration in the IL upon the CO solubility in the IL is quite significant. When the HCl partial pressure was increased from 19.7 (135 kPa) to 44.7 psia (0.31 MPa), the "apparent" dissolved CO concentration increased by 61% (Eq. 2); whereas, the predicted amount of super acidic Brønsted chloroaluminate anion in the IL increased by only 24%. Measurements of dissolved CO and ($ClHAl_2Cl_7^-$) concentrations in the IL as a function of HCl partial pressure will be necessary to elaborate further the ideas described here.

Titration of IL with a Lewis base. It is possible to confirm the assumed stoichiometry of one aldehyde sequestered for every $Al_2Cl_7^-$ by a simple titration experiment. One equivalent of *p*-tolualdehyde per mol of Al in the sample was added to separate IL's which were prepared having the Al/$\mathbb{O}^+$ ratio of 1/2, 1/1, 1.5/1 and 2/1. Since no HCl was added to this system, we presume that very little Bronsted acid was present. The amount of base and Al was the same in each sample; whereas the amount of EMIM-Cl was varied to develop the desired Al/$\mathbb{O}^+$ ratio. These first two IL's were basic, and neutral (Al/$\mathbb{O}^+$ = 1/2, 1/1); whereas, the last two were acidic (Al/$\mathbb{O}^+$ = 1.5/1 and 2/1). The mixture of *p*-tolualdehyde and IL was heated to 413 K and placed under a vacuum (200 milliT, 26.7 Pa) for 1/2 hour so as to remove the weakly absorbed base. The vaporized base was condensed into a trap held at 77 K. The amount of base remaining in the IL was determined by weighing the amount of base found in the trap and subtracting this amount from the initial mass of base placed in the IL. These results are shown in Figure 10.

For the basic and neutral IL's, the amount of *p*-toluadehyde not found in the LN2 trap was ~ 10% of the amount of Al in the system. One might expect that these two IL's would not retain any of the aldehyde as a result of their intrinsic chemistry and this expectation could be realized if 1) all of the base vaporized from the IL was found in the LN2 trap and 2) the IL's were dry and had not reacted with adventitious water vapor. We speculate that the small amounts of aldehyde not found in the LN2 trap may be explained by a combination of these two reasons. The amount of *p*-tolualdehyde estimated to be retained in the IL increased when increasing the Al/$\mathbb{O}^+$ ratio above unity. On the same figure we show the predicted moles $Al_2Cl_7^-$/mol Al in the IL. Notice that the amount of *p*-tolualdehyde retained in the sample was always slightly greater than the amount of $Al_2Cl_7^-$ predicted to be in the sample. Again, we speculate that a combination of loss of base and/or adventitious moisture may account for the unexpectedly larger amount of base retained in the IL. From the trend with increasing amount of Al in the sample, we conclude that $Al_2Cl_7^-$ does sequester *p*-tolualdehyde in the proportion of 1 mol of aldehyde for every 1 mol of $Al_2Cl_7^-$ (slope of Figure 10 = 1/2 mol p-tolualdehyde/1/2 mol of $Al_2Cl_7^-$). This finding suggests a stoichiometry of 1 mol of the aldehyde for every mole of $Al_2Cl_7^-$ in the IL, and it confirms our use of this stoichiometry (*vide supra*) in predicting the ultimate conversion of toluene.

Discussion

Simple equilibrium thermodynamic calculations were used to predict the composition of chloroaluminate IL's derived from EMIM-Cl and $AlCl_3$ in contact with HCl gas at room-temperature. Equilibrium constants developed by Chandler and Johnson[2] were used in these simulations. Our calculations showed $ClHAl_2Cl_7^-$ was the major Brønsted acidic species while $ClHAlCl_4^-$ and $HAlCl_4$ appeared in very small concentrations. The mole fraction of $ClHAl_2Cl_7^-$ approaches unity for the IL having $[AlCl_3/\mathbb{O}^+]° = 2$ and when the HCl partial pressure approached 500 psia (3.45 MPa). The equilibrium to form $ClHAl_2Cl_7^-$ is favorable as its mole fraction is predicted to be 0.663 when the HCl partial pressure was 19.7 psia (135 kPa), and our calculations suggest that most of the benefit for adding HCl to produce super acidity is realized for HCl partial pressures less than 100 psia (0.69 MPa). Others[2] speculate that $ClHAl_2Cl_7^-$ is a Brønsted super acid and the results shown here for toluene carbonylation are consistent with this speculation. Additionally, the predicted response of the Lewis acidic chloroaluminate species, $Al_2Cl_7^-$, for increasing HCl partial pressure showed that the mole fraction of the Lewis acid decreased as the mole fraction of the Brønsted superacid increased.

When changing the $[AlCl_3/\mathbb{O}^+]°$ from 2 to 3 mol/mol it has been observed that not all of the Al_2Cl_6 dissolved into the liquid, and our calculations suggest that applying HCl gas above the two-phase mixture does not change the solubility of the Al_2Cl_6. The predicted amount of super acidic Brønsted species, $ClHAl_2Cl_7^-$, apparently is not different when P_{HCl} = 500 psia (3.45 MPa) as we increase the $[AlCl_3/\mathbb{O}^+]°$ from 2 to 3 mol/mol: 0.96 vs. 0.92 mol, although the *mole fraction* of $ClHAl_2Cl_7^-$ does decrease from 1/2 to 1/3. If these predictions can be verified by spectroscopic means, the implication is that the super acidic mixture with the largest number of moles of

$ClHAl_2Cl_7^-$ that can be developed results from an IL showing $[AlCl_3/\mathbb{C}^+]^\circ = 2$.

With this simple model we were able to predict the data of ultimate toluene conversion when changing the $[AlCl_3/\mathbb{C}^+]^\circ$ ratio at a constant $P_{HCl} = 44.7$ psia (0.31 MPa), thus, confirming that this reaction is not catalytic, but rather it is a stoichiometric reaction. This prediction assumed that the product aldehyde was sequestered by both ($ClHAl_2Cl_7^-$) and ($Al_2Cl_7^-$) with a stoichiometry of one mole of aldehyde per mole of chloroaluminate species. A simple titration with *p*-tolualdehyde in acidic IL without HCl in the gas phase confirmed this assumption for the ($Al_2Cl_7^-$) species.

The data of initial reaction rate of toluene conversion were correlated with the molar amounts of superacidic Brønsted species, $ClHAl_2Cl_7^-$, by assuming that CO solubility into the IL could be simulated by a simple Henry's law model where the Henry's law constant $\mathcal{H}$, increased with increasing amounts of super acidic Brønsted species, $ClHAl_2Cl_7^-$, in the IL. This favorable CO solubility with increasing acid strength has been observed in other superacidic systems.[13]

The small, positive value observed for $k[CO][ClHAl_2Cl_7^-]$ at zero HCl partial pressure in gas phase may be a result of water contaminating the IL before the reaction was initiated. This water could have reacted with the IL to form HCl *in situ* and, thus, produce the acidity required to initiate the reaction. The magnitude of the reactivity can be estimated by ratoing values of the ordinate of the integrated rate plot (Table 1, $k[CO][ClHAl_2Cl_7^-]$) for the runs with and without HCl added. The reactivity of the samples for which HCl was added was 15–40 times that of the sample for which no HCl was added. Thus, we speculate that the effect of adventitious water was small (~2–7%) upon the observed reaction rates in those runs for which HCl was added. While the effect of this adventitious water was small, it does not alter the essential conclusions that arise from this modeling study: dimeric Al species are largely responsible for the reactivity observed in these IL's.

These calculations predict that the $AlCl_4^-$ mole fraction depends only on the ratio of $AlCl_3/\mathbb{C}^+$ in the starting mixture, and it is also unaffected by the HCl partial pressure. This prediction is contrary to the interpretation of ^{27}Al NMR data reported by Nara et al[6] who showed two peaks in the ^{27}Al NMR spectra of an acidic chloroaluminate/EMIM-Cl melt ($AlCl_3/\mathbb{C}^+ = 2$) whose intensities changed with increasing partial pressure of HCl above the melt. The peak at 73.9 ppm decreased steadily with increasing P_{HCl}, while the peak at 79.3 ppm increased. The peak at 73.9 ppm was attributed to $Al_2Cl_7^-$, while the peak at 79.3 ppm was assigned to $AlCl_4^-$. These species were reported to be influenced by HCl according the equilibrium described in Eq. 1 earlier. This equilibrium would explain the decrease in the NMR signal attributed to the Lewis acid, $Al_2Cl_7^-$, but it would not explain the existence of the superacidic activity documented by the toluene carbonylation reaction since $H^+AlCl_4^-$ is said to exhibit an acidity similar to HF.[2] The acidity of HF alone is not sufficient to catalyze the arene carbonylation reaction. The predictions shown here and the results of the carbonylation reaction suggest that a re-examination is necessary of the NMR assignments reported by Nara et al.[6]

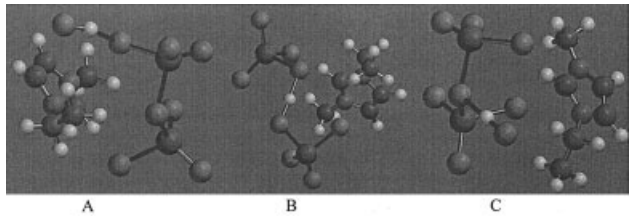

Figure 11. Optimized geometries, at the AM1 level, for (a) $ClHAl_2Cl_7^-$ (b) $AlCl_4HAlCl_4^-$, and (c) $(AlCl_3)_2$-HCl^-.

Each structure is shown with the ethyl-methyl imidazolium cation.

The calculations completed here assumed one structure existed for the dimeric, Bronsted acidic, anionic species: $ClHAl_2Cl_7^-$ (Figure 11a). In the review process for this manuscript, it was suggested that another structure shared the same stoichiometry: $AlCl_4HAlCl_4^-$ (Figure 11b). This new structure prompted us to propose as yet another new structure (Figure 11c).

We determined the enthalpy, entropy and free energy of formation for these anionic structures with the $EMIM^+$ using three semiempirical models: AM1, PM3 and MNDO (Table 2).

These simulations suggest that the new structure proposed by the reviewer shows a free energy of formation that is comparable to the structure found by Chandler and Johnson,[2] although it is from 1/2 to 9 kcal/mol less stable than the established structure, depending on the model used to predict its properties; whereas the new structure that we propose here can be as much as 4 kcal/mol more stable than the structure reported by Chandler and Johnson,[2] depending on the quantum mechanical model that was used to calculate the free energy of formation. Given the uncertainty in the model predictions for these energy functions, we must admit that both new structures are possible and they may exist in equilibrium with the structure proposed by Chandler and Johnson.[2] Additionally, we can examine the effect of these free energies of formation upon the equilibrium constant for reaction 6 in the manuscript

$$HCl + Al_2Cl_7^- \Leftrightarrow ClHAl_2Cl_7^-; \quad K_6 = 0.1$$

Table 2. Energy Functions for the Formation of the Dimeric Al, Bronsted Acidic Species Having the Stoichiometry: $\{Al_2Cl_8H\}^-$

	AM-1 T = 298 K				PM3 T = 298 K				MNDO T = 298 K			
Structure	ΔH_f	ΔS_f	ΔG_f	kcal/mol	ΔH_f	ΔS_f	ΔG_f	kcal/mol	ΔH_f	ΔS_f	ΔG_f	kcal/mol
$ClHAl_2Cl_7^-$	−333.008	0.19669	−391.622		−370.078	0.201886	−430.24		−316.098	0.201552	−376.16	
$AlCl_4HAlCl_4^-$	−328.767	0.194425	−386.706		−368.635	0.204897	−429.694		−304.811	0.21138	−367.802	
$AlCl_3-Cl$—HCl—$AlCl_3^-$	−331.55	0.199699	−391.061		−366.936	0.204178	−427.781		−316.297	0.213872	−380.031	

We recalculated the equilibrium constant for the same reaction but with the proposed new structures, and their free energies of formation according to these reactions

$$HCl + Al_2Cl_7^- \Leftrightarrow AlCl_4—H—AlCl_4^-; \quad K_6' = ?$$

$$HCl + Al_2Cl_7^- \Leftrightarrow AlCl_3—Cl—HCl—AlCl_3^-; \quad K_6'' = ?$$

The new equilibrium constants are different by only 1–2% from that reported by Chandler and Johnson,[2] depending on the model used to determine the free energy of formation. Thus, we conclude that our predictions for the existence of a dimeric, Al Bronsted acidic species will not be changed when one considers this proposed new structures and as the reviewer suggested, the speciation of these agents will likely involve an equilibrium between these structures, each having the same stoichiometry: $\{Al_2Cl_8H\}^-$.

Conclusions

Simple equilibrium thermodynamics can be used to identify the species in the IL, superacidic Brønsted ($ClHAl_2Cl_7^-$) and Lewis acidic ($Al_2Cl_7^-$) chloroaluminate anions, that are responsible for the observed ultimate conversion of toluene to tolualdehyde. These calculations predict the systematic increase in the *ultimate* toluene conversion as the ratio $[AlCl_3/\mathbb{C}^+]^o$ was varied from 1 to 2. The initial rates of the carbonylation reaction in the IL were correlated with the predicted molar amounts of the superacidic Brønsted chloroaluminate anions assuming that the CO solubility also depended on the molar amounts of an acidic species having the stoichiometry: $HAl_2Cl_8^-$. Our predictions suggest that the solubility of Al_2Cl_6 in the IL cannot be changed by increasing the HCl partial pressure above it. While these predictions were not contradicted by visual observations, more accurate direct measurements of the species must be completed to confirm our predictions.

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Literature Cited

1. Wasserscheid P, Welton T. *Ionic Liquids in Synthesis*.Weinheim: Wiley-VCH; 2003.
2. Chandler WD. Johnson KE. Thermodynamic Calculations for Reactions Involving Hydrogen Halide Polymers, Ions, and Lewis Acid Adducts. 3. Systems Constituted from Al^{3+}, H^+ and Cl^-. *Inorg Chem*. 1999;38:2050-6.
3. Olah GA, Ohannesian L, Arvanaghi M. Formylating agents. *Chem Rev*. 1980;87:671; Olah GA, Laali K, Farooq O. Aromatic substitution. 52. Superacid-catalyzed carbonylation of aromatics with carbon monoxide. *J Org. Chem*. 1985;50:1483-6.
4. Toniolo M, Graziani J, *Organometallic Chemistry*. 1980;194:221-228; Smith BM. *Integrated Laboratory Systems, Aluminum Compounds*. Review of Toxicological Literature, Abridged Final Report; October 2000.
5. Wasserscheid P, Keim W. Ionic Liquids-New Solutions for Transition Metal Catalysis. *Angew Chem Int Ed*. 2000;39:3772-89.
6. Nara SJ, Harjani JR, Salunkhe MM. Friedel–Crafts Sulfonylation in 1-Butyl-3-methylimidazolium Chloroaluminate Ionic Liquids. *J Org Chem*. 2001;66:8616-8620.
7. Takahashi S, Curtiss LA, Gosztola D,. Koura N, Saboungi ML. Molecular Orbital Calculations and Raman Measurements for 1-Ethyl-3-methylimidazolium Chloroaluminates. *Inorg Chem*. 1995;34:2990-3.
8. Angueira EJ, White MG, AIChE. Annual Meeting, San Francisco, CA, November, 2003;pp 511a.
9. Angueira EJ, White MG. Arene Carbonylation in Acidic, Chloroaluminate Ionic Liquids. *J Mol Catal. A: Chemical,* 2005;227:51–58.
10. Doug Gordon, private communication, Hoechst Celanese Corporation, Technical Center, Corpus Christi, Texas; May 30;1995.
11. Sood DS, Sherman SC, Iretskii AV, Kenvin JC, Schiraldi DA, MG White, Formylation of toluene in triflic acid. *J Catalysis.* 2001;199:149.
12. DeLaplane RG, Lundgren JO, Olovson I, Acta Crystallogr. Sect. B. 1975;31:2202.
13. Booth BL, Fekky El. A comparison of the effectiveness of sulfuric acid and trifluoromethanesulfonic acid in Koch carboxylation reactions. *J C S Perkin I*, 1979;2441-6.

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