THERMODYNAMICS OF 1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE — ALUMINUM CHLORIDE MIXTURES

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ABSTRACT

A thermodynamic model for liquid mixtures of 1-methyl-3-ethylimidazolium chloride — aluminum chloride is presented. The model is based on EMF and vapor pressure measurements. It assumes the presence of the anions, Cl⁻, AlCl₄⁻, Al₂Cl₇⁻, Al₃Cl₁₀⁻, as well as Al₂Cl₆ and equilibria between them. The most remarkable feature of this system is the strong dependence of AlCl₃ activity on composition in the acidic region and the presence of Al₃Cl₁₀⁻ as a dominant species around 75 mol % AlCl₃.

INTRODUCTION

Melt mixtures of 1-methyl-3-ethylimidazolium chloride (MEICl) — aluminum chloride are molten at room temperature for aluminum chloride concentrations between 30 and 67 mole % (1). Its Lewis acidity varies within a wide range from the very basic melt with excess MEICl to the acidic melts with excess aluminum chloride. The melt mixtures are of interest as a battery electrolyte, a solvent for unusual oxidation states, and as a homogeneous catalyst for organic reactions.

Recently the melts have been characterized thermodynamically between 46 and 68 mole % AlCl₃ by EMF measurements using aluminum electrodes (2). A study extended further into the acidic range is of importance to obtain a complete thermodynamic description of the melts and to clarify which species are present throughout the composition range. Using a vapor pressure method, activities with respect to liquid aluminum chloride can be calculated and a thermodynamic model can be constructed which predicts vapor pressure, activities, and the EMF's of galvanic cells.

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EXPERIMENTAL

The vapor pressure was obtained by a boiling point method. The principle and theory of this method have been given by Motzfeldt, Kvande, and Wahlbeck (3) and only a short outline is presented here. The sample is contained in a cell with a capillary opening, in the present case made from pyrex glass (cf. Fig. 1). The cell is placed in a recording thermobalance and brought to temperature under N\textsubscript{2} pressure. Theoretical treatment of the transport processes (3) gave the following expression for the rate of weight change \( \dot{w} \):

\[
-\dot{w} = C \left( \frac{P \exp(\dot{w}/B)}{1-\exp(\dot{w}/A)} - P_F^2 \right)
\]

In this equation, \( P_F \) is the external pressure, and \( P \) is the equilibrium vapor pressure of the melt. The parameters \( A \), \( B \), and \( C \) are related to gas diffusivity, heat transfer and gas viscosity, respectively, but for the present purpose may be considered empirical constants for a given experiment at constant temperature. What is important here is that Eqn. 1 allows calculation of \( P \) from the experimental quantities, \( P_F \) and \( \dot{w} \).

A commercial thermogravimetric analyzer was used for our studies (Perkin-Elmer TGA7 Thermogravimetric analyzer). It was connected to a MENSOR Quartz manometer/controller™ with a nitrogen reservoir and a vacuum pump. The TGA7 was fully computerized but could only take total weight of 5 grams including the crucible. To accommodate the crucible and achieve a larger zone of constant temperature, the low-temperature furnace of the TGA7 was replaced with a larger furnace made of a quartz tube with externally wound 0.2 mm Pt wire having the same resistance as the original furnace, 8.5Ω.

In earlier work on chloroaluminates (4,5,6), the initial outer pressure was larger than the vapor pressure and the outer pressure was then stepwise lowered, the weight loss increasing markedly when the outer pressure becomes lower than the equilibrium vapor pressure. The vapor pressure was obtained by a fitting of the mass loss data to Eqn. 1. As the evaporating gas had a composition different from that of the melt, a continuous change in melt composition resulted. This was accounted for by correction procedures (5,6).

The problem with a changing composition of the melt during the present experiment is much more serious due to the smaller sample size (2 g versus 40 g) and a very strong dependence of vapor pressure on composition. Using the procedure mentioned above led to having to "chase" a rapidly diminishing pressure. The resulting break in the weight loss curve was not sufficiently pronounced and the correction procedure was difficult to employ. It was then decided to change the
procedure and turn this apparent weakness of the present set-up into an advantage.

The first modification was to lower the initial external pressure below the equilibrium pressure, and then let the sample boil itself toward the composition which corresponds to the external pressure. The equilibrium pressure was determined from the weight loss as follows:

In the chosen pressure range where \( P_f < P \), Eqn. 1 is simplified to

\[ - \dot{w} = C[P_{\exp}(\dot{w}/B)^2 - P_f^2] \]  

neglecting diffusive gas flow.

As the weight change \( \Delta w \) for one experiment with constant \( P_f \) is small relative to the total weight and the gas consists only of aluminum chloride

\[ \Delta X_A = k' \Delta w \]  

where

\[ k' = \frac{X_A(1-X_A) + (1-X_A)^2}{w} \frac{(M_{MEICl}/M_{AlCl3})}{w} \]

where \( M \) is the molecular weight of the subscripted species, \( X_A \) denotes the stoichiometric mole fraction of \( AlCl_3 = n_{AlCl3}/(n_{AlCl3} + n_{MEICl}) \), and \( w \) is the sample weight.

For a limited range, the vapor pressure of \( Al_2Cl_6 \) is assumed to follow the relation

\[ d \ln P = k'' d X_A \]  

Eqns. 2-4 gives the following differential equation for the weight change rate

\[ - \dot{w} = C[P_0^2 e^{a\Delta w} e^{aw} - P_f^2] \]  

where \( P_0 \) is the pressure at the start of the experiment at time \( t=0 \) and \( \Delta w=0 \), \( a=2k'k'' \) and \( \alpha=2/B \). This equation can only be solved for \( |aw| < 1 \), so that

\[ e^{aw} = 1 + aw \]
This gives

\[
\dot{w} = \frac{C_P^2 e^{a\Delta w} - C_P^2}{1 + aC_P^2 e^{a\Delta w}}
\]  \hspace{1cm} (6)

and integration of Eqn. 6 gives:

\[
\frac{\Delta w}{C_P^2} - \frac{1}{a} \left[ \frac{1}{C_P^2} + \alpha \right] \ln \left( \frac{p_0^2 e^{a\Delta w} - p_F^2}{p_0^2 - p_F^2} \right) = t
\]  \hspace{1cm} (7)

The quantities \(p_0\) and \(a\) can be obtained in an iterative fashion and the constants \(C\) and \(\alpha\) by fitting of Eqn. 5, 6 or 7. A two point fitting is most easily done by the use of Eqn. 5 as the experiments give both \(w\) and \(\Delta w\) and no approximation is involved. The fitting is done for \(t=0\) where \(\Delta w=0\) and for the end time, \(t\).

After determination of \(\alpha\) and \(C\), \(\Delta w\) for \(\dot{w} = -0.1\ \text{mg/min}\) is calculated. The composition of the melt which has this weight change \(\Delta w\) is now taken to be the melt which has a vapor pressure \(p_F\). The rationale for setting \(\dot{w} = -0.1\ \text{mg/min}\) instead of 0 was justified from calibration experiments with ethyleneglycol combined with the fact that Eqn. 5 will extrapolate the data too far due to neglect of diffusive gas flow. Examples of experimental data are shown in Fig. 2. This procedure worked well for external gas pressures in the range 0.4 - 0.7 atm., but at lower external pressures, the time \(t\) for \(\dot{w} = -0.1\ \text{mg/min}\) becomes exceedingly long making the extrapolation procedure uncertain.

In the second modification, the initial external pressure was again lowered below the equilibrium vapor pressure resulting in boil-off of \(\text{AlCl}_3\). But the external pressure was increased in steps until boiling stopped as indicated by the levelling off of the rate of weight loss. The composition at that point corresponded to a melt which had the vapor pressure \(p_F\). For both methods, melt mixtures from 80 to 66 mol % could be studied with a single experimental sample. It was however necessary to raise the temperature when the vapor pressure became too low for easy measurements (< 0.05 atm).

III. THERMODYNAMIC MODEL AND CALCULATIONAL PROCEDURES

The model assumed the following melt species to be present in the melt: 1-methyl-3-ethylimidazolium (MEI+), Cl-, \(\text{AlCl}_4^-\), \(\text{Al}_2\text{Cl}_7^-\), \(\text{Al}_3\text{Cl}_{10}^-\), and \(\text{Al}_2\text{Cl}_6\).
Three independent equilibria are formulated between the species:

\[ \text{AlCl}_4^- = \text{Cl}^- + 0.5 \text{Al}_2\text{Cl}_6 \quad \frac{a_1 a_6^{0.5}}{a_4} = K_I \] (8)

\[ \text{Al}_2\text{Cl}_7^- = \text{AlCl}_4^- + 0.5 \text{Al}_2\text{Cl}_6 \quad \frac{a_4 a_6^{0.5}}{a_7} = K_{II} \] (9)

\[ \text{Al}_3\text{Cl}_{10}^- = \text{Al}_2\text{Cl}_7^- + 0.5 \text{Al}_2\text{Cl}_6 \quad \frac{a_7 a_6^{0.5}}{a_{10}} = K_{III} \] (10)

where  

\[ a_i = Y_i X_i \] (11)

the subscript referring to the number of Cl's present in each species, and

\[ K_I = \exp \left\{ \frac{\Delta H_I^\circ (T)}{RT} + \frac{\Delta S_I^\circ (T)}{R} + \frac{\Delta C_{p,I}^\circ}{R} \left[ \ln \frac{T}{T_0} + \frac{T_0 - T}{T} \right] \right\} \] (12)

where \( T \) is the temperature of the experiment and \( T_0 \) is the standard temperature.

\( X_i \) is defined as a modified Temkin ion fraction (7), i.e. as an anion fraction where the neutral \( \text{Al}_2\text{Cl}_6 \) is counted among the anions. From this definition the following mass balance equilibria are obtained:

\[ X_4 + 2X_7 + 3X_{10} + X_6 (2 - X_A)/(1 - X_A) = X_A/(1 - X_A) \] (13)

and

\[ X_1 + X_4 + X_7 + X_{10} + X_6 = 1 \] (14)

where \( X_A \) is defined as at Eqn. 3.

Presently the activity coefficients \( Y_i \) in Eqn. 5 are set equal to unity. This is equivalent to setting them to be constant and incorporating them into the equilibrium constants. The \( \Delta C_{p,I}^\circ \) in Eqn. 12 is set equal to zero. Knowing \( K_I, K_{II}, \) and \( K_{III}, \) as functions of temperature, Eqns. 8-14 can then be used to calculate the five ion fractions as well as the activity \( a_6. \)
The program MODFIT (8) programmed for a personal computer was used to determine the equilibrium constants $K_I$, $K_{II}$, and $K_{III}$, by minimizing

$$F = \sum (\log a_6 [\text{exp}] - \log a_6 [\text{calc}])^2$$

This criteria is equivalent to a relative least square fit of the values proper, but avoids the very small numbers for basic melts.

The experimental total vapor pressures were converted to activities utilizing data from the JANAF tables (9) as well as considering the small amount of $\text{AICI}_3$ in the vapor phase:

$$\text{AlCl}_3 (1) = \text{AlCl}_3 (g) \quad (15)$$

$$K_{15} = \exp \{76.65 - 13159.6 \ T^{-1} - 9.474 \ \ln T + 7.93 \times 10^{-3}T$$
$$- 3.903 \times 10^{-6}T^2 + 1.3 \times 10^{-9}T^3 - 0.1929.10^{-12}T^4\}$$

$$2 \ \text{AlCl}_3 (g) = \text{Al}_2\text{Cl}_6 (g) \quad (16)$$

$$K_{16} = \exp \{-23.6162 + 15588.4 \ T^{-1} + 0.5482 \ \ln T + 3.32 \times 10^{-3}T$$
$$- 1.96 \times 10^{-6}T^2 + 0.774.10^{-9}T^3 - 0.137.10^{-12}T^4\}$$

The activity $a_6$ is then given as:

$$a_6 = \frac{P_{\text{Al}_2\text{Cl}_6}}{P_{\text{AlCl}_3}} \cdot \frac{B - \sqrt{B^2 - 4P^2_{\text{tot}}}}{2K_{15} \cdot K_{16}^2} \quad (17)$$

where $B = 2P_{\text{tot}} + 1/K_{15}$. As the internal transport number of $\text{MEI}^+$ is unity (10,11), the EMF data can be transferred to activity by the relationship (12):

$$d \ln a_6 = -\frac{6F}{RT} \left[\frac{1 - X_A}{1 + 2X_A}\right]dE \quad (18)$$

The integration constant was chosen so that this EMF data overlaps with the vapor pressure data.

Although Eqns. 8-14 are a straightforward set of equations to solve for the anion fractions and the $a_6$ activity in an iterative fashion, the solution may easily diverge if proper starting values and restrictive conditions are not introduced, especially near the equivalence points, $X_A(\text{eq}) = 0.50, 0.667$ and 0.75. The following procedure was successful. Close to the equivalence points, $X_A =$
$X_{A(eq)} \pm 0.02$, the majority species was first calculated for the equivalence composition assuming only the three most prominent species present. Then the second most prominent species was calculated for the same composition. The three remaining species were calculated from Eqns. 8-10. A better value for the second species was then calculated from Eqn. 13 by requiring the ratio between the two most prominent species to be unchanged, and an improved value was then obtained for the first species from Eqn. 14. The process was repeated until all mole fractions changed with less than ±0.00001. Further apart from the equivalence point, the iteration procedure was less critical and the starting values were calculated considering only the two major species. Using this procedure the final result for each composition was usually obtained with less than 10 iterations. To find the best set of $K_1$, $K_{II}$, and $K_{III}$, the constants were first varied one at a time and afterwards all constants were varied simultaneously.

IV. RESULTS

The original EMF data were averaged from two or three independent experiments and integrated to obtain activities using Eqn. 18 and are given below. For the three different temperatures, the activities of $\text{Al}_2\text{Cl}_6$ for $X_A = 0.60$ have been arbitrarily set equal to unity.

40°C

| $X_A$  | 0.4745 | 0.4798 | 0.4853 | 0.4903 | 0.4952 |
|-------|--------|--------|--------|--------|--------|
| log $a_6$ | -29.983 | -29.755 | -29.446 | -29.085 | -28.533 |

| | 0.5204 | 0.5310 | 0.5415 | 0.5504 | 0.5595 | 0.5691 |
|---|---|---|---|---|---|---|
| | -1.869 | -1.465 | -1.168 | 0.902 | -0.696 | -0.506 |

| | 0.5798 | 0.5904 | 0.6003 | 0.6102 | 0.6205 | 0.6308 |
|---|---|---|---|---|---|---|
| | -0.324 | -0.141 | 0.041 | 0.209 | 0.430 | 0.689 |

| | 0.6411 | 0.6511 | 0.6612 | 0.6714 |
|---|---|---|---|---|
| | 1.039 | 1.435 | 2.036 | 2.873 |

50°C

| $X_A$  | 0.4850 | 0.4906 | 0.4948 | 0.5211 | 0.5288 | 0.5387 |
|-------|--------|--------|--------|--------|--------|--------|
| log $a_6$ | -29.222 | -28.567 | -28.048 | -1.806 | -1.541 | -1.283 |

| | 0.5509 | 0.5598 | 0.5698 | 0.5791 | 0.5897 | 0.5999 |
|---|---|---|---|---|---|---|
| | -0.972 | -0.767 | -0.562 | -0.372 | -0.175 | 0.002 |

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The vapor pressure data were transformed into $a_g$ by Eqn. 17 ignoring the presence of AlCl$_3$ i.e. $a_g = \frac{P_{tot}}{K_{9Kg^2}}$:

$t^\circ C$ | 206 | 236 | 267 | 191 | 191 | 191
--- | --- | --- | --- | --- | --- | ---
$X_A$ | 0.7572 | 0.7281 | 0.7114 | 0.7788 | 0.7665 | 0.7383
$log a_g$ | -0.611 | -0.961 | -1.360 | -0.427 | -0.552 | -1.030

219 | 219 | 265
0.7233 | 0.7118 | 0.7049
-1.278 | -1.676 | -1.701

In order to get a smooth overlap between the EMF and the vapor pressure data, the value 6.5 was subtracted from all log $a_g$ data obtained by EMF measurement. The fit gave the following parameters:

| | I | II | III |
--- | --- | --- | --- |
$\Delta H$ (kJ) | 55.40 | 2.81 | 6.21 |
$\Delta S$ (J/K) | -191 | -53 | 0.9 |
$log K$ (40°C) | -19.2 | -3.2 | -1.0 |

with a standard deviation in the fit equal to 0.107. Figure 3 shows the activity $a_g$ for $t=40^\circ C$ and $t=250^\circ C$ and the calculated concentration of the different species for $t=250^\circ C$. It must, however, be stressed that the data are preliminary and more accurate data are expected to be obtained after performing further experiments. It should also be remembered that the mole fraction is calculated assuming the activity coefficients to be constants. Higher polymeric anions with four or more Al atoms may also be present.

Nevertheless three features stand out:
1. Acidic melts are stable versus gaseous decomposition up to at least 300°C even if they attain a dark color.

2. Not only is the activity change tremendous around 50 mol % AlCl₃, but the AlCl₃ activity changes much more strongly with composition in the acidic region than for alkali chloroaluminate melts.

3. Substantial amounts of higher polymers like Al₃Cl₁₀⁻ must be present to explain the strong change in AlCl₃ activity around Xₐ = 0.75.

Raman spectroscopic studies are under way to clarify the presence of higher polymers.

ACKNOWLEDGEMENT

The expert glassblowing and other help from Mr. Fred C. Kibler is greatly appreciated as well as the sample preparation by Mr. Steve Keeley. We also thank Missy Landess for expert word processing and assisting in editing this manuscript.
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Figure 1. Capillary cell used for vapor pressure measurements.

Figure 2. Experimental weight loss data. $T = 191{}^\circ$C, outer pressure of 0.5613 atm, and composition at equilibria of $X_A = 0.7675$. 

To Thermal Balance

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TGA File Name: in10
Sample Weight: 0.000 mg
Fri Apr 17 22:50h 24 1987

7 Series Thermal Analysis System

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TGA 1st Derivative in10
Sample Weight: 0.000 mg
Fri Apr 17 22:50h 24 1987

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Figure 3. Activity of Al$_2$Cl$_6$ at 40 and 250°C and species concentration at 250°C from model calculations.