

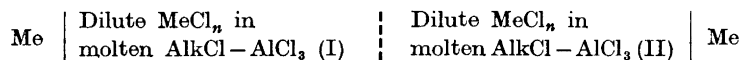
## EMF Studies in Aluminium Chloride Systems

### I. Utilization of Concentration Cells with Dilute Metal Chlorides

HARALD A. ØYE

*Universitetet i Trondheim, Norges tekniske høgskole, Institutt for uorganisk kjemi,  
N-7034 Trondheim-NTH, Norway*

The information to be gained from studies of concentration cells:



is discussed. The emf of the cell is given as:

$$\Delta E = \frac{1}{F} \int_I^{II} \frac{1}{n} (1 - t_{\text{Me}}) d\mu_{\text{MeCl}_n} - t_{\text{Alk}} d\mu_{\text{AlkCl}} - \frac{1}{3} t_{\text{Al}} d\mu_{\text{AlCl}_3}$$

It is shown that the cell is useful in determining the free energy of complexation in these melts and what kinds of statistical models for the melt mixture can be chosen.

Dilute solution of transition metal ions may be used as a structural probe for molten salts, revealing the conditions and the structure of the bulk melt as well as the local structure around the probe ions.

Previously Øye and Gruen<sup>1,2</sup> used dilute solutions of  $\text{CoCl}_2$  as a probe for molten chlorides. From studies of the coordination of  $\text{Co}^{2+}$  and utilizing a general acid-base concept

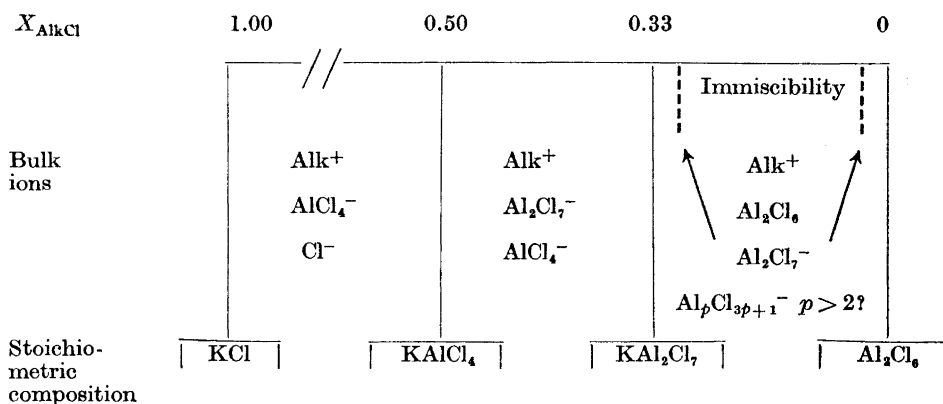


the salts could be divided in three classes with decreasing acidity.<sup>2</sup> These are:



All three classes were realized within the system  $\text{KCl} - \text{AlCl}_3$  which was studied in detail. The bulk melt structure found for  $\text{KCl} - \text{AlCl}_3$  is expected to be similar for mixtures of all the alkali chlorides with aluminium chloride, and the radically changing electrostatic and acid-base characteristics in  $\text{AlkCl} - \text{AlCl}_3$  systems make them desirable systems for studying coordination equilibria of  $\text{Co}^{2+}$  as well as using  $\text{Co}^{2+}$  as dilute probe ions for the bulk melt structure.

The structure may be summarized as follows:



The existence of the species Al<sub>2</sub>Cl<sub>6</sub>, Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> and AlCl<sub>4</sub><sup>-</sup> are firmly established. The Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> species, the existence of which has been subject to discussion, has recently been identified by Raman spectroscopy.<sup>3a,b</sup> This paper also gives further references to structural studies of AlkCl–AlCl<sub>3</sub> systems.

In addition, the Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> might possibly appear together with further polymerized species<sup>3b</sup> Al<sub>p</sub>Cl<sub>3p+1</sub><sup>-</sup>,  $p > 2$ . We do not expect these species to be a predominant constituent except possibly in the composition range close to pure aluminium chloride. Raman studies are in progress for determining the extent of such species.\*

In order to bring the spectroscopic studies on firmer ground, it is necessary to have more information of the free energies of these systems. The present paper aims to point out what information can be gathered by means of electrochemical concentration cells using the transition metal as electrode and dilute indicator constituent.

#### CALCULATION OF EMF

The following concentration cell will be considered:



The general expression for the emf,  $\Delta E$ , of such a concentration cell may be written<sup>4</sup>

$$\Delta E = -\frac{1}{F} \int_{\text{II}}^{\text{I}} \sum_{i=1}^k t_i \left( -\frac{d\mu_i}{z_i} + \frac{d\mu_k}{z_k} \right) \quad (\text{const. } T) \quad (1)$$

where  $F$  is Faraday constant,  $t$  external transport number,  $\mu$  chemical single ion potential,  $z$  charge number. The summation is carried over all ions in the

\* Note added in proof: Newer studies confirm the existence of further polymerized species.

system including the ion reversible to the electrodes. This ion is marked with the subscript  $k$ . The equation is composed of quantities experimentally not amenable, but the single ion chemical potentials can always be combined to the chemical potentials of neutral salts, *i.e.* eqn. (2).

For binary systems which this system approximates, it can be shown that the emf is independent of the form of the concentration gradient or the reference system <sup>5,6</sup> for the transport number, *i.e.* whether the transport numbers are external or internal.

The right hand electrode (II) is the positive pole when the cell reaction takes place spontaneously, and the equation gives a positive  $\Delta E$  for this reaction.

Carrying out the summation for the concentration cell and combining single ion potentials to those of the neutral compounds, we obtain:

$$F\Delta E = \int_I^{II} \frac{1}{n} (1 - t_{Me}) d\mu_{MeCl_n} - t_{Alk} d\mu_{AlkCl} - \frac{1}{3} t_{Al} d\mu_{AlCl_3} \quad (2)$$

To simplify the expressions, the charge signs have been omitted when the ion is used as a subscript, *i.e.*

$$t_{Me^{n+}} = t_{Me}$$

For dilute solutions of  $Me^{n+}$ ,  $t_{Me} \simeq 0$  and hence:

$$F\Delta E = \int_I^{II} \frac{1}{n} d\mu_{MeCl_n} - t_{Alk} d\mu_{AlkCl} - \frac{1}{3} t_{Al} d\mu_{AlCl_3} \quad (3)$$

In view of the dilute solution of  $MeCl_n$ , the Gibbs-Duhem relation may approximately be formulated for the two major constituents,  $AlkCl$  and  $AlCl_3$  only:

$$X_{AlkCl} d\mu_{AlkCl} + X_{AlCl_3} d\mu_{AlCl_3} = 0 \quad (4)$$

where  $X$  denotes the mol fraction.

Combining eqns. (4) and (3) yields:

$$F\Delta E = \int_I^{II} \frac{1}{n} d\mu_{MeCl_n} + \left( -t_{Alk} + \frac{t_{Al} X_{AlkCl}}{3X_{AlCl_3}} \right) d\mu_{AlkCl} \quad (5)$$

Eqn. (5) summarizes how the emf is related to experimental quantities. It uses only thermodynamic reasoning with the additional assumption of the noninterference of the dilute  $MeCl_n$  on the bulk properties.  $t_{Alk}$  and  $t_{Al}$  may here be visualized as external transport numbers but can equally well be the transport numbers relative to the  $Cl^-$  ions. This concentration cell is useful in testing different models for the melt, *i.e.* which species and equilibria are prevalent in the melt, as well as for the dilute ions.

We will in the following demonstrate how different expressions for the emf are obtained depending on the model chosen.

From spectroscopy <sup>3a,b</sup> it was found that the  $Al^{3+}$  ion either exists as the neutral species  $Al_2Cl_6$  or as the anionic monovalent species  $AlCl_4^-$ ,  $Al_2Cl_7^-$ ,

and possibly  $\text{Al}_p\text{Cl}_{3p+1}^-$ ,  $p \geq 3$ . In view of this, it is reasonable to assume that negligible current will be carried by the  $\text{Al}^{3+}$  ions, the carriers being only  $\text{Alk}^+$  for  $X_{\text{AlkCl}} \leq 0.5$  and  $\text{Alk}^+$  and  $\text{Cl}^-$  for  $X_{\text{AlkCl}} > 0.5$ .

Hence by introducing:

$$t_{\text{Alk}} + t_{\text{Cl}} = 1 \quad (6)$$

$$F\Delta E = \int_I^{II} \frac{1}{n} d\mu_{\text{MeCl}_n} - t_{\text{Alk}} d\mu_{\text{AlkCl}} \quad (7)$$

This reasoning tacitly implies external transport numbers. The argument will be just as valid, however, using relative transport numbers with  $\text{Cl}^-$  ions as a reference, but then the relative transport number of  $\text{Al}^{3+}$  will only be negligible for  $X_{\text{AlkCl}} \leq 0.5$ .

Transforming to activities and giving eqn. (7) in its differential form we have:

$$\frac{FdE}{RT} = \frac{1}{n} d \ln a_{\text{MeCl}_n} - t_{\text{Alk}} d \ln a_{\text{AlkCl}} \quad (8)$$

We will then introduce the Temkin model <sup>7</sup> for the system. In the Temkin model the activity is set equal to:

$$a_{\text{Me}_a\text{A}_b} = a_{\text{Me}}^a a_{\text{A}}^b = X'_{\text{Me}}{}^a X'_{\text{A}}{}^b \quad (9)$$

where  $X'_{\text{Me}}$  and  $X'_{\text{A}}$  are the cation and anion fraction, respectively.

The Temkin model will be suitable for  $\text{AlkCl}$ -rich mixtures where only ionic species are assumed. For  $\text{AlCl}_3$ -rich mixtures, where also uncharged species as  $\text{Al}_2\text{Cl}_6$  may be present, we would like to introduce a modified Temkin model where uncharged species are classified together with anionic species. As  $\text{Alk}^+$  will be the only cation present in this melt system except for a possible minute amount of  $\text{Me}^{2+}$  we will according to the Temkin model set  $X'_{\text{Alk}} = 1$  and hence  $d \ln X'_{\text{Alk}} = 0$ .

Eqns. (8) and (9) then simplify to:

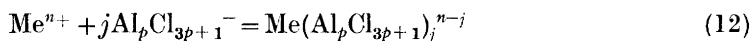
$$\begin{aligned} \frac{FdE}{RT} &= \frac{1}{n} d \ln X'_{\text{Me}} + d \ln X'_{\text{Cl}} - t_{\text{Alk}} d \ln X'_{\text{Alk}} - t_{\text{Alk}} d \ln X'_{\text{Cl}} \\ \frac{FdE}{RT} &= \frac{1}{n} d \ln X'_{\text{Me}} + (1 - t_{\text{Alk}}) d \ln X'_{\text{Cl}} \end{aligned} \quad (10)$$

*Model A.* The dilute metal ion does not interact with the melt and exists as weakly solvated ions. The amount of  $\text{Cl}^-$  ions is assumed negligible, *i.e.*  $t_{\text{Alk}} = 1$ . This is a model that might be close to physical realities for  $X_{\text{AlkCl}} < 0.5$ . The change in emf from eqn. (10) is then given as:

$$\frac{FdE}{RT} = \frac{1}{n} d \ln X'_{\text{Me}} \quad (11)$$

If this is a proper model no change in the emf with composition should be observed if the mol fraction of the metal ion is kept constant.

*Model B.* The dilute metal ion interacts strongly with the bulk melt species. The amount of  $\text{Cl}^-$  ions is assumed negligible, *i.e.*  $t_{\text{Alk}} = 1$ . This is an alternate model for  $X_{\text{AlkCl}} < 0.5$ .



$$\frac{X'_{\text{Me-Al-Cl}}}{X'_{\text{Me}} X'^j_{\text{Al-Cl}}} = K' \quad (13)$$

$$d \ln X'_{\text{Me}} = d \ln X'_{\text{Me-Al-Cl}} - j d \ln X'_{\text{Al-Cl}} \quad (14)$$

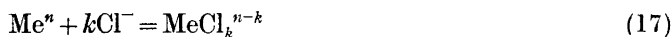
Combining eqns. (10) and (14) setting  $t_{\text{Alk}} = 1$ :

$$\frac{nF dE}{RT} = d \ln X'_{\text{Me-Al-Cl}} - j d \ln X'_{\text{Al-Cl}} \quad (15)$$

*Model C.* The saturated concentration of  $\text{MeCl}_n$  is reached and  $\text{MeCl}_n(\text{s})$  is present. We still assume the amount of  $\text{Cl}^-$  ions negligible and  $t_{\text{Alk}} = 1$ . This is a model that can be realized experimentally close to the composition  $\text{AlkAlCl}_4$  the metal chloride being for instance  $\text{NiCl}_2$ . From eqn. (10):

$$\begin{aligned} \frac{F dE}{RT} &= \frac{1}{n} d \ln X'_{\text{Me}} = \frac{1}{n} d \ln X'_{\text{MeCl}_n} - d \ln X'_{\text{Cl}} \\ \frac{F dE}{RT} &= -d \ln X'_{\text{Cl}} \end{aligned} \quad (16)$$

*Model D.*  $\text{Cl}^-$  ions present and  $t_{\text{Alk}} \leq 1$ . The dilute metal ions form chloride complexes  $\text{MeCl}_k^{n-k}$ .



$$\frac{X'_{\text{Me-Cl}}}{X'_{\text{Me}} X'^k_{\text{Cl}}} = K'' \quad (18)$$

$$d \ln X'_{\text{Me}} = d \ln X'_{\text{Me-Cl}} - k d \ln X'_{\text{Cl}} \quad (19)$$

Combining eqns. (10) and (19):

$$\frac{nF dE}{RT} = d \ln X'_{\text{Me-Cl}} - (nt_{\text{Alk}} + k - n) d \ln X'_{\text{Cl}} \quad (20)$$

## DISCUSSION

For melts where  $X_{\text{AlkCl}}/X_{\text{AlCl}_3} < 1$  the  $\text{Cl}^-$  ions from  $\text{AlkCl}$  will be bonded to  $\text{AlCl}_3$  forming  $\text{Al}_2\text{Cl}_7^-$  and  $\text{AlCl}_4^-$  species.<sup>3a,b</sup> As  $\text{Al}^{3+}$  has a higher ionic strength than most transition ions, the transition ions will not be able to coordinate directly with chloride ions but will be strongly or weakly solvated with the  $\text{Al-Cl}$  species formed in the bulk melt. The most important feature of the present concentration cells is that they will reveal the energetics of solvation of the transition ion.

Models A and B represent two different statistical models for the solvation. In model A it is implied that the solvation is weak and the emf should then

to the first approximation be given by eqn. (11). A very slight change of emf due to dilution should be observed when varying the composition. If, however, the Me-Al-Cl species should be considered as a separate entity, then the emf should be given by eqn. (15) reflecting the change of activity of the coordinated solvent species. If this model is appropriate, the emf may further be used for evaluation of the equilibria between the solvent species.

When solid  $\text{MeCl}_n$  is present (Model C) the study of the concentration cell becomes a way of measuring the chloride activity in the melt (eqn. (16)). This also gives information about the equilibria between solvent species in the bulk melt.

$\text{AlCl}_4^-$  is the Al-Cl species with the highest  $\text{Cl}^-/\text{Al}^{3+}$  ratio known, and  $\text{Cl}^-$  ions not bonded to  $\text{Al}^{3+}$  will be present for  $X_{\text{AlkCl}}/X_{\text{AlCl}_3} > 1$ . Melts in this composition range will be similar to mixtures of alkali chlorides and most transition metals which form negative  $\text{MeCl}_k^{n-k}$  complexes.<sup>8,9</sup> By considering this complex a species the emf of the cell will be given by eqn. (20). The emf will mainly give information about chloride activity. It is, however, here necessary to know the transport number  $t_{\text{Alk}}$  as a function of composition in order to perform a more quantitative analysis of the data.

The studied concentration cell may also be useful in evaluating the free energy of complexation of the transition metal ions. This enables us to make a comparison between the behaviour of the different transition metal ions and alkali chloride in the bulk melt. For this purpose, the large change in emf around the composition  $\text{AlkAlCl}_4$  can be utilized. The electrostatics of the bulk melt changes here radically as demonstrated by the very abrupt change in coordination of the transition metal ions.<sup>1,9,13,14</sup>

Close to the composition  $\text{AlkAlCl}_4$ , the amount of  $\text{Cl}^-$  relative to  $\text{K}^+$  will be so small that  $t_{\text{K}}=1$ . When the composition changes from, e.g.,  $X_{\text{AlkCl}}=0.45$ (II) to  $X_{\text{AlkCl}}=0.515$ (I), the emf is given by eqn. (11). Although  $d \ln X'_{\text{Cl}}$  does undergo large variations in this region, the justification for neglecting the term with  $d \ln X'_{\text{Cl}}$  can be seen by introducing the Temkin model directly into the exact eqn. (2). The coefficient before  $d \ln X'_{\text{Cl}}$  becomes then  $1 - t_{\text{Me}} - t_{\text{Alk}} = t_{\text{Cl}} \approx 0$ .

By integration:

$$\Delta E = \frac{RT}{nF} \int_{\text{I}}^{\text{II}} d \ln X'_{\text{Me}} \quad (21)$$

Assuming that  $\text{Me}(\text{Al}_p\text{Cl}_{3p+1})_j^{n-j}$  according to eqn. (13) forms on the  $\text{AlCl}_3$ -rich side II and  $\text{MeCl}_k^{n-k}$  according to eqn. (18) forms on the  $\text{AlkCl}$ -rich side

$$\Delta E - \frac{RT}{nF} \ln \frac{K''}{K'} = \frac{RT}{nF} \ln \frac{X'^{\text{II}}_{\text{Me-Al-Cl}} (X'^{\text{I}}_{\text{Cl}})^k}{X'^{\text{I}}_{\text{MeCl}_k} (X'^{\text{II}}_{\text{Al-Cl}})^j} \quad (22)$$

Using the Temkin model and introducing ion fractions, the right hand side of the eqn. (22) may be calculated from known amount of  $\text{Me}(\text{Al}_p\text{Cl}_{3p+1})_j^{n-j}$ ,  $\text{MeCl}_k^{n-k}$  and stoichiometrically calculated amounts of Cl and  $\text{Al}_p\text{Cl}_{3p+1}^-$ . The change in emf for the present cell will hence give information about the ratio between the two equilibrium constants  $K''/K'$  (eqns. (18) and (13)) where

an ion fraction standard states have been introduced by using the Temkin model. By studying different transition metal ions as well as different alkali ions in the bulk mixture it is possible to determine how the complexation changes with these parameters.

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