Coion–Interactions in Molten Salt Systems (M1,M2)X3

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The association–model of binary molten salt systems (M1,M2)X3 is criticized and the friction coefficients r13, r23, and r12 of the system (6Li,7Li)Cl are calculated from ancient mobility measurements, showing that the coion–interactions, represented by r12, are about as strong as the ion–counterion–interactions, represented by r13 and r23.

There exist many experimental results on the migration of cations with respect to anions (internal mobilities) in binary molten halide and nitrate mixtures. The models, however, that should enable to understand and predict quantitatively such mobilities are still unsatisfactory.

One of the models is based on the conjecture that melts of the type (M1,M2)X are not completely dissociated but contain neutral biatomic molecules [1 - 3]. In this model, from four experimental data on the internal mobilities, for instance the mobilities b1(0) and b2(1) of the pure salts and the mobilities b1(0.5) and b2(0.5) at the mole fraction 0.5, or b1(0), b2(1), b1(x) = b2(x) and the mole fraction x at the Chemla point, if there exists any, one evaluates the association constants K1 and K2 of the two salts and the internal mobilities u1 and u2 of the not associated cations, and from these one evaluates the theoretical internal mobilities b1 and b2 in dependence on the mole fractions. Hereby not only K1 and K2 but also u1 and u2 are independent of the mole fractions.

In [3], dealing with (Li,Cs)Cl, it was shown that the agreement of b1 and b2, obtained in [4], with b1 and b2, respectively, is not satisfactory. Evidently the assumptions that u1 and u2 are independent of the mole fractions and that the interaction of the coions can be neglected are not adequate.

The situation is different, however, if the coions are isotopes. In this case, the temperature of the melt being high, structural differences between the two salts can be neglected. One would, e. g. in the association–model have K1 = K2. Due to their different masses, however, the isotopes differ in their dynamic properties. These can be approximated by the three friction coefficients r13, r23, and r12.

For one mole of a salt M1X3 of monovalent ions one has

\[ FE = r_{13}(v_1 - v_3), \]

where F is Faraday's constant, E the external electric field, r13 the friction coefficient and (v1 − v3) the difference of the migration velocities of the ions 1 and 3. In case of a mixture (M1,M2)X3 we introduce the mole fractions x1, x2 and x3 of the ions, where x1 + x2 = x3 = 1/2, and the friction coefficients r13, r23 and r12 = r21, writing

\[ \frac{x_1}{x_3} FE = 4[x_1 x_3 r_{13}(v_1 - v_3) + x_1 x_2 r_{12}(v_1 - v_2)], \]

\[ \frac{x_2}{x_3} FE = 4[x_2 x_3 r_{23}(v_2 - v_3) + x_2 x_1 r_{21}(v_2 - v_1)]. \]

(2a,b)

Note that (1) is recovered if x2 = 0. In this paper it is assumed that the friction coefficients are independent of the mole fractions, which is only approximately true even for isotopic mixtures (cf. [5]).

By replacement of the ionic mole fractions x1, x2 and x3 by the mole fractions x13 and x23 of the salts,

\[ x_1 = \frac{x_{13}}{2}, \quad x_2 = \frac{x_{23}}{2}, \quad x_3 = \frac{1}{2}, \]

and by the introduction of the reduced internal mobilities b1' and b2',

\[ b_1' = \frac{b_1}{F} = \frac{v_1 - v_3}{EF}, \quad b_2' = \frac{b_2}{F} = \frac{v_2 - v_3}{EF}, \]

(4a,b)

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(2a,b) becomes
\[
\begin{align*}
    r_{13}b_1' + x_{23}r_{12}(b_1' - b_2') &= 1, \\
    r_{23}b_2' + x_{13}r_{21}(b_2' - b_1') &= 1.
\end{align*}
\]

From (5b) follows
\[
b_2' = (1 + x_{13}r_{12}b_1')/(r_{23} + x_{13}r_{12}).
\]

Introduction of (6) into (5a) yields
\[
b_1' = (r_{23} + r_{12})/[r_{13}r_{23} + (x_{13}r_{13} + x_{23}r_{23})r_{12}],
\]
and correspondingly
\[
b_2' = (r_{13} + r_{12})/[r_{13}r_{23} + (x_{13}r_{13} + x_{23}r_{23})r_{12}].
\]

From (7a,b) follows
\[
\begin{align*}
    b_1' &= (r_{23} + r_{12})/(r_{13} + r_{23}), \\
    b_2' &= (r_{13} + r_{12})/(r_{13} + r_{23}).
\end{align*}
\]

and
\[
(b_1'/b_2') = (r_{13} + r_{12})/(r_{13} + r_{23}),
\]
so that
\[
r_{12} = [r_{23} - (b_1/b_2)r_{13}] / [(b_1/b_2) - 1].
\]

In the following we shall for the system \(^6\text{Li},^7\text{Li})\text{Cl}\) at 610 and 780 °C calculate \(r_{13}\) and \(r_{23}\) from measurements of \(b_1'\) and \(b_2'\), using (8a,b), and \(r_{12}\) from measurements of \(b_1/b_2\) in natural \(^6\text{Li},^7\text{Li})\text{Cl}\) \(x_{23} = 0.921\) [6], using (9) with the found values of \(r_{13}\) and \(r_{23}\).

In [6] one finds for LiCl, where for the isotops 6 and 7
\[
(2m_1 - m_2)/(m_1 + m_2) = -0.154
\]
\[
\mu^o = -[0.335 + 0.000138(t - 610)]
\]
for \(620 \leq t \leq 750 \text{ °C},
\]
\[
\mu = -[0.111 + 0.000263(t - 610)]
\]
for \(670 \leq t \leq 900 \text{ °C}\) and \(x_{23} = 0.921\).

The internal mobility of Li in LiCl as a function of the temperature is still not known very precisely, cf. [4]. Here, \(b_2\) in units of \(10^{-4}\text{cm}^2/\text{sV}\) is chosen to be 16.68 at 610 °C and 20.12 at 780 °C. With these values and those of the first column of Table 1 follow the values of \(b_1\), and through (8a,b) the values of \(r_{13}\) and \(r_{23}\).

The experimental values of \(\mu\) at 610 and 780 °C for \(x_{23} = 0.921\) are given in the first column of Table 2. According to (11) and (12)
\[
b_1/b_2 = (1 - 0.077\mu)/(1 + 0.077\mu).
\]

The values of \(b_1/b_2\) for the two temperatures are given in the second column of Table 2, and the values of \(r_{12}\), obtained from (9) and the \(r_{13}\) and \(r_{23}\) values of Table 1, are given in the third column of Table 2.

Having determined \(r_{13}\), \(r_{23}\), and \(r_{12}\), values of \(b_1\) and \(b_2\) as functions of \(x_{23}\) can be evaluated by means of (4a,b) and (7a,b). Such values are given in Table 3, and the corresponding almost linear curves are shown in Figure 1.
Conclusion

1. The association–model in its present form for a system \((M_1,M_2)X_3\) is not satisfactory because it assumes that the internal mobilities \(u_1\) and \(u_2\) of the free cations with respect to the anions are independent of the mole fractions and that coion–interactions are absent, while the application of this model to published mobility–measurements on the system \((Li,Cs)Cl\) shows that \(u_1\) and \(u_2\), the mobilities of the free ions depend on the mole fractions, and published mobility–measurements on the system \((^{6}Li,^{7}Li)Cl\) show that coion–interactions are present.

2. Due to the negligibility of the difference in the molar volumes of molten \(^{6}LiCl\) and \(^{7}LiCl\), the three friction coefficients of \((^{6}Li,^{7}Li)Cl\) can be taken to be approximately independent of the mole fractions and it is possible to evaluate them from published mobility–measurements on \(^{6}LiCl\), \(^{7}LiCl\) and natural \((^{6}Li,^{7}Li)Cl\). It turned out that the coionic friction coefficient is of the same order of magnitude as the two counterionic friction coefficients, and that these friction coefficients decrease with temperature.

[3] A. Klemm and L. Schäfer, Z. Naturforsch. 51a, 1229 (1996). The last sentence of the section ending on page 1233 should be read: Once \(K_1\) and \(K_2\) are determined, \(u_1\) and \(u_2\) result from (18a,b).