Coion–Interactions in Molten Salt Systems $(M_1,M_2)X_3$

Alfred Klemm and Lutz Schäfer

Max-Planck-Institut für Chemie (Otto Hahn Institut), Postfach 3060, D-55020 Mainz

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The association–model of binary molten salt systems $(M_1,M_2)X_3$ is critizised and the friction coefficients r_{13}, r_{23}, and r_{12} of the system (^{6}Li,^{7}Li)Cl are calculated from ancient mobility measurements, showing that the coion–interactions, represented by r_{12}, are about as strong as the ion-counterion–interactions, represented by r_{13} and r_{23}.

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 $(M_1,M_2)X$ 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 $b_1(0)$ and $b_2(1)$ of the pure salts and the mobilities $b_1(0.5)$ and $b_2(0.5)$ at the mole fraction 0.5, or $b_1(0)$, $b_2(1)$, $b_1(x) = b_2(x)$ and the mole fraction x at the Chemla point, if there exists any, one evaluates the association constants K_1 and K_2 of the two salts and the internal mobilities u_1 and u_2 of the not associated cations, and from these one evaluates the theoretical internal mobilities $^\circ b_1$ and $^\circ b_2$ in dependence on the mole fractions. Hereby not only K_1 and K_2 but also u_1 and u_2 are independent of the mole fractions.

In [3], dealing with (Li,Cs)Cl, it was shown that the agreement of b_1 and b_2, obtained in [4], with $^\circ b_1$ and $^\circ b_2$, respectively, is not satisfactory. Evidently the assumptions that u_1 and u_2 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 $K_1 = K_2$. Due to their different masses, however, the isotopes differ in their dynamic properties. These can be approximated by the three friction coefficients r_{13}, r_{23}, and r_{12}.

For one mole of a salt M_1X_3 of monovalent ions one has

$$FE = r_{13}(v_1 - v_3), \tag{1}$$

where F is Faraday's constant, E the external electric field, r_{13} the friction coefficient and $(v_1 - v_3)$ the difference of the migration velocities of the ions 1 and 3. In case of a mixture $(M_1,M_2)X_3$ we introduce the mole fractions x_1, x_2 and x_3 of the ions, where $x_1 + x_2 = x_3 = 1/2$, and the friction coefficients r_{13}, r_{23} and $r_{12} = r_{21}$, writing

$$\frac{x_1}{x_3} FE = 4[x_1x_3r_{13}(v_1 - v_3) + x_1x_2r_{12}(v_1 - v_2)],$$

$$\frac{x_2}{x_3} FE = 4[x_2x_3r_{23}(v_2 - v_3) + x_2x_1r_{21}(v_2 - v_1)]. \tag{2a,b}$$

Note that (1) is recovered if $x_2 = 0$. 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 x_1, x_2 and x_3 by the mole fractions x_{13} and x_{23} of the salts,

$$x_1 = \frac{x_{13}}{2},\ x_2 = \frac{x_{23}}{2},\ x_3 = \frac{1}{2}, \tag{3}$$

and by the introduction of the reduced internal mobilities b_1' and b_2',

$$b_1' \equiv \frac{b_1}{F} \equiv \frac{v_1 - v_3}{EF},\ b_2' \equiv \frac{b_2}{F} \equiv \frac{v_2 - v_3}{EF}, \tag{4a,b}$$

Reprint requests to Prof. A. Klemm, Fax: +49 6131 305388.

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(2a,b) becomes

$$r_{13}b_1' + x_{23}r_{12}(b_1' - b_2') = 1,$$
$$r_{23}b_2' + x_{13}r_{21}(b_2' - b_1') = 1. \quad (5a,b)$$

From (5b) follows

$$b_2' = (1 + x_{13}r_{12}b_1')/(r_{23} + x_{13}r_{12}). \quad (6)$$

Introduction of (6) into (5a) yields

$$b_1' = (r_{23} + r_{12})/[r_{13}r_{23} + (x_{13}r_{13} + x_{23}r_{23})r_{12}], \quad (7a)$$

and correspondingly

$$b_2' = (r_{13} + r_{12})/[r_{13}r_{23} + (x_{13}r_{13} + x_{23}r_{23})r_{12}]. \quad (7b)$$

From (7a,b) follows

$$b_1'(x_{23} = 0) \equiv b_1^\circ/F = 1/r_{13},$$
$$b_2'(x_{13} = 0) \equiv b_2^\circ/F = 1/r_{23}. \quad (8a,b)$$

One also has from (7a,b)

$$b_1/b_2 = (r_{23} + r_{12})/(r_{13} + r_{12}),$$

so that

$$r_{12} = [r_{23} - (b_1/b_2)r_{13}]/[(b_1/b_2) - 1]. \quad (9)$$

In the following we shall for the system (^{6}Li,^{7}Li)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}Li,^{7}Li)Cl ($x_{23} = 0.921$) [6], using (9) with the found values of r_{13} and r_{23}.

In [6] one finds for

$$\mu^\circ \equiv \frac{2(b_1^\circ - b_2^\circ)}{b_1^\circ + b_2^\circ} \cdot \frac{m_1 + m_2}{2(m_1 - m_2)} \quad (10)$$

and

$$\mu \equiv \frac{2(b_1 - b_2)}{b_1 + b_2} \cdot \frac{m_1 + m_2}{2(m_1 - m_2)} \quad (11)$$

of LiCl, where for the isotops 6 and 7

$$2(m_1 - m_2)/(m_1 + m_2) = -0.154 : \quad (12)$$

$$\mu^\circ = -[0.335 + 0.000138(t - 610)] \quad \text{for } 620 \leq t \leq 750\ ^\circ\text{C}, \quad (13)$$

Table 1.

Temp. [°C]	$2(b_1^\circ - b_2^\circ)\cdot(b_1^\circ+b_2^\circ)^{-1}$	b_2° [$10^{-4}\frac{cm^2}{sV}$]	b_1° [$10^{-4}\frac{cm^2}{sV}$]	r_{13} [$10^7\frac{sVC}{cm^2}$]	r_{23} [$10^7\frac{sVC}{cm^2}$]
610	0.0516	16.68	17.54	5.502	5.785
780	0.0551	20.12	21.23	4.545	4.796

Table 2.

Temp. [°C]	$-\mu$	b_1/b_2	r_{12} [$10^7\frac{sVC}{cm^2}$]
610	0.111	1.0172	10.951
780	0.156	1.0243	5.141

Table 3.

Temp. [°C]	x_{23}	b_1 [$10^{-4}\frac{cm^2}{sV}$]	b_2 [$10^{-4}\frac{cm^2}{sV}$]
610	0	17.54	17.24
	0.25	17.39	17.10
	0.50	17.24	16.96
	0.75	17.11	16.82
	1	16.96	16.68
780	0	21.23	20.70
	0.25	21.09	20.56
	0.50	20.93	20.41
	0.75	20.79	20.27
	1	20.65	20.14

$$\mu = -[0.111 + 0.000263(t - 610)] \quad \text{for } 670 \leq t \leq 900\ ^\circ\text{C and } x_{23} = 0.921. \quad (14)$$

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}cm^2/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)

$$b_1/b_2 = (1 - 0.077\mu)/(1 + 0.077\mu). \quad (15)$$

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.

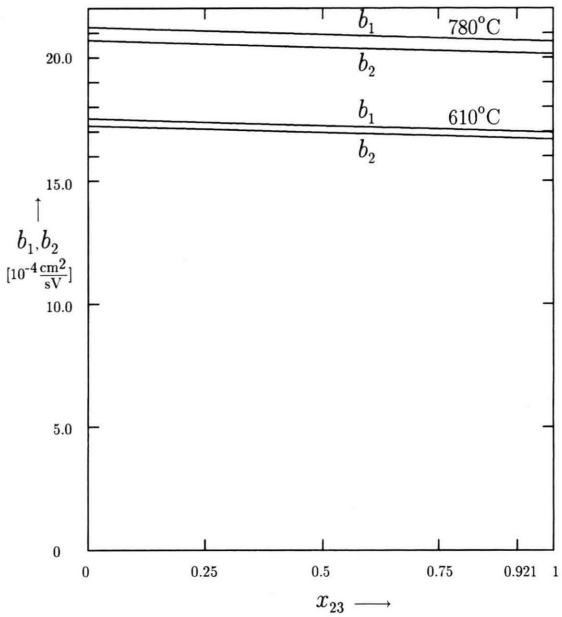

Fig. 1. Mobility isotherms of ^{6}Li (b_1) and ^{7}Li (b_2) in molten (^{6}Li,^{7}Li)Cl. x_{23} is the mole fraction of ^{7}LiCl.

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 neglibility 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.

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