Association in Molten Salts and Mobility Isotherms showing the Chemla Effect

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In 1984 a model for additive binary molten salt mixtures had been proposed that allowed for a qualitative understanding of the occurrence of the Chemla effect (equal internal mobilities at a certain mixing ratio of the salts). In that model the presence of three ions (1, 2 and 3) and two neutral molecules (4 and 5) consisting of two ions is assumed, and the ratios \( K_1 = x_4 / x_1 x_3 \) and \( K_2 = x_5 / x_2 x_3 \) of their mole fractions are assumed to be independent of the mixing ratio of the salts. In the present paper, that model is compared with recent experimental results on the system \((\text{Li, Cs})\text{Cl}\) obtained in Japan. The comparison shows that the model is too simple for a quantitative description of systems showing the Chemla effect. Rather a dependence of \( K_1 \) and \( K_2 \) on the mixing ratio of the salts must be assumed.

Introduction

After the discovery of nuclear fission in 1939 [1] it became evident that the separation of the isotopes of hydrogen, lithium [2] and uranium would be needed for the utilization of nuclear energy. Therefore various methods of isotope separation were tested, among these electromigration in molten lithium chloride [3]. Although with that method, using lithium nitrate, \(^6\text{Li}\) was enriched from 7% to 91.2% in 39 days with a small apparatus [4], industrial use of the method seemed problematic because the heat produced by the direct current in the separation tube can not be removed by thermoconvection of the melt, convection needs being prevented by some diaphragm material.

In order to reduce the temperature of the melt, in one experiment in 1960 [5] a mixture of \(\text{LiBr}\) and \(\text{KBr}\) was applied, not bothering that this way not only \(^6\text{Li}\) and \(^7\text{Li}\), but with a larger speed lithium and potassium should separate. It came as a surprise that in the separation tube a zone developed where the concentration of the two salts stood constant, i.e. the mobilities of lithium and potassium were equal. Futher experiments did show that at a certain mixing ratio of \(\text{LiBr}\) and \(\text{KBr}\) the mobility isotherms of the system \((\text{Li, K})\text{Br}\) cross [6]. This interesting effect, now called Chemla effect, has stimulated many more experiments on cation mobilities in various molten halide - and nitrate systems.

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In 1984 [7] the Chemla effect had been explained qualitatively in the following way:

In molten lithium bromide, although it has a larger conductivity than potassium bromide, more ions are associated to neutral molecules \(\text{LiBr}\) than are in potassium bromide to neutral molecules \(\text{KBr}\) because \(^{\text{Li}}^+\) is smaller than \(^+\text{K}\). In the mixtures, \(^+\text{Li}\) and \(^+\text{K}\) compete in the formation of molecules \(\text{LiBr}\) and \(\text{KBr}\), respectively, the smaller \(^+\text{Li}\) being more successful. Therefore in the mixtures the internal mobility of lithium decreases faster with increasing content of potassium bromide than the mobility of potassium, and thus the mobility isotherms may cross.

According to Fig. 1, the existence of the Chemla effect of a system \((\text{M}_1, \text{M}_2)\text{X}\) depends on the temperature.

Experimentally, for the chlorides and bromides of \((\text{Li, Rb}), (\text{Li, Cs}), (\text{Na, K}), (\text{Na, Rb}), (\text{Na, Cs}), (\text{K, Rb}), (\text{K, Cs}), \) and \((\text{Rb, Cs})\) and the iodides of \((\text{Na, K}), (\text{Na, Rb}), (\text{Na, Cs}), (\text{K, Rb}), (\text{K, Cs}), \) and \((\text{Rb, Cs})\) the ratio \( b_1(0)/b_2(1) \), where \( b_1(0) \) and \( b_2(1) \) are the internal mobilities of the pure salts, decreases with increasing temperature. For the missing systems to the left, in the literature there are no data for the two salts at the same two temperatures.

Coion-interactions are absent in mixtures having the mole fraction \( x_{23} = x \) coresponding to the Chemla point because there the migration-velocities of the coions are equal \( b_1(x) = b_2(x) = b \). At other
The mole fractions of the particles add up to unity:
$$x_1 + x_2 + x_3 + x_4 + x_5 = 1. \quad (1)$$

The neutrality of the melt is expressed by
$$x_1 + x_2 = x_3, \quad 0 < x_3 < 1/2. \quad (2)$$

Also the mole fractions of the salts add up to unity:
$$x_{13} + x_{23} = 1. \quad (3)$$

When writing (1) in the form \( \left[ \frac{x_1 + x_4}{1 - x_3} \right] + \left[ \frac{x_2 + x_5}{1 - x_3} \right] = 1 \), comparison with (3) shows that
$$x_{13} = \frac{x_1 + x_4}{1 - x_3}, \quad x_{23} = \frac{x_2 + x_5}{1 - x_3}. \quad (4a, b)$$

In the following \( x_{23} \) will be used to define the composition of the melt. We now define \( K_1 \) and \( K_2 \) by
$$K_1 = \frac{x_4}{x_1 x_3}, \quad K_2 = \frac{x_5}{x_2 x_3}. \quad (5a, b)$$

From (3), (4a, b) and (5a, b) follows
$$x_1 = \frac{(1 - x_{23})(1 - x_3)}{1 + K_1 x_3}, \quad x_2 = \frac{x_{23}(1 - x_3)}{1 + K_2 x_3}. \quad (6a, b)$$

By adding (6a) and (6b), and using (2) one obtains
$$x_3 = \left[ \frac{1 - x_{23}}{1 + K_1 x_3} + \frac{x_{23}}{1 + K_2 x_3} \right] (1 - x_3), \quad (7)$$

a cubic equation in \( x_3(x_{23}) \):
$$x_3^3(x_{23}) + \alpha x_3^2(x_{23}) + \beta x_3(x_{23}) + \gamma = 0 \quad (8)$$

with
$$\alpha = \left( \frac{2}{K_1} + \frac{1}{K_2} \right) - \left( \frac{1}{K_1} - \frac{1}{K_2} \right) x_{23}, \quad (9a, b, c)$$
$$\beta = \left( \frac{2}{K_1 K_2} - \frac{1}{K_1} \right) + \left( \frac{1}{K_1} - \frac{1}{K_2} \right) x_{23}, \quad (9a, b, c)$$
$$\gamma = -\frac{1}{K_1 K_2}. \quad (9a, b, c)$$

molefractions, coion-interactions are active. Such interactions have been shown to exist in \((^6\text{Li},^7\text{Li})\text{Cl}\) by a comparison of the mobilities \( b_1(0) \) and \( b_2(1) \) of the pure salts with the mobilities \( b_1(0.93) \) and \( b_2(0.93) \) in the natural mixture of the two salts [8]. Since the temperature of the melt is high, quantum effects can be neglected, i.e. the structure of the melt is independent of \( x_{23} \), and only coion-interactions are active. The result was \( b_1(0.93) - b_2(0.93) = 0.42[b_1(0) - b_2(1)] \) at 750°C, i.e. by the coion interactions the difference of the mobilities of \(^6\text{Li}\) and \(^7\text{Li}\) in the pure chlorides \(^6\text{LiCl}\) and \(^7\text{LiCl}\) is reduced in the mixture by more than 50%.

The simplest model for ion-counterion-interactions

It is assumed that the mixture consists of five kinds of particles, three of which are charged and two are neutral:

\[ M_1^+, M_2^-, X^-, M_1 X, \text{ and } M_2 X. \]
We now turn to the internal mobilities \( b_1(x_{23}) \) and \( b_2(x_{23}) \). These transport properties of the melt are defined as

\[
\begin{align*}
    b_1(x_{23}) &= \frac{v_1(x_{23}) - v_3(x_{23})}{E}, \\
    b_2(x_{23}) &= \frac{v_2(x_{23}) - v_3(x_{23})}{E}, 
\end{align*}
\]

(10a, b)

where \( v_1, v_2 \) and \( v_3 \) are average velocities of \( M_1, M_2 \) and \( X \), respectively, in the direction of the applied electric field \( E \). The conductivity of the mixture is

\[
\kappa(x_{23}) = \frac{[(1 - x_{23}) b_1(x_{23}) + x_{23} b_2(x_{23})]}{F/V_m(x_{23})} 
\]

(11)

with \( F \) being Faraday’s constant and \( V_m \) the molar volume of the melt.

In diluted aqueous solutions of two additive, monovalent salts, the equilibrium constants \( K_1 \) and \( K_2 \) and the mobilities \( u_1 \) and \( u_2 \) of the ions \( M_1^+ \) and \( M_2^+ \) are independent of \( x_{23} \). It is the essential assumption of the simplest model for ion – counterion interactions, that this holds also for additive binary molten salt mixtures. One introduces degrees of dissociation

\[
D_1 = x_1/(x_1 + x_3), \quad D_2 = x_2/(x_2 + x_3), 
\]

(12a, b)

which according to (5a, b) depend on \( x_{23} \):

\[
\begin{align*}
    D_1(x_{23}) &= 1/[1 + K_1 x_3(x_{23})], \\
    D_2(x_{23}) &= 1/[1 + K_2 x_3(x_{23})], 
\end{align*}
\]

(13a, b)

and writes

\[
\begin{align*}
    o b_1(x_{23}) &= u_1/[1 + K_1 x_3(x_{23})], \\
    o b_2(x_{23}) &= u_2/[1 + K_2 x_3(x_{23})]. 
\end{align*}
\]

(14a, b)

The prefix \( o \) is added to indicate that no coion interactions are taken account of.

It can be shown that \( b_1(0) \) and \( b_2(1) \) are functions of \( u_1 \) and \( K_1 \), respectively \( u_2 \) and \( K_2 \) :

From (3), (4a) and (12a), and (4b) and (12b), respectively, follows

\[
(1 - x_{23}) D_1 = \frac{x_1}{1 - x_3}, \quad x_{23} D_2 = \frac{x_2}{1 - x_3}, 
\]

(15a, b)

and adding (15a) and (15b) yields with (2)

\[
x_{23} = \frac{[(1 - x_{23}) D_1 + x_{23} D_2]}{1 + (1 - x_{23}) D_1 + x_{23} D_2}. 
\]

(16)

Especially for the pure salts \((x_{23} = 0 \text{ and } x_{23} = 1)\), where e.g. for \( x_{23} = 0 \) according to (2) and (1) \( x_1 = x_3 \) and \( x_4 = 1 - 2x_3 \), and according to (16) \( x_3 = D_1 / (1 + D_1) \), (5a, b) becomes

\[
K_1 = 1 - \frac{2x_3(0)}{x_3^2(0)}, \quad K_2 = 1 - \frac{2x_3(1)}{x_3^2(1)}. 
\]

(17a, b)

Elimination of \( x_3(0) \) in (14a) and (17a), and of \( x_3(1) \) in (14b) and (17b) yields

\[
\begin{align*}
    b_1(0) &= u_1/\sqrt{1 + K_1}, \quad b_2(1) = u_2/\sqrt{1 + K_2}. 
\end{align*}
\]

(18a, b)

For four experimental values we introduce the symbols \( b_1, b_2, b \) and \( x: b_1 \equiv b_1(0), b_2 \equiv b_2(1), b \equiv b_1(x) = b_2(x), x \equiv x_{23} \) at the Chemla point. These four experimental values, obtained in the absence of coion interactions, allow for the calculation of \( K_1, K_2, u_1 \) and \( u_2 \).

Using these symbols, one obtains from (14a, b) and (18a, b) by elimination of \( u_1 \) and \( u_2 \) the relations

\[
\frac{b}{b_1} = \frac{\sqrt{K_1 + 1}}{K_1 x_3(x) + 1}, \quad \frac{b}{b_2} = \frac{\sqrt{K_2 + 1}}{K_2 x_3(x) + 1}. 
\]

(19a, b)

Since by definition \( b_2 < b < b_1 \), \( K_2 \) is a function of \( b/b_2 \) in the range \( 1 < b/b_2 < \infty \) and \( K_1 \) is a function of \( b/b_1 \) in the range \( 0 < b/b_1 < 1 \). Also \( 0 < x_3(x) < \frac{1}{2} \). The solid curves in Fig. 2 show for seven values of \( x_3(x) \) the dependence of \( K_2 \) on \( b/b_2 \) and the dependence of \( K_1 \) on \( b/b_1 \). Only the solid curves to the right of the dashed curve have physical meaning because \( x_3(x) \) must, at constant \( b/b_2 \), decrease with increasing \( K_2 \).

In the following it will be shown that, according to the simplest model, the Chemla point lies in an area of the \( b_1(x_{23}) - b_2(x_{23}) \) diagram which is limited by a lower curve \( b_1(x_{23}) \) and an upper curve \( b_2(x_{23}) \), both curves running from \( b_1(0) \) to \( b_2(1) \), and their formulas containing the parameters \( b_1 \) and \( b_2 \) only. These curves result from the fact that the functions \( K_2(b/b_2) \) have maxima for given values of \( x_3(x) \), cf. Figure 2. Extrema due to these maxima will be marked with the subscript “e”, and use will be made of the abbreviations

\[
\begin{align*}
    Q_1 &= \frac{b_1}{b_2} + \sqrt{\left(\frac{b_1}{b_2}\right)^2 - 1}, \quad Q_e = \frac{b_e}{b_2} + \sqrt{\left(\frac{b_e}{b_2}\right)^2 - 1}. 
\end{align*}
\]

(20a, b)
where according to (19b), (22) and (23)

$$
\frac{b_1}{b_c} = \frac{b_1}{b_2} = \frac{2Q_e}{Q_e^2 + 1}.
$$

From (19a), (24) and (25) follows

$$
K_{1e} = Q_1^2Q_e^2 - 1.
$$

For the construction of the curves $1b(x_{23})$ and $2b(x_{23})$ also the $x_{e}$ - values must be known. These one finds from (7) when putting $x_3 = x_{3e}$, $K_2 = K_{2e}$, $K_1 = K_{1e}$ and expressing $x_{3e}$, $K_{2e}$ and $K_{1e}$, using (22), (23) and (26), by $Q_1$ and $Q_e$:

$$
x_e = \frac{2(Q_1^2 - Q_e^2)}{(Q_1^2 - 1)(Q_e^2 + 1)}.
$$

From (22) and (27) follows that the function $x_3(x_e)$ is linear:

$$
x_3(x_e) = \frac{1}{2} x_e + \frac{1}{Q_1^2 - 1}.
$$

From (20b) and (27) follows

$$
Q_e^2 = \frac{2Q_1^2 - (Q_1^2 - 1)x_e}{2 + (Q_1^2 - 1)x_e},
$$

and since according to (20b)

$$
\frac{b_c}{b_2} = \frac{Q_e^2 + 1}{2Q_e},
$$

one obtains from (29)

$$
\frac{b_e}{b_2} = \left\{1 - \left[\frac{Q_1^2 - 1}{Q_1^2 + 1}\right]^2 (1 - x_e)^2\right\}^{-\frac{1}{2}}.
$$

Also

$$
\left[\frac{Q_1^2 - 1}{Q_1^2 + 1}\right]^2 = 1 - \left(\frac{b_1}{b_2}\right)^2.
$$

From (30) and (31) results the formula of the lower curve:

$$
1b(x_{23}) = b_2 \left\{1 - \left[1 - \left(\frac{b_1}{b_2}\right)^2\right] (1 - x_{23})^2\right\}^{-\frac{1}{2}}.
$$

Fig. 2. The solid curves show for seven values of $x_3(x)$, the relation between $K_2$ and $b_2$, and between $K_1$ and $b_1$, where $b$ and $x$, respectively, are $b(x_{23})$ and $x_{23}$ of a Chemla point. Only the solid curves to the right of the dashed curve have physical meaning because $x_3(x)$ must at constant $b$ decrease with increasing $K_2$. First we find for given values of $x_3(x)$ the extrema of $K_1$ and $K_2$. According to (19a, b), the equation

$$
(\partial x_3(x)/\partial K_2)_{b=\text{const}} = 0
$$

is fulfilled if

$$
x_{3e}(x_e) = 1/(Q_e^2 + 1),
$$

$$
K_{2e} = Q_e^2 - 1.
$$

To find the corresponding values of $K_{1e}$, we obtain from (19a), (20b) and (22) the equation

$$
\frac{1}{K_{1e}} \left[\frac{b_1}{b_e} \sqrt{K_{1e} + 1} - 1\right] = \frac{1}{Q_e^2 + 1}.
$$

From (30) and (31) results the formula of the lower curve:
To obtain the formula of the upper curve, very large values of \( K_2 \) must be considered. Since

\[
\lim_{K_2 \to \infty} \frac{\sqrt{K_2 + 1}}{x_3(x)K_2 + 1} = \frac{1}{x_3(x)\sqrt{K_2}}.
\] (33)

(19b) yields

\[
u_b(x_{23}) = b_2 \left( u_x(x_{23})\sqrt{K_2} \right).
\] (34)

From (22) and (23) one obtains

\[
x_3(x) = 1 / (K_2 + 2).
\] (35)

Since \( K_2 \to \infty \) for the upper curve, one has

\[
u_x(x_{23}) = 1 / K_2.
\] (36)

Thus (34) becomes

\[
u_b(x_{23}) = b_2 \left[ u_x(x_{23}) \right]^{-\frac{1}{2}}.
\] (37)

According to (28), \( u_x(x_{23}) \) is a linear function of \( x_{23} \).

Putting

\[
u_b(x_{23}) = b_2 \left[ \eta + \zeta(1 - x_{23}) \right]^{-\frac{1}{2}}
\] (38)

one obtains, since \( \nu_b(0) = b_1 \) and \( \nu_b(1) = b_2 \):

\[\eta = 1, \quad \zeta = -\left[ 1 - \left( \frac{b_1}{b_2} \right)^2 \right].\] (39a, b)

From (38) and (39a, b) results the formula for the upper curve:

\[
u_b(x_{23}) = b_2 \left[ 1 - \left[ 1 - \left( \frac{b_1}{b_2} \right)^2 \right] \left( 1 - x_{23} \right) \right]^{-\frac{1}{2}}.
\] (40)

Figure 3 shows, according to (32) and (40), the functions \( \nu_b(x_{23})/b_2 \) and \( \nu_b(x_{23})/b_2 \) for four values of \( b_1/b_2 \). The simplest model can only be applied if the experimental Chemla point lies between the corresponding lower and upper curve. If it does not, the simplest model of ion-coion interactions can not be applied.

If the experimental Chemla point lies in the range which is allowed by the simplest model, then \( K_1 \) and \( K_2 \) can be determined:

\[
u_b(x_{23}) = b_2 \left[ 1 - \left[ 1 - \left( \frac{b_1}{b_2} \right)^2 \right] \left( 1 - x_{23} \right) \right]^{-\frac{1}{2}}.
\] (40)

From (19a, b) results

\[
x_3(x) = \frac{1}{K_1} \left[ \left( \frac{b_1}{b} \right) \sqrt{K_1 + 1} - 1 \right]
\] (41)

When setting \( x_{23} = x \) in (9a, b) and solving (8), one gets \( x_3(x) \) for a given pair of values \( K_1 \) and \( K_2 \). One has to find a pair of \( K_1 \) and \( K_2 \) that satisfies (41). To find this pair, the cubic equation (8) must be solved repeatedly.

Once \( D_1 \) and \( D_2 \) are determined, \( u_1 \) and \( u_2 \) from (18a, b).

**Conductivity – and mobility – isotherms and the simplest model for ion - counterion interactions**

Extensive calculations of \( K \) – values from published conductivities of binary mixtures have been performed in 1989 – 1991 [8 – 13] using the simplest model for ion – counterion interactions, although
Table 1. Juxtaposition of the symbols in [8 - 13] with those used in the present paper.

<table>
<thead>
<tr>
<th>[8 - 13]</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_{A^+}$</th>
<th>$x_{B^+}$</th>
<th>$x_{X^-}$</th>
<th>$x_{A^+}X^-$</th>
<th>$x_{B^+}X^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present paper</td>
<td>$x_{23}$</td>
<td>$x_1$</td>
<td>$x_2$</td>
<td>$x_3$</td>
<td>$x_4$</td>
<td>$x_5$</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>[8 - 13]</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\alpha_{01}$</th>
<th>$\alpha_{02}$</th>
<th>$K_1$</th>
<th>$K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present paper</td>
<td>$D_1$</td>
<td>$D_2$</td>
<td>$D_1(0)$</td>
<td>$D_2(0)$</td>
<td>$1/K_1$</td>
<td>$1/K_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[8 - 13]</th>
<th>$\alpha_1(u_{A^+}+u_{X^-})$</th>
<th>$\alpha_2(u_{B^+}+u_{X^-})$</th>
<th>$u_{A^+}+u_{X^-}$</th>
<th>$u_{B^+}+u_{X^-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present paper</td>
<td>$b_1$</td>
<td>$b_2$</td>
<td>$u_1$</td>
<td>$u_2$</td>
</tr>
</tbody>
</table>

Fig. 4. The lower, $^b(b_{\text{CsCl}})$ and upper $^b(b_{\text{CsCl}})$, bounds of $b$, divided by $b_{\text{Cs}}$ for the system (Li,Cs)Cl at 640°C and 700°C, as functions of the mole fraction $x_{\text{CsCl}}$. The experimental Chemla points from [14] are marked as cross and diamond at 640°C and 700°C, respectively.

conductivities of course depend on coion interactions, though weekly. As expected for this model, widely varying $K$ – values were found for the same salt, depending on the second salt with which it is combined to form a system. The symbols used in [8 – 13] differ from those used in the present paper. Therefore a juxtaposition of the symbols is given in Table 1.

Mobility measurements on the system (Li, Cs)Cl in 1995 [14] have yielded the following values needed for a comparison with the simplest model of ion – counterion interactions:

At 640 °C: $b_1 = 17.29$, $b = 10.86$, $b_2 = 6.80$, $x = 0.247$,
At 700 °C: $b_1 = 18.49$, $b = 12.45$, $b_2 = 7.87$, $x = 0.226$.

The internal mobilities $b_1$, $b$ and $b_2$ are given in units of $10^{-4}$ cm$^2$/sV. Figure 4 shows that the Chemla points lie in the allowed ranges, that is the simplest model of ion – counterion interactions can be applied. From the above values, by numerical calculation the following values of $K_1$, $K_2$, $u_1$ and $u_2$ were obtained:

At 640 °C: $K_1 = 705.6$, $K_2 = 77.9$, $u_1 = 459.6$, $u_2 = 60.4$,
At 700 °C: $K_1 = 438.5$, $K_2 = 52.6$, $u_1 = 387.6$, $u_2 = 57.6$.

The mobilities $u_1$ and $u_2$ are given in $10^{-4}$ cm$^2$/sV.

With these $K_1$ and $K_2$ values, solving (8) and using (14a, b), the isothermes $^o b_1(x_{23})$ and $^o b_2(x_{23})$ shown in Figs. 5 and 6 were obtained. Figures 5 and
6 also show the experimental points for the mobility isotherms $b_1(x_{23})$ and $b_2(x_{23})$. Since the curves $b_1(x_{23})$ and $b_2(x_{23})$, obtained by neglecting the coion interactions, should be far apart from each other then the curves $b_1(x_{23})$ and $b_2(x_{23})$, which of course include the coion interactions, while in the Figs. 5 and 6 they are closer together, it is to be concluded that the simplest model for ion – counterion interactions is not fit for reproducing the experimental facts in a quantitative way.

**Conclusion and Suggestion**

The simplest model of ion – counterion interactions, though fit for a qualitative understanding of the existence of the Chemla effect, can not be used for quantitative calculations because the assumption that the $K$ – and $u$ – values are independent of $x_{23}$ is not realised in nature.

Proposal for further research: Measure at the same temperature the $x$ – and $u$ – values of the Chemla points of three connected binary systems, such as (Li, Rb)Cl, (Li, Cs)Cl and (Rb, Cs)Cl, and calculate for these by means of the simplest model the pairs of $K_1$ – and $K_2$ – values. Then, for an advanced model, accept these $K_1$ – and $K_2$ – values for the three Chemla points but not for the three pure salts. Instead, take for pure LiCl the average of the $K_{Li}$ values found by the simplest model from the systems (Li, Rb)Cl and (Li, Cs)Cl, in the same way for pure RbCl $K_{Rb}$ from (Li, Rb)Cl and (Rb, Cs)Cl, and for pure CsCl $K_{Cs}$ from (Li, Cs)Cl and (Rb, Cs)Cl. One thus gets for each of the three systems four $K$ – values, those of the two pure salts and those of the Chemla point, and one can apply for the three systems an advanced model of ion – counterion interactions in which the $K$ – values depend linearly on $x_{LiCl}$, $x_{RbCl}$ and $x_{CsCl}$, respectively.