

# Dissociation model of the electrical conductivity of molten salt mixtures

## VI. Systems containing bivalent cation

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The dissociation model of the electrical conductivity of molten salt mixtures, based on the idea of an incomplete dissociation of electrolyte components, was applied in binary systems containing bivalent cation. The systems of the  $M^I\text{Cl}-M^{II}\text{Cl}_2$  ( $M^I = \text{Li, Na, K, Rb, Cs}$ ;  $M^{II} = \text{Mg, Ca, Ba, Cd, Pb}$ ) type were chosen. It was found that in the given systems the dissociation model may be successfully used. The formation of complex compounds and their dissociation was not considered, as the ionic pair  $M^{2+} 2\text{Cl}^-$  may be also formally considered as a complex compound. Alkali metal chlorides are in these systems completely dissociated, whereas the values of the dissociation degree of the chlorides of bivalent metals are substantially lower. The difference of the dissociation degrees of the pure components is directly proportional to the dimension of the alkali cation, which indicates that the bivalent cations possess a higher tendency to form complex anions in the presence of an alkali cation with higher electronegativity.

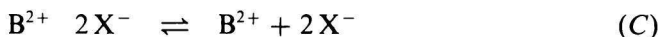
The dissociation model of the electrical conductivity of the molten salt mixtures, based on the idea of an incomplete dissociation of electrolyte components was proposed and theoretically derived in [1]. The validity of this model was verified in a number of binary [2] and ternary [3] univalent systems with a common ion, in univalent reciprocal systems [4] and in the systems containing trivalent cation [5].

In contradiction to the univalent systems the application of the dissociation model of the electrical conductivity of the molten salt mixtures in systems containing a bivalent cation is more complicated with regard to the tendency of these cations to form complex anions. For instance, in a number of  $\text{AX}-\text{BX}_2$  systems the presence of the complex anions like  $\text{BX}_3^-$ , or  $\text{BX}_4^{2-}$  has been evidenced by cryoscopic or spectroscopic method. In simple calculations of the activity of components in such systems it may be assumed that at mixing of *e.g.*  $\text{BX}_4^{2-}$  and  $\text{X}^-$  anions in the presence of  $\text{A}^+$  and  $\text{B}^{2+}$  cations only the change in the configurational entropy takes place, *i.e.* the thermal effect is absent. On the

other hand, the possibility of the dissociation of the complex anions according to the scheme



must be always considered, especially in the region of low content of the  $\text{BX}_2$  component. With regard to these facts, by the application of the dissociation model of the electrical conductivity in these systems a certain hypothetic value of the molar conductivity of the pure undissociated  $\text{ABX}_3$ , resp.  $\text{A}_2\text{BX}_4$  compounds should be considered, which would lead to the introduction of an additional adjustable parameter into the calculation. In the uni-bivalent systems with a common anion the equilibrium between the ionic pairs and the ions according to the schemes



was therefore considered. The formation of the  $\text{ABX}_3$ , resp.  $\text{A}_2\text{BX}_4$  complex compounds and their dissociation was not taken into account, as the  $\text{B}^{2+} 2\text{X}^-$  ionic pair may be considered as a complex compound as well.

For the equilibrium constants of the dissociation reactions (B) and (C) the following relations may be obtained from the material balance

$$K_1 = \frac{\alpha_{01}^2}{1 - \alpha_{01}^2} = \frac{\alpha_1}{1 - \alpha_1} \cdot B \quad (1)$$

$$K_2 = \frac{4\alpha_{02}^3}{1 + 3\alpha_{02} - 4\alpha_{02}^3} = \frac{\alpha_2}{1 - \alpha_2} \cdot B^2 \quad (2)$$

where

$$B = \frac{x_1\alpha_1 + 2x_2\alpha_2}{1 + x_1\alpha_1 + 2x_2\alpha_2}$$

$\alpha_{0i}$  and  $\alpha_i$  are the dissociation degrees of the pure components and of the components in the binary mixture with the composition given by the mole fractions  $x_i$ . By analogy with the procedure given in [1] for the molar conductivity of the uni-bivalent mixture with a common anion the relation

$$\lambda_{\text{mix}} = x_1 \frac{\alpha_1}{\alpha_{01}} \lambda_1 + x_2 \frac{\alpha_2}{\alpha_{02}} \lambda_2 \quad (3)$$

may be derived, where  $\lambda_i$  are the molar conductivities of the pure components. The solution of eqns (1–3) along with the condition

$$\sum_{j=1}^n (\lambda_{j,\text{exp}} - \lambda_{j,\text{calc}})^2 = \min \quad (4)$$

enables to find such values of  $\alpha_{01}$  and  $\alpha_{02}$  for which the difference between the measured and calculated values of the molar conductivity is lower than the experimental error.

The validity of the dissociation model of the molten salt mixtures for the calculation of the molar conductivity in uni-bivalent systems was verified in binary systems of alkali metal chlorides with chlorides of alkali earth metals, lead and cadmium.

### Computational procedure

The experimental data on the density and conductivity of the investigated systems were taken from [6]. In many cases the published values of the density and conductivity were not measured at the same composition. Therefore interpolated values have been used. In some cases the values of the molar conductivity of the pure components were not consistent. At their adjustment the values given in [7] were considered as the right ones.

In Table 1 the values of the dissociation degrees of the pure components in the investigated binary uni-bivalent systems with a common chloride anion are given. In the table also the values of the standard deviations of the experimental and calculated values of the molar conductivity are given.

### Discussion

From the calculated values of the dissociation degrees of the pure components in the investigated uni-bivalent systems it follows that the alkali metal

Table 1

The calculated values of the dissociation degrees of the pure components for the binary uni-bivalent systems with a common chloride anion

System	T/K	$\alpha_{01}$	$\alpha_{02}$	$s/(S\text{ cm}^2\text{ mol}^{-1})$
LiCl—MgCl <sub>2</sub>	1050	0.99	0.18	2.52
LiCl—CaCl <sub>2</sub>	1073	0.99	0.20	1.06
LiCl—BaCl <sub>2</sub>	1200	0.99	0.32	2.17
LiCl—CdCl <sub>2</sub>	1000	0.99	0.33	4.15
NaCl—MgCl <sub>2</sub>	1050	0.99	0.36	4.42
NaCl—CaCl <sub>2</sub>	1070	0.99	0.192	2.84
NaCl—BaCl <sub>2</sub>	1073	0.99	0.25	0.51
NaCl—CdCl <sub>2</sub>	973	0.99	0.29	2.65
NaCl—PbCl <sub>2</sub>	1070	0.99	0.31	1.86
KCl—CaCl <sub>2</sub>	1070	0.99	0.128	4.86
KCl—PbCl <sub>2</sub>	1000	0.99	0.25	5.44
RbCl—CaCl <sub>2</sub>	1173	0.99	0.123	2.86
RbCl—PbCl <sub>2</sub>	1000	0.99	0.205	3.17
CsCl—PbCl <sub>2</sub>	1000	0.99	0.195	6.46

chlorides are completely dissociated ( $\alpha_{01}$  practically equals one). On the other hand, the values of the association degrees of the second component, *i.e.* the chlorides of bivalent metals, are substantially lower and they do not surpass the value of 0.36. From this fact it follows that the bivalent cations bond the chloride anions stronger than the univalent ones and then they show greater tendency to the formation of ionic pairs and of complex anions, respectively. The component with the lower field intensity (the charge to radius ratio) exhibits again a higher value of the dissociation degree, which is in agreement with the conclusions resulting from the calculation of the dissociation degrees in binary univalent systems [2].

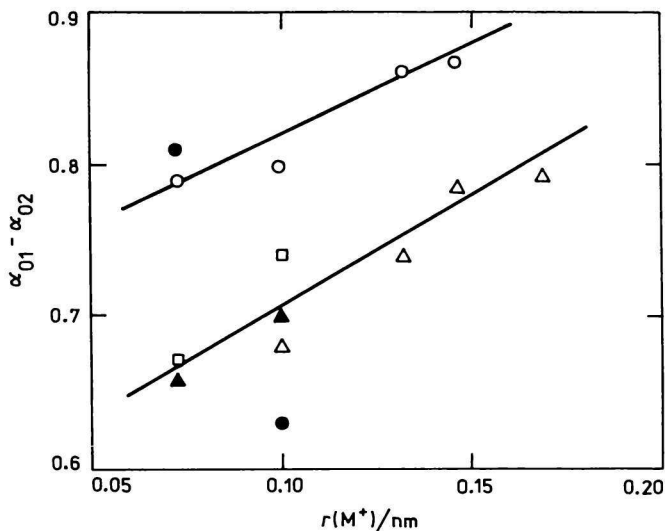


Fig. 1. Dependence of the difference of the dissociation degrees of the pure components on the size of the alkali metal cation. ● MCl—MgCl<sub>2</sub>; ○ MCl—CaCl<sub>2</sub>; □ MCl—BaCl<sub>2</sub>; ▲ MCl—CdCl<sub>2</sub>; △ MCl—PbCl<sub>2</sub>.

The dependence of the difference of the dissociation degrees of the pure components on the radius of the alkali metal cation is shown in Fig. 1. The values of the ionic radii of the alkali metals are taken from [8]. From the dependence shown in Fig. 1 it follows that the difference of the dissociation degrees of the pure components is directly proportional to the size of the alkali metal cation. This indicates that also in the uni-bivalent systems there is a dependence between the difference of the dissociation degrees ( $\alpha_{01} - \alpha_{02}$ ) and the relative difference in the interatomic distances, which have been quantitatively determined for the univalent systems [2]. It is obvious that the bivalent cations show a greater tendency to the formation of complex anions in the presence of

a more electronegative alkali metal cation. However, quantitative conclusions may be done only on the basis of reliable data on the density and the conductivity of the investigated systems.

It was confirmed that the dissociation model of the electrical conductivity of the molten salt mixtures describes well the course of the concentration dependence of the molar conductivity in the uni-bivalent systems. From the standard deviations  $s$  given in Table 1 it follows that the calculated values of the molar conductivity are in a good accordance with the experimental values for properly chosen values of the dissociation degrees of pure components. Larger differences were found only in systems containing KCl and CsCl. These differences may be caused by the following factors:

- i) the low accuracy of the experimental values of the molar conductivity of the binary systems;
- ii) the neglecting of the formation of the complex compounds and their dissociation.

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