

# Dissociation model of the electrical conductivity of molten salt mixtures

## V. Systems containing trivalent cations

V. DANĚK and M. CHRENKOVÁ

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,  
CS-842 36 Bratislava*

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*Dedicated to Associate Professor K. Matiašovský, DrSc.,  
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The dissociation model of the electrical conductivity of molten salt mixtures, based on the assumption of an incomplete dissociation of electrolyte components was applied in some pseudobinary systems containing trivalent cations. The  $\text{MeX—AlX}_3$  ( $\text{Me} = \text{Li, Na, K; X} = \text{Cl, F}$ ) and  $\text{Na}_3\text{AlF}_6\text{—NaCl}$  systems were chosen. It was found that the dissociation model may be successfully used in the systems containing trivalent cations if the real equilibrium composition is taken into account. In such a way the positive deviations from the additivity of the molar conductivity may be rationally explained.

In [1] the dissociation model of the electrical conductivity of molten salt mixtures, based on the assumption of an incomplete dissociation of electrolyte components was proposed and theoretically derived. Owing to the mutual interaction, the dissociation degrees of the components are not constant but they change with the composition of the system. Consequently, the content of "free" ions in the melt changes with the composition as well. The validity of the dissociation model was verified in a number of binary [2] and ternary [3] univalent systems with a common ion as well as in binary reciprocal univalent systems [4]. It was found that in the systems with a common anion the component with the larger cation has always the higher dissociation degree while in the systems with a common cation the component with the smaller anion has always the higher dissociation degree. The difference between the dissociation degrees of components is proportional to the fractional difference in the ionic radii of the similarly charged ions. A close similarity in the course of the molar conductivity and the enthalpy of mixing was found.

The application of the dissociation model of the electrical conductivity of molten salt mixtures in the systems containing polyvalent ions meets with certain difficulties caused by their strong tendency to form complex compounds.

Thus it is necessary to know which new compounds are formed in the system under study and to consider the dissociation of each component.

Since the experimental data of the density and of the electrical conductivity of systems containing trivalent cation, are rather scarce in the literature the systems MeCl—AlCl<sub>3</sub>, MeF—AlF<sub>3</sub> (Me = Li, Na, K) and Na<sub>3</sub>AlF<sub>6</sub>—NaCl were chosen for the verification of the dissociation model in this work. In the MeCl—AlCl<sub>3</sub> systems the compound MeAlCl<sub>4</sub> is formed. The subsystems MeAlCl<sub>4</sub>—AlCl<sub>3</sub> are simple eutectic systems for which the needed data are known. Therefore the dissociation of MeAlCl<sub>4</sub> can be considered in this system only.

In the MeF—AlF<sub>3</sub> systems two complex compounds, Me<sub>3</sub>AlF<sub>6</sub> and MeAlF<sub>4</sub>, are formed. The congruently melting Me<sub>3</sub>AlF<sub>6</sub> compounds, however, undergo at melting a considerable thermal dissociation according to the scheme



and the equilibrium composition of Me<sub>3</sub>AlF<sub>6</sub>, MeF, and MeAlF<sub>4</sub> constitutes in the melts. The dissociation of all three components must be taken into account by the calculation. Similarly, in the Na<sub>3</sub>AlF<sub>6</sub>—NaCl system the cryolite dissociates partly in the liquid state according to the scheme (A). Thus the dissociation of all four components must be considered.

## Procedure and results

### A. The MeCl—AlCl<sub>3</sub> systems (Me = Li, Na, K)

As mentioned earlier in the MeCl—AlCl<sub>3</sub> systems the density and the conductivity data are known only for the subsystems MeAlCl<sub>4</sub>—AlCl<sub>3</sub> [5, 6]. From the Raman spectroscopic investigations [7, 8] it follows that MeAlCl<sub>4</sub> and Al<sub>2</sub>Cl<sub>6</sub> are the most frequent species in this part of the system. Let us consider a mixture of (1 - x) mol MeAlCl<sub>4</sub> and x mol AlCl<sub>3</sub> in which an equilibrium constitutes between the ionic pairs Me<sup>+</sup> AlCl<sub>4</sub><sup>-</sup> and the "free" Me<sup>+</sup> and AlCl<sub>4</sub><sup>-</sup> ions according to the scheme



If  $\alpha$  is the dissociation degree of the reaction (B) and considering the dimerization of AlCl<sub>3</sub> the following amounts of individual particles are present in an arbitrary mixture:  $x(\text{Me}^+) = x(\text{AlCl}_4^-) = \alpha(1 - x)$ ,  $x(\text{Me}^+ \text{AlCl}_4^-) = (1 - \alpha)(1 - x)$  and  $x(\text{Al}_2\text{Cl}_6) = 0.5x$ . For the equilibrium constant of the dissociation equation (B) we get

$$K = \frac{\alpha_0^2}{1 - \alpha_0^2} = \frac{\alpha}{(1 - \alpha)} \frac{\alpha(1 - x)}{(1 + \alpha(1 - x) - 0.5x)} = \frac{\alpha}{1 - \alpha} B \quad (1)$$

where  $\alpha_0$  is the dissociation degree of pure  $\text{MeAlCl}_4$ . Rearranging eqn (1) we get for the dissociation degree the implicit equation

$$\alpha = \frac{K}{K + B} \quad (2)$$

By analogy with the procedure shown in [1] the following relation can be derived for the molar conductivity of the  $\text{MeAlCl}_4$ — $\text{AlCl}_3$  mixture

$$\lambda_{\text{mix}} = (1 - x) \frac{\alpha}{\alpha_0} \lambda(\text{MeAlCl}_4) \quad (3)$$

where  $\lambda(\text{MeAlCl}_4)$  is the molar conductivity of pure  $\text{MeAlCl}_4$ . Solving eqns (1—3) along with the condition

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

we get the value of  $\alpha_0$  for which the standard deviation  $s$  of the experimental values of the molar conductivity from the calculated ones is less than the experimental error. The results of the calculations are given in Table 1. The comparison of the calculated course of the molar conductivity and the experimental data is shown in Fig. 1.

Table 1

The calculated values of the dissociation degrees of the pure components in systems containing  $\text{Al}^{3+}$

System	$T/\text{K}$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$s$
$\text{LiAlCl}_4$ — $\text{AlCl}_3$	480	—	0.93	—	—	0.83
$\text{NaAlCl}_4$ — $\text{AlCl}_3$	480	—	0.51	—	—	1.38
$\text{KAlCl}_4$ — $\text{AlCl}_3$	540	—	0.02	—	—	4.90
$\text{LiF}$ — $\text{AlF}_3$	1270	0.60	0.62	0.54	—	2.18
$\text{NaF}$ — $\text{AlF}_3$	1280	0.60	0.51	0.71	—	2.28
$\text{KF}$ — $\text{AlF}_3$	1290	0.52	0.50	0.45	—	3.28
$\text{Na}_3\text{AlF}_6$ — $\text{NaCl}$	1273	0.45	0.94	0.43	0.20	2.72

$s$  in  $\text{S cm}^2 \text{ mol}^{-1}$

$\alpha_1 = \alpha(\text{Me}_3\text{AlX}_6)$ ;  $\alpha_2 = \alpha(\text{MeAlX}_4)$ ;  $\alpha_3 = \alpha(\text{MeX})$ ;  $\alpha_4 = \alpha(\text{NaCl})$ .

### B. The $\text{MeF}$ — $\text{AlF}_3$ systems (Me = Li, Na, K)

The equilibrium mole fractions of  $\text{MeF}$ ,  $\text{MeAlF}_4$ , and  $\text{Me}_3\text{AlF}_6$  denoted as  $x_1$ ,  $x_2$ , and  $x_3$ , respectively, may be easily calculated on the basis of the known

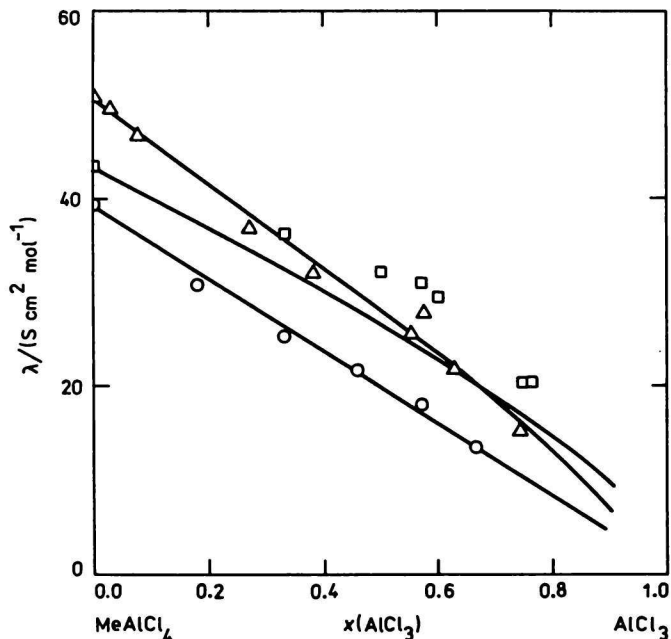


Fig. 1. The molar conductivity of the  $\text{MeAlCl}_4\text{--AlCl}_3$  systems.  
 ○  $\text{LiAlCl}_4\text{--AlCl}_3$ ; △  $\text{NaAlCl}_4\text{--AlCl}_3$ ; □  $\text{KAlCl}_4\text{--AlCl}_3$ ; — calculated.

values of the respective dissociation constants  $K_{\text{dis}}$  [9]. The individual components of the  $\text{MeF--AlF}_3$  system dissociate electrolytically according to the schemes



with the dissociation degrees  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$ , respectively. For the equilibrium constants of the dissociation reactions  $K_i$  we get the following equations

$$K_1 = \frac{\alpha_{01}^2}{1 - \alpha_{01}^2} = \frac{\alpha_1}{1 - \alpha_1} B \quad (5)$$

$$K_2 = \frac{\alpha_{02}^2}{1 - \alpha_{02}^2} = \frac{\alpha_2}{1 - \alpha_2} B \quad (6)$$

$$K_3 = \frac{27\alpha_{03}^4}{(1 - \alpha_{03})(1 + 3\alpha_{03})^3} = \frac{\alpha_3}{1 - \alpha_3} B \quad (7)$$

where

$$B = \frac{x_1 \alpha_1 + x_2 \alpha_2 + 3x_3 \alpha_3}{1 + x_1 \alpha_1 + x_2 \alpha_2 + 3x_3 \alpha_3} \quad (8)$$

Rearranging eqns (5—7) we get for the dissociation degrees of the individual components the following relations

$$\alpha_1 = \frac{K_1}{K_1 + B}; \quad \alpha_2 = \frac{K_2}{K_2 + B}; \quad \alpha_3 = \frac{K_3}{K_3 + B^3} \quad (9)$$

According to the dissociation model we get for the molar conductivity of the MeF—AlF<sub>3</sub> systems the equation

$$\lambda_{\text{mix}} = \sum_{i=1}^3 x_i \frac{\alpha_i}{\alpha_{0i}} \lambda_i \quad (10)$$

where  $\lambda_i$  are the molar conductivities of the pure components ( $\lambda_3$  are the hypothetical values for the pure thermally undissociated cryolites — the values 440 S cm<sup>2</sup> mol<sup>-1</sup>, 240 S cm<sup>2</sup> mol<sup>-1</sup>, and 360 S cm<sup>2</sup> mol<sup>-1</sup> for Li<sub>3</sub>AlF<sub>6</sub>, Na<sub>3</sub>AlF<sub>6</sub>, and K<sub>3</sub>AlF<sub>6</sub>, respectively, were used). The solution of eqns (5—10) along with the condition (4) enables finding of such values of  $\alpha_{0i}$  for which the standard deviation of the experimental and calculated values of the molar conductivity is less than the experimental error. The experimental density and conductivity data were taken from [5, 6]. The calculated values of the dissociation degrees of the pure components are given in Table 1. The comparison of the calculated course of the molar conductivity with the experimental data is shown in Fig. 2.

### C. The Na<sub>3</sub>AlF<sub>6</sub>—NaCl system

Similarly as in the previous case the cryolite in the Na<sub>3</sub>AlF<sub>6</sub>—NaCl melts is thermally dissociated. Thus at least four constituents must be considered to dissociate electrolytically. Due to the presence of the chloride anions two different reciprocal exchange reactions may further occur



However, according to the values of the reaction standard Gibbs energies (547 kJ mol<sup>-1</sup> for reaction (F) and 450 kJ mol<sup>-1</sup> for reaction (G) at the temperature of 1200 K [10]) these reactions are mostly improbable in the melt.

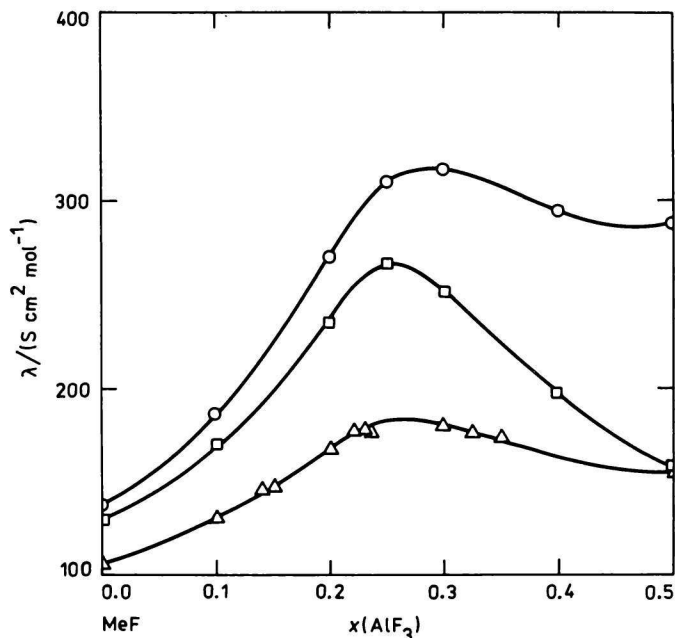


Fig. 2. The molar conductivity of the MeF—AlF<sub>3</sub> systems.  
 ○ LiF—AlF<sub>3</sub>; △ NaF—AlF<sub>3</sub>; □ KF—AlF<sub>3</sub>; — calculated.

Let us consider a mixture of  $(1 - x)$  mol Na<sub>3</sub>AlF<sub>6</sub> and  $x$  mol NaCl. Denoting the degree of thermal dissociation of cryolite as  $b$  the following equilibrium mole fractions of components are present in the melt

$$\begin{aligned}
 x_1 = x(\text{Na}_3\text{AlF}_6) &= \frac{(1-x)(1-b)}{1+2b(1-x)}; & x_2 = x(\text{NaF}) &= \frac{2b(1-x)}{1+2b(1-x)} \\
 x_3 = x(\text{NaAlF}_4) &= \frac{b(1-x)}{1+2b(1-x)}; & x_4 = x(\text{NaCl}) &= \frac{x}{1+2b(1-x)}
 \end{aligned}
 \quad (11)$$

For the equilibrium constant of the thermal dissociation of cryolite in the Na<sub>3</sub>AlF<sub>6</sub>—NaCl mixture the equation

$$K_{\text{dis}} = \frac{b}{1-b} \left( \frac{2b(1-x)}{1+2b(1-x)} \right)^2 \quad (12)$$

may be derived. For the known value of  $K_{\text{dis}}$  the equilibrium mole fraction of components can then be calculated.

The four components present in the melt partially dissociate according to the schemes



For the dissociation degrees  $\alpha_i$  of the reactions (H—K) the following equations may be derived

$$\begin{aligned} \alpha_1 &= \frac{K_1}{K_1 + B^3} & \alpha_2 &= \frac{K_2}{K_2 + B} \\ \alpha_3 &= \frac{K_3}{K_3 + B} & \alpha_4 &= \frac{K_4}{K_4 + B} \end{aligned} \quad (13)$$

where

$$B = \frac{3x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3 + x_4\alpha_4}{1 + 3x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3 + x_4\alpha_4} \quad (14)$$

$$K_1 = \frac{27\alpha_{01}^4}{(1 - \alpha_{01})(1 + 3\alpha_{01})^3}; \quad K_i = \frac{\alpha_{0i}^2}{1 - \alpha_{0i}^2} \quad i = 2, 3, 4 \quad (15)$$

Therefore it follows that with the procedure given in [1], the molar conductivity of the  $\text{Na}_3\text{AlF}_6$ — $\text{NaCl}$  mixture is given by the relation

$$\begin{aligned} \lambda_{\text{mix}} &= x_1 \frac{\alpha_1}{\alpha_1^*} \lambda(\text{Na}_3\text{AlF}_6) + x_2 \frac{\alpha_2}{\alpha_2^*} \lambda(\text{NaF}) + \\ &+ x_3 \frac{\alpha_3}{\alpha_3^*} \lambda(\text{NaAlF}_4) + x_4 \frac{\alpha_4}{\alpha_4^*} \lambda(\text{NaCl}) \end{aligned} \quad (16)$$

where  $\alpha_1^*$ ,  $\alpha_2^*$ , and  $\alpha_3^*$  are the dissociation degrees of the respective components in the pure cryolite (not in the pure components),  $\alpha_{04}$  is the dissociation degree of pure  $\text{NaCl}$ ,  $\lambda(\text{Na}_3\text{AlF}_6)$  is the molar conductivity of hypothetical undissociated cryolite (the same value as in the  $\text{NaF}$ — $\text{AlF}_3$  system was used) and  $\lambda(\text{NaF})$ ,  $\lambda(\text{NaAlF}_4)$ , and  $\lambda(\text{NaCl})$  are the experimental values of the molar conductivities of the pure components. The solution of eqns (12—16) along with the condition (4) allows the finding of such values of  $\alpha_{0i}$  for which the standard deviation of the experimental values of molar conductivity from the calculated ones is less than the experimental error for all mixtures with the

known value of the molar conductivity. The experimental data of the density and the conductivity of the  $\text{Na}_3\text{AlF}_6\text{—NaCl}$  system were taken from [5, 6]. The comparison of the calculated course of the molar conductivity with the experimental data is shown in Fig. 3.

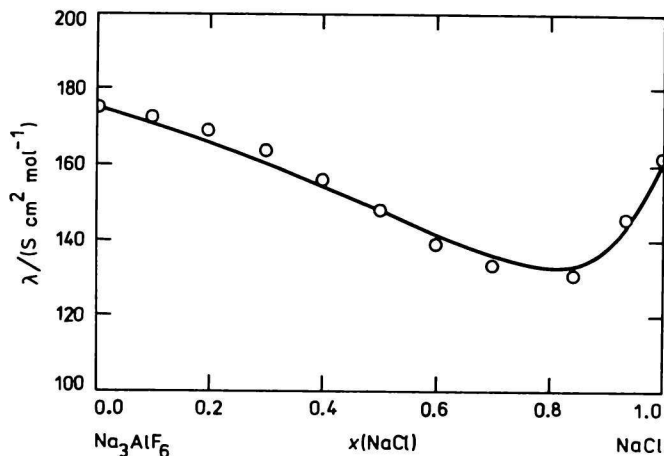


Fig. 3. The molar conductivity of the  $\text{Na}_3\text{AlF}_6\text{—NaCl}$  system.  
 ○ Experimental, — calculated.

## Discussion

From the values of the standard deviations of the experimental and the calculated values of the molar conductivity it follows that the dissociation model also very well describes the course of the molar conductivity in systems containing trivalent cation, *e.g.*  $\text{Al}^{3+}$ . The only exception is the system  $\text{KAlCl}_4\text{—AlCl}_3$ , where the relatively high standard deviation may be due to both the relatively high inaccuracy of the experimental data (*cf.* Fig. 1) and the neglecting of the presence of other possible anions such as *e.g.*  $\text{Cl}^-$  or  $\text{Al}_2\text{Cl}_7^-$ . The improbable low value of the dissociation degree of  $\text{KAlCl}_4$  and its incongruent melting character refers rather to the prevailing influence of the latter fact.

The calculated dependences of the molar conductivity on composition of the  $\text{MeF—AlF}_3$  systems (*cf.* Fig. 2) show an expressive maximum which is due to the formation of the new compounds ( $\text{Me}_3\text{AlF}_6$  and  $\text{MeAlF}_4$ ) and the constitution of the equilibrium composition of the melt. It is obviously not possible to describe such complicated dependences of the molar conductivity on composition using the existing phenomenological models [11—13]. Moreover, they do not consider the positive deviations from the additivity, as it is seen *e.g.* in



the  $\text{MeAlCl}_4\text{—AlCl}_3$  systems. The physical reason for the positive deviation of the molar conductivity from the additivity in these systems results from the concentration dependence of the dissociation degree of the component given by the equation for the dissociation equilibrium constant. In systems without a common ion the dissociation degree of the component increases with the decreasing mole fraction of the component, which results in the relatively increasing content of “free” ions. Similar behaviour may be seen also in the  $\text{Na}_3\text{AlF}_6\text{—NaCl}$  system. In spite of the fact that it is a system with a common cation the equilibrium mole fractions of  $\text{NaF}$  and  $\text{NaAlF}_4$  decrease only slightly with increasing mole fraction of  $\text{NaCl}$ . This is apparently because of the shifting of the equilibrium of the reaction (A) to the right due to the presence of  $\text{NaCl}$  (cf. eqn (12)). Consequently the molar conductivity in the  $\text{Na}_3\text{AlF}_6\text{—NaCl}$  system shows the S-shaped course (Fig. 3).

Finally it should be noted that the dissociation model of the electrical conductivity of molten salt mixtures also rationally explains the dependence of the molar conductivity on composition also in the rather complex systems containing a trivalent cation. However, the actual equilibrium composition of the melt must be taken into account in every case. The dissociation model has an evident physical background and offers a more detailed view on the structure with respect to the ionic composition of the mixture.

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