

# Dissociation model of the electrical conductivity of molten salt mixtures

## I. Theory of univalent electrolytes

V. DANĚK

*Institute of Inorganic Chemistry, Centre for Chemical Research,  
Slovak Academy of Sciences, CS-842 36 Bratislava*

Received 18 May 1988

A new model of electrical conductivity of molten salt mixtures, based on the idea of an incomplete dissociation of electrolyte components, is proposed. In systems with a common ion the dissociation degree of the component is affected by the presence of the second component. Consequently, the dissociation degree of both components is not constant, but changes with the composition of the mixture, which affects the concentration of the conducting particles in the electrolyte. On examples of the KCl—NaCl and KF—LiF binary systems it was shown that the "dissociation model" describes very well the course of the molar conductivity of binary systems with a common ion.

Предложена новая модель электропроводности расплавов смесей солей, основанная на идее неполной диссоциации электролитических компонентов. В системах с общим ионом степень диссоциации одного компонента подвержена влиянию второго компонента. Следовательно, степень диссоциации обоих компонентов не постоянна, а определяется составом смеси, от которого зависит концентрация проводящих частиц в электролите. На примерах бинарных систем KCl—NaCl и KF—LiF показано, что «диссоциативная модель» очень хорошо описывает процесс молярной проводимости бинарных систем с общим ионом.

The experimental study of the electrical conductivity of multicomponent molten systems is generally pretentious and with regard to the relative character of the measurement the results of various authors differ considerably. Therefore numerous attempts have been made to elaborate a theoretical model enabling the calculation of the electrical conductivity of a mixture on the basis of the knowledge of conductivities of the pure components.

The principal problem in the elaboration of a theoretical model of the electrical conductivity is the problem of an ideal behaviour. In the case of the molar conductivity the assumption of the additive ideal behaviour has been frequently used. However, this assumption is not acceptable owing to the existence of the interaction of the components in the mixture, given by the nature of the repulsive forces between the ions and determining the coordination

sphere of each kind of ions. As a matter of fact, no system with an additive course of the molar conductivity may be found in the literature. All investigated systems exhibit molar conductivities lower than additive.

The model of the molar conductivity of binary systems based on the assumption of a mutual interaction of the components has been proposed by *Markov* and *Shumina* [1]. They supposed that in the molten binary mixture AX—BX interactions of the type AXAX, BXBX and AXBX or BXAX are possible. The probability of the interactions of the AXAX and BXBX type is proportional to the square of the mole fraction of the respective component  $x_i$ , the interactions of the AXBX and BXAX type are proportional to the product  $2x_1 x_2$ . For the molar conductivity of an ideal binary molten mixture it holds (for  $\lambda_1 > \lambda_2$ )

$$\lambda_{\text{mix}} = x_1^2 \lambda_1 + x_2^2 \lambda_2 + 2x_1 x_2 \lambda_2 \quad (1)$$

The application of the model proposed by *Markov* and *Shumina* to different systems shows that this model is acceptable only in some simplest cases of the systems with a common ion, such as NaCl—KCl, PbCl<sub>2</sub>—PbBr<sub>2</sub>, and KNO<sub>3</sub>—NaNO<sub>3</sub>.

More universal model of the molar conductivity of the binary systems which supposes the interaction of  $k$  ions in systems with a common ion has been theoretically derived by *Kvist* [2] in the form

$$\lambda_{\text{mix}} = x_1^k \lambda_1 + (1 - x_1^k) \lambda_2 \quad (2)$$

The expression  $x_1^k$  represents the probability of the interaction of  $k$  ions of the component AX in a mixture with the mole fraction  $x_1$ . It may be easily shown that for  $k = 2$  eqn (2) transforms to eqn (1). Thus the model proposed by *Markov* and *Shumina* [1] is only a special case of the *Kvist*'s model, according to which the molar conductivity is determined by the polycationic and polyanionic interactions, respectively. The *Kvist*'s model describes well e.g. the systems of alkali and silver sulfates for  $k$  ranging from 2.7 up to 4.3.

The next two models of the electrical conductivity of binary and multicomponent systems have been proposed by *Fellner* [3]. On the basis of the idea of two possible ways of resistance coupling, he proposed the series and parallel models of the electrical conductivity of a mixture. He supposed that in an ideal mixture the mutual influence of conducting particles does not occur. According to *Fellner* [3] the conductivity of a mixture may be calculated as a sum of the contributions of the pure components placed in separated conductance cells linked either in series or parallelly. Denoting the conductivities of the components in a binary system by  $\kappa_1$  and  $\kappa_2$  and their molar volumes by  $V_1^\circ$  and  $V_2^\circ$ , *Fellner* derived for the conductivity of a mixture according to the series model the relation

$$\kappa_{\text{mix},s} = (x_1 \nu_1^\circ + x_2 \nu_2^\circ) / \left( \frac{x_1 \nu_1^\circ}{\kappa_1} + \frac{x_2 \nu_2^\circ}{\kappa_2} \right) \quad (3)$$

After rearrangement of eqn (3) we get for the molar conductivity of a mixture according to the series model

$$\lambda_{\text{mix},s} = (x_1 \nu_1^\circ + x_2 \nu_2^\circ)^2 / \left( x_1 \frac{\nu_1^{\circ 2}}{\lambda_1} + x_2 \frac{\nu_2^{\circ 2}}{\lambda_2} \right) \quad (4)$$

It has been shown [4] that the series model gives a good accordance with the experimentally determined molar conductivity of a molten mixture in such cases, when the system behaves ideally also from the thermodynamic point of view. If the system, however, deviates from the thermodynamic ideality, the series model fails.

For the parallel model *Fellner* [3] derived the relation

$$\kappa_{\text{mix},p} = (x_1 \kappa_1 \nu_1^\circ + x_2 \kappa_2 \nu_2^\circ) / (x_1 \nu_1^\circ + x_2 \nu_2^\circ) \quad (5)$$

By definition  $\kappa \cdot \nu^\circ = \lambda$ , consequently the parallel model of the conductivity is obviously identical with the additive model of the molar conductivity. As shown in [4], the parallel model represents a limiting case, in which no interaction of components takes place. Therefore, the real molar conductivity is always lower than that one calculated according to the parallel model.

In the present work, the "dissociation model" of the molar conductivity of molten binary systems with a common ion, based on the idea of an incomplete dissociation of components, is proposed. The validity of the dissociation model is verified in the KCl—NaCl and KF—LiF systems.

### Theoretical

Let us consider a binary system with a common anion of the type AX—BX. Let us further assume that each component in the molten mixture is incompletely dissociated and that an equilibrium between the ionic pairs  $A^+ X^-$ , or  $B^+ X^-$  and the "free" ions  $A^+$  and  $X^-$ , and  $B^+$  and  $X^-$  constitutes in the melt



If we denote the dissociation degrees of the components in the mixture by  $\alpha_1$  and  $\alpha_2$  and their mole fractions by  $x_1$  and  $x_2$ , then in one mole of an arbitrary mixture of  $x_1(\text{AX})$  and  $x_2(\text{BX})$  the following equilibrium amounts of substances of particles are present

$$\begin{aligned}
 n_{A^+} &= x_1 \alpha_1 & n_{B^+} &= x_2 \alpha_2 \\
 n_{X^-} &= x_1 \alpha_1 + x_2 \alpha_2 \\
 n_{A^+ X^-} &= x_1(1 - \alpha_1) & n_{B^+ X^-} &= x_2(1 - \alpha_2)
 \end{aligned}
 \tag{6}$$

The total amount of substance of all particles is then  $n = 1 + x_1 \alpha_1 + x_2 \alpha_2$ . For the equilibrium mole fractions of individual particles we get

$$\begin{aligned}
 x_{A^+} &= \frac{x_1 \alpha_1}{1 + x_1 \alpha_1 + x_2 \alpha_2} & x_{B^+} &= \frac{x_2 \alpha_2}{1 + x_1 \alpha_1 + x_2 \alpha_2} \\
 x_{X^-} &= \frac{x_1 \alpha_1 + x_2 \alpha_2}{1 + x_1 \alpha_1 + x_2 \alpha_2} \\
 x_{A^+ X^-} &= \frac{x_1(1 - \alpha_1)}{1 + x_1 \alpha_1 + x_2 \alpha_2} & x_{B^+ X^-} &= \frac{x_2(1 - \alpha_2)}{1 + x_1 \alpha_1 + x_2 \alpha_2}
 \end{aligned}
 \tag{7}$$

The equilibrium constants of the dissociation reactions according to eqns (A) and (B) are given by the relations

$$K_1 = \frac{\alpha_{01}^2}{1 - \alpha_{01}^2} = \frac{\alpha_1(x_1 \alpha_1 + x_2 \alpha_2)}{(1 - \alpha_1)(1 + x_1 \alpha_1 + x_2 \alpha_2)}
 \tag{8}$$

$$K_2 = \frac{\alpha_{02}^2}{1 - \alpha_{02}^2} = \frac{\alpha_2(x_1 \alpha_1 + x_2 \alpha_2)}{(1 - \alpha_2)(1 + x_1 \alpha_1 + x_2 \alpha_2)}
 \tag{9}$$

where  $\alpha_{01}$  and  $\alpha_{02}$  are the dissociation degrees of the pure components AX and BX at the given temperature. By rearranging eqns (8) and (9) we get for  $\alpha_1$  and  $\alpha_2$  in an arbitrary mixture the following relations

$$\alpha_1^2 \cdot x_1 + \alpha_1 \cdot x_2(\alpha_2 + \alpha_{01}^2) - \alpha_{01}^2(1 + x_2 \alpha_2) = 0
 \tag{10}$$

$$\alpha_2^2 \cdot x_2 + \alpha_2 \cdot x_1(\alpha_1 + \alpha_{02}^2) - \alpha_{02}^2(1 + x_1 \alpha_1) = 0
 \tag{11}$$

These implicit equations for the concentration dependences of  $\alpha_1$  and  $\alpha_2$  can be solved analytically. Separating  $\alpha_2$  in eqn (10)

$$\alpha_2 = \frac{\alpha_{01}^2 - x_1 \alpha_1^2 - x_2 \alpha_1 \alpha_{01}^2}{x_2 \alpha_1 - x_2 \alpha_{01}^2}
 \tag{12}$$

and inserting it into eqn (11), we get for  $\alpha_1$  the cubic equation

$$\begin{aligned}
 \alpha_1^3[x_1 \cdot x_2(\alpha_{01}^2 - \alpha_{02}^2)] + \alpha_1^2\{x_2[x_1(\alpha_{01}^2 \cdot \alpha_{02}^2 - \alpha_{01}^2) + x_2(\alpha_{01}^4 - \alpha_{02}^2)]\} + \\
 + \alpha_1[x_2(1 + x_2)(\alpha_{01}^2 \alpha_{02}^2 - \alpha_{01}^4)] + \alpha_{01}^4(1 - \alpha_{02}^2)x_2 = 0
 \end{aligned}
 \tag{13}$$

This equation can be solved either analytically or, preferably, using the Newton—Raphson's method. As starting values for  $\alpha_1$  and  $\alpha_2$  it is advantageous to choose the values of the dissociation degrees of the pure components  $\alpha_{01}$  and  $\alpha_{02}$ . In this way it is possible to calculate the values of  $\alpha_1$  and  $\alpha_2$  for an arbitrary composition of the mixture and for arbitrary values of the dissociation degrees of the pure components.

For the conductivity of the electrolyte the general equation is valid

$$\kappa = \sum_{i=1}^k F z_i c_i u_i \quad (14)$$

where  $c_i$  are the molar concentrations of the particles with the mobility  $u_i$  and with the charge  $F z_i$ . For the uni-univalent electrolytes  $z_i = 1$  and  $F u_i = \lambda_i$ . Eqn (14) has then the form

$$\kappa = \sum_{i=1}^k c_i \lambda_i = \sum_{i=1}^k \frac{n_i}{V} \cdot \lambda_i \quad (15)$$

where  $n_i$  are the amounts of substances of the conducting particles in the mixture and  $V$  is the total volume of the mixture. In the case of the molten electrolytes it may be assumed that the ionic pairs  $A^+ X^-$  and  $B^+ X^-$ , present in the mixture, are electroneutral and do not contribute to the conductivity of the electrolyte. The whole charge is transported by "free" ions, *i.e.* by cations  $A^+$  and  $B^+$  and anions  $X^-$ . In such a case eqn (15) may be written in the form

$$\kappa_{\text{mix}} = \frac{n_{A^+}}{V} \lambda_{A^+} + \frac{n_{B^+}}{V} \lambda_{B^+} + \frac{n_{X^-}}{V} \lambda_{X^-} \quad (16)$$

If we consider one mole of the mixture, then according to eqn (8)  $n_{A^+} = x_1 \alpha_1$ ,  $n_{B^+} = x_2 \alpha_2$ ;  $n_{X^-} = x_1 \alpha_1 + x_2 \alpha_2$  and  $V = V_{\text{m,mix}}$  (the molar volume of the mixture). For the molar conductivity of the mixture we get

$$\lambda_{\text{mix}} = \kappa_{\text{mix}} V_{\text{m,mix}} = x_1 \alpha_1 \lambda_{A^+} + x_2 \alpha_2 \lambda_{B^+} + (x_1 \alpha_1 + x_2 \alpha_2) \lambda_{X^-} \quad (17)$$

and by rearranging

$$\lambda_{\text{mix}} = x_1 \alpha_1 (\lambda_{A^+} + \lambda_{X^-}) + x_2 \alpha_2 (\lambda_{B^+} + \lambda_{X^-}) \quad (18)$$

As the molar conductivities of the individual ions are not a priori known, their sum can be expressed on the basis of the limiting conditions

$$\lambda_{A^+} + \lambda_{X^-} = \frac{\lambda_1}{\alpha_{01}}, \quad \lambda_{B^+} + \lambda_{X^-} = \frac{\lambda_2}{\alpha_{02}} \quad (19)$$

and we get for the molar conductivity of the molten mixture the final expression

$$\lambda_{\text{mix}} = x_1 \cdot \frac{\alpha_1}{\alpha_{01}} \cdot \lambda_1 + x_2 \cdot \frac{\alpha_2}{\alpha_{02}} \cdot \lambda_2 \quad (20)$$

From eqn (20) it follows that if the dissociation degrees do not change with composition, *i.e.*  $\alpha_1 = \alpha_{01}$  and  $\alpha_2 = \alpha_{02}$ , eqn (20) is identical with the parallel model [3]. Thus the expression  $x_i(\alpha_i/\alpha_{0i})$  may be considered as a certain expression for the "conductance activity" of the components in the mixture.

The calculation procedure is as follows: For the chosen values of the dissociation degrees of the pure components  $\alpha_{01}$  and  $\alpha_{02}$ , the values of  $\alpha_1$  and  $\alpha_2$  were calculated according to eqns (12) and (13) for each composition of the mixture with the known value of the molar conductivity  $\lambda_{i,\text{exp}}$ . The theoretical value of the molar conductivity  $\lambda_{i,\text{calc}}$  is calculated according to eqn (20). In such a way for each couple of  $\alpha_{01}$  and  $\alpha_{02}$  values a set of theoretical values of molar conductivities for a given composition of the mixture is obtained. The criterion for the selection of the right values of  $\alpha_{01}$  and  $\alpha_{02}$  is given by the relation

$$\sum_{i=1}^n (\lambda_{i,\text{exp}} - \lambda_{i,\text{calc}})^2 = \min \quad (21)$$

It is obvious that the derived eqns (12), (13), and (20) can be used in the binary systems with common cation, too.

## Results and discussion

For the verification of the applicability of the proposed model of the electrical conductivity of the molten salt mixtures, the binary systems KCl—NaCl and KF—LiF were selected. The experimental values of the molar conductivities of both systems were calculated on the basis of the conductivity and density data given in [5]. The course of the concentration dependences of the molar conductivities in these systems is essentially different. While the KCl—NaCl system behaves rather "rationally" and the molar conductivity monotonically increases with the increasing content of NaCl, there is an expressed minimum in the KF—LiF system. From the point of view of the volume properties, both systems are close to the ideal one (for  $x = 0.5$  in the KCl—NaCl system  $V_{\text{excess}} = 0.26 \text{ cm}^3 \text{ mol}^{-1}$ , *i.e.* 0.58 % and in the KF—LiF system  $V_{\text{excess}} = 0.02 \text{ cm}^3 \text{ mol}^{-1}$ , *i.e.* ca. 0.1 % [5]), but the enthalpy of mixing in the KF—LiF system for  $x = 0.5$  attains the value of  $4.91 \text{ kJ mol}^{-1}$  [6], which indicates a strong interaction of the components.

Fig. 1 shows the experimental values of the molar conductivity of the molten KCl—NaCl system at the temperature of 1100 K and the theoretical courses calculated according to the individual models. It is obvious that the parallel



— with regard to the general level of the measuring technique — in the range from 1 to 2 %. The dissociation model, however, describes the experimental results most accurately.

The experimental values of the molar conductivity of the KF—LiF system at the temperature of 1300 K and the theoretical courses calculated according to the various models are compared in Fig. 2. It is obvious that none of the previously proposed models describes the real course of the molar conductivity in this system. The minimum on the concentration dependence of the molar conductivity is attained only with the series model. As follows from Table 1, the standard deviations of the experimental values from the theoretical ones calculated by use of those models surpass substantially the experimental error, most probably due to the unadequate consideration of the interaction of the components. On the other hand, the dissociation model describes the experimental course very well, as it is possible to find such values of  $\alpha_{01}$  and  $\alpha_{02}$ , for which the standard deviation is comparable with the experimental error of  $2.7 \text{ S cm}^2 \text{ mol}^{-1}$

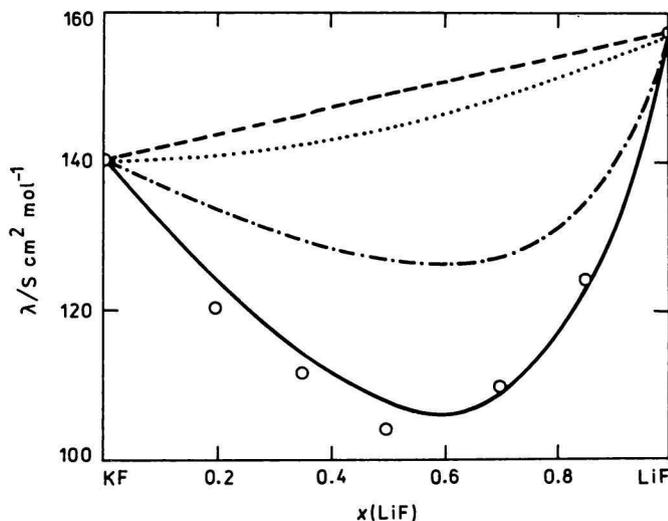


Fig. 2. Molar conductivity of the molten KF—LiF system at the temperature of 1300 K.

○ Experimental values [5]; — — — parallel model; — · — · — Markov and Shumina [1] model;  
— · — · — series model; — — — dissociation model.

The values of the dissociation degrees of the pure components in the KCl—NaCl system at the temperature of 1100 K are  $\alpha_{0,\text{KCl}} = 0.97$  and  $\alpha_{0,\text{NaCl}} = 0.49$ . The corresponding values in the KF—LiF system at the temperature of 1300 K are  $\alpha_{0,\text{KF}} = 0.985$  and  $\alpha_{0,\text{LiF}} = 0.175$ . These values comply

with the fact that the component with smaller radius of the cation, *i.e.* with higher electronegativity, is always less dissociated in a molten mixture. This means that the cations with higher field strength (the charge to radius ratio) bind the surrounding anions stronger and, consequently, exhibit a greater tendency to formation of the ionic pairs or associates. The dissociation of the component in the molten mixture is then affected by the properties of the second component. Thus, *e.g.* the dissociation degree of NaCl in the mixtures with LiCl and KCl, respectively, will be probably different. Then it can be expected that the value of the equilibrium constant of dissociation of the component will depend on the system under investigation. This is understandable, because as a matter of fact it is not possible to consider the formation of the ionic pairs only, but in general the formation of the more complex clusters of the  $A_rX_s^{(r-s)}$  type with a mobility substantially lower than is the mobility of "free" ions. The average

Fig. 3. Dependence of the dissociation degree of KCl and NaCl on the composition in the KCl—NaCl system at the temperature of 1100 K.

○  $\alpha_{\text{KCl}}$ ; △  $\alpha_{\text{NaCl}}$ .

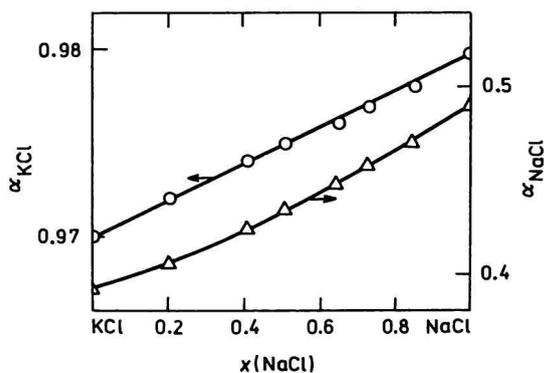
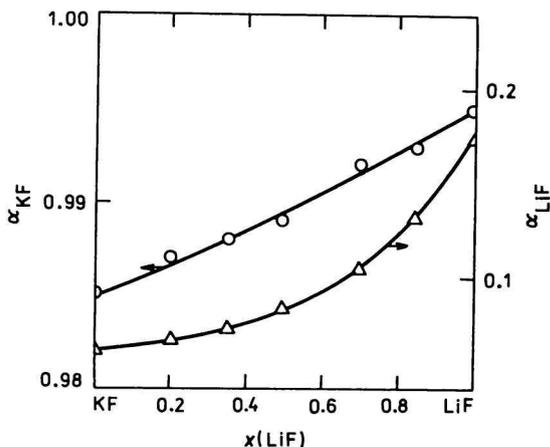


Fig. 4. Dependence of the dissociation degree of KF and LiF on the composition in the KF—LiF system at the temperature of 1300 K.

○  $\alpha_{\text{KF}}$ ; △  $\alpha_{\text{LiF}}$ .



magnitude of the clusters obviously depends also on the properties of the second component. For each cluster of an arbitrary magnitude it is possible to write formally the correspondent dissociation equation with the corresponding value of the dissociation constant. For simplification of the calculation, in this work the dissociation equations of the clusters were formally substituted by simple eqns (A) and (B).

The dependences of the dissociation degrees of individual components on the composition in the KCl—NaCl and KF—LiF systems are shown in Figs. 3 and 4. It can be seen that the dissociation degree of the more dissociated component slightly increases with increasing content of the second component whereas an opposite tendency is observed for the less dissociated component. The observed dependences also point to the fact that the dissociation of the given component in the mixture is strongly affected by the properties of the added “foreign” ion.

### References

1. Markov, B. F. and Shumina, L. A., *Dokl. Akad. Nauk SSSR* 110, 411 (1956).
2. Kvist, A., *Z. Naturforsch.* 22A, 208 (1967).
3. Fellner, P., *Chem. Zvesti* 38, 159 (1984).
4. Fellner, P. and Chrenková, M., *Chem. Papers* 41, 13 (1987).
5. Janz, G. J., Allen, C. B., Bansal, N. P., Murphy, R. M., and Tomkins, R. P. T., *Physical Properties Data Compilations Relevant to Energy Storage. II. Molten Salts: Data on Single and Multi-Component Salt Systems*. Nat. Stand. Ref. Data System, NBS (U.S.), April 1979; *IV Molten Salts: Data on Additional Single and Multi-Component Salt Systems*. Nat. Stand. Ref. Data System, NBS (U.S.), July 1981.
6. Lumsden, J., *Thermodynamics of Molten Salt Mixtures*, p. 28. Academic Press, London, 1966.

Translated by V Daněk