

# Dissociation model of the electrical conductivity of molten salt mixtures

## II. Binary univalent systems with common ion

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The dissociation model of the electrical conductivity of molten salt mixtures, based on the assumption of an incomplete dissociation of components, was verified in a number of binary univalent systems with a common anion as well as with a common cation, such as systems of alkali halides, of alkali metal nitrates and of silver halides. It was found that in the systems with the common anion the component with a larger cation is always more dissociated. In systems with a common cation the higher value of the dissociation degree always belongs to the component with the lower polarizability of anion. The linear dependence of the difference of the dissociation degrees of components ( $\alpha_{01} - \alpha_{02}$ ) on the geometrical parameter  $\Delta$  was found. This parameter represents the fractional difference in the ionic radii of the like charged ions. The correlation between the course of the molar conductivity and the enthalpy of mixing in the studied systems is discussed.

Диссоциационная модель электропроводности расплавов смесей солей, основанная на предположении неполной диссоциации компонентов, была проверена на ряде бинарных одновалентных систем с общим анионом, а также с общим катионом, например, в системах галогенидов щелочных металлов, нитратов щелочных металлов и галогенидов серебра. Обнаружено, что в системах с общим анионом компонент с более размерным катионом всегда более диссоциирован. В системах с общим катионом более высокое значение степени диссоциации имеет всегда компонент с более низкой поляризуемостью аниона. Найдена линейная зависимость разности степеней диссоциации компонентов, ( $\alpha_{01} - \alpha_{02}$ ), от геометрического параметра  $\Delta$ . Этот параметр представляет собой фракционную разность ионных радиусов одинаково заряженных ионов. Обсуждается взаимосвязь между мольной электропроводностью и энтальпией смешения в изучаемых системах.

In the previous paper [1] the dissociation model of the electrical conductivity of the molten salt mixture was proposed and theoretically derived. This model is based on the idea of the incomplete dissociation of the electrolyte com-

ponents. In systems with a common ion the mutual influence of the dissociation equilibria of the components takes place. Consequently the dissociation degrees of the components are not constant but they change with the composition of the system.

In the systems with a common ion the constitution of the equilibrium between the individual ions and of the ionic pairs is assumed for each component (*e.g.* in systems with a common anion)



For the equilibrium constant of the dissociation reactions (A) and (B) the following relations result from the material balance

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

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

where  $\alpha_{0i}$  and  $\alpha_i$  are the dissociation degrees of the pure components and those of the components in the mixture with the composition given by the mole fractions  $x_i$ , respectively. The set of eqns (1) and (2) is implicit with respect to  $\alpha_i$  and its analytical solution is given in [1].

For the molar conductivity of the binary mixture with a common ion the following relation was derived in [1]

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

where  $\lambda_i$  are the molar conductivities of the pure components. The solution of eqns (1—3) along with the condition

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

allows to find such values of  $\alpha_{01}$  and  $\alpha_{02}$  that for all figurative points of the system with known value of the molar conductivity the difference of the measured and calculated values of the molar conductivity is lower than the experimental error.

The validity of the dissociation model of the electrical conductivity of the molten salt mixtures was verified in a number of univalent systems with a common ion. The systems of alkali halides with a common anion as well as with a common cation, further the systems of alkali metal nitrates and of silver halides were chosen.

### Procedure and results

The experimental data on the molar conductivity of the systems under examination were taken from [2—9]. It should be noted that in prevailing cases the molar conductivity of a given mixture was calculated using the published values of the density and of the conductivity of melts with nonequal composition. Therefore the interpolated values had to be used. Further, in many cases the data on the conductivity and the density of pure components measured by different authors do not coincide which required either to correct the values of the pure components or in some cases to shift the values of the molar conductivity of all figurative points inside the system. By the corrections the data given in [10] were considered to be the correct values of the molar conductivity of the pure components.

The calculated values of the dissociation degrees of the pure components of the binary systems with a common anion are given in Table 1. The values for

Table 1

The calculated values of the dissociation degrees of the pure components of the binary systems with common anion

System	<i>T</i> /K	$\alpha_{01}$	$\alpha_{02}$	$\Delta$	Ref.
LiF—NaF	1200	0.21	0.42	0.052	[2]
LiF—KF	1200	0.17	0.91	0.116	[2]*
NaF—KF	1200	0.47	0.80	0.065	[2]
LiCl—NaCl	1100	0.28	0.52	0.050	[3]
LiCl—KCl	1100	0.19	0.83	0.104	[3]*
LiCl—CsCl	1100	0.24	0.95	0.158	[3]*
NaCl—KCl	1100	0.42	0.81	0.054	[3]
NaCl—RbCl	1100	0.19	0.50	0.075	[3]
NaCl—CsCl	1100	0.19	0.63	0.109	[3]
KCl—RbCl	1100	0.37	0.57	0.022	[3]
RbCl—CsCl	1100	0.41	0.58	0.034	[3]
LiI—NaI	1000	0.23	0.45	0.044	[4]
LiI—KI	1000	0.21	0.56	0.090	[4]
LiI—RbI	1000	0.19	0.84	0.109	[4]
LiI—CsI	1000	0.13	0.74	0.139	[4]
NaI—KI	1000	0.41	0.74	0.047	[4]
LiNO <sub>3</sub> —NaNO <sub>3</sub>	640	0.42	0.52	0.044	[5]
LiNO <sub>3</sub> —KNO <sub>3</sub>	640	0.43	0.85	0.092	[5]
NaNO <sub>3</sub> —KNO <sub>3</sub>	640	0.53	0.81	0.048	[5]

\* Corrected values.

Table 2

The calculated values of the dissociation degrees of the pure components of the binary systems with common cation

System	T/K	$\alpha_{01}$	$\alpha_{02}$	$\Delta$	Ref.
LiF—LiCl	1100	0.73	0.24	0.099	[6]
LiF—LiBr	1100	0.99	0.19	0.130	[6]
LiF—LiI	1100	0.999	0.155	0.174	[6]
LiCl—LiBr	1100	0.67	0.44	0.030	[6]
LiCl—LiI	1100	0.705	0.33	0.076	[6]
LiBr—LiI	1100	0.79	0.59	0.046	[6]
KF—KBr	1100	0.99	0.46	0.111	[7]
KF—KI	1100	0.99	0.325	0.148	[7]
CsF—CsCl	1100	0.81	0.35	0.077	[8]
CsF—CsBr	1100	1.00	0.28	0.099	[8]
CsF—CsI	1100	0.95	0.21	0.133	[8]
AgCl—AgBr	850	0.54	0.40	0.025	[9]
AgCl—AgI	850	0.50	0.21	0.064	[9]*
AgBr—AgI	850	0.455	0.21	0.039	[9]*

\* Corrected values.

the binary systems with a common cation are given in Table 2. In both tables also the values of the simple geometrical parameter  $\Delta$ , the so-called Tobolsky parameter [11], are given. This parameter represents the fractional difference of the ionic radii of both like charged ions

$$\Delta = \frac{d_1 - d_2}{d_1 + d_2} \quad (5)$$

where  $d_1$  and  $d_2$  are the interatomic distances (the sum of the ionic radii of the cation and anion) of the individual components. The values of the ionic radii were taken from [12, 13].

## Discussion

As follows from Table 1, in systems with a common anion always the component with larger cation, *i.e.* with lower field strength (the charge to radius ratio) has the higher value of the dissociation degree. It means that the more electronegative cations bind the surrounding anions stronger and thus they possess a larger tendency to form ionic pairs, resp. associates. In systems with a common cation (*cf.* Table 2) always the component with the lower polariza-

bility of anion, *i.e.* the component with the smaller anion has the higher value of the dissociation degree. It is due to the fact that the entrance of a strange ion into the pure molten component causes a nonrandom mixing and thus the lowering of the configurational entropy of the melt. The entrance of a strange ion causes the change of the coulombic, the polarization and the dispersion energy of the system resulting from the substitution of ions of different size in the coordination sphere of ions and the distortion of the symmetry of the electrical field of ions. As has been shown by *Førland* [14], *Lumsden* [15], and *Blander* [16] on the basis of a simple geometrical model and by *Reiss et al.* [17] and *Davis and Rice* [18] on the basis of the theory of the conformal solutions the measure of this energetical change is the dimensionless parameter  $\Delta$  (*cf.* eqn (5)), which represents the fractional difference in the ionic radii of the like charged ions. On the basis of the mentioned theories the negative values of the mixing enthalpy may be expected, the magnitude of which increases with increasing difference of the ionic radii

$$\Delta H_{\text{mix}} \approx Ex_1x_2(U_0 + U_1\Delta + U_2\Delta^2) \quad (6)$$

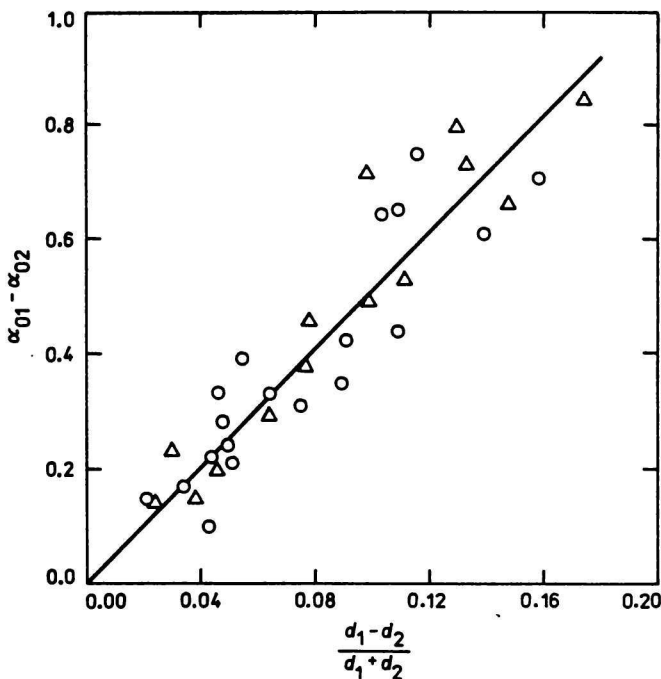


Fig. 1. The dependence of the difference of the dissociation degrees ( $\alpha_{01} - \alpha_{02}$ ) of the components on the parameter  $\Delta$ . O Systems with common anion;  $\Delta$  systems with common cation.

where  $U_0$  is the change in the dispersion energy resulting from the change of the induced dipoles of the second coordination sphere of cations,  $U_1$  is the change in the polarization energy caused by the asymmetry of the electrical field of anions owing to the different electronegativity of cations with different radius and  $U_2$  is the change in the coulombic energy resulting from the different cation—anion distance of both components. It is evident that these effects affect also the concentration of the “free” ions in the mixture which is determined by the values of  $\alpha_{01}$  and  $\alpha_{02}$ . Therefore the linear plot of the difference of the dissociation degrees of both components *vs.* the geometrical parameter  $\Delta$ , resp.  $\Delta^2$ , depending on that which energetic therm is the decisive one, may be expected. In Fig. 1 the dependence of the difference of the dissociation degrees of the components ( $\alpha_{01} - \alpha_{02}$ ) on the parameter  $\Delta$  for all the studied binary systems is shown. By means of the regression analysis the equation

$$\alpha_{01} - \alpha_{02} = 5.095 \Delta \quad (7)$$

with the standard deviation  $s = 8.5 \times 10^{-2}$  was obtained for this dependence. A very good correlation of both quantities is obvious from this figure, which

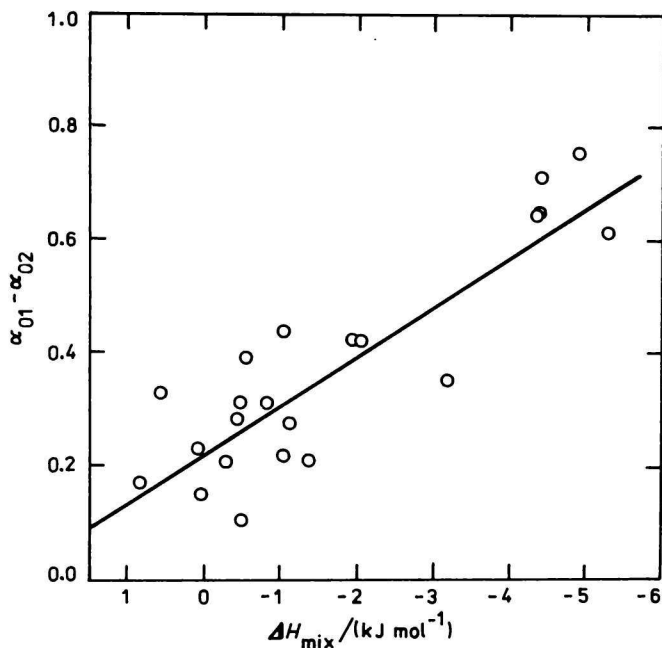


Fig. 2. The dependence of the difference of the dissociation degrees ( $\alpha_{01} - \alpha_{02}$ ) of the pure components on the enthalpy of mixing  $\Delta H_{\text{mix}}$  at  $x_1 = x_2 = 0.5$  for some systems with common ion.

Table 3

The standard deviations of the experimental values of the molar conductivity from those calculated according to the individual models for the systems with common anion

System	$s/(S\text{ cm}^2\text{ mol}^{-1})$			
	Dissociation	Markov	Series	Parallel
LiF--NaF	2.31	2.74	3.23	7.98
LiF--KF	4.50	27.55	14.23	29.68
NaF--KF	1.03	2.77	1.88	2.44
LiCl--NaCl	0.25	3.05	2.15	8.19
LiCl--KCl	1.94	17.75	4.10	32.78
LiCl--CsCl	4.18	9.89	20.65	29.89
NaCl--KCl	0.49	1.47	1.09	6.00
NaCl--RbCl	0.24	5.52	1.61	12.66
NaCl--CsCl	1.87	10.00	2.05	17.11
KCl--RbCl	0.35	1.64	0.35	1.49
RbCl--CsCl	0.09	0.98	0.82	1.20
LiI--NaI	1.73	4.99	2.83	14.08
LiI--KI	2.78	4.05	17.82	24.72
LiI--RbI	2.83	11.31	16.94	33.72
LiI--CsI	12.77	25.75	15.52	44.45
NaI--KI	0.29	3.21	2.38	5.05
LiNO <sub>3</sub> --NaNO <sub>3</sub>	0.13	0.19	0.12	0.25
LiNO <sub>3</sub> --KNO <sub>3</sub>	0.41	1.14	1.68	2.46
NaNO <sub>3</sub> --KNO <sub>3</sub>	0.08	2.24	1.53	1.06

refers to the prevailing influence of the polarization energy change on the dissociation of both components at mixing. The change in the coulombic energy is not so important as the regression analysis of the  $\alpha_{01} - \alpha_{02} = f(\Delta^2)$  plot gives lower value of the correlation coefficient. In spite of the good correlation of the dependence shown in Fig. 1 the dispersion of the  $\alpha_{01} - \alpha_{02}$  values is given by several factors:

- i) the precision and the correctness of the molar conductivity values of the mixtures,
- ii) the uncertainty of the ionic radii values,
- iii) the neglecting of the coulombic energy change between the more distant ions,
- iv) the simplifying of the three-dimensional interaction to the linear one,
- v) the neglecting of the dissociation of the more complex clusters of the  $A_m X_n^{(m-n)}$  type.

Table 4

The standard deviations of the experimental values of the molar conductivity from those calculated according to the individual models for the systems with common cation

System	$s/(S\text{ cm}^2\text{ mol}^{-1})$			
	Dissociation	Markov	Series	Parallel
LiF—LiCl	1.92	7.43	18.44	21.81
LiF—LiBr	1.82	23.16	38.29	40.81
LiF—LiI	8.71	41.33	62.78	67.87
LiCl—LiBr	1.11	1.61	2.99	3.72
LiCl—LiI	1.33	4.71	10.85	13.28
LiBr—LiI	0.89	4.25	1.85	2.28
KF—KBr	1.38	3.38	15.45	5.47
KF—KI	1.99	8.24	5.42	11.23
CsF—CsCl	1.34	1.69	5.10	5.72
CsF—CsBr	2.09	3.55	4.36	10.74
CsF—CsI	8.53	10.67	2.79	17.75
AgCl—AgBr	0.25	2.37	1.01	0.67
AgCl—AgI	1.85	1.92	1.81	4.94
AgBr—AgI	3.14	2.09	0.94	0.75

It is thus obvious that for the deeper theoretical analysis of the mutual interaction of the components more precise and more intact experimental data on the electrical conductivity of the molten salt systems are needed. The above-mentioned factors cause most probably also the differences between the values of the dissociation degrees of the pure components in dependence on the second one.

From the results of the calculation it further follows that there exists a very close coherence between the course of the dependence of the molar conductivity and the enthalpy of mixing on the composition. This follows also from the linear dependence of the difference of the dissociation degrees of pure components ( $\alpha_{01} - \alpha_{02}$ ) on the mixing enthalpy  $\Delta H_{\text{mix}}$  at  $x_1 = x_2 = 0.5$  which is for some systems given in Fig. 2. The respective values of the mixing enthalpy were taken from [13, 19, 20].

The dissociation model of the electrical conductivity of the molten salt mixture enables to interpret also the unsymmetrical course of the composition dependence of the molar conductivity, which is given by the values of both dissociation constants. The dissociation model explains rationally the course of the composition dependence of the molar conductivity also in such cases if due



to the strong interaction of the components this dependence shows an expressed minimum. In Tables 3 and 4 the standard deviations of the experimental values of the molar conductivity from the theoretical course calculated according to the dissociation model, the model of *Markov* and *Shumina* [21], the series and the parallel models [22] are given. From the tables it follows that using the dissociation model the standard deviations are in each case better or comparable with the experimental error. However, it should be noted that the model of *Markov* and *Shumina* and the series and parallel models do not involve adjustable parameters as it is in the dissociation model.

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