Dissociation model of the electrical conductivity of molten salt mixtures
III. Ternary univalent systems with common ion

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday
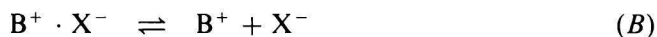
The dissociation model of the electrical conductivity of molten salt mixtures, based on the idea of an incomplete dissociation of electrolyte components was applied in some ternary univalent systems with a common anion as well as with a common cation. The systems of alkali halides, of alkali metal nitrates, and of silver halides were examined. It was found that in the systems with a common anion the dissociation degree increases with the increasing radius of the cation. In the systems with a common cation the dissociation degree increases with the decreasing radius of the anion. The dissociation model describes the course of the molar conductivity of ternary univalent systems with a common ion very well. The standard deviations of the experimental values from the calculated ones are lower or comparable with the experimental error.

Диссоциативная модель электропроводности расплавленных смесей солей, основанная на предположении неполной диссоциации составных частей электролита, была применена для изучения некоторых тройных одновалентных систем с общим анионом, а также с общим катионом. Были изучены системы галогенидов щелочных металлов, нитратов щелочных металлов и галогенидов серебра. Было найдено, что в системах с общим анионом степень диссоциации возрастает при увеличении радиуса катиона. В системах с общим катионом степень диссоциации возрастает при уменьшении радиуса аниона. Диссоциативная модель очень хорошо описывает ход молярной электропроводности тройных одновалентных систем с общим ионом. Стандартные отклонения экспериментальных величин от рассчитанных ниже или сравнимы по величине с ошибкой эксперимента.

In [1] the dissociation model of the electrical conductivity of the binary 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 in the systems with a common ion are not constant but they change with the composition causing the change of the content of the "free" ions in the system. The validity of the dissociation model of the electrical conductivity was verified in a number of binary univalent systems with a common ion [2].

The dissociation model of the electrical conductivity of molten salt mixtures may be easily applied also in the ternary systems with a common ion. The constitution of the equilibrium between the individual ions and the ionic pairs may be considered for each component (*e.g.* in systems with a common anion)

$$A^+ \cdot X^- \rightleftharpoons A^+ + X^- \qquad (A)$$

$$B^+ \cdot X^- \rightleftharpoons B^+ + X^- \qquad (B)$$

$$C^+ \cdot X^- \rightleftharpoons C^+ + X^- \qquad (C)$$

For the equilibrium constants cf the simultaneous dissociation reactions (A—C) the following relations may be derived from the material balance

$$K_1 = \frac{\alpha_1}{1 - \alpha_1} \frac{(x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3)}{(1 + x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3)} = \frac{\alpha_1}{1 - \alpha_1} \cdot B \qquad (1)$$

$$K_2 = \frac{\alpha_2}{1 - \alpha_2} \frac{(x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3)}{(1 + x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3)} = \frac{\alpha_2}{1 - \alpha_2} \cdot B \qquad (2)$$

$$K_3 = \frac{\alpha_3}{1 - \alpha_3} \frac{(x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3)}{(1 + x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3)} = \frac{\alpha_3}{1 - \alpha_3} \cdot B \qquad (3)$$

where α_i are the dissociation degrees of the individual components in the mixture with the composition given by the mole fractions x_i. The set of the implicit eqns (*1*—*3*) may be solved with advantage iteratively. Rearranging eqns (*1*—*3*) we get a set of equations

$$\alpha_i = \frac{K_i}{K_i + B} \qquad i = 1, 2, 3 \qquad (4)$$

The values of the equilibrium constants K_i are determined by the values of the dissociation degrees of the pure components

$$K_i = \frac{\alpha_{0i}^2}{1 - \alpha_{0i}^2} \qquad i = 1, 2, 3 \qquad (5)$$

As the input values for α_i, the values of the dissociation degrees of the pure components, α_{0i}, were used. The set of eqns (*4*) converges fastly to the resulting values of α_i for each composition of the ternary system.

By analogy with the procedure shown in [1] for the molar conductivity of the ternary mixture with a common ion the following relation can be derived

$$\lambda_{mix} = x_1 \frac{\alpha_1}{\alpha_{01}} \lambda_1 + x_2 \frac{\alpha_2}{\alpha_{02}} \lambda_2 + x_3 \frac{\alpha_3}{\alpha_{03}} \lambda_3 \qquad (6)$$

where λ_i are the molar conductivities of the pure components. The solution of the set of eqns (4—6) along with the condition

$$\sum_{j=1}^{k} (\lambda_{j,\,exp} - \lambda_{j,\,calc})^2 = min \qquad (7)$$

enables to find such values of α_{0i} for which the standard deviation of the experimental values of the molar conductivity from the calculated ones is less than the experimental error for all mixtures of the ternary system with the known value of the molar conductivity.

In the present work the dissociation model of the electrical conductivity of molten salt mixtures was verified in the ternary univalent systems with a common anion as well as with a common cation. The systems of alkali halides, of alkali metal nitrates, and of silver halides were selected.

Table 1

The calculated values of the dissociation degrees of the pure components in the ternary univalent systems with a common anion

System	T/K	α_{01}	α_{02}	α_{03}	s	Ref.
LiF—NaF—KF	1200	0.17	0.38	0.92	3.79	[3]
LiF—NaF		0.21	0.42	—	2.31	
LiF—KF		0.17	—	0.92	4.50	
NaF—KF		—	0.47	0.80	1.03	
LiCl—NaCl—KCl	1073	0.205	0.418	0.88	1.64	[4]
LiCl—NaCl		0.28	0.52	—	0.25	
LiCl—KCl		0.19	—	0.83	1.94	
NaCl—KCl		—	0.42	0.81	0.49	
LiI—NaI—KI	1000	0.21	0.39	0.58	2.43	[5]
LiI—NaI		0.23	0.45	—	1.73	
LiI—KI		0.21	—	0.56	2.75	
NaI—KI		—	0.41	0.74	0.29	
$LiNO_3$—$NaNO_3$—KNO_3	640	0.43	0.54	0.85	0.34	[6]
$LiNO_3$—$NaNO_3$		0.42	0.52	—	0.13	
$LiNO_3$—KNO_3		0.43	—	0.85	0.41	
$NaNO_3$—KNO_3		—	0.53	0.81	0.08	

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

Table 2

The calculated values of the dissociation degrees of the pure components in the ternary univalent systems with a common cation

System	T/K	α_{01}	α_{02}	α_{03}	s	Ref.
LiF—LiCl—LiBr	1100	0.97	0.30	0.19	2.08	[7]
LiF—LiCl		0.73	0.24	—	1.92	
LiF—LiBr		0.99	—	0.19	1.82	
LiCl—LiBr		—	0.67	0.44	1.11	
LiF—LiBr—LiI	1100	1.00	0.19	0.15	4.81	[7]
LiF—LiBr		0.99	0.19	—	1.82	
LiF—LiI		0.999	—	0.155	8.71	
LiBr—LiI		—	0.79	0.59	0.89	
LiCl—LiBr—LiI	1100	0.67	0.43	0.32	1.23	[7]
LiCl—LiBr		0.67	0.44	—	1.11	
LiCl—LiI		0.705	—	0.33	1.33	
LiBr—LiI		—	0.79	0.59	0.89	
AgCl—AgBr—AgI	850	0.52	0.46	0.22	2.47	[8]
AgCl—AgBr		0.54	0.40	—	0.25	
AgCl—AgI		0.50	—	0.21	1.85	
AgBr—AgI		—	0.455	0.21	3.14	

s in S cm^2 mol^{-1}.

Table 3

The standard deviations of the experimental values of the molar conductivity of the ternary systems from those calculated according to the individual models

System	$s/(\text{S cm}^2\,\text{mol}^{-1})$		
	Model		
	dissociation	series	parallel
LiF—NaF—KF	3.79	9.29	19.09
LiCl—NaCl—KCl	1.64	2.69	21.85
LiI—NaI—KI	2.43	10.69	17.87
LiNO$_3$—NaNO$_3$—KNO$_3$	0.34	1.41	1.79
LiF—LiCl—LiBr	2.08	25.54	27.15
LiF—LiBr—LiI	4.81	38.80	41.94
LiCl—LiBr—LiI	1.23	6.65	8.17
AgCl—AgBr—AgI	2.47	3.15	4.67

Results

The experimental data on the molar conductivity of the ternary systems are very scarce in the literature. Whereas in some cases the conductivity values in the ternary system are known, the density data are missing. In such cases the approximate rule on the additivity of the molar volumes can be used. This approach, however, does not give sufficiently reliable values of the molar conductivity. Therefore in some cases the experimental values of the molar conductivity of the boundary binary systems were used only. Similarly as in the binary systems it was necessary, with respect to the inconsistency of the conductivity data of the pure components as well as of the binary and ternary mixtures, to use interpolated, or adjusted values in order to get the likely course of the molar conductivity in the ternary system. The available data on the density and the conductivity of the systems under investigation were taken from [3—8].

The calculated values of the dissociation degrees of the pure components in the investigated ternary systems with a common anion are given in Table 1. The values for the systems with a common cation are given in Table 2. In both tables the values of the dissociation degrees of pure components calculated in [2] for the respective boundary binary systems are shown for comparison as well. In Table 3 the standard deviations of the experimental values of the molar conductivity from those calculated according to the dissociation, series, and parallel models [9] are shown.

Discussion

From the values given in Table 1 it follows that in the ternary systems with a common anion the dissociation degree of the components increases with the increasing radius of the cation, *e.g.* with its decreasing field strength (the charge to radius ratio). In the case of the ternary systems with a common cation (*cf.* Table 2) the dissociation degree of the components increases with the decreasing radius of the anion, *e.g.* with its decreasing polarizability. Such behaviour was already found in [2], which is supported also by the comparison of the respective values in the binary and ternary systems. It is obvious that the change of the dissociation degree of the component owing to the presence of different strange ions is not very significant.

Comparing the ternary system with a common anion like LiF—NaF—KF with the system with a common cation like LiF—LiCl—LiBr it is evident that the influence of different cations — Li, Na, and K — on the change of the dissociation degree of the individual components is roughly the same as the influence of different anions — F, Cl, and Br. The differences between the dissociation degrees $(\alpha_{0i} - \alpha_{0j})$ remain in prevailing cases nearly the same. This indicates again that the difference of the dissociation degrees of the components is probably a linear function of the fractional difference in the interatomic

distances. However, such simple geometrical model for the ternary systems has not been proposed till now.

In Tables 1 and 2 the standard deviations of the experimental values of the molar conductivities from the calculated ones are shown as well. It is evident that the values for the ternary systems are on the same level as those for the boundary binary systems [2] and that they are also less than or comparable with the experimental error. From Table 3 it follows that when using the dissociation model the standard deviations of the experimental values are always less than in the case when using the series or parallel model. However, it should be noted that these models do not involve adjustable parameters as it is in the dissociation model.

The dissociation model of the electrical conductivity of molten salt mixtures explains rationally the concentration dependence of the molar conductivity also in the ternary univalent systems namely in the cases if due to the strong interaction of the components this dependence passes through an expressed minimum. The dissociation model enables to describe also a nonsymmetrical concentration dependence of the molar conductivity by appropriate choice of the equilibrium constants K_i of the dissociation reactions. In comparison with the present phenomenological approaches in which the molar conductivity of the ternary mixture was calculated by means of the additive summation of the excess contributions of the boundary binary systems [10, 11], or the contribution of the three-component interaction was taken into account [11], the dissociation model has the physical background and it gives a more detailed view on the structure and the ionic composition of the molten mixture, respectively. However, for an exact theoretical processing and generalizing of the results of calculation more intact and precise experimental data on the physicochemical properties of the molten inorganic systems are needed. It may be assumed that using more reliable experimental data the differences between the values of the dissociation degrees of pure components will not depend on the nature of the second component.

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