The series and parallel models of electrical conductivity of molten salt mixtures
II. Multicomponent systems

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The series and parallel models of electrical conductivity of molten salt mixtures are extended to multicomponent systems. On the examples of the ternary systems LiCl—NaCl—KCl and $LiNO_3$—$NaNO_3$—KNO_3 it will be shown that the series model predicts satisfactorily the conductivity of molten mixtures assuming that it predicts reasonably well conductivity of the boundary binary systems. If this is not the case the deviations observed in binary systems have to be considered at the calculation of conductivity of the multicomponent system. The proposed method of calculation of conductivity of nonideal systems is demonstrated on the examples of the molten mixtures NaCl—$CaCl_2$—$BaCl_2$ and NaCl—$MgCl_2$—$CaCl_2$.

Рядовая и параллельная модели электропроводности расплавов смеси солей расширены на многокомпонентные системы. На примерах тройных систем LiCl—NaCl—KCl и $LiNO_3$—$NaNO_3$—KNO_3 показано, что рядовая модель удовлетворительно предсказывает электропроводность расплавленных смесей в том случае, если она хорошо предсказывает электропроводность пограничных двойных систем. В противном случае следует отклонения, наблюдающиеся в двойных системах, учитывать при вычислении многокомпонентных систем. Предлагаемый метод расчета электропроводности неидеальных систем демонстрируется на примерах расплавленных смесей NaCl—$CaCl_2$—$BaCl_2$ и NaCl—$MgCl_2$—$CaCl_2$.

Molten electrolytes used in technical applications are often multicomponent systems. For optimizing composition of the electrolyte one needs to know the dependence of its physicochemical properties on composition and temperature. The experimental determination of these properties is a time-consuming procedure and thus the data on multicomponent systems are rare and in many cases they do not exist at all. Therefore it may be useful to work out a procedure

which will allow to predict properties of multicomponent electrolyte on the basis of knowledge of this property for pure components or for binary systems which can be derived from components of the multicomponent system. When a suitable model for calculation is available it is often sufficient to carry out only several measurements which prove if the given model predicts behaviour of the whole system with required precision.

In paper [1] two models of electrical conductivity of molten electrolytes have been proposed: the series and the parallel models. It has been shown that the conductivity calculated according to the series model gives good agreement with experiment when the system is ideal from the thermodynamic point of view. Because the models have a physical background it is possible to extend them readily to the multicomponent systems. When we denote the number of components as k it holds

$$\varkappa_s = \sum_{i=1}^{k} (x_i . V_i^\circ) / \sum_{i=1}^{k} \frac{x_i . V_i^\circ}{\varkappa_i} \qquad (1)$$

$$\varkappa_p = \sum_{i=1}^{k} (x_i . V_i^\circ . \varkappa_i) / \sum_{i=1}^{k} (x_i . V_i^\circ) \qquad (2)$$

where $\varkappa_s$ and $\varkappa_p$ are the conductivities of the electrolyte calculated according to the series and parallel model, respectively. $\varkappa_i$ is the conductivity of the i-th pure component, V_i° is its molar volume and x_i is the mole fraction of the i-th component in the molten mixture. We will show on examples of ternary and quaternary systems that the extension of the models to the multicomponent electrolytes is justified.

Calculation of conductivity for the systems which are ideal from the thermodynamic point of view

The system LiCl—NaCl—KCl

The experimental and calculated data on the conductivity of this system at the temperature of 800 °C are summarized in Table 1. In this table also the conductivities and molar volumes of pure components used for calculation are given. The deviations between the experimental and calculated values of conductivity are expressed by the relationship

$$\Delta/\% = 100(\varkappa_{exp} - \varkappa_{calc})/\varkappa_{calc} \qquad (3)$$

where Δ_p denotes the deviation from the parallel model and Δ_s the deviation from the series model of electrical conductivity. From Table 1 it follows that except one case the conductivity calculated according to the series model does

Table 1

Experimental [2] and calculated data of conductivity of the molten ternary system LiCl—NaCl—KCl at 800 °C

x/%			$\varkappa_{exp}$	$\varkappa_s$	$\varkappa_p$	Δ_s	Δ_p
LiCl	NaCl	KCl	S cm^{-1}	S cm^{-1}	S cm^{-1}	%	%
100	—	—	6.610	—	—	—	—
50	50	—	4.564	4.522	4.942	0.92	−8.28
—	100	—	3.613	—	—	—	—
19.96	—	80.04	2.362	2.450	2.811	−3.73	−19.01
40.45	—	59.55	2.635	2.771	3.511	−5.16	−33.24
58.80	—	41.20	3.123	3.226	4.264	−3.30	−36.54
70.36	—	29.64	3.203	3.667	4.817	−14.48	−50.39
81.77	—	18.23	4.261	4.331	5.435	−1.64	−27.55
—	—	100	2.237	—	—	—	—
—	15.23	84.77	3.222	3.233	3.350	−0.34	−3.97
—	27.06	72.94	2.973	3.007	3.162	−1.14	−6.36
—	34.85	65.15	2.847	2.881	3.045	−1.19	−6.95
—	48.77	51.23	2.639	2.692	2.848	−2.01	−7.92
	59.00	41.00	2.535	2.576	2.713	−1.62	−7.02
—	79.96	20.04	2.335	2.385	2.461	−2.14	−5.40
	50.00	50.00	2.630	2.677	2.831	−1.79	−7.64
5.77	47.11	47.11	2.721	2.743	2.984	−0.81	−9.67
13.69	43.15	43.15	2.832	2.844	3.203	−0.42	−13.10
25.41	37.30	37.30	2.982	3.018	3.549	−1.21	−19.01

$V°$(LiCl) = 29.85 cm^3 mol^{-1}; $V°$(NaCl) = 37.54 cm^3 mol^{-1}; $V°$(KCl) = 49.37 cm^3 mol^{-1}

not deviate from experimental data more than by 5 %. As can be seen from Fig. 1 the disagreement in one point (x(LiCl) = 0.7036) of the binary system LiCl—KCl is caused probably by an error in experimental data. In the ternary

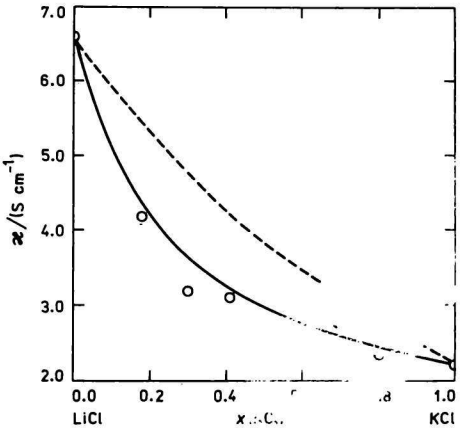

Fig. 1. Conductivity of the binary system LiCl—KCl at the temperature of 800 °C.
○ Experimental data [2]; — the series model; --- the parallel model.

system LiCl—NaCl—KCl the experimental conductivity data are known only for three compositions [2]. (The data published in [2] and [3] are critically evaluated. Thus we will not discuss the methods used for measurement of conductivity and their accuracy. Reader is referred to the cited literature.) As follows from Table 1 (see the last three rows) the deviation between the experimental and calculated conductivity is in the case of the series model lower than 1.5 %. Thus it may be assumed that the series model is suitable for calculation of conductivity in the whole concentration range.

The system $LiNO_3$—$NaNO_3$—KNO_3

In Table 2 the experimental and calculated conductivity data for pure components, boundary binary systems and one point in the ternary system $LiNO_3$—$NaNO_3$—KNO_3 are presented. All data are related to the temperature of 367 °C. The data on molar volume of pure components used in the calculation are given under the table. In this ternary system only one value of conductivity is reported in the literature [2, 3]. It can be seen that the agreement between this experimental value and the conductivity calculated according to the series model is better than 3 %. Because also the agreement between the experimental and calculated data in binary systems is reasonable (better than 5 %) we may assume that the series model predicts conductivity in the whole ternary system $LiNO_3$—$NaNO_3$—KNO_3 with good precision (better than 5 %).

Table 2

Experimental [2, 3] and calculated data of conductivity of the molten ternary system $LiNO_3$—$NaNO_3$—KNO_3 at 367 °C

x/%			$\varkappa_{exp}$	$\varkappa_s$	$\varkappa_p$	Δ_s	Δ_p
$LiNO_3$	$NaNO_3$	KNO_3	S cm^{-1}	S cm^{-1}	S cm^{-1}	%	%
100	—	—	1.433	—	—	—	—
74.3	25.3	—	1.371	1.372	1.378	−0.07	0.50
50.0	50.0	—	1.319	1.322	1.329	−0.23	−0.76
25.0	75.0	—	1.282	1.277	1.282	−0.39	0.0
—	100	—	1.238	—	—	—	—
23.3	—	76.7	0.817	0.784	0.842	4.04	−3.06
50.1	—	49.9	0.950	0.906	1.018	4.63	−7.16
74.8	—	25.2	1.141	1.087	1.206	4.73	−5.70
—	—	100	0.713	—	—	—	—
—	24.85	75.15	0.811	0.786	0.827	3.08	−1.97
—	50.31	49.69	0.924	0.886	0.955	4.11	−3.35
—	75.09	24.91	1.066	1.025	1.090	3.85	−2.25
37.50	18.00	44.50	0.956	0.929	1.032	2.82	−7.94

$V°(LiNO_3) = 40.13\,cm^3\,mol^{-1}$; $V°(NaNO_3) = 46.11\,cm^3\,mol^{-1}$; $V°(KNO_3) = 54.71\,cm^3\,mol^{-1}$

Calculation of conductivity of the multicomponent systems which are nonideal from the point of view of given model

The conductivity of the ternary systems LiCl—NaCl—KCl and $LiNO_3$—$NaNO_3$—KNO_3 does not deviate substantially (more than 5 %) from the ideality defined by the series model. These systems are close to ideality also from the thermodynamic point of view. This follows from the study of volume properties [4] and solid—liquid equilibria [5] of these systems. It seems that there is a correlation between an ideal thermodynamic behaviour and good agreement between experimental and calculated conductivity according to the series model.

In many cases the molten systems are nonideal. Even then the series or parallel models of conductivity can be useful as reference models with respect to which the deviations are evaluated. As the series model gives better agreement with experiment in the case of thermodynamically ideal systems we will discuss in the next only this model.

Table 3

Experimental [6] and calculated data of conductivity of the binary systems NaCl—$CaCl_2$, NaCl—$BaCl_2$, and $CaCl_2$—$BaCl_2$ at the temperature of 800 °C

x/%			$\varkappa_{exp}$	$\varkappa_s$	Δ_s
$BaCl_2$	$CaCl_2$	NaCl	S cm^{-1}	S cm^{-1}	%
100	0	—	1.47	—	—
80	20	—	1.530	1.549	−1.23
60	40	—	1.605	1.643	−2.31
40	60	—	1.695	1.758	−3.58
20	80	—	1.830	1.900	−3.68
0	100	—	2.080	—	—
—	80	20	2.060	2.212	−6.87
—	60	40	2.125	2.384	−10.86
—	40	60	2.270	2.617	−13.26
—	20	80	2.600	2.951	−11.89
—	0	100	3.470	—	—
20	—	80	2.700	2.471	9.27
40	—	60	2.175	2.017	7.83
60	—	40	1.805	1.756	2.80
80	—	20	1.610	1.588	1.38

$V°(BaCl_2) = 63.41\ cm^3\ mol^{-1}$; $V°(CaCl_2) = 53.54\ cm^3\ mol^{-1}$; $V°(NaCl) = 37.53\ cm^3\ mol^{-1}$

As an example of nonideal systems the ternary system NaCl—$BaCl_2$—$CaCl_2$ and the quaternary system NaCl—KCl—$MgCl_2$—$CaCl_2$ were chosen. In Table 3 the experimental conductivity data are compared with calculated con-

ductivity of the binary systems NaCl—$CaCl_2$, NaCl—$BaCl_2$, and $CaCl_2$—$BaCl_2$. It can be seen that in the case of the system NaCl—$CaCl_2$ the deviation between experimental and calculated data is almost 15 % and in the system NaCl—$BaCl_2$ about 10 %. (At the calculation the values of conductivity of pure components given by the authors who measured the ternary system were used.) In Table 4 the experimental and calculated data of the ternary system NaCl—$CaCl_2$—$BaCl_2$ are compared. It follows that also in this case the deviation is about 10 %, which exceeds significantly the unaccuracy of experiment.

Table 4

Experimental [6] and calculated data of conductivity of the molten ternary system NaCl—$CaCl_2$—$BaCl_2$ at 800 °C

x / %			$\varkappa_{exp}$	$\varkappa_s$	Δ_s	$\varkappa_{s,cor}$	$\Delta_{s,cor}$
$BaCl_2$	$CaCl_2$	NaCl	S cm^{-1}	S cm^{-1}	%	S cm^{-1}	%
10	63	27	1.990	2.141	−7.05	1.993	−0.13
30	49	21	1.810	1.910	−5.24	1.851	−2.23
50	35	15	1.689	1.741	−2.99	1.721	−1.88
20	40	40	1.931	2.112	−8.57	1.999	−3.41
40	30	30	1.772	1.867	−5.09	1.861	−4.81
10	27	63	2.275	2.458	−7.45	2.254	0.92
20	24	56	2.164	2.231	−3.00	2.159	0.25
35.5	19.35	45.15	2.007	1.979	1.41	2.012	−0.20
10	70	20	1.925	2.095	−8.11	1.980	−2.79
7.5	52.5	40	2.070	2.272	−8.89	2.044	1.27
6.25	43.75	50	2.180	2.383	−8.56	2.107	3.49
20	60	20	1.870	1.994	−6.22	1.905	−1.89
15	45	40	2.015	2.172	−7.23	2.015	0.00
10	30	60	2.240	2.425	−7.63	2.210	1.36
32	48	20	1.781	1.889	−5.72	1.836	−2.99
24	36	40	1.940	2.067	−6.14	1.989	−2.41
16	24	60	2.200	2.326	−5.41	2.214	−0.65

The deviation from ideality (which is defined by the used model) in a ternary system can be estimated if we know the deviations in boundary binary systems. Let us assume that in a binary system it holds

$$\Delta\varkappa_s^E = \varkappa_{exp} - \varkappa_s = x_i x_j (A_{ij} + x_j B_{ij}) \qquad (4)$$

where $\Delta\varkappa_s^E$ is the excess conductivity determined with respect to the series model and A_{ij}, B_{ij} are the empirical constants. In ternary system it holds

$$\Delta\varkappa_s^E = x_1 x_2 (A_{12} + x_2 B_{12}) + x_2 x_3 (A_{23} + x_3 B_{23}) + x_3 x_1 (A_{31} + x_1 B_{31}) \qquad (5)$$

This procedure is formally similar to that used by *Redlich* and *Kister* [7] for calculation of the thermodynamic excess data. Similar procedure has been used also for calculation of excess molar volumes [4, 8, 9] and excess molar conductivities [9—11]. Using the relationships (*1*) and (*5*) one can calculate the corrected values of conductivities $\varkappa_{s(cor)}$ of the ternary mixture

$$\varkappa_{cor} = \varkappa_s + \varkappa_s^E \qquad (6)$$

As can be seen from Table 4 the corrected calculated data approached the experimental values better than by 5 %, which may be considered as a good fit comparable with reliability of measurement of conductivity of the discussed system. The values of the constants A_{ij} and B_{ij} used in the calculation are summarized in Table 5.

Table 5

Coefficients of the empirical relationship (*5*) used for calculation of $\Delta\varkappa_s^E$ in the systems NaCl—$CaCl_2$—$BaCl_2$ and NaCl—KCl—$BaCl_2$—$CaCl_2$ at the temperature of 800 °C

System	$A/(S\,cm^{-1})$	$B/(S\,cm^{-1})$
$BaCl_2$—$CaCl_2$	5.20221×10^{-2}	−0.66351
$CaCl_2$—NaCl	−0.40670	−2.12531
NaCl—$BaCl_2$	1.74973	−2.16437
KCl—$CaCl_2$	−2.68947	3.1399×10^{-2}
$MgCl_2$—$CaCl_2$	2.19042	−0.51952
KCl—$MgCl_2$*	−0.7	0
$MgCl_2$—NaCl*	5.0	0
NaCl—KCl	0	0

* The coefficient was determined on the basis of conductivity determined only at one composition.

Calculation of conductivity of the quaternary system NaCl—KCl—$MgCl_2$—$CaCl_2$ (only the section corresponding to the content of 10 mass % $MgCl_2$ has been published [12]) confirmed that the proposed procedure can be applied also to this system. It should be pointed out that the deviations between the experimental and calculated data in the binary system KCl—$CaCl_2$ reached −30 % and the deviations in the system $MgCl_2$—$CaCl_2$ 35 %. As the content of $MgCl_2$ in the quaternary system never exceeded 11 mole % only the deviations from ideality in the system NaCl—KCl—$CaCl_2$ were considered. The influence of $MgCl_2$ was considered to be ideal with respect to the series model. In Table 6 the experimental and calculated conductivity data are compared. The values of molar volumes and conductivities of pure components used in calculation are given under the table. Without correction the deviations between the experi-

Table 6

Experimental [12] and calculated data of conductivity of the molten quaternary system NaCl—KCl—$MgCl_2$—$CaCl_2$ at the temperature of 800 °C

x/%				$\varkappa_{exp}$	$\varkappa_s$	Δ_s	$\varkappa_{s,cor}$	$\Delta_{s,cor}$
KCl	$MgCl_2$	$CaCl_2$	NaCl	S cm^{-1}	S cm^{-1}	%	S cm^{-1}	%
92.0	8	—	—	1.955	2.000	−2.25	1.961	−0.31
76.7	8.6	14.7	—	1.610	1.975	−18.48	1.664	−3.25
49.1	9.6	41.2	—	1.365	1.932	−29.61	1.443	−5.72
14.0	10.9	75.1	—	1.300	1.883	−9.72	1.748	−2.41
—	11.5	88.5	—	2.038	1.864	9.33	2.040	−0.10
—	6.9	—	93.6	3.19	2.901	9.96	3.200	−0.33
—	7.5	19.3	73.2	2.54	2.511	1.15	2.549	−0.39
—	9.7	58.5	31.8	2.01	2.063	−6.7	2.154	−2.6
63.8	8.3	14.3	13.6	1.665	2.047	−18.66	1.793	−7.11
41.3	9.4	40.5	8.8	1.462	1.974	−25.94	1.513	−3.36
22.7	10.4	62.2	4.8	1.550	1.922	−19.35	1.537	0.87
59.9	7.8	6.7	25.5	1.950	2.135	−8.66	2.014	−3.18
35.6	9.3	39.9	15.2	1.520	2.007	−24.27	1.592	−4.69
19.7	10.3	61.7	8.4	1.640	1.938	−15.37	1.594	2.85
34.7	7.8	13.3	44.3	2.100	2.254	−6.83	2.060	1.94
23.0	9.0	38.6	29.4	1.760	2.089	−15.75	1.750	0.34
12.9	10.1	60.6	16.4	1.750	1.978	−11.5	1.714	2.09
14.9	7.8	20.1	57.2	2.230	2.344	−4.86	2.090	6.68
11.2	8.7	37.5	42.7	1.955	2.179	−10.27	1.879	4.02
6.3	9.9	59.2	24.2	1.860	2.019	−7.87	1.813	2.60
7.4	8.1	27.8	56.7	2.170	2.315	−6.26	2.024	7.2
3.6	9.8	59.1	27.5	1.900	2.038	−6.77	1.850	2.73
1.9	10.6	72.7	14.8	1.890	1.950	−3.07	1.857	1.74

$V°$(KCl) = 49.37 cm^3 mol^{-1}; $\varkappa$(KCl) = 2.17 S cm^{-1};
$V°$($MgCl_2$) = 57.64 cm^3 mol^{-1}; $\varkappa$($MgCl_2$) = 1.13 S cm^{-1};
$V°$($CaCl_2$) = 53.54 cm^3 mol^{-1}; $\varkappa$($CaCl_2$) = 2.05 S cm^{-1};
$V°$(NaCl) = 37.53 cm^3 mol^{-1}; $\varkappa$(NaCl) = 3.47 S cm^{-1}

mental and calculated data were similar as in the binary systems (about −25 %). When the proposed correction was introduced the deviation did not exceed 7.5 %. For the ratio n(NaCl):n(KCl) = 1 : 1 the agreement between experimental and calculated conductivity was better than 3 %. These results show that the proposed procedure can be used also for calculation of conductivity of the systems which are rather far from the behaviour defined by the series model.

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