The electrical conductivity, density and surface tension of molten salts containing zirconium fluoride

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Abstract. The temperature dependencies of specific electric conductivity, density and surface tension of molten LiF-KF-ZrF$_4$ mixtures in a wide concentration range were investigated using relative capillary method and method of maximum pressure in a gas bubble. The obtained values of molar electric conductivity, molar volumes and excess thermodynamic functions of melt surface layer have noticeable deviations from those calculated for ideal mixtures. This phenomenon can be explained by some specific interaction between the components of studied ternary mixtures. Mixing the components in such melts is accompanied by a noticeable interaction with predominant formation of stable zirconium fluoride complex ions. The values of deviations depend on the ionic composition of the salt mixtures.

1. Introduction
Molten alkali fluorides, having high electric conductivity, stability towards hydrolysis and capable of dissolving considerable amounts of zirconium fluoride can find prospective application for electrowinning and electrorefining of metallic Zr. Addition of LiF into the melts considerably increases their electric conductivity and surface tension and thus can considerably improve the parameters of the electrolysis process. Lack of the literature data concerning physical and chemical properties of molten mixtures of Zr and alkali metals fluorides slows down their practical application and does not allow to draw conclusions about processes taking place in the melts upon mixing pure individual salts and about the coordination state of zirconium ions at various ratios of the components.

The aim of the present study was to obtain new experimental data on electric conductivity, density and surface tension of Zr containing fluoride melts. Investigating physical and chemical properties of LiF-KF and LiF-KF-ZrF$_4$ melts is undoubtedly of practical interest because such data can be used for optimising the conditions of electrolytic production and refining of metallic Zr.

2. Experimental
Specific electric conductivity (χ) of all studied melts was measured using relative capillary method at 50 Hz frequency [1] using AC bridge P5083, a capillary made of sintered beryllium oxide and nickel or platinum wire electrodes. The cell constant was 60-65 cm^{-1}. The cell was calibrated at working temperatures before each measurement in KCl or LiCl-KCl melt using the data from [2, 3]. A cell made of a nickel alloy was employed for studying electric conductivity. Density (ρ) and surface tension (σ) of LiF-KF, LiF-ZrF$_4$, KF-ZrF$_4$ and LiF-KF-ZrF$_4$ systems were determined using the method of maximal pressure in a gas (argon) bubble. The data were recorded using a MPXV5004G microprocessor and a PC. Platinum tube (2.0 mm in diameter) served as a capillary in the

measurements. Maximal errors of density, specific electric conductivity and surface tension did not exceed 1.0; 1.5 and 2 %, respectively.

Considerable attention was paid to preparation of anhydrous salts. Chemically pure LiF and KF were dried under vacuum with gradual increasing temperature to melting points, the melts then were allowed to crystallise [4]. Additional purification was achieved by zone melting [5]. Dried zirconium fluoride was twice sublimed under vacuum. All salt mixtures were prepared in a dry box.

3. Results and discussion

The experimental data were treated using least squares method. The results of the treatment are presented in tables 1 and 2 in the form of equation coefficients, standard deviations S and temperature intervals. Obtained experimental data were employed for calculating molar volumes in the entire concentration range as well as the deviation from additivity ($\Delta V/V_{add}$). The character of the deviation of the molar volume of molten salt mixtures from the additive values allows, to some degree, to draw conclusions about the interaction of the components, because the formation of the ideal mixtures is not accompanied by any compression or expansion (figure 1).

Table 1. Specific electric conductivity of molten mixtures LiF-KF-ZrF$_4$ at 1150 K.

mol. %			$\chi = a + b \cdot T + c \cdot T^2$, S·m^{-1}				T, K
LiF	KF	ZrF$_4$,	a	b	$c \cdot 10^6$	$S \cdot 10$	
25.0	75.0	0.0	-1215.2	2.3401	-856	1.6	1113-1323
23.8	71.2	5.0	-832.0	1.9230	-800	1.3	913-1243
22.5	67.5	10.0	-532.2	1.0039	-300	1.4	963-1213
20.0	60.0	20.0	-528.4	1.0672	-400	3.2	1013-1243
17.5	52.05	30.0	-352.7	0.6474	-180	4.0	763-1243
15.0	45.0	40.0	-211.7	0.3596	-30	3.1	773-1273
12.5	37.5	50.0	-188.6	0.2935	6	3.4	813-1253
10.0	30.0	60.0	-103.4	0.1421	42	4.2	923-1183
7.5	22.5	70.0	-60.5	1.6844	-580	1.4	753-1103
50.0	50.0	0.0	-844.1	1.6844	-580	1.4	753-1100
47.5	47.5	5.0	-733.8	1.4808	-500	3.7	943-1245
45.0	45.0	10.0	-488.7	0.9021	-236	1.6	973-1313
40.0	40.0	20.0	-445.6	0.8198	-225	3.3	993-1293
35.0	35.0	30.0	-183.1	0.3117	-27	2.5	763-4263
30.0	30.0	40.0	-192.1	0.3482	-56	0.8	743-1273
25.0	25.0	50.0	-344.0	0.6248	-188	0.8	743-1263
20.0	20.0	60.0	-255.2	0.3828	-43	1.1	883-1313
15.0	15.0	70.0	-240.6	0.3973	-51	2.8	763-1173
75.0	25.0	0.0	-955.2	1.9581	-603	0.2	1033-1313
71.2	23.8	5.0	-674.0	1.6339	-590	1.8	1013-1153
67.5	22.5	10.0	-39.6	0.3145	-200	1.5	1003-1243
60.0	20.0	20.0	-730.1	1.3963	-500	3.0	773-1273
52.5	17.5	30.0	-276.0	0.6844	-300	2.8	773-1273
45.0	15.0	40.0	-493.4	1.0008	-300	1.2	823-1273
37.5	12.5	50.0	-286.2	0.5322	-100	2.6	823-1273
30.0	10.0	60.0	-138.6	0.2950	-36	2.6	823-1273
22.5	7.5	70.0	-96.8	0.0664	100	3.1	823-1263

Table 2. Density and surface tension of molten mixtures LiF-KF-ZrF$_4$ (LiF/KF=1/1).

| mol. %			$\rho = a - b \cdot T$, g/cm^3			$\sigma = \sigma_O - c \cdot T$, mJ/m^2			T, K
LiF	KF	ZrF$_4$	a	b	$S \cdot 10^3$	σ_O	$c \cdot 10^3$	$S \cdot 10$	
50.0	50.0	0.0	2.5698	0.6582	1	189.0	44.6	3	948-1136
47.5	47.5	5.0	2.2267	0.2087	1	245.7	100.6	3	1025-1296
45.0	45.0	10.0	2.6276	0.4235	2	252.1	108.7	2	1025-1271
40.0	40.0	20.0	3.2942	0.8594	1	237.8	100.5	4	1035-1291
35.0	35.0	30.0	2.7976	0.4235	4	219.1	94.0	5	1078-1312
30.0	30.0	40.0	2.6904	0.2347	5	215.6	96.1	6	1007-1245
25.0	25.0	50.0	3.73007	0.9788	3	144.2	44.4	5	1038-1321
20.0	20.0	60.0	4.1706	1.1525	2	171.2	73.0	4	1015-1200
15.0	15.0	70.0	4.7430	1.2152	3	190.2	93.2	2	1087-1225
0.0	0.0	100	5.3677	1.223	5	162.9	79.1	5	1200-1280
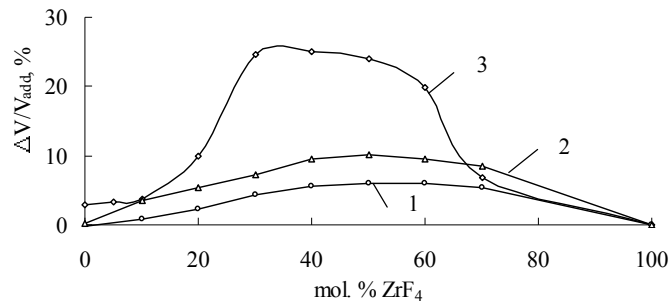
Figure 1. Relative deviations of molar volumes from additive values for molten mixtures LiF-ZrF$_4$ (1), KF-ZrF$_4$ (2) and LiF-KF-ZrF$_4$ (3) at 1150 K.

The calculations indicate a considerable positive deviation of the molar volumes from the additive values, and this can be connected to the increase of the fraction of covalent bonding in the melts and the formation of complex ions ZrF_5^-, ZrF_6^{2-} and ZrF_7^{3-} [6, 7]. In the ternary LiF-KF-ZrF$_4$ system the deviations of the molar volumes from the additive values exceed those found for the binary systems.

The molar electric conductivity exhibit considerable negative deviations from the ideal behaviour (figure 2). This also points out to strengthening inter-particle interactions in mixtures with the formation of zirconium complex ions.

Surface tension decreases with increasing zirconium fluoride concentration (figure 3), and this is connected to the formation of surface active zirconium complex ions.

4. Conclusions

Thus the values of electric conductivity, density and surface tension in molten salts are determined by concentration of zirconium fluoride. The experimental deviations of molar electric conductivity and molar volume from additive values are in good agreement with the principal explanation in frames of complex model of ionic liquids structure.
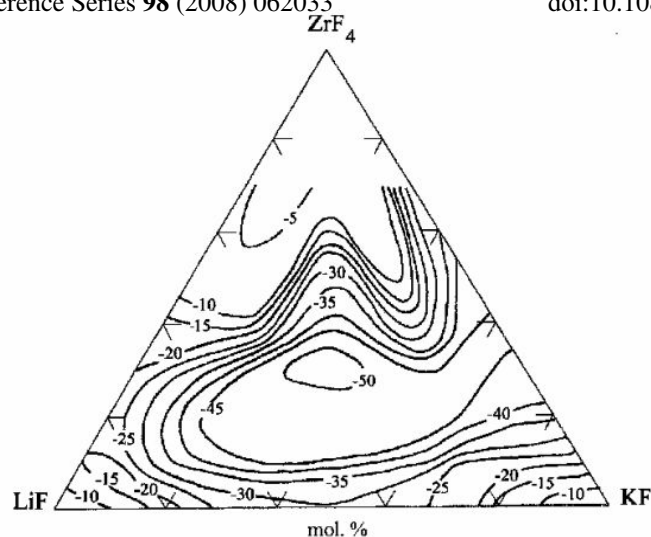
Figure 2. Relative deviations of molar electroconductivity from additive values (%) for molten mixtures LiF-KF-ZrF$_4$ at 1150 К.
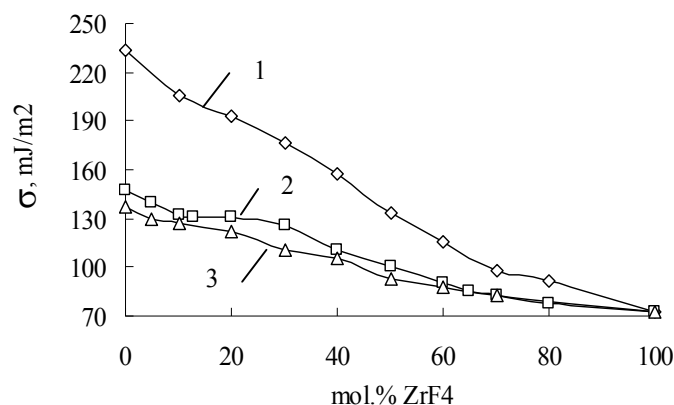

Figure 3. Isoterms of surface tension of molten mixtures LiF-ZrF$_4$ (1), KF-ZrF$_4$ (2) and LiF-KF-ZrF$_4$ (3) at 1150 К.

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