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Calorimetric study of melts in the system KCl–K_2TaF_7

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ABSTRACT

Enthalpy increment measurements on melts in the system KCl–K_2TaF_7 were carried out by drop calorimetry at temperatures between 298 and 1053, 1093 and 1133 K and selected compositions. The heat capacities of melted mixtures and enthalpies of mixing were determined using the experimental data. Calorimetric experiments showed nonideality of the melts in several properties. The molar relative enthalpy and molar heat capacity of melts exhibited small negative divergence from additivity. The molar enthalpy of mixing of melts showed exothermic deviation from ideality which increased with increasing temperature. The thermal effect at mixing was assigned predominantly to addition and substitution reactions producing heteroligand complex anions TaF_6Cl^{2-}. The nonideality was also confirmed by evaluating of activities considering Margules type model for excess Gibbs energy of mixing.

1. Introduction

The fused salt systems containing heptafluorotantalate(V) of potassium and alkali halides can be used for electrowinning and electrorefining of tantalum, and production of tantalum coatings. In the molten salt electrolyte K_2TaF_7 is used as the solvent of the tantalum pentoxide, while alkali halides help to modify some physicochemical properties of the electrolyte like melting temperature, electrical conductivity, viscosity, etc. and also to raise the solubility of tantalum pentoxide in the electrolyte [1]. The KCl–K_2TaF_7 system plays the most important role in the electrolyte fused bath.

The equilibrium diagram of the KCl–K_2TaF_7 system has been reported for the first time by Iuchi et al. [2] and Iuchi and Ono [1,3]. This phase diagram, along with later published ones, shows that in this system, the compound KCl·K_2TaF_7 (K_3TaF_7Cl) is formed in solid state. This compound melts congruently at 1031 K. The system has two eutectic points. The first one at 20 mol% of K_2TaF_7 and 969 K and the second one at 78 mol% of K_2TaF_7 and 970 K. According to Ziu Bin-Sin et al. [4] KCl·K_2TaF_7 melts congruently at 1049 K and the liquidus curve of the system shows temperature minima at 973 and 985 K with 17.6 and 84.0 mol% of K_2TaF_7, respectively. According to Kovalev et al. [5] this compound solidifies at 1044 K. The eutectic temperature minima are at 968 and 983 K and the corresponding compositions are 22.5 and 84.0 mol% of K_2TaF_7, respectively. KCl·K_2TaF_7 crystallizes in the cubic system with $a = 6.046$ Å [6]. The complete structural data for this substance are not available. The ionic form of the components in the electrolytic fused bath has initially been investigated by Iuchi and Ono [7,8]. On the basis of the freezing point depression on the alkali halide side of the phase diagram, using Temkin's ionic mole fractions, the complex ionic equilibria in the fused state were deduced as follows: $TaF_7{}^{2-} + Cl^- = TaF_7Cl^{3-}$. The assumption on the presence of $TaF_7{}^{2-}$ and TaF_7Cl^{3-} complexes in KCl–K_2TaF_7 melts was later supported by further thermodynamic calculations, but the presence of octacoordinated TaF_7Cl^{3-} complexes was not confirmed by spectroscopic methods [9,10].

Frequently, the ionic composition of molten salt systems was estimated by coupled analysis of melting diagrams and physicochemical properties like density, surface tension, viscosity, electrical conductivity and mixing thermodynamic properties. Surprisingly, in spite of the technical importance of the KCl–K_2TaF_7 system, not enough information on physicochemical properties of its melts is available in accessible literature today. Density measurements of the molten system KCl–K_2TaF_7 have been reported by Agulyansky et al. [11]. Molar volume in this system shows a small positive deviation in the order of magnitude of several cm^3/mol. From the point of view of the parent system KF–KCl–TaF_5, Agulyansky et al. [10,11] did not observe any strong interaction in the region of potential production of octacoordinated complexes. In this system, distinct deviation from ideality in molar conductivity versus mole fraction of KCl has also been reported [12]. In [12] the molar conductivity of the ideal system was calculated using Markov's equation [13]. Agulyansky et al. [9,10,12] interpreted these results with formation of TaF_6Cl^{2-} ions in the melt by F–Cl exchange in the fluorotantalate complex ions, and did not suppose formation of the TaF_7Cl^{3-} complexes. IR spectra were also interpreted in the same sense [14]. Density, surface tension, viscosity

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and electrical conductivity of the molten mixtures of alkali metal chlorides with potassium fluorotantalate have been reported in Refs. [15–17]. The temperature dependences of density and surface tension were described by the linear equations. Positive deviation of molar viscosity from the ideal behavior, observed in molten mixtures of potassium chloride with potassium heptafluorotantalate, testified to interaction between components. Experimental data about fusibility, density and viscosity of the fluoride–chloride melts containing tantalum have been reported by Darienko et al. and Zobnin [18,19]. They concluded that the presence of tantalum in the anionic complexes with coordination 7 and possibly also more than 7 in the studied melts is most probable.

Generally, the properties of KCl–K_2TaF_7 melts are similar to those of KF–K_2TaF_7 melts with slightly more distinct deviations from ideality. So far, no measurements of mixing enthalpic properties in KCl–K_2TaF_7 system have been reported in the literature. The deviations from ideality in these properties can also be used to estimate mainly the types of interactions between the initial components and to draw some conclusions on the ionic composition of the melts. From this point of view the analysis of thermochemical properties of mixing and of the magnitude of their deviation from ideality is of most interest.The main goals of the present study were to obtain missing thermodynamic data, including heat capacities, enthalpies of mixing and activities of components and to extend understanding of the relationships between phase equilibria, structure and bonding in the melts of this system.

2. Experimental

2.1. Samples

Samples were mixtures of 99.5 wt% pure K_2TaF_7 obtained from the Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Russian Academy of Sciences, Apatity, Russia and specpure KCl (JMC). The used K_2TaF_7 was investigated by X-ray diffraction and IR spectroscopy. X-ray powder diffraction pattern was in good agreement with that in PDF-2 database (PDF No. 84-1255). No foreign diffractions were observed. The IR absorption band near 900 cm^{-1}, typical for Ta–O bond, was not found. This indicated the absence of oxofluorotantalates in the sample. K_2TaF_7 was dried in the presence of P_2O_5 under reduced pressure at 393 K for 24 h. KCl was dried for 16 h at 393 K. The dried substances were stored in a glove box, in which further manipulation was carried out. The calorimetric experiments were performed with samples in hermetically sealed containers. Pt 90% Rh 10% crucibles (10 mm diameter, 15 mm high, 0.2 mm thick sheet) with welded lids were used as containers. The substances were loaded into the containers in the glove box through a small hole drilled in the welded lid. The hole was then sealed using gold. The weight of the mixtures was about 1 g and both components were weighed to 0.001 g accuracy. The containers with samples weighed about 4 g. In order to check the airtightness and to homogenize the samples, the containers were heated 3 h at 1173 K and weighed. Only absolutely airtight containers which maintained constant weight were used for calorimetric measurements.

2.2. Enthalpy measurements

Enthalpy increments $H_{\mathrm{rel}} = H(T) - H(298\,\mathrm{K})$ were measured by an isoperibolic high temperature drop calorimeter. The equipment was constructed at the calorimetry laboratory of the Institute of Inorganic Chemistry of the Slovak Academy of Sciences [20]. The measurement starts with annealing of the sample in the calorimetric furnace. After at least 1 h of heating at constant temperature the sample is dropped into the massive calorimetric copper block in which the heat released is measured. The surrounding jacket of the block is kept at constant temperature 298 K and stabilized to ±0.003 K by a battery of thermostats. The whole calorimetric equipment is placed in a separate room tempered to 298 ± 0.3 K. The temperature increase of the calorimetric block, usually about 0.5–1 K, is measured in the form of the voltage difference by the Wheatstone bridge consisting of two temperature dependent and two temperature independent resistors made of copper wire and manganine wire, respectively. Windings of the resistors are placed in a groove at the surface of the block. Output voltage of the bridge varies linearly with temperature. The temperature sensitivity of the measuring system is about 600 μV/K. Heat capacity of the calorimetric system is determined by calibration using the calorimetric standard – synthetic sapphire, and using electric energy. For electrical calibration, a special precise manganine resistor is installed inside the block. By the isoperibolic principle, the enthalpy is measured as the amount of heat transferred from the block to its surroundings, while the block cools down to its base line temperature. It is determined by evaluating the temperature difference between the block and its surroundings as a function of time. After dropping the sample the temperature of the block is recorded for approximately 1 h. The evaluation of the amount of heat is performed by integration of the calorimetric curve. The evaluation method is described in detail in [21]. The typical measured enthalpy is 1–4 kJ, the typical relative error of a single measurement is about 0.3%.

Table 1
Molar relative enthalpy of melts.

$x(K_2TaF_7)$	T (K)	H_{rel} (kJ/mol)	$x(K_2TaF_7)$	T (K)	H_{rel} (kJ/mol)
0	1053	70.2 [23]	0.70	1053	191.4
0	1093	73.2 [23]	0.70	1053	190.6
0	1133	76.1 [23]	0.70	1093	202.5
0.20	1053	105.4	0.70	1093	200.7
0.20	1053	105.4	0.70	1093	203.2
0.20	1053	104.4	0.70	1133	212.4
0.20	1093	110.6	0.70	1133	210.6
0.20	1093	110.3	0.70	1133	211.3
0.20	1133	115.4	0.80	1053	213.1
0.40	1053	137.4	0.80	1053	212.9
0.40	1053	137.6	0.80	1053	213.2
0.40	1093	144.7	0.80	1093	222.9
0.40	1093	145.1	0.80	1093	222.2
0.40	1133	151.7	0.80	1133	235.2
0.40	1133	152.6	0.80	1133	235.8
0.50	1053	154.4	0.90	1093	245.1
0.50	1093	161.5	0.90	1133	258.9
0.50	1093	161.5	0.90	1133	259.3
0.50	1093	161.4	0.90	1053	231.8
0.50	1093	163.2	1	1093	266.2
0.50	1093	161.0	1	1133	282.0
0.50	1133	169.4	1	1053	252.7
0.50	1133	170.4			

3. Results

Enthalpy increments of melts with 0.2, 0.4, 0.5, 0.7, 0.8 and 0.9 mole fractions of K_2TaF_7 as well as of the pure K_2TaF_7 melt were measured at temperatures between 298 and 1053, 1093 and 1133 K. The measured data are summarized in Table 1. The reference state is crystals of individual compounds at $T = 298$ K. Enthalpies of K_2TaF_7 melt obtained in this study are about 0.6–2% higher than values reported in [22]. The calculations were made using presently observed values. Data for KCl are from [23].

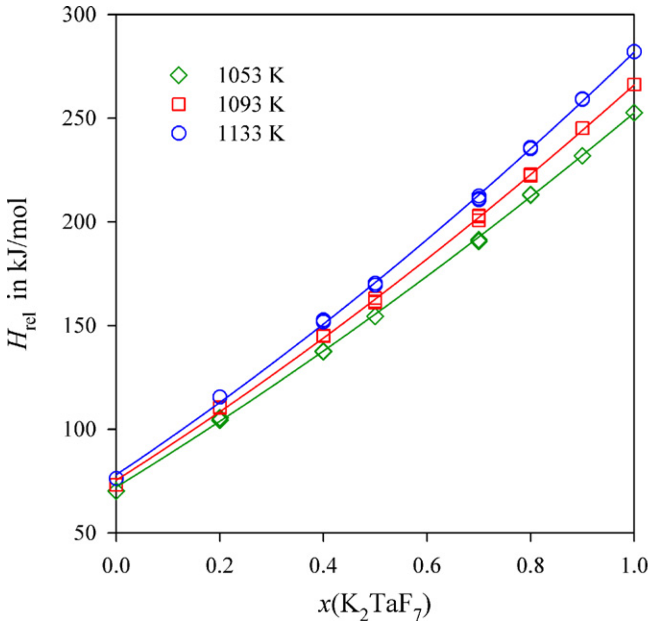

Fig. 1. Composition dependences of relative enthalpy of melts in the system KCl–K_2TaF_7.

The polynomials fitted to the molar enthalpy increments to express the composition dependences are as follows:

$$H_{rel}(1053\,\mathrm{K})/(\mathrm{kJ\,mol^{-1}}) = (72.1 \pm 1.1) + (153.1 \pm 4.9)x + (27.4 \pm 4.6)x^2, \quad 0.5 \le \sigma(H_{rel}) \le 1.1\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

$$H_{rel}(1093\,\mathrm{K})/(\mathrm{kJ\,mol^{-1}}) = (75.4 \pm 1.2) + (158.5 \pm 4.6)x + (32.2 \pm 4.3)x^2, \quad 0.4 \le \sigma(H_{rel}) = 1.2\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

$$H_{rel}(1133\,\mathrm{K})/(\mathrm{kJ\,mol^{-1}}) = (78.0 \pm 1.4) + (167.0 \pm 5.5)x + (36.8 \pm 5.1)x^2, \quad 0.5 \le \sigma(H_{rel}) = 1.4\,\mathrm{kJ\,mol^{-1}} \tag{3}$$

where x is mole fraction of K_2TaF_7. The regression coefficients in these equations are given in parentheses along with their standard deviations. The standard deviations of H_{rel}, $\sigma(H_{rel})$, were calculated using variances and covariances of regression coefficients by the error propagation law. They depend on the composition of the melt and may thus be calculated for arbitrary compositions of the melts, including pure components KCl and K_2TaF_7. This was employed later by evaluation of uncertainties of the enthalpies of mixing. Variation of the enthalpy with composition is presented in Fig. 1.

The obtained experimental data allowed to examine dependences of the relative enthalpy on temperature and to determine heat capacities of melts. The straight line fits of the measured enthalpy data versus temperature are shown in Fig. 2. The molar heat capacities obtained as the first derivatives of the straight line fits with respect to temperature are presented in Fig. 3. The evaluated C_p data show negative deviation from additivity.

Combined temperature and composition dependence of the relative enthalpy was obtained by multiple least squares fit of the measured enthalpy data:

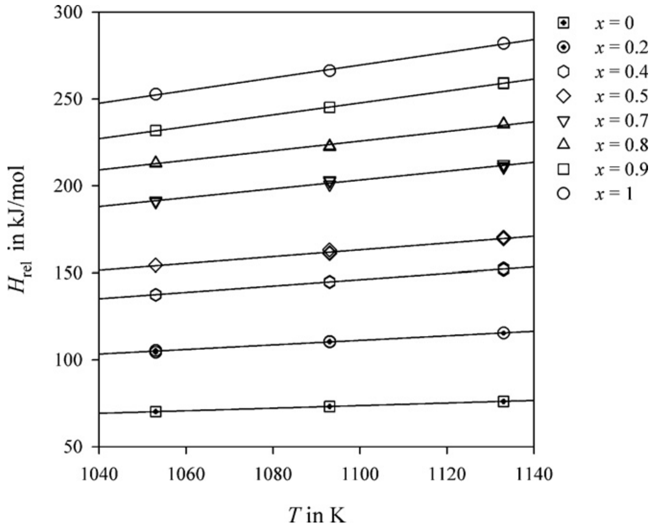

Fig. 2. Temperature dependences of relative enthalpy of melts in the system KCl–K_2TaF_7; x is mole fraction of K_2TaF_7.

$$H_{rel}/(\mathrm{kJ\,mol^{-1}}) = (6.88 \times 10^{-2} \pm 6 \times 10^{-4})T/\mathrm{K} - (115 \pm 11)x + (0.251 \pm 1.1 \times 10^{-2})x\,T/\mathrm{K} + (3.01 \times 10^{-2} \pm 2.4 \times 10^{-3})x^2\,T/\mathrm{K}$$

For calculation of the molar enthalpies of mixing measured enthalpies of melted mixtures, enthalpies of liquid KCl [23] and measured enthalpies of K_2TaF_7 melt were used. The enthalpy of undercooled melt of KCl at 1053 K was obtained by extrapolation. The obtained enthalpies of mixing are plotted in Fig. 4 as individual data points. The uncertainties were evaluated using standard deviations of enthalpies of melted mixtures and pure component melts. Standard deviations of the pure component melts were determined by extrapolation of the standard deviations of the molar relative enthalpies of melted mixtures, as mentioned above. The standard deviations of the individual $\Delta_{mix}H$ data points, $\sigma(\Delta_{mix}H)$, were 1.4–1.6 kJ/mol.

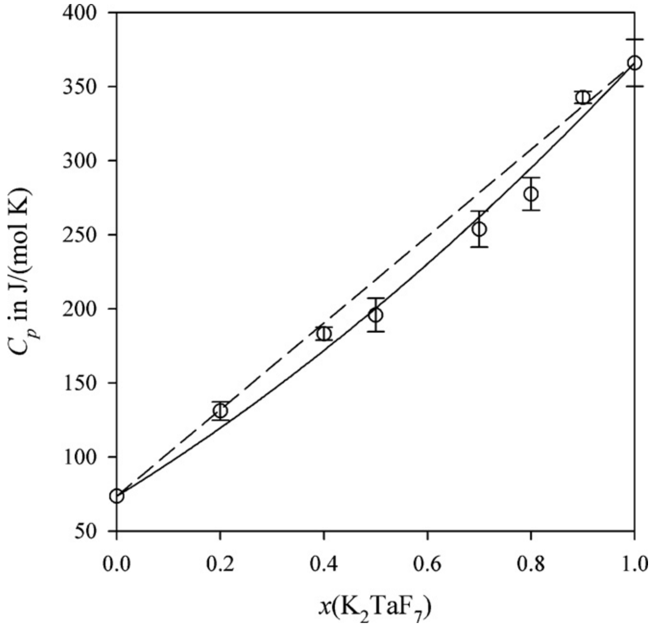

Fig. 3. Molar heat capacity of melts in the system KCl–K_2TaF_7. The dashed line represents additivity.

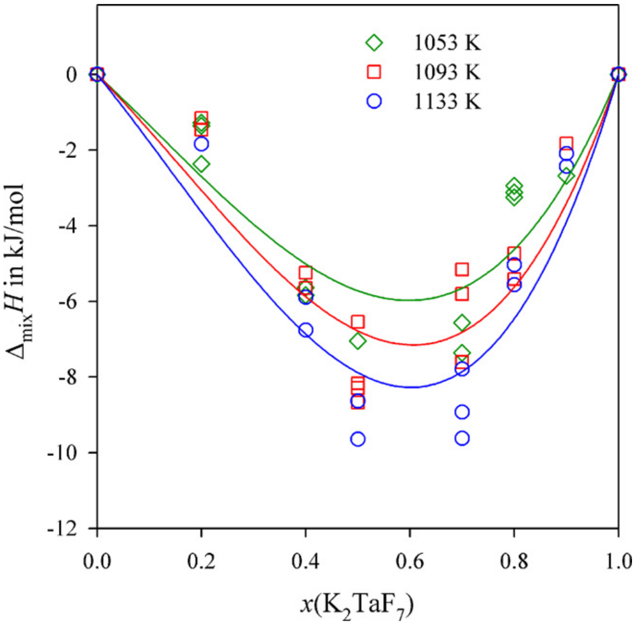

Fig. 4. Enthalpy of mixing of melts in the system KCl–K_2TaF_7.

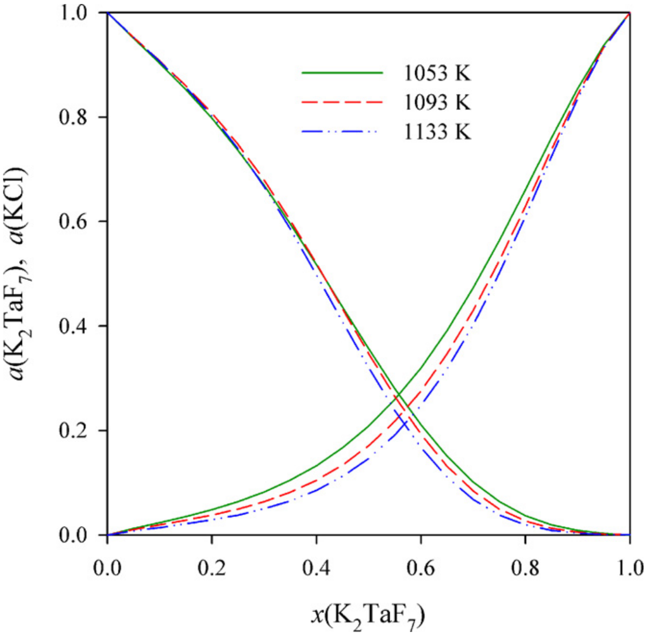

Fig. 5. Activities of components in melts of the system KCl–K_2TaF_7.

For analytical expression of the composition dependence of the enthalpy of mixing the equation:

$$\Delta_{mix}H/(\mathrm{kJ\,mol^{-1}}) = ax(1-x)^2 + bx^2(1-x) \quad (4)$$

was chosen. The regression coefficients with standard deviations obtained by the least squares fits of the enthalpy of mixing values are summarized in Table 2. Eq. (4) is represented by curves in Fig. 4. This figure shows negative deviation from ideality, due to exothermic enthalpy of mixing in this system.

Considering two parameter Margules type model for excess Gibbs energy of mixing and assuming regular behavior of the melts, activity coefficients have been calculated using the relations:

$$\ln \gamma_1 = \frac{1}{RT}x_2^2[a + 2x_1(b-a)]$$

$$\ln \gamma_2 = \frac{1}{RT}x_1^2[b + 2x_2(a-b)]$$

where x_1 and x_2 are mole fractions of K_2TaF_7 and KCl, respectively. The resulting activities of components are shown in Fig. 5.

4. Discussion

Extensive studies of tantalum containing fluoride melts, mainly by IR spectroscopy [9,14,24], showed that ionic composition of these melts is determined by the ionic equilibrium between hepta- and hexacoordinated complexes. In the K_2TaF_7 melt, the following anionic equilibrium is assumed:

$$TaF_7{}^{2-} \leftrightarrows TaF_6{}^{-} + F^{-}$$

Both of the present complex ions are ready to interact with Cl^- anions at mixing with molten KCl. Negative deviation of the enthalpy of mixing from additivity observed in the present study indicates a tendency to compound formation in the solution. It may be attributed to the addition reaction of the fluorotantalate anions, present in the K_2TaF_7 melt, with Cl^- anions. The formation of TaF_6Cl^{2-} complexes according to the reaction:

$$TaF_6{}^{-} + Cl^{-} \leftrightarrows TaF_6Cl^{2-} \quad (A)$$

was suggested by Agulyansky et al. [12]. However, the contribution of the addition reaction to the enthalpy of mixing is probably limited by the dissociation of the heteroligand anions TaF_6Cl^{2-}. With increasing temperature, the dissociation degree increases, the equilibrium (A) is shifted to the left, and the influence of the reaction (A) on thermal effect of mixing diminishes. This kind of behavior, a decrease of the mixing enthalpy with increasing temperature, was observed in the KF–K_2TaF_7 melts where only addition reaction is supposed [22]. Another factor which may influence the enthalpy of mixing in KCl–K_2TaF_7 melts substantially is the enthalpy of substitution reaction and its temperature dependence. It may be expected that the following substitution reaction occurs in the studied system:

$$TaF_7{}^{2-} + Cl^{-} = TaF_6Cl^{2-} + F^{-} \quad (B)$$

The formation of the TaF_6Cl^{2-} ions by reaction (B) is as mentioned in Agulyansky [10]. One may expect that with increasing temperature, the equilibrium of reaction (B) is shifted to the right, having the opposite influence on the temperature dependence of the mixing enthalpy as the addition reaction (A). This influence becomes energetically dominant, causing increase of the total thermal effect of mixing at increasing temperature in this system, as observed in the present study. As shown in Fig. 4 the curves of enthalpy of mixing are not symmetrical. The minima are shifted to the K_2TaF_7 rich side of the system near composition of $x(K_2TaF_7) = 0.6$. The asymmetry of the mixing enthalpy and the character of temperature dependence make it evident that ionic equilibria in the melts are quite complicated and several processes run simultaneously at mixing. The asymmetry was observed also in KF–K_2TaF_7 system [22] which suggests that probably association processes contribute substantially to this effect. This may indicate that apart from the association processes resulting in formation of the TaF_6Cl^{2-} anions, TaF_7Cl^{3-} complexes may also be

Table 2
Regression coefficients with respective standard deviations in Eq. (4).

T (K)	a	$\sigma(a)$	b	$\sigma(b)$
1053	−12.8	5.0	−32.9	4.5
1093	−13.8	5.4	−40.4	4.9
1133	−16.8	6.4	−46.2	5.2

created in the melts by addition reaction of TaF_7^{2-} with Cl^- ions. K_3TaF_7Cl ($KCl{\cdot}K_2TaF_7$) was identified in the solidified melts after calorimetric experiments by X-ray diffraction (PDF No 25–682). Besides K_3TaF_7Cl, a phase with X-ray pattern similar to K_2TaF_7 was also observed. However, as already mentioned, TaF_7Cl^{3-} complexes were not observed in the melts by spectroscopic methods. According to a recent structural study [25] the presence of octacoordinated complexes was denied in crystalline K_3TaF_8 and questioned even in Na_3TaF_8. This makes the presence of TaF_7Cl^{3-} ions in the melt unlikely too.

To assess possible contamination by Rh or Pt from the Pt 90% Rh 10% containers the solidified melt with 80 mol% K_2TaF_7 and 20 mol% of KCl was examined by EDX method. In several heating and cooling cycles this sample spend about 15 h in the container in the molten state. No detectable amount of the Rh or Pt was observed.

5. Conclusions

The calorimetric measurements of enthalpy increments on melts in the $KCl–K_2TaF_7$ system at temperatures between 298 and 1053, 1093 and 1133 K have shown that the variation of the molar relative enthalpy with composition is slightly nonlinear. In the considered temperature interval, the enthalpy of mixing shows negative deviation from ideality and becomes more negative at higher temperatures. The negative deviation in the studied system may be explained by a tendency to clustering or compound formation in the melts due to addition reaction at mixing. The increasing negative deviation of the enthalpy of mixing with increasing temperature indicates that the addition reaction is accompanied by substitution of chlorine for fluorine in fluorotantalate anions, producing heteroligand complexes. The formation of TaF_6Cl^{2-} anions produced either by addition interaction and/or F–Cl exchange reactions may be responsible for this nonideality. F–Cl exchange probably becomes energetically dominant, causing increase of the total thermal effect of mixing at increasing temperature. The present study showed that enthalpic properties of the $KCl–K_2TaF_7$ melts may be explained without necessarily assuming the presence of octacoordinated complex ions.

A similar concept may be applied also to $KF–K_2TaF_7$ melts, where formation of the TaF_8^{3-} ions was often assumed [22].

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References

[1] T. Iuchi, K. Ono, Sci. Rep. Res. Tohoku A 13 (1961) 456–465.
[2] T. Iuchi, T. Matsuchima, K. Ono, Bull. Res. Inst. Miner. Dress. Metall. Tohoku Univ. 15 (1960) 87–90.
[3] T. Iuchi, K. Ono, Bull. Res. Inst. Miner. Dress. Metall. Tohoku Univ. 16 (1961) 133–138.
[4] Z. Bin-Sin, N.P. Lushnaya, V.I. Konstantinov, Zh. Neorg. Khim. 8 (1963) 389–395.
[5] F.V. Kovalev, V.E. Kvartsev, V.M. Ioffe, M.E. Leonov, Zh. Neorg. Khim. 18 (1973) 1352–1355.
[6] J.J. Remeau, Rev. Int. Hautes Temp. Refract. 8 (1971) 59–70.
[7] T. Iuchi, K. Ono, Bull. Res. Inst. Miner. Dress. Metall. Tohoku Univ. 16 (1961) 139–145.
[8] T. Iuchi, K. Ono, Sci. Rep. Res. Tohoku A 14 (1962) 42–49.
[9] A. Agulyansky, J. Fluorine Chem. 123 (2003) 155–161.
[10] A. Agulyansky, The Chemistry of Tantalum and Niobium Fluoride Compounds, Elsevier, Amsterdam, 2004.
[11] A.I. Agulyansky, P.T. Stangrit, V.I. Konstantinov, Zh. Prikl. Khim. 51 (1978) 789–792.
[12] A.I. Agulyansky, P.T. Stangrit, V.I. Konstantinov, Zh. Prikl. Khim. 51 (1978) 2720–2724.
[13] B.F. Markov, L.A. Shumina, Dokl. AN SSSR 110 (1956) 411–413.
[14] A.I. Agulyansky, S.A. Kirilov, V.D. Prisyagny, Ukrain. Khim. Zh. 46 (1980) 457–460.
[15] A.A. Klimenkov, B.V. Kokarev, Yu.F. Chervinskij, 6. Kola Seminar on Electrochemistry of Rare and Non-ferrous Metals, Apatity (USSR), 15–17 July 1989. Summaries of Reports, 1989, p. 26. AN SSSR, Apatity (USSR), Inst. Khimii i Tekhnologii Redkikh Ehlementov i Mineral'nogo Syr'ya, Short Communication.
[16] A.V. Kozyukov, S.P. Raspopin, V.Yu. Chervinskij, Yu.F. Chervinskij, Rasplavy (4) (1997) 74–77.
[17] A.V. Kozyukov, S.P. Raspopin, V.Yu. Chervinskij, Yu.F. Chervinskij, Rasplavy (6) (1997) 87–89.
[18] S.E. Darienko, S.S. Zobnin, Yu.F. Chervinskij, 6. Kola Seminar on Electrochemistry of Rare and Non-ferrous Metals, Apatity (USSR), 15–17 July 1989. Summaries of Reports, 1989, p. 25. AN SSSR, Apatity (USSR), Inst. Khimii i Tekhnologii Redkikh Ehlementov i Mineral'nogo Syr'ya, Short Communication.
[19] S.S. Zobnin, Physical-chemical Properties of Fluoride–chloride Melts Containing Tantalum and Niobium, U-Thesis, 1992 (http://hdl.handle.net/10068/345884).
[20] I. Proks, M. Eliášová, I. Zlatovský, J. Záuška, Silikáty 21 (1977) 253–264.
[21] I. Zlatovský, Silikáty 21 (1977) 71–75.
[22] I. Nerád, E. Mikšíková, Z. Balogová, Cent. Eur. J. Chem. 7 (2009) 774–779.
[23] O. Knacke, O. Kubashewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances I, 2nd ed., Springer-Verlag, Berlin, 1991.
[24] A.I. Agulyansky, Zh. Neorg. Khim. 25 (1980) 2998–3002.
[25] Ľ. Smrčok, R. Černý, M. Boča, I. Macková, B. Kubíková, Acta Crystallogr. C66 (2010) i16–i18.