The Charge Transfer for Nb(V)/Nb(IV) and Ta(V)/Ta(IV) Redox Couple in Electrode Surface: Experimental and Calculation Methods

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The diffusion coefficients and Standard rate constants k_s of charge transfer for Nb(V)/Nb(IV) and Ta(V)/Ta(IV) in NaCl–KCl (the equimolar mixture)–$K_2Nb(Ta)F_7$, KCl–$K_2Nb(Ta)F_7$, and CsCl–$K_2Nb(Ta)F_7$ melts are determined by using cyclic voltammetry. An unconventional series of the standard rate constants is found: k_s (KCl) < k_s (CsCl) < k_s (NaCl–KCl). Ab initio calculations carried out by using a PC Gamess/Firefly quantum-chemical program showed that the charge transfer activation energy can change not monotonically in the Na–K–Cs series, in compliance with the reorganization energy relationship. This leads, in its turn, to nonmonotonic change in the charge transfer rate constants. The diffusion coefficients decrease when the composition of the second coordination sphere changes from sodium to cesium. Logarithms of the diffusion coefficients of the com plexes Nb(V) and Nb(IV) or Ta(V)/Ta(IV) are the linear functions of the alkali metal cation radius. Such changes of D values are well known. They are due to a weakening of the counter-polarizing effect when passing from Na to Cs, which, in its turn, leads to the shortening of the metal–ligand bond in the complexes. The diffusion coefficients decrease as the oxidation degree increases, while the activation energy of the diffusion process increases. Thus, with the increasing of the ionic potential of the diffusing particles the values of D decrease, while ΔU increases. The obtained results agree with numerous data on the effect of the central atom oxidation degree on the diffusion coefficients and activation energy of diffusion processes. Quantum-chemical calculations showed that the charge transfer activation energies can actually change in nonmonotonic manner in the series sodium–potassium–cesium, which leads to nonmonotonic change of the charge transfer rate constants.

Keywords: Melt, Redox couple, Niobium complexes, Cyclic voltammetry, Diffusion coefficients, Quasireversible process, Standard rate constants of charge transfer, Quantumchemical calculations.

1. INTRODUCTION

Despite extensive electrochemical studies carried out in salt melts, still no data on the standard rate constants ks of charge transfer for redox couples and on the effect of second coordination sphere on the charge transfer rate constants is at hand. We showed [1, 2] that the standard rate constants of charge transfer for Hf(IV)/Hf and Cr(III)/Cr(II) redox couples decreased when passing from NaCl–KCl melt to KCl and CsCl melts. According to the theory of the elementary act of charge transfer, smaller and stronger complexes require higher energy for the reorganization preceding the electron transfer process proper; hence, the electrode reaction is slower [3]. When passing from NaCl–KCl melt to KCl and CsCl melts, the complex size and metal–ligand bond length decrease and the complex strength increases because of the weakening of the counter-polarizing effect of outer-sphere cations in the Na–K–Cs series. Thus, the decrease in the ks value for the Hf(IV)/Hf and Cr(III)/Cr(II) redox couples caused by the changes in the second coordination sphere composition from Na$^+$ toward Cs$^+$ agrees with the principal concepts of the theory of the elementary act of charge transfer [4].

Whereas it was shown during the studies of the effects of the second coordination sphere on the standard rate constants of charge transfer for Eu(III)/Eu(II) [2, 5], Sm(III)/Sm(II), and Yb(III)/Yb(II) [6] redox couples in alkali metal chlorides that ks values increase with the increasing of the outer-sphere cation size from sodium to cesium. In the above-listed redox couples the charge transfer may involve an outer-sphere cation; the largest

values of ks in the CsCl melt may be explained by the Cs larger polarizability as compared with other alkali metal cations [5].

This work [6] is part of our systematic research concerning the effects of composition of the first and second coordination spheres on the standard rate constants of charge transfer involving the Nb(V)/Nb(IV) and Ta(V)/Ta(IV) redox couple.

2. RESULTS AND DISCUSSION

2.1 The Diffusion Coefficients of Nb(V)/Nb(IV) and Ta(V)/Ta(IV) Complexes in Chloride–Fluoride Melts

The temperature dependence of the diffusion coefficients was determined over the 1073-1173 K interval,with due allowance for all data obtained by the linear voltammetry (Table 1). We see from Tables 1 that the diffusion coefficients decrease when the composition of the second coordination sphere changes from sodium to cesium. Logarithms of the diffusion coefficients of the complexes Nb(V)/Nb(IV) and Ta(V)/Ta(IV) are the linear functions of thealkali metal cation radius. Such changes of D values are well known [9]. They are due to a weakening of the counter-polarizing effect when passing fromNa to Cs, which, in its turn, leads to the shortening ofthe metal–ligand bond in the complexes. The diffusion coefficients decrease as the oxidation degree increases, while the activation energy of the diffusion process increases.

Table 1 – The values of the diffusion coefficients for the studied objects against the background of the KCl/NaCl melt, obtained at different temperatures by the method of linear voltammetry

Temperature	1073 K		1123 K		1173 K		Activation energy of the diffusion process, kJ/mol
KCl/NaCl	$D_{Nb}(V)$	$D_{Nb}(IV)$	$D_{Nb}(V)$	$D_{Nb}(IV)$	$D_{Nb}(V)$	$D_{Nb}(IV)$	49.7
	1.37	1.79	1.79	2.31	2.29	2.93	
CsCl	1.01	1.35	1.35	1.99	1.81	2.55	62.2
KCl/NaCl	$D_{Ta}(V)$	$D_{Ta}(IV)$	$D_{Ta}(V)$	$D_{Ta}(IV)$	$D_{Ta}(V)$	$D_{Ta}(IV)$	
	1.60	2.03	1.84	2.70	2.37	3.01	51.9
CsCl	1.41	1.83	1.57	2.48	2.01	2.84	69.4
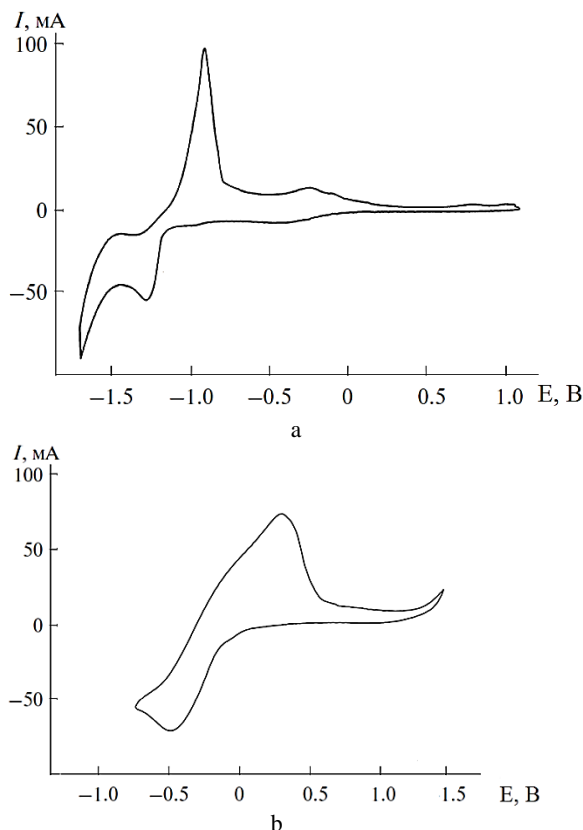
Fig. 1 – Cyclic voltamperogram of the (a) KCl–$K_2NbF_7^{2-}$ and (b) KCl–$K_2TaF_7^{2-}$ melts. The platinum electrode surface area is 0,378 cm², the potential scan rate is 0,1 V s^{-1}, T = 1073 K, $c(K_2NbF_7^{2-})$ = 1.11 × 10^{-4} mol·cm^{-3}; platinum quasireference electrode for niobium melt; the potential scan rate is 0,5 V·s^{-1}, T = 1023 K, $c(K_2TaF_7^{2-})$ = 3.11 × 10^{-5} mol cm^{-3}; platinum quasireference electrode for tantal-contain melt

Thus, with the increasing of the ionic potential of the diffusing particles the values of D decrease, while ΔU increases. The obtained results agree with numerous data on the effect of the central atom oxidation degree on the diffusion coefficients and activation energy of diffusion processes [7].

2.2 Quantum-Chemical Calculations

One of the reasons of the changes in the rate constants of charge transfer we observed in the series of the outersphere cations can be the nonmonotonic change of the electron transfer activation energy in this series; the values of the activation energies, in their turn, are determined by the complex particles reorganization energies. When the latter are known, it is possible to evaluate the charge transfer activation energies (Eact) by using the Marcus formula. This approach is prevailing nowadays [8, 9]. The complex particle here is the NbF_7^{2-} and TaF_7^{2-} complex with its outer-sphere shell comprising alkali metal cations. It is well-known that this approximation gives more realistic description of the properties of particles in the alkali-metal chloride melts [11]. In this work the calculations were performed for the Nb(V)/Nb(IV) and Ta(V)/Ta(IV) complexes with taking into consideration their outersphere shell, that is, for particles of the type $nM^+ \cdot Nb(Ta)F^{2-}$ and $nM^+ \cdot Nb(Ta)F^{3-}$, where M = Na, K, Cs and n is the number of the outer-sphere cations (n = 1 to 6). At n = 6 the particles become unstable.

In Table 2 we give the bond order for the particles $nM^+ \cdot Nb(Ta)F_7^{2-}$ and $nM^+ \cdot Nb(Ta)F_7^{3-}$ (M = Na, K, Cs). We see from Table 2, that the Nb(V) and Ta(V) particles are most stable at n = 4; the Nb(IV) and Ta(V) particles, at n = 5.

Table 2 – Values of bond orders B_{ij} for heptafluoro-(tantalates)niobates of alkali and alkaline earth metals (selective data)

Type of particles	The meaning of B_{ij}					
	Nb–F$_{(1)}$	Ta–F$_{(1)}$	Nb–F$_{(6)}$	Ta–F$_{(6)}$	M–F$_{(6)}$	M–F$_{(6)}$
$Nb(Ta)F_7^{2-}$	0.654	0.545	0.654	–	–	–
$\{K^+[Nb(Ta)F_7]^{2-}\}^-$	0.665	0.554	0.372	0.310	0.057	0.048
$\{Li^+[Nb(Ta)F_7]^{2-}\}^-$	0.717	0.598	0.208	0.173	0.208	0.170
$\{Mg^{2+}[Nb(Ta)F_7]^{2-}\}$	0.801	0.679	0.218	0.185	0.232	0.193

Because the most stable particles of Nb(V)/Nb(IV) and Ta(V)/Ta(IV) differ in the composition of their outer-sphere shell, the electron transfer process is likely to pass in two stages. One stage is the electron transfer proper; the other, the changing of the shell composition (from four outer-sphere cations to five cations). The change in the composition of the initial particle from $4M^+ \cdot NbF_7^{2-}$ to $5M^+ \cdot NbF_7^{2-}$, which precedes the electron transfer, is energetically unfavorable: it consumes as much as 250 (for Cs) to 420 (for Na) kJ/mol. In other words, of the

two particles it is $4M^+ \cdot Nb(Ta)F_7^{2-}$ that seems to be the most probable electroactive particle. It is evident that in our case the taking into consideration of the long-order environment whose effect is less strong than that from the first two coordination spheres cannot radically change the interrelation between the stabilities of the discussed particles. At the same time the passing from the composition of the initial particle with four outer-sphere cations to that with three outer-sphere cations is more probable because it requires only 4 (for Cs) to 25 (for Na) J/mol. Because of the great excess of the alkali metal cations in the melt, all equilibriums must be shifted to the formation of the particles $4M^+ \cdot NbF_7^{2-}$, indeed; hence, the probability of the particles $3M^+ \cdot Nb(Ta)F_7^{2-}$ formation must be less than the value that follows from the calculations. The passing of a reduced particle $4M^+ \cdot NbF_7^{3-}$ to the most stable composition $5M^+ \cdot Nb(Ta)F_7^{3-}$ is spontaneous: the energy of the transition changes from -14 (for Cs) to -72 (for Na) kJ/mol. It seems quite doubtful that the transition can limit the charge transfer process because the attaching of the fifth outer-sphere cation (unlike the attaching of electron) does not require any significant rearrangement of the niobium's first coordination sphere. We conclude, that at the current stage of the model most probable is the electron transfer to the particle $4M^+ \cdot Nb(Ta)F_7^{2-}$, with subsequent transition of the composition of the reduced form $4M^+ \cdot Nb(Ta)F_7^{3-}$ to $5M^+ \cdot Nb(Ta)F_7^{3-}$.

In Table 2 we give the calculated values of the activation energies for the charge transfer for particles with different composition of the outer-sphere shell.

Under the conditions of electrochemical experiment the charge transfer occurs near the equilibrium state when the Gibbs energy of electron transfer (ΔGr) can be thought of as zero. As a result the Marcus general formula can be simplified [4]:

$$E_{act} = (E_r + \Delta G_r)2/4E_r \approx E_r/4. \qquad (2)$$

The reorganization energy E_r in this case is the difference of the initial $nM^+ \cdot NbF_7^{2-}$ (or $nM^+ \cdot TaF_7^{2-}$) particle's energies in the equilibrium geometry of the final particle $nM^+ \cdot Nb(IV)F^{3-}$ (or $nM^+ \cdot TaF_7^{2-}$) and in its intrinsic equilibrium geometry.

The comparison of the energies E_{act} for M = Na, K, Cs (Table 3) at different values of n showed that their ratio corresponds to the experimental ratio of the charge

transfer rate constants only at the values of n equal to 4 and 5; here the activation energy grows in the series Na < Cs < K. We mentioned above that the electron transfer to the particle $5M^+ \cdot Nb(Ta)F_7^{2-}$ is improbable. The only acceptable variant that remains is the electron transfer to the particle $4M^+ \cdot Nb(Ta)F_7^{2-}$. This corroborates the assumption on the prevailing effect in the melt of those niobium(V) complexes whose energy of the outer-sphere shell formation is maximal.

Table 3 – Calculated electron transfer activation energies for the particles $nM^+ \cdot NbF_7^{2-}$ and $nM^+ \cdot TaF_7^{2-*}$

	M+					
n	Na		K		Cs	
1	19.2	21.5*	2.2	2.8*	3.1	4.0*
2	17.7	18.0	7.5	8.7	1.5	2.3
3	13.4	14.7	27.4	29.0	2.3	2.9
4	18.2	19.1	27.7	29.1	24.5	25.7
5	18.5	18.9	29.1	30.1	23.4	24.9
6	50.1	51.4	67.4	69.0	48.1	49.9

* – evaluations for $nM^+ \cdot TaF_7^{2-*}$

The above-given calculated data also evidences that the charge transfer activation energies really can change in nonmonotonic manner in the series Na–K–Cs in compliance with the ratio of the reorganization energies. This leads, in its turn, to nonmonotonic change of the charge transfer rate constants, which is observed in the experiment, indeed.

3. CONCLUSIONS

The effect of the second coordination sphere composition on the standard rate constants of charge transfer for Nb(V)/Nb(IV) and Ta(V)/Ta(IV) redox couple in chloride–fluoride melts is studied. Quantum-chemical calculations showed that the charge transfer activation energies can actually change in nonmono-tonic manner in the series sodium–potassium–cesium, which leads to nonmonotonic change of the charge transfer rate constants. Thus, the calculations corroborate the experimentally found series of changes in the rate constants k_s for fluoride complexes that make up the Nb(V)/Nb(IV) and Ta(V)/Ta(IV) redox couple in the alkali metal halide melts.

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