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Electrochemically active species and multielectron processes in ionic melts

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Abstract. The model concepts for the mechanisms of formation of electrochemically active species and multielectron processes in ionic nitrate-, carbonate-, boron- and titanium-containing fluoride melts are generalised. The fundamental importance of the acid-base properties of a melt in the mechanism of formation of electrochemically active species is shown for nitrate- and carbonate-containing melts. This fact is confirmed by electrochemical measurements and by calculations of force constants for oxyanions. The optimum form of electrochemically active species has been established; their reduction abilities depend on the cationic composition of a melt, the adsorption properties of the electrode surface and the electric field strength. The bibliography includes 218 references.

I. Introduction

Complex multicomponent systems containing ions of polyvalent metals are used as reaction media in the preparation of inorganic and organic compounds by high-temperature electrochemical synthesis, for the implementation of processes in high-temperature current sources, in electrometallurgy, in electroplating and other areas where a specific approach to the control of chemical processes in melts is required. Molten salts are widely used in practice, that is why the study on their structures, chemical and electrochemical properties is an issue of current interest.[1–3]

This review covers the state-of-the-art of a fundamental problem of electrochemistry of ionic melts, *viz*., determination of the nature of electrochemically active species (EAS) involved in electrochemical reactions and the conditions required for multielectron transformations at electrode – electrolyte interfaces. The electrochemically active species are groups of ions formed in a melt due to acid-base interactions and possessing the highest abilities to accept electrons in the double electric layer. To date, this problem got both the theoretical background and was confirmed comprehensively by experiment for not-too-complicated electrochemical systems with simple one-element ions. If the components of a system arise from complexes, the electrode reactions are supposed to involve multiple-charged ions with complex compositions. Such systems can exist both in aqueous electrolytes and in ionic melts. The problem of theoretical description of multielectron electrochemical reactions in ionic melts has not been solved unambiguously so far. In order to describe experimental results on multielectron transformations at interfaces of electrochemical systems, one mainly uses the concepts on acid-base equilibria and the concepts on electron density redistribution mechanisms during the formation of new chemical bonds or under the influence of the outer-sphere cations and anions on the intracomplex bonds.

The concepts of the mechanism of formation of electrochemically active species in ionic melts based on the analysis of thermodynamic and kinetic parameters are phenomenological. The lack of systematic studies on the relationship between chemical reactions of EAS formation in the bulk melt and their electrochemical reduction and on the effect of the adsorption properties of electrode surfaces and the external electric field on the acid-base interactions in ionic melts not only predetermines the existence of controversial results in the interpretation of the relationships obtained experimentally but also prevents the formulation of basic principles of EAS formation and control of electrochemical processes. The most abundant information on the interaction between the species in a melt and on the processes of their electrochemical reduction can be obtained from data on the changes in the electronic state of the species.[4–7] Therefore, it seems expedient to use the results of both theoretical and modern experimental research methods for the substantiation of EAS formation mechanisms in ionic melts. Once this mechanism has been established, it will be possible to develop a theoretical basis for creating the general principles for control over multielectron processes.

In ionic liquids (ionic melts), the acid-base interactions manifest themselves explicitly,[8,9] but it is difficult to conceive their mechanisms because of their complexity. A cation – anion interaction model is used for the description of this mechanism. In accordance with this model, the acid-base properties of a medium with respect to a particular anion are changed by addition of different types of cations to a dilute solution. Let us consider how this model 'operates' for such anions as NO_3^-, CO_3^{2-}, TiF_6^{2-}, BF_4^-, WO_4^{2-} and MoO_4^{2-} (hard bases) and such cations as Cs^+, Rb^+,

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K^+, Na^+, Li^+, Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Be^{2+} (hard acids) in nitrate-, carbonate-, boron- and titanium-containing fluoride melts that are widely used in practice.[2–4]

II. Model concepts on the structures of ionic melts

The physicochemical properties of ionic melts containing polycoordinated anions, *viz*., NO_3^- and CO_3^{2-}, are determined by the electronic structures of the oxygen-containing anions and the character of their interactions with the melt cations. There is only the near-range order in ionic liquids, which creates problems both for the interpretation of the experimental relationships and for the theoretical descriptions of the melt structures. This can explain the existence of various model concepts as to the structures of ionic melts.

Studies on the changes in the intra-anion bonds depending on the cationic environment (changes in the force constants of the bonds and in bond angles were analysed) in melts of monovalent metal nitrates have led to the conclusion that contact cation–anion pairs exist in these melts.[10, 11] Based on this conclusion, a model of an ion pair was built. This model has been used, *e.g*., for the explanation of the features of IR and Raman spectra of $LiNO_3$ and alkaline-earth nitrate melts, namely, the low-frequency component of the spectrum resulting from the M–O vibrations and splitting of one of the frequencies in the NO_3^- spectrum.

The quasi-lattice model of the melt structure accounts for the concerted vibrational movement of the ions. Considering the mean statistical distribution of the inter-ion potential, the existence of two sublattices, namely, cationic and anionic, was assumed.[12, 13] This model denies the existence of ion pairs due to the comparability of lifetimes of the vibrational levels and the diffusional migration of species. Based on this quasi-lattice model, the existence of $[M(NO_3)_4]^{3-}$ complexes was assumed;[14] this was confirmed by spectroscopic data.[15]

The Kucharski–Flengas quasi-chemical model[16] and the three-sphere Ferland model[17] account for the statistical exchange of cations in sublattices of mixed nitrate melts. Complex ions existing in the melt are regarded as fragments of the ionic structure rather than isolated species of an anionic sublattice.[16] The asymmetry of the cation-anionic environment and the existence of independent kinetic species are explained[18] by effects of various cations, in agreement with the assumptions made elsewhere.[10, 11]

For objective reasons, the above models cannot claim to provide full description of the structures of ionic melts, but each of them states unambiguously that the structure depends significantly on the cationic compositions. This dependence has been confirmed by spectroscopic data for systems with polycoordinate anions, *viz*., complexation products. In fact, the geometries and types of complex species in melts containing insignificant amounts of transition metal salts as well as in melts with oxygen-containing anions have been established based on spectroscopic data.[19] Analysis of the spectra of sulfate melts revealed a considerable contribution of π-interactions to the chemical bonds of the metal complexes studied.[15] The characteristic vibration frequencies were found to depend on the cationic composition for individual and mixed melts containing molecular ions as the starting structural elements. In many cases, C–O and S–O vibration frequency shifts for outer-sphere cations $Cs^+ > K^+ > Na^+ > Li^+$, accompanied by band broadening due to the polarising effect of the cations, were observed in carbonate- and sulfate-containing solutions.[15]

However, the reasons for the frequency shifts in the spectra of melts were explained either qualitatively[20, 21] or on the basis of various model assumptions on the melt structures (the quasi-lattice model,[13] the ion-pair model,[10, 11] *etc*.). In addition, mutually exclusive interpretations of the same data can be found as well.

The use of spectroscopic methods for the study on dilute oxygen-containing melts encounters considerable difficulties in the interpretation of the bands because of their low intensities. On the other hand, information on the acid-base interactions in ionic liquids can be obtained by studying electrode processes. Let us consider certain specific features of electrode processes in melts, in particular those containing nitrate and carbonate ions.

Neglecting of the role of acid-base properties of the medium has traditionally led researchers to mutually exclusive conclusions in the explanation of the same features of electrode processes. For example, Delimarskii *et al*.[22, 23] showed that a cathodic process with a 100% yield of carbon was possible in the electrolysis of a molten equimolar mixture of lithium and potassium carbonates. They noted a specific feature of the voltammetric curves, *viz*., the existence of a region with a distinct limiting current at potentials 0.4–0.5 V, and considered that this region corresponded to the evolution of carbon preceding that of the alkali metal.[23] The existence of limiting currents in voltammograms has also been reported in other studies on cathodic processes in molten carbonates (see, *e.g*., Refs 24–27), but these features have been interpreted differently by different authors. Studies on the possibility of carbon evolution preceding the discharge of alkali metal cations[28, 29] showed that cathodic carbon evolution depends on the electrolyte cationic composition and can occur not only from carbonates but also from chlorides, either supplemented with thermally unstable carbonates or saturated with gaseous CO_2. The dependence of the amount of carbon evolved on the cationic composition of the carbonate electrolyte showed the dominating role of the reducing ability of CO_2 formed in the redox reaction

$$(2/m)\,M^{m+} + CO_3^{2-} \rightleftharpoons M_{2/m}O + CO_2\,. \qquad (1)$$

As in the case of carbonate-containing melts, the development of concepts on the mechanism of formation of electrochemically active species in nitrate-containing melts was facilitated by the existence of many different interpretations of the features of cathodic processes. In fact, the nature of the electrode process preceding the electrochemical reduction of alkali metals, which has first been reported by Lyalikov and Karamzin,[30] was interpreted in different manners. Rust and Duke,[31] who studied acid-base equilibria, assumed that it is the dissociation product of the anion, *viz*., the nitronium ion NO_2^+, that is reduced in electrochemical and chemical reactions. A similar conclusion was reached by Delimarskii *et al*.[32] However, no direct measurements could prove the existence of NO_2^+ in nitrate melts. It was also found[33] that noticeable amounts of NO_2^+ cannot be formed in the presence of strong acids; instead, a compound is formed the properties of which coincide with those of NO_2. This subsequently undergoes one-electron reduction into nitrite. Usanovich[34] believes that $[H_2NO_3]^+$ ions rather than NO_2^+ exist in aqueous melts.

A different viewpoint regarding the nature of the electrode process preceding the alkali metal evolution was given by Delimarskii *et al*.:[35] this process results from direct NO_3^- reduction, irrespective of the electrolyte cationic composition. A similar interpretation has been given in other studies,[36–38] but the reasons for the direct electrochemical nitrate ion reduction have not been explained.

The currently available experimental results on electrode processes in molten salts, particularly in nitrate melts, are used as a base for the simulation of various schemes of formation of electrochemically active species and the corresponding electrode processes. Let us consider some of the models.

Tkalenko *et al*. applied the regularities of the electrochemical reduction of NO_3^- in aqueous solutions[39] to melts;[40–43] this allowed them to propose a model scheme of the cathodic process in concentrated nitrate melts. According to this scheme, the NO_3^- ion in the bulk melt is an ellipsoid with the negative charge distributed over the periphery. Near the electrode surface, the ion is subjected to a combined effect of the cation and electrode fields, therefore its state differs from that in the bulk. It is believed that at negative potentials (cathodic polarisation) the NO_3^- ions are polarised additionally by the electrode force field in such a way that the positively charged nitrogen atom is displaced towards the

electrode relative to the oxygen atoms. The nitrate ion polarised by the electrode field is regarded as an activated complex. Species that form activated complexes under the action of both the electrode field and cation field in the double electric layer are considered electrochemically active.[43] It is the NO_3^- ions that undergo discharge upon cathodic polarisation, hence they can be regarded as electrochemically active species.

We feel that the above scheme of the formation of electrochemically active species has a number of drawbacks. First, though the authors do not deny the effect of the electrolyte cationic composition, they believe that the cation–anion interaction is limited to indirect anion polarisation (through variation of the field potential). They rule out the formation of metal complexes as electrochemically active species; this disagrees with the concept on the chemical interaction of species in melts. In addition, this assumption contradicts the results of studies on the electrochemical reduction of oxygen-containing anions [4, 44, 45] and spectroscopic data.[15, 19, 46] Second, the unreasonable overestimation of the electrode field effect requires a thorough consideration. And, finally, while noting the possible effect of both the electrode field and cations, the authors do not estimate the contributions of each of the effects to the formation of the activated complex.

A different model of the formation of electrochemically active species in melts has been proposed by Chernukhin *et al.*[47, 48] The model is based on the concept on inter-species interactions in condensed media. It was suggested [48] that inter-species interactions result in concerted groups of ions consisting of one anion and surrounding cations. The anion can be transformed to the activated state and undergo electrochemical transformation. In their study on electrode processes in ternary mixtures, Chernukhin *et al.* assumed that the inter-species interactions in the double electric layer and in the melt bulk have similar natures.

Within the framework of the concept that melts are dynamic systems † and based on the results reported by Belen'kaya *et al.*[50] (see footnote ‡), it was assumed [48] that the state of an anion depends on the concerted action of the ionic environment. The activation of anion discharge was explained by the polarising action of the electrode field resulting in a definite anion orientation and, subsequently, localisation of its pairwise inter-species interactions, preferably with cations having the strongest polarising effect. This enhances the non-equivalence of the N–O bonds and prolongs considerably the life-time of the group consisting of the anion and the first-sphere cations. Such a group has been called the activated complex.[48] For example, the formation of an activated complex is given by the following scheme for a binary melt containing potassium and calcium:

$$K^+_{n-x}Ca^{2+}_{x-1}\{Ca^{2+}[ONO_2]^-\} \xrightarrow{-E} K^+_{n-x}Ca^{2+}_{x-1}\{Ca^{2+}...O...[(NO_2]^+\}, \quad (2)$$

where n is the coordination number (c.n.) of the anion during discharge, which is constant irrespective of the cationic composition; $K^+_{n-x}Ca^{2+}_{x-1}\{Ca^{2+}[ONO_2]^-\}$ is the binary melt formula which emphasises the polarising effect of the cation on the NO_3^- anion by designating the anion as $[ONO_2]^-$. Within the scope of Scheme (2), the electrode reaction has the form:

$$Ca^{2+} + NO_3^- \xrightarrow{-E} \{Ca^{2+}...O...[NO_2]^+\} \xrightarrow{2e^-} CaO + NO_2^- . \quad (3)$$

For similar lithium-containing melts, an intermediate compound LiO^- can be formed:

$$Li^+ + NO_3^- \xrightarrow{-E} \{Li^+...O...[NO_2]^+\} \xrightarrow{2e^-} LiO^- + NO_2^- . \quad (4)$$

Based on the above model for the formation of electrochemically active species, the appearance of additional cathodic waves in the voltammograms upon addition of strongly polarising cations, *e.g.*, in melts of sodium and potassium nitrates, can be explained by an increase in anion asymmetry. The shift of the reduction wave upon addition of strongly polarising cations to the melt occurs due to the gradual replacement of the background cations in the nitrate ion environment by cations with a higher polarising strength. This scheme, unlike that proposed by Tkalenko,[43] is generally consistent with the concept on the chemical interactions between species in melts and with the data of numerous spectroscopic studies on concentrated nitrate melts. However, certain aspects of the mechanism discussed above are debatable.

Shapoval *et al.*[4, 44] generalised their own results and other data and explained some features of the electrochemical reduction of oxygen-containing anions. It was assumed that electrode processes in molten salts with oxygen-containing anions are limited by a preceding chemical reaction. For example, the formation of electrochemically active species in the reduction of the carbonate ion in lithium-containing melts was represented by the scheme:

$$n\,Li^+ + CO_3^{2-} \rightleftharpoons [Li_nCO_3]^{n-2} \rightleftharpoons Li_nO^{n-2} + CO_2 . \quad (5)$$

A similar scheme of the preceding acid-base reaction has been proposed for nitrate-containing melts based on data for NO_3^- reduction in a KCl–LiCl eutectic as the background:[45]

$$2\,Li^+ + NO_3^- \rightleftharpoons [Li_2NO_3]^+ \rightleftharpoons Li_2O + NO_2^+ . \quad (6)$$

As follows from Eqns (5) and (6), it is not anions but their reaction products with cations of the molten media that are electrochemically active species.

The proposed anion–cation interaction scheme agrees most closely with the concepts on the chemical reactions of species in ionic melts, but this has a phenomenological character.[51] The anion–cation interaction mechanism can be comprehended more precisely by studying it at an electronic level with the use of quantum-chemical calculations and by comparing them with experimental data. The CO_3^{2-} and NO_3^- anions which are most sensitive to variations of the acid-base properties of a melt are most convenient for the comparison of the electrochemical reduction characteristics.

The scheme for the formation of electrochemically active species in oxygen-containing melts proposed by Shapoval *et al.*[4, 44] does not account fully for the function of cations as acids which, like protons in aqueous media, can add to anions and thus accelerate electrochemical reduction. The complex nature of interaction between species in ionic media creates difficulties for their theoretical description. Therefore, it is expedient to consider a model scheme of cation–anion interaction which makes it possible to change the acid-base properties of the medium with respect to a selected anion by gradual accumulation of cations in the anion's first solvation shell (cationised anion).[52] The cation–anion interaction for carbonate- and nitrate-containing melts can be represented as follows:

$$n\,M^{m+} + CO_3^{2-} \rightleftharpoons \begin{matrix} \{M_n^{m+}[CO_3]^{2-}\}^{(mn-2)+} \\ M_{2/m}O + CO_2 + (n-2/m)M^{m+} \end{matrix} , \quad (7)$$

$$n\,M^{m+} + NO_3^- \rightleftharpoons \begin{matrix} \{M_n^{m+}[NO_3]^-\}^{(mn-1)+} \\ M_{2/m}O + NO_2^+ + (n-2/m)M^{m+} \end{matrix} , \quad (8)$$

where m is the cation charge, n is the reaction order with respect to the cation (coordination number). Thus, cation–anion interaction can result either in cationised anions (metal complexes) or in anion dissociation (both under direct influence of cations and *via* intermediate formation of 'short-lived' metal complexes).

Earlier quantum-chemical calculations [53] and electrochemical data [51, 54] showed that cation–anion interactions in nitrate-containing melts result mostly in nitrate metal complexes, whereas in carbonate-containing melts, two mechanisms of the EAS formation in accordance with Scheme (7) are equally probable. On the

† These views have later been generalised by Delimarskii *et al.*[49]

‡ Belen'kaya *et al.*[50] used Raman spectroscopy to study the changes in the geometry and the potential function of nitrate ion in molten alkali nitrates. It was shown that the bond lengths and strengths in molecular ions can be changed with strengthening of inter-species interactions in the melt. Therefore, the reactivities of species in molten media can be controlled directly by varying their compositions.

other hand, the model proposed, which is valid in dilute melts as the background, does not account for the effects of the electrode surface adsorption properties and the electric field on the character of acid-base interactions and on the charge transfer elementary act.

A calculation of the total energies, charges and populations for carbonate ions showed [55] that the presence of uncharged electrode surface atoms (this surface was simulated by a linear cluster of three carbon atoms) favours the electron density redistribution in an isolated CO_3^{2-} anion according to the σ,π-mechanism (where the σ-component predominates), which, in turn, weakens the intra-anion bonds. Estimates of contributions from the electrode surface and from the cation field to the changes in the C–O bond energy showed that the latter contribution predominates, *i.e.*, the electrode surface does not affect in principle the mechanism of the EAS formation within this model. This mechanism is primarily determined by the melt cationic composition.

The cation–anion interactions are affected considerably not only by the adsorption effects but also by electric fields.[56] Comparison of the energy characteristics and atomic charges and orbital populations in an isolated CO_3^{2-} anion and in an anion located near the electrode surface under the effect of the cation field and an external electric field ($E = 2 \times 10^{10}$ V m^{-1}) showed that cleavage of C–O bonds occurs with formation of CO_2. It is believed [57] that the effect of the electrode surface lowers the activation barriers for two- and four-electron CO_3^{2-} reduction in comparison with the similar magnitudes for an isolated anion. The additional effect of the electric field increases the effect discovered (by a factor of ~2) and favours the direct discharge of the CO_2 molecule

$$CO_2 + 4e^- \longrightarrow C + 2O^{2-} . \quad (9)$$

The geometric sizes of metal complexes resulting from cation–anion interactions in nitrate-containing melts are much larger than that of the linear cluster of three carbon atoms mentioned above. This fact prompted a search for new clusters simulating the electrode surface.[58] The optimum four-cluster variant selected is an aromatic system of 12 carbon atoms (48 basis orbitals) which ensures an adequate representation of the donor-acceptor properties of an uncharged electrode surface. Interaction of a surface cluster with an NO_3^- anion initiates the electron density redistribution in it according to the σ,π-mechanism (with the σ-component predominating) which weakens the intra-anion bonds. An additional influence of the field from the melt cations, *e.g.*, Li^+ and Be^{2+}, on the NO_3^- anion results in a considerable (three- to fourfold) increase in the N–O bond energies. In this case, the π-component predominates in the σ,π-mechanism. Both of these factors increase the N–O bond energy. The trend towards strengthening the N–O bonds is preserved as the c.n. of the cation is increased. Solov'ev *et al.*[59] emphasised that the overall effect of the electrode surface and melt cations on the EAS formation mechanism is determined by competition of two opposite trends in electron density redistribution in NO_3^- and concluded that the electrode surface effect on the mechanism of formation of EAS, such as metal complexes $\{M_n^{m+}[NO_3]^-\}^{(mn-1)+}$, is insignificant within the framework of Scheme (8).

Calculations carried out by Solov'ev *et al.*[60] showed that the external electric field (2×10^{10} V m^{-1}) imposed on a cationised nitrate ion located near the electrode surface virtually does not change the energy of N–O intra-anion bonds against the background of the rather strong interaction of NO_3^- with Li^+ or Be^{2+}. It was found that the contributions of both electric field and electrode surface do not greatly affect the cation–anion interaction.

It has been found [58] (from activation barrier calculations) that the effect of the electrode surface increases considerably the reactivity of metal complexes with respect to two-electron reduction. This effect increases with increase in the cation specific charge and coordination number. The trend towards lowering of activation barriers is preserved under an external electric field. An estimate of the electrode surface effects, the cation field and the external electric field on the elementary charge transfer act showed that the adsorption properties of the electrode surface play the most significant role in these processes. The optimum coordination numbers were found to be 2 for NO_3^- surrounded by Li^+ cations and 3 for the same anion surrounded by Be^{2+} cations. Taking electrochemical measurement data into account,[61] electrochemical reduction can be represented as follows

$$\{M_n^{m+}[NO_3]^-\}^{(mn-1)+} + 2e^- \longrightarrow NO_2^- + n M_{2/m}O + (n-2/m) M^{m+} . \quad (10)$$

Experimental studies [62] not only confirm the formation of EAS according to Scheme (8) but also suggest unambiguously the catalytic nature (caused by the depolariser regeneration) of nitrate reduction waves in the presence of strongly polarising cations. An excess of the latter is believed to result in regeneration of the original EAS

$$3NO_2^- \xrightarrow{M^{m+},\ -E} NO_3^- + 2NO + O^{2-} . \quad (11)$$

The possible realisation of Scheme (11) follows from quantum-chemical calculations of interactions between $M_n^{m+} \cdots NO_2^-$ ($M = Li^+, Be^{2+}$) in an electric field with a strength of $E = 0; 0.2; 2 \times 10^{10}$ V m^{-1} (see Ref. 55). Similar calculations showed the priority of cation–anion interactions in the EAS formation in ionic melts. This fact was confirmed in IR and Raman spectroscopic studies on the effect of the melt cationic composition on the force constants of the N–O, C–O, W–O and Mo–O bonds in NO_3^-, CO_3^{2-}, WO_4^{2-} and MoO_4^{2-} anions. The force constants calculated for the $[MNO_3]^0$ and $[M_2CO_3]^0$ systems ($M = Cs^+$, Rb^+, K^+, Na^+, Li^+) suggest [53, 62] a trend towards an increase in the stretching force constants of the N–O and C–O bonds compared with the same bonds in isolated NO_3^- and CO_3^{2-} anions as the cation specific charge increases in the series from Cs^+ to Li^+. The observed effect of the increase in the N–O bond strength due to anion cationisation was confirmed by quantum-chemical calculations and by analysis of electronic absorption spectra.[15, 19] In carbonate melts containing the Cs^+, Rb^+ and K^+ cations, the C–O force constants tend to increase, which also agrees with quantum-chemical calculations.

Calculations of force constants for $[MEO_4]^0$ systems ($M = Na_2^+, Li_2^+, Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}$; E = W, Mo) showed [61] that the E–O bond stretching force constants and the deformation force constants in EO_4^{2-} increase with the increase in the cation specific charge. The increase in the force constants of these interactions is believed to result from an increase in the degree of delocalisation of the valence electrons of the EO_4^{2-} anion on the cation orbital. In turn, this stabilises the electronic energy levels of the inner shells in EO_4^{2-}.

III. Structures, chemical and electrochemical properties of titanium-containing fluoride melts

To date, data on the structure of dilute titanium-containing melts in fluoride–chloride systems are very scarce, therefore even the simplest models of the structures of these melts are unavailable. However, there are a number of publications devoted to the studies of these melts.

Analysis of the electronic absorption spectra of the fluoride-containing system KCl–NaCl–NaF with the use of the ligand field theory [63] revealed transient coordination forms of the Ti^{3+} ion resulting from mixed coordination with Cl^- and F^- anions. In the presence of a 100-fold excess of F^- with respect to TiF_3, the formation of a trigonally distorted complex was detected. Complexation of lower titanium compounds with fluoride ions in KCl–NaCl melts was reported [64–66] and it was noted that the c.n. with respect to the F^- ligand in the complexes formed is 3–4.

The existence of $[TiF_4Cl_2]^{2-}$ complexes, presumably with distorted octahedral symmetry, in K_2TiF_6–NaF melts was stated.[67] The possible formation of titanium tetrafluoride in these melts was also reported by Rolin.[68] The formation of poorly soluble compounds $MTiF_4$ in titanium-containing melts cannot be ruled out.[69, 70]

Thus, based on the results of the few studies on the structure of titanium-containing fluoride–chloride melts, one can assume that they contain the mixed $[TiF_4Cl_2]^{2-}$ complex and that the interaction mechanism of the melt species, which results in the compounds $MTiF_4$, depends considerably on the cationic composition.

The electrochemical reduction of titanium-containing fluorides in the presence of chlorides was studied by Smirnov *et al.*[70] The steady-state polarisation curve method was used to study the reduction of Ti^{4+} in the 0.14 K_2TiF_6–0.86 NaCl melt at 1033 K. The titanium deposition mechanism was studied by recording the potentiometric voltammetric characteristics of electrochemical reduction on steel, graphite and titanium electrodes (tetravalent titanium ions were assumed to be the EAS). A polarographic study on the electrochemical reduction of K_2TiF_6 with a KCl–NaCl melt as the background was first carried out by Vitlaci and Nechel[71] who have established the two-electron nature of the charge transfer to the TiF_4^{2-} anion.

Analysis of results reported in these studies[70, 71] suggests unambiguously the possibility of formation of new titanium-containing species upon dissociation of the original complex, *viz.*, chloride–fluoride titanium complexes with titanium in various valent states and cationised titanium-containing anions. These species can react with the melt components. In such cases, a multistep electrode process is observed, and the transfer act can involve several species.

A higher level of experimental data interpretation (with calculation of diagnostic criteria of electrochemical reduction) distinguishes a series of studies[65, 66, 72] which served as a basis for the assumption on the formation of TiF_4 molecules from the original species TiF_6^{2-} and the cationised anion $\{M_n^{m+}[TiF_6]^{2-}\}^{(mn-2)+}$. However, the studies discussed above and those by Juman and White[73] do not report any quantitative data on the electrochemical reduction kinetics and merely suggest the electrode reaction mechanisms.

The most comprehensive data on the electrochemical properties of titanium-containing fluoride melts have been obtained in the studies on the electrochemical reduction of the TiF_6^{2-} anion with a KCl–NaCl melt as the background.[74–76] The possible formation of new EAS, *viz.*, dissociation products of the original complex, was also reported in these studies. Three reduction waves were found in the cathodic polarisation curves. The first wave was interpreted as a result of charge transfer to the dissociation product, *i.e.*, the TiF_4 molecule, and the second one, as a result of four-electron charge transfer directly to the complex anion. The third wave could not be interpreted on the basis of the experimental data.

The authors of the majority of studies discussed above did not relate the results obtained to the effect of the melt cationic composition on the EAS formation mechanism. It seems most reasonable to study this mechanism with the use of quantum-chemical methods which enable the simulation of EAS formation at the electronic level by relating it to electron transfer during electrochemical reduction.

The successful application of the cation–anion interaction model to the studies on carbonate- and nitrate-containing melts stimulated the use of this model for the study on melts containing complex anions. A scheme of the cation–anion interaction in titanium-containing fluoride melts was represented as follows:[77]

$$n\mathrm{M}^{m+} + \mathrm{TiF}_6^{2-} \rightleftharpoons \{\mathrm{M}_n^{m+}[\mathrm{TiF}_6]^{2-}\}^{(mn-2)+} \rightleftharpoons \mathrm{TiF}_4 + 2\mathrm{F}^- + n\,\mathrm{M}^{m+}. \quad (12)$$

According to this scheme, the cation–anion interaction can involve the formation of cationised anions (metal complexes) $\{M_n^{m+}[TiF_6]^{2-}\}^{(mn-2)+}$ or dissociation of the TiF_6^{2-} anion to give titanium tetrafluoride.

Calculations showed[78] that dissociation of an isolated TiF_6^{2-} anion is impossible for energetic reasons: comparative analysis of atomic orbital populations in an isolated TiF_6^{2-} anion and that in cationic environment showed that electron density redistribution cannot result in cleavage of the Ti–F bond in this anion. Reactions of the Na^+ or Li^+ cations with the TiF_6^{2-} anion yield metal complexes with coordination numbers equal to 2, 4 and 6. The Ti–F bond energies decrease with the increase in the c.n. under the influence of cations, whereas the energies of the cation–anion bonds increase. The interaction between Mg^{2+} cations and TiF_6^{2-} at c.n. = 2 results in cleavage of two Ti–F bonds. Further increase in the number of Mg^{2+} cations in the first solvate shell results in further dissociation of the TiF_6^{2-} anion.

Weakening of Ti–F bonds due to the cation–anion interaction results from electron density redistribution in the TiF_6^{2-} anion according to the σ,π-mechanism. The electron density redistribution increases with the increase in both c.n. and the cation specific charge.

It was noted[79] that the cation–anion interaction lowers the activation barriers for two- and four-electron reduction of metal complexes of the TiF_6^{2-} anions and titanium tetrafluoride molecular associates in comparison with the corresponding values for isolated TiF_6^{2-} and TiF_4. Predominance of four-electron reduction was established for metal complexes; on the contrary, two-electron charge transfer predominates for isolated TiF_4.

Volkov[80] does not rule out that the EAS formation mechanism is affected by chloride anions of the background electrolyte. The existence of stable ion-molecular associates $\{Cl_2^-[TiF_4]^0\}^{2-}$ in the melt bulk is probable. This follows from an estimate (based on quantum-chemical calculations) of the interaction of Cl^- ions with the TiF_4 molecule. The activation barriers for two- and four-electron reduction of TiF_4 increase considerably in the presence of chloride anions. Hence, anionic environments (unlike cationic ones) do not increase the reducing ability of EAS.

It has been shown[81] that the electrode surface effect results in electron density redistribution in cationised TiF_6^{2-} anions and in TiF_4 molecular associates, as well as in isolated TiF_4, according to the σ,π-mechanism with predominance of the σ-component. Hence, the electrode surface does not affect considerably the EAS formation mechanism but only enhances the cation–anion interaction effect. Comparative analysis of atomic charges and atomic orbital populations[82] showed that the electric field initiates electron density redistribution in the TiF_6^{2-} anion with predominance of the σ-component and in TiF_4 with predominance of the π-component. The combined effect of the electrode surface and the electric field results in considerable lowering of the activation barrier for EAS four-electron reduction. A TiF_6^{2-} anion surrounded by six cations and a TiF_4 molecule surrounded by four alkali metal cations have the optimum reducing ability. In our opinion, these results are in full compliance with the idea of outer-sphere cationisation in melts containing anions with complex compositions[3, 44, 45] confirmed by electrochemical studies on tungstate- and molybdate-containing systems.[83]

IV. Structures, chemical and electrochemical properties of boron-containing fluoride melts

Much less data are currently available on the structures and properties of boron-containing fluoride melts than on titanium-containing fluoride melts; these data have almost not been interpreted.

Raman spectroscopic studies on the $NaBF_4$ and $NaF–NaBF_4$ melts[84] showed that the structure of the BF_4^- anion remains unchanged at temperatures up to 880 K. A similar conclusion was made by Prostakov *et al.*[85] who also noted that various complex associates can exist in $KBF_4–KF–CsF$ melts. Pirina and

Prostakov[86] used data on the specific densities and electric conductivities of the $KBF_4-KF-CsF$ system to calculate the stabilisation energies of these complex associates. They also stated that complex anions $[M(BF_4)_4]^{3-}$ with tetrahedral configurations were formed predominantly and noted that mixing of salts having the same cation resulted in gradual substitution of anions to give mixed complexes of the types $[MF_4]^{3-}$, $[M_4F]^{3+}$, $[M(BF_4)_4]^{3-}$, $[M(BF_4)_6]^{3-}$, $[M(BF_4)_3F]^{3-}$ and $[M(BF_4)_2F_2]^{3-}$.

A study on solubility of BF_3 in $KCl-KF$ melts at 870–970 K showed[87] that after dilution of the melt with respect to fluoride or after addition of strongly polarising cations (Li^+, Mg^{2+}, Ba^{2+}, Ca^{2+}), the system contains (in addition to the BF_4^- species) mixed fluoride–chloride boron complexes and BF_3 molecules in equilibrium with halide ions. Based on data on boron equilibrium potentials in $KCl-KF-KBF_4$ melts,[88,89] it was concluded that the majority of boron ions exist as higher fluoride and fluoride–choride complexes, *viz*., $[BF_4]^-$ and $[BF_3Cl]^-$, respectively. It was assumed[90] taking account of viscosity and specific density data for $NaCl-NaBF_4$ and $NaCl-RbBF_4$ melts that the structures of tetrafluoroborate melts comply with the model of 'solids' (with retention of the short order arrangement of species).

The ambiguous interpretation and scantiness of data on the structures and physicochemical properties of boron-containing melts often result in conflicting concepts on the electrochemical reduction processes in these melts. Studies on the cathodic process in the $LiF-KBF_4-KF$ system showed that reduction of the BF_4^- anion involves simultaneous transfer of three electrons.[91] It was assumed that diffusion of the BF_4^- anions from the melt bulk is not a limiting step of electrochemical reduction, and this is an indication of the process complexity. Myshalov[92] who studied the electrochemical reduction in boron-containing melts concluded that boron reduction follows a two-step mechanism. Vasil'eva *et al*.[93] studied the possibility of electrochemical preparation of boron from borax-containing melts; they detected several waves on the polarisation curves originating from the stepwise reduction of the oxygen-containing anion.

The reduction kinetics of boron compounds in fluoride-containing melts have been studied most thoroughly by Tsiklauri *et al*.[94–96] Analysis of reduction chronovoltammograms and interpretation of the spectral characteristics of the ternary molten system $KCl-NaCl-KBF_4$ suggest that the chloride–fluoride melt contains several boron-containing equilibrium forms. Reduction of three of them, *viz*., BF_4^-, BF_3Cl^- and BF_3, is believed to account for two waves in the voltammetric curves. This conclusion does not contradict the data by Zarutskii *et al*.[97] On the other hand, the EAS formation mechanism was not related to the melt cationic composition[98] which is important in EAS formation in the melt bulk.

The EAS formation scheme in fluoride boron-containing melts is represented as follows:[99]

$$n\,M^{m+} + BF_4^- \rightleftharpoons \begin{matrix} \{M_n^{m+}[BF_4]^-\}^{(mn-1)+} \\ BF_3 + F^- + n\,M^{m+} \end{matrix} \qquad (13)$$

Preliminary calculations showed that dissociation of an isolated BF_4^- anion is impossible for energetic reasons. It was found that the interaction of this anion with Na^+ and Mg^{2+} cations demonstrates a trend towards a decrease in the intra-anion bond energies, while the interaction with the Li^+ cations, the trend is towards their increase. Distribution of atomic charges and populations of the atomic orbitals of these systems indicates strengthening of the B–F bonds in metal complexes of the anion with Li^+ cations due to predominance of the π-component in the σ,π-mechanism of electron density redistribution in BF_4^-. In metal complexes with Na^+ and Mg^{2+} cations, the σ-component was found to predominate.

The possible dissociation of the BF_4^- anion upon cation–anion interaction cannot be ruled out. The interaction of one of the products of reaction (13), *viz*., the BF_3 molecule, with the melt cations has been studied.[100] Analysis of the interaction energies of BF_3 with Na^+ or Li^+ for the cases where the coordination numbers of these cations are equal to 1, 2 and 3 showed that cleavage of the B–F bonds does not occur, though they are weakened considerably. On the other hand, interaction of two Mg^{2+} cations with BF_3 results in decomposition of the BF_3 molecule; in this case, the formation of $\{Mg_2^{m+}[BF_3]^0\}^{2m+}$ associates in the melt bulk is possible.

It was noted[101] that the cationic environment lowers the activation barriers for two- and four-electron reduction of the products of reaction (13), *i.e*., metal complexes of the BF_4^- anion and associates of the BF_3 molecule, in comparison with the corresponding values for the isolated BF_4^- and BF_3 species. Predominance of two-electron reduction over four-electron reduction is observed both for cationised anions and for BF_3.

Spectroscopic studies on the molten ternary system $KCl-NaCl-KBF_4$ suggest that mixed chloride–fluoride complex ions $[BF_{4-x}Cl_x]^-$ exist in the melt.[102] Analysis of the effect of the background electrolyte chloride anions on the interaction of the BF_4^- species with one or two lithium cations (carried out by quantum-chemical calculations) showed the possible formation of both $[BF_{4-x}Cl_x]^-$ complexes and their associates in the cationic environment. The $\{[BF_3]^0Cl^-\}^-$ species is the most reduction-stable. The activation barrier for two-electron reduction of these associates is lower than that of the BF_4^- anion without the cationic environment. The maximum decrease is achieved for the $\{Li^+[BF_3Cl]^-\}^0$ system. However, though the effect of the activation barrier decrease for BF_4^- and BF_3 in a cationic environment is greater than that for the $\{Li^+[BF_3Cl]^-\}^0$ associate, one cannot rule out a possible decrease in the latter.

Solov'ev[103] assumed that the effect of the electrode surface in boron-containing fluoride melts causes electron density migration in EAS according to the σ-mechanism, resulting in an insignificant weakening of the B–F bonds. It was therefore concluded that, within the model scheme selected, the electrode surface does not affect greatly the EAS formation mechanism.

Imposed electric field ($E = 2\times10^{10}$ V m^{-1}) enhances the trend towards weakening of the B–F bonds in $\{M_n^{m+}[BF_4]^-\}^{(mn-1)+}$ and strengthens slightly these bonds in other EAS.[104] On the other hand, the decrease in the activation barriers for reduction due to the surface and electric field effects results in a considerable increase in the reducing ability of cation–anion interaction products. Taking this into consideration, the following EAS forms can be assumed: $\{M_4^{m+}[BF_4]^-\}^{(4m-1)+}$, $\{M_2^{m+}[BF_3]^0\}^{2m+}$, BF_3, $\{M^+[BF_3Cl]^-\}^0$. Thus, the EAS formation mechanism was complemented as follows:

$$n\,M^{m+} + BF_3 \rightleftharpoons \{M_n^{m+}[BF_3]^0\}^{mn+}, \qquad (14)$$

$$n\,M^{m+} + [BF_{4-x}Cl_x]^- \rightleftharpoons \{M_n^{m+}[BF_{4-x}Cl_x]^-\}^{(mn-1)+}. \qquad (15)$$

Analysis of electrochemical measurements of BF_4^- and BF_3 reduction with the $KCl-NaCl$ melt as the background has been carried out by Tsiklauri *et al*.[95,96] without interpretation of the EAS reduction waves. Based on the calculations, the existence of an additional EAS (besides BF_3 and associates of chloride–fluoride complexes) was assumed,[104] namely, $\{M_n^{m+}[BF_3]^0\}^{mn+}$; the probability of its reduction is higher than that of mixed chloride–fluoride associates.

V. Effect of cations on the mechanisms of chemical and electrochemical reactions in ionic melts

The effect of the solvent nature on the mechanism and rate of chemical reactions in ionic melts was first discovered by Rust and Duke[31] in a study on acid-base equilibria in nitrate-containing melts. It was shown that replacement of a solvent with weakly polarising cations by a solvent with strongly polarising cations accelerates the reactions. This effect was explained by activation of the reacting molecules by the cationic environment. In other studies, the role of the melt cationic composition was ignored. For example, in studies on the electrochemical reduction of oxygen-

containing anions [26, 35, 36] it was assumed that, irrespective of the electrolyte cationic composition, the anions themselves participate in the cathodic reaction. The specific features of the cathodic reduction of anions in the presence of cations were explained by various factors excluding the acid-base interaction.

Certain model concepts used in studies on aqueous solutions were applied to ionic melts. In an analysis of the possible direct discharge of the nitrate ion in aqueous solutions, Lopatin[105] used the 'cationic bridges' concept which makes it possible to explain the effect of the solution cations on the cathodic process. Having studied the anion discharge kinetics near the zero charge potential of the electrode, he explained the effect of cations on the discharge rate by a decrease in the negative reduction potential of the nitrate ion with increase in the concentration and the cation charge. The possibility of direct discharge of the nitrate ion has also been noted.[106] Kvaratskheliya [39] studied the effect of the cation nature on the shift of NO_3^- cathodic reduction waves in aqueous electrolyte solutions. In his opinion, one of the reasons for the effect of salts with polyvalent cations on the positive shift of the cathodic wave is the formation of cation–anion pairs in which one of the N—O bonds is weakened under the effect of the cationic environment.

In studies on electrode processes in melts of individual nitrates with various cationic compositions,[40–42] it was concluded that the activity of the nitrate ion is determined by its environment and hence depends on the acid-base properties of the melt. Differences in the positions of the NO_3^- electrochemical reduction wave were explained by the different charge densities of the cations whose force field affects both the NO_3^- anions and the O^{2-} ions formed in the cathodic process. Attempts were made to find an empirical relationship between the composition of a nitrate-containing melt and the reactivities of its components. For example, Fletcher *et al.*[107] reported an inverse dependence of the isobaric potential of activation of NO_3^- electrochemical reduction on the solvent cation radius.

In a study on the self-diffusion and charge transfer in carbonate- and nitrate-containing melts, the existence of metal complexes such as MCO_3^-, MNO_3^- and $M_2NO_3^+$ (the latter being most probable for the lithium cation) in the melt was assumed and the possibility of the following elementary chemical reactions in a melt was noted:[108]

$$M^{n+} + \text{base} \rightleftharpoons \text{acid}. \qquad (16)$$

Of interest are the studies by Shams El Din *et al.*[109, 110] reporting a comparative estimate of the acidities of alkali and alkaline-earth metal cations. According to these data, the acidity changes in the series of cations: $Ca^{2+} > Li^+ > Sr^{2+} > Ba^{2+} > Na^+, K^+$.

One of the first theoretical studies on the effect of the medium on the elementary act of chemical reactions in the condensed phase can be found in a series of works.[98, 111–113] They considered certain classes of chemical and electrochemical processes and calculated the kinetic parameters of the elementary act of charge transfer, the mechanism of which being dynamically affected by the macroscopic medium. In their opinion, the dynamic effect is determined by fluctuations or changes in the ionic environment surrounding the reacting species; chemical reactions are assumed to occur in a polar liquid and to be accompanied by a considerable charge density redistribution in the reacting species.[110] It was noted [111] that short-range effects predominate in reactions in ionic melts.

Proof that the cationic composition of the medium affects the mechanisms of electrochemical reactions in nitrate-containing melts was obtained in a series of studies [47–49] where a different scheme for the EAS formation mechanism in such melts was suggested (see Section II). However, we feel many statements of this scheme to be debatable because of the doubtful assumption that the nature of inter-species interactions in the electric double layer is the same as in the melt bulk. The electrochemical reaction mechanisms have also been found to be affected by cations for titanium-[66, 69, 70] and boron-containing [84–86, 97] halide melts. Unfortunately, the results obtained were not accompanied by conclusions or generalisations.

The results of experimental studies [28–30, 44, 45] on the kinetics of electrode processes with conjugate acid-base reactions in oxychloride molten salts demonstrate that the cationic composition of the melt affects the rate and mechanism of the reactions occurring in the melt. These studies are based on the idea that the electrochemical activities of oxygen-containing anions originate from the cation–anion mechanism of the EAS formation specific for molten salts (see Section II). This mechanism can be regarded as acid-base interaction where the decisive role belongs to the acid properties of the cations. The formation of EAS and their reactions in the near-electrode layer occur at a limited rate since these processes involve complete restructuring of the reacting species.

The assumption on the cation–anion interaction in molten electrolytes was confirmed in studies on the electrochemical reduction kinetics of oxygen-containing anions in chloride and oxide melts. Detailed studies on the electrochemical reduction of WO_4^{2-} with an equimolar KCl–NaCl melt as the background [4] and of a sodium tungstate melt [114] showed that the tungstate ion itself is not an electrochemically active species but it can generate such species. Owing to the cation–anion interaction, a sufficient excess of strongly polarising cations results in outer-sphere cationisation of the WO_4^{2-} anion to give symmetrically cationised species. Thus, the electrochemical reduction of oxygen-containing anions in the presence of molten chlorides as the background is preceded by a slow acid-base reaction which is the rate-determining step of the electrode process. The EAS are formed due to the interaction of the oxygen-containing anion with the molten electrolyte according to the cation–anion interaction mechanism determined by the acid-base properties of the medium.

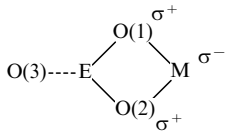
VI. Theoretical and experimental studies of cation–anion interactions in nitrate- and carbonate-containing melts

The results of experimental studies discussed above [28–30, 39–42, 44–49, 108–110] suggest that the reduction of oxygen-containing anions depends on the cationic composition of the melt. Hence, it is necessary, first, to estimate the possibility of the formation of cationised anions (metal complexes) in principle and second, to study the effect of cations on the reducing abilities of anions. In application to nitrate- and carbonate-containing melts, the cation–anion interaction was represented by Schemes (7) and (8).

The CO_3^{2-} anion, the CO_2 molecule and their complexes with the lithium cations (up to five-coordinate complexes) were selected as model compounds for preliminary quantum-chemical calculations. A preliminary energy-based estimate of cation–anion interaction pathways for carbonate-containing melts based on a semiempirical calculation showed [115, 116] the possibility of formation of a broad spectrum of metal complexes of the CO_3^{2-} anion with lithium cations and the effect of the cation nature on the increase in the reducing ability of cation–anion interaction products.

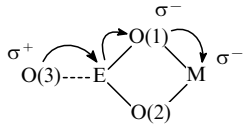
Analysis of the energy profiles of potential surfaces of the interaction of NO_3^- and CO_3^{2-} with Li^+ or Be^{2+} showed that the interaction of cations preferentially occurs along the bisecting line of any bond angle of the anion; there are local energy minima in the monodentate position of the cation with respect to the anion.[117, 118] If interaction between cations and anions is sufficiently strong (it is more efficient in the case of Be^{2+}), the weakening of N—O intra-anion bonds under the effect of the cation was found to differ noticeably from that of C—O bonds. As calculations showed, bidentate interaction of an anion with a cation results in electron density migration from the $2s$, $2p_x$ and $2p_y$ orbitals of the O(1) and O(2) atoms to the corresponding

cation orbitals with formation of σ-bonds. As a result, an effective positive charge σ^+ is transferred to the oxygen atoms.



(17)

In turn, this favours the electron-donating effect of the $2p_2$ orbitals of O(3)



(18)

with formation of π-bonds.

In complexes formed by the nitrate ion, electron density redistribution along the π-bonds under the effect of cations occurs within the NO_3^- anion and causes strengthening of the N—O bond. On the contrary, the σ-mechanism of electron density redistribution predominates in the carbonate ion and in the corresponding complexes, resulting in a considerable weakening of the C—O bonds. Thus, the role of metal cations is to effect the polarisation of an anion as a whole according to the σ,π-interaction mechanism with predominance of one of the interaction types in the isoelectronic ions NO_3^- and CO_3^{2-} (see Refs 119, 120). The results of semiempirical and *ab initio* calculations coincided qualitatively, which afterwards permitted the use of semiempirical calculations which are less laborious.

The gradual increase in the number of the first solvate shell cations, results in the weakening of C—O bonds in CO_3^{2-} with an increase in the coordination number. For the coordination number equal to 2, cleavage of one C—O bond occurs. Conversely, a trend towards strengthening of the N—O bonds is observed for NO_3^-. This conclusion was confirmed by data on charge transfer and electron density migration within anions for the entire coordination number range and by spectroscopic data.[121]

Analysis of the energies of the frontier molecular orbitals showed that the ability of NO_3^- to undergo reduction is higher than that of CO_3^{2-}. Cationisation results in a decrease in the energy gap between the highest occupied and lowest unoccupied molecular orbitals in these anions, which suggests that the cation–anion interaction has a favourable effect on the ability of anions to undergo reduction.[122, 123] Comparison of the reduction activation barriers for NO_3^- and CO_3^{2-} and their metal complexes also indicates an increase in the ability of anions to undergo reduction due to the cation–anion interaction. This interaction decreases the reduction activation barriers for the entire series of complexes.[123]

Electric field is one of the most important factors affecting the reduction in melts. The results of quantum-chemical calculations were used to estimate the effect of the electric field on the acid-base interaction and on the elementary charge transfer act. A uniform electric field was simulated by a system of opposite charges located symmetrically at a long distance from the molecule. The calculations were carried out using a programme developed for this purpose.[124] It was shown[125] that a field which enhances the specificity of cation–anion interaction (predominantly, σ-type in carbonate ion and π-type in nitrate ion) affects considerably the reducing ability of the interaction products; specifically, it lowers the activation barrier.

Shapoval *et al.*[126] reported the results of an experimental examination of the acid-base interaction mechanism by determining a number of electrochemical parameters of the electrode process affected most strongly by the acidity of the melt. The model, Scheme (8), determined the choice of the starting system for the study on cation–anion interaction in melts. Studies on NO_3^- electrochemical reduction in a K, Na, Cs/Cl eutectics as the background (T = 793 K) showed that, like the K, Na, Rb/Cl eutectics, it is weakly acidic with respect to the NO_3^- anion and is suitable for studies on NO_3^- anions with strongly polarising cations. Introduction of Mg^{2+}, Ca^{2+} or Li^+ cations to a nitrate-containing chloride melt at concentrations no higher than a two-, four- and hundred-fold excess, respectively, with respect to NO_3^- shifted the electrochemical reduction wave towards negative potentials.[127–129] Further increase in the concentration of the added anions shifted the discharge potential to more positive region. Analysis of the chronovoltammograms for the NO_3^- anion in the presence of, *e.g.*, a strongly polarising Ca^{2+} cation suggested unambiguously the catalytic character of nitrate reduction waves in the presence of excess Ca^{2+}. It was shown[127, 129] that the excess of these cations is not only consumed in the formation of qualitatively new electrochemically active species, *viz.*, metal complexes, but also results in regeneration of the depolariser in agreement with the experimental Scheme (11).

The coordination number of the Ca^{2+} cations determined in the presence of a considerable excess of these cations equalled 2, while that in the case of excess magnesium cations equalled 3. Calculations of heterogeneous rate constants of charge transfer and regeneration of the original EAS indicate that introduction of cations to the melt catalyses the overall process,[127, 130] while the EAS formation during the electrochemical reduction of NO_3^- in the presence of Li^+, Ca^{2+}, Mg^{2+} occurs according to the cation–anion interaction mechanism in accordance with Scheme (8).

Experimental studies on the cation–anion interaction of CO_3^{2-} with strongly polarising cations[131–133] indicate that this can be described by Scheme (7).

Experimental studies confirmed certain regularities obtained from quantum-chemical calculations.[134] For example, an increase in the rate constants of charge transfer and regeneration of the original EAS with an increase in the specific charges and concentrations of cations in a melt corresponded to a decrease in the activation barrier for EAS reduction. The reduction potential shift by more than 0.6 V upon replacement of Na^+ by Mg^{2+} correlated with the calculated changes in the N—O bond energies in metal complexes formed by the nitrate ion. The absence of electrochemical activity in CO_3^{2-} in the presence of weakly polarising cations in a melt correlates with high activation barriers of two- and four-electron reduction. The experimentally found reduction of CO_3^{2-} in the same potential range in the presence of cations with various polarising strengths correlates with the calculated data, according to which CO_3^{2-} is characterised by a trend towards dissociation. Similar results were also obtained in other studies[51, 135] on the electrochemical reduction of CO_3^{2-} in tungstate melts with various cationic compositions.

The results of a theoretical and experimental study on the mechanism of cation–anion interaction in carbonate and nitrate-containing melts were reviewed by Solov'ev.[136] It is generally acknowledged that this mechanism includes the formation of cationised anions (metal complexes) $[M_nNO_3]^{(mn-1)+}$ and dissociation of CO_3^{2-} under the effect of cationic environment. However, this mechanism being applied to dilute melts did not account for the effect of the electrode surface and the electrical field on both the character of cation–anion interaction and the elementary charge transfer act.

The electrochemical reduction characteristics measured depend on a combination of various factors. The adsorption properties of the electrode surface (together with the temperature mode and the electrical field) affect strongly the character of electrochemical reduction in melts. Considering the surface of a solid electrode as possessing a discrete structure and the differences in the structures of the melt–electrode interfaces (at zero charge potential) caused by individual features of the electrode and melt surfaces, one should take into account the interaction of the surface atoms with adsorbed species of the melt. In accordance with the general physical concepts, this results in changes in the electronic properties of the interface. A preliminary estimate (quantum-chemical calculations) of the electrical field effect on the reactivity of cation–anion interaction products[125] agrees with

real processes of electrochemical reduction in melts. Such processes occur on electrode – melt interfaces where a certain potential gradient exists. Electrochemical reduction and cation – anion interaction are influenced not only by adsorption effects but also by the electrical field (external field and double layer field). Therefore, more detailed studies of the field effect on electrochemical reduction (on the energy parameters of cation – anion interaction products and on their reactivities) are necessary.

Thus, three basic factors should be taken into account in the analysis of the EAS formation mechanism and electrochemical reduction in nitrate- and carbonate-containing melts, *viz*., the acid-base properties of a melt, the electrode surface properties and the effect of the electric field.

VII. Multielectron electrochemical reduction of oxoanions of high-melting metals and non-metals in ionic melts

Multielectron electrochemical discharge – ionisation reactions can occur with simultaneous charge transfer or through a number of consecutive steps, with transfer of one or several electrons involved in each of the steps. It was noted [137–139] that the mechanisms of these reactions can be described by determining experimentally the effective transfer factors or the stoichiometric factors of the elementary steps. However, due to the diversity of ionic states in electrolytes and structures of cathodic deposits, it is unlikely that a general (common) mechanism for the electrochemical deposition of polyvalent metals and non-metals will ever be established.[140, 141] One can govern the reactivities, solubilities and electrochemical properties of the starting and transient forms by changing, *e.g*., the temperature and electrolytes.

There are several viewpoints on the mechanisms of electrochemical reduction of high-melting polyvalent metals from ionic melts. According to one of them (*cf.* Ref. 141), electrochemical reactions result in cathodic deposition of high-melting metals as solid oxygen-containing compounds (oxides and bronzes). A different viewpoint was expressed by Spitsyn *et al*.[142] who believe that the deposits in question consisted of products of electrochemically initiated polymerisation of high-melting metal ions. At the moment, it is hardly possible to prefer the involvement of one particular species over another in reduction. However, there is no doubt that after multicharged species obtain the first electrons, they become reactive and initiation of polymerisation of the species becomes possible. In this case, the situation resembles that observed in aqueous solutions.[141] It is believed that the alkali metal acts as the reduced state stabiliser in melts and in non-aqueous solutions; in aqueous solutions, this role is played by hydrogen. However, the mechanism suggested is questionable, especially in the case where solid oxygen-containing compounds are not formed on the cathode.

It was assumed in certain publications (see, *e.g*., Refs 143 and 144) that the discharge and ionisation of polyvalent metals in aqueous solutions occur *via* transient ions with intermediate valence, the kinetic and thermodynamic stabilities of which depend on the nature of the metal and the electrolyte. Many of the intermediates formed in the bulk of the near-electrode layer possess high reactivities; they react with each other (disproportionation) and with the solution components (redox reactions). As a consequence, the life-times of these ions are small. It is a matter of discussion whether these concepts can be applied to ionic melts.

Polyakov [145] analysed the studies on the electrochemical behaviour of niobium in chloride, oxochloride, chloride – fluoride, oxochloride – fluoride, chloride and oxofluoride melts. It was concluded that both multistep discharge (according to virtually every possible scheme for pentavalent metals, including the transient formation of clusters and intermediates) and single-step discharge of niobium-containing ions are possible. It is generally acknowledged that niobium is reduced in two or three steps in chloride – fluoride electrolytes. The number of steps of niobium reduction in oxochloride – fluoride melts depends on the O : Nb ratio (for $O : Nb \leqslant 1$, a single-step process is observed).

The diversity of niobium oxofluoride and fluoride complexes existing in melts based on NaCl – KCl and the variety of mechanisms of their electrochemical reduction have been noted in a number of studies.[146–151] To date, much remains unclear in the chemistry and electrochemistry of niobium in salt melts.[145] A general problem, as in studies on other metals, is the establishment of correlations between the data from physicochemical and spectroscopic studies and the results of electrochemical measurements obtained by linear voltammetry, chronopotentiometry and other related methods. In addition, discharge of different-ligand complexes and release of their anionic shells in the near-cathode layer can involve the formation of species with compositions other than those of species in the melt bulk.

The laws of electrochemical behaviour of tantalum resemble those of niobium in similar melts.[147]

In their surveys Kuznetsov *et al*.[152, 153] noted diverse views on the electrochemical reduction mechanism of zirconium in fluoride, chloride, fluoride – chloride and oxofluoride melts. Some researchers consider that discharge of ZrF_6^{2-} to give the metal is preceded by various intermediate steps (formation of complex fluorides $n\,MF \cdot ZrF_2$, poorly soluble complex salts $MZrF_4$, *etc*.). Others believe that the reduction of ZrF_6^{2-} is a multistep (involving two or even three steps) or a one-step process. The existing disagreement can be explained by differences in the experimental conditions and in techniques for the interpretation of results.[154, 155] It is presently believed [155, 156] that the electrochemical reduction of zirconium in chloride – fluoride melts occurs either according to the auto-inhibition scheme or with four-electron reversible single-step charge transfer, depending on the concentration of the F^- ion.

Of particular interest are theoretical studies on the stepwise character of charge transfer. For non-adiabatic reactions, the discharge of polyvalent ions is usually represented by a sequence of single-electron charge transfer steps with concomitant intervalent interactions, which are also considered to be one-electron processes.[157, 158] However, a series of studies on the features of electrochemical reduction of the elements in question did not reveal any steps in the discharge of the corresponding oxo, oxohalide and halide complexes. Studies on adiabatic electrochemical electron transfer reactions showed [157, 158] that at a certain ratio between the energy of environment reorganisation accompanying the electron transfer and the Coulombic interaction energy of valence electrons in the reagent, the consecutive single-electron discharge can become multi-electron discharge. In this case, the elementary charge transfer act can be compared to a continuous stream of electrons which cannot be separated into separate steps.

To date, the stepwise character of multielectron processes could not be detected by methods of electrochemical analysis. The use of quantum-chemical methods was suggested for this purpose.[57, 79, 101, 104] A specially developed technique was used for comparison of the activation barriers of multi- and single-step electrochemical EAS reduction with optimal compositions and forms in carbonate-, nitrate-, boron- and titanium-containing melts.[57, 104] For boron-containing melts it was found [57, 101] that the activation barriers for two-step reduction of BF_4^- anions and BF_3 molecules are lower than those for single-step reduction. This law is no longer valid in the case of boron-containing metal complexes. It was concluded for titanium-containing fluoride melts [57, 79] that single-step reduction is more favourable than multi-step reduction.

Thus, no common mechanism of electrochemical reduction of multivalent metals and non-metals has been established to date. Different states of the ions of these metals in electrolytes, structures of cathodic deposits and conditions of the process (temperature and the nature of the electrolyte) can favour one or another electrochemical reduction mechanism. The ambiguity

and diversity of electrochemical reduction mechanisms of EAS can also be due to differences in the melt compositions (different anionic and cationic compositions, admixtures) and in features of experimental techniques (for example, electrode polarisation rates, purity of reagents, materials of electrodes and atmosphere in voltammetry). The possible 'masking' of the apparent stepwise mechanism by autoinhibition should also be noted. Therefore, in each particular case of single-step electrochemical reduction, one should speak of a narrow potential range, which practically cannot be resolved by the existing methods.

The processes of electrochemical evolution of high-melting metals and non-metals from ionic melts underlie a new promising method for the preparation of carbides, borides and silicides of Group IV–VIA metals, *i.e.*, high-temperature electrochemical synthesis.[3, 159] It should be noted that there is as yet no generally accepted opinion on the mechanism of EAS formation involving these compounds. In this Section, we survey the results of experimental studies on the mechanisms of formation and structures of the EAS of high-melting metals.

1. MoO_4^{2-} and WO_4^{2-} anions with chloride melts as the background in the presence of strongly polarising cations

Systematic studies on the electrochemical behaviour of molybdate and tungstate ions in oxohalide electrolytes were carried out by many research groups. Electrochemists from the Sverdlovsk scientific school studied the electrochemical deposition from melts based on alkaline-earth metal chlorides. It was found[160] that anodic dissolution of molybdenum in $CaCl_2$–CaO melts produces MoO_4^{2-} ions; if an admixture of MoO_3 is present, the formation of $Mo_2O_7^{2-}$ ions is more probable. Depending on the melt temperature on the cathode, either molybdenum oxide Mo_2O_3 or metallic molybdenum are deposited.[161] Deposition of molybdenum occurs from electrolytes with acidic properties caused by the presence of calcium cations.[160–162]

It has been shown by electrochemists from the Kiev scientific school[163, 164] that EO_4^{2-} anions (E = Mo, W) in an equimolar KCl–NaCl melt as the background (973–1073 K) do not manifest electrochemical activity up to decomposition potentials of the background electrolyte. The equilibrium potential of molybdenum (tungsten) is not reached in these systems, as noticeable metallic corrosion occurs. The acidic character of alkali and alkaline-earth metal cations (Li^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}) was established.[165, 166] Introduction of cations with high polarising strength (Li^+, Ba^{2+}, Ca^{2+}) to melts containing EO_4^{2-} anions gives rise to a reduction wave at more positive potentials than the decomposition potential of the background electrolyte.[167, 168] Acidification of the melt results in a considerable increase in the reduction wave of molybdate (tugstate) ions and its displacement to the positive range of potentials. If the melt is acidified with a small concentration of Ca^{2+} cations, one wave is observed; two waves are observed at $[Ca^{2+}] \approx (4-5)\,[WO_4^{2-}]$: the first wave reaches a maximum, and a second wave appears at more negative potentials. Upon acidification with Li^+, Ba^{2+} or Ca^{2+} cations, the WO_4^{2-} reduction waves maintain their kinetic nature. This follows from the absence of a linear dependence of the limiting current on the cation concentration and from the activation energy of the limiting current (88.2 kJ mol^{-1} for $[Ca^{2+}] \to 0$). As the melt is acidified, the surface kinetic constant increases by an order of magnitude and reaches the values comparable to the diffusion constant, while the activation energy of the limiting current decreases to 12.4 kJ mol^{-1} (see Ref. 169).

If a 3.5–4.0-fold excess of Mg^{2+} cations with respect to EO_4^{2-} is introduced, an almost proportional relationship between the limiting current of the reduction waves and the concentration of these cations is observed.[170, 171] The maximum limiting current is reached at $[Mg^{2+}] \approx 4\,[EO_4^{2-}]$. Under these conditions, the mass transfer rate constant $[(1.5-2.0)\times 10^{-3}$ cm s$^{-1}]$ is comparable to the diffusion constant; this suggests the diffusion nature of the steady-state waves.

Introduction of Al^{3+} cation also resulted in a proportional dependence of the limiting current on the concentration of this cation. At $[AlCl_3] > 0.5\,[EO_4^{2-}]$, strong evolution of gases (chlorine, chlorine oxides) and a decrease in the limiting current were observed.

In a chloride melt as the background, the electrochemical reduction of MoO_4^{2-} and WO_4^{2-} anions to the metals in the presence of various cations (Li^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}) occurs at various potentials. On going from Li^+ to Al^{3+}, the reduction potentials are shifted in the positive direction by more than 1 V. The limiting current of MoO_4^{2-} and WO_4^{2-} electrochemical reduction is reached at a non-equivalent concentration of cations. The shift of the reduction half-wave potentials ($E_{1/2}$) upon a ten-fold increase in cation concentration is 0.2–0.4 V. Such a significant $E_{1/2}$ shift upon changing the concentration and the cation polarising strength results from the different compositions of the electrochemically active species due to changes in the acid-base properties of the melt. As Shapoval *et al.*[170, 171] report, this shows that, first, variations of the acid strength and the cation concentration change the acid-base reaction stoichiometry, which cannot be described by dissociation of the anion; second, it cannot be described by a reaction resulting in the complete loss of oxygen ions by the metal.

The EAS formation mechanism in melts with various cationic compositions can be presented by the following scheme:

$$x\mathrm{M}^{z+} + \mathrm{EO}_4^{2-} \rightleftarrows \begin{matrix} \{\mathrm{M}_x^{z+}[\mathrm{EO}_4^{2-}]\}^{zx-2} \\ \mathrm{EO}_{4-x}^{2(x-1)} + x\mathrm{M}^{z+}\mathrm{O}^{2-} \end{matrix}, \qquad (19)$$

where E = Mo, W; $M^{z+} = Li^+$, Ba^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}.

The direction of shift of equilibrium (19) is determined by the polarising strength and concentration of the cation and by the anion strength. In any case, the cation–anion interaction occurs through a step of the formation of metal complexes.

Acidification of a melt containing MoO_4^{2-} or WO_4^{2-} by Li^+, Ba^{2+}, Ca^{2+} or Mg^{2+} cations results in outer-sphere cationisation of anions giving metal complexes $\{M_x^{z+}[EO_4^{2-}]\}^{(xz-2)+}$. Acidification of the same melts by the Al^{3+} cation results in decomposition of the anions to give $EO_{4-x}^{2(x-1)-}$ species.

The outer-sphere cationisation of WO_4^{2-} anion by the Ca^{2+} cation was studied by IR emission spectroscopy.[172] It was shown that at $[Ca^{2+}] > [WO_4^{2-}]$, symmetric cationisation occurs to give the $\{Ca_4^{2+}[WO_4^{2-}]\}^{6+}$ species.

Shapoval *et al.*[170, 171] also observed an increase in the electron-accepting properties of molybdate and tungstate ions with increase in their degree of cationisation and increase in the acid strength of the cation. This indicates that multielectron processes might have occurred. Apparently, the specific features of multielectron processes are caused by the particular structure of the cationised EAS. For example, in the case of Ca^{2+} and Li^+ cations, two electrons are transferred in the electrode process

$$\{\mathrm{Ca}_x[\mathrm{WO}_4^{2-}]\}^{2(x-1)} + 2\mathrm{e}^- \rightleftharpoons \mathrm{WO}_2 + x\,\mathrm{CaO} + (2-x)\,\mathrm{O}^{2-}, \qquad (20)$$

where $1 \leqslant x \leqslant 2$.

For $x = 4$ in the presence of Mg^{2+}, Al^{3+} in the melt, transfer of six electrons occurs in a practically unresolvable range of potentials. The multielectron electrochemical processes are described by the following overall reactions:

$$\{\mathrm{Li}_4^+[\mathrm{EO}_4^{2-}]\}^{2+} + 6\mathrm{e}^- \longrightarrow \mathrm{E} + 2\,\mathrm{Li}_2\mathrm{O} + 2\mathrm{O}^{2-}, \qquad (21)$$

$$\{\mathrm{Ca}_4^{2+}[\mathrm{EO}_4^{2-}]\}^{6+} + 6\mathrm{e}^- \longrightarrow \mathrm{E} + 4\,\mathrm{CaO}, \qquad (22)$$

$$\{\mathrm{Mg}_4^{2+}[\mathrm{EO}_4^{2-}]\}^{6+} + 6\mathrm{e}^- \longrightarrow \mathrm{E} + 4\,\mathrm{MgO}. \qquad (23)$$

In the case of acidification by the Al^{3+} cations

$$\mathrm{AlO}_2\mathrm{Cl}_{2+x}^x + 6\mathrm{e}^- \rightleftharpoons \mathrm{Al} + 2\,\mathrm{O}^{2-} + (2+x)\,\mathrm{Cl}^-. \qquad (24)$$

2. CO_3^{2-} anions with chloride and carbonate melts as the background

The cathodic evolution of carbon upon electrolysis of molten carbonates has first been reported by Haber and Tolloczko [173] who obtained carbon deposits from a $BaCl_2-BaCO_3$ melt at 853 K. Systematic studies on electrolysis and electrode processes involving carbonates have been carried out by electrochemists from the Kiev and Sverdlovsk scientific schools. Delimarskii *et al.*[22] have found that graphite powder is the only cathodic product in the electrolysis of an equimolar $Li_2CO_3-K_2CO_3$ mixture at 853–873 K (current efficiency ~100%); carbon dioxide and oxygen (in 2:1 ratio) are the anodic products. The cathodic process is believed [174, 175] to include the reaction

$$CO_3^{2-} \rightleftharpoons CO_2 + O^{2-} \quad (25)$$

and reaction (9), while the anodic process includes the reactions

$$CO_3^{2-} \longrightarrow CO_2 + (1/2)O_2 + 2e^- , \quad (26)$$

$$O^{2-} \longrightarrow (1/2)O_2 + 2e^- . \quad (27)$$

The ratio of the parallel reactions (26) and (27) is determined by the current density. It has been noted that carbon is not formed in the electrolysis of pure K_2CO_3. If this melt is saturated with CO_2 (under pressure), carbon is precipitated on the cathode. Shapoval *et al.*[176, 177] concluded that a certain CO_2 concentration is required for carbon deposition from molten chlorides; it can be achieved by addition of thermally unstable carbonates or by saturation of the melt with gaseous carbon dioxide.

Trunov and Stepanov [178, 179] showed that a platinum electrode which contacts with a mixed stream of carbon dioxide and oxygen is reversible with respect to a carbonate melt. They believe that an equilibrium (between carbonate ions and molecules of CO_2 and O_2) is established on the electrode. Smirnov *et al.*[180] studied the polarisation of platinum and nickel electrodes in a melt of alkali metal carbonates. It was shown that, depending on the current density, various electrode reactions occur resulting in formation of carbides, evolution of free carbon and carbon(II) oxide, as well as discharge of alkali metal cations. The polarisation depends on the concentration of carbonate ions and is due to their diffusion from the bulk melt to the surface. The mechanisms of anodic processes in chloride–carbonate melts in various atmospheres (He, CO, CO_2 or $2CO_2 + O_2$ mixture) have been studied in detail.[181]

Bartlett and Johnson [27, 182] calculated the decomposition potential of alkali and alkaline-earth metal carbonates and considered all possible variants in the reduction of carbonate ions. Based on the calculations, it was concluded that the precipitation of the alkali metal is energetically more favourable at all temperatures for K_2CO_3; for Na_2CO_3, the evolution of carbon is possible up to 1143 K, while that of sodium is possible above 1143 K. Reduction of lithium, calcium, magnesium and barium carbonates gives carbon.

In a series of studies,[183–187] the formation of new species upon dissolution of carbon dioxide in molten $Li_2CO_3-Na_2CO_3-K_2CO_3$ eutectics was reported. The formation of dicarbonate ions was confirmed by potentiometric titration, by structural studies on a melt and by determination of the free energy ($\Delta H = -142$ kJ mol^{-1}) of the reaction between CO_2 and CO_3^{2-} to give $C_2O_5^{2-}$ (see Ref. 183). The possible existence of such species as CO_4^{2-} (see Refs 184, 185), $C_2O_6^{2-}$ (see Ref. 184), $C_2O_4^{2-}$ (see Ref. 186) and CO_2^{2-} (see Ref. 187) was noted.

In K, Na, Rb/Cl melts as the background, the carbonate ion does not show electrochemical activity.[188] An increase in temperature to 700 °C does not favour the electrochemical reduction of CO_3^{2-} either. The addition of a 500-fold excess of LiCl with respect to CO_3^{2-} does not produce a wave on the voltammograms. As the Li^+ concentration is increased, a small wave of CO_3^{2-} electrochemical reduction stretched along the potential axis is observed in the potential range from 0.7 to 0.9 V. The Ca^{2+} cation affects the electrochemical reduction of CO_3^{2-} more strongly than Li^+ does. A noticeable wave is observed even with a 200-fold excess of Ca^{2+}. The waves in the presence of Ca^{2+} are also extended along the potential axis. The wave heights were not found to depend explicitly on the cation concentration. The effect of the Mg^{2+} cation was found to be most pronounced. A distinct wave appears even with a four-fold excess of Mg^{2+}. Further increase in the Mg^{2+} concentration increases the wave height, and it reaches a maximum with a 100-fold excess of Mg^{2+}. Evacuation of the system after reaching the maximum wave height decreases the latter. The addition of Mg^{2+} after evacuation increases the wave again.

It should be noted that the electrochemical reduction of CO_3^{2-} in molten chlorides as the background occurs in the same potential range, irrespective of the polarising force of the cation. Hence, the electrode processes in melts with different cationic compositions involve the same species, namely, CO_2. The electrochemical reduction of CO_3^{2-} under the action of strongly polarising cations occurs at much lower temperatures than the thermal decomposition temperatures of the corresponding carbonates. Hence, the formation of CO_2 does not result from thermal decomposition but is a consequence of the polarising effect of cations.

3. MoO_4^{2-}, WO_4^{2-} and CO_3^{2-} anions in oxide melts as the background in the presence of strongly polarising cations

It is known [189–192] that polytungstate and polymolybdate melts $Na_2EO_4-EO_3$ (E = Mo, W) can be considered as melts of eutectic mixtures $Na_2EO_4-Na_2E_2O_7$ containing the Na^+, EO_4^{2-} and $E_2O_7^{2-}$ ions. The ratio between the concentrations of EO_4^{2-} and $E_2O_7^{2-}$ ions is determined by the equilibrium

$$2\,EO_4^{2-} \rightleftharpoons E_2O_7^{2-} + O^{2-} . \quad (28)$$

Presumably, the introduction of Li_2WO_4 or $ZnWO_4$ as well as of WO_3 in a sodium tungstate melt complicates the structure of tungsten–oxygen groups, for example, owing to the reaction

$$2\,WO_4^{2-} + x\,Li^+ \longrightarrow Li_xO^{(2-x)-} + W_2O_7^{2-} . \quad (29)$$

However, if this concept is applied to molten $M^{I}EO_4-M^{II}EO_4$ mixtures (M^{I} = Li, Na, K; M^{II} = Ca, Zn, Ba, Sr, Mg, Al), some contradictions arise. First, if the equilibrium (28) took place upon introduction of tungstates of strongly polarising cations, *e.g.*, $CaWO_4$, in a sodium tungstate melt, this would have occurred in melts containing an excess of the Ca^{2+} cation with formation of the tungstate ion dimer. However, studies on the electrochemical behaviour of the $CaCl_2-CaWO_4-CaO$ system at high temperatures [152] and the IR spectra of a $KCl-NaCl-Na_2WO_4-CaCl_2$ melt (for $[Ca^{2+}] > [WO_4^{2-}]$) [14] indicate that the tungstate ion retains its tetrahedral structure. Second, the solubility of tungstates (molybdates) with strongly polarising cations in sodium or potassium tungstate (molybdate) decreases with the increase in the cation specific charge.[193] These facts can imply that the strength of $M^{z+}-EO_4^{2-}$ interaction increases with increase in the specific charge and that the concentration of oxygen ions in the molten mixtures decreases.

In our opinion, the cationic composition of tungstate and molybdate mixtures, like that of oxochloride melts, should affect considerably the EAS composition and the parameters of the electrode process. Kushkhov *et al.*[194, 195] studied the melts of $Na_2WO_4-MEO_4$ mixtures (M = Li, Ca, Zn, Ba, Sr, Mg, Al; E = Mo, W). The addition of tungstates and molybdates with strongly polarising cations shifts the oxygen electrode potential towards more positive values, *i.e.*, decreases the activity of the O^{2-} ion. An increase in the cation specific charge in the series Ba^{2+}, Sr^{2+}, Li^+, Mg^{2+}, Al^{3+} leads to a more significant shift. In the cases of addition of aluminium tungstate (molybdate) and tungsten (molybdenum) trioxide, the concentration dependences of the oxygen electrode potential practically coincide. It can thus be assumed that if a strongly polarising cation is present in a melt, an acid-base reaction of the molybdate (tungstate) ion with the Al^{3+} cation is possible

$$2\,Al^{3+} + 3\,EO_4^{2-} \longrightarrow 3\,EO_3 + Al_2O_3\,. \quad (30)$$

According to reactions (28) and (29), the parameters (potentials, rates) of electrochemical evolution of tungsten and molybdenum should be virtually identical in melts with identical acidities, irrespective of the cationic composition. However, an increase in the cation specific charge shifts the electrochemical reduction wave towards more positive potentials. For example, the shift upon transition from Na^+ to Al^{3+} is $\sim$1.0 V.

This fact cannot be explained using the viewpoint that EAS are formed in melts of sodium tungstate containing molybdates and tungstates of strongly polarising cations according to reaction (28). In melts with equal acidities, the specific charge on cations affects considerably the electrochemical reduction potential. In fact, the electrochemical reduction potentials of tungstate ion in the presence of barium, magnesium and aluminium cations are within 1.8–1.9, 1.5–1.7 and 1.0–1.2 V, respectively. A similar situation is observed for molybdate ion.

The acid-base (cation–anion) interactions occurring in a melt of sodium tungstate upon addition of the carbonate ion are judged by changes in the e.m.f. of a cell with oxygen electrodes.[135] Upon addition of carbonates, the oxygen electrode potential is shifted towards negative values, indicating an increase in the oxygen ion activity in the melt. The addition of lithium carbonate shifts the oxygen electrode potential much more strongly than that of sodium carbonate. This is due to the fact that the stability constant of sodium carbonate is higher than that of lithium carbonate.[196] For the same reasons, a melt of sodium tungstate containing lithium carbonate has a lower pCO_2.

The electrochemical reduction of carbonate ion in sodium tungstate as the background can be detected only upon addition of lithium carbonate. The absence of a linear dependence of the reduction wave current on the lithium carbonate concentration and the decrease in the diagnostic criterion $j_p/V^{1/2}$ (where j_p is the peak current density, V is the potential sweep rate) with an increase in the polarisation rate implies the kinetic nature of electrochemical reduction waves of carbonate ion. Electrochemically active CO_2 species are formed as a result of cation-anionic interaction of the strongly polarising Li^+ cation with the carbonate ion. The formation of CO_2 can be described by the above scheme [see Eqn (5)]. The addition of sodium carbonate increases pCO_2 considerably, therefore the CO_2 reduction wave is not observed in the voltammetric curves.

4. Effect of PO_3^- anions on the formation of electrochemically active species in the presence of MoO_4^{2-} and WO_4^{2-} anions

Introduction of PO_3^- in $KCl-NaCl-Na_2WO_4$ (Na_2MoO_4) melts gives two waves on the voltammograms.[197, 198] An increase in PO_3^- concentration within $0.01 < [PO_3^-]/[EO_3^{2-}] < 0.2$ increases the current of the second wave, whereas the potentials and currents of the first wave remain unchanged. The current of the second wave is proportional to the PO_3^- concentration. Potentiostatic electrolysis of molybdate (tungstate)-containing melts with the specified concentration ratio of molybdate (tungstate) and metaphosphate anions gives a deposit of the corresponding high-melting metal on the cathode.

Our assumption on the participation of the dimeric ionic forms of molybdenum and tungsten in the electrode processes in question is based on the following data. It has been shown [199] that introduction of sodium metaphosphate in a purely tungstate melt shifts the potential of the tungsten electrode from -1.8 to -1.0 V. It is at -1.0 V that discharge of $W_2O_7^{2-}$ ions occurs; the existence of these ions has been proven both electrochemically [200] and by high-temperature radiography.[201]

Based of voltammetric data,[197, 198] the effect of PO_3^- on the electrochemical reduction of MoO_4^{2-} and WO_4^{2-} can be interpreted as follows. The role of PO_3^- involves the formation of two EAS forms according to the scheme

$$PO_3^- + 2EO_4^{2-} \rightleftharpoons \begin{matrix} E_2O_7^{2-} + PO_4^{3-} \\ 2EO_3 + PO_4^{3-} + O^{2-}\,. \end{matrix} \quad (31)$$

The formation of ditungstate ions in a sodium tungstate melt in the presence of PO_3^- anions has also been reported by Malyshev.[202]

5. Effect of neutral MoO_3, WO_3 and B_2O_3 molecules on the formation of electrochemically active species in the presence of MoO_4^{2-} and WO_4^{2-} anions

The effect of tungsten trioxide on the electrode processes in tungstate melts has been studied in detail by a research group directed by Academician A N Baraboshkin.[189, 191, 200] Contradictory opinions on the ionic composition of tungstate melts exist at present. It has been noted above that the melts of the $Na_2WO_4-WO_3$ system can be regarded as melts of the $Na_2WO_4-Na_2W_2O_7$ eutectic mixture and that they mostly consist of a mixture of Na^+, WO_4^{2-} and $W_2O_7^{2-}$ ions.

The discharge of $W_2O_7^{2-}$ occurs more easily than that of the tungstate ion. This is evident from a thermodynamic calculation of the decomposition potentials of the corresponding compounds [203, 204] and from experimental data:[190, 191] introduction of small amounts of WO_3 increases abruptly the potential of tungsten evolution and decreases the decomposition potential of polytungstate melts.

The effect of MoO_3 on electrode processes in the sodium tungstate melt and the EAS formation mechanism were studied by potentiometric and voltammetric measurements (a cell with oxygen electrodes was used).[205, 206] Measurements of the equilibrium potentials of the oxygen electrode showed that in the presence of up to 2 mol.% – 3 mol.% MoO_3 in the sodium tungstate melt, the pre-logarithmic factor of the dependence of the oxygen electrode potential on MoO_3 concentration is 0.120 V. This means that in this concentration range molybdenum exists mainly as MoO_4^{2-} ions. The pre-logarithmic factor of this dependence at concentrations 7 mol.% – 20 mol.% is 0.112 V. Hence, molybdenum is present mainly as dimolybdate ions $Mo_2O_7^{2-}$ in this concentration range. The experimental dependences match the calculated ones, which confirms the validity of the chosen model of the ionic composition of the melt.

Measurements of the potential of a molybdenum electrode *versus* MoO_3 concentration showed the existence of two equilibria.[206, 207] At MoO_3 concentration up to 4 mol.% – 5 mol.%, metallic molybdenum is in equilibrium with a melt containing $Mo_2O_7^{2-}$ ions. The concentration dependence of the equilibrium potential is well described by the Nernst equation. The number of electrons per one electroactive species calculated from the slope of the plot of the molybdenum electrode potential against MoO_3 concentration, ($dE/d\log[MoO_3]$), equals 1.5. This value is consistent with the equilibrium

$$4\,Mo_2O_7^{2-} + 6\,e^- \rightleftharpoons Mo + 7\,MoO_4^{2-}\,. \quad (32)$$

At high MoO_3 concentrations (> 5 mol.%), the activity of $Mo_2O_7^{2-}$ increases, and a tungstate–molybdate melt is in equilibrium with the dioxide MoO_2 rather than with metallic molybdenum

$$2\,Mo_2O_7^{2-} + 2\,e^- \rightleftharpoons MoO_2 + 3\,MoO_4^{2-}\,. \quad (33)$$

The number of electrons per one electroactive species, also calculated from the slope $dE/d\log[MoO_3]$, equals 1. This value describes the equilibrium (33).

The formation of dimolybdate and ditungstate ions in tungstate–molybdate melts in the presence of B_2O_3 was noted.[208, 209]

6. Effect of fluoride and fluoroaluminate ions on the formation of electrochemically active species in the presence of CrO_3, MoO_3, WO_3, CrO_4^{2-}, MoO_4^{2-} and WO_4^{2-} in chloride–fluoride melts

Tungsten and molybdenum trioxides can be stabilised in chloride melts by binding them in oxofluoride complexes which are more

stable. Such complexes have been described in the literature; they are obtained by treatment of tungstates and molybdates with hydrofluoric acid. We were able to find data on the existence of these compounds in melts in only one publication.[210]

The composition range of oxohalide melts where tungsten and molybdenum exist as stable oxofluoride complexes was determined by studying $KCl-NaCl-NaF-EO_3$ melts (E = Mo W) with different [NaF]/[EO_3] concentration ratios.[211,212] Based on the results of these studies, the overall electrode process of electrochemical reduction of the oxofluorotungstate complex can be presented as follows:

$$[WO_2F_4]^{2-} + 6e^- \rightleftharpoons W + 2O^{2-} + 4F^- , \quad (34)$$

$$2O^{2-} + [WO_2F_4^-]^{2-} \rightleftharpoons WO_4^{2-} + 4F^- , \quad (35)$$

$$2[WO_2F_4]^{2-} + 6e^- \rightleftharpoons W + WO_4^{2-} + 8F^- . \quad (36)$$

As noted above, MoO_4^{2-} and WO_4^{2-} in melts of chlorides of weakly polarising cations (Na^+, K^+) as the background manifest no electrochemical activity up to decomposition potentials of the background electrolyte. The addition of fluoride ion to a sodium chloride melt containing molybdate and tungstate ions does not change the shapes of the voltammetric curves. The molybdate and tungstate ions are stable in NaCl–NaF melts; the O^{2-} is not replaced by F^- with the formation of oxofluoride complexes, and they do not manifest electrochemical activities up to decomposition potentials of the background electrolyte.[213,214]

It is known that aluminium fluoride complexes possess acceptor properties with respect to O^{2-} ions and hence can be used for controlling the acid-base properties. On introduction of AlF_6^{3-} in a sodium chloride melt containing MoO_4^{2-} and WO_4^{2-} anions, waves at 0.7–1.0 V appear on the voltammetric curves.[163,164] Acid-base interaction of EO_4^{2-} with AlF_6^{3-} is accompanied by replacement of F^- by O^{2-} in the aluminium environment to give $AlOF_x^{1-x}$ complexes ($x = 2-5$), while EO_4^{2-} is bound in oxofluoride complexes. For example, for $x = 2$

$$EO_4^{2-} + 2AlF_6^{3-} \longrightarrow EO_2F_4^{2-} + 2AlOF_2^- . \quad (37)$$

The proof that tungsten and molybdenum are evolved from oxofluoride complexes in the $NaCl-Na_3AlF_6-Na_2EO_4$ systems is as follows. First, the deposition potentials of tungsten and molybdenum from these systems correlate well with the deposition potentials of these elements from WO_2F_2, MoO_2F_2 relative the oxygen electrode calculated from thermodynamic data.[203,204] Second, the deposition potential of tungsten (molybdenum) from the system in question coincides with the deposition potential of tungsten (molybdenum) from the $NaCl-KCl-NaF-EO_3$ system, in which the high-melting metal exists as $EO_2F_4^{2-}$ (see Refs 215, 216). The formation of $EO_2F_4^{2-}$ and its subsequent electrochemical reduction to the metal in a $KF-MoO_3-B_2O_3$ melt was assumed by Japanese researchers.[213] The electrochemical reduction waves recorded for a $NaCl-Na_3AlF_6$ melt containing EO_3 and Na_2EO_4 both separately and simultaneously are virtually identical. Hence, the reaction between tungstate (molybdate) and fluoroaluminate ions results in $EO_2F_4^{2-}$ and $AlOF_x^{1-x}$.

Taking into account the linear dependences of the reduction wave peak current on the EO_3 (EO_4^{2-}) concentration and on the polarisation rate and using the mass transfer constant of $(5-6)\times10^{-3}$ cm s^{-1}, Malyshev *et al.*[214] reached a conclusion on the diffusion nature of the limiting current. The dependence of the potential of molybdenum or tungsten electrode in a $NaCl-Na_3AlF_6$ melt on the EO_3 or EO_4^{2-} concentration *vs.* the Pt, O_2/NaCl–0.05 Na_2MO_4 half-cell is well described by the Nernst equation. The number of electrons per one electroactive species calculated from the slope of plots of the metal electrode potential against the EO_3 (or EO_4^{2-}) concentration equals 5.8±0.2. For these melts, the polarisation curves of the molybdenum and tungsten electrodes are characterised by low overvoltage; the cathodic and anodic segments of polarisation curves are symmetric up to the overvoltage of 0.35 V. Based on the slopes of the polarisation curves in the current–overvoltage coordinates, the number of electrons participating in the electrode process was found to be 5.5–6.1. These data suggest the reversibility of the charge transfer step. The overall electrochemical reaction can be represented as follows:

$$EO_2F_4^{2-} + 2AlF_6^{3-} + 6e^- \rightleftharpoons E + 2AlOF_4^{3-} + 8F^- . \quad (38)$$

Several studies[214,217,218] deal with the effect of fluoride complexes AlF_6^{3-} and SiF_6^{2-}, manifesting acid properties with respect to O^{2-} ions on the electrochemical reduction of CrO_4^{2-} in K, Na/Cl, F melts as the background. The chromate ion in halide melts as the background with weakly polarising cations, such as Na^+ and K^+, does not manifest electrochemical activity up to the decomposition potentials of the support electrolyte. The formation of EAS can be represented by an equation analogous to Eqn (38). The Cr_2O_3 formation potential coincides with its evolution potential from $CrO_2F_4^{2-}$ *vs.* the oxygen electrode calculated from thermodynamic data.[203,204] The dependence of the chromium electrode potential in a $NaCl-Na_3AlF_6$ melt (50 mass % : 50 mass %) on CrO_4^{2-} concentration at 1173 K obeys well the Nernst equation with the number of electrons per EAS equal to 3.0±0.1. The electrochemical deposition of Cr_2O_3 occurs without a noticeable overvoltage; analysis of polarisation curves gives 5.7–6.1 electrons. These data suggest the reversibility of the charge transfer step. The overall electrochemical equilibrium can be expressed as follows:

$$2CrO_2F_4^{2-} + AlF_6^{3-} + 6e^- \rightleftharpoons Cr_2O_3 + AlOF_4^{3-} + 10F^- . \quad (39)$$

Studies on the electrochemical reduction of oxoanions of high-melting metals in the presence of chloride, chloride–fluoride and oxide melts with various acid-base properties made it possible to reveal three mechanisms of EAS formation:[3,4] anion cationisation with formation of $\{M_x^{z+}[EO_{n/2+1}]^{2-}\}^{(xz-2)+}$ species, oxoanion decomposition to give $\{EO_{[(n+2(1-x)]/2}Hal_{2(x-1)+y}\}^{y-}$ oxohalide complexes, formation of $[E_{(1+x)}O_{n(1+x)/2+1}]^{2-}$ dimer complexes where E = Cr, Mo, W, C; M = Li^+, Ba^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}.

The direction of EAS formation is determined by the acid properties and the concentration of M^{z+}, EO_n, PO_3^-, F^- and the stability of the EO_n^{2-} anion.

One can create conditions enabling various multielectron electrochemical processes to favour a particular reduction mechanism in ionic melts, by constructing electrochemically active species with various structures and compositions (in other words, by controlling the cation–anion interactions).

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