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On regularities of some carbohalogenation processes in chloride and bromide melts of various cation composition

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The generalization of course of halogenation and carbohalogenation processes (purification from oxygen-containing admixtures) in chloride and bromide melts was performed on the basis of physicochemical imaginations. The carbohalogenation processes were shown to be more thermodynamically profitable comparing with simple halogenation since oxygen yielding as a result of carbohalogenation is fixed in CO (or CO_2). The features of CX_4 (X=Cl, Br) application as carbohalogenating agents are discussed. From the viewpoint of chemical kinetics, the kinetic order of chemical stage (n) is dependent on the composition of the product of oxide ion interaction with the most acidic cation of melt. For Y^{3+} containing melts it is equal to 1 whereas for alkali and alkaline earth melts n=2. In the case of performing carbobromination (‘C+Br_2’ Red-Ox pair) the limit of purification from oxygen-containing admixtures is not dependent on the surface area of carbon that means that system achieves true chemical equilibrium. The approach allowing to estimate limits of halide melts purification from oxygen-containing admixtures is described.

Kewords: melts, chlorides, bromides, deoxidization, carbohalogenationю

Закономірності деяких процесів карбогалогенування хлоридних та бромідних розплавів різного катіонного складу *Т.П. Реброва, В.Л. Чергинець, О.Л. Ребров, Т.В. Пономаренко, В.В.Соловйов, О.І. Юрченко*

На основі фізико-хімічних уявлень проведено узагальнення даних про перебіг процесів галогенування та карбогалогенування (очищення від кисневмісних домішок) у розтоплених хлоридах та бромідах. Показано, що процеси карбогалогенування є більш термодинамічно вигідними, ніж просте галогенування, завдяки зв’язуванню кисню, що виділяється в процесі галогенування в CO (або CO_2). Обговорено особливості застосування CX_4 (X=Cl, Br) для карбогалогенування. Що стосується кінетичних особливостей, кінетичний порядок хімічної стадії процесу (n) залежить від складу продукту взаємодії оксид-іонів з найбільш кислотним катіоном розплаву. Для Y^{3+}-вмісних розплавів порядок реакції дорівнює 1 в той час, як для галогенідних розплавів, що містять катіони лужних та лужноземельних металів, n=2. При проведенні карбобромування з застосуванням окислювально-відновної пари ‘C+Br_2’) ліміт очищення розплаву від кисневмісних домішок не залежить від величини питомої поверхні вуглецю, що означає, що система досягає стану хімічної рівноваги. Описано підхід, що дозволяє оцінювати ліміт очищення розплавів від кисневмісних домішок.

Introduction

Molten ionic halides are widely used for numerous fundamental and applied purposes as media for performing different processes connected with the obtaining of various final and half-products, such as single crystals [1, 2], active metals and non-metals [3, 4], refractory binary (carbides, nitrides) and complex compounds [5] etc.

Due to reactions with the aggressive components of atmosphere (oxygen O_2, water vapor) the halide charge and the obtained molten media (halide melts) are contaminated with the oxygen-containing admixtures:

$$2X^- + 1/2O_2 \uparrow = X_2 \uparrow + O^{2-}, \quad (1)$$

$$2X^- + H_2O \uparrow = 2HX \uparrow + O^{2-}. \quad (2)$$

The presence of carbon dioxide leads to carbonization of the charge or melt according to the following equation

$$CO_2 \uparrow + O^{2-} = CO_3^{2-} \quad (3)$$

that causes additional shift of Eqn. (1) and (2) rightwards according to Le Chatelier principle. Additionally, there are organic admixtures which usually contain oxygen and hydrogen in the halide charge (especially this concerns bromides and iodides) decomposing at the heating of solid salts to 700 K with the evolution of CO_2 and H_2O that also favors the contamination processes (1)–(3).

The oxygen-containing admixtures (oxides, hydroxides and carbonates) are undesirable for a majority of processes performed in molten salts since they supply oxide ions in the melt and the latters interact with the constituent cations or cationic dopants used for different applications. For example, if the melt is used for performing electrochemical processes oxide ion admixtures reduce concentration of depolarizator that results in the retarding of the process and the decreasing of the current yield. Oxygen-containing admixtures formed at the stage of halide melt preparation for growth of cation-activated optical materials (e.g., scintillators) react with the activator forming oxides or other oxo-derivatives:

$$Eu^{2+} + O^{2-} = EuO(\downarrow), \quad (4)$$

$$Ce^{3+} + O^{2-} = CeO^+, \quad (5)$$

that results in the loss of an activator, changes of the composition of luminescent centers and, hence, the deterioration of the functional characteristics of the materials [6].

It means that before the usage these molten halide media should be thoroughly purified from oxygen-containing compounds and fixing them in gaseous or insoluble in the melt products seems the most desirable.

These requirements force developing new methods of deep deoxidization of halide melts using reagents providing the formation of gaseous or solid compounds as a result of the melt treatment. Additionally, the approaches permitting to extend the obtained for a particular melt data for the case of melts of different compositions deserve to be developed.

The obvious division of the methods in the relation to the aggregate state of the purification products is as follows:

– treatment in reactive gas atmosphere (the treatment leads to the formation of gaseous products);

– precipitating deoxidization (deposition of oxide ions in the form of metal oxides practically insoluble in the treated melt).

The former variant consists in performing processes reverse to reactions (1) or (2) and the latter one means that oxide-containing compounds in halide melts must react with cation dopants or solid metals possessing extremely high affinity to oxide ions forming practically insoluble products.

The purpose of the present work is to consider some factors permitting to predict the course of the carbohalogenation (treatment by perhalogenated hydrocarbons or action of halogen vapor on melts containing suspension of carbon) of halide melts of various cation and anion compositions.

Such a kind of the melt treatment seems very attractive for the media used for crystal growth since the products of the interactions are volatile (gases) and, therefore, they can be removed by flow of inert gas-carrier (nitrogen or argon) or using vacuum pump.

1. Common remarks

Treatment with free halogen or carbohalogenation are considered as the most available methods since the reaction products, as a rule, are practically insoluble in the treated melt. Ditto, the final oxocompounds contain multiple bonds (O=O, O=C=O) that practically prevent the running of the reverse reactions.

Since the equilibrium position of reactions of (1) kind is determined by Red-Ox potentials of

$X_{2,gas}/X^-$ and $O_{2,gas}/O^{2-}$ pairs, the corresponding estimations of the purification efficiency can be performed using these data alone. The most appropriate for this purpose are the data presented in monograph [7] where Red-Ox potentials for 'halogen/halide-ion' pairs with respect to the reference $\varphi^0_{Na^+/Na}$ electrode at 973 K are presented:

$$X_2\uparrow + 2\bar{e} = 2X^- . \qquad (6)$$

where X=*Cl, Br, I* and $\varphi^0_{Cl_2/Cl^-} = +3.89$ V, $\varphi^0_{Br_2/Br^-} = +2.98$ V, $\varphi^0_{I_2/I^-} = +2.42$ V, respectively.

To estimate the Red-Ox potential for gaseous oxygen the data of [7] are also available. So, the standard potential for silver electrode $\varphi^0_{Ag^+/Ag}$ is estimated as *ca.* +2.5 V. Our studies of the reversibility of oxygen electrode with the use of reference silver electrodes give values of $\varphi^0_{O_2/O^{2-}}$ within 0÷+0.2V range at the temperature of 973 K [8]. That means that potential value of $\varphi^0_{O_2/O^{2-}}$ electrode *vs.* sodium one lies within 2.5÷2.7 V and increases with the strengthening of oxoacidic properties of the halide melts. So, it is placed between the potentials of $\varphi^0_{Br_2/Br^-}$ and $\varphi^0_{I_2/I^-}$.

From the above data it can be concluded that equilibrium of the following reaction:

$$X_2\uparrow + O^{2-} = 2X^- + 1/2O_2\uparrow \qquad (7)$$

which is reverse to (1) is the most shifted to the right in the case of using chlorine for purification of chloride melts, the purification by iodine is thermodynamically unfavorable and proceeds relatively hard and the bromination of bromide melts proceeds merely.

The efficiency of the halide melts purification can be raised in the case of the use of Red-Ox pair 'carbon+ halogen' or perhalogenated derivatives of alkanes since carbon suspended in the melt or supplied in the form of halogenated alkanes reacts with yielding oxygen and provides its fixation into CO_2 or *CO*. This provides the removal of O_2 from the atmosphere over the melt.

The easiest media for the implementation of the carbohalogenation using perhalogenated alkanes are chloride melts since the boiling point of CCl_4 is 76.8 °C and its partial pressure at 293 K is 11.94 kPa and 15.06 kPa at 298 K [9]. The activation energy of this process is estimated as ca. 200 kJ·mol^{-1} that correlates with the strength of '*C-Cl*' bond (ca. 327±29 kJ·mol^{-1} [10]), therefore, the temperature rise essentially effects the course of the corresponding purification processes.

Carbobromination using CBr_4 is a hard process since its melting point is 363.25 K that requires worming up the communications providing supply of CBr_4 vapor into bromide melts. According to [11] the dependence of CBr_4 pressure *vs.* temperature is described by the following equation:

$$\log p(torr) = 7.97 - 2347.7/\mathrm{T(K)} \qquad (8)$$

That gives 4.28 kPa at the melting point of CBr_4. Therefore, the use of 'C+Br_2' for the deoxidization of the bromide melts seems more available since the vapor pressure of bromine is 8.6 kPa at 273 K. The purification limit for bromide melts is slightly dependent on temperature due to lower activation energy of the purification process (30–40 kJ·mol^{-1} for different melts). It was connected with the lower strength of '*Br–Br*' bond (199 kJ·mol^{-1} [10]) comparing with '*C–Cl*' one [12].

Performing carboiodination is practically impossible since it also requires heating both iodine and the supplying communications to temperatures above 373 K.

2. Kinetic aspects of carbohalogenation

Now let us consider the running of the carbohalogenation processes in melts of different cation compositions. The efficiency of the purification and the kinetic order of the reaction are dependent on forms of oxide complexes in the melts. The most noticeable examples are presented below. For estimations of the kinetic parameters the dependences of $\log m_{O^{2-}}$ ($m_{O^{2-}}$ the oxide-ion molality, mol·kg^{-1}) *vs.* the time and $m^{-1}_{O^{2-}}$ *vs.* time were built. The linearity (or practical linearity) of the corresponding dependence gives us possibility to refer the process to 1st or 2nd kinetic order, respectively.

The dependence of $\log\left(m_{O^{2-}}/m^0_{O^{2-}}\right)$ *vs.* time in molten mixture 2C*sCl-LiCl-YCl*$_3$ is presented in Fig.1 (here $m^0_{O^{2-}}$ the initial molality of oxide ion, mol·kg^{-1}). The correlation coefficients for dependences 1 and 2 (both R=0.987) permit to consider them as linear ones. This fact gives the evidence that the purification processes run according to the kinetics of the first order and we can believe that the rate-determining process can be described by the formula:

$$YO^+ = Y^{3+} + O^{2-} \qquad (9)$$

and the strength of 'Y=O' bond retards the total process which lasts more than 6 h [13].

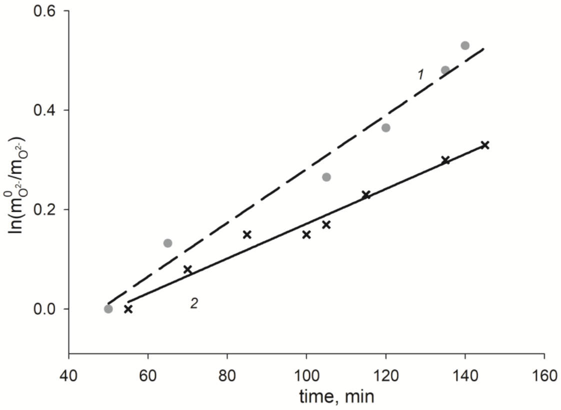

Fig. 1. The dependence of $\ln\left(m^0_{O^{2-}} / m_{O^{2-}}\right)$ *vs.* time of treatment of $2CsCl\text{-}LiCl\text{-}YCl_3$ melt by CCl_4 vapor at 973 K. CCl_4 carriers: 1 – high purity argon preliminary passed through P_2O_5, 2 – high purity argon as supplied.

The data of Fig.1 show that the preliminary preparation of the gas-carrier for the halogenation agent is important and the removal of water traces dives possibility to accelerate the rate of the purification: in the 'wet carrier' the rate constant, k is $3.5 \cdot 10^{-3}$ min^{-1} and after drying it becomes $5.4 \cdot 10^{-3}$ min^{-1}, i.e. increases by a factor of 1.5.

However, such a situation takes place in the case of melts possessing very high affinity to O^{2-} (due to the presence of Y^{3+}). For instance, let us consider the dependencies obtained at the purification of melts consisting of single charged cations: equimolar mixtures of *KCl-NaCl* (with CCl_4) and *KBr-NaBr* (with '$C+Br_2$' Red-Ox pair). In these melts the formation of Na_nO^{n-2} complexes as the main form of O^{2-} existence is preferable and their dissociation with the formation of oxide ions is easier than that of YO^+ one.

The dependence of $-\log m_{O^{2-}}$ *vs.* time is not linear (see Fig.2) that is explained by the existence of several sections with own rate-determining processes.

The first sections from 0 to 5÷7 min corresponds to considerable excess of oxide ions comparing with CCl_4 or Br_2 and the supplied gaseous deoxidant reacts with O^{2-} very rapidly. Here the rate of CCl_4 or Br_2 supply or their dissolution in the treated melt is the rate determining process.

The next section corresponds to the situation when oxide ion concentration becomes so low that the chemical process becomes the rate determining stage. The data obtained for this stage are presented in Fig.3.

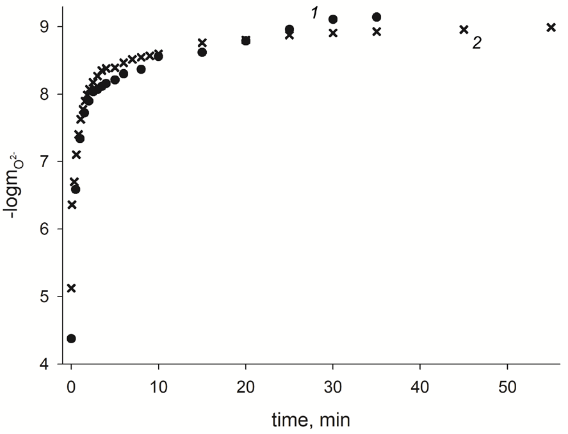

Fig. 2. The dependence of negative logarithm of oxide ion molality $-\log m_{O^{2-}}$ *vs.* time of treatment of equimolar mixtures *KCl-NaCl* (with CCl_4) and *KBr-NaBr* ('$C+Br_2$'Red-ox pair) at 973 K.

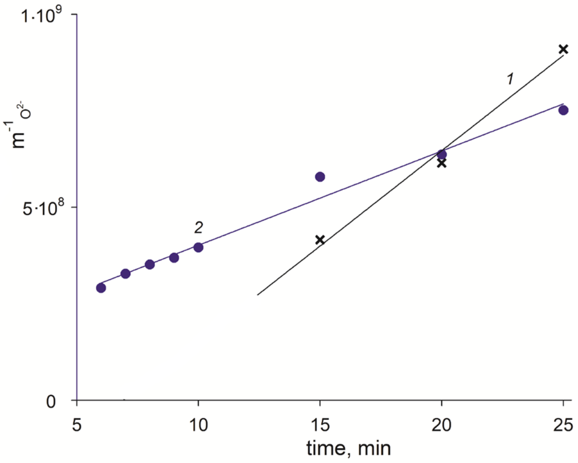

Fig. 3. The dependence of inverse molality $m^{-1}_{O^{2-}}$ *vs.* time of treatment of equimolar mixtures KCl-*NaCl* (with CCl_4) and *KBr-NaBr* ('C+Br_2' red-ox pair) at 973 K.

Since these dependences are linear in '$m^{-1}_{O^{2-}}$ – time' coordinates the chemical reactions in the melts are subjected to the kinetics of the 2nd order. It is interesting that the O^{2-} concentrations corresponding to beginning and end of the second sections are close, although the rate constant (the slope of the dependence) for bromide melt is appreciably lower than in the chloride one. This can be explained by the fact that in the bromide melt the deoxidization reaction is heterogeneous (carbon is suspended in the melt with dissolved bromine and oxide ions) and it is limited by the surface of carbon whereas in the chloride melt reaction is homogeneous (saturated solution of CCl_4 or products of its pyrolysis and dissolved O^{2-}).

A question arises: why does the dependence of oxide ion concentration from the time reaches a plateau in the purified melts? Is it caused by the equalization of rates of purification (deoxidization) and contamination (oxygen-containing admixtures in gaseous phase or coming from the construction materials) processes or by achieving the chemical equilibrium.

This question was answered in [14] where the carbobromination process of *KBr-2SrBr*$_2$ at 973 K was studied. The deoxidization was performed by bubbling '*Ar-Br*$_2$' gaseous mixture and two kinds of carbon were used for a comparison: grinded graphite and active coal. It was shown that although the active coal possesses more developed surface than grinded graphite (1800–2200 $m^2 \cdot g^{-1}$ vs. 700 $m^2 \cdot g^{-1}$) the plateaus were achieved at practically equal oxide ion concentrations: $3.6 \cdot 10^{-7}$ mol·kg^{-1}. Independence of the purification limit on surface area of carbon is an argument in favor of achieving equilibrium conditions in the purified systems.

3. The dependences limits of the purification of halide melts from their oxoacidic properties

It is obvious that the limit of halide melts' purification from oxide ion admixture should be dependent on the strength of bonding between the most acidic cation of the melt (Kt^{m+}) and oxide ion. Let us consider the system of equations:

$$C + X_2 \uparrow + O^{2-} = 2X^- + CO \uparrow \qquad (10)$$

$$Kt^{m+} + O^{2-} \rightleftharpoons KtO^{m-2}, K. \qquad (11)$$

It follows that the increase of the equilibrium constant value (*K*) causes the shift of equilibrium (10) to the left due to fixation of additional amount of oxide ions into KtO^{m-2} complexes. It is obvious that *K* reflects oxoacidic properties of the melt. The equilibrium (and the residual) concentration of oxide ions after the oxidization increases by a factor of *K*.

The direct determination of *K* is impossible; therefore, the relative values should be used. In our work [14] pI_L index was proposed as a measure of the oxoacidic properties of the melts and equimolar mixture KCl-NaCl was chosen as the reference melt since it is the most extensively studied. The pI_L for the said melt is equal to 0. In terms of consideration of Eqn. (10) and (11):

$$\log K_x = pI_{L,x}, \qquad (12)$$

where *x* the designation of the given melt. So K value for *KCl-NaCl* melt which we designate as K* is equal to 1 and the purification limit at 973 K is: $\log m_{O^{2-},lim} = -9.24$. The purification limit for the melt of x composition can be estimated using the formula:

$$\log m_{O^{2-},lim} = \\ = -9.24 + \log\left(K_x / K^*\right) \equiv -9.24 + pI_L \qquad (13)$$

The investigations of the deoxidization of chloride and bromide melts performed earlier [15, 16] give us possibility to estimate the limit of oxide ion concentration if its pI_L value is known. So for temperature 973 K the limiting concentration of O^{2-} is calculated according to the next equation:

$$\log m_{O^{2-},lim} = \\ = -8.67\left(\pm 0.37\right) + 1.20(\pm 0.18) \cdot pI_L. \qquad (14)$$

For chloride melts the corresponding dependence is as follows:

$$\log m_{O^{2-},lim} = \\ = -9.34\left(\pm 0.17\right) + 1.17(\pm 0.08) \cdot \leq pI_L. \qquad (15)$$

Since the statistical treatment was performed in the melts which pI_L lies in 0÷3.5 range the Eqn. (14), (15) can be used for all chloride and bromide melts based on salts of alkali and alkaline earth metals possessing pI_L values in this range.

4. Conclusions

The carbohalogenation processes are more thermodynamically profitable comparing with simple halogenation due to fixation of oxygen yielding as a result of carbohalogenation in *CO* (or *CO*$_2$).

The kinetic order of chemical stage of the carbohalogenation process (n) is dependent on composition of the product of interaction of oxide ions with the most acidic cation of melt. For Y^{3+} containing melts it is equal to 1 whereas for melts containing halides of alkali and alkaline earth metal cations n=2.

At the performing of carbobromination ('*C+Br*$_2$' Red-Ox pair) the limit of the purification from oxygen-containing admixtures is not dependent on the surface area of carbon that means that the system achieves true chemical equilibrium.

The limits of purification of halide melts from oxygen-containing admixtures using carbohalogenation can be estimated going from their relative oxoacidic properties.

References

1. J. Glodo, E. van Loef, N. Cherepy, S. A. Payne, C. M. Wilson, K. S. Shah, I*EEE Trans. Nucl. Sci.*, **57**, 128 (2010). https://doi.org/10.1109/TNS.2009.2036352.
2. K.S. Pestovich, L. Stand, C.L. Melcher, E. Van Loef, M. Zhuravleva, *J. Cryst. Growth,* **627**, (127540) 2024. https://doi.org/10.1016/j.jcrysgro.2023.127540.
3. G. Yang, H. Yan, Z. Liu, W. Ma, S. Guo, Y. Yang, *Solid State Sci.* **148**, 107328 (2024). https://doi.org/10.1016/j.solidstatesciences.2023.107328.
4. D. Yang, M. Yu, Y. Mubula, W. Yuan, Zh. Huang, B. Lin, G. Mei, T. Qiu, *J. Rare Earths*, 2023. https://doi.org/10.1016/j.jre.2023.08.013.
5. M. Hu, R. Tan, T. Ma, M. Hu, *Materials Today Commun.*, **35**, 105531 (2023). https://doi.org/10.1016/j.mtcomm.2023.105531.
6. V.L. Cherginets, T.P. Rebrova, Yu.N. Datsko, T.G. Deineka, E.N. Kisil, N.N. Kosinov, E.E. Voronkina, , *J. Chem.Eng.Data*, **55**, 5696 (2010). (https://doi.org/10.1021/je100643g).
7. Yu.K. Delimarsky, Chemistry of ionic melts, Kiev: Naukova Dumka, 1980.
8. V.L. Cherginets, Oxoacidity: reactions of oxocompounds in ionic solvents, Amsterdam-Boston-Heidelberg-London-New York-Oxford-Paris-San Diego-San Francisco-Singapore-Sydney-Tokyo: Elsevier, 2005.
9. http://www.microkat.gr/msds/Carbon%20tetrachloride.html.
10. https://www.wiredchemist.com/chemistry/data/bond_energies_lengths.html.
11. https://dockchemicals.com/wp-content/uploads/2020/11/DOCK-C_Product_Datasheet_CBr4.pdf.
12. V.L.Cherginets,T.P.Rebrova, T.V.Ponomarenko, V.A.Naumenko, Yu.N. Datsko, *RSC Adv.,* **4**, 52915 (2014). https://doi.org/10.1039/C4RA07806C.
13. V.L. Cherginets, T.P. Rebrova, T.V. Ponomarenko, E.P. Kisil, L.I. Filippovich, *J.Chem.Eng.Data*, **56**, 3897 (2011). https://doi.org/10.1021/je200603c.
14. V.L. Cherginets, T.P. Rebrova, *Electrochim.Acta*. **45**, 469 (1999). https://doi.org/10.1016/S0013-4686(99)00274-1.
15. V.L. Cherginets, T.P. Rebrova, T.V. Ponomarenko, V.A. Naumenko, Yu.N. Datsko, *RSC Adv.*, **4**, 52915 (2014). https://doi.org/10.1039/C4RA07806C).
16. V.L. Cherginets, T.P. Rebrova, V.A. Naumenko, A.L. Rebrov, O.I. Yurchenko, *RSC Adv.*, **6**, 58780 (2016). https://doi.org/10.1039/C6RA11551A.