RSC Advances

Paper

Polythermal investigation of course of molten ionic bromide deoxidization by action of 'bromine + carbon' red-ox pair

Victor L. Cherginets*, Tatyana P. Rebrova, Tamara V. Ponomarenko, Vyacheslav A. Naumenko and Yuri N. Datsko

Process of removal of oxide ion admixtures by the action of 'C+Br_2' red-ox pair (usually called as carbohalogenation) from bromide melts of KBr-NaBr (0.5:0.5), $BaBr_2$-KBr (0.51:0.49) and KBr-LiBr (0.4:0.6) compositions at 943, 973, 1000 and 1023 K was studied by the potentiometric method using
10 Pt(O_2)|YSZ oxygen electrode as an indicator one. The chemical stage of this process in all the molten mixtures is characterized by the 2nd kinetic order with respect to oxide ions. The thermal dependences of the conditional rate constants are described by the equations: ln k=22.06 (±1.5) – 4880 (±1400)·T^{-1} for KBr-NaBr, ln k=15.5 (±0.8) – 3700 (±800)·T^{-1} for $BaBr_2$-KBr and ln k=12.02(±1)-4011(±900)·T^{-1} for KBr-LiBr that makes it possible to estimate the activation energies of the carbohalogenation as 42±12 kJ
15 mol^{-1}, 31±7 kJ mol^{-1} and 33±8 kJ mol^{-1}, respectively. Thermodynamic characteristics of the activation complex formation ($\Delta H^{\#}$, $\Delta S^{\#}$) are estimated. The purification limits (residual concentration of O^{2-}) of the said melts in 943-1023 K temperature range are (1÷2)·10^{-9} mol kg^{-1} for KBr-NaBr, (2÷3)·10^{-7} mol kg^{-1} for $BaBr_2$-KBr (1.4÷1.8)·10^{-5} mol kg^{-1} for KBr-LiBr. There exists a good correlation between the purification limits and oxoacidic properties (the oxobasicity indices) of the studied melts.

20 Introduction

Nowadays molten bromide mixtures to be used as media for crystal growth attract considerable attention of investigators working at the development of recently discovered highly-efficient Eu^{2+}-doped scintillation materials, e.g., $CsBa_2Br_5$:Eu^{2+},[1]
25 BaBrI:Eu^{2+} [2] and $CsCaBr_3$:Eu^{2+}.[3] One of the most important stages of treatment of the charge for crystal growth is its drying and purification of the melt from oxygen-containing admixtures. Their presence results in the loss of the activator (Eu^{2+}) caused by precipitation of EuO or Eu_2O_3 from the growth melt. A priori, the
30 process of carbohalogenation, i.e., the treatment of a melt containing carbon (suspended graphite or soot) by free halogen:

$$nO^{2-} + C\downarrow + nX_2\uparrow = 2nX^- + CO_n\uparrow, \quad (n=1;2), \qquad (1)$$

(where X denotes halogen) is considered to be the most convenient deoxidization procedure for the purification of halide
35 melts, especially if they contain Li^+ or multicharged metal cations.[4] However, there are no literature data on the duration of the purification processes in ionic halide melts and the efficiency of carbohalogenation from the viewpoint of residual concentration of oxygen-containing admixtures. There is no
40 information about kinetic features of the mentioned chemical reaction in molten salts at all. So, any estimations of conditions of optimal performing the purification process remain impossible. This makes topical the goal of this work: to obtain information about course of the carbohalogenation process in bromide melts

45 of KBr-NaBr (0.5:0.5, the melting point 911 K[5]), $BaBr_2$-KCl (0.51:0.49, the melting point 906 K[6]) and KBr-LiBr (0.4:0.6, the melting point 601 K[5]) compositions in 943-1023 K temperature range that allows tracing the effect of the oxoacidic properties of the melt and the temperature on the rate and completeness of the
50 purification from oxide ion impurities.

Experimental

The following chemicals ($BaBr_2$, KBr, LiBr and NaBr) of reagent quality ('Reakhim', Russia) were used to prepare the charge of the bromide melts. The charge compositions (mass fractions)
55 were 0.536:0.464 for KBr-NaBr equimolar mixture, 0.72:0.28 for $BaBr_2$-KBr eutectic and 0.48:0.52 for KBr-LiBr eutectic. For each experiment 50 g of salt mixtures were weighted.
KOH (99.9%) was melted in alundum crucible and kept for 1 h at 700 °C in argon atmosphere that provided complete removal of
60 absorbed water.
To create inert atmosphere in the potentiometric cell we used high-purity Ar (the volume fraction of the main substance was 0.9999), preliminarily dried by passing over P_2O_5 that provided deep purification from H_2O traces. This gas was used as a gas-
65 carrier for performing the carbohalogenation process.
The scheme of the potentiometric cell for determination of equilibrium O^{2-} molality is presented by the scheme:

$$(-)Pt\,|\,Ag\,|\,Ag^+ + \text{melt}\,||\,\text{melt} + O^{2-}\,|\,YSZ\,|\,Pt(O_2)(+), \qquad (2)$$
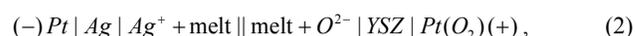
(where *YSZ* is the solid electrolyte membrane of 0.9 ZrO_2+0.1

RSC Advances Accepted Manuscript

Y_2O_3 composition produced at the Kharkov Plant of Refractory Materials). Its construction is described in detail elsewhere.[7] Cell (2) was initially calibrated with known amounts of KOH as a strong base (oxide ion donor)

$$2\,KOH \rightarrow 2K^+ + O^{2-} + H_2O \uparrow \qquad (3)$$

to obtain the dependences of *emf* vs. the equilibrium oxide ion molality ($m_{O^{2-}}$). In this work we also used the oxide ion index, $pO \equiv -\log m_{O^{2-}}$. The molalities of oxide ion during the carbohalogenation process were calculated using the calibration data.

The carbohalogenation routine consisted in the following. After calibration the oxide ion concentration in the studied melt was reduced to *pO* values within 3-4 by the addition of ammonium bromide which action is expressed by the following common scheme:

$$2NH_4Br + O^{2-} \rightarrow H_2O \uparrow + 2NH_3 \uparrow + 2Br^- . \qquad (4)$$

Then ground graphite powder (~0.5 g) was added to the melt and the gas-carrier saturated by bromine vapour at 273 K (p=8630 Pa) was bubbled through the melt at a rate of 75 ml min^{-1}. The carbohalogenation process was controlled by *emf* measurements performed each 30 sec during the initial 5 min, each 1 min in 5-10 min time period, each 2 min in 10-20 min time period and the next each 5 min up to the *emf* stabilization.

Results and Discussion

1   Molten KBr-NaBr equimolar mixture

Now let us consider the features of carbohalogenation of the molten KBr-NaBr equimolar mixture. Studying this process in the time we meet some essential difficulties, since it includes several stages. They are: dissolution of gaseous bromine in the melt, its reaction with oxide ions dissolved in the melt and insoluble graphite, removal of CO or CO_2 from the melt into gas phase. Another problem is contamination of the melt by the oxygen-containing admixtures from the crucible, electrodes and argon. And, finally, kinetic investigations usually imply creation of certain initial concentrations of the reagents. In the considered case we cannot saturate the melt with bromine and simultaneously prevent its reaction with other components before a certain starting moment. Therefore, the main task of the investigation consisted in separation of the chemical stage of this process and its investigation.

As is known, the rate of chemical reaction *w* is expressed using the reagent concentrations in such a manner:

$$w = k'' \cdot m_{Br_2}^{n_1} \cdot m_C^{n_2} \cdot m_{O^{2-}}^{n_3} . \qquad (5)$$

where k' is the rate constant; m_{Br_2}, m_C and $m_{O^{2-}}$ the concentrations of bromine, carbon and oxide ions in the melt and n_1, n_2 and n_3 the orders of the reactions with respect to the corresponding reagent. As to the acting concentrations, we can assert that the concentration of carbon in its saturated solution is constant (since the melt contacts with solid graphite) that permits
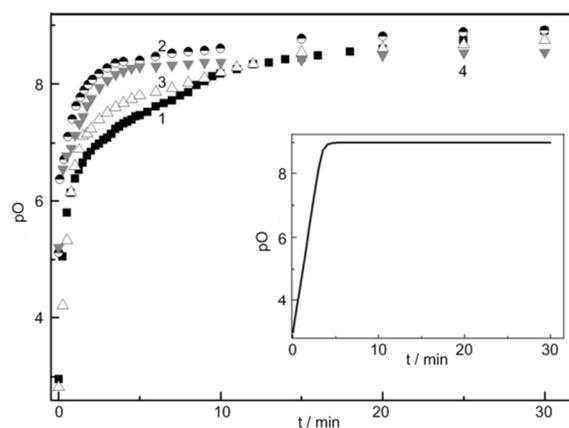

Fig. 1. pO − time (*t*) dependences obtained at carbohalogenation of the molten KBr-NaBr equimolar mixture at 943 (1), 973 (2), 1000 (3) and 1023 K (4).

to include this concentration into the rate constant and rewrite equation (5) as:

$$w = k'' \cdot m_{Br_2}^{n_1} \cdot m_{O^{2-}}^{n_3} . \qquad (6)$$

Further, the concentration of O^{2-} is varying till the rates of the melt purification and contamination become equal. Therefore, if we fit the conditions under which the concentration of bromine will be constant, we will be able to determine the order of this reaction with respect to the oxide ion and calculate the corresponding conditional rate constant. Since the constant partial pressure of bromine over the melt is provided, in the absence of the carbohalogenation process its concentration in the melt should be constant (the Henry law). This should be true if the consumption of the dissolved bromine for the melt treatment is negligible. In its turn, this means extremely low oxide ion concentrations. In this case equation (6) may be rewritten in the final form convenient for estimations:

$$w = k \cdot m_{O^{2-}}^{n_3} . \qquad (7)$$

The experimental dependences of *pO* vs. time (*t*) for the carbohalogenation process at different temperatures are presented in Fig.1. Within 30-40 min of the treatment they reach a plateau, which lies within *pO*=8.7-9. This corresponds to residual O^{2-} concentrations in the melt from $1\cdot10^{-9}$ to $2\cdot10^{-9}$ mol kg^{-1}. Although the shapes of these dependences are similar to the usual kinetic dependences, there are appreciable deviations. In particular, the curves presented in Fig.1 are constructed in 'log *m* - *t*' coordinates, and even in the case of the existence of the reverse process they should have the shape presented in the inset in Fig.1 for 1st kinetic order of the main process. Therefore, the carbohalogenation of the bromide melt is a complex multistage process which does not obey the kinetics of the 1st order.

To analyse it in detail, let us consider the same data, but presented in 'inverse concentration – time' coordinates which should be linear if the reaction running obeys the kinetics of the 2nd order (Fig.2).

This dependence divides the kinetic curve into three pronounced sections. The first of them lying in 0-7 min time range is convex towards the abscissa axis. The observed result is explained by the
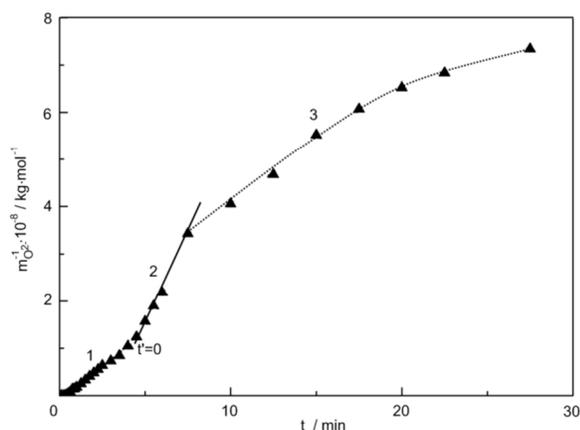
Fig. 2. $m_{O^{2-}}^{-1} - t$ dependence obtained at carbohalogenation of the molten KBr-NaBr equimolar mixture at 1000 K: section 1: the rate of the process is limited by the dissolution of Br_2 in the melt; section 2: the rate of the process is limited by the chemical reaction; t' the zero time for this section; section 3: a 'plateau', where the rates of the processes of purification of the melt from oxide ion traces and contamination by O^{2-} equalize.

fact that dissolution of gaseous bromine is accompanied with its simultaneous fast interaction with oxide ions in the melt. This reaction is similar to acid-base titration and, since bromine is supplied to the melts at a constant rate one can observe such a convex due to reduction of the buffer capacity of the solution with the subsequent decrease of the oxide ion concentration.

The beginning of the second section corresponds to low concentrations of O^{2-}, pO=7-8. Here the consumption of bromine for the reaction with oxide ions becomes negligible, its concentration is practically constant that permits to describe the reaction by Eq.(7). Since this section is linear in $m_{O^{2-}}^{-1} - t$ coordinates, we can ascribe the 2nd kinetic order to chemical interaction in the melt.

And finally, section 3 corresponds to the plateau in Fig.2. Here the rates of removal of the oxide ions from the melt and contamination of the melt by O^{2-} from oxygen-containing admixtures in argon and oxide constructional materials (alundum, *YSZ*) equalize.

So, we can select only the middle sections from all the dependences in Fig.1 as those which yield essential information about the course of the process of carbohalogenation. These sections in $m_{O^{2-}}^{-1} - t'$ coordinates (where t' is the time counted from the beginning of the section 2, as shown in Fig.2) are presented in Fig.3, and all of them are linear.

As is known, the slopes of such dependences are nothing but the rate constants. The slopes are seen from Fig.3 to increase with the temperature that agrees with the well-known phenomenon of the rise of the reaction rate with the temperature. The treatment of the plots from Fig.3 by the least square method yields the following conditional rate constants k (kg mol^{-1} min^{-1}): (2.20±0.2)·10^7 at 943 K, (2.44±0.3)·10^7 at 973 K, (2.86±0.4)·10^7 at 1000 K and (3.32±1)·10^7 at 1023 K. Using these values we construct the plot of ln k against the inverse temperature, which is described by the following equation:

$$\ln k = 22.06(\pm 1.5) - 4880\ (\pm 1400) \cdot T^{-1}. \tag{8}$$

The slope of this plot makes it possible to estimate the activation energy of this process as 41±12 kJ mol^{-1}. Just a relatively low
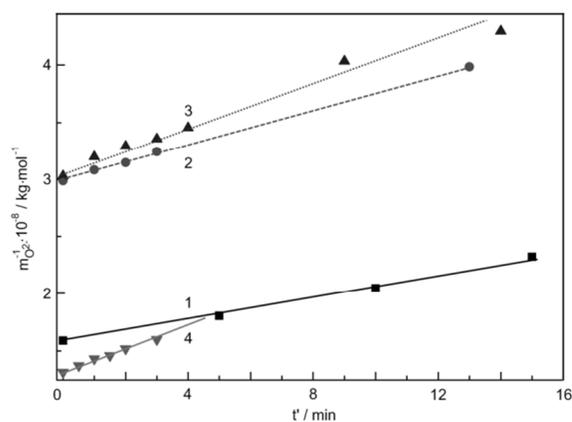

Fig. 3. $m_{O^{2-}}^{-1} - t$ dependences obtained at the carbohalogenation of molten KBr-NaBr mixture at 943 (1), 973 (2), 1000 (3) and 1023 K (4).

value of the activation energy gives rise to a slow growth of the rate of the studied deoxidization process with the temperature. So, the temperature does not essentially effect the duration and efficiency of the treatment of molten alkali metal bromides by 'C+Br$_2$' red-ox pair.

As for the thermodynamic characteristics of the formation of the activation complex (transition state), the value of $\Delta H^{\#}$ in the studied temperature range slightly decreases from 33.2 to 32.5 kJ mol^{-1}, and the entropy $\Delta S^{\#}$ is negative and decreases from -78.8 to -79.4 J mol^{-1}K^{-1}.

2 Molten BaBr$_2$-KBr and KBr-LiBr eutectic mixtures

The pO-t curves for these melts are similar to those obtained in the KBr-NaBr melt excluding ordinates of the plateau. The examples of these dependences are presented in Fig.4.
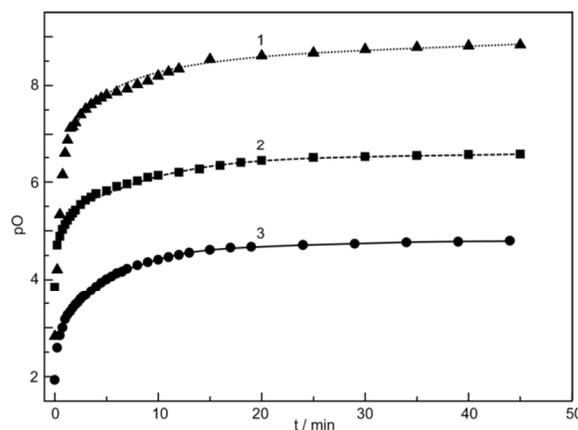

Fig. 4. pO − time (t) dependences obtained at carbohalogenation of the molten KBr-NaBr equimolar mixture (1), BaBr$_2$-KBr eutectic (2) and KBr-LiBr eutectic (3) at 1000 K.

As is seen, for molten KBr-NaBr the plateau is placed at pO=8.7, whereas the corresponding pO values are 6.6 for BaBr$_2$-KBr and 4.8 for KBr-LiBr. Such a decrease of pO takes place due to the rise of oxoacidic properties of the constituent cations of the melts in Na$^+$-Ba^{2+}-Li$^+$ sequence, and the strength of O^{2-} fixation considerably increases. The recent investigations of relative acidities of bromide melts[8,9] allow us to estimate the primary medium effects for oxide ions $-\log \gamma_{0,O^{2-},L}$ (where L is the designation of ionic melt) using its concentration analogue the
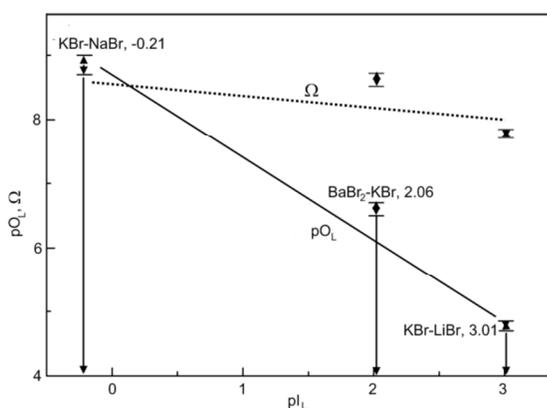
Fig. 5. Dependence of the purification limits of some bromide melts (expressed via instrumental pO_L and common oxoacidity function Ω) on their oxobasicity indices pI_L.

oxobasicity index $pI_L = -\log \gamma_{0,O^{2-},L}$ with respect to the molten KCl-NaCl equimolar mixture as the reference melt ($pI_{KCl-NaCl}=0$). On the basis of this estimation the melts discussed here are arranged in the sequence: KBr-NaBr ($pI_L=-0.21$)→BaBr$_2$-KBr ($pI_L=2.06$)→KBr-LiBr ($pI_L=3.01$).

Concerning the main task of the present paper it should be noted that the calculated oxoacidity parameters can be used to predict the limit of the melt purification depending on its acidity. From common considerations one can conclude that the increase of melt acidity retards the rate of purification and the stronger are the oxoacidic properties of the melt the higher is the residual concentration of oxide ions remaining after termination of the purification. However, the values of the common oxoacidity function of the purified melts, introduced by Tremillon et al.[10]

$$\Omega = pO_L + pI_L \, . \qquad (9)$$

(where pO_L is the instrumentally measured pO in a solvent of 'L' composition) are only slightly changed. The calculated data on purification of the bromide melts are presented in Fig.5. As is seen, the values of pO_L sequentially reduce together with the increase of the melt acidity (pI_L). Nevertheless, the degree of Ω changes is considerably lower (8-8.5) in comparison with the experimental errors. Thus, the purification threshold of bromide melts from oxygen-containing admixtures by carbohalogenation method expressed via Ω values is practically independent of the melt composition. This fact gives possibility to predict the purification limit (pO_L) for arbitrary melt if we know its oxoacidic properties (pI_L value) according to Eq.(9).

However, let us return to the kinetic data. Similarly to the KBr-NaBr melt, only the data belonging to the middle section of the 'concentration - time' curves can yield reliable information about the kinetics of the chemical stage of the purification process. These data for the mentioned BaBr$_2$-KBr and KBr-LiBr melts are presented in Fig.6, a and b, respectively.

The increase of the melt temperature results in somewhat increasing slopes of $m_{O^{2-}}^{-1} - t'$ dependences in both melts. The rate of the melt purification slightly increases with the temperature similar to the KBr-NaBr melt. The rate constants k (kg mol^{-1} min^{-1}) for the BaBr$_2$-KBr melt are: $(1.05\pm0.1)\cdot10^5$ at 943 K, $(1.33\pm0.06)\cdot10^5$ at 1000 K and $(1.42\pm0.2)\cdot10^5$ at 1023 K. As for the KBr-LiBr melt, the corresponding values are:

a

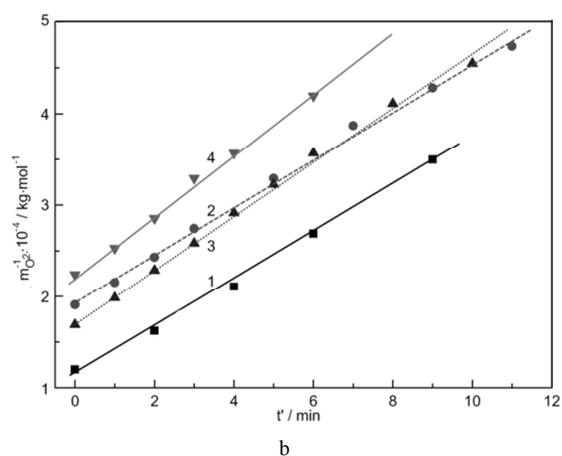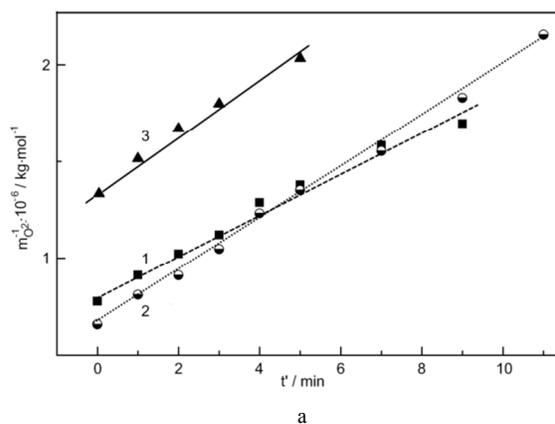b

Fig. 6. $m_{2-}^{-1} - t'$ dependences obtained at carbohalogenation of: a) molten BaBr$_2$-KBr mixture at 943 (1), 1000 (2) and 1023 K (3); b) molten KBr-LiBr mixture at 943 (1), 973 (2), 1000 (3) and 1023 K (4).

$(2.38\pm0.15)\cdot10^3$ at 943 K, $(2.62\pm0.15)\cdot10^3$ at 973 K, $(2.93\pm0.16)\cdot10^3$ at 1000 K and $(3.31\pm0.25)\cdot10^3$ at 1023 K.

The dependences of $\ln k$ vs. the reciprocal temperature can be presented by the following plots:

$$\ln k = 15.5 \, (\pm0.8) - 3700 \, (\pm800)\cdot T^{-1}, \qquad (10)$$

for the BaBr$_2$-KBr melt, and

$$\ln k = 12.02(\pm1) - 4011(\pm900)\cdot T^{-1} \qquad (11)$$

for the KBr-LiBr melt. Their slopes make it possible to estimate the values of the activation energies of the carbohalogenation process in all the melts and the thermodynamic characteristics of the activated complex formations in 943-1023 K temperature range. These values are presented in Table 1.

Table 1. Thermodynamic characteristics of activated complex formation at carbohalogenation of some bromide melts by 'C+Br$_2$' red-ox pair

Parameter\Melt	KBr-NaBr	BaBr$_2$-KBr	KBr-LiBr
E_a, kJ mol^{-1}	42±12	31±7	33±8
$\Delta H^{\#}$, kJ mol^{-1}	33.2÷32.5	23.2÷22.5	25.5÷24.8
$\Delta S^{\#}$, J mol^{-1} K^{-1}	-78.8÷-79.4	-133.8÷-134.5	-162.9÷-163.5

As is seen, the values of the activation energies of the carbohalogenation process in the studied bromide melts are close (30-40 kJ mol^{-1}). The elevation of the melt temperature from 943 to 1023 K gives rise to the increase of the purification rate only

by a factor of 1.4-1.5, whereas for the case of molten chlorides the rate of the carbochlorination process increases by a factor of 7 (compare, the activation energy of carbochlorination is *ca.* 200 kJ mol^{-1}).[11] This difference in the temperature effect on the carbohalogenation rate in molten chlorides and bromides is explained by different energies of bonding in substances used as halogen sources. In the case of bromide melts the halogenating agent is bromine and the strength of bonding in Br_2 molecule is 199 kJ mol^{-1}.[12] Chloride melts are treated by vapour of CCl_4 and breaking C-Cl bond in this molecule the energy *ca.* 340 kJ mol^{-1} is required.[13] Just the difference of the energies in Br–Br and C–Cl bonds estimated as 140 kJ mol^{-1} is the main cause of the observed distinction of activation energies of melt purification processes by action of CCl_4 and 'C+Br_2' red-ox pair (*ca.* 170 kJ mol^{-1}).

As for the enthalpies, they are positive since the process of the activated complex formation is endothermic. Negative values of the entropies of the activated complex formation show that the formation of the transmission state is accompanied with ordering. The trend for the ordering becomes more pronounced with the rise of the oxoacidic properties of the melts.

Conclusions

In the frames of this work, some questions connected with kinetic aspects of the processes lying in the basis of bromide melt purification are answered at first.

The kinetic order and rates of chemical interaction of oxide ions with halogenating agents were determined. The chemical stage of the carbohalogenation is described by the kinetic equation of the 2nd order with respect to oxide ions. The thermal dependences of the rate constants: ln k=22.06 ($\pm$1.5) – 4880 ($\pm$1400)$\cdot T^{-1}$ for KBr-NaBr, ln k=15.5 ($\pm$0.8) – 3700 ($\pm$800)$\cdot T^{-1}$ for BaBr$_2$-KBr and ln k=12.02($\pm$1)-4011($\pm$900)$\cdot T^{-1}$ for KBr-LiBr make it possible to estimate the activation energies of the carbohalogenation as 42$\pm$12 kJ mol^{-1}, 31$\pm$7 kJ mol^{-1} and 33$\pm$8 kJ mol^{-1}, respectively. Thermodynamic characteristics of the activated complex formation are also estimated.

The limits of purification for melts of different oxoacidic properties are determined. The obtained results give possibility to predict the similar characteristics for the purification of arbitrary melts in the case if its oxoacidic properties are known.

Notes and references

^{a} Institute for Scintillation Materials, National Academy of Sciences of Ukraine, 60, Lenin Ave., Kharkov, 61001, Ukraine.
Fax: +38 057 3404474 XXXX; Tel: XX +38 057 3410218; E-mail:
v_cherginets@ukr.net

1   B. Ramesh, E. Bourret-Courchesne and S. Derenzo, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2011, **652**, 260.
2   E. Bourret-Courchesne, G. Bizarri, S.M. Hanrahan, G. Gundiah, Z. Yan and S. Derenzo, *Nucl. Instrum. Methods Phys. Res., Sect. A,* 2010, **613**, 95.
3   A.Yu. Grippa, N.V. Rebrova, T.E. Gorbacheva, V.Yu. Pedash, N.N. Kosinov, V.L. Cherginets, V.A. Tarasov, O.A. Tarasenko and A.V. Lopin, *J. Cryst. Growth*, 2013, **371**, 112.
4   R.C. Pastor and A.C. Pastor, *Mat.Res. Bull.*, 1976, **11**, 1043.
5   I.I. Iliasov, *Zhurn. Neorg. Khim.*, 1962, **7**, 169.
6   R. Riccardi, C. Sinistri, G. Campari and A. Magistris, *Z. Naturforsch., A: Phys.Sci.*, 1970, **25**, 781.
7   V.L. Cherginets, *Oxoacidity: reactions of oxocompounds in ionic melts*, Elsevier, Amsterdam, 2005.
8   V.L. Cherginets, O.V. Demirskaya and T.P. Rebrova, *Molten salts forum*, 2000, **7**, 163.
9   R.G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.
10   R. Combes, J. Vedel and B. Tremillon, *Electrochim.Acta*, 1975, **20**, 191.
11   V.L. Cherginets, V.A. Naumenko, T.V. Ponomarenko and T.P. Rebrova, *Probl. Chem. Chem. Technol.*, 2012, No **5**, 154.
12   *Chemical Encyclopedia* (in 5 v.). V.1, Ed. L.I. Knunyants et al., Sovetskaya Entsyklopediya, Moscow, 1988.
13   *Short handbook of physicochemical magnitudes*, Ed. A.A. Ravdel and A.M. Ponomaryova, Khimiya, Leningrad, 1983.

$$C\downarrow + 2\ O^{2-} + 2\ Br_2\uparrow = CO_2\uparrow + 4\ Br^-$$
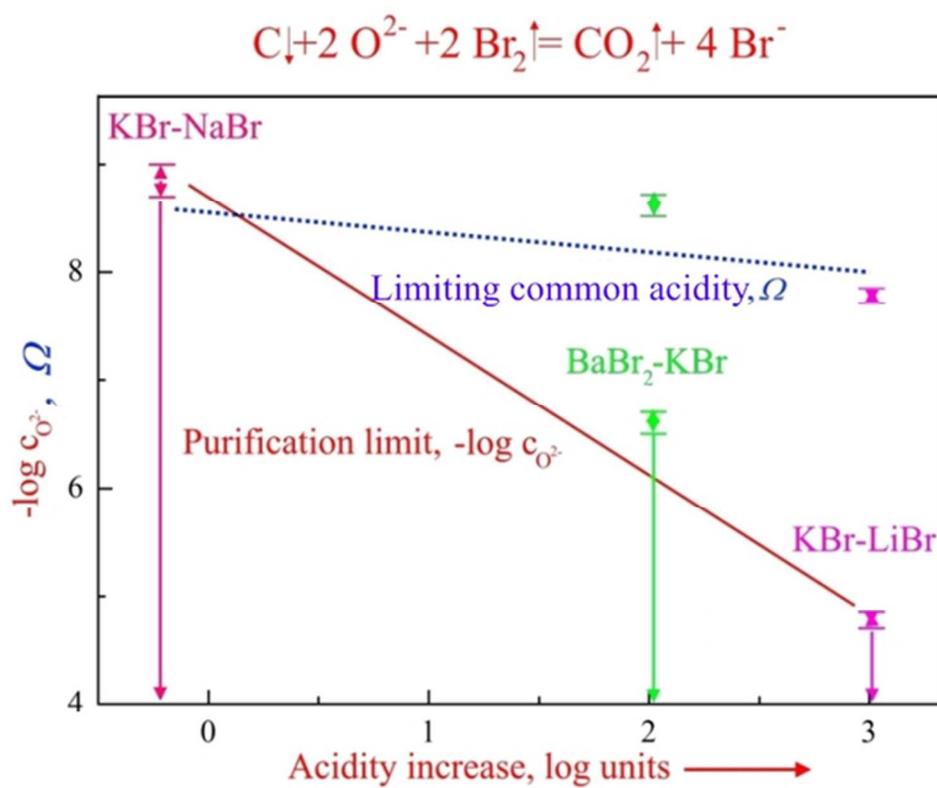
54x44mm (300 x 300 DPI)

The effect of bromide melt composition (oxoacidity) and temperature on carbohalogenation process course is studied. The corresponding kinetic order, rate constants and the activation energies are determined.