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Oxoacidic Properties of Melts of the $CsCl-LiCl-YCl_3$ System and Features of Their Purification from Oxide Ion Traces

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ABSTRACT: Acidic properties of $CsCl-yLiCl$ ($y = 0/0.5$) and $2CsCl-LiCl + yYCl_3$ ($y = 0/0.5$) melts at 700 °C were studied by the potentiometric method using an $Pt(O_2)|ZrO_2(Y_2O_3)$ membrane oxygen electrode. The acidity of these melts is found to rise together with y. The values of oxobasicity indices (pI_L or Ω for standard solutions) are 3.84 for the $CsCl-0.5LiCl$ melt and 5.55 for the $(2CsCl-LiCl)-0.5YCl_3$ melt. The main forms of fixation of O^{2-} by the studied melts are Li_2O in the $CsCl-LiCl$ system (the stability constant is $7.5 \cdot 10^4$, molar fraction) and YO^+ in the $CsCl-LiCl-YCl_3$ system (the stability constant is $1.9 \cdot 10^4$, molar fraction). The solubility of YOCl in the melt of the $2CsCl-LiCl-YCl_3$ composition is equal to 0.022 (molar fraction). Carbochlorination of the $2CsCl-LiCl-YCl_3$ melt by the products of CCl_4 pyrolysis in argon flow is described by a pseudo-order equal to 1, and the rate constant of this process is $(5.4 \pm 0.2) \cdot 10^{-3}$ min^{-1} at 700 °C. The time required for 10-fold and 100-fold purification from oxide ion traces is (420 and 840) min, respectively.

INTRODUCTION

Recent progress in the research of modern scintillation materials is connected with the development of materials based on mixed alkali and rare-earth (Ln) halides, in particular, K_2LaX_5:Ce^{3+} (where X is Cl, Br, or I)[1] or Cs_2LiYCl_6:Ce^{3+} (CLYC).[2] As a rule, the preparation routine of the corresponding single crystals includes the "wet" stage of the raw preparation, that is, the dissolution of oxide-based precursors (Li_2CO_3, Ln_2O_3, or LnO_2, where Ln is a lanthanide) in the corresponding aqueous hydrogen halides with subsequent drying of the synthesized raw under relatively soft conditions, melting, and the growth of the single crystals. The stage of drying is accompanied with interactions of the obtained mixed halides (mainly, their Ln-based component) with the residual water and oxygen traces according to the following equations:

$$LnX_3 + H_2O\uparrow \rightarrow LnOX + 2HX\uparrow \qquad (1)$$

or for Ln able to form compounds with the oxidation degree +4 (CeX_3):

$$2LnX_3 + 3H_2O\uparrow + 0.5O_2\uparrow \rightarrow 2LnO_2 + 6HX\uparrow \qquad (2)$$

Careful drying of the synthesized material (which means steady-equilibrium conditions) permits us to reduce the effect of the mentioned processes. Nevertheless, reactions 1 and 2 must not be neglected. Therefore, commercial obtaining of the mentioned material requires the data on the peculiarities of the above said oxidation or hydrolysis processes in the melts based on "alkali metal halide + rare-earth metal halide" mixtures. Such information will facilitate production of the said materials provided that procedures of the suppression of reactions 1 and 2 are found and investigated. In particular, there are two generally accepted ways of chloride melt purification from the traces of oxo-compounds which ensure the fixation of oxide ions in volatile compounds. The first and faster of them consists in passing HCl through the purified melt that shifts equilibrium (1) to the left; H_2O is the product of oxide ion fixation. Another way is the cocalled carbochlorination which consists in the action of "$C+Cl_2$" pair on the treated melt. The latter routine is realized in different ways, for example, passing CCl_4 or $CHCl_3$ through the melt or the action of Cl_2 on the melt containing suspended carbon black,[3] and CO or CO_2 are formed owing to the O^{2-} fixation. The main features of these purification methods are considered in ref 4.

The rate of the purification processes and completeness of their running is dependent on the oxoacidic properties of the melt, that is, its ability regarding oxide ions. The increase of the melt acidity results in a stronger fixation of O^{2-} (the common base) by the melt cation (acid) that, in its turn, impedes the purification process or makes it impossible. The principal scheme of this acid−base interaction may be presented by the following equation:

$$Me^{n+} + mO^{2-} \leftrightarrow MeO_m^{n-2m} \qquad (3)$$

The acidity of the given melt is a relative magnitude. Therefore, it should be determined with respect to a definite standard (reference melt). In earlier works[5,6] two Na^+-based melts, the equimolar mixture KCl−NaCl and CsCl−KCl−NaCl (0.455/0.245/0.30) eutectic, have been proposed as reference melts. For

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them the primary medium effect for O^{2-} ($\log \gamma_{0,O^{2-}}$) is considered to be 0. So, oxoacidic properties of a given melt "L" can be quantitatively estimated from the equilibrium constant (K_L) of the following reaction:

$$MeO^{(n-2)+} + 2Na^+ \rightleftharpoons Me^{n+} + Na_2O, K_L \quad (4)$$

The index of the K_L, $pI_L = -\log K_L$ (which is called "oxobasicity index"), may serve as a concentration analogue of ($\log \gamma_{0,O^{2-}}$).[6] The authors of ref 5 propose the Ω function (an analogue of the well-known Hammett function H_0) with the following physical sense: $\Omega = \log \gamma_{0,O^{2-}} - \log a_{L,O^{2-}}$ (where $a_{L,O^{2-}}$ is the activity of O^{2-} in melt "L"). In relation to mixed melts based on alkali and rare earth halides it should be emphasized that only one paper devoted to estimation of oxoacidic properties of the KCl−NaCl−$CeCl_3$ system has been published before.[7]

The purpose of the present work was to study the processes with the participation of oxide ions in the melts of the CsCl−LiCl−YCl_3 system at 700 °C. The melt of composition of 2CsCl−LiCl−YCl_3 is used for the growth of CLYC scintillation material (see ref 2). Therefore, the investigation was performed in the CsCl → 2CsCl−LiCl → 2CsCl−LiCl−YCl_3 sequence.

EXPERIMENTAL SECTION

Anhydrous YCl_3 was obtained by dissolution of "pure" Y_2O_3 (99.5 %) in "extra pure" HCl. Then NH_4Cl of reagent quality was added to the formed solution in the proportion of 4 mol of NH_4Cl to 1 mol of YCl_3.[8] Then the obtained mixture was slowly heated in vacuum (the pressure at the heating maintained lower than 10 Pa) with two 2 h stops at (200 and 400) °C up to complete sublimation of NH_4Cl. The obtained YCl_3 powder was melted and treated at 900 °C by argon saturated with vapor of CCl_4 at 20 °C (Ar and CCl_4 were preliminarily dried by P_2O_5) for a period of 10 h. Than molten YCl_3 was quenched to the room temperature and crushed in a drybox.

CsCl of reagent quality (99.9 %) was used for the experiments without additional purification. LiCl (99.9 %) was dried in vacuum (~1 Pa) at a slow increase of the temperature from room temperature to 400 °C. Afterward the dry salt was melted and treated by argon saturated with CCl_4 to remove oxide ion traces. Such a routine provided approximately equal concentrations of oxygen-containing admixtures in CsCl, LiCl, and YCl_3 (ca. 10^{-4} mol·kg^{-1}). This was especially important for the estimation of the oxoacidic properties of the mixed melts since the addition, for example, of LiCl to CsCl the concentration of O^{2-} in the obtained melts, remained practically the same.

"Extra pure" KOH (99.9 %) was melted in an alundum crucible and kept for 1 h at 700 °C in argon atmosphere for the removal of absorbed water.

The scheme of the potentiometric cell for the determination of equilibrium O^{2-} molality is as follows:

$$(-)\mathrm{Pt}|\mathrm{Ag}|\mathrm{Ag}^+ + \mathrm{melt}||\mathrm{melt} + O^{2-}|\mathrm{YSZ}|\mathrm{Pt}(O_2)(+) \quad (5)$$

(where YSZ is the solid electrolyte of 0.9 ZrO_2 + 0.1 Y_2O_3 composition, a production of the Kharkov plant of refractory materials). Its construction is described in detail elsewhere.[9] Cell 5 was initially calibrated with known amounts of KOH as a strong base

$$2KOH \rightarrow 2K^+ + O^{2-} + H_2O\uparrow \quad (6)$$

to obtain the dependences of emf (E) versus equilibrium oxide ion content. For estimation of the melt acidity we used the molar fraction of O^{2-} ($x_{O^{2-}}$), whereas for determination of the main products of reaction 3 in the studied melts molality, $m_{O^{2-}}$, or its negative index $pO \equiv -\log m_{O^{2-}}$ was more convenient. The potentiometric titration routine is described elsewhere.[9] To provide inert atmosphere in the cell, we used high-purity Ar (the volume fraction of the main substance was 0.9999). This gas was preliminarily dried by passing over P_2O_5 which provided deep purification from H_2O traces. For some kinetic experiments the initial gas was used without such drying.

RESULTS AND DISCUSSION

1. Oxoacidic Properties of the Mixtures of CsCl−LiCl−YCl_3 System. Since the 2CsCl−LiCl melt is intermediate in the studied CsCl → 2CsCl−LiCl → 2CsCl−LiCl−YCl_3 sequence, the calibration parameters of this melt are the most appropriate for the quantitative estimations. The dependence $E = f(-\log x_{O^{2-}})$ is expressed by the following equation (the experimental errors correspond to the confidence level 0.95):

$$E = 0.029(\pm 0.02) - 0.139(\pm 0.01)\cdot\log x_{O^{2-}} \quad (7)$$

The value of E for the initial 2CsCl−LiCl melt permits us to estimate the molar fraction of oxygen traces in it as approximately $5\cdot10^{-5}$.

We studied the oxoacidic properties of two systems: $(1-y)$(CsCl) + yLiCl (where y was varied from $9.12\cdot10^{-4}$ to $2.97\cdot10^{-1}$) and $(1-y)$(2CsCl−LiCl) + $y$$YCl_3$ (where y was varied from $1.14\cdot10^{-3}$ to $3.08\cdot10^{-1}$). The values of the initial amounts of Li^+ and Y^{3+} corresponded to the relation: $x_{Me^{n+}} \gg x^0_{O^{2-}}$. This gave us the possibility to consider the traces of O^{2-} as an indicator admixture (since its initial concentration underwent only small oscillations after the addition of the salts with practically the same concentration of oxygen admixtures) on the background of the studied melts. Taking into account that $pI_{CsCl} = -0.3$,[10] all of the oxobasicity indices were calculated with respect to this value as the reference one. For pI_L calculations, the following formula was used:

$$pI_L = -0.3 + \frac{E - E^*}{0.139} \quad (8)$$

where −0.3 was the oxobasicity index of CsCl; $E^* = 0.07$ V was the emf value of cell 5 measured in pure CsCl melt at 700 °C; 0.139 was the slope of the calibration plot (eq 7), V. The obtained and calculated data for CsCl−LiCl and CsCl−LiCl−YCl_3 systems are presented in Tables 1 and 2, respectively. Here w_{LiCl} and w_{YCl_3} are the weights of LiCl and YCl_3 (g), and m_{Li^+} and $m_{Y^{3+}}$ are the molalities of Li^+ and Y^{3+} (mol·kg^{-1}). The dependences $E = f(-\log x_{Me^{n+}})$ for the studied systems are presented in Figure 1. As is seen, both plots include a linear section at $-\log x_{Me^{n+}} < 2$, that is, the above-said condition $x_{Me^{n+}} \gg x^0_{O^{2-}}$ becomes true if $x_{Me^{n+}} \geq 100\, x^0_{O^{2-}}$. In all of the cases the oxoacidic properties of melts strengthen with the increase of the content of the cation possessing the strongest acidity (i.e., Li^+ for plot 1 and Y^{3+} for plot 2 in Figure 1). Thereat, $pI_{2CsCl-LiCl}$ is equal to 3.84, which is somewhat higher than the corresponding value for KCl−LiCl eutectic ($pI_{KCl-LiCl} = 3.5$[6]). The addition of Y^{3+} to 2CsCl−LiCl melt (that results in the formation of CsCl−LiCl + YCl_3 ternary melts) is accompanied with the strengthening of their acidity, and the oxobasicity index $pI_{2CsCl-LiCl+YCl_3}$ reaches a value of 5.55 at $x_{Y^{3+}} = 0.31$.

Table 1. Experimental and Calculated Data Obtained from the Study of Oxoacidic Properties of the CsCl (50 g) + LiCl System at 700 °C

w_{LiCl}	m_{Li^+}			E	$E - E^*$	
g	mol·kg^{-1}	x_{Li^+}	$-\log x_{Li^+}$	V	V	pI_L
0				0.070		−0.30
0.012	0.0003	0.0009	3.04	0.094	0.024	−0.13
0.215	0.005	0.0166	1.78	0.270	0.200	1.14
0.444	0.010	0.0336	1.47	0.343	0.273	1.66
0.634	0.015	0.0474	1.32	0.384	0.314	1.96
1.035	0.0244	0.0751	1.12	0.447	0.377	2.41
1.569	0.037	0.1096	0.96	0.499	0.429	2.79
2.131	0.050	0.1432	0.84	0.544	0.474	3.11
2.824	0.066	0.1814	0.74	0.569	0.499	3.29
3.902	0.092	0.2344	0.63	0.607	0.537	3.56
4.930	0.116	0.2789	0.55	0.642	0.572	3.82
5.397	0.127	0.2975	0.53	0.646	0.576	3.84

Table 2. Experimental and Calculated Data Obtained from the Study of Oxoacidic Properties of the CsCl−LiCl + YCl_3 System at 700 °C

w_{YCl_3}	$m_{Y^{3+}}$			E	$E - E^*$	
g	mol·kg^{-1}	$x_{Y^{3+}}$	$-\log x_{Y^{3+}}$	V	V	pI_L
0.031	0.0028	0.0011	2.94	0.663	0.593	3.97
0.087	0.0080	0.0032	2.5	0.677	0.607	4.07
0.301	0.0277	0.0108	1.97	0.699	0.629	4.23
1.642	0.1511	0.0562	1.25	0.752	0.682	4.61
2.881	0.2653	0.0947	1.02	0.787	0.717	4.86
6.014	0.5541	0.1794	0.75	0.836	0.766	5.21
11.983	1.1037	0.3033	0.52	0.878	0.808	5.51
12.304	1.1331	0.3089	0.51	0.883	0.813	5.55

The juxtaposition of the linear section of plot 2 (Figure 1) to the value $-\log x_{Y^{3+}}$ equal to 0.3 (that corresponds to CLYC composition) yields pI_{CLYC} = 5.86. According to the results of ref 4, the melts possessing p$I_L \geq 6$ cannot be purified from oxygen traces by passing HCl, and only carbohalogenation is suitable for this purpose. In contrast, for the melts of CsCl−LiCl system with p$I_L > 4$ oxide ion admixtures can be removed by treatment in HCl flow.

2. Composition of Oxide Ion Complexes in the CsCl−LiCl−YCl$_3$ System. In frame of the current study we can answer another question about the composition of the complexes formed by the oxide ion with constituent cations of the melts of the CsCl−LiCl−YCl$_3$ system. It is obvious that in melts of the CsCl−LiCl system the most acidic cation is Li$^+$, and at $x_{L^+} \gg x^0_{O^{2-}}$ its oxoacidic properties are determined by running of the following interactions:

$$n\mathrm{Li}^+ + \mathrm{O}^{2-} \rightleftharpoons \mathrm{Li}_n\mathrm{O}^{n-2}, K_{\mathrm{Li},n} \tag{9}$$

where $n = 1, 2, 3$. The material balance of O^{2-} can be presented as:

$$x^{\mathrm{o}}_{\mathrm{O}^{2-}}/x_{\mathrm{O}^{2-}} = 1 + \sum_{n=1}^{3} K_{\mathrm{Li},n} \cdot x^n_{\mathrm{Li}^+} \tag{10}$$

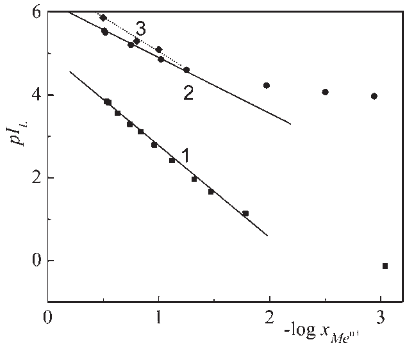

Figure 1. Dependence of the oxobasicity index (pI_L) of chloride melts vs the molar fraction index of the most acidic cation of melts ($-\log x_{Me^{n+}}$) at 700 °C. 1: CsCl + yLiCl (Me^{n+} = Li$^+$), 2: 2CsCl−LiCl + yYCl$_3$ (Me^{n+} = Y^{3+}), 3: literature data on KCl−NaCl + yCeCl$_3$.[7]

As for the melts of the CsCl−LiCl−YCl$_3$ system, the most acidic cation of these melts is Y^{3+}, and at $x_{Y^{3+}} \gg x^0_{O^{2-}}$ oxide ions may be fixed in complexes because of the following reactions:

$$n\mathrm{Y}^{3+} + \mathrm{O}^{2-} \rightleftharpoons \mathrm{Y}_n\mathrm{O}^{3n-2}, K_{\mathrm{Y},n} \tag{11}$$

where n = 2/3, 1, meaning that $Y_{2/3}O$ = 1/3Y_2O_3. The material balance of O^{2-} is as follows:

$$x^{\mathrm{o}}_{\mathrm{O}^{2-}}/x_{\mathrm{O}^{2-}} = 1 + K_{\mathrm{Y},2/3} \cdot x'^2 + K_{\mathrm{Y},1} \cdot x'^3 \tag{12}$$

Here $x' = x^{1/3}_{Y^{3+}}$. For both material balances (eqs 10 and 12) the value of $x^0_{O^{2-}}$ is known, and the $x_{O^{2-}}$ value is calculated from the calibration data of cell 5.

The mathematical treatment of the obtained data according to the above-said polynomial models (10 and 12) gives the following results. For the CsCl−LiCl system the values of $K_{Li,1}$ (corresponding to the formation of LiO$^-$) and $K_{Li,3}$ (corresponding to the formation of Li$_3$O$^+$) are statistically insignificant, and the interactions in this system may be described only by $K_{Li,2}$, which is equal to $(7.5 \pm 0.2) \cdot 10^4$ (P = 0.95) in the molar fraction scale. This means that Li$_2$O is the main product of O^{2-} fixation by Li$^+$ cations in CsCl−LiCl melts.

As to the CsCl−LiCl−YCl$_3$ system, the treatment shows that under the above-mentioned condition ($x_{Y^{3+}} \gg x^0_{O^{2-}}$ the value of $K_{Y,2/3}$ corresponding to formation of Y$_2$O$_3$ is statistically insignificant, and YO$^+$ is the only product of O^{2-} fixation. The stability constant of this complex on the background of 2CsCl−LiCl melt is $(1.9 \pm 0.3) \cdot 10^4$ (P = 0.95) in molar fraction scale. Taking into account the oxobasicity index of 2CsCl−LiCl melt (4.1) we can estimate the corresponding value for, say, the standard KCl−NaCl melt as $4.27 \cdot 10^{-9}$.

It should be noted that some questions connected with the formation of oxocompounds of rare earth elements in acidic melts (CaCl$_2$−KCl at 550 °C and KCl−LiCl at 450 °C) were considered earlier.[11−13] Authors of ref 11 studied the process of CeO$_2$ dissolution in the said melts. They found that the dissolution of this oxide after the treatment by gaseous HCl was practically complete and it was accompanied with the formation of the transparent solution of CeCl$_3$ in the KCl−LiCl melt. However, the interaction of CeCl$_3$ ($x_{Ce^{3+}} \approx 2.4 \cdot 10^{-3}$ in the CaCl$_2$−NaCl melt and $x_{Ce^{3+}} \approx 5 \cdot 10^{-3}$ in the KCl−LiCl melt) leads to the formation of CeOCl precipitate. Taking into account data of Table 2 we can assume that the pI_L index does not exceed 5; that is, such acidity of the melts gives HCl to be appropriate for the purification from O^{2-} traces.

Investigations of the dissolution of several other oxides in the KCl−LiCl melt[12] shows that La^{3+} and Pr^{3+} interact with O^{2-} forming the corresponding oxochlorides, whereas Y^{3+} forms Y_2O_3. This agrees with the data of ref 13 where lanthanides possessing ionic radii close to 0.1 nm according to ref 14 ($r_{La^{3+}} \approx 0.104$ nm, $r_{Ce^{3+}} \approx 0.102$ nm, $r_{No^{3+}} \approx 0.099$ nm, Belov/Bokii radii) form LnOCl and Gd_2O_3 formed by smaller cations ($r_{Gd^{3+}} \approx 0.094$ nm,[14] compare to $r_{Y^{3+}} \approx 0.097$ nm[14]) which did not react with the KCl−LiCl melt.

The obtained thermodynamic data permit us to interpret the practical data on the purification of the mixed melts based on alkali and rare earth metal chlorides. If carbohalogenation of the melt containing suspension of Ln_2O_3 is performed up to clearing of the melt, then the final product of this stage is not only $LnCl_3$ formed according to the reaction:

$$Ln_2O_3\downarrow + 3C + 3Cl_2\uparrow \rightarrow 2LnCl_3 + 3CO\uparrow \qquad (13)$$

but $LnCl_3$ and the saturated solution of oxohalide LnOCl:

$$Ln_2O_3\downarrow + C + Cl_2\uparrow \rightarrow 2LnOCl + CO\uparrow \qquad (14)$$

That is, only a third of the fraction of O^{2-} is actually removed in such a way. Taking into account that LnO^+ complexes are extremely stable, one can expect that its destruction by carbohalogenation process will be slower than breaking down of Ln_2O_3 due to both thermodynamic (the stability constant) and kinetic (escape of negatively charged O^{2-} ion from positively charged LnO^+ ion) reasons.

Now let us clear the problem of appropriateness of the distribution of the obtained results on other melts based on alkali and rare earth chlorides. For this purpose let us compare the data of this work with those of ref 7. The oxobasicity index of 0.9(KCl−NaCl) + 0.1$CeCl_3$ melt, taking into account the correlation made in our paper,[4] is estimated as 5.81, and the similar characteristic of 0.875 (2CsCl−LiCl) + 0.125YCl_3 melt is equal to 5.55. So, the acidic properties of different rare earth cations in halide melts could be considered as close. Ditto, the presence of Li^+ cations in these melts does not result in an appreciable change of their oxoacidic properties because of the leveling of the acidic properties of the Li^+ cation to those of the essentially stronger Ln^{3+}, which is a constituent cation of these melts, too.

It is of interest to determine YOCl solubility in molten Cs_2LiYCl_6, that is, the limiting content of this substance at which the melt for growing CLYC single crystals remains transparent. For this purpose we grew a single crystal from the melt being in the contact with YOCl and Y_2O_3 precipitates. The investigation was performed in an ampule providing separation of the precipitate in the bottom section. The melt was kept at 700 °C for a day and then quenched to the room temperature. The grown crystal was then dissolved in water, the precipitate was separated, and a quantity of Y in it was determined using voltamperometric method. The analysis show that a sample of CLYC (17.756 g) contains 0.060 g of Y in the insoluble in water form that corresponds to the molar fraction of the latter equal to 0.022 or 2.2 molar percent. So, visually transparent melts based on rare earth halides may contain traces of fixed oxygen on the level of several molar percent.

3. Some Kinetic Parameters of Purification of CsCl−LiCl−YCl_3 from Oxide Ion Traces. Finally, we would like to return to measurements of the rate of the carbohalogenation process taking place on the background of the Cs_2LiYCl_6 melt:

$$O^{2-} + (\text{pyrolized } CCl_4) \rightarrow \text{products} \qquad (15)$$

The experiment was performed by bubbling argon saturated with CCl_4 vapor at 20 °C through the said melt at 0.2 $dm^3 \cdot min^{-1}$. This should provide a constant concentration of the pyrolysis products (in ref 4 it is demonstrated that they are mainly Cl_2 and C_2Cl_4) in the atmosphere over the melt and, hence, in the melt. The measurements of E during this process using cell 5 make it possible to estimate $x_{O^{2-}}/x_{O^{2-}}{}^{o}$ ratio from the calibration data.

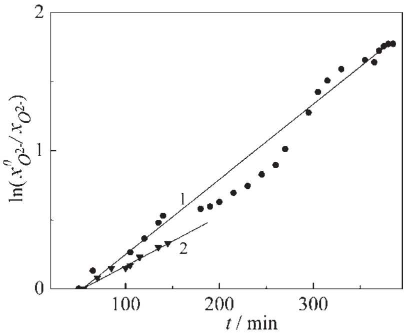

Figure 2. Dependence of ln $x_{O^{2-}o}/x_{O^{2-}}$ vs time of treatment of 2CsCl−LiCl−YCl_3 melt by the products of CCl_4 pyrolysis at 700 °C.

The rate constant of reaction 5 is expressed as:

$$v = k \cdot p_{pyr} \cdot x_{O^{2-}} = k' \cdot x_{O^{2-}} \qquad (16)$$

where v is the rate of reaction 5; k, its rate constant; p_{pyr}, the pressure of CCl_4 pyrolysis products over the melt. Since p_{pyr} remains unchanged during the experiment, it can be entered into the rate constant value yielding the conditional rate constant k'. So, under the experimental conditions the running of the said reaction should obey that of the first-order process. For these processes the dependence of ln $x^0_{O^{2-}}/x_{O^{2-}}$ versus time should be linear. Such dependences for the said process are presented in Figure 2.

Statistical treatment of the dependence 1 (Figure 2) obtained using dry argon confirms its linearity ($r_{xy} = 0.989$ at 23 degrees of freedom) at the confidence probability 0.9999. Plot 2 for as-supplied argon is linear at the same confidence probability ($r_{xy} = 0.986$ at 6 degrees of freedom). This confirms that the rate of the gas mixture bubbling is enough to provide the constant partial pressures of CCl_4 pyrolysis products over the melt.

From the slopes of dependences 1 and 2 (Figure 2) the values of the conditional rate constants can be estimated as $(5.4 \pm 0.2) \cdot 10^{-3}$ min^{-1} and $(3.5 \pm 0.3) \cdot 10^{-3}$ min^{-1}, which corresponds to half-transformation periods of the purification process equal to (128 and 198) min.

The obtained parameters permit us to estimate the duration of the purification processes. For instance, it is approximately 420 min for 10-fold purification of the melt from O^{2-} traces and about of 840 min for the 100-fold purification.

It is interesting to note that the carbochlorination process of Y_2O_3 precipitate in molten KCl−LiCl was studied in ref 12. The authors found that the treatment of the melt by C + Cl_2 Red−Ox pair led to the efficiency of the process of about of 0.97 for 60 min treatment (i.e., 30-fold purification). The estimation of the rate constants (ref 12, Table 11, the data for Nd_2O_3, 700 °C) yields (0.01 to 0.015) min^{-1}. From our data it follows that the 30-fold purification can be achieved after 600 min of the treatment; that is, the purification is slower by a factor of 10. This can be explained by the fact that the pI_L index for KCl−LiCl + Y_2O_3 after chlorination approaches 5, whereas the corresponding value for the CsCl−LiCl + YCl_3 + Y_2O_3 (or YOCl) system exceeds 6. Owing to this reason, the acidity of the latter system exceeds that of KCl−LiCl + Y_2O_3 by a factor of 10, too. So, the obtained results are in a good agreement with the data of ref 12.

CONCLUSIONS

Investigations of the oxoacidic properties of CsCl−yLiCl (y = 0/0.5) and 2CsCl−LiCl + $y$$YCl_3$ (y = 0/0.5) melts at 700 °C show that their acidity rises with the concentration of the most acidic component (Li^+ and Y^{3+}, respectively) in the molten mixtures. The oxobasicity index values (pI_L or Ω for standard solutions) change from −0.3 for pure CsCl to 3.84 for the CsCl−0.5LiCl melt and 5.55 for the (2CsCl−LiCl)−0.5YCl_3 melt.

This work permits us to identify the main products formed by oxide ions in the studied melts. They are Li_2O in the CsCl−LiCl system (the stability constant is $7.5 \cdot 10^4$, molar fraction) and YO^+ in the CsCl−LiCl−YCl_3 one (the stability constant is $1.9 \cdot 10^4$, molar fraction).

The solubility of YOCl in the melt of the 2CsCl−LiCl−YCl_3 composition used for the growth of scintillation crystals is determined as 0.022 (molar fractions). Therefore, the visually transparent growth melt can contain a considerable amount of oxygen-containing admixtures, worsening the quality of the final product.

Carbochlorination of the 2CsCl−LiCl−YCl_3 melt by the products of CCl_4 pyrolysis in argon is characterized by a pseudo-order equal to 1, and the rate constant is $(5.4 \pm 0.2) \cdot 10^{-3}$ min^{-1} at 700 °C. The times required for 10-fold and 100-fold purification from oxide ion traces are estimated as (420 and 840) min. The use of supporting gas (Ar) without additional purification by P_2O_5 retards the purification process because of the presence of H_2O traces.

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