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Some physicochemical aspects of oxo-species formation in melts of CsBr–LiBr and CsBr–LiBr–YBr_3 systems at 973 K

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Interactions between the admixture oxo-species (as O^{2-} donors) and the most acidic cations being the basis of the melts of CsBr + LiBr and (2CsBr–LiBr) + YBr_3 systems containing different amounts of LiBr and YBr_3, respectively, were studied at 973 K by the potentiometric method with the use of $Pt(O_2)|YSZ$ membrane oxygen electrode as reversible to O^{2-}. The addition of LiBr to CsBr melt up to $x_{LiBr} = 0.33$ (x is mole fraction) results in the formation of Li_2O as the main product, $K_{(x,Li2O)} = (6.1\pm1)\cdot10^4$. The formation of LiO^- is almost statistically insignificant 2CsBr–LiBr melt at 973 K is characterized by the upper limit of basicity due to the limited solubility of Li_2O ($1.23\cdot10^{-2}$ mol·kg^{-1}). The addition of YBr_3 to 2CsBr–LiBr melt leads to the formation of YO^+ complex and its stability constant is $K_{(x,YO+)} = 2.4(\pm0.1)\cdot10^2$. Together with the composition of the oxo-species the oxobasicity indices, pI_L of the said systems were estimated as 3.62 for 2CsBr–LiBr melt and 4.74 for 0.99(2CsBr–LiBr)–0.01YBr_3 one. The obtained characteristics are close to those of the analogous chloride systems.

Keywords: cesium bromide, lithium bromide, yttrium bromide, melts, potentiometry, oxoacidity, complexation, solubility.

Деякі фізико-хімчні аспекти утворення оксосполук у розтопах систем CsBr–LiBr і CsBr–LiBr–YBr_3 при 973 К. *В.Л.Чергинець, О.Л.Ребров, О.Ю.Гриппа, Т.П.Реброва, Т.В.Пономаренко, Н.В.Реброва, А.Г.Варич, О.І.Юрченко, В.В.Соловйов*

Взаємодії між домішковими оксосполуками (донорами оксид-іонів) і найбільш кислотними катіонами що входять до основи розтопів CsBr + LiBr та (2CsBr–LiBr) + YBr_3 зі змінним вмістом LiBr і YBr_3, відповідно, були досліджені при 973 К потенціометричним методом з використанням мембранного електроду $Pt(O_2)|YSZ$ у якості індикаторного до іонів O^{2-}. Додавання LiBr до розтопленого CsBr до $x_{LiBr} = 0,33$ (x — молярна частка) веде до утворення Li_2O як основного продукту взаємодії $K_{(x,Li2O)} = (6.1\pm1)\cdot10^4$. Утворення комплексу LiO^- в цих умовах є статистично незначимим. Розтоп 2CsBr–LiBr при 973 К має верхню межу основності (концентрації O^{2-}) що обумовлено обмеженою розчинністю в ньому Li_2O ($1,23\cdot10^{-2}$ моль·кг$^{-1}$). Додавання YBr_3 до розтопу 2CsBr–LiBr приводить до утворення комплексу YO^+ з константою стійкості $K_{(x,YO+)} = 2.4(\pm0.1)\cdot10^2$. Було розраховано індекси оксоосновності (міра кислотних властивостей розтопу), pI_L досліджених систем, вони дорівнюють 3,62 для розтопу 2CsBr–LiBr і 4,74 для розтопу 0.99(2CsBr–LiBr)–0.01YBr_3. Одержані характеристики є близькими до відповідних параметрів аналогічних хлоридних систем.

1. Introduction

Molten alkali metal halide mixtures containing lithium halides, such as CsX–LiX or KX–LiX (X = Cl,Br), or those doped with a rare earth (Ln) halide are of great interest for modern industry and material science. The reason consists, mainly, in the low melting point of the similar multicomponent eutectics that provides the wide use of this mixtures as the main electrolytes in high-temperature power sources [1] and for the separation of spent nuclear fuel components [2, 3]. As for rare earth halide doped systems, they can be used as growth melts for obtaining single crystals of $Cs_2LiLnX_6{:}Ce^{3+}$ composition which are used as common scintillators or neutron detectors (if the ^6Li-enriched lithium salts are used for the material preparation) [4, 5].

Naturally, the present-day prospective of the above-said molten mixtures application requires additional studies devoted to the determination of the essential physicochemical characteristics of these melts and the corresponding investigations are known [6, 7]. The use of rare earth or heavy metal salts as components of the practically important systems requires information about the affinity of their main components to oxide-ions which originates due to the interactions of raw chemicals or charge with water and oxygen from atmosphere since the obtaining process of these melts usually pass through the stages of wet synthesis, drying (dehydration) and melting. If these melts are used for the obtaining of crystals the stages of melting, crystal growth from the melt and final treatment (cutting, polishing etc.) are added.

The contamination of rare earth halide containing growth melts results in the presence of appreciable amounts of LnO^+ (LnOX) and Ln^{3+} (LnX_3) ions in them that can cause distortion /worsening of the functional properties of the final product. The course of oxygen-containing admixture removal is considerably dependent on the affinity of the main charge materials (and their melts) to oxide-ions and the corresponding information should be very helpful for estimation of the efficiency of the common deoxidization processes [8].

Unfortunately, such information is rare and the works [9, 10] where some oxoacidic properties of $KCl–NaCl–CeCl_3$ and $CsCl–LiCl–YCl_3$ systems were reported can be presented as examples. Similar bromide mixtures were not studied before.

The goal of this work is to investigate the interactions of melts of CsBr+yLiBr and $(2CsBr–LiBr)–YBr_3$ compositions with O^{2-} (originated from admixture oxygen-containing substances), to determine the main forms of oxocomplexes and the corresponding equilibrium constants and the estimate the oxoacidic properties of $CsBr–LiBr–YBr_3$ melts of different compositions.

2. Experimental

Cesium bromide of 4N purity,"Reakhim" was used without purification. The preliminary measurements showed that due to the presence of oxygen-containing admixtures the equilibrium concentration of O^{2-} was ca. $x_{O^{2-}} = 2{\cdot}10^{-5}$ (x meant mole fraction scale). The said concentration serves as inner standard lying in the basis of calculation of the interactions running in the saline mixtures.

Extra pure Li_2CO_3, 4N, was the starting material for obtaining lithium bromide. This compound taken with 5 % excess was dissolved in aqueous HBr of reagent quality. The solution was filtered from the excess of Li_2CO_3 and acidified with HBr to pH of *ca.*3. Then, NH_4Br of reagent quality was added in a ratio of 0.5 mole per 1 mole of LiBr and the obtained solution was evaporated, dried and heated at vacuum of 5 Pa at stepwise increase of the temperature up to 500°C with stops at 200 and 400°C for an hour. After 2 h holding at 500°C the salt was cooled to the room temperature and kept in the glove box.

YBr_3 was prepared by the dissolution of Y_2O_3 (reagent quality) in the excess (5 %) of aqueous HBr of reagent quality and extra pure NH_4Br (6 mole per 1 mole of YBr_3) was added to the formed solution. This solution was dried and heated in vacuum up to 600°C with stops at 200 and 400°C for an hour. After 2 h holding at 600°C the salt was cooled to the room temperature, repacked and kept in the glove box.

Potassium hydroxide, KOH (reagent quality) was melted and kept in Ar atmosphere for 2 h at 600°C that provided quantitative removal of the absorbed water.

The Lux-Flood acid-base equilibria in CsBr+LiBr and $(2CsBr–LiBr)+YBr_3$ systems were studied on the basis of controlling the O^{2-} equilibrium molality in the melt after addition of known amounts of LiBr to molten CsBr or YBr_3 to CsBr–LiBr melt, respectively. The principal scheme of potentiometric cell for oxide ion determination is as follows

$$(-)\mathrm{Pt}|\mathrm{Ag}|\mathrm{Ag}^{+} + melt \vdots\vdots\ melt + \mathrm{O}^{(2-)}|\mathrm{YSZ}|(\mathrm{O_2})\mathrm{Pt}(+), \quad (1)$$

where YSZ is 0.9 ZrO_2 + 0.1 Y_2O_3 ceramics test-tube and its construction is described in detail in [8]. The descriptions of the experimental routine and the sequential addition method (SAM) are also presented there.

High-purity argon, 5N, additionally purified by passing over P_2O_5 was used to prevent an interaction between the melt and the atmosphere. O_2 and H_2O concentrations in the inert gas were $3 \cdot 10^{-3}$ vol.% and $2 \cdot 10^{-3}$ vol.%, respectively.

3. Results and discussion

We chose 2CsBr–LiBr composition as the reference one since it is an intermediate in the CsBr → 2CsBr–LiBr → 2CsBr–LiBr–YBr_3 sequence. This melt is neither eutectic (the eutectic point corresponds to $x_{\mathrm{LiCl}} = 0.62$) nor peritectic (there is and incongruent compound of $CsLiBr_2$ composition in CsBr–LiBr system) [11]. The plot of emf (E, mV) of cell (1) vs.pO ($pO \equiv -\log a_{\mathrm{O}^{2-}} \approx -\log m_{\mathrm{O}^{2-}}$, $a_{\mathrm{O}^{2-}}$ and $m_{\mathrm{O}^{2-}}$ are activity and molality of O^{2-}, respectively) is presented in Fig. 1.

As is seen, the E–pO plot contains some features. Sections a and b are usual for the calibrations of the membrane oxygen electrode Pt(O_2)|YSZ in molten halides [7]. The section a above the inflection point isreferred to the region with low oxide ion concentration and here the oxygen electrode is reversible to O^{2-} according to the equation

$$\frac{1}{2}\mathrm{O_2} \uparrow + 2\bar{e} = \mathrm{O^{2-}} \quad (2)$$

and it can be approximated by the following equation:

$$E = 23(\pm 20) + 91(\pm 8) \cdot pO, \text{ mV}. \quad (3)$$

These data were used for the calculation of the equilibrium molalities of oxide ions in the melts and for the estimation of the oxoacidic properties of the latter since the common content of oxide ions was low and their equilibrium concentration in the studied melts only reduced due to additions of acidic cations like Li^+ or Y^{3+}.

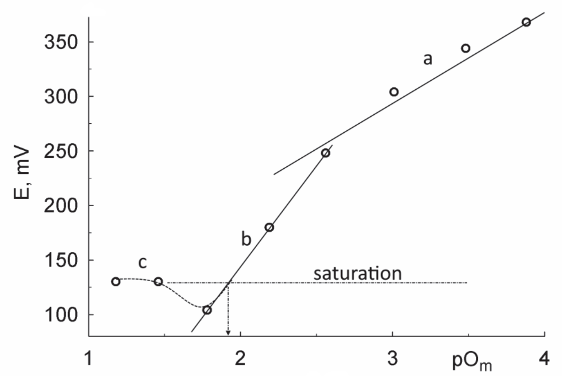

Fig. 1. The dependence of E of cell (1), mV vs.pO_m (molalities) in 2CsBr–LiBr melt at 700°C: a — the calibration plot, upper section (Eq. 2 and 3), b — the calibration plot, lower section (Eq. 4 and 5), c — the saturated solution region.

The increase of oxide ion concentration in 2CsBr–LiBr melt results in the slope change and the section b corresponds to the electrochemical process:

$$\frac{1}{2}\mathrm{O_2^{2-}} \uparrow + 2\bar{e} = \mathrm{O^{2-}} \quad (4)$$

called "peroxide function" and the approximation equation is as follows:

$$E = -224(\pm 5) + 185(\pm 2) \cdot pO, \text{ mV}. \quad (5)$$

At the decrease of pO the dependence passes through the minimum and reaches the plateau where the equilibrium concentration of oxide ion remains constant.Similarly to other investigations [12] it can be concluded that at this point the melt becomes saturated with respect to Li_2O. The existence of the minimum in the calibration plot gives a certain information about interaction between KOH with CsBr–LiBr melt. The addition of the solid alkali leads to the immediate formation of solid Li_2O:

$$2\mathrm{KOH}(\downarrow) + 2\mathrm{Li^+} \rightarrow \mathrm{Li_2O}\downarrow + 2\mathrm{K^+} + \mathrm{H_2O}\uparrow \quad (6)$$

which further dissolves in the melt. If the added amount of O^{2-} corresponds to points at sections 1 and 2 (excluding the minimum point) then Li_2O dissolves completely, however, the addition corresponding to the saturation point results only in partial dissolution of the formed Li_2O powder. So, under the equilibrium conditions there exists the saturated melt in contact with powder consisting of particles with considerably smaller final sizes than initial ones. Such powder possesses higher solubility comparing to the initial one due to the Ostwald-Freundlich rule:

$$\frac{2.3RTd}{2\sigma M}\log\frac{s_2}{s_1} = \frac{1}{r_2} - \frac{1}{r_1}, \qquad (7)$$

where s_1 and s_2 are the solubilities of powders of the particle radii r_1 and r_1, respectively, R the universal gas constant, T the absolute temperature, d the density, σ surface energy and M the molar mass.

The following additions of KOH result in the formation of Li_2O powder whose particles do not undergo dissolution and, therefore, the average particle radius increases causing the decrease of the solubility. As is seen from Fig. 1, the minimum depth is 26 mV (0.14 *pO* units) that agrees with the data obtained in KCl–NaCl melt at 1000 K [13]. We can conclude from this agreement that common regularities of solid oxide dissolution in alkali halide melts remains practically the same regardless cation and anion melt composition. On the basis of the minimum depth the mole surface energy on "Li_2O-melt" boundary can be estimated within 35–40 $J \cdot m^{-2}$.

It is obvious that for the Li_2O solubility we should choose the lowest values, corresponding to the particles with the smallest size changes and using the calibration data the value of *pO* in the saturated solution region can be estimated as 1.91 and the solubility product of Li_2O according to the following equilibrium:

$$Li_2O \leftrightarrows 2Li^+ + O^{2-},\ K_{s,Li_2O} = c^2_{Li^+} \cdot c_{O^{2-}} \qquad (8)$$

is equal to $4.6 \cdot 10^{-2}$ $mol^3 \cdot kg^{-3}$ that corresponds to $2.3 \cdot 10^{-4}$ in mole fractions. The obtained solubility parameters are lower than those in 2CsCl–LiCl melt at 973 K ($2.2 \cdot 10^{-1}$ $mol^3 \cdot kg^{-3}$ and $4.5 \cdot 10^{-4}$, respectively). This can be explained by lower oxoacidic properties of bromide melts comparing with their chloride analogs [14] that results in the oxide solubility decrease.

The interactions between Li^+ and O^{2-} ions in CsBr (basic melt) — LiBr (addition) + O^{2-} (residual admixtures) system were studied by sequential additions of LiBr to CsBr melt. To determine equilibrium constants we assumed that the addition of Li^+ to CsBr melt leads to interactions:

$$n,Li^+ + O^{2-} \leftrightarrows Li_nO^{n-2}, K_{Li,n},\ n = 1,2. \qquad (9)$$

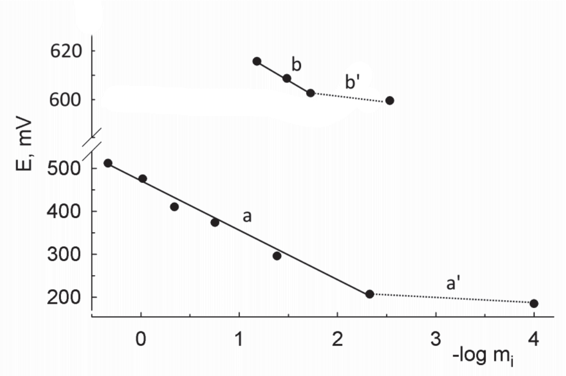

Fig. 2. The dependence of E of cell (1) vs. concentration of the most acidic cation of the melt ($-\log m_i$) at 700°C: a, a′ — CsBr + LiBr, $i = Li^+$, b, b′ — 2CsBr–LiBr + YBr_3, $i = Y^{3+}$.

For this system of equilibriums the material balance with the respect to oxide ions can be presented by the following equation:

$$\frac{m^0_{O^{2-}}}{m_{O^{2-}}} = 10^{(E^* - E_{CsBr})/91} = 1 + K_{Li,1} \cdot m_{Li^+} + K_{Li,2} \cdot m^2_{Li^+}, \qquad (10)$$

where E^* is emf value of melt after Li^+ addition to pure CsBr, E_{CsBr} is emf value of cell (1) in "pure" CsBr (185 mV) and 91 is the slope of *E–pO* plot (3), mV.

The dependence of E vs. logarithm of Li^+ molality in CsBr–LiBr melts is presented in Fig. 2 (dependence a′, a).

The slope of the linear section of this plot is equal to 116±10 mV, i.e., it is essentially higher than the calibration plots one (Fig. 1, section a). This can be explained by the formation of Li_2O as one of the products of Li^+–O^{2-} interactions in the melts of CsBr–LiBr system. As it was explained in [10], the dependence of E vs.$\log m_{Li}{}^+$ becomes linear in the case where the concentrations of Li^+ ion considerably exceed that of O^{2-} (dependence "a"), therefore, the deviations at $\log m_{Li}{}^+$ (dependence "a′") are explained by the fact that in the vicinity of this point Li^+ and O^{2-} concentrations become comparable (experiment gives $\log m_O{}^{2-} \approx 2.7$ and $m_O{}^{2-} = 1.7 \cdot 10^{-3}$ $mol \cdot kg^{-1}$).

The processing of the obtained potentiometric data results in the following equilibrium constant values (in mole fraction scale): $K_{Li,1} = 1.3(\pm 1) \cdot 10^4$ and $K_{Li,2} = 6.1(\pm 1) \cdot 10^4$ at good coincidence of the experimental data (points of dependence "a") with the calculated one (line "a"). It is seen that the value of constant of LiO^- complex formation is practically equal to the statistical zero. Nevertheless, comparing with the analogous chloride system this equilibrium becomes pronounced due to some weakening

Table 1. The experimental and calculated data on oxoacidic properties estimations of (1–y)CsBr–yLiBr and (1–y)[2CsBr–LiBr] + yYBr$_3$ systems at 973 K ("y" the mole fraction)

y	E, mV	pI_L
System (1–y)CsBr–yLiBr		
$8.76 \cdot 10^{-3}$	296	1.22
$3.73 \cdot 10^{-2}$	374	2.08
$9.58 \cdot 10^{-2}$	410	2.47
$1.98 \cdot 10^{-1}$	476	3.20
$4.31 \cdot 10^{-1}$	512	3.59
(1–y)[2CsBr–LiBr] + yBr$_3$		
$4.92 \cdot 10^{-4}$	600	4.56
$3.16 \cdot 10^{-3}$	603	4.59
$5.48 \cdot 10^{-3}$	609	4.66
$1.11 \cdot 10^{-2}$	616	4.74

of acidic properties of bromide system. The study of the chloride system CsCl–LiCl [10] confirmed only one equilibrium of Li_2O formation with $K_{Li,2} = 7.5(\pm 0.2) \cdot 10^4$.

Due to the fixation of oxide ion in the above oxo-complexes the addition of LiBr to CsBr melt results in the increase of its oxoacidic properties. The oxobasicity index [6] for the studied systems can be estimated according to the following formula [10]:

$$pI_L = (E^* - E_{CsBr})/91, \qquad (11)$$

i.e.,it is the difference between acidity of pure CsBr and the melt obtained after addition of LiBr amount. The values of the oxoacidity estimations for some of the studied systems are presented in Table 1.

The oxobasicity index pI_L for 2CsBr–LiBr melt can be estimated by juxtaposition of the obtained plot "a" (Fig. 1) as 3.62 that is lower than the corresponding value for 2CsCl–LiCl melt — 4.1 that also confirms the weakling of the oxoacidic properties going from bromide melts to the chloride ones with the same cation composition.

To complete the oxoacidity data for CsBr–LiBr–YBr$_3$system we performed the similar potentiometric investigations of [2CrBr–LiBr] (basic melt) — YB$_3$ (addition) + O^{2-} (residual admixtures) system (the logarithmic dependence is presented in Fig. 2, dependence 2). However, the extremely high sensitivity of YBr$_3$ to moisture and oxygen in pure argon gave possibility to make investigations in relatively narrow concentration range. We found that the values of the oxobasicity indices for 2CsBr–LiBr melt containing $5.48 \cdot 10^{-3}$ and $1.11 \cdot 10^{-2}$ mole fractions of YBr$_3$ are 4.59 and 4.74 that agrees with the corresponding parameters of (1– y)[2CsCl–LiCl] + yYCl$_3$ system (4.37 for $y = 3.2 \cdot 10^{-3}$ and 4.53 for $y = 1.0 \cdot 10^{-2}$). The complex composition corresponds to YO$^+$ and the constant of the process:

$$Y^{3+} + O^{2-} \leftrightarrows YO^{+};\ K_{Y,1}, \qquad (12)$$

on the background of 2CsBr–LiBr melt was estimated as $2.4(\pm 0.1) \cdot 10^2$. This value is close to the corresponding value for YO$^+$ in 2CsCl–LiCl melt ($3.1 \cdot 10^2$) [10].

4. Conclusions

Interaction of Li$^+$ cations with O^{2-} in molten CsBr–LiBr results in the formation of Li_2O in the solution, $K_{Li,2} = =(6.1 \pm 1) \cdot 10^4$ (mole fractions) while the formation of other product of LiO$^-$ composition is not entirely confirmed, $K_{Li,1} = (1.3 \pm 1) \cdot 10^4$. The solubility product of Li_2O in 2CsBr–LiBr melt is 0.046 mol^3·kg^{-3} that corresponds to $2.3 \cdot 10^{-4}$ in mole fraction scale.

Investigations of the oxoacidic properties of (1–y)CsBr–yLiBr ($y = 0 \div 0.5$) and (1–y)[2CsBr–LiBr]+yYBr$_3$ ($y = 0 \div 0.01$) melts at 700°C shows that their acidity rise with the concentration of the most acidic component(Li$^+$ and Y^{3+}, respectively) in the molten mixtures. The oxobasicity index values (pI_L) is 3.62 for 2CsBr–LiBr melt, and 4.74 for 0.889[2CsBr–LiBr] + 0.011YBr$_3$ melt. The obtained oxoacidity estimations correspond to the similar parameters of the analogous chloride melts. The formation constant of YO$^+$ complex on the background of 2CsBr–LiBr melt is $2.4(\pm 0.1) \cdot 10^2$.

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