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On metal oxide solubilities in some molten alkali metal bromides at $T = 973$ K

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Reactions of Me^{2+} cations with O^{2-} in molten (KBr + NaBr) (0.5:0.5) and (KBr + LiBr) (0.4:0.6) mixtures at $T = 973$ K were studied by potentiometric titration method using $Pt(O_2)|ZrO_2(Y_2O_3)$ indicator electrode. In the former melt, the set of cations available for investigation was wide enough (Me = Sr, Ca, Mn, Co, Ni and Pb) and the corresponding solubility product indices ($pK_{s,MeO}$, molalities) were found to be (3.81 ± 0.3) (SrO), (5.00 ± 0.3) (CaO), (7.85 ± 0.3) (MnO), (8.80 ± 0.1) (CoO), (9.72 ± 0.04) (NiO) and (5.20 ± 0.3) (PbO). A correlation between $pK_{s,MeO}$ and the polarisation action of the metal cation by Goldschmidt ($Zer_{Me^{2+}}^{-2}$) was obtained. The oxide solubilities on the mole fraction scale were shown to be close to those obtained in molten (KCl + NaCl) equimolar mixture. On the basis of the solubility data the oxobasicity index (primary medium effect for oxide ion) for the (KBr + NaBr) melt was estimated as $pI_{\{KBr-LiBr\}} = -0.24$. Due to considerable oxoacidic properties of Li^+ cation in the molten (KBr + LiBr) eutectic, it was possible to study only three from the above cations (Me = Mn, Co and Ni) and their $pK_{s,MeO}$ values were (4.36 ± 0.2), (5.19 ± 0.05) and (6.25 ± 0.03), respectively. Comparison with the corresponding data for (KBr + NaBr) equimolar mixture showed that the Li^+-based melt dissolved all the studied oxides in more extent. On the basis of the data obtained, the oxobasicity index value $pI_{\{KBr-LiBr\}}$ was estimated as (3.01 ± 0.5), that was close to the similar parameter of the chloride analogue (KCl + LiCl) (3.36). The change of the constituent anion of the melt in $Cl^- \rightarrow Br^-$ does not result in appreciable changes of the melt acidity. Oxoacidic properties of the bromide melts rise in the following sequence: (2CsBr + KBr), $pI_L = -1.15 \rightarrow$ (KBr – NaBr), $pI_L = -0.24 \rightarrow$ (KBr – LiBr), $pI_L = +3.01$.

1. Introduction

Extensive use of molten alkali metal halides for numerous basic and applied purposes necessitates wide investigations of their physicochemical properties. In particular, the ability of a melt to dissolve different oxygen-containing materials is an important characteristic which allows prediction of the behaviour of the melt contacting oxide-based constructional materials, or treated substances. For example, the melts used for the growth of optical single crystals should be unsuitable solvents for oxide materials and, hence, should possess oxoacidic properties with minimum effects as low as possible. This minimizes their interaction with the atmosphere and growth crucible materials and facilitates any purification from oxide ion traces by generally accepted chemical methods. On the contrary, the melts used as electrolytes for obtaining active metals should have relatively high acidity to prevent the formation of suspensions of oxides at the electrolysis.

Although the common approaches to determination of halide melt oxoacidity were proposed rather long ago [1,2], the results were only obtained for chloride melts [3,4]. Bromide and iodide melts remain practically unstudied. Oxide solubilities were studied only in the (2CsBr + KBr) melt [5].

The goal of this work was to determine the solubilities of several oxides of MeO composition in molten (KBr + NaBr) equimolar mixture and the (KBr + LiBr) (0.4:0.6) eutectic at $T = 973$ K by the potentiometric titration method. This makes it possible to trace the influence of cation (2CsBr + KBr) → (KBr + NaBr) → (KBr + LiBr) and anion ($Cl^- \rightarrow Br^-$) composition of the melts on their oxoacidic properties and, hence, their ability to dissolve oxide materials.

2. Experimental

The process of metal cation titration inverse to dissolution of the corresponding oxide can be described by the following equation:

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$$Me^{2+} + O^{2-} \underset{dissolution}{\overset{titration}{\rightleftarrows}} MeO \downarrow . \tag{1}$$

2.1. Solvent and reagents

Each experiment required 50 g of (KBr + NaBr) or (KBr + LiBr) mixture. The equimolar mixture of (KBr + NaBr) was obtained by mixing KBr and NaBr taken in 0.536:0.464 mass ratio. For preparation of (KBr + LiBr) charge KBr and LiBr were taken in the mass ratio 0.48:0.52. The melts before experiment were additionally dried from oxide ion traces (admixtures of the corresponding hydroxides, carbonates and sulfates in the chemicals) by adding NH_4Br of reagent quality. The residual concentration of O^{2-} in the melts was *ca* $5 \cdot 10^{-5}$ mol · kg^{-1}.

Before the experiments, KBr, NaBr, LiBr, $CaCl_2$ and $SrCl_2$ were dried by careful heating of commercial chemicals of reagent quality in vacuum (p = 5 Pa) with slow elevation of the temperature to T = 473 K. Anhydrous $CoCl_2$ and $MnCl_2$ were prepared by drying the mixtures of ($CoCl_2{\cdot}6H_2O + NH_4Cl$) ($MnCl_2{\cdot}4H_2O + NH_4Cl$) composition made of chemicals of reagent quality in vacuum with stepwise elevation of the temperature to T = 673 K. Anhydrous $NiCl_2$ was prepared by drying the corresponding hydrate of reagent quality in vacuum (p = 5 Pa) to 673 K with subsequent sublimation within the temperature range from 975 K to 1053 K. That provided separation of $NiCl_2$ from the NiO remaining in the hot zone. $PbCl_2$ of reagent quality was used without purification.

The compound KOH (mass fraction purity 0.999) was melted in an alumina crucible and kept for 1 h at T = 973 K in an argon atmosphere for complete removal of absorbed water.

To create the 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. The residual concentration of oxygen in the gas did not exceed $2 \cdot 10^{-3}$ volume per cent. The provenance and mass fraction purity are summarised in Table S1 of the Supplementary Information file.

2.2. Features of calibration and titration procedures

The saline mixture was melted in an electrochemical cell with a silver reference electrode Ag|Ag$^+$ and an indicator that was reversible to oxide ions, $Pt(O_2)$|YSZ, where YSZ was yttria stabilized zirconia ($\{0.9ZrO_2 + 0.1Y_2O_3\}$):

$$Ag|Ag^+ + melt \mid melt + Me^{2+} + O^{2-}|YSZ|Pt(O_2). \tag{2}$$

Its construction is described in detail in [6]. This cell was preliminarily calibrated by known additions of O^{2-} donor KOH of chemical quality

$$2OH^- \rightleftarrows H_2O\uparrow + O^{2-}, \tag{3}$$

to obtain the dependence of *emf* (E, V) of cell (2) vs. the equilibrium molality of O^{2-} ($m_{O^{2-}}$) or its index ($pO = -\log m_{O^{2-}}$). Examples of the calibration plots are presented in figure 1.

These dependences are approximated by linear plots (the confidence ranges are presented at the confidence level 0.95). For the (KBr + NaBr0 melt (figure 1(a)), they are:

$$E(V) = -0.044(\pm 0.020) + 0.097(\pm 0.006) \cdot pO \text{ (at } E > 0.250V), \tag{4}$$

$$E(V) = -0.521(\pm 0.050) + 0.245(\pm 0.020) \cdot pO \text{ (at } E < 0.250V). \tag{5}$$

For the (KBr + LiBr) eutectic (figure 1(b)), the plot is as follows:

$$E(V) = 0.240(\pm 0.020) + 0.114(\pm 0.009) \cdot pO. \tag{6}$$

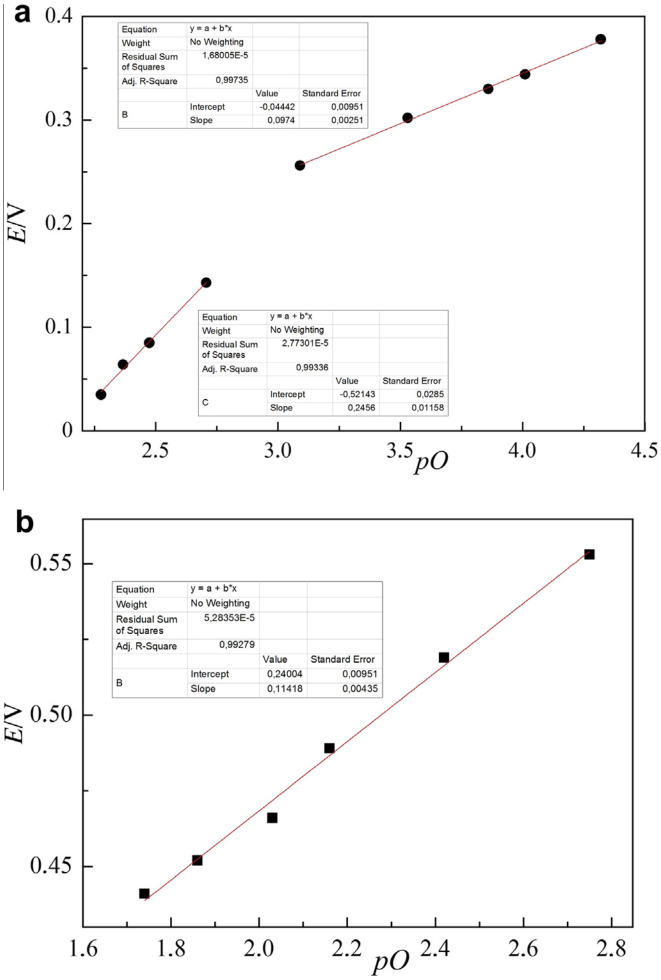

FIGURE 1. Plot to show the dependence of *emf* (E, V) of cell (2) *vs.* pO in the molten (KBr + NaBr) equimolar mixture (a) and (KBr + LiBr) eutectic (b) at T = 973 K with the results of their statistical treatment (insets).

These plots were used for pO calculation from the potentiometric data. Their features concerning the electrochemical behaviour of $Pt(O_2)$|YSZ electrode were discussed in detail earlier in Electrochimica Acta [7,8] and here we should not restate them.

The titration procedure was as follows. After stabilization of the temperature and *emf*, the weight of $MeCl_2$ corresponding to a molality of *ca* 0.05 mol · kg^{-1} was added to the melt (this initial molality is denoted further as $m^0_{Me^{2+}}$), and the equilibrium *emf* value was measured. The *emf* measurements were performed each 5 min before three sequential values become the same. At the $\theta < 1$ the equilibrium was achieved after 30 min, whereas at $\theta > 1$ the equilibrium state was observed after 1 h.

Then a sequence of the weights of KOH (the initial molality of O^{2-}, $m^0_{O^{2-}}$) was added to the melts till the initial molality of O^{2-} become considerably greater than $m^0_{Me^{2+}}$ (from 0.07 to 0.1 mol · kg^{-1}, i.e., $\theta > 1.85$) and the equilibrium *emf* values were registered after each addition. For each experimental point, we calculated the value of pO, the ligand number, $\bar{n}$:

$$\bar{n} = \left(m^0_{O^{2-}} - 10^{-pO}\right) \Big/ m^0_{Me^{2+}}, \tag{7}$$

corresponding to the average number of oxide ions fixed by one Me^{2+} cation, the dissociation constant, K'_{MeO}:

$$K'_{MeO} = \left(m^0_{Me^{2+}} - m^0_{O^{2-}} + 10^{-pO}\right) \cdot 10^{-pO} \Big/ \left(m^0_{O^{2-}} - 10^{-pO}\right),$$

$$pK'_{MeO} = -\log K'_{MeO},$$