Contents lists available at ScienceDirect

J. Chem. Thermodynamics

Polythermal study of magnesium oxide solubility in molten K$_2$SrCl$_4$

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A B S T R A C T

Solubility products of MgO in molten (KCl + SrCl$_2$) with composition corresponding to congruent compound K$_2$SrCl$_4$ at T = 923, 973 and 1023 K were determined by a potentiometric titration method using Pt(O$_2$)|ZrO$_2$(Y$_2$O$_3$) indicator electrode. The solubility product indices ($pK_{s,MgO}$, mole fractions) were found to decrease with the temperature elevation by such a manner (9.92 ± 0.13) at 923 K, (9.34 ± 0.11) at 973 K and (9.08 ± 0.13) at 1023 K. The slope of $logK_{s,MgO} - T^{-1}$ plot in the studied temperature range (ca. 76 kJ·mol^{-1}) corresponds to value of fusion enthalpy of MgO (77 kJ·mol^{-1}). A comparison of MgO solubilities in the molten K$_2$SrCl$_4$ with the similar results obtained for (CsCl + KCl + NaCl) (0.455:0.245:0.300) and (KCl + LiCl) (0.41:0.59) eutectic melts shows that the values for K$_2$SrCl$_4$ melt are intermediate between those for low-acidic (CsCl + KCl + NaCl) and merely acidic (KCl + LiCl). The oxobasicity indices pI_L of K$_2$SrCl$_4$ in the studied temperature range change from 2.26 to 2.45 with the temperature rise.

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1. Introduction

Nowadays molten saline mixtures on the basis of alkali and alkaline earth metal halides are often used as initial media for obtaining single crystals of promising luminescent (scintillation) materials [1–3]. Eu^{2+} ions entered in the melt in form of the corresponding europium dihalide serve as activator and in the case of Sr^{2+}-based melts the distribution coefficient is close to 1 due to very close ionic radii of Eu^{2+} and Sr^{2+} [4]. Since initial halides, as a rule contain traces of hardly removable oxygen-containing admixtures europium ions interact with oxide ions formed as a result of dissociation of these admixtures that results in the formation of non-dissociated EuO in the melt:

$$Eu^{2+} + O^{2-} \rightarrow EuO(\downarrow) \tag{1}$$

and, at high concentration of the admixtures, in its precipitation. This causes loss of the activating substance. Therefore, preliminary treatment of the matrix (the molten halide mixture) seems very desirable. Such a treatment provides addition of a stronger cation acid forming oxide with solubility product value lower than that of EuO or supply of gaseous halogenating agent into the melt. In any case the efficiency of the purification is dependent on the affinity of constituent cations of the halide melt to oxide ion which can

be characterized by the oxobasicity index pI_L (concentration analog of the primary medium effect for oxide ion in the given melt) [5].

Taking into account all the above-written, it seems very interesting to perform the investigation of MgO solubility in the molten (KCl + SrCl$_2$) mixture for two reasons. The first one consists in the fact that data on MgO solubility can be used for estimation of the oxobasicity indices of SrCl$_2$-based saline mixtures on the basis of the solubility data. The second reason is to estimate the efficiency of Mg^{2+} as one of the most powerful deoxidizing cation acids. K$_2$SrCl$_4$ melt is chosen since it presents a congruent compound which single crystals can be easily grown from the melt. Unfortunately, the said solubility values are absent.

2. Experimental

The process of Mg^{2+} titration with the addition of an oxide ion donor is reversed to the dissolution of the precipitated oxide and it can be presented as follows:

$$Mg^{2+} + O^{2-} \rightarrow MgO \downarrow . \tag{2}$$

2.1. Solvent and reagents

The reagents and methods used for their preparation are presented in Table 1. The saline mixture (K$_2$SrCl$_4$) was prepared by mixing KCl and SrCl$_2$ in 48.4:51.6 mass ratio, both salts was of reagent quality. A total of 50 g of the mixture was used for each experiment.

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Table 1
Chemicals used in the experiments and methods of their treatment.

Formula	Supplier	Purity, Main Substance, Mass Fraction	Purification Method	Final Mass Fraction Purity	Method of Analysis
Ammonium chloride	Merck	0.998	None	–	–
Argon of high purity	PASS, Ukraine	0.9999	Drying over P_2O_5	0.9999	'Baikal' (analyser of water in gases) Zircon (analyser of O_2 in gases)
Potassium hydroxide	Reakhim, Russia	0.999	Drying in argon atmosphere at 600 °C	0.999	Stated by supplier
Magnesium chloride	Synthesis		Crystallization + vacuum drying, melting	0.99	CT[a]
Potassium chloride	Reakhim, Russia	0.995	None	–	–
Strontium chloride	Reakhim, Russia	0.995	None	–	–
Tetrachloromethane	Reakhim, Russia	0.995	Drying over anhydrous $CaCl_2$ with distillation	–	–

[a] Complexometric titration.

To obtain anhydrous $MgCl_2$, $MgCl_2 \cdot 6H_2O$ of reagent quality was mixed with NH_4Cl in mole ratio of 1:1 and dried by careful heating in vacuum (2 Pa) to 673 K to complete sublimation of ammonium chloride. Then the residue was melted and treated at 1073 K by CCl_4 vapour in argon flow (carbohalogenation):

$$2MgO + CCl_4 \uparrow \rightarrow 2Mg^{2+} + 4Cl^- + CO_2 \uparrow . \tag{3}$$
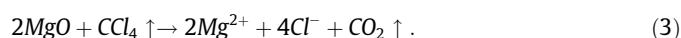
Obtained $MgCl_2$ free of oxygen-containing admixtures was cooled to room temperature and kept in dry box.

KOH (fraction of the main substance was 0.999) was melted in an alumina crucible and kept for 1 h at T = 973 K in anargon atmosphere that provided complete removal of absorbed water. It should be mentioned that the reaction of KOH with Al_2O_3 practically did not run since the fraction of Al in the resulting KOH did not exceed 0.003 that could not affect the following investigations.

We used high-purity Ar for creation inert atmosphere in the potentiometric cell (the volume fraction of the main substance was 0.9999). This gas was preliminarily dried by passing over P_2O_5 that provided deep purification from H_2O traces. The residual volume part of oxygen in the gas did not exceed 2×10^{-5}.

2.2. Features of the titration procedure

The chloride mixture was melted and heated to the temperature of the experiment in an electrochemical cell including a silver reference electrode $Ag|Ag^+$ and the indicator one reversible to oxide ions, $Pt(O_2)|YSZ$, where YSZ was yttria stabilized zirconia ($\{0.9ZrO_2 + 0.1Y_2O_3\}$):

$$Ag|Ag^+, K_2SrCl_4 \vdots K_2SrCl_4 + O^{2-}|YSZ|(O_2)Pt. \tag{4}$$

The cell construction is described in detail in [6]. The melt before the experiment was purified from a majority of oxide ion traces (admixtures of the corresponding hydroxides, carbonates and sulfates in the initial chemicals) by adding NH_4Cl of reagent quality:

$$2NH_4Cl + O^{2-} \rightarrow 2NH_3 \uparrow + H_2O \uparrow + 2Cl^-. \tag{5}$$
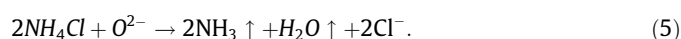
Then the cell was preliminarily calibrated by a sequence of known additions of KOH to obtain the dependence of the *emf* of cell (4) *vs.* the equilibrium molality of O^{2-}, $m_{O^{2-}}$ (mol kg^{-1}) or its index $pO = -\log m_{O^{2-}}$. At temperatures near 1000 K, potassium hydroxide in molten halides undergoes dissociation:

$$2KOH \rightarrow 2K^+ + H_2O \uparrow + O^{2-}, \tag{6}$$

i.e., 112 g of KOH corresponds to 1 mol of O^{2-} in a melt. The plots obtained at 923, 973 and 1023 K were used for pO calculations from the corresponding potentiometric data.

The potentiometric titration procedure was fulfilled by such a manner. After stabilization of the temperature and *emf* of cell (4), the weight of $MgCl_2$ corresponding to initial molality of Mg^{2+} $m^0_{Mg^{2+}} = 0.04$ mol·kg^{-1} was added to the melt and the equilibrium *emf* was measured. The *emf* measurements were performed every 5 min until three sequential values of *emf* became the same. Then a sequence of the weights of KOH was added to the melts till $m^0_{O^{2-}}$ (the initial molality of oxide ion, mol·kg^{-1}) became somewhat greater than $m^0_{Mg^{2+}}$ (θ > 1.5, where θ the ratio of initial molalities of oxide ion and metal cation, namely, $m^0_{O^{2-}}/m^0_{Mg^{2+}}$) and the equilibrium *emf* values were registered after each addition. The *emf* value gave us the possibility to calculate the corresponding oxygen index, pO.

For each titration point we calculated the solubility product, $K'_{s,MgO}$, mol²·kg^{-2}:

$$K'_{s,MgO}/(\text{mol}^2 \cdot \text{kg}^{-2}) = (m^0_{Mg^{2+}} - m^0_{O^{2-}} + 10^{-pO}) \cdot 10^{-pO}/(\text{mol}^2 \cdot \text{kg}^{-2}). \tag{7}$$

Statistical treatment of the obtained results was performed using the generally accepted routines [7] and all the confidence ranges are the standard deviations.

3. Results and discussion

The potentiometric titration curves of Mg^{2+} with KOH at all temperatures studied are presented in Fig. 1.

All titration curves correspond to formation of oxide slightly soluble in the melt. As is seen, the increase of the temperature causes a sequential decrease of pO values in sections where θ < 1. The lower are pO values in this section the higher are the solubility products of the oxide. Therefore, the temperature rise causes the increase of solubility of MgO in the K_2SrCl_4 melt. Examples of the treatment of the experimental values are presented in Tables 2–4. The calculated values of the index of the solubility products for MgO are practically constant within negligible oscillations near average values: $pK_{s,MgO} = (7.82 \pm 0.13)$ at 923 K, $pK_{s,MgO} = (7.31 \pm 0.06)$ at 973 K and $pK_{s,MgO} = (6.98 \pm 0.14)$ at 1023 K. This confirms the saturation of the solution formed with MgO at all the titrant additions. All the values of the solubility product obtained are presented in Table 5.