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CRYOSCOPIC BEHAVIOUR OF SOME COMPLEXES OF Si, Cr, Al, V AND Ti IN MOLTEN POTASSIUM NITRATE AND POTASSIUM DICHROMATE

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ABSTRACT

Freezing point depression measurements were taken on dilute solutions of the following solutes: K_2SiF_6 and $KM(SO_4)_2$, where M = Al(III) or Cr(III), and $MOSO_4$ where M = V(IV) or Ti(IV), in molten KNO_3 and $K_2Cr_2O_7$ as solvents. The number of foreign ions obtained, ν, showed that the $(SiF_6)^{2-}$ ion is partially dissociated in molten KNO_3, while it is completely dissociated in molten $K_2Cr_2O_7$. With respect to the other solutes, the results indicated that certain reactions may occur between their dissociation products in the melt and in the studied solvent.

INTRODUCTION

When applied to molten salt mixtures, cryoscopy is convenient for investigations of ionization processes, reaction and interaction phenomena in molten electrolytes. For the very dilute solution range, Raoult van't Hoff's law of freezing point depression, $\Delta T = T_1 - T = \nu m(RT_1^2/L_1)$, is applied.

T_1 and T are the absolute freezing point temperature of the pure solvent and the salt mixture, respectively. ΔT is the freezing point depression, ν is the number of ions "foreign" to the solvent furnished by one molecule of the solute, R is the ideal gas constant (1.986 cal mol^{-1} deg^{-1}), L_1 is the melt enthalpy of the solvent in cal mol^{-1} and m is the mole fraction of the solute. The value of (RT_1^2/L_1) is the molar depression of the freezing point or cryoscopic constant, K_0, of the pure solvent.

EXPERIMENTAL

The experimental technique used in this work was the same as that described before [1]. The depression in the freezing point of molten KNO_3 (f.p. = 334°C) or that of molten $K_2Cr_2O_7$ (f.p. = 400°C) was measured for a

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series of salts. The change of freezing point as a function of concentration, m, for all solutes used is shown in Figs. 1–3. The 1 ×, 2 ×, 3 ×,... lines represent theoretical lines for one-, two-, threefold,... lowerings and are calculated from the known value of K_0 ($K_0 = 318$ and 101.1 for KNO_3 and $K_2Cr_2O_7$ respectively [2,3]). All chemicals used in this study were of high quality reagent grade (Merck and BDH).

RESULTS AND DISCUSSION

KNO_3 systems

KNO_3–K_2SiF_6

The number of foreign ions produced by potassium fluorosilicate in molten KNO_3 was found to be two ($\nu = 2$) as shown in Fig. 1. This suggests the following reaction

$$KNO_3 + K_2SiF_6 \rightarrow 3\ K^+ + SiF_4 + 2\ F^- + (NO_3)^-$$

Accordingly, the $(SiF_6)^{2-}$ ion may dissociate into SiF_4 and 2 F^-. SiF_4 seems to be insoluble in KNO_3 melt, in contrast to its behaviour in high melting point solvents, e.g., alkali metal bromides [4], where the $(SiF_6)^{2-}$ ion dissociates into 2 F^- and soluble SiF_4 ($\nu = 3$).

Moreover, this proposed dissociation for the $(SiF_6)^{2-}$ ion is analogous to the dissociation of the $(TiF_6)^{2-}$ ion in molten alkali halides [5] and $(AlF_6)^{2-}$ ion in cryolite [6,7] or in sodium sulphate [8] melts.

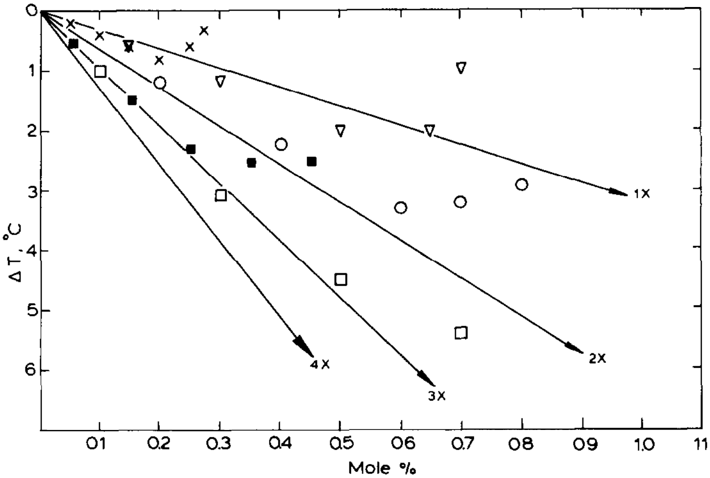

Fig. 1. Depression of the freezing point of molten KNO_3 by: (○), K_2SiF_6; (×), $VOSO_4 \cdot H_2O$; (▽), $TiOSO_4 \cdot H_2O$; (□), $KCr(SO_4)_2 \cdot 12\ H_2O$; (■), $KAl(SO_4)_2 \cdot 12\ H_2O$.

KNO_3–$VOSO_4 \cdot H_2O$

According to the number of foreign species found ($\nu = 1$; Fig. 1), the reaction may proceed in 2 steps (a) Transformation of the vanadyl sulphate in KNO_3 melt into V_2O_5 and SO_2 and SO_3 gases [9]

$$2\,VOSO_4 \cdot H_2O \rightarrow V_2O_5 + SO_2\uparrow + SO_3\uparrow + H_2O\uparrow$$

(b) V_2O_5 behaves as a strong Lux acid and accepts oxide ions from the nitrate melt to form the basic $(VO_4)^{3-}$ ion [10]

$$6\,KNO_3 + V_2O_5 \rightarrow 6\,K^+ + 6\,NO_2\uparrow + 2(VO_4)^{3-} + 3/2\,O_2\uparrow$$

Accordingly, one can write the overall reaction as follows

$$6\,KNO_3 + 2\,VOSO_4 \cdot H_2O \rightarrow 6\,K^+ + 2(VO_4)^{3-} + SO_2\uparrow + SO_3\uparrow + H_2O\uparrow + 6\,NO_2\uparrow + 3/2\,O_2\uparrow$$

KNO_3–$TiOSO_4 \cdot H_2O$

The titanyl sulphate gave $\nu = 1$, which may be explained on the basis that titanyl sulphate is first decomposed into TiO_2 and SO_3. Then, TiO_2 behaves as a Lux acid, which takes oxide ions from the nitrate base–electrolyte to yield the $(TiO_4)^{4-}$ ion. Such a reaction is analogous to that of TiO_2 in alkali metal sulphate melts [11,12]. The mechanism of the reactions involved in this system may be written as follows

$$TiOSO_4 \cdot H_2O \rightarrow TiO_2 + SO_3\uparrow + H_2O\uparrow$$

$$4\,KNO_3 + TiO_2 \rightarrow 4\,K^+ + (TiO_4)^{4-} + 2\,N_2O_5\uparrow$$

$$2\,N_2O_5 \rightarrow 4\,NO_2\uparrow + O_2\uparrow$$

$$4\,KNO_3 + TiOSO_4 \cdot H_2O \rightarrow 4\,K^+ + (TiO_4)^{4-} + SO_3\uparrow + H_2O\uparrow + 4\,NO_2\uparrow + O_2\uparrow$$

KNO_3–$KCr(SO_4)_2$ –12 H_2O

From cryoscopic measurements on this system (Fig. 1; $\nu = 3$) it follows that in molten KNO_3 the chromium alum is at first dissociated as follows

$$2\,K\,Cr(SO_4)_2 \cdot 12\,H_2O \rightarrow 2\,K^+ + (SO_4)^{2-} + Cr_2O_3 + 3\,SO_3\uparrow + 24\,H_2O\uparrow$$

Many elements, including chromium, cannot exist in a lower oxidation state, because they form scarcely soluble oxides in their high oxidation state [13]. Moreover, formation of the $(CrO_4)^{2-}$ ion by the reaction of Cr_2O_3 in KNO_3 melt or in $LiNO_3$–KNO_3 eutectic [14,15] was also suggested previously. Accordingly, Cr_2O_3 reacts in the KNO_3 melt to give 2 $(CrO_4)^{2-}$ ions, via the formation of $(Cr_2O_7)^{2-}$ ions

(a) $2\,KNO_3 + Cr_2O_3 \rightarrow 2\,K^+ + (Cr_2O_7)^{2-} + 2\,NO\uparrow$

(b) $4\,KNO_3 + (Cr_2O_7)^{2-} \rightarrow 4\,K^+ + 2(CrO_4)^{2-} + 4\,NO_2\uparrow + 3/2\,O_2\uparrow$

Therefore, the resulting three foreign ions may be visualized as being 2 $(CrO_4)^{2-}$ and $(SO_4)^{2-}$ ions.

KNO_3-$KAl(SO_4)_2 \cdot 12\ H_2O$

The experimental ΔT measurements (Fig. 1) agree with the theoretical value of $\nu = 3$. This can be explained by assuming that the aluminium alum is simply dissociated in the nitrate melt as follows

$$KNO_3 + KAl(SO_4)_2 \cdot 12\ H_2O \rightarrow 2\ K^+ + Al^{3+} + 2(SO_4)^{2-} + 12\ H_2O\uparrow + (NO_3)^-$$

$K_2Cr_2O_7$ systems

$K_2Cr_2O_7$-K_2SiF_6

The number of foreign ions, ν, was found to be 7 (Fig. 2). This suggests that the fluorosilicate anion is completely dissociated in the dichromate melt as follows

$$K_2Cr_2O_7 + K_2SiF_6 \rightarrow 4\ K^+ + Si^{4+} + 6\ F^- + (Cr_2O_7)^{2-}$$

$(SiF_6)^{2-}$ ion was previously found to dissociate into 2 F^- and SiF_4, which then partially dissociates into Si^{4+} and 4 F^- in alkali metal bromides [4].

$K_2Cr_2O_7$-$KCr(SO_4)_2 \cdot 12\ H_2O$

The measured ΔT coincide with theoretical line of $\nu = 1$ (Fig. 2). This

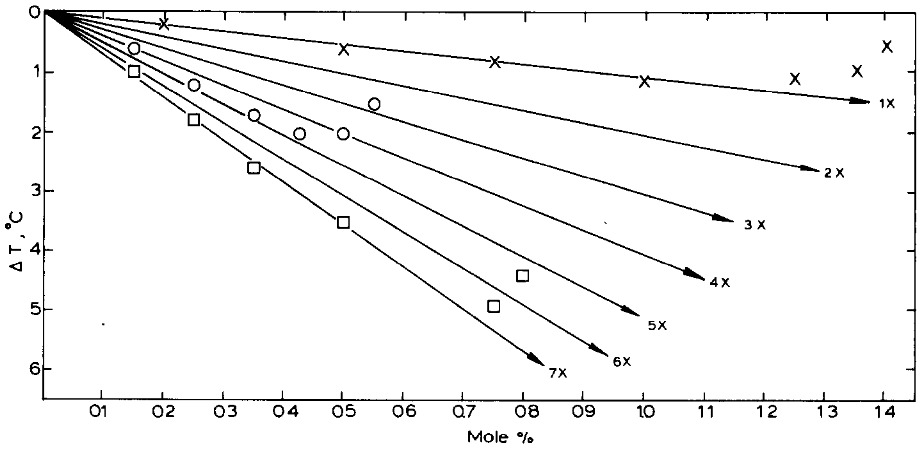

Fig. 2. Depression of the freezing point of molten $K_2Cr_2O_7$ by: (□), K_2SiF_6; (×), $KCr(SO_4)_2 \cdot 12\ H_2O$; (○), $KAl(SO_4)_2 \cdot 12\ H_2O$.

suggests the following stepwise reaction mechanism

(a) $K_2Cr_2O_7 \rightarrow 2\,K^+ + CrO_3 + (CrO_4)^{2-}$

(b) $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\,H_2O \rightarrow 2\,K^+ + (SO_4)^{2-} + Cr_2O_3 + 3\,SO_3 \uparrow + 24\,H_2O$

(c) $CrO_3 + (SO_4)^{2-} \rightarrow (CrSO_7)^{2-}$

$$K_2Cr_2O_7 + 2\,KCr(SO_4)_2 \cdot 12\,H_2O \rightarrow 4\,K^+ + (CrO_4)^{2-} + (CrSO_7)^{2-} + Cr_2O_3 + 3\,SO_3 \uparrow + 24\,H_2O \uparrow$$

Cr_2O_3 was found to be insoluble in $K_2Cr_2O_7$ melt [16]. Moreover, the displacement of $(SO_4)^{2-}$ ion within the $(CrO_3 \cdot CrO_4)^{2-}$ ion to give the $(CrSO_7)^{2-}$ heteropolyion and the $(CrO_4)^{2-}$ ion was also known before [17]. Therefore, the depression in the freezing point of molten $K_2Cr_2O_7$ may be due to $(CrO_4)^{2-}$ and $(CrSO_7)^{2-}$ ions.

$K_2Cr_2O_7$–$KAl(SO_4)_2 \cdot 12\ H_2O$

The dissociation state of the aluminium alum in molten $K_2Cr_2O_7$, according to the experimentally obtained $\nu = 5$, can be understood as proceeding via the following reactions

(a) $4\,K_2Cr_2O_7 \rightarrow 8\,K^+ + 4(CrO_4)^{2-} + 4\,CrO_3$

(b) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O \rightarrow 2\,K^+ + 2\,Al^{3+} + 4(SO_4)^{2-} + 24\,H_2O \uparrow$

(c) $4\,CrO_3 + 4\,SO_4^{2-} \rightarrow 4(CrSO_7)^{2-}$

$$4\,K_2Cr_2O_7 + 2\,KAl(SO_4)_2 \cdot 12\,H_2O \rightarrow 10\,K^+ + 2\,Al^{3+} + 4(CrO_4)^{2-} + 4(CrSO_7)^{2-} + 24\,H_2O$$

Thus, from the overall reaction one can deduce that the foreign ions are 2 Al^{3+}, $4(CrO_4)^{2-}$ and $4(CrSO_7)^{2-}$ ions.

$K_2Cr_2O_7$–$VOSO_4 \cdot H_2O$

From the results obtained in the cryoscopic studies of this sytem (Fig. 3), it can be seen that in the concentration range 1.5–2.5 mol% $VOSO_4 \cdot H_2O$ the number of new particles per molecule of solute is reduced from 2.5 to 2. This suggests that $VOSO_4 \cdot H_2O$ is decomposed in the dichromate melt as follows

$$2\,VOSO_4 \cdot H_2O \rightarrow V_2O_5 + SO_2 \uparrow + SO_3 \uparrow + H_2O \uparrow$$

Then, the following 2 reaction mechanisms may be postulated at lower and higher concentrations, respectively, as previously suggested [1]

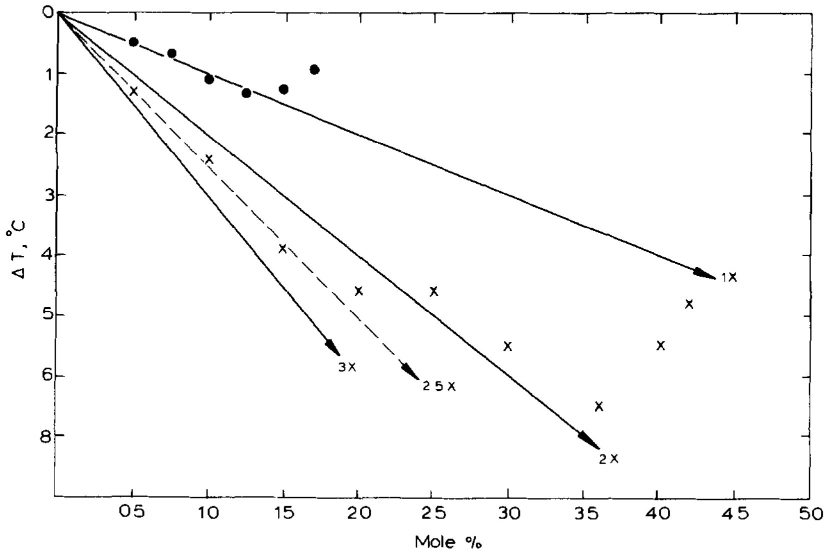

Fig. 3. Depression of the freezing point of molten $K_2Cr_2O_7$ by: (×), $VOSO_4 \cdot H_2O$; (●), $TiOSO_4 \cdot H_2O$.

At low concentration

$$6\ K_2Cr_2O_7 + V_2O_5 \rightarrow 12\ K^+ + (CrVO_7)^{3-} + (Cr_2VO_{10})^{3-} + 3(Cr_3O_{10})^{2-}$$

At high concentration

$$5\ K_2Cr_2O_7 + V_2O_5 \rightarrow 10\ K^+ + (CrV_2O_{10})^{4-} + 3(Cr_3O_{10})^{2-}$$

$K_2Cr_2O_7$–$TiOSO_4 \cdot H_2O$

The cryoscopic behaviour of titanyl sulphate in dichromate melt (Fig. 3) shows that $\nu = 1$. On this basis, one can postulate the following stepwise reactions

(a) $2\ K_2Cr_2O_7 \rightarrow 4\ K^+ + 2(CrO_4)^{2-} + Cr_2O_3 + 3/2\ O_2 \uparrow$

(b) $2\ TiOSO_4 \cdot H_2O \rightarrow 2\ TiO_2 + 2\ SO_3 \uparrow + 2\ H_2O \uparrow$

(c) $2\ TiO_2 + Cr_2O_3 \rightarrow Cr_2O_3 \cdot 2\ TiO_2$

$$2\ K_2Cr_2O_7 + 2\ TiOSO_4 \rightarrow 4\ K^+ + 2(CrO_4)^{2-} + 2\ SO_3 \uparrow + 2\ H_2O \uparrow + 3/2\ O_2 \uparrow + Cr_2O_3 \cdot 2\ TiO_2$$

Reaction (a) was suggested previously [3]. According to the last overall reaction, the depression in the freezing point of $K_2Cr_2O_7$ was due only to the $2(CrO_4)^{2-}$ ions. Formation of the complex $Cr_2O_3 \cdot 2\ TiO_2$ [18] in the melt is also probable, but it may not affect the freezing point of the molten dichromate owing to its insolubility in the solvent.

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