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REACTIONS OF SINGLE Cr(III)–P(V)Mo(VI) AND DOUBLE Cr(VI)–P(V)Mo(VI) PHASE SYSTEMS IN MOLTEN KNO_3

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ABSTRACT

Dilute solutions of single-phase ($K_6Cr_2(P_2O_7)_3$, $Na_2KCr_2(PO_4)_3$, $K_2Cr_2Mo_3O_{13}$) and double-phase ($K_2Cr_2O_7$–$K_4P_2O_7$, $K_2Cr_2O_7$–$Na_5P_3O_{10}$, K_2CrO_4–MoO_3, $K_2Cr_2O_7$–MoO_3) solutes were studied cryoscopically in molten KNO_3 solvent at 350 ° C. The depression in the freezing point ΔT of the solvent was measured using the DTA method. The calculated number of foreign ions ν suggested the presence of $(CrO_4)^{2-}$ groups together with the isopolyions $(P_3O_{10})^{5-}$ or $(Mo_3O_{10})^{2-}$ in the corresponding single-phase solute–solvent melts. However, the double-phase solutes, Cr(VI)–P(V) and Cr(VI)–Mo(VI), seemed to react differently in molten KNO_3, giving rise to the foreign species $(CrO_4)^{2-}$, $(PO_4)^{3-}$, $(P_3O_{10})^{5-}$ and the heteropolyion $(CrMoO_7)^{2-}$, respectively. The formation of such simple, isopolyions and heteropolyions is discussed in view of previous results obtained using different experimental methods.

INTRODUCTION

In very dilute solutions of a solute in a molten solvent, a depression in the freezing point ΔT of the solvent may be observed. In such a case, a number of foreign ions ν are formed in the solvent–solute melt, which differ from the dissociation products of the melted pure solvent. The relation between ΔT (° C) and ν is given by the simplified Raoult–van't Hoff law of freezing point depression, $\Delta T = T_1 - T = \nu x_2 \, [RT_1^2/\Delta H_1] = \nu x_2 K_0$, which is obeyed in very dilute solutions. T_1 and T are the crystallization temperatures in K of the pure solvent and the solvent–solute mixture, respectively; x_2 is the mole fraction of the solute and K_0 is the molar depression of freezing point or cryoscopic constant of the solvent obtained from its heat of fusion and freezing point. A K_0 value of 318 was obtained for KNO_3 [1] from $\Delta H_1 = 2300$ cal mol^{-1}, $T_1 = 607$ K and the ideal gas constant $R = 1.986$ cal K^{-1} mol^{-1}.

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EXPERIMENTAL

The solutes $K_2Cr_2O_7$, K_2CrO_4, MoO_3 (P.A.) and $K_4P_2O_7$ (pure), together with the solvent KNO_3 (purest) were obtained from Merck. $Na_5P_3O_{10}$ was kindly provided by Prof. E. Thilo (Berlin). Single solute phases, namely $K_6Cr_2(P_2O_7)_3$, $Na_2KCr_2(PO_4)_3$ and $K_2Cr_2Mo_3O_{13}$, were prepared and identified as reported previously [2–4]. Depression of the freezing point ΔT (°C) of the solvent KNO_3 was measured using the DTA technique as described earlier [1,5].

RESULTS AND DISCUSSION

Generally, in view of the dissociation equilibria of molten KNO_3 [6,7], $NO_3^- \rightleftharpoons NO_2^+ + O^{2-}$ and $NO_3^- + NO_2^+ \rightarrow N_2O_5 \rightarrow 2NO_2 + 0.5O_2$, the nitrate can be considered as an oxide ion donor. The shift of the basic equilibria to the right in the presence of solutes behaving as Lux–Flood acids (oxide ion acceptors) has been generally accepted and confirmed by thermogravimetric techniques [8], acid–base reactions [9] and cryoscopic methods [10].

The numbers of foreign ions ν produced by the single-phase solutes $K_6Cr_2(P_2O_7)_3$ and $Na_2KCr_2(PO_4)_3$ were found to be 4 and 5, respectively (Fig. 1). Accordingly, the following general reactions can be assumed

$$8KNO_3 + K_6Cr_2(P_2O_7)_3 \rightarrow 14K^+ + 2(CrO_4)^{2-} + 2(P_3O_{10})^{5-} + 8NO_2 + 0.5O_2 \quad (1)$$

$$6KNO_3 + Na_2KCr_2(PO_4)_3 \rightarrow 7K^+ + 2Na^+ + 2(CrO_4)^{2-} + (P_3O_{10})^{5-} + 6NO_2 \quad (2)$$

It is evident that the nature of the foreign particles formed in the melt suggests the oxidation of Cr(III) to Cr(VI) and formation of the stable isopolyion $(P_3O_{10})^{5-}$ during reactions between the nitrate (oxide ion donor) and the constituents Cr_2O_3 and $x(P_3O_9)^{3-}$ of the solute (oxide ion acceptor). However, an alternative complex reaction in the melt between $(P_3O_9)^{3-}$ and $(NO_3)^-$ ions as assumed previously [9] will not change the ν value as can be seen from the reactions

$$(P_3O_9)^{3-} + (NO_3)^- \rightarrow [(P_3O_9)\cdot NO_3]^{4-}$$

$$[(P_3O_9)\cdot NO_3]^{4-} + (NO_3)^- \rightarrow (P_3O_{10})^{5-} + N_2O_5 (N_2O_5 \rightarrow 2NO_2 + 0.5O_2)$$

The species proposed ($(CrO_4)^{2-}$ and $(P_3O_{10})^{5-}$) as reaction products of the single-phase solutes Cr(III)–P(V) in the nitrate melt are in good agreement with previous results of melt spectra (presence of CrO_4^{2-}) and IR spectra of the quenched melt [11] (identification of CrO_4^{2-} and $P_3O_{10}^{5-}$) and with the stability of the isopolyion $(P_3O_{10})^{5-}$ as confirmed cryoscopically [12], electrochemically [13] and by acid–base reactions [9].

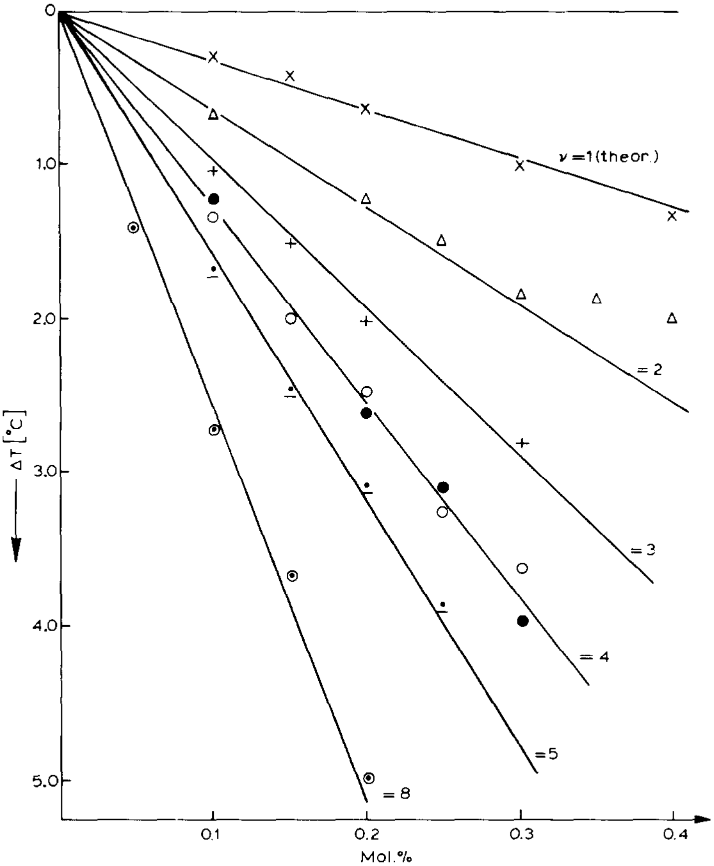

Fig. 1. Depression of the freezing point of molten KNO_3 by: $K_6Cr_2(P_2O_7)_3$ (○), $Na_2KCr_2(PO_4)_3$ ($\dot{-}$), $K_2Cr_2O_7$–$K_4P_2O_7$ (●), $K_2Cr_2O_7$–$Na_5P_3O_{10}$ (◉), $K_2Cr_2Mo_3O_{13}$ (+), K_2CrO_4–MoO_3 (×) and $K_2Cr_2O_7$–MoO_3 (△).

The double-phase solutes $K_2Cr_2O_7$–$K_4P_2O_7$ and $K_2Cr_2O_7$–$Na_5P_3O_{10}$ induced a depression in the freezing point of the KNO_3 melt corresponding to ν values of 4 and 8, respectively (Fig. 1). Thus, their reactions in the nitrate melt can be assumed to be

$$4KNO_3 + (K_2Cr_2O_7\text{–}K_4P_2O_7) \rightarrow 10K^+ + 2(CrO_4)^{2-} + 2(PO_4)^{3-} + 4NO_2 + 0.5O_2$$

$$2KNO_3 + (K_2Cr_2O_7\text{–}Na_5P_3O_{10}) \rightarrow 4K^+ + 5Na^+ + 2(CrO_4)^{2-} + (P_3O_{10})^{5-} + 2NO_2 + 0.5O_2$$

It seems, therefore, that the transformation of the relatively acidic groups $(Cr_2O_7)^{2-}$ and $(P_2O_7)^{4-}$ to the more basic groups $2(CrO_4)^{2-}$ and $2(PO_4)^{3-}$ and the dissociation of $Na_5P_3O_{10}$ with the formation of the stable isopolyion $(P_3O_{10})^{5-}$ are the dominant reactions occurring in the nitrate melt. This conclusion is in agreement with previous results of the separate phases $K_2Cr_2O_7$, $K_4P_2O_7$ and $Na_5P_3O_{10}$ in molten nitrate [10,12], thus indicating that no apparent prior reactions of $K_2Cr_2O_7$ with either $K_4P_2O_7$ or $Na_5P_3O_{10}$ occur in the melt. If such prior reactions did occur in the melt to give water-insoluble $K_6Cr_2(P_2O_7)_3$ or $Na_2KCr_2(PO_4)_3$ together with water-soluble phases (as known in solid state reactions) one would expect different values of ν than those found.

The single-phase solute $K_2Cr_2Mo_3O_{13}$ gave a ν value of 3 (Fig. 1), according to which a proposed general reaction can be given as $4KNO_3 + K_2Cr_2Mo_3O_{13} \rightarrow 6K^+ + 2(CrO_4)^{2-} + (Mo_3O_{10})^{2-} + 2NO_2 + 2NO + 0.5O_2$. The mechanism of the reaction between each constituent of the dissociation products [Cr_2O_3, $(Mo_3O_9)^{2-}$] of the solute and the KNO_3 melt, and hence the nature of the foreign species formed, seem to be similar to those suggested previously for the solute $Cr_2Mo_3O_{12}$ [14]. Moreover, the presence of $(CrO_4)^{2-}$ groups in the present melt mixture was confirmed by measuring the absorption spectrum of the melt (absorption maximum of $(CrO_4)^{2-}$ at 26531 cm^{-1}). The IR spectrum of the quenched melt also confirmed the formation of CrO_4^{2-} groups together with the isopolyion $(Mo_3O_{10})^{2-}$ [11].

The numbers of foreign ions ν obtained in the double-phase solute systems K_2CrO_4–MoO_3 and $K_2Cr_2O_7$–MoO_3 were found to be 1 and ≈ 2, respectively (Fig. 1). It is obvious that these values of ν (1 and ≈ 2) are lower than the summation of the individual ν values produced separately by each phase within the corresponding double-phase solute. This observation might indicate that some kind of reaction occurs between the two phases of the solute in the nitrate melt. By considering the behaviour of MoO_3 and $K_2Cr_2O_7$ separately in the KNO_3 melt [10], and the solid state reaction between K_2CrO_4 and MoO_3 (in equimolar ratio) [4], it may be possible to explain the results achieved. It was reported previously [10] that MoO_3 showed little tendency to dissolve in the KNO_3 melt at 350 °C. However, its dissolution and reaction with KNO_3 increased with an increase in the temperature of the nitrate melt (450 °C). In contrast, the reaction of the solute $K_2Cr_2O_7$ in the KNO_3 melt at 350 °C was observed to be rapid (in terms of the period of time required to observe a depression in the freezing point of the solvent) with the formation of the more basic $(CrO_4)^{2-}$ groups. Moreover, the mixed crystal $2(K_2CrMoO_7)$ was obtained and identified as a result of a solid state reaction between K_2CrO_4 and MoO_3 as described earlier [4]. As seen from the previous observations and results concerning the velocity of the reactions of MoO_3 and $K_2Cr_2O_7$ in the KNO_3 melt at 350 °C and the tendency of K_2CrO_4 to react with MoO_3 (equimolar ratio) in the solid state to give a defined phase (the above-mentioned mixed crystal), one can propose the following general reactions for the two double-phase solutes under investigation

$$KNO_3 + 2(K_2CrO_4\text{–}MoO_3) \rightarrow 5K^+ + 2(CrMoO_7)^{2-} + NO_3^- \quad (3)$$

Accordingly, it seems obvious that a reaction occurs first between K_2CrO_4 and MoO_3 in the nitrate melt presumably to give the mixed crystal $2(K_2CrMoO_7)$, followed by its simple dissociation to produce the stable foreign heteropolyion $(CrMoO_7)^{2-}$.

$$4KNO_3 + 2(K_2Cr_2O_7\text{–}MoO_3) \rightarrow 8K^+ + 2(CrMoO_7)^{2-} + 2CrO_4^{2-} + 4NO_2 + O_2 \qquad (4)$$

Again, it is clear that $K_2Cr_2O_7$ reacts first with KNO_3 to give the more basic $2(CrO_4)^{2-}$ groups which react simultaneously with MoO_3 in a similar way as in the $K_2CrO_4\text{–}MoO_3$ double-phase solute, leading to the same stable heteropolyion $(CrMoO_7)^{2-}$. Other previous reactions between $K_2Cr_2O_7$ and MoO_3 in the nitrate melt can be excluded, since the ν value found for this system is much less than that expected for any such reaction.

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