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References

Cryoscopic Studies in Molten Salts: Dissociation of Some Alkali Isopolymolybdates & Some Related Molybdenum(VI) Compounds in Molten Potassium Dichromate & Potassium Nitrate

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The dissociation of the solutes, viz. M₂MoO₇, M₂MoO₅, M₂MoO₄, M₂MoO₃, K₂Cr₂O₇, K₂MoO₄, Cr₂MoO₇, and V₂MoO₇, in molten K₂Cr₂O₇ and KNO₃ as solvents has been studied employing cryoscopic methods. The values of number of foreign ions (n) show that all the solutes, except V₂MoO₇, are either simply dissociated in the melt, or, in some cases after dissociation undergo rearrangement to heteropolymolybdates of the type (CrMoO₄)₃⁻. The solute V₂MoO₇, dissolves without any apparent dissociation. An agreement between the experimental and calculated values of activity (a) based on the Temkin and random mixing models and that of Vant Hoff’s equation support the proposed simple dissociation scheme for K₂Cr₂O₇–Cs₂MoO₇ system.

It is well known that the freezing point of a pure solvent is lowered provided the foreign ions or species present are different from those of the dissociation products of the solvent. The factor, υ, gives only the number of such foreign species formed, rather than the effects of the forces they exert, i.e. it expresses a molecular property of the solute. The υ-value is evaluated by measuring the freezing point depression (ΔT) of solvents induced by solutes, in very dilute solutions, where Raoult–Vant Hoff’s law (1) of freezing point depression is obeyed.

\[ \Delta T = T_1 - T = \nu \cdot x_2 \left[ \frac{R T^4}{L_1} \right] \]  …(1)

In Eq. (1), T, and T are the crystallisation temperatures in K of the pure solvent and the mixture, respectively; L₁ is the melt enthalpy (in cal/mol) of the solvent; x₂ is the mole fraction of the solute; and R is the ideal gas constant (1.986 cal. deg.⁻¹ mol⁻¹).
The $RT/L_1$ represents the molar depression of freezing point or the cryoscopic constant, $K_0$, of the pure solvent.

In this note the dissociation behaviour of some alkali isopolymolybdates and some related molybdenum (VI) compounds in molten potassium dichromate ($K_0 = 101.1$) and potassium nitrate ($K_0 = 318.0$) has been investigated employing the cryoscopic method. The experimental technique used was the same as described earlier. The working temperature was 450 and 350°C for molten $K_2Cr_2O_7$ and $KNO_3$ respectively. The solvents $K_2Cr_2O_7$ (pro-analysis) and $KNO_3$ (purest) were obtained from E. Merck. The solutes employed in the present investigation were prepared and identified as reported.

(A) The number ($v$) of foreign ions produced by the solutes, $M_2Mo_8O_{21}$, $M_2Mo_4O_{13}$ and $M_2Mo_7O_{18}$ ($M = Rb$ or $Cs$) in the two solvents comes out to be 3, as revealed by the plots of $\Delta T$ versus mol fraction ($x_3$) of the solute. This indicates that the dissociation of the solutes in these melts follows Eqs (2) and (3).

$$K_2Cr_2O_7 + M_2Mo_8O_{21} \rightarrow 2K^+ + (Cr_2O_7)^{2-} + 2M^+ + (Mo_8O_{21})^{2-} \quad \text{(2)}$$

$$KNO_3 + M_2Mo_8O_{21} \rightarrow K^+ + (NO_3)^{-} + 2M^+ + (Mo_8O_{21})^{2-} \quad \text{(3)}$$

where $M = Rb$ or $Cs$ and $x/y = 1/4$, $3/10$, $4/13$ and $5/16$.

The present results on rubidium and cesium orthomolybdates are analogous to those of sodium and potassium orthomolybdates in the same solvents. However, isopolyorthomolybdates ions, viz. $(Mo_8O_{21})^{2-}$ or $(Mo_8O_{13})^{2-}$ and $(Mo_7O_{18})^{2-}$ do not seem to undergo any reaction with the solvent anions, presumably because of their stability in the melt under the present experimental conditions.

The formation and stability of one of the isopolyorthomolybdates ions in molten $KNO_3$ reported earlier are based on a different method. The Cs$_8$Mo$_8$O$_{21}$-rich (1.5 mol%) mixture of $K_2Cr_2O_7$ has been chosen, as an example of this group of solutes, to calculate its activity ($\alpha$) using Temkin and random mixing models as well as Vant Hoff's equation. The experimental and calculated activities are given in Table 1.

The data in Table 1 demonstrates an excellent agreement between the experimental and calculated values of activity ($\alpha$), thus supporting the proposed dissociation scheme (Eqs 1 and 2). However, the choice of a specific model is not possible, since such an agreement depends on the same ideality criteria used rather than the model chosen.

(B) (i) Although the solutes $K_2Cr_2O_7 .2MoO_3$ and $V_2MoO_8$ give the same number of foreign ions, i.e. $v = 1$ in both the solvents, they show obviously a different behaviour in the melt. The solute $K_2Cr_2O_7 .2MoO_3$ appears to be dissociated, while $V_2MoO_8$ presumably dissolves without dissociation. The corresponding reactions may consequently be represented by Eqs (4-7)

$$K_2Cr_2O_7 + K_2CrO_4 .2MoO_3 \rightarrow 4K^+ + (Cr_2O_7)^{2-} + (CrMoO_7)^{2-} \quad \text{(4)}$$

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

$$K_2Cr_2O_7 + V_2MoO_8 \rightarrow 2K^+ + (Cr_2O_7)^{2-} + V_2MoO_8 \quad \text{(6)}$$

$$KNO_3 + V_2MoO_8 \rightarrow K^+ + (NO_3)^{-} + V_2MoO_8 \quad \text{(7)}$$

The above scheme for the dissociation of $K_2Cr_2O_7 .2MoO_3$ and that for the dissolution of $V_2MoO_8$ is supported by the fact that the value of $\nu = 1$, is smaller than that required for their constituents : $K_2Cr_2O_7 .2MoO_3$ and $V_2MoO_8$ studied separately in the same solvents as reported earlier.

(ii) The dissociation of $Na_2CrO_4 .MoO_3$ in both the molten solvents give $\nu = 3$, suggesting the reactions to take place through dissociation and simultaneous rearrangement of ions as shown in Eqs (8-11)

$$K_2CrO_4 + 2Na_2CrO_4 .MoO_3 \rightarrow 2K^+ + 4Na^+ + 2(CrMoO_7)^{2-} + (CrO_4)^{2-} \quad \text{(8)}$$

$$2(CrMoO_7)^{2-} \rightarrow (CrMoO_7)^{2-} + (CrO_4)^{2-} \quad \text{(ii)}$$

$$K_2CrO_4 + 2Na_2CrO_4 .MoO_3 \rightarrow 2K^+ + 4Na^+ + (CrMoO_7)^{2-} + (CrO_4)^{2-} + (CrO_4)^{2-} \quad \text{(8)}$$

$$KNO_3 + 2Na_2CrO_4 .MoO_3 \rightarrow K^+ + (NO_3)^{-} + 4Na^+ + (CrMoO_7)^{2-} + (CrO_4)^{2-} \quad \text{(9)}$$

It can be seen from Eqs (8) and (9) that the number of foreign ions, $\nu = 3$, does not change after rearrangement of the heteroions $2(CrMoO_7)^{2-}$ to $2(CrO_4)^{2-}$. Such a rearrangement seems probable because the remaining $(CrMoO_7)^{2-}$-ions in the melt will lead to a lower and a higher value of $\nu$ in the cases of molten $K_2Cr_2O_7$ and $KNO_3$ solvents, respectively. This assumption can be explained by considering the heteroion $2(CrMoO_7)^{2-}$ as mixed crystals of $(Cr_2O_7)^{2-}$ and $(MoO_7)^{2-}$. The resulting $(MoO_7)^{2-}$-ion then tends to undergo isomorphous substitution within the $K_2Cr_2O_7$ lattice, thus leading to $\nu < 3$.

### Table 1 — Experimental and Calculated Activities ($\alpha$)

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NOTES
Also the same heteroions may dissociate in KNO₃ solvent giving 2(CrO₄)²⁻ and 2(MoO₄)²⁻ ions, leading to $v > 3$ which is not the case here. The behaviour of dimolybdate anion (MoO₄)²⁻ of Rb and Cs has, therefore, been studied in molten KNO₃. The $v$-value comes out to be 4 in this case. Thus, the resulting species are unstable and give rise to two basic monomolybdate anions analogous to the reactions of K₂Cr₂O₇ and K₂Mo₃O₁₂ in molten KNO₃ (ref. 5). These solutes behave as Lux-acids and take up oxide ions from the nitrate base electrolyte lead to the formation of more basic CrO₄²⁻ and MoO₄²⁻ ions, respectively. Accordingly, the reaction may be written as shown in Eq. (10).

$$2\text{KNO}_3 + \text{M}_2\text{MO}_3\text{O}_{12} \rightarrow 2\text{M}^+ + 2\text{K}^+ + 2(\text{MoO}_4)^2^- + 2\text{CrO}_4^- + \frac{1}{2} \text{O}_2$$

(M = Rb or Cs) \hspace{1cm} (10)

The results obtained using the ions, (Cr₂O₇)²⁻ and (MoO₃O₁₀)²⁻, separately in the two solvents support the above mechanism for the heteroions rearrangement process.

(ii) The mechanism of dissociation of Cr₂Mo₃O₁₂ in the two solvents seems to be obviously different, though the value of $v$ comes out to be 3, as in the cases B-i and B-ii above.

Consequently, the mechanism of dissociation of Cr₂Mo₃O₁₂ in molten K₂Cr₂O₇ may be expressed by Eq. (11).

$$\text{Cr}_2\text{Mo}_3\text{O}_{12} \rightarrow \text{Cr}_2\text{O}_7^- + \text{Mo}_2\text{O}_9^- \quad \text{(i)}$$

$$\text{K}_2\text{Cr}_2\text{O}_7 + \text{Mo}_2\text{O}_9^- \rightarrow 2\text{K}^+ + (\text{MoO}_4)^2^- + 2\text{CrO}_4^- \quad \text{(ii)}$$

$$3\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{Cr}_2\text{O}_7^- \rightarrow 6\text{K}^+ + \text{Cr}_2\text{O}_7^- + (\text{MoO}_4)^2^- + 2(\text{CrO}_4)^2^- \quad \text{(iii)}$$

It has already been pointed out that the first dissociation product, Cr₂O₇⁻, (step-i) is stable and insoluble in molten K₂Cr₂O₇ (ref. 5) and hence it does not contribute to the freezing point depression. The second dissociation product may then react with the solvent (step-ii) by taking its oxide-ion from the (CrO₄)²⁻ group, to form the trimolybdate anion (MoO₄)²⁻ and the two CrO₄⁻ ions. The stability of (MoO₄)²⁻ ion in molten K₂Cr₂O₇ has already been demonstrated in the present work. Finally, a reaction may occur between he CrO₄⁻ molecules and (CrO₄)²⁻ ions (step-iii) to form the well known, stable (CrO₄)²⁻ ion in such solvent.

In addition to the above studies, the behaviour of Cr₂O₇⁻ has also been investigated in molten KNO₃ to provide support for the formation of chromate ion. Thus, the experimentally determined value of $v = 2$ for this system suggests the following sequence of reactions:

$$2\text{KNO}_3 + \text{Cr}_2\text{O}_7^- \rightarrow 2\text{K}^+ + (\text{CrO}_4)^2^- + 2\text{NO} \quad \text{(12)}$$

$$4\text{KNO}_3 + (\text{Cr}_2\text{O}_7)^2^- \rightarrow 4\text{K}^+ + 2(\text{CrO}_4)^2^- + 4\text{NO}_2 + \frac{1}{2} \text{O}_2$$

Moreover, the yellow solution obtained as a result of dissolution of Cr₂O₇⁻ as well as that of Cr₂Mo₃O₁₂ in molten KNO₃ shows an absorption maximum at 27100 cm⁻¹, thus confirming the formation of (CrO₄)²⁻ ions. Similar results were also obtained for the reaction of Cr₂O₇⁻ in molten lithium-potassium nitrate eutectic.

References


Formation Constants of Cyanohydrins of Substituted Acetylphenyls

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The formation constants of cyanohydrins of 2' - and 3'-substituted 4-acetylphenyls have been determined at 30° in 80% dioxan-water (v/v). The 3'-substituted 4-acetylphenyls obey the Hammett equation giving a $p$-value of 0.52; 2'-substituted cyanohydrins do not obey the Hammett equation. The formation constants of 3'-substituted 4-acetylphenyls and the rate constants for the reduction by sodium borohydride reveal a linear relationship ($r = 0.990$). The influence of 2'-substituents reveals the existence of $\pi$-electron steric effect.

During addition of hydrogen cyanide to carbonyl group in ketones and aldehydes the carbonyl carbon in $sp^2$ hybrid state (trigonal planar) undergoes transition to $sp^3$ hybrid state (tetrahedral). When the change in the coordination of the reaction centre occurs the development of steric strain will be reflected in rate or equilibrium constant.