

Kinetic Studies of the Solvent Extraction of Molybdenum(VI) by 2-Thenoyltrifluoroacetone

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Received 27 January 1979; revised 18 April 1979; re-revised and accepted 30 July 1979

The rate of extraction of molybdenum (VI) from halide medium by 2-thenoyltrifluoroacetone (TTA) in carbon tetrachloride is first order with respect to the initial concentration of the metal in the aqueous phase, second order with respect to the chelate concentration in the organic phase and inversely second order with respect to hydrogen ion concentration. The rate determining step is the 1:2 complex formation in the aqueous phase. The species extracted is $\text{MoO}_2(\text{TTA})_2$. The rate constant for this reaction is $8.4 \times 10^{-3} \text{ min}^{-1}$. The addition of a solvating solvent helps to attain the extraction equilibrium immediately. Synergistic studies with mixtures of TTA and di-*n*-pentyl sulphoxide (DPSO) have established the extraction of metal species $\text{MoO}_2(\text{TTA})_2 \cdot 2\text{DPSO}$ in the perchlorate medium; $\text{HMoO}_2(\text{TTA})\text{Cl}_2 \cdot \text{DPSO}$ and $\text{HMoO}_2\text{Cl}_3 \cdot 3\text{DPSO}$ are the additional species in the chloride medium.

A survey of literature shows that little attention has been paid to the study of the solvent extraction of Mo(VI) by chelates under non-equilibrium conditions. In addition to the use of distribution phenomena as a means of studying chelate formation equilibria, in favourable cases, it provides a simple technique for the determination of rate constants of chelation reactions. The extraction of the metal from halide medium by acetylacetone,¹ dibenzoylmethane² and 2-thenoyltrifluoroacetone³ chelates have been studied under equilibrium conditions. The steps involved in the formation of the chelate are loss of water molecules from the metal hydrate and addition of the first and second ligands. The present paper deals with a kinetic investigation of the extraction of Mo(VI) from halide medium by TTA with a view to elucidating the mechanism of extraction and identifying the rate-determining step. The slow rate of extraction by the chelate may be improved by the addition of a solvating solvent; studies have been made on the extraction of Mo(VI) from both perchlorate and chloride media using mixtures of TTA and di-*n*-pentyl sulphoxide (DPSO).

Materials and Methods

Di-*n*-pentyl sulphoxide was synthesised according to the procedure already described⁴. TTA was a Fluka A. G. reagent and was used as such. Molybdenum(VI) was estimated spectrophotometrically using a Toshniwal spectrophotometer.

Determination of extraction coefficients — After shaking equal volumes of the two phases at $30 \pm 1^\circ$ for different intervals of time, they were separated. The phases were agitated rapidly so that the rate of extraction was independent of the shaking of the phases. The metal content in the aqueous phase was determined spectrophotometrically by dithiol method⁵. In extraction systems containing the sulphoxide, the extraction equilibrium was attained

within 5 min. The distribution coefficient, *D*, was taken as the ratio of the metal concentration in the organic phase to that present in the aqueous phase.

The rate of extraction of Mo(VI) into the aqueous phase with TTA may be represented⁶ by Eq. 1.

$$-\frac{d[\text{Mo}^{6+}]}{dt} = k [\text{Mo}^{6+}]^a [\text{TTA}]_{\text{org}}^b [\text{H}^+]^c [\text{Cl}^-]^d \dots (1)$$

If the extractant, hydrogen and chloride ions are in large excess in relation to Mo(VI), the rate expression can be written as,

$$-\frac{d[\text{Mo}^{6+}]}{dt} = q [\text{Mo}^{6+}]^a \dots (2)$$

where *q* is the product of rate constant, *k*, and the other concentrations which are kept constant. When the reaction order with respect to Mo^{6+} is unity, Eq. (2) takes the form,

$$-\log [\text{Mo}^{6+}] = qt + C_0 \dots (3)$$

where *C*₀ is a constant. As seen from Eq. (3), the plot of $-\log [\text{Mo}^{6+}]$ against *t* should be linear with a slope of *q*.

The reaction order with respect to other species in Eq. (1) can be determined when three of the concentrations out of four are kept constant.

$$\log q_{\text{H}^+} = \log k [\text{TTA}]_{\text{org}}^b [\text{Cl}^-]^d + c \log [\text{H}^+] \dots (4)$$

$$\log q_{\text{Cl}^-} = \log k [\text{TTA}]_{\text{org}}^b [\text{H}^+]^c + d \log [\text{Cl}^-] \dots (5)$$

$$\text{and } \log q_{\text{TTA}} = \log k [\text{H}^+]^c [\text{Cl}^-]^d + b \log [\text{TTA}] \dots (6)$$

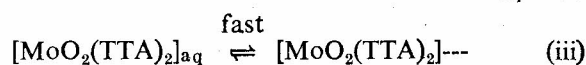
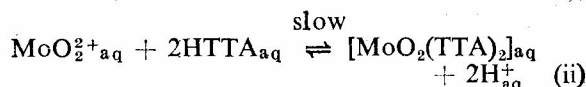
Results and Discussion

The plot of $-\log [\text{Mo}^{6+}]$ against *t* is linear showing (Eq. 3) that the order with respect to the metal is always unity. Again the linear plot of $\log q_{\text{TTA}}$ against $\log [\text{TTA}]$ has a slope equal to 2 indicating the second order dependence of TTA concentration of the organic phase (Eq. 6). Further the slope of the linear plot of $\log q_{\text{H}^+}$ against $-\log [\text{H}^+]$ is 2;

confirming the inverse second order with respect to the H^+ ion concentration in the aqueous phase (Eq. 4).

The effect of chloride ion concentration on the rate of extraction in the range 5.3-6.3 M was studied with 0.1 M TTA at 0.1 M H^+ ion concentrations. It is found that the rate of extraction is independent of the concentration of the salt in the aqueous phase. Under the present experimental conditions rate constant, k , has been evaluated as $8.4 \times 10^{-3} \text{ min}^{-1}$.

The foregoing results suggest the following overall extraction mechanism:



The low rate of extraction of MoO_2^{2+} ion in the aqueous phase with the chelate may not be due to the slow substitution of the hydrated water; this is important only for such metal ions with larger charge and/or small radius. A second order dependence upon the concentration of the chelate shows that step (ii) is the rate determining step.

Studies under equilibrium conditions : Extraction by TTA — The extraction of Mo(VI) from perchlorate and chloride media by TTA can be represented by Eq. (7),



The equilibrium constant, K , is given by

$$K = \frac{[\text{MoO}_2(\text{TTA})_2][\text{H}^+]^2}{[\text{MoO}_2^{2+}][\text{HTTA}]^2} \quad (8)$$

$$= D \cdot [\text{H}^+]^2 [\text{HTTA}]^{-2}$$

where D is the distribution coefficient of Mo(VI). A second order dependence of $\log D$ on $\log M$ TTA has been observed (Fig. 1) from ($H^+ = 0.1M$ and $Cl^-/ClO_4^- = 6.0M$) chloride/perchlorate media, as expected. The value of the equilibrium constant is 0.326.

Extraction by DPSO — The slope analysis method for the extraction of Mo(VI) from hydrochloric acid solutions by DPSO (studied by varying $[DPSO]$, $[\text{Mo(VI)}]$, $[Cl^-]$ and $[H^+]$ in the range of experimental conditions) showed the transfer of $\text{HMoO}_2Cl_3 \cdot 3DPSO$ into the organic phase.

Synergistic extraction of Mo (VI) by TTA + DPSO mixtures — The addition of neutral extractant, DPSO enhances the extraction and the extraction equilibrium is attained within 5 min. The rapid rate of extraction may be due to the extraction of the first complex, $\text{MoO}_2(\text{TTA})Cl$, as a mixed adduct, $\text{MoO}_2(\text{TTA})Cl \cdot nDPSO$, in the presence of DPSO. In the organic phase TTA rapidly substitutes the anion of the metal adduct completing the

chelation ($\text{MoO}_2(\text{TTA})_2 \cdot nDPSO$). The synergistic extraction may be attributed to the formation of extractable mixed ligand complex, generally represented by the Eq. (9),



Distribution studies were carried out from perchlorate medium ($H^+ = 0.1M$ and $ClO_4^- = 6.0M$) by keeping $[DPSO]$ at 0.03 M and varying $[TTA]$ in the range 0.01-0.06 M . The natures of the metal species transferred into the organic phase have been established by plotting $\log D_{\text{syn,TTA}}$ ($D_{\text{obs}} - D_{\text{DPSO}}$) against $\log [TTA]$. The log-log plot is linear with a slope of 2 (Fig. 2). At constant $[TTA] = 0.03M$, the linear plot (Fig. 3) of $\log D_{\text{syn,DPSO}}$ against $\log [DPSO]$ has a slope equal to 2. Thus the species, $\text{MoO}_2(\text{TTA})_2 \cdot 2DPSO$, seems to be involved in the extraction, without the association of the anion, ClO_4^- .

On the other hand, the extraction of Mo(VI) from chloride medium ($H^+ = 0.1M$ and $Cl^- = 6.0M$) by mixtures of DPSO and TTA involves chloride ion participation (Fig. 4). The effect of Cl^- concentration over the range 5.0-7.0 M has been studied at

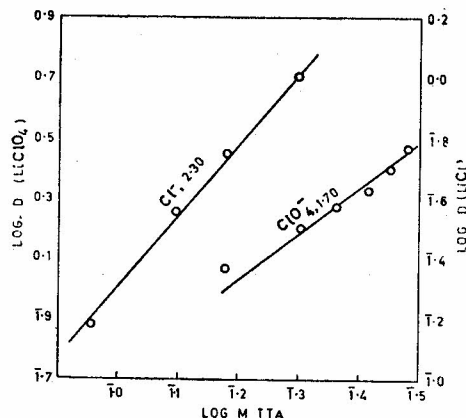


Fig. 1 — Variation of D of Mo (VI) with concentration of TTA. [Aq. Phase : $H^+ = 0.1M$; $Cl^-/ClO_4^- = 6.0M$]

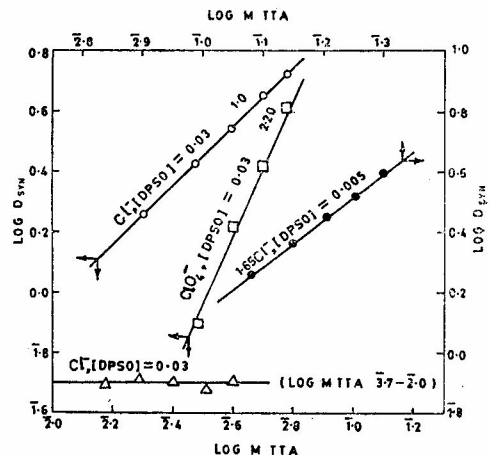


Fig. 2 — Variation of D of Mo (VI) with concentration of TTA at a fixed DPSO concentration. [Aq. phase : $H^+ = 0.1M$; $Cl^-/ClO_4^- = 6.0M$]

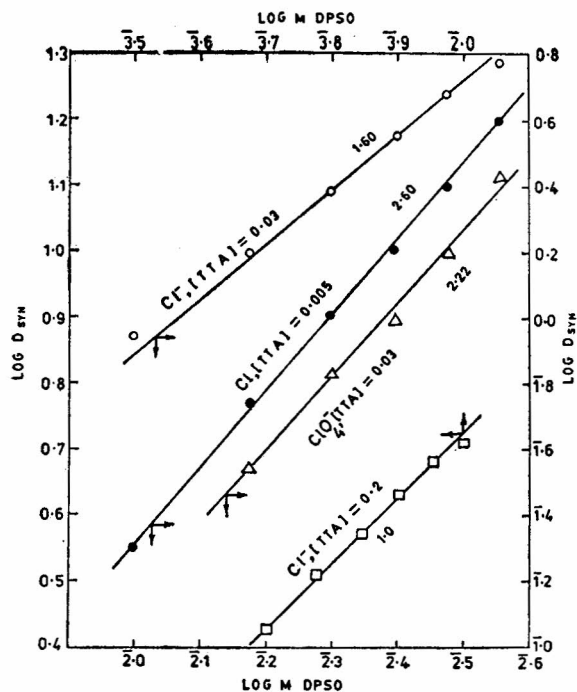


Fig. 3 — Variation of D of Mo (VI) with concentration of DPSO at a fixed TTA concentration. [Aq. phase : $H^+ = 0.1M$; $Cl^-/ClO_4^- = 6.0M$]

constant molarity of H^+ ($0.1M$) from mixtures of $HCl + LiCl$. The mean ionic activity coefficients of this mixed electrolyte system have been calculated⁷. The slopes of $\log D - \log a_{Cl^-}$ (logarithm of mean ionic activity of HCl at constant H^+ concentration) are nearly 2 and 3.

Fig. 2 presents data on the variation of $D_{SYN,TTA}$ of Mo(VI) with the concentration of TTA, at fixed concentration of DPSO. Depending on the composition range of the mixture, the slopes of log-log plots vary between zero and two indicating that 0–2 molecules of TTA are associated with the extraction of the metal from the chloride medium. For example at a given high concentration of DPSO ($0.03M$) and at low concentration range of TTA ($0.005M$ – $0.01M$) the log-log plot with zero slope shows the negligible participation of TTA in the extraction process. As the concentration range of TTA is increased while decreasing the given concentration of DPSO, the participation of TTA in the extraction of the metal becomes more pronounced. Fig. 3 shows data on the variation of $D_{SYN,DPSO}$ of Mo(VI) with the concentration of DPSO at a fixed concentration of TTA. It is seen that depending on the

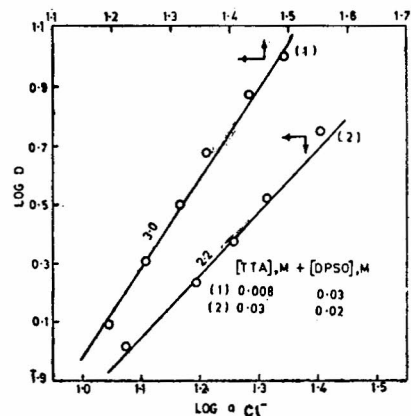


Fig. 4 — Variation of D of Mo (VI) with activity of chloride ion at constant composition of DPSO and TTA at $H^+ = 0.1M$

concentration of TTA used as compared to that of DPSO, the slopes of log-log plots vary from 1 to 3; these observations clearly suggest the presence of three complexes with average DPSO solvation numbers one $\{[TTA] \gg [DPSO]\}$, two $\{[TTA] \approx [DPSO]\}$, and three $\{[TTA] \ll [DPSO]\}$.

Thus, on the basis of the data in Figs. 1–4, the metal species $MoO_2(TTA)_2$, $HMoO_2(TTA)Cl_2$, $DPSO$, $MoO_2(TTA)_2 \cdot 2DPSO$ and $HMoO_2Cl_2 \cdot 3DPSO$ seem to be simultaneously involved in various proportions in the extraction of Mo(VI) from chloride medium into mixtures of TTA and DPSO. The species that are common in the extraction of Mo (VI), both from perchlorate and chloride media, are $MoO_2(TTA)_2$ and $MoO_2(TTA)_2 \cdot 2DPSO$.

Acknowledgement

The authors thank the UGC, New Delhi for awarding a junior research fellowship to one of them (BRR).

References

1. MCKAVANEY, J. P. & FREISER, H., *Analyt. chem.*, **29** (1957), 290.
2. STARY, J. & HLADKY, E., *Analyt. chim. Acta*, **28** (1963), 227.
3. DE, A. K. & SAHU, C., *J. inorg. nucl. Chem.*, **31** (1969), 2257.
4. MOHANTY, S. R. & REDDY, A. S., *J. inorg. nucl. Chem.*, **37** (1975), 1791.
5. CLARK, L. K. & AXLEY, J. H., *Analyt. Chem.*, **27** (1955), 2000.
6. SEKINE, T., YUMIKURA, J. & KOMATSU, Y., *Bull. chem. Soc. Japan*, **46** (1973), 2356.
7. REDDY, A. S. & SAYI, Y. S., *J. inorg. nucl. Chem.*, **40** (1978), 1125.