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Thermodynamics of extraction of MoO_4^{2-} from aqueous sulfuric acid media with TBP dissolved in kerosene

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Abstract

Molybdenum distribution between TBP dissolved in kerosene and aqueous sulfuric acid media is investigated. The influential parameters are temperature, molarity of sulfuric acid and concentration of TBP. The results show that the extraction reaction is exothermic. Increasing the TBP concentration at sulfuric acid molarities greater than 4 M does not change the distribution factor of molybdenum. The distribution factor of molybdenum in sulfuric acid media with TBP has a maximum at 0.03 mol/l of H_2SO_4 and a minimum near 0.2 mol/l of H_2SO_4 . The stoichiometric reaction indicates neutralization of 2 mol of H^+ with 1 mol of MoO_4^{2-} and solvating a neutral molecule with 3 mol of TBP. At the lower acidity, the complex structure may be $3\text{TBP} \cdot \text{H}_2\text{Mo}_2\text{O}_5(\text{SO}_4)_2$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: TBP; MoO_4^{2-} ; Sulfuric acid

1. Introduction

The conventional method for extraction of molybdenum involves roasting of molybdenite concentrate, containing molybdenum sulfide, into molybdenum oxides. Molybdenum dioxide sublimes with other volatile materials such as Re_2O_7 and SeO_2 . The

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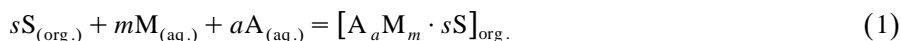
valuable compounds can then be recovered by cleaning and scrubbing of the gas [1,2]. These compounds accompanied by SO_2 and excess oxygen can be dissolved in water. The scrubbing solution contains MoO_4^{2-} , ReO_4^- and SeO_4^{2-} dissolved in sulfuric acid with a pH less than 2 [2]. Solvent extraction is a commercial method for production of pure materials such as molybdenum, rhenium, selenium and their compounds from multi-component scrubber solution. Many organic extractants have the ability to selectively extract the ions dissolved in a dilute acid solution. Determination of distribution factors of the ions present in the solution is, therefore, an important parameter in selection of the appropriate extractant.

Many investigations have so far been made on the solvent extraction of molybdenum from aqueous media containing sulfuric acid [2–11], hydrochloric acid [11–15] and nitric acid [5,11,16–20]. The published data include those using different organic reagents such as TBP [12,13,15,20–26], D2EHPA [10,26–33], Aliquat 336 [19,34,35], Alamine 336 [4,5,19,27,36–38] and Alamine 310 [21–23,39]. These papers provide useful insight into the extraction of molybdenum from solutions containing U, W, Re, V, Al, Co, Ni and Fe.

There are, however, no quantitative details on effect of temperature, TBP concentration and sulfuric acid molarity on distribution factors given in the literature. Thermodynamic properties such as enthalpy, entropy and equilibrium constant of extraction reaction are, however, required for detailed scientific studies and industrial applications. These properties can conveniently be utilized for estimation of the distribution factor prevailing under practical extraction conditions. Extensive research has been carried out during the past few years in our laboratory to evaluate these properties. Sample results corresponding to extraction of MoO_4^{2-} from sulfuric acid media with TBP are given in this paper.

2. Chemical equilibria

The extraction reaction has the following general form:



where S is the extractant, M is the ion being extracted (anion or cation) and A is any counter ion or other species that may be present in the aqueous phase. The equilibrium constant of reaction 1 may be written as:

$$K = \frac{a_{[\text{A}_a\text{M}_m \cdot s\text{S}]_{\text{org.}}}}{a_{\text{S}}^s a_{\text{M}}^m a_{\text{A}}^a} = \frac{[\text{A}_a\text{M}_m \cdot s\text{S}]_{\text{org.}}}{[\text{S}]^s [\text{M}]^m [\text{A}]^a} \frac{\gamma_{[\text{A}_a\text{M}_m \cdot s\text{S}]_{\text{org.}}}}{\gamma_{\text{S}}^s \gamma_{\text{M}}^m \gamma_{\text{A}}^a} = \frac{[\text{A}_a\text{M}_m \cdot s\text{S}]_{\text{org.}}}{[\text{S}]^s [\text{M}]^m [\text{A}]^a} Q \quad (2)$$

where Q is the quotient of the activity coefficients and square brackets indicate the molar concentrations. The distribution factor of species M may be written as:

$$D_{\text{M}} = \frac{\Sigma [\text{M}]_{\text{org.}}}{\Sigma [\text{M}]_{\text{aq.}}} \quad (3)$$

By substituting Eq. (3) into Eq. (2) and considering that solubilities of aqueous/organic phases in each other are negligible, thus:

$$\frac{K}{Q} = K' = \frac{D_M}{[S]^s[A]^a} \quad (4)$$

Re-arranging and taking logarithms yields:

$$\ln D_M = \ln K' + s \ln[S] + a \ln[A]. \quad (5)$$

Since $\ln K'$ is a function of temperature, Eq. (5) can be written as:

$$\ln D_M = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + s \ln[S] + a \ln[A] \quad (6)$$

where ΔH° and ΔS° are called the apparent standard changes of enthalpy and entropy of the reaction 1, respectively [40]. By measuring the distribution factor of an ion, one can determine the relationship between the stoichiometric coefficients and the apparent standard enthalpy and entropy of the reaction.

3. Experimental

3.1. Materials and reagents

Stock of molybdenum ion (5 g/l solution) was prepared by dissolving analytical grade sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$) produced by Merck in distilled water. In order to avoid the reduction of metal ions, 5 M sulfuric acid was prepared by diluting analytical grade sulfuric acid from Baran Chemical of Iran in distilled water. Acidic solutions of molybdenum were prepared by diluting 5 g/l aliquot solution with 5 M sulfuric acid to produce the required final concentrations. Corresponding quantities of analytical grade TBP were dissolved in aromatic kerosene, both obtained from Fluka, Switzerland.

3.2. Experimental procedure

Batch experiments were carried out in a flask containing equal volumes (20 ml) of aqueous and organic phases. The mixture was agitated at a constant temperature with a mechanical shaker. The experiments were allowed to run for 1 h, even though equilibrium could be obtained within 15 min [41]. The samples were retained for three more hours to allow complete separation of phases and the two phases were then removed with a separation funnel. Equilibrium was attained at different temperatures (25, 40 and $60 \pm 0.5^\circ\text{C}$).

The initial concentration of molybdenum in the aqueous phase in all experiments was 1 g/l. Molybdenum content of the aqueous phase was analyzed with the thiocyanate spectrophotometric adsorption method. Chemical composition of the organic phase was determined through mass balance calculations. Spectrophotometric measurements were done with a Unicam 8700 series UV/VIS spectrophotometer.

4. Result and discussion

4.1. Effect of temperature

The effect of temperature on the extraction of molybdenum was determined by changing temperature between 25°C and 60°C at a constant TBP concentration. It can be seen from Fig. 1 that D_{Mo} increases with decreasing temperature. Similar effect is observed at all acid and TBP concentrations. The values of the slopes for different TBP concentrations and acid molarities are given in Table 1. These values are 9023, 8922, 9098, 9320 and 9125 for 20%, 30%, 40%, 60% and 80% TBP, respectively. The average of the slopes is 9130. The apparent standard enthalpy of the extraction reaction 1 is, therefore, -75.90 kJ/mol. So the extraction of molybdenum from sulfuric aqueous media with TBP is an exothermic reaction.

4.2. Effect of extractant concentration

Eq. (6) shows that at a constant temperature and acid molarity, the distribution factor of molybdenum is proportional to the concentration of TBP. This effect is shown in Fig. 2, for 25°C, and is summarized, for other temperatures, in Table 2 at TBP concentrations ranging from 0.365 to 2.923 M (10 to 80 vol.%). The results indicate a constant slope at different temperatures and acid molarities. At acid molarities greater than 0.3 M, however, the slope tends asymptotically to zero. This result shows that at molarities greater than 0.3, changing TBP concentration, does not significantly influence the amount of extraction. The average slopes at 25°C, 40°C and 60°C are all 2.9. The

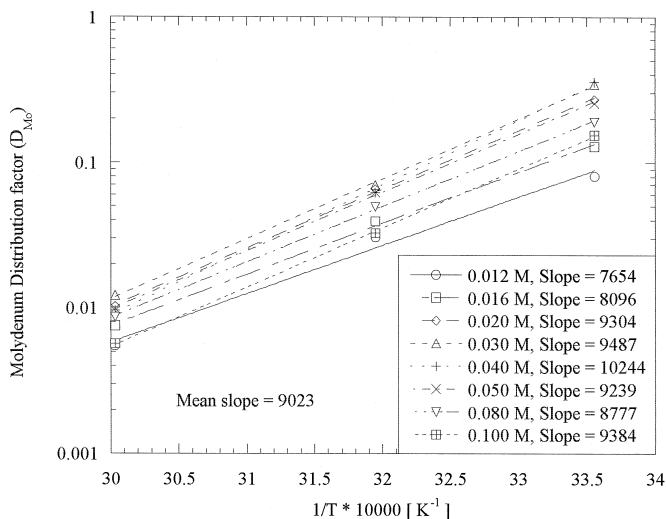


Fig. 1. Effect of temperature and molarity of sulfuric acid on molybdenum distribution factor with 20 vol.% TBP in kerosene.

Table 1

Values of the slopes of $\ln D_{\text{Mo}}$ vs. $1/T$ evaluated at different TBP concentrations and acid molarities

Acid molarity (mol/l)	TBP concentration (%)				
	20	30	40	60	80
0.004	–	–	8154	10232	9570
0.008	–	8818	9264	9014	9337
0.010	–	8341	9282	9372	9051
0.012	7657	8794	8010	9476	8862
0.016	80956	8587	7964	8874	8490
0.020	9304	9512	9191	8877	9410
0.030	9487	9551	9808	8987	9415
0.040	10244	9004	9045	9162	9597
0.050	9239	8902	8995	8603	9908
0.080	8777	9096	9528	9804	9512
0.100	9384	9526	10282	9504	9414
0.120	–	9162	9845	8910	9115
0.160	–	7769	8296	9696	8582
0.200	–	–	9096	9736	9563
0.300	–	–	9714	9548	7042
Mean	9023	8922	9098	9320	9125

stoichiometric constant of the extractant (s value in Eq. 1) is an integer number. We assume this value to be 3.

Hanson and Patel [42] have shown that the $[(\text{TBP})_3 \cdot \text{H}_2\text{SO}_4]$, $[(\text{TBP})_2 \cdot \text{H}_2\text{SO}_4]$ and $[\text{TBP} \cdot \text{H}_2\text{SO}_4]$ are the complexes formed in the extraction system containing TBP at sulfuric acid with molarities of less than 4, equal to 6 and between 8 and 9, respectively.

4.3. Effect of sulfuric acid concentration

Plotting the molybdenum distribution factor at constant temperature and TBP concentration vs. acid molarity, gives a straight line with a constant slope equal to a (Eq. 6). The effect of the concentration of sulfuric acid on the extraction of molybdenum anion has been investigated between 0.002 and 4 M, keeping the extraction temperature constant at 25°C, 40°C or 60°C and using TBP concentrations ranging from 10% to 80%. Based on the experimental results, shown in Fig. 3, an increase in acid concentration of the aqueous phase affects the extraction of molybdenum at every temperature and TBP concentration according to the following four regimes.

Regime one — increasing acid concentration from 0.002 to 0.03 M has an increasing effect on the distribution factor.

Regime two — increasing acid concentration from 0.03 to 0.2 M decreases the distribution factor.

Regime three — increasing acid molarity from 0.2 to 0.4 M and TBP concentration from 10% to 40% has a positive effect on the slope of the distribution factor. Changing TBP concentration from 60% to 80% results in variation of the slope of the distribution factor from a slightly positive to a negative value.

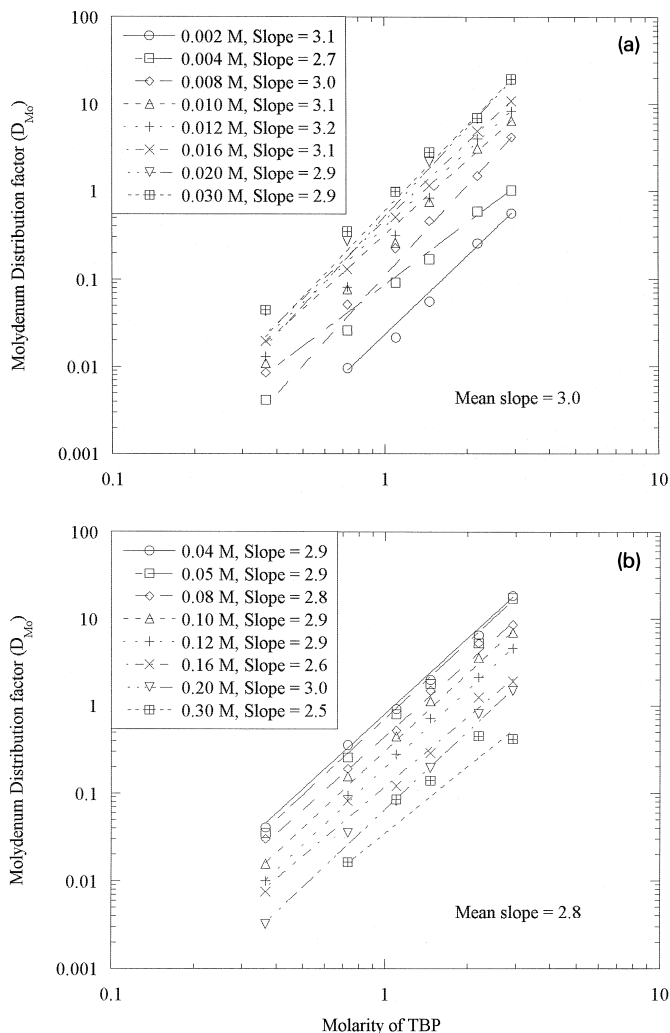


Fig. 2. Effect of molarity of TBP on the distribution factor of molybdenum at 25°C for aqueous sulfuric acid media. (a) 0.002 to 0.030 M, (b) 0.04 to 0.30 M.

Regime four — increasing the acid molarity does not significantly affect the extraction of molybdenum and thus the distribution factor.

In some special cases of practical importance, the complex formed has multiplicative dissolving behavior in organic and/or aqueous media. For these cases $\ln D_{Mo}$ depends on such parameters as acid molarities, TBP concentration and organic and/or aqueous volume change. So the assumptions for re-writing Eqs. (3) and (4) are not precise. Hence, the molybdenum distribution factor vs. acid molarity relationship does not

Table 2

Values of the slopes $\ln D_{M_0}$ vs. $\ln[\text{TBP}]$ evaluated at different temperatures and acid molarities

Acid molarity (mol/l)	Temperature °C		
	25	40	60
0.002	3.1	–	–
0.004	2.7	2.6	–
0.008	3.0	2.7	2.9
0.010	3.1	3.0	3.1
0.012	3.2	3.1	3.1
0.016	3.1	3.1	3.1
0.020	2.9	3.0	3.1
0.030	2.9	3.0	3.0
0.040	2.7	2.9	3.0
0.050	2.9	2.9	2.9
0.080	2.8	2.9	2.6
0.100	2.9	2.7	2.7
0.120	2.9	2.6	2.6
0.160	2.6	–	–
0.200	3.0	–	–
0.300	2.5	–	–
Mean	2.9	2.9	2.9

exactly obey Eq. (6). A better correlation is derived in Section 4.4 for prediction of the molybdenum distribution factor under practical conditions of interest.

4.4. Approximate equation for computation of the distribution factor

We can compute constants of Eq. (6) excluding a . We re-write Eq. (6) as:

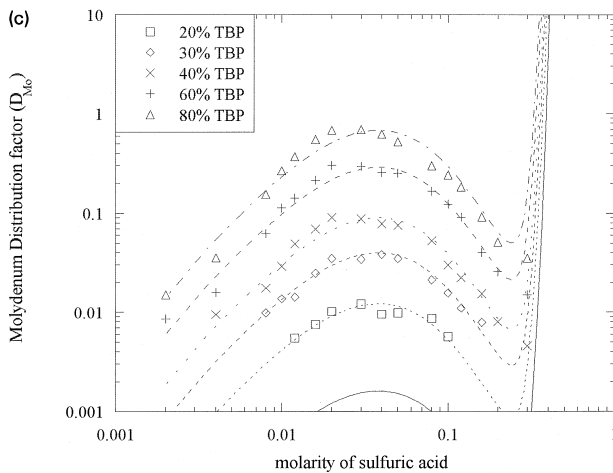
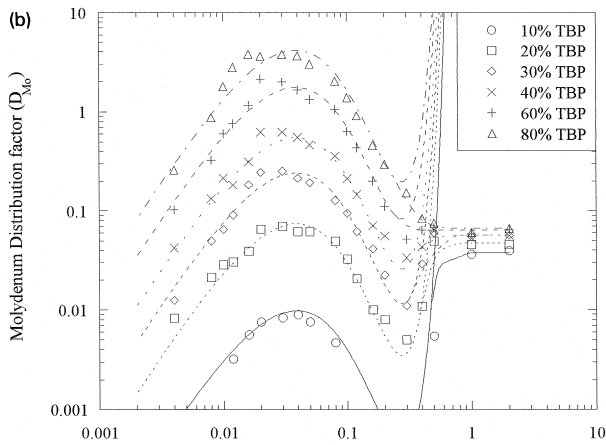
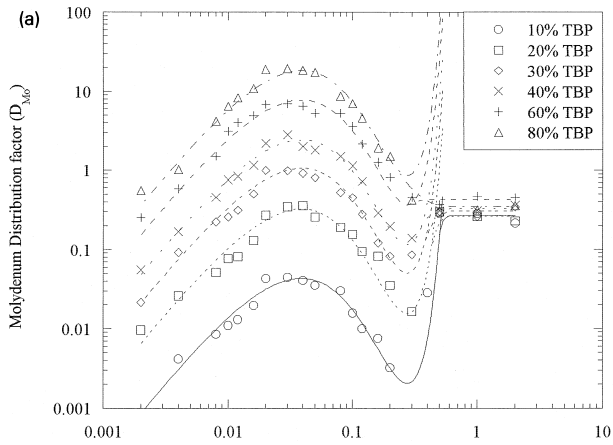
$$\ln D_M = \frac{9130}{T} + \frac{\Delta S}{R} + a \ln[\text{H}^+] + 2.9 \ln[\text{TBP}]. \quad (7)$$

Pruett [40] proposes that in systems which show a maximum in the extraction curve, a free TBP term ($[\text{TBP}]_f$) can be used instead of the initial TBP term ($[\text{TBP}]_0$). Thus we have:

$$[\text{TBP}]_f = [\text{TBP}]_0 - [\text{Acid}] - d[\bar{X}] \quad (8)$$

where d is a constant, $[\text{Acid}]$ is acid concentration in the organic phase and $[\bar{X}]$ is the concentration of metal in the organic phase. Under conditions of our experiments, the third term in Eq. (8) is negligible; the acid term is, however, large enough to affect $[\text{TBP}]_f$ [40]. With a theoretical and/or semi empirical analysis, it can be shown that with initial TBP concentration of $[\text{TBP}]_0$ and equilibrated aqueous acid concentration of $[\text{H}_2\text{SO}_4]_{\text{aq}}^{\text{equilibrium}}$, we have [40]:

$$[\text{TBP}]_f = [\text{TBP}]_0 + c[\text{H}_2\text{SO}_4]_{\text{aq}}^{\text{equilibrium}} [\text{TBP}]_0 \quad (9)$$



where c is a constant. So Eq. (9) can be re-written as:

$$[\overline{\text{TBP}}]_f = [\overline{\text{TBP}}]_0 \left(1 + c[\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \right) \quad (10)$$

or

$$\ln[\overline{\text{TBP}}]_f = \ln[\overline{\text{TBP}}]_0 + \ln\left(1 + c[\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \right). \quad (11)$$

Using Taylor's approximation:

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \quad -1 < x \leq 1. \quad (12)$$

When sulfuric acid concentration is much less than 1, Eq. (11) can be re-written as follows:

$$\begin{aligned} \ln[\overline{\text{TBP}}]_f = \ln[\overline{\text{TBP}}]_0 + c[\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} - \frac{c^2}{2} \left\{ [\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \right\}^2 \\ + \frac{c^3}{3} \left\{ [\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \right\}^3 - \frac{c^4}{4} \left\{ [\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \right\}^4 + \dots \end{aligned} \quad (13)$$

At very low sulfuric acid concentrations, those terms having large powers tend to zero. Hence, with replacement of $[\overline{\text{TBP}}]_f$ from Eq. (13) in Eq. (6) we have:

$$\begin{aligned} \ln D_{\text{Mo}} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + a \ln[\text{H}^+] + s \ln[\overline{\text{TBP}}]_0 + d[\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \\ + e \left\{ [\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \right\}^2 - f \left\{ [\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \right\}^3 \\ + g \left\{ [\text{H}_2\text{SO}_4]_{\text{aq.}}^{\text{equilibrium}} \right\}^4. \end{aligned} \quad (14)$$

In order to determine the coefficients of Eq. (14), we have collected a data bank with acid molarities of less than 0.4 M. We have then analyzed the data through application of SPSS for windows V 8.0. The results are shown in Table 3. From these data, the equation for molybdenum distribution factor would become:

$$\begin{aligned} \ln D_{\text{Mo}} = -25.55 + \frac{9790}{T} + 2.00 \ln[\text{H}^+] + 2.90 \ln[\overline{\text{TBP}}]_0 - 64.26[\text{H}_2\text{SO}_4] \\ + 146.46[\text{H}_2\text{SO}_4]^2 - 120.72[\text{H}_2\text{SO}_4]^3. \end{aligned} \quad (15)$$

The values measured for molybdenum distribution factor are compared with the calculated ones in Fig. 4. These data confirm the estimated equation for computation of the distribution factor of the aqueous media with molarities less than 0.4 M.

Fig. 3. Effect of sulfuric acid molarity on molybdenum distribution factor with TBP in kerosene at (a) 25°C, (b) 40°C and (c) 60°C. Note that the points show the experimental data, while the lines (plotted based on Eq. 15) indicate the estimated values. Horizontal lines demonstrate the P_{RMoO_4} values.

Table 3

Coefficients calculated for determination of distribution factor of molybdenum with TBP diluted in kerosene and sulfuric acid aqueous media at different temperatures

Value	Computed coefficient	Standard error
$1/T$	9790	105
$\ln[H^+]$	2.00	0.05
$\ln [TBP]_0$	2.90	0.02
$[H_2SO_4]$	-64.26	3.15
$[H_2SO_4]^2$	146.46	20.22
$[H_2SO_4]^3$	-120.72	40.48
Equation constant	-25.55	0.39

Comparing Eqs. (14) and (15) indicates that the apparent standard molar enthalpy of extraction of molybdenum anions is -75.90 kJ/mol and the apparent standard entropy of molybdenum extraction with TBP from sulfuric acid aqueous media is -0.21 kJ/mol.

The apparent standard Gibbs free energy of extraction of molybdenum from the solution is, therefore:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -75.90 + 0.21T \text{ kJ/mol.} \tag{16}$$

The equilibrium constant of the extraction reaction can be calculated from:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_p \tag{17}$$

Based on Eq. (16), the apparent equilibrium constant at 25°C , 40°C and 60°C is, therefore, 162.6, 37.5 and 6.5, respectively.

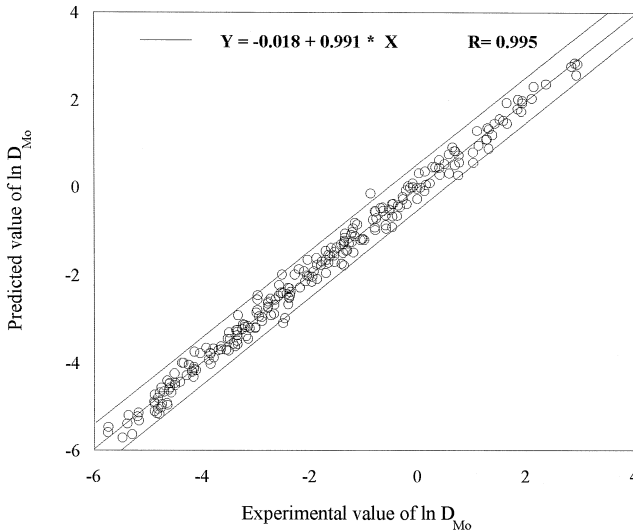


Fig. 4. Comparison of the measured and the calculated values for molybdenum distribution factor for TBP in kerosene in aqueous sulfuric acid media with molarities less than 0.4 at different temperatures.

4.5. Organic complex partition factor

Cox and Flett [43] have shown that at equilibrium between organic and aqueous phase an organic substance (RX) is present in both phases:

$$\overline{\text{RX}} = \text{RX}. \quad (18)$$

One can define an organic partition factor such as:

$$P_{\text{RX}} = \frac{[\overline{\text{RX}}]}{[\text{RX}]}. \quad (19)$$

After the extraction of the metal, an organic complex RMe is formed at equilibrium between the two phases:

$$\overline{\text{RMe}} = \text{RMe}. \quad (20)$$

Define an organic complex partition factor, P_{RMe} , as follows:

$$P_{\text{RMe}} = \frac{[\overline{\text{RMe}}]}{[\text{RMe}]}. \quad (21)$$

If solubility of the complex formed in the aqueous media is large, the distribution factor of the metal ion is, therefore, given by:

$$D_{\text{Me}} = \frac{[\overline{\text{RMe}}]}{[\text{RMe}] + [\text{Me}]}. \quad (22)$$

Hence, we assume that the extracted complex can be produced through the combination of a molybdenum anion MoO_4^{2-} , and a complex organic agent and then is ionized according to the following ionization reaction:



The equilibrium constant of Eq. (12) is:

$$K_{\text{D}} = \frac{[\text{R}^{2+}][\text{MoO}_4^{2-}]}{\text{RMO}_4}. \quad (24)$$

hence:

$$\begin{aligned} D_{\text{Mo}} &= \frac{\overline{\text{RMO}_4}}{[\text{RMO}_4] + [\text{MoO}_4^{2-}]} = \frac{[\overline{\text{RMO}_4}]}{[\text{RMO}_4] \left(1 + \frac{[\text{MoO}_4^{2-}]}{[\text{RMO}_4]} \right)} \\ &= P_{\text{RMO}_4} \frac{1}{1 + \frac{K_{\text{D}}}{[\text{R}^{2+}]}}. \end{aligned} \quad (25)$$

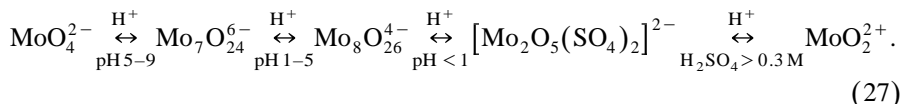
Taking logarithms yields:

$$\ln D_{\text{Mo}} = \ln P_{\text{RMoO}_4} - \ln \left\{ 1 + \frac{[K_D]}{[R^{2+}]} \right\}. \quad (26)$$

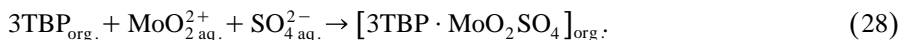
The value of $\log P_{\text{RMoO}_4}$ can be calculated by plotting the changes of $\log D_{\text{Mo}}$ vs. logarithm of the acid molarity and characterization of the horizontal part of the obtained curve. So the values of P_{RMoO_4} at temperatures 25°C and 40°C are 0.318 and 0.053, respectively. These values indicate that the complex formed at the higher acid concentration would have higher solubility in water. This phenomenon depends on the nature of complex and the solubility of water in the complex.

4.6. Estimation of the extraction stoichiometric equation

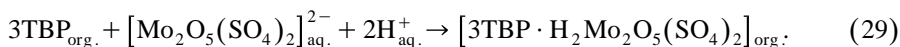
The structure of molybdenum ions depends on pH and molarity of the acid in aqueous media [44–48]. The change of ionic structure of molybdenum is defined by:



In the upper acidity range ($\text{H}_2\text{SO}_4 > 0.3 \text{ M}$) the stable molybdenum cation is MoO_2^{2+} . So in the present test, which is carried out in sulfuric acid media, the molybdenum ion complex is MoO_2SO_4 with TBP and the extraction molecules may have a structure such as $3\text{TBP} \cdot \text{MoO}_2\text{SO}_4$. The stoichiometric equation for the extraction reaction may, therefore, be:



Regression analysis of the data given in Table 3 shows that the constant (a) is equal to 2, so at the lower acidity, the complex structure may be $3\text{TBP} \cdot \text{H}_2\text{Mo}_2\text{O}_5(\text{SO}_4)_2$ and the extraction stoichiometric equation may be written as:



Based on the experimental data and the above discussion, it may be said that for sulfuric acid molarities greater than 0.002 (pH approximately 2.4) the stable molybdenum ion is $[\text{Mo}_2\text{O}_5(\text{SO}_4)_2]^{2-}$.

5. Conclusions

Based on the data presented in this paper, one can deduce that the molybdenum extraction reaction with TBP is an exothermic reaction. The apparent standard molar enthalpy for extraction of molybdenum anions is -75.90 kJ/mol and the apparent standard entropy of molybdenum extraction with TBP from sulfuric acid aqueous media is -0.21 kJ/mol K . So the apparent standard Gibbs free energy of extraction of molybdenum from the solution presented in this paper is:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -75.90 + 0.21T \text{ kJ/mol.}$$

The apparent equilibrium constant of extraction reaction at 25°C, 40°C and 60°C is 162.6, 37.5 and 6.5, respectively. The investigation of extraction of molybdenum for acid concentration with molarities less than 0.4 M at constant temperature and TBP concentration indicates that neutralization of every mole of molybdenum anion needs 2 mol of H⁺ cations. At these molarities, the molecules formed react with 3 mol of TBP and the complex formed may be 3TBP · H₂Mo₂O₅(SO₄)₂. Results of this study show that by increasing the acid molarity above 0.4 M, the molybdenum extraction factor, D_{Mo} , does not significantly change. Under these circumstances, the extraction molecules may have a structure such as 3TBP · MoO₂SO₄ and the values of the organic complex partition factor (P_{RMoO_4}) are 0.317 and 0.053 at temperatures 25°C and 40°C, respectively. Based on the regression analysis of the data, the following equation is obtained for prediction of the distribution factor of molybdenum:

$$\ln D_{Mo} = -25.55 + \frac{9790}{T} + 2.00\ln[H^+] + 2.90\ln[TBP]_0 - 64.26[H_2SO_4] + 146.46[H_2SO_4]^2 - 120.72[H_2SO_4]^3.$$

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