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# Determination and modeling for the solubility of $Na_2MoO_4{\cdot}2H_2O$ in the $(Na^+ + MoO_4^{2-} + SO_4^{2-})$ system

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ABSTRACT

The solubility of $Na_2MoO_4{\cdot}2H_2O$ in $(Na^+ + MoO_4^{2-} + SO_4^{2-})$ system was carried out using a dynamic method within the temperature range from 293.15 K to 343.15 K. The new model was established via regression of the published and the determined values to predict the solubility. From the results, the solubility of sodium molybdate increases with the temperature increase, however, it decreases with the increasing concentration of sodium sulfate. The Pitzer parameters and the solubility product constant of sodium sulfate and sodium molybdate in aqueous solution were obtained using the literature data. The solubilities of the sodium molybdate in the sodium sulfate solution as well as the thermodynamic parameters were calculated based on the experimental values obtained. The new model was also applied to estimate the solubility of the sodium molybdate under various conditions. The calculated values agree well with the experiment results.



## 1. Introduction

Molybdenum is one of the rare and high-melting metals, which is applied widely in many industries, such as steel, general electronic, agrochemical, and nuclear. The smelting and extraction of molybdenum attracts much more researcher's attention. The usual methods of dealing with the resources containing molybdenum are precipitation [1], ion exchange [2], adsorption [3] and solvent extraction [4]. For these methods, the solvent extraction was more promising due to its advantages including high purity of products, high efficiency of extraction and simple operation procedures. There are many kinds of separation techniques based on different extraction principles among molybdenum and other metals [5,6]. Many studies have been concerned with the extraction of tungsten and molybdenum using primary amine as the extractant [7]. The related thermodynamics was also researched [8]. However, the predicted results for the established model had more deviations from the experimental values and the separation factor between the two metals still needed to be promoted, resulting from the complicated species of molybdenum in the solution.

There are many species of molybdenum in the aqueous solution containing molybdenum formed by hydrolysis or polymerization [9]. The species of molybdenum were determined chiefly by pH value and the concentration of molybdenum. The major species was $MoO_4^{2-}$ in the molybdenum-bearing aqueous solution with pH over 7.0. However, $MoO_4^{2-}$ polymerizes with each other and becomes isoplyacid ions in the weak acid solution when the concentration of molybdenum is beyond $10^{-4}$ mol · $L^{-1}$. The precipitation of $MoO_3$ forms in the acid solution with pH below 1.5. In view of variety of results obtained by many researchers, Beas and Mesmer summarized the aqueous chemistry of molybdenum and drew the diagram on the species change of isoplyacid dependently on pH value shown in figure 1 [10]. Moreover, other salts like sodium sulfate often exist in the aqueous solution used to extract molybdenum. The existing of these ions may increases the complexities of species in the aqueous solution. Thus, it is necessary to discuss the interaction and species distribution in this complex system. The ideal way to resolve this problem is to establish a new model referring to these ions, and then predict the interaction parameters between two ions using the new model. The priority species in different situations can be obtained by comparing the parameters. Based on the results, the studies on the solvent extraction of molybdenum will become much easier.

The related studies were carried out to determine the solubility of sodium molybdate in the $(Na^+ + MoO_4^{2-} + SO_4^{2-})$ system [11,12]. They emphasized the phase diagram of sodium sulfate and sodium molybdate under the condition of nearly saturated sodium sulfate, where it provided less information for the species research and

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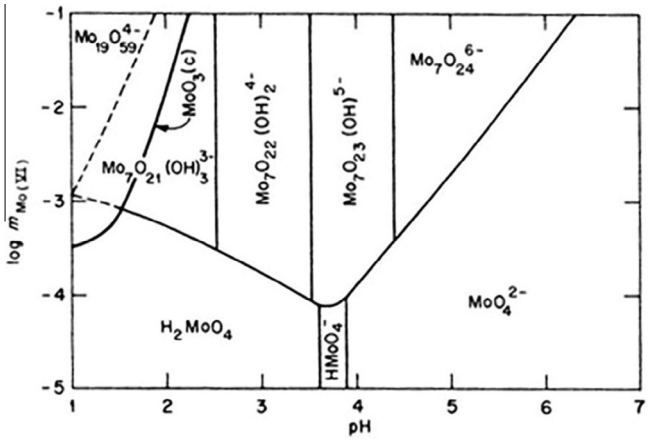


**FIGURE 1.** Predominance diagram for Mo(VI)-$OH^-$ species at 25 °C.

molybdenum extraction. New solubility results and a new model need to be researched over a wide range. Up to now, additional thermodynamics results for sodium sulfate were obtained. For example, Hovey [13] investigated the thermodynamics of sodium sulfate over the temperature range from 273 K to 373 K using Pitzer model. Marliacy [14] studied the thermodynamics of sodium sulfate as well as sodium chloride using Pitzer equations. The new model of Hovey was highly precise under a comprehensive consideration, while the parameter *b* was 1.7 rather than the value of 1.2 used usually in Pitzer model. Compared to sodium sulfate, the thermodynamic properties of sodium molybdate were studied rarely. Wu [15] and Rard [16] reported the osmotic coefficient of sodium tungstate and sodium molybdate at $T = 298.15$ K. Rard also explained that molybdate polymerization would happen if the concentration of sodium molybdate were within the range of 0.2 mol · $kg^{-1}$ to 0.9 mol · $kg^{-1}$ based on the theory and mathematics.

In terms of the reports, the solubility of sodium molybdate in the ($Na^+ + MoO_4^{2-} + SO_4^{2-}$) system was measured. The regression of the parameters were obtained using the solubility results. Then the new model was established with the regressed parameters and the calculated parameters in the binary system of the ($Na_2SO_4 + H_2O$) system and the ($Na_2MoO_4 + H_2O$) system. The application of the new model was also studied.

## 2. Experimental

### 2.1. Materials

The $Na_2SO_4$ and $Na_2MoO_4{\cdot}2H_2O$ (analytical grade, AG) was purchased from the Xilong Chemical Engineering Company, China. The source and mass purity of all reagents used in this work are listed in table 1 without further purification.

### 2.2. Experimental apparatus

The experimental apparatus is described a follows: electronic balance ML104 (Mettler Toledo, Switzerland) with uncertain to ±0.0001 g, Thermostat DC-0510 (Ningbo Scientz Biotechnology

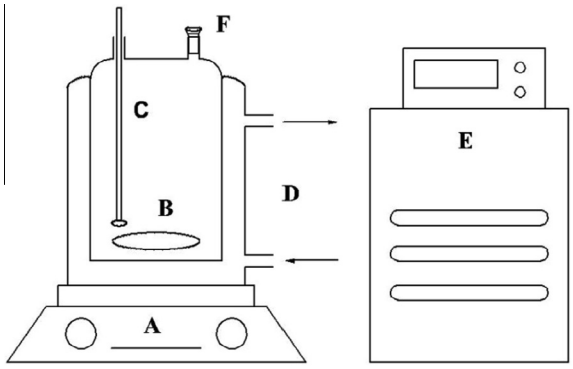


**FIGURE 2.** Apparatus for the solubility of sodium molybdate in sodium sulfate at temperatures from 293.15 K to 343.15 K. (A) magnetic stirring apparatus; (B) magnetic rotor; (C) thermometer; (D) vessel; (E) thermostat; (F) bottle plug.

Poltroon Technologies Inc., China) with its accuracy being ±0.1 °C, magnetic agitator 84-1A (Shanghai SileInstrument Co., Ltd. China), a 250 mL self-made jacketed equilibrium still, pipette tube; beaker; pipette gun.

The experimental setup shown in figure 2 includes a thermostat, a magnetic stirrer, a equilibrium still, and a rubber pipe.

The analytical instruments used for Mo in the aqueous phase were an OPTIMA 5300DV inductively couple plasma-optical emission spectrometer (ICP-OES, Perkin-Elmer, USA) at the wavelength of 209.86 nm with the correlation degree of standard curve ⩾99.99%, and anions were determined using the ion chromatograph DX-500 (Dionex, USA).

### 2.3. Experimental method and steps

The experiment was carried out using the isothermal dissolution method which has been applied frequently as noted in the literature. The solubility of $Na_2MoO_4{\cdot}2H_2O$ in the aqueous solution was measured using a dynamic method within the temperature range of 293.15 K to 343.15 K. A jacketed glass vessel with a volume of 250 mL, a thermostat and a magnetic stirrer were used in this work as shown in figure 2. A known mass of doubly distilled water was firstly put into the vessel and the facility was maintained at a desired temperature with an accuracy of ±0.1 K for 10 min through a thermostat connected with the glass vessel. Simultaneously, the temperature was monitored by a calibrated thermometer immersed in the inner chamber of the vessel. Then a certain mass of sodium sulfate was added into the vessel and rigorously stirred by magnetic stirrer until the salt was dissolved completely. Thereafter, a known mass of $Na_2MoO_4{\cdot}2H_2O$ was added to the solvent little by little until the last trace of salt was observed to remain undissolved. The total mass of $Na_2MoO_4{\cdot}2H_2O$ before the last adding is the solubility of it under given conditions. All the chemical reagents were prepared by weighing the analytically pure components with an accuracy of ±0.0001 g.

### 2.4. Reproducibility

To assess the accuracy and reproducibility of the apparatus and procedure adopted above, the solubility of $Na_2MoO_4{\cdot}2H_2O$ in pure

**TABLE 1**
Source and purity of chemicals.

| Substance | Molar mass | Source | Purity (mole fraction) | Purity analysis method |
|---|---|---|---|---|
| $Na_2MoO_4{\cdot}2H_2O$ | 241.95 | Xilong Chemical Engineering Company, China | 0.9732 | As stated by the supplier |
| $Na_2SO_4$ | 142.04 | Xilong Chemical Engineering Company, China | 0.9897 | As stated by the supplier |
| Ultra-pure water | 18.016 | Homemade by millipore ultrapure water machine | 0.9996 | Conductance method and ICP-MS |