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State of Molybdenum Clusters in Solutions: I. Stability of the $[Mo_2(SO_4)_4]^{4-}$ Ion in H_2SO_4 Solutions

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Abstract—Regions of the $[Mo_2(SO_4)_4]^{4-}$ ion stability in H_2SO_4 solutions were determined spectroscopically. Standard enthalpies of formation of the crystal hydrate $K_4[Mo_2(SO_4)_4]_4 \cdot 2H_2O$ and of anhydrous $K_4[Mo_2(SO_4)_4]$ were determined by a direct calorimetric method.

Keywords: molybdenum clusters, calorimetry, enthalpy of formation, oxidation of clusters, ligand environment

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Stable interest to the state in solutions of coordination compounds containing a cluster fragment is caused in many respects by the role of such compounds in biological systems. As a rule, these are enzymes of various nature containing metals in active groups. A great number of molybdenum-containing enzymes are also known, for example, nitrogenase [1] or xanthiteoxidoreductase [2].

Behavior of clusters in solutions is of interest for both the fundamental and the applied chemistry [3, 4]. Forms of molybdenum existence in solutions are highly diversified and depend not only on the metal oxidation state, but also on the solvent nature and the presence of various ions and donor ligands. Often the nature of a particular molybdenum form in solution is complicated by resolvation processes and various donor-acceptor interactions. A detailed description of complicated processes in solutions of such complexes requires not only knowledge of forms of intermediates, but also a thermodynamic description of separate stages of many-stage transformations. However such a description has received little attention. Calorimetry is one of the most sensitive methods capable to characterize a species actually existing in a solution. This method makes it possible not only to determine thermodynamic characteristics of molybdenum complexes, but also to trace variations of coordination spheres of both mononuclear and polynuclear molybdenum species resulted from redox or exchange reactions in solutions. At present a procedure of differential calorimetric titration for direct experimental determination of energy effects of multistage transformations has been developed and successfully applied to the study of molybdenum complexes [5–7].

To determine correctly thermodynamic characteristics of reactions involving cluster molybdenum complexes it is necessary to know not only particular forms of molybdenum complexes in certain conditions, but also values of standard enthalpies of formation of these complexes. The present work consists in the determination of stability regions of the ion $[Mo_2(SO_4)_4]^{4-}$ in H_2SO_4 solutions, and also in the determination of enthalpies of formation of the binuclear molybdenum complexes $K_4[Mo_2(SO_4)_4] \cdot 2H_2O$ and $K_4[Mo_2(SO_4)_4]_4$.

Boundaries of H_2SO_4 concentrations in solutions limiting the existence of the sulfate ion $[Mo_2(SO_4)_4]^{4-}$ were determined by the method of electron absorption spectroscopy in visible region.

The absorption band of $[Mo_2(SO_4)_4]^{4-}$ solutions corresponds in its shape and maximum position (510 nm) to the known spectral data [8]. The results obtained are presented in Fig. 1.

Molar extinction coefficients were measured at the wavelength of 510 nm. As the acid concentration decreased to 0.1 M, the extinction coefficient slightly increases up to 235 L mol^{-1} cm^{-1} (Fig. 2), suggesting that when the total absorption of solution changes from 190 up to 250 L mol^{-1} cm^{-1} the ion $[Mo_2(SO_4)_4]^{4-}$ is preferentially present in solution. In solutions with

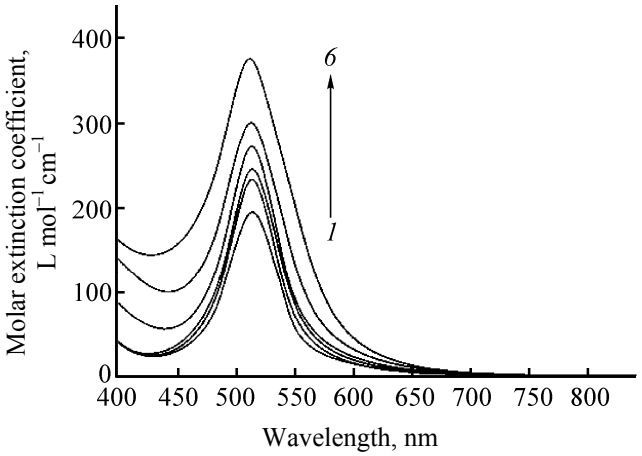

Fig. 1. Electron absorption spectra (*1*→*6*) of $[Mo_2(SO_4)_4]^{4-}$ solutions in sulfuric acid of various concentration, M: (*1*) 1, (*2*) 0.3, (*3*) 0.1, (*4*) 0.01, (*5*) 0.003, and (*6*) 0.001.

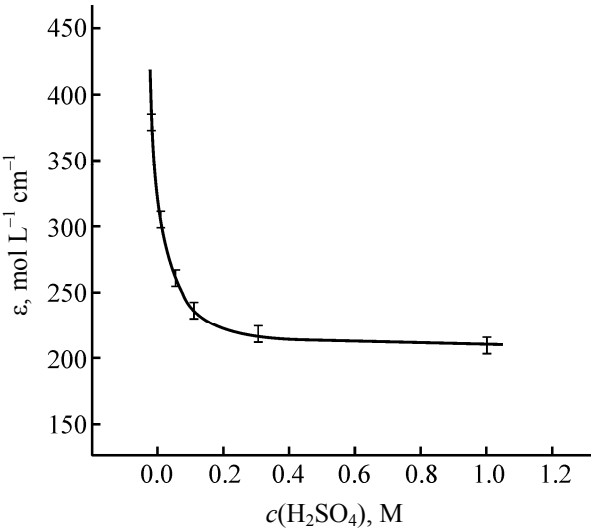

Fig. 2. Molar extinction coefficient (λ 510 nm) of $[Mo_2(SO_4)_4]^{4-}$ solutions in sulfuric acid of various concentration.

sulfuric acid concentration from 1.0 up to 0.1 M the predominant form of Mo(II) is the ion $[Mo_2(SO_4)_4]^{4-}$, whereas in solutions with the concentration of 0.001 M and lower it is the aquacation $[Mo_2(H_2O)_8]^{4+}$ [9]. In the concentration region from 0.1 to 0.001 M a sequential substitution of water molecules for sulfate groups apparently takes place and a mixture of complex ions $[Mo_2(H_2O)_{8-2x}(SO_4)_x]^q$ is present. Further calorimetric experiments were carried out in solutions of 1.0 M sulfuric acid.

Check of reliability of the calorimetric procedure. Determination of the standard enthalpy of $K_2Cr_2O_7$(cryst.) formation. Reliability of the procedure has been confirmed by the determination of the standard enthalpy of $K_2Cr_2O_7$(cryst.) formation, which was calculated using thermochemical equation (1). The result was compared with a reference value. The enthalpy of process (1) was determined experimentally. The initial solution contained $FeSO_4$, H_2SO_4, and H_2O in the molar ratio 1 : 60 : 800. A weighted sample of $K_2Cr_2O_7$ was added to the solution. The error of calorimetric measurements did not exceed 1–2%. The enthalpy ΔH_1^0 of the reaction of $K_2Cr_2O_7$(cryst.) reduction in the solution containing a $FeSO_4$ excess in the medium of 1.0 M sulfuric acid was determined experimentally.

$$K_2Cr_2O_7(cryst.) + 6FeSO_4(soln.) + 7H_2SO_4(soln.) = Cr_2(SO_4)_3(soln.) + K_2SO_4(soln.) + 3Fe_2(SO_4)_3(soln.) + 7H_2O,\ \Delta H_1^0. \quad (1)$$

The calculation of $\Delta_f H^0$ for $K_2Cr_2O_7$(cryst.) was carried out using values of standard enthalpies of formation of corresponding compounds (Table 1) given in [10] and values of standard enthalpies of reaction components dissolution (Table 2).

The found value of $\Delta_f H^0[K_2Cr_2O_7(cryst.)]$ –2050± 15 kJ/mol is in agreement with the value –2061.9± 2.6 kJ/mol given in [10], which confirms validity of the $K_2Cr_2O_7$ application for the calorimetric study of oxidation reactions of molybdenum complex compounds.

Table 1. Standard enthalpies of formation ($\Delta_f H^0$) of reactions components

Compounds	$-\Delta_f H^0$, kJ/mol [10]
H_2O	285.83±0.01
$Cr_2(SO_4)_3$(solid)	3307.9±0.5
$K_2Cr_2O_7$(solid)	2061.9±0.01
K_2SO_4(solid)	1439.1±0.4
$Fe_2(SO_4)_3$(solid)	2580.1±0.01
$FeSO_4$	927.6±0.03
H_2SO_4	814.2±0.8
K_2MoO_4	1498±1

Calorimetry of $K_4[Mo_2(SO_4)_4]_4$(cryst.) dissolution in 1.0 M sulfuric acid containing an excess of $K_2Cr_2O_7$. Determination of $\Delta_f H^0$ for {$K_4[Mo_2(SO_4)_4]$(cryst.)}. The final product of the ion $[Mo_2(SO_4)_4]^{4-}$ oxidation in acid solutions is the ion MoO_4^{2-} [2]. The enthalpies of $K_4[Mo_2(SO_4)_4]\cdot 2H_2O$(cryst.) and $K_4[Mo_2(SO_4)_4]$(solid) dissolution in 1.0 M sulfuric acid (ΔH_2^0 and ΔH_3^0), the enthalpy of $K_4[Mo_2(SO_4)_4]$(solid) oxidation (ΔH_4^0) by a solution containing a $K_2Cr_2O_7$ excess, and the enthalpies of dissolution of reaction components were determined using the same procedure as that for the

Table 2. Enthalpies of dissolution of reactions components

Compounds	Conventional notation of forming solution	Number of experiments	ΔH^0, kJ/mol
1.0 M H_2SO_4	A0		–73.8±0.6 [10]
$K_4[Mo_2(SO_4)_4]\cdot 2H_2O$ + A0	A1	3	49±1 (ΔH^0_2)
$K_4[Mo_2(SO_4)_4]$ + A0	A1	3	–29±1 (ΔH^0_3)
$K_2Cr_2O_7$(solid) + A0	A2	5	77.1±0.5
K_2SO_4(solid) + A0	B1	5	23.0±0.1
$Cr_2(SO_4)_3$(solid) + B1	B2	5	116.1±0.7
K_2MoO_4 + B2	B3	3	–2.0±0.3
$K_4[Mo_2(SO_4)_4]$(cryst.) + A2	B3	3	–1148±8(ΔH^0_4)
$FeSO_4$(solid) + A0	C1	3	–48.8±0.7
K_2SO_4(solid) + C1	D1	5	23.0±0.1
$Fe_2(SO_4)_3$(solid) + A0	D2	5	–142±2
$Cr_2(SO_4)_3$(solid) + D2	D3	5	116.1±0.7
$K_2Cr_2O_7$(solid) + C1	D3	5	–654±4(ΔH^0_1)

determination of the enthalpy of $K_2Cr_2O_7$ reduction by iron(II) sulfate.

$$K_4[Mo_2(SO_4)_4]\cdot 2H_2O(cryst.) = K_4[Mo_2(SO_4)_4](soln.),\ \Delta H^0_2,$$

$$K_4[Mo_2(SO_4)_4](cryst.) = K_4[Mo_2(SO_4)_4](soln.),\ \Delta H^0_3,$$

$$K_4[Mo_2(SO_4)_4](cryst.) + 4/3K_2Cr_2O_7(soln.) + 4/3 = 4/3Cr_2(SO_4)_3(soln.) + 4/3K_2SO_4(soln.) + 2K_2MoO_4(soln.) + 4/3H_2O,\ \Delta H^0_4.$$

The initial solution contained $K_2Cr_2O_7$, H_2SO_4, and H_2O in the molar ratio 1 : 60 : 1200, respectively. The results are presented in Table 2.

Calculation of the standard enthalpies of $K_4[Mo_2(SO_4)_4]$(cryst.) and $K_4[Mo_2(SO_4)_4]\cdot 2H_2O$ formation. The enthalpy of $K_4[Mo_2(SO_4)_4]$(cryst.) formation was calculated from the thermochemical equation presented below.

$$\Delta_f H^0 = 4/3(\Delta_f H^0 + \Delta H^0_{dis})Cr_2(SO_4)_3 + 4/3(\Delta_f H^0 + \Delta H^0_{dis})K_2SO_4 + 2(\Delta_f H^0 + \Delta H^0_{dis})K_2MoO_4 + 4/3(\Delta_f H^0 + \Delta H^0_{dis})H_2O - 4/3(\Delta_f H^0 + \Delta H^0_{dis})K_2Cr_2O_7 - 4/3(\Delta_f H^0 + \Delta H^0_{dis})H_2SO_4 - \Delta H^0_4.$$

Standard enthalpy of the $K_4[Mo_2(SO_4)_4]$(cryst.) formation $\Delta_f H^0$ was found to be –4556±12 kJ/mol. On the basis of the experimental data the enthalpy of the reaction: $K_4[Mo_2(SO_4)_4]$(cryst.) + $2H_2O$ = $K_4[Mo_2(SO_4)_4]\cdot 2H_2O$(cryst.), ΔH^0_5 −78.0±2 kJ/mol was determined, and the standard enthalpy of formation of the crystal hydrate $K_4[Mo_2(SO_4)_4]\cdot 2H_2O$(solid) $\Delta_f H^0$ –5206±15 kJ/mol was calculated.

The boundaries of the ion $[Mo_2(SO_4)_4]^{4-}$ stability in H_2SO_4 solutions were determined from the spectral data. The predominant form of Mo(II) existence in sulfuric acid solutions with concentrations from 1.0 to 0.1 M was shown to be the ion $[Mo_2(SO_4)_4]^{4-}$. The further decrease in the acid concentration results in the sequential substitution of water molecules for sulfate ions in the coordination sphere of Mo(II) up to the formation of the aquacation $[Mo_2(H_2O)_4]^{4+}$ [11].

EXPERIMENTAL

Dried up in vacuum analytical-grade crystal hydrate $K_4[Mo_2(SO_4)_4]\cdot 2H_2O$(solid) was obtained from analytical-grade MoO_3 by the procedure [8]. Dehydrated $K_4[Mo_2(SO_4)_4]$ was prepared by heating the crystal hydrate in a vacuum (p 10^{-2} at) at 140°C. The purity of the $K_4[Mo_2(SO_4)_4]$ samples was proved by the X-ray analysis fulfilled in the Center of X-ray diffraction studies at St. Petersburg State University.

Work solutions of 1.0 M sulfuric acid were preliminarily deaerated. For this purpose the solutions were boiled under reduced pressure, saturated with argon, and cooled. A weighted sample of $K_4[Mo_2(SO_4)_4]$(cryst.) was dissolved in a deaerated sulfuric acid solution. Spectral measurements were carried out on an SF-103 Akvilon spectrophotometer in quartz cells 1 cm thick.

Calorimetric measurements were carried out on a custom made differential heat-conducting calorimeter [12] with calorimetric cages of 80.0 cm^3 in volume. Stability of a calorimeter basic line was maintained by a water thermostat (T 298.15 K), the signal drift did

not exceed ±(15–20) μV a day. The calorimeter constant (k 0.151±0.002 V/W) was determined by electric current calibration and was multiply checked by measuring the enthalpy of crystalline KCl (ultrapure grade) dissolution in water with dilution of resulting solutions ≥ 1 : 400 (ΔH^0 17.2±0.2 kJ/mol). The construction of calorimetric cells provided a possibility of operating with aggressive materials in hermetic conditions and in an inert-gas atmosphere.

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