Vigasina M.F., Orlov R.Yu. Equilibrium constants for MoO_4^{2-} + H^+ = $HMoO_4^-$ and WO_4^{2-} + H^+ = HWO_4^- from the data on CD-spectroscopy using the quantum-chemical calculations.

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	observed frequency, ν	quantum-mechanical calculation [1]		
		ν	σ	r
MoO_4^{2-}	896 (1)	898	35	3,07
$HMoO_4^-$	941	944	41	3,14
WO_4^{2-}	931 (1)	916	30	3,08
HWO_4^-	960	950	35	3,19

Note: (1) - reference data similar to the observed values

Application of the molecular spectroscopy together with the quantum-chemical calculations gives interesting perspectives for the study of hydrothermal systems.

Owing to the least level of interferences resulted from solvent and thermal flux from the heating equipment, the combinational dissipation spectroscopy is more valuable than the IR-spectroscopy. This method uses autoclaves of volume of 0.5-50 ml with sapphire windows. Spectrum registration proceeds with multi-channel optical detector.

Qualitative identification of molecular components of a solution needs the presence of reference data or possibility of calculation of an oscillation spectrum. In order to calculate relative concentrations, intensities of corresponding lines are necessary to calculate. Both these problems can be solved by the quantum-chemical methods. In such procedure, oscillation frequencies can be determined with accuracy of ±10%.

In some cases, determination of the molal concentration of components is possible from the results of preliminary study of standards, where water (its spectrum) serves as an internal standard. A possibility to calculate equilibrium constants appears further.

The above approach was applied for determination of the second dissociation constant K_2 for H_2MoO_4 and H_2WO_4 complexes at normal conditions.

An equilibrium $HMoO_4^-$ = MoO_4^{2-} + H^+ was investigated at concentrations of 0.1 M and 0.05 M within the pH interval from 5 to 9.

The experimental frequencies of the most intense lines, as well as calculated frequency values ν (cm^{-1}), of the combination dissipation σ (E^4/amu) and radiuses of the first coordination sphere r (E) for the above complexes are shown in Table:

One intense line at 896 cm^{-1} is observed in the initial 0.1M solution of $Na_2MoO_4 \cdot 2H_2O$. Acidification of the solution with hydrochloric acid results in appearance of the second line at 941 cm^{-1}, while the first line weakens. The results of the quantum-chemical calculation show that this line belongs to the $HMoO_4^-$ complex. Ratio of intensities (I) of these lines at varying pH within 5-7 is linear
$$\log(I_{896}/I_{941}) = pH + const$$
with the inclination 45 ± 5°. Two intensities are equal at pH = 5.9±0.1.

The ratio of intensities of two lines was also considered at constant pH = 6.2 and varying concentration of 0.1, 0.05, 0.025 M. In this experiment, the ratio of intensities was retained with accuracy of ±10%. It is possible only in the case, then both lines belong to simple monomers.

In order to calculate an equilibrium constant

$$logK_2 = = log[MoO_4^{2-}] / [HMoO_4^-] + log\gamma(MoO_4^{2-}) / \gamma(HMoO_4^-) - pH,$$

where γ - activity coefficient, the relation I(M) $\sim$ [M]$\cdot\sigma$(M)/ν(M)
should be regarded, where [M] is concentration, σ(M) is cross-section of M scattering in vibrational mode ν(M). Regarding this relation, $[MoO_4^{2-}]$ = $[HMO_4^-]$ corresponds to pH^0 = 5.8±0.1, and subsequently

$$logK_2 = log\gamma(MoO_4^{2-}) - log\gamma(HMoO_4^-) - 5,8$$

Activity coefficients were calculated within the second approach of the Debye-Hückel theory using the radius of the first coordination sphere of the complexes, calculated from the quantum-chemical model EFP.

For a solution with the initial concentration 0.1 M:

$$log\gamma(MoO_4^{2-}) = -0,64 ; \quad log\gamma(HMoO_4^-) = -0,16$$

It is follows that $logK_2 = -5.8 - 0.48 \approx = -6.3$ and $\Delta_rG^0 \approx 8.6$ kcal/mol.

Using the published value Δ_rG^0 (MoO_4^{2-}) = -200.4 kcal/mol [2], we obtain a new constant

$$\Delta_rG^0 (HMoO_4^-) = -209 \text{ kcal/mol.}$$

The maximal error could be created by calculation of σ, that is a new section in the quantum chemistry, proposed in the 2001 year [3, 4]. An error of the $log\sigma(MoO_4^{2-})/\sigma(HMoO_4^-)$ can be ±0.2. Accounting for the maximal errors in the determination of pH (±0.1), the relative intensity (±20 %), and the effective radius of the complexes (0.2 A), the $logK_2$ is determined with an accuracy of ±0.35, whereas the Δ_rG^0 and Δ_fG^0 values are determined with an accuracy of 0.5 kcal/mol.

Similar procedure for the system $Na_2WO_4 \cdot 2H_2O$-HCl-H_2O gave the following results:

pH^0 = 6.9; $logK_2$ = -7.3; Δ_rG^0 = 10±0.5 kcal/mol; $\Delta_fG^0(HWO_4^-)$ = -228.5±0.5 kcal/mol.

References:

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