Journal scientific and applied research, vol. 3, 2013
Association Scientific and Applied Research
International Journal

Original Contribution
ISSN 1314-6289

TETRAHEDRAL AND OCTAHEDRAL COMPLEXES OF MN^{2+} IN THE AQUEOUS SOLUTIONS OF MNCL$_2$.4H$_2$O

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ABSTRACT

In this work, the absorption spectra of the aqueous solutions of $MnCl_2.4H_2O$ are investigated. The concentration of these solutions is in the interval 30-38 %. The experiment is conducted at the room temperature in the spectral region 350 – 650 nm. The asymmetric vibration values and the strength of the oscillator are calculated for all investigated aqueous solutions.

KEY WORDS: tetrahedral complexes, Racah's parameters, exchange integrals, Jahn-Teller effect, spin-orbit interaction

INTRODUCTION

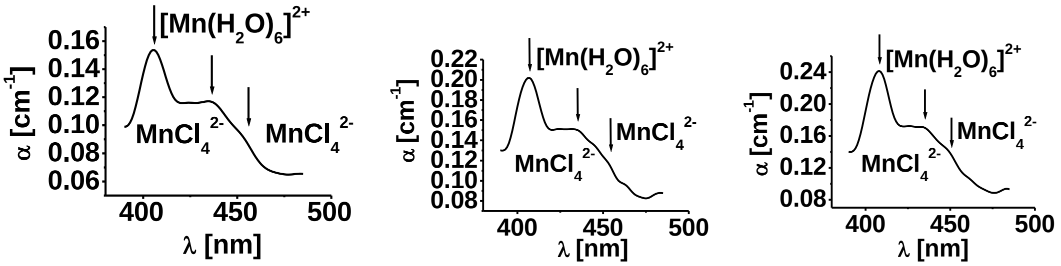
The aim of this work is connected with the determination of the optical parameters of the complex ions where Mn^{2+} cation is in the center. We are investigated the aqueous solution of $MnCl_2.4H_2O$ with different concentrations. Our experiment will be usefull for the clarification of the growth conditions of the crystals $MgSO_3.6H_2O$ from aqueous solution [1, 2]. These materials have application in the nonlinear optics.

EXPERIMENT, RESULTS AND DISCUSSION

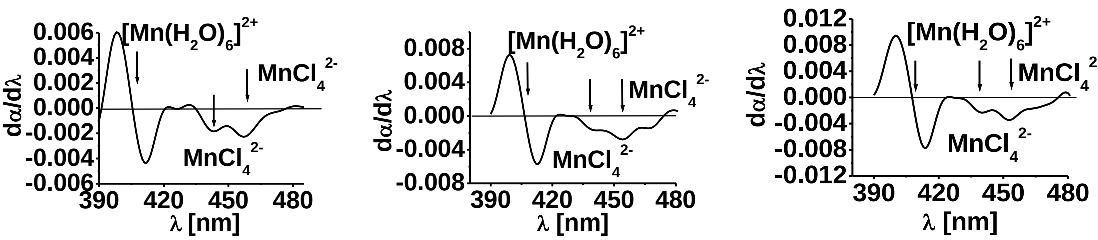
The solutions are investigated with spectrophotometer "BOECO", model S-26, in the cuvette with thickness b = 1 cm. The absorbance A is calculated by the formula $A(\lambda) = \ln(I_0/I) = a(\lambda)cb$, where I_0 is the intensity of the incident light, I is the intensity of the passed light, b is the thickness of the cuvette, a(λ) is the absorption, which characterizes the interaction of the substance with the radiation (i.e. a(λ) determines the probability of the transition) and c is the concentration of the solutions. The first derivative of the absorbance to the energy of the photons is calculated in the spectral region 400-600 nm. The derivative [dA/dλ] determines only the number of the electron transitions in the cation Mn^{2+} and it not informs us about the exact value of the energy of these transitions. This is the reason for the calculation of the second derivative of the absorbance $[d^2A/d\lambda^2]$.

It is known that the complex ions $[Mn(H_2O)_6]^{2+}$ and $[MnCl_4]^{2-}$ are in the aqueous solution of $MnCl_2.4H_2O$ [3]. The other authors made investigations of the aqueous solutions with very small concentration of the salt. Thus it appears the influence of one or the other complex. This fact was very interesting for us and we decided to check what is happen in the same solutions with big concentration? We established the simultaneous expression of both complexes in the visible region.

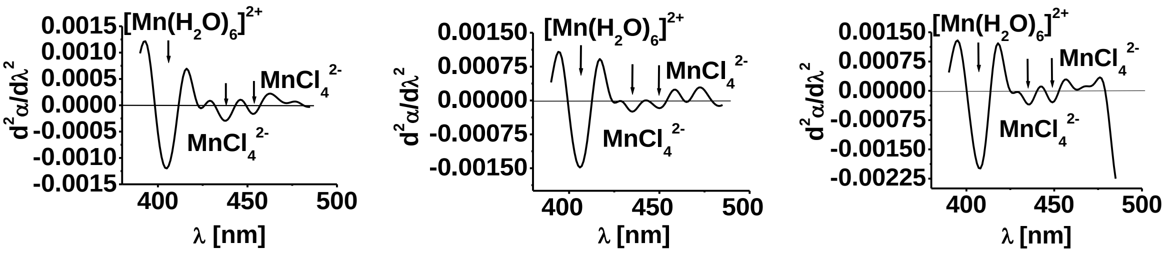
The absorption spectra of the complex ions $[Mn(H_2O)_6]^{2+}$ and $[MnCl_4]^{2-}$ are shown on fig. 1A. The first derivative of the absorbance to wave length (fig. 1B) and second derivative of A(λ) (fig. 1C) are presented in the spectral region 400-500 nm for the aqueous solutions with concentration respectively 30%, 34% and 38%. It is shown (fig. 1C) that the solutions with the concentration 30%, 34% and 38% combine one electron transition in the octahedral complex of Mn^{2+} and two electron transitions in the tetrahedral complex of the cation Mn^{2+}.



1A



1B

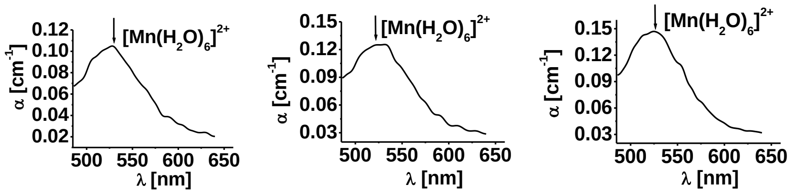


1C

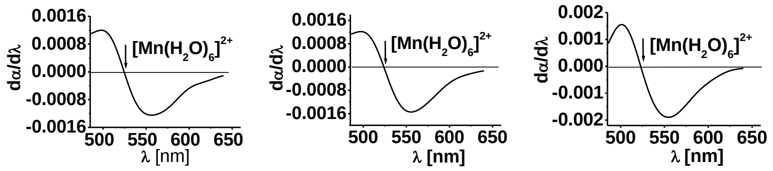
30% 34% 38%

Figure 1. The experimental data of the absobance A(λ) (1A), the calculated dA/dλ (1B) and $d^2A/d\lambda^2$ (1C) for the aqueous solutions of $MnCl_2.4H_2O$ with concentration 30%, 34% and 38% in the spectral region 400-500 nm.

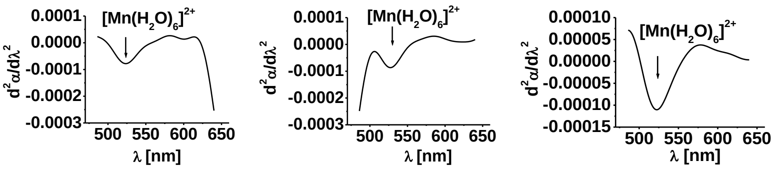
The spectra of $[Mn(H_2O)_6]^{2+}$ are presented on fig. 2 in the wave length region 500-650 nm together with the first and second derivatives of the absorbance dA/dλ and $d^2A/d\lambda^2$.



2A



2B



2C

30% 34% 38%

Figure 2. The experimental data of the absobance A(λ) (2A), the calculated dA/dλ (2B) and $d^2A/d\lambda^2$ (2C) for the aqueous solutions of $MnCl_2.4H_2O$ with concentration 30%, 34% и 38% in the spectral region 500-650 nm.

It is shown, that the electron transition is one in the octahedral complex of Mn^{2+} in the same part of the visible spectral region.

The strength of the three-dimensional harmonic oscillator determines from the ratio of the real intensity and the intensity of the radiation of the electron. f = 1 for such “ideal electron”. The transitions of the oscillator classify by the strength f and this connects the theory with the experiment. f = 1 for the allowed transition; for single symmetric band (table 1):

$$f = 4.32 * 10^{-9} \int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda) d\lambda,$$

where $\varepsilon(\lambda)$ not depends on the concentration of the solutions [4]. The next equation $Q_i = \sqrt{\frac{f_i}{\nu_i * 1{,}096 * 10^{11}}}$ explains the connection between the oscillator strength f_i and the transition moment of the impurity band Q_i, where ν_i is the frequency of the band centre.

$f_0 = f/[1 + \exp(-\theta/T)]$, where θ is the frequency of the total asymmetric vibration (table 3).

In our case, it is registered asymmetric vibration due to the available deformation of the aqueous solution. The deformation is consequence of the simultaneous manifestation of the Jahn-Teller effect and the spin-orbit interaction. The frequency of the vibration ω of the complexes is connected with θ by the equality $\omega = \theta/1.44$ [cm^{-1}] ($\omega = 2\pi c/\lambda$, $c = 3.10^8$ m/s).

Table 1. The strength of the oscillator f_1 (400-500 nm) and f_2 (500-600 nm) for the aqueous solution of $MnCl_2.4H_2O$ with concentration 30%, 34% and 38% at temperature T = 300K; The strength of the oscillator $f^{01}{}_1$ (400-500 nm) and $f^{02}{}_2$ (500-600 nm) for aqueous solutions of $MnCl_2.4H_2O$ with concentration 30%, 34% and 38% at temperature T = 0K.

solution	$f_1.10^{-4}$	$f_2.10^{-4}$	$f_{01}^{1}.10^{-4}$	$f_{01}^{2}.10^{-4}$	$f_{02}^{1}.10^{-4}$	$f_{02}^{2}.10^{-4}$
30%	1.198	1.159	0.867	1.088	0.839	1.052
34%	1.370	1.274	0.991	1.244	0.922	1.157
38%	1.381	1.280	0.999	1.254	0.926	1.162

Table 2. The transition moment of Mn^{2+} structures in the spectral regions 400-500 nm and 500-650 nm.

solution	$f_1.10^{-4}$	$f_2.10^{-4}$	$Q_1.10^{-10}$	$Q_2.10^{-10}$
30%	1.198	1.159	2.2178	2.4659
34%	1.370	1.274	2.3717	2.5267
38%	1.381	1.280	2.3812	2.5914

The basic conclusion from the table 2 is that the values of the transition moment Q are bigger for the smaller wavelengths for the all investigated solutions.

Table 3. The asymmetric vibration values, characteristic for the octahedral and tetrahedral complex of Mn^{2+}.

at 400 nm	at 500 nm
Θ_1 = 36 923 cm^{-1}	Θ_1 = 29 629 cm^{-1}
Θ_2 = 29 691 cm^{-1}	Θ_2 = 22 500 cm^{-1}

CONCLUSIONS

The strength of the oscillator “f” increases with the increasing of the concentration of the solution and this is typical for the octahedral and the tetrahedral complex ions in the aqueous solution of $MnCl_2$.

When we analyze the absorption bands in the spectrum of the investigated samples, we can conclude that the ions $[Mn(H_2O)_6]^{2+}$ and $[MnCl_4]^{2-}$ observe in the solutions.

An equilibrium observes between the complex ions $[Mn(H_2O)_6]^{2+}$ and $[MnCl_4]^{2-}$ at concentrations above 30% in the investigated aqueous solutions.

The Jahn-Teller effect is strong as the result of the high concentration of the investigated solutions.

ACKNOWLEDGMENTS

Partial financial support by project of Shumen University (2013) is gratefully acknowledged.

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