

MANGANESE(II) COMPLEXES WITH DIETHYLAMINE IN AQUEOUS SOLUTIONS

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Interaction between MnCl_2 and diethylamine (DEA) in aqueous solutions has been studied by UV, IR, and EPR spectroscopy as part of the design and research program on models of natural photosystems. The composition of the precipitate for comparable concentrations of reagents and solute oxygen has been investigated. Mn(II) was found to be oxidized with oxygen to give $\text{MnO}_2 \cdot \text{H}_2\text{O}$ as a precipitate. In the solution over the precipitate, Mn(III) complexes with DEA are formed; the complex molecule has four and six amine molecules in the coordination sphere.

Keywords: manganese complexes, diethylamine, UV, IR, and EPR spectra, modeling of natural photosystems.

INTRODUCTION

In the course of photosynthesis, solar energy is transformed into chemical energy during carbon dioxide reduction. Concurrently, water is oxidized at the reaction center of photosystem II (PSII) [1, 2]. This occurs in an oxygen-liberating center (OLC) containing four manganese ions. The structure of the OLC is not known exactly; however, much effort has been taken to model processes of water decomposition [3-8].

One of approaches to OLC simulation employs donor-acceptor complexes formed by the incorporated components and water molecules [9-11]. Irradiation of solutions containing associates of porphyrins and their donor-acceptor complexes with water leads to proton-liberating photochemical reactions [10]. The source of protons is assumed to be water molecules. Previously, a system of associates of meso-tetra(*n*-aminophenyl)porphyrin (TAPP) and a bi- or multinuclear complex formed by triethylamine (TEA) and manganese ions has been studied [11]. This combined complex, which may include water molecules, exhibits photochemical activity. Photolysis products are additionally protonated, water molecules being an additional source of protons [10, 11]. Thus the combined complex may prove to be a promising system for photocatalytic decomposition of water.

For a model system of water photodecomposition, a detailed study of the components of a system including associates and donor-acceptor complexes of porphyrin with water and manganese complexes with alkylamines is needed in order to determine the mechanism of functioning of this model system and to develop methods of its optimization. While porphyrin complexes were examined in sufficient detail [9-11], data on complexation in the manganese ions–aliphatic amine system have recently been unavailable. It would be interesting to seek binuclear or polynuclear complexes of manganese in solutions since natural OLC is a polynuclear complex.

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Recently, it was shown that reactions of Mn^{2+} with triethylamine (TEA) [11] and diethylamine (DEA) [12] in aqueous solutions occur according to complex schemes. The product composition depends on the proportion between the initial concentrations of reagents and solute oxygen. For the MnCl_2 -TEA system, it was found [11] that EPR inactive compounds, which may appear to be polynuclear complexes, form under certain conditions in both solution and precipitate. However, the structure of these compounds has not been investigated; at the same time, there was no experiment to reject the alternative reason for the absence of EPR spectra (formation of polynuclear Mn(III) compounds).

Our preliminary results on reactions in the MnCl_2 -DEA system are published in a brief communication [12]. At Mn(II) and DEA concentrations substantially higher than the oxygen content, Mn(II) compounds are settled as a precipitate. For comparable concentrations of reagents and oxygen, the precipitate is Mn(IV) compounds. After prolonged storage, the Mn(IV) precipitate is dissolved, presumably forming manganese(III) complexes with amine [12]. The aim of this work is to study the structure of these complexes.

EXPERIMENTAL

Reagents. To prepare the starting solutions of Mn(II) we used the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt (Reakhim, analytical grade). Diethylamine (Reakhim, pure grade) was used after distillation. The purity of amine after distillation was controlled spectrophotometrically. Manganese dioxide was synthesized according to the literature [13]. The solutions were prepared from bidistilled water.

Sample preparation. The reaction between Mn(II) chloride and DEA was studied in a mode of comparable reagent concentrations and solute oxygen. For reagent concentrations of the order of 10^{-3} M, a solution of reagents (250 ml) was stirred for 60 min in a flask placed in an ultrasonic bath. Then the solution was allowed to settle for 30 min. The top layer of liquid from the flask not containing a suspended precipitate was decanted, and the bottom layer with the precipitate was centrifuged. The precipitate was dried with a flow of warm air or by evacuation with a forepump in a closed vessel. The drying procedure did not affect the results of experiments.

Sample analysis. The IR spectra of solid reaction products were recorded on a Vectra 22 (Bruker) IR Fourier spectrometer ($400\text{-}4000\text{ cm}^{-1}$). KBr was used as a diluent. A pellet contained 200 mg of KBr per 1 mg of the reagent. Simultaneously, a pellet of pure KBr was prepared, whose spectrum was subtracted from the spectrum of the sample.

Percent of manganese in the precipitates was determined by atomic emission spectrometry with inductively coupled plasma (AES ICP).

EPR spectra were measured on a Bruker EMX-300 spectrometer. The aqueous solutions were analyzed in ampules 1 mm in diameter at room temperature, using aqueous MnCl_2 of known concentration as a standard.

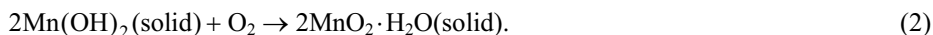
Electronic absorption spectra were recorded on an HP8453 (Hewlett Packard) spectrophotometer.

SOLID PRODUCT OF THE REACTION OF MnCl_2 WITH DEA

When MnCl_2 was mixed with diethylamine in concentrations comparable to the concentration of solute oxygen ($2.5 \cdot 10^{-4}$ M [15]), the solution immediately became tawny-colored, and a fine precipitate formed throughout the volume (the amount of the precipitate depends on the initial ratio of reagent concentrations). The color of the solution was the result of product absorption and light scattering on the fine particles of the precipitate. After drying, the precipitate became dark brown. The appearance of the solid product and its IR spectrum [12] fully coincide with the appearance and spectrum of the solid that precipitated after solutions of MnCl_2 and NaOH were mixed under the same conditions. According to element analysis data, the manganese content in the sample is 53.4 wt.% for $\text{MnCl}_2 + \text{DEA}$ and 52.1 wt.% for $\text{MnCl}_2 + \text{NaOH}$. These values are in satisfactory agreement with the manganese content in manganese(IV) dioxide hydrate $\text{MnO}_2 \cdot \text{H}_2\text{O}$ (52.3 wt.%).

The primary reactions of Mn^{2+} with aliphatic amines in aqueous solutions depend on the alkaline nature of the

amines. For DEA, the basicity constant is 10^{-3} M [14]. For $c_{\text{DEA}} = 10^{-3}$ M, pH of the initial solution is 10.8 ($c_{\text{OH}^-} = 6.2 \cdot 10^{-4}$ M). Therefore, it is conceivable that at reagent concentrations of a few millimoles per liter, manganese(II) hydroxide is the primary product in Mn^{2+} -DEA systems, as well as in the Mn^{2+} -NaOH system (note that at reagent concentrations of the order of several moles, reactions of Mn^{2+} with NaOH and DEA occur differently [12]). The formation of $\text{MnO}_2 \cdot \text{H}_2\text{O}$ (or H_2MnO_3 , manganous acid) probably results from oxidation of $\text{Mn}(\text{OH})_2$ with air oxygen [16, 17]:



STATE OF MANGANESE IONS IN SOLUTION

The precipitate ($\text{MnO}_2 \cdot \text{H}_2\text{O}$) that formed at the first stage of the reaction gradually dissolved after storage in dark. The amount of the initially precipitated and dissolved solid depends on the ratio of the initial reagent concentrations. At $c_{\text{Et}_2\text{NH}}^0 \approx 0.005$ M and $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0 \leq 2$, a substantial amount of manganese dioxide hydrate formed, which partially dissolved after several dozen hours. At $c_{\text{Et}_2\text{NH}}^0 \approx 0.005$ M and $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0 \approx 4$, the $\text{MnO}_2 \cdot \text{H}_2\text{O}$ precipitate did not form. Finally, at $c_{\text{Et}_2\text{NH}}^0 \approx 0.0005$ M the initial precipitate dissolved completely even when the initial reagent ratio was 1:1.

The state of manganese ions in solutions was studied by EPR and UV spectroscopy. Figure 1 shows the EPR spectra of the solutions after the precipitate dissolved completely or partially and the dependence of the concentration of Mn^{2+} ions in solution on the ratio $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0$. Except the case with ligands creating a strong crystal field, nearly all Mn(II), Mn(III), and Mn(IV) complexes are in the high-spin state [18]. The bivalent manganese ion in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ has a $3d^5$ electron configuration; as in the case of many other Mn(II) complexes, net electron spin is $5/2$. In water the Mn^{2+} ion has an EPR signal of six lines (Fig. 1a, curves 1-3), resulting from hyperfine interaction with the spin of the nucleus ($I = 5/2$). The Mn(II) ion with a $3d^4$ configuration forms high-spin complexes with even spin ($S = 2$), which have no EPR lines in X band (10 GHz) because of high splitting in the zero field. For spectrum recording for such systems, one uses EPR spectrometers with a frequency of 90 GHz and higher [19].

At low contents of alkylamine ($c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0 \approx 1$), about 50% manganese was in solution (in the form of Mn(II) ions, curve 1, Fig. 1a) after the precipitate partially dissolved. The rest of manganese probably remained in the undissolved precipitate. As the content of DEA increased, the precipitate dissolved to a greater extent, but the EPR spectrum did not increase (as might be thought in view of the transition of manganese(II) ions from precipitate to solution); on the contrary, it decreased in intensity. At $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0 \approx 4$, the EPR spectrum of the solution vanished completely (Fig. 1b). Since a precipitate does not form at these concentrations, manganese ions should be EPR inactive in solution. This is in line with the previously observed [11] formation of an EPR inactive complex of manganese with TEA.

The absence of an EPR spectrum is explained by Mn(II) oxidation to Mn(III). When the EPR signal vanishes, a complex of manganese(III) ions with DEA is formed in solution, which shows itself in the electronic absorption spectrum. The absorption band of the complex has a maximum at 280 nm (Fig. 2). This band cannot be due to the complexation of manganese(III) ions with inorganic ligands (water molecules, OH^- and Cl^- ions). $\text{Mn}(\text{OH})_3$ is sparingly soluble in water (the product of solubility is $1 \cdot 10^{-36}$ M^4) [20]. When $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ is added to a NaOH solution, the precipitate does not dissolve, and stable UV absorption does not occur. In this case, one can observe only the spectrum that is due to light scattering on the small particles of the precipitate, which vanishes when they settle.

At alkylamine concentrations ten or more times higher than the concentration of manganese(III) ions, one more complex, which absorbs in the region 380-390 nm, is formed in the solution (Fig. 2, curve 4).

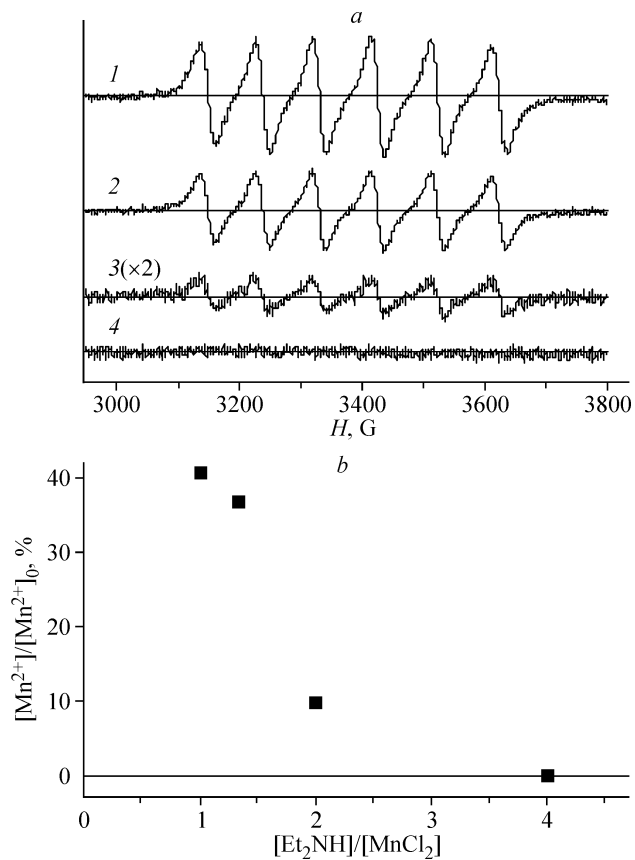


Fig. 1. EPR spectra of solution over the precipitate formed by the reaction of MnCl₂ with DEA (0.004 M) in aqueous solution at low reagent concentrations: *a* — spectra 1-4 correspond to the concentrations of MnCl₂: 0.004 M, 0.003 M, 0.002 M, 0.001 M, respectively; *b* — dependence of Mn²⁺ content (percent) in solution on the ratio $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0$.

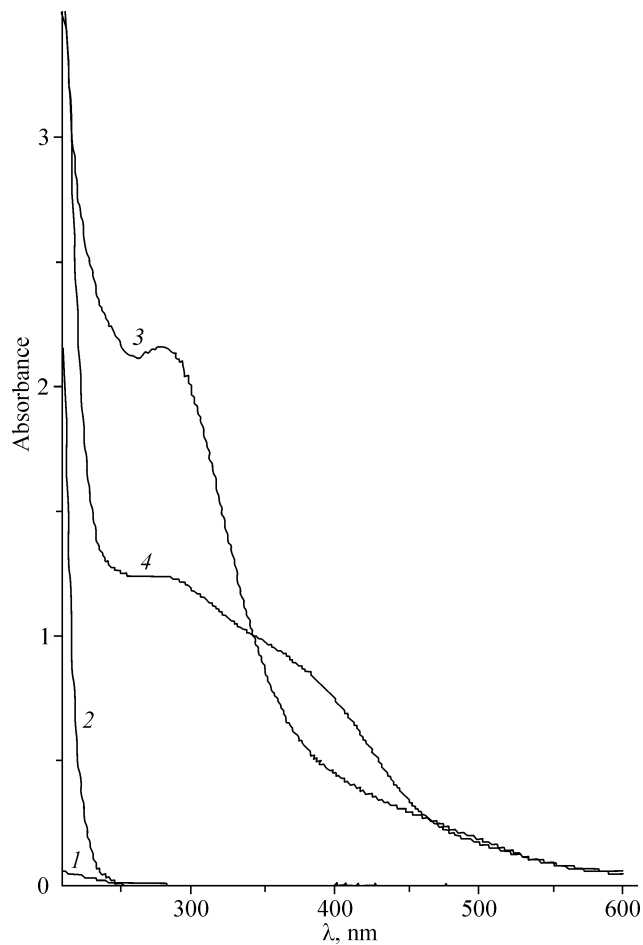


Fig. 2. Optical absorption spectra of manganese complexes with DEA in aqueous solutions. 1 — 0.001 M MnCl₂; 2 — 0.02 M DEA; 3 — spectrum of the solution after mixing 0.001 M MnCl₂ and 0.02 M DEA after storage in the dark for 145 h (twice dilute); 4 — spectrum of the solution after mixing 2·10⁻⁴ M MnCl₂ and 0.02 M DEA after storage in the dark for 145 h.

COMPOSITION OF Mn(II) COMPLEXES WITH DEA

To establish the composition of manganese(III) complexes with DEA we studied the dependences of their optical spectra on reagent concentrations. Experiments were conducted under conditions of complete solution of the precipitate. Figure 3*a* demonstrates the dependence of absorbance at 280 nm on the relation $x = c_{\text{Et}_2\text{NH}}^0 / (c_{\text{MnCl}_2}^0 + c_{\text{Et}_2\text{NH}}^0)$ (Job plot [21]) with a maximum $x_{\text{max}} \approx 0.8$.

With only one stable complex in solution, the position of the maximum on the Job curve would make it possible to determine the ratio of the number of ligands (*n*) to the number of metal ions (*m*) in the manganese complex with DEA: $n/m = x_{\text{max}} / (1 - x_{\text{max}}) \approx 4$. As the reagents (except the complex with a maximum at 280 nm) form at least one more stable complex (absorbing at 380-390 nm, Fig. 2), interpretation of the Job curve demands special analysis. Following [22], we consider the equilibrium in a system with two complexes:



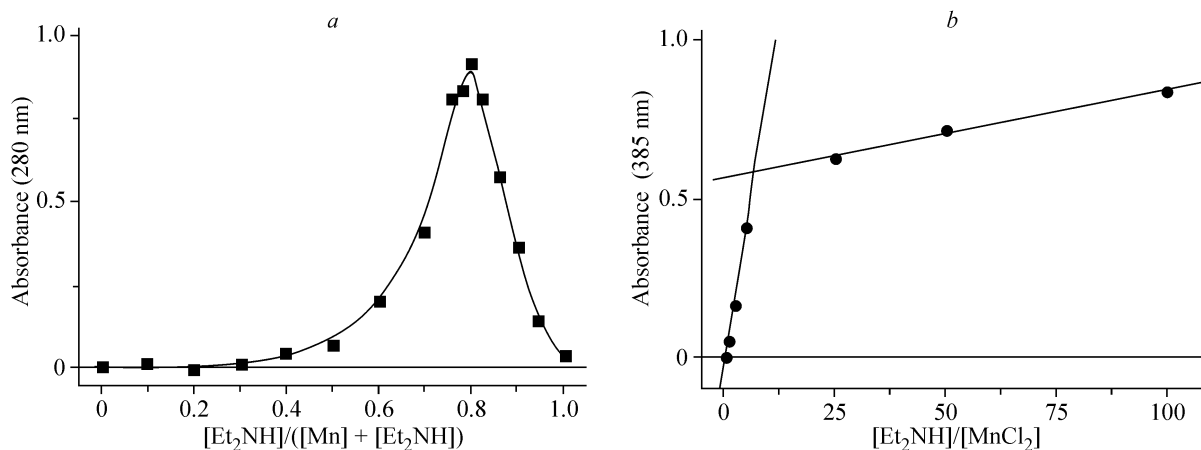


Fig. 3. Determination of the composition of Mn(III) complexes with DEA. Treatment of UV data; cell thickness 1 cm, spectra recorded 3 h after mixing of reagents and complete solution of the residue; *a* — determination of the composition of the Mn(III) complex with DEA from the dependence of absorbance at a maximum 280 nm on the ratio $x = c_{\text{Et}_2\text{NH}}^0 / (c_{\text{MnCl}_2}^0 + c_{\text{Et}_2\text{NH}}^0)$ (Job curve); total concentration of reagents $1 \cdot 10^{-3}$ M; *b* — dependence of absorbance at 385 nm on the ratio of initial concentrations $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0$; initial concentration of MnCl_2 is $2 \cdot 10^{-4}$ M.

For this system, the position of the maximum on the Job curve is defined by an expression [22]

$$\frac{x_{\max}}{1-x_{\max}} = n - \frac{p(n+p)c_2}{C(1-x_{\max})} + \frac{pc_2}{\frac{(\varepsilon_1 - \varepsilon_0)}{(\varepsilon_2 - \varepsilon_0)} c_1 + c_2} \left[1 + \frac{n(c_1 + c_2) + pc_2}{C(1-x_{\max})} \right], \quad (5)$$

where C is the total concentration of the starting reagents; c_1 and c_2 are the concentrations of the ML_n and ML_{n+p} complexes, respectively; ε_0 is the extinction coefficient of the solution in the absence of complexes; ε_1 , ε_2 are the molar absorption coefficients of ML_n and ML_{n+p} at an appropriate wavelength. In our case, the extinction coefficient at 280 nm does not change when large amounts of the ligand are added (Fig. 4a). Therefore, in formula (5) we set that $\varepsilon_1 = \varepsilon_2$:

$$\frac{x_{\max}}{1-x_{\max}} = n - \frac{p(n+p)c_2}{C(1-x_{\max})} + \frac{pc_2}{c_1 + c_2} \left(1 + \frac{n(c_1 + c_2) + pc_2}{C(1-x_{\max})} \right). \quad (6)$$

Equation (6) was used for Job curve simulation in a system containing two Mn(III) complexes with DEA. The “true” number of ligands in a complex was calculated from the position of the maximum on the Job curve. Figure 4b shows the result of simulation for the case of $C = 1 \cdot 10^{-3}$ M, $x_{\max} \approx 0.8$ (which corresponds to the maximum on the Job curve, Fig. 3a) provided that $p = 1$ (curve 1) and 2 (curve 2) and that the concentration of free metal ions is small compared to the concentrations of ML_n and ML_{n+p} . We actually calculated a correction to the ratio $n/m = 4$ determined from the position of the maximum on the Job curve (Fig. 2a). From Fig. 4b it follows that under conditions of our experiment, the amount of 50% ML_5 or ML_6 complexes in addition of ML_4 in solution cannot substantially affect the composition of the main complex to be determined.

Now we assess the assumptions made during calculation of curves 1 and 2 in Fig. 4b. First, it was assumed that the concentration of the free metal ions (or hydroxo complexes) in an equilibrium system is much lower than the concentration of ML_n complexes. From Eq. (6) it is clear that the presence of uncomplexed metal ions (or hydroxo complexes) in the system will only lead to decreased c_1 and c_2 ; as a result, the experimental value of $x_{\max}/(1-x_{\max})$ will still show less difference from n . Second, Eq. (6) suggests that the forms ML_i , which do not show themselves in the UV spectrum, are absent. If they are present, the right part of Eq. (6) will contain additional terms proportional to c_i/C , i.e., having the same order of magnitude as

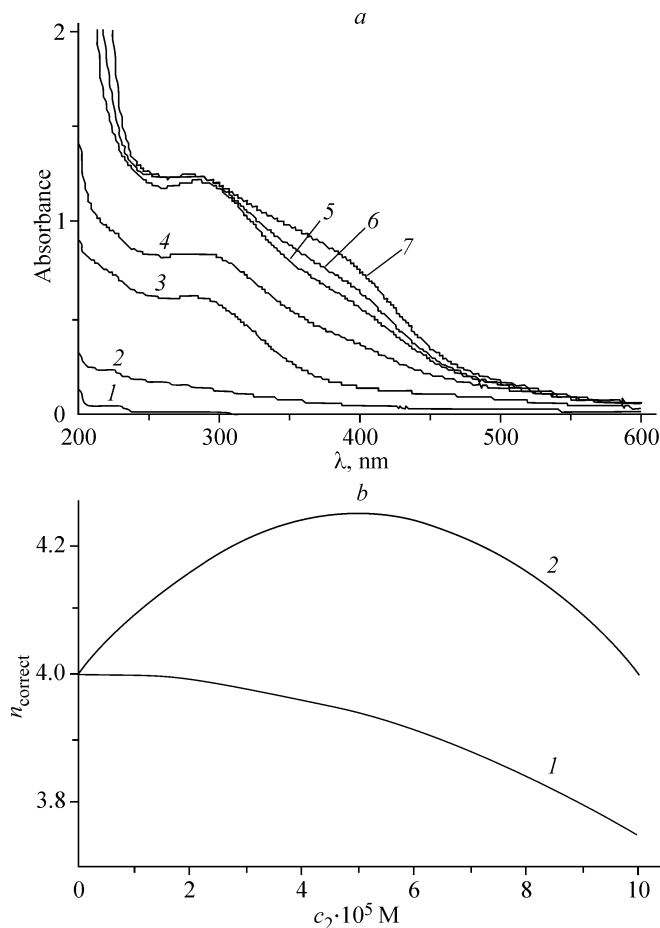


Fig. 4. Justification of the application of the Job method for determining the composition of the Mn(III)–DEA complex having an absorption maximum at 280 nm; *a* — UV spectra of Mn(III)–DEA complexes; concentration of MnCl₂ is $2 \cdot 10^{-4}$ M; curves 1–7 correspond to the concentrations of Et₂NH: $1 \cdot 10^{-4}$ M, $2 \cdot 10^{-4}$ M, $5 \cdot 10^{-4}$ M, $1 \cdot 10^{-3}$ M, $5 \cdot 10^{-3}$ M, $1 \cdot 10^{-2}$ M, and $2 \cdot 10^{-2}$ M; cell thickness 1 cm; 15 h after the initial solutions were mixed; *b* — simulation of the dependence of the true value of *n* for the Job curve for a system with two equilibrating complexes (Eqs. 3, 4) for $\varepsilon_1 = \varepsilon_2$ (Eq. 6); parameters of the model: $C = 1 \cdot 10^{-3}$ M $x_{\max} = 0.8$ (metal ion concentration is $2 \cdot 10^{-4}$ M), no uncomplexed ions, $p = 1$ (curve 1) and 2 (curve 2).

the available terms. From Fig. 4*b* it is clear that the maximum on the Job curve will not be shifted substantially (at least if the total concentration of ML_{n+p} and “dark” complexes does not exceed 50%).

This analysis indicates that, indeed, the maximum on the Job curve (Fig. 2*a*) corresponds to absorption of the 1:4 complex. Since Mn(III) generally forms complex compounds with coordination number 5 or 6 [18], one can suggest various structures for the complex having an absorption band with a maximum at 280 nm. For coordination number 6, structures of this kind are $Mn(DEA)_4(H_2O)_2^{3+}$, $Mn(DEA)_4(OH)_2^+$, and $MnCl_2(DEA)_4^+$, and other complexes with four DEA molecules and with various sets of H₂O, OH[−], and Cl[−] ligands.

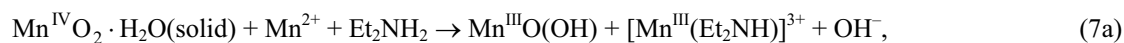
With a tenfold excess of ligand over metal, absorbance at 280 nm does not change any longer as the concentration of DEA increases further (Fig. 4*a*). This value of absorbance permits one to evaluate the lower bound of the molar absorption

coefficient for the Mn(III) complex with four DEA molecules. Assuming that this complex is dominant, we obtain $\varepsilon^{280} \geq 6000 \text{ M}^{-1}\text{cm}^{-1}$.

To determine the composition of the complex absorbing at 385 nm, we obtained a dependence of absorbance at 385 nm on the ratio $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0$ (molar ratio method [21]) (Fig. 3b). The lines through points at high and low concentrations of DEA intersect at $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0 = 6.6 \pm 1.0$. Hence it follows that the complex is likely to have a composition $\text{Mn}(\text{DEA})_6^{3+}$ (similar construction at 280 nm using the molar ratio technique gives $c_{\text{Et}_2\text{NH}}^0 / c_{\text{MnCl}_2}^0 = 4.4 \pm 0.7$, which agrees with the result obtained by the Job method). Thus the optical spectrum has absorption from two complexes of trivalent manganese with DEA with four and six alkylamine molecules in the coordination sphere.

FORMATION MECHANISM OF Mn(III) COMPLEXES

Formation of Mn(III) complexes due to solution of the precipitate containing Mn(IV) may be attributed to the comproportionation reaction between Mn(IV) of the solid and Mn(II) in solution. The hypothetical mechanism that illustrates the possibility of formation of these complexes is presented by Eqs. (7)-(9) (in which for simplicity we omitted ligands except Et_2NH). The initial process may include the molecular (7a) and protonated (7b) forms of amine:



CONCLUSIONS

The results of this work and [12] demonstrate that trivalent manganese can form complexes with aliphatic amines. The character of interactions and the form of complexes in the $\text{MnCl}_2 + \text{DEA}$ system depend on the relative concentrations of reagents and solute. At concentrations much higher than the oxygen concentration, the manganese ions remain bivalent in both solid reaction products and in solution [12]. At comparable concentrations of reagents and solute, the $\text{Mn}(\text{IV})-\text{MnO}_2 \cdot \text{H}_2\text{O}$ compound precipitates, and Mn(III) complexes with diethylamine form in solution.

It was interesting to examine if polynuclear manganese complexes (involving tri- and tetranuclear ions) can form as components of active complexes for oxidation of water. In this work, we did not obtain any evidence that polynuclear complexes can form in the $\text{MnCl}_2 + \text{DEA}$ system at low reagent concentrations. Analysis of UV spectra shows that 1:4 and 1:6 complexes can exist in solution. One of them may be binuclear. However, experimental proof of this possibility (for example, a UV band that might be assigned to the dimerization product) is unavailable. At high (1-5 M) initial concentrations of reagents, the precipitate contains only mononuclear manganese compounds [12].

An AFM/SNOM study [12] showed that films that form after evaporation of water from solutions of Mn(III) complexes with DEA and TEA contain compounds of two types. Apart from the major compound, presumably $\text{Mn}(\text{Et}_2\text{NH})_3\text{Cl}_3$ ($\text{Mn}(\text{Et}_3\text{N})_3\text{Cl}_3$ for the case of TEA), macroscopic (typically sized 1 μ) regions with a different chemical structure are formed. It was assumed [12] that these regions consist of polynuclear complexes of manganese coupled with water molecules. The possibility of clusterization of manganese(III) complexes with DEA and TEA due to solution concentration should be investigated in a separate study.

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