INFLUENCE OF POLY(ETHYLENE GLYCOL) WITH DIFFERENT MOLECULAR WEIGHT ON THE ESR SPECTRA OF Mn²⁺ IONS IN THE SYSTEM Mn(NO₃)₂·6H₂O/H₂O/POLY(ETHYLENE GLYCOL)

E.A. MASIMOV, E.G. ISMAILOV, V.I. GUSEINOV

Baku State University
Z. Khalilov, st.23, Baku, 370145, Azerbaijan

The structure of the local arrangement of Mn^{2+} ions in the system PEG/H_2O/Mn(NO₃)₂·6H₂O with the PEG of different molecular weights (200, 300, 400, 1500) in the temperature range 293-363 K was investigated using ESR spectroscopy. It was shown that connection of PEG with Mn^{2+} ions is as in the case of H_2O and has nonvalent character and at higher temperature ($T>343$ K for PEG-200 and $T>315$ K for PEG-1500) the local arrangement of Mn^{2+} ions in this system consists of only the water molecules.

1. INTRODUCTION

The structure and thermodynamic characteristics of Poly(ethylene glycol) (PEG) and its water solutions were widely investigated and are investigated nowadays. It is related both to practical application of PEG and with importance of research of its properties for the decision of fundamental tasks of the theory of solutions of water-soluble polymers. The interest to PEG is stimulated also by its application in molecular biology and biochemistry, where this polymer is widely used in various researches. There are a number of researches on influence of PEG on some processes proceeding in alive objects. It in turn puts a question on study of molecular mechanisms of such influences and opens new prospects in study of physical and chemical properties of PEG and in possibilities of its applications [1,2]. There are data on systems Polymer/Water/Inorganic Salt in the literature in present. Such systems find an application in pharmaceutics, medicine, etc. Among these systems, the systems PEG/Water/ Inorganic Salt are interesting also that they are capable to division into two liquid phases under certain conditions (temperature, concentrations of components). These biphase systems are used for division of biomacromolecules, cell particles, viruses and membranes for cleaning substances from impurities by their distribution between phases [3,4]. In the present work the structure of local arrangement of transition metal ions in the system PEG/H_2O/Mn(NO₃)₂·6H₂O for PEG with different molecular weight and changes in the system at the temperature range 293-363 K using ESR spectroscopy are investigated.

2. EXPERIMENTAL

In this work PEG HO(-CH₂-CH₂-O-)ₙH with molecular weights 200, 300, 400, 1500 from Loba-Chemie (Austria), the salt Mn(NO₃)₂·6H₂O qualified as "chemically clear" and distilled water as a solvent were used.

ESR spectra were registered using JES-PE-3X radiospectrometer (JEOL, Japan) with the working frequency 9300 MHz. The temperature dependence of the ESR spectra was studied in the range 293-363 K using temperature variator JES-VT-3A.

Theoretical spectra were built using PentiumII-300 MHz computer. Program, which is written by us for this purpose, allows fitting the theoretical spectra to experimental by optimization of parameters using the method of least squares. The derivative spectra were calculated using the formula [5]:

$$\frac{dF(H)}{dH} = \int_0^{2\pi} d\varphi \int_0^{\pi} \left[\sum_{m_1=-I_1}^{+I_1} \sum_{m_2=-I_2}^{+I_2} \cdots \sum_{m_N=-I_N}^{+I_N} \frac{\partial f[H - H_{(m_v)}(\vartheta, \varphi)]}{\partial H} \right] P(\vartheta, \varphi) W(\vartheta, \varphi) \sin \vartheta d\vartheta \ ,$$

where all notions are generally ones and these are described in previous paper [6]. The width of ESR line was determined as $\Delta H = C(1/T_1 + 1/T_2)$, where T_1 and T_2 are spin-lattice and spin-spin relaxation time, consequently and C – constant. The following expressions [7,8]

$$\frac{1}{T_1} = \frac{32}{25} \Delta^2 \left(\frac{\tau_r}{1 + \omega_0^2 \tau_r^2} + \frac{4\tau_r}{1 + 4\omega_0^2 \tau_r^2} \right), \quad \frac{1}{T_2} = \frac{16}{25} \Delta^2 \left(3\tau_r + \frac{5\tau_r}{1 + \omega_0^2 \tau_r^2} + \frac{2\tau_r}{1 + 4\omega_0^2 \tau_r^2} \right),$$

where τ_r – rotational correlation time, ω_0 – electron spin-resonance frequency, Δ – zero field splitting, were used in written program for calculating the width of the Mn^{2+} ESR lines.

which are very sensitive to changes of geometry and structure of a local environment of an Mn(II) ion [8]. The introduction at room temperature of PEG in a solution Mn(NO₃)₂·6H₂O/H_2O results in distortion of an initial spectrum. The spectrum, measured at room temperature, is not described satisfactorily by uniform set of magnetic-resonance parameters (MRP) and represents, at least, superposition of two signals concerning to various paramagnetic centres of the ions Mn^{2+}. These paramagnetic centres represent ions Mn^{2+} with a various local

3. RESULTS AND THEIR DISCUSSION

The water solutions of salts Mn(II) characterized by well-described sextet of ESR lines, width and relative intensity

environment, i.e. complexes $[Mn(H_2O)_6]^{2+}$ and complexes of a kind $[Mn(H_2O)_{6-n}(PEG)_n]^{2+}$, where n=1;2. It is clear, that the percentage of these complexes variously and depends on the contents in system of PEG, H_2O and $Mn(NO_3)_2 \cdot 6H_2O$.

Table. Magnetic-resonance parameters obtained by computer simulation of ESR spectra at C_{Mn}=0.2 mol/l, C_{PEG}=0.1 mol/l

$Mn(NO_3)_2 \cdot 6H_2O/H_2O/PEG$-200			
T, K	g, ±0.001	A, ±0.5 Gs	ΔH, ±1 Gs
293	1.995	95.5	90
315	1.995	95.5	70
343	1.999	95.5	47
363	1.999	95.5	40
$Mn(NO_3)_2 \cdot 6H_2O/H_2O/PEG$-1500			
T, K	g, ±0.001	A, ±0.5 Gs	ΔH, ±1 Gs
303	1.998	95.5	84
315	2.000	95.5	66
325	2.000	95.5	54
335	2.000	95.5	46
345	1.998	95.5	44
363	1.998	95.5	42
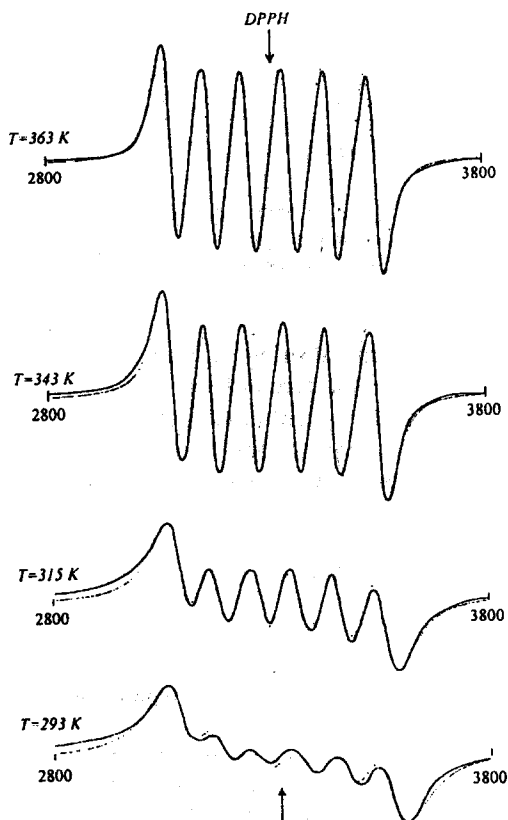
Fig.1. Temperature dependence of ESR spectra of the system $Mn(NO_3)_2 \cdot 6H_2O/H_2O/PEG$-200:
continuous line – experimental spectra measured at temperature range 293-363 K and C_{Mn}=0.2 mol/l, C_{PEG}=0.1 mol/l;
dashed line – calculated with Lorenz type of individual line shape and with magnetic-resonance parameters given in table.

The analysis of ESR spectra of system $Mn(NO_3)_2 \cdot 6H_2O/H_2O/PEG$ shows, that at room temperature these spectra for PEG of various molecular weights are practically identical. The distinction in influence of PEG with different molecular weights is precisely traced with increase of measurement temperature of ESR signals of these systems.

At fig.1 and fig.2 the experimental ESR spectra of systems $Mn(NO_3)_2 \cdot 6H_2O/H_2O/PEG$ are given for various temperatures of measurement and their theoretically designed variants in the assumption of Lorenz type of line form. The analysis of the signal form from PEG-200 (fig.1) and PEG-1500 (fig.2) at various temperatures shows the following: for ESR spectra registered at low temperatures (293-343 K for PEG-200 and 293-315 K for PEG-1500) it fails to pick up uniform MRP, with which the designed spectrum coincides with experimental. It means, that for these temperatures the spectrum of system is a superposition of several spectra. Nevertheless we for each temperature have tried to pick up uniform values of magnetic-resonance parameters (see table) and to calculate these spectra as single, so that to give the nearest by the form of theoretical to experimental spectrum. As it is visible from figures 1 and 2, as the temperature is

higher the coincidence of experimental and designed with uniform set of MRP theoretical spectra is better. At temperatures 343-363 K for PEG-200 and 315-363 K for PEG-1500 the theoretical and experimental spectra completely coincide. Such behaviour of system $Mn(NO_3)_2 \cdot 6H_2O/H_2O/PEG$ is possible to explain as follows. From the literature it is known [8], that the time of life of a water molecule in the coordination sphere of an Mn^{2+} ion is equal to 10^{-7} s. Means, in pure
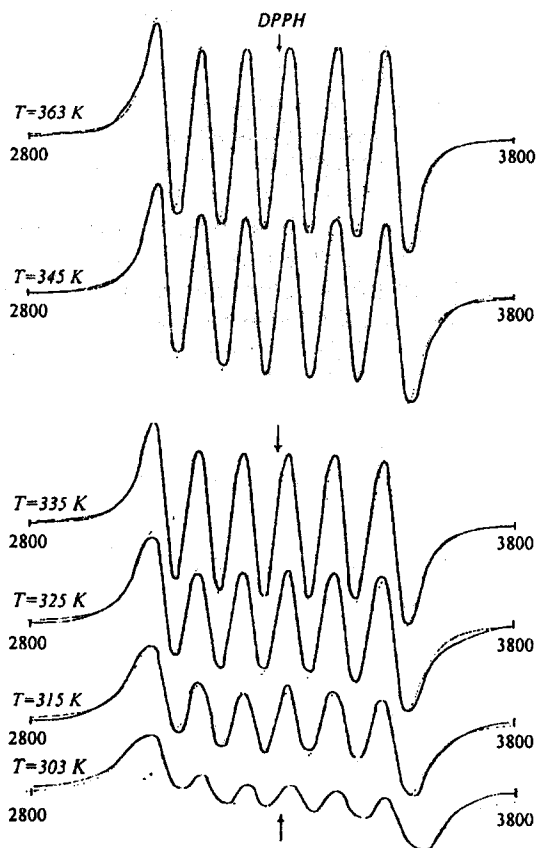

Fig.2. Temperature dependence of ESR spectra of the system $Mn(NO_3)_2 \cdot 6H_2O/H_2O/PEG$-1500:
continuous line – experimental spectra measured at temperature range 293-363 K and C_{Mn}= 0.2 mol/l, C_{PEG}=0.1 mol/l;
dashed line – calculated with Lorenz type of individual line shape and with magnetic-resonance parameters given in table.

water solution aquacomplexes of an Mn^{2+} ion have the not rigidly connected structure, and there is a continuous fast exchange between the water molecules of aquacomplexes and volumetric water. In the presence of PEG in solution, there is the exchange process with participation also of PEG molecules. Thus, in this case we have also the PEG-containing complexes, where the connection of PEG molecules to Mn^{2+} ion is carried out through oxygen atoms of a PEG molecule. However mobility of PEG molecules owing to their large sizes is much less than mobility of water molecules. Therefore PEG molecules first participate in an exchange less effectively, than the molecules of water, secondly, having built in the first coordination sphere of metal ion, cannot long move with a complex at high temperatures. From told follows, that at low temperatures, formation of complexes of PEG molecules with Mn^{2+} ion is facilitated in comparison with high temperatures. At low temperatures there are complexes of various structures ($[Mn(H_2O)_6]^{2+}$ and $[Mn(H_2O)_{6-n}(PEG)_n]^{2+}$, where n=1;2), giving various ESR spectra. With increase of temperature the probability of the formation of complexes of

PEG with Mn^{2+} decreases, and the formation of water complex $[Mn(H_2O)_6]^{2+}$ is more probably. It explains the complete coincidence between experimental and designed with a uniform set of MRP spectra at high temperatures. Furthermore, we take into account the lower temperature limit of existence of various complexes for PEG-1500 (315 K) in comparison with PEG-200 (343 K), as PEG-1500 is much more heavy and has the large geometrical size, than PEG-200. At the fixed contents of the initial components the percentage of complexes with different number of PEG molecules in the coordination sphere of a metal ion and of pure water complexes depends on temperature. With increase of temperature the equilibrium is displaced in the direction of formation of pure water complexes. With return cooling of system $Mn(NO_3)_2 \cdot 6H_2O/H_2O/PEG$ down to room temperature, its ESR spectrum accepts an initial kind. From here follows that with the formation of complexes in the investigated system the connection of Mn^{2+} ions with PEG as with H_2O has non-valent character.

[1] *E.A. Bekturov*, Synthetic Water-soluble Polymers in Solution,Huethig & Wepf Verlag,Basel, Germany,1986, p.135ff.

[2] *V. Fischer, W. Borchard, and M. Karas*. J. Phys. Chem., 100, 1996, 15992-15999.

[3] *I.N. Topchieva*. Uspekhi Khimii, v. XLIX, № 3, 1980, 494-517.

[4] *S.P. Rojkov*. Jurnal Fizicheskoy Khimii, v. 70, № 11, 1996, pp. 1982-1986.

[5] *A.V. Ilyasov, I.D. Morozova, A.A. Vafina, M.B. Zuev.* Spektri EPR i stereokhimia fosforsoderjashikh svobodnikh radikalov, Nauka, Moscow, 1985.

[6] *E.A.Masimov, V.I.Guseinov, E.G.Ismailov*. Baki Universitetinin Heberleri, № 4, 1998, (in a seal).

[7] *S. Ristori, E. Ottomani, M. Romanelli, and G. Martini.* J. Phys. Chem., v. 99, 1995, pp. 17886-17890.

[8] *G.P. Vishnevskaja*. "Electron Relaxation and Resonance of Paramagnetic Ions in Solutions", in the Collection of the survey articles: "Radiospectroscopy of Condensed Matter", "Science", Moscow, 1990, p.13-45.

E.Ə. Məsimov, E.H. İsmayılov, V.İ. Hüseynov

MÜXTƏLİF MOLEKULYAR KÜTLƏLİ POLİETİLENQLİKOLUN Mn(NO₃)₂·6H₂O/H₂O/ POLİETİLENQLİKOL SİSTEMİNDƏ Mn²⁺ İONLARININ EPR SPEKTRLƏRİNƏ TƏ'SİRİ

EPR spektroskopiyasının tətbiqi ilə, tərkibində müxtəlif molekulyar kütləli PEQ (200,300,400,1500) olan, Mn(NO₃)₂·6H₂O/H₂O/PEQ sistemində 293-363 K temperatur intervalında Mn²⁺ ionlarının lokal ətrafının quruluşu tədqiq edilimişdir. Göstərilmişdir ki, PEQ Mn²⁺ ilə H₂O molekulları kimi rabitələnir, və bu rabitə qeyri valent xarakteri daşıyır.Yüksək temperaturlarda (T>343 K PEQ-200 üçün və T>315 K PEQ-1500 üçün) bu sistemində Mn²⁺ ionlarının lokal ətrafı yalnız su molekullarından ibarətdir.

Э.А. Масимов, Э.Г. Исмаилов, В.И. Гусейнов

ВЛИЯНИЕ ПОЛИЭТИЛЕНГЛИКОЛЯ С РАЗЛИЧНЫМИ МОЛЕКУЛЯРНЫМИ МАССАМИ НА ЭПР СПЕКТРЫ ИОНОВ Mn²⁺ В СИСТЕМЕ Mn(NO₃)₂·6H₂O/H₂O/ПОЛИЭТИЛЕНГЛИКОЛЬ

С использованием ЭПР спектроскопии в температурном интервале 293-363 К исследована структура локального окружения ионов Mn²⁺ в системе ПЭГ/H₂O/Mn(NO₃)₂·6H₂O с ПЭГ различных молекулярных масс (200, 300, 400, 1500). Показано, что ПЭГ связывается с Mn²⁺ подобно H₂O, и эта связь имеет невалентный характер. При высоких температурах (T>343 К для ПЭГ-200 и T>315 К для ПЭГ-1500) локальное окружение ионов Mn²⁺ в этой системе состоит только из молекул воды.