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Spectroscopic Characteristics of Highly Selective Manganese Catalysis in Acqueous Polyurethane Systems

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Abstract: The latest investigations on producing more efficient catalytic aqueous polyurethane systems are in the domain of metal complexes with mixed ligands. In our previous research works, the high selectivity for the isocyanate-hydroxyl reaction in aqueous polyurethane systems has been shown by the manganese(III) mixed-ligand complexes. The two new complexes have been prepared with two acetylacetonate (acac) ligands and one maleate ligand and its hydroxylamine derivative of the general formula $[Mn(C_5H_7O_2)_2L]$. Their structures have been established by using the fundamental analyses, the FTIR and UV/VIS spectroscopic methods, as well as the magnetic measurements. In order to explain the different selectivity of the manganese(III) mixed-ligand complexes, the UV and ESR spectroscopy have been employed to determine the kinetics of the complexes' decomposition. The thermal stability of the complexes has been determined by way of the dynamic TG method at the heating rate of $5°C·min^{-1}$ and at the temperature ranged 20-550°C. It suggests the decomposition of the

complexes by loss of acid ligand. The main factor in the selective catalysis control in the aqueous polyurethane systems is the nature of the acid ligands and their impact on the manganese(II)/manganese(III) equilibrium.

Keywords: catalyst's selectivity, manganese(III) complexes, fourier transform infrared spectra (FTIR), electronic spectra (UV), electron spin resonance (ESR).

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Introduction

The main problem in formulating the aqueous polyurethane systems is the isocyanate-water side reaction, which can lead to gassing/foaming, pinholes, loss of isocyanate functionality, low gloss, and a reduced pot life. The formation of carbon dioxide also lowers the pH of the emulsion or dispersion, which can reduce the stability of the aqueous formulations [1,2]. A new approach in monitoring the water side reaction is the use of catalysts which selectively catalyze the isocyanate-polyol reaction but not the isocyanate-water reaction [3] (Figure 1).
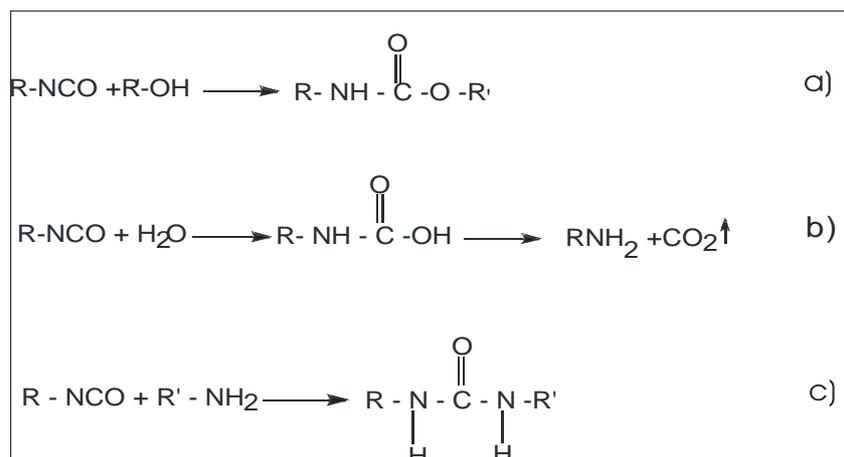

Figure 1. Isocyanate reactions with alcohol (a) and with water (b,c).

In the previous works of Blank [4], the selectivity of different compounds compared to model compounds has been investigated. Butyl isocyanate and 2-ethyl-1-hexanol have been chosen as model compounds due to their similarity to the aliphatic polyisocyanate and hydroxyl resins, as well as because of the simplicity of their FTIR spectra. The reaction product ratio, urethane/urea, has been used as a measure of the relative selectivity. In our previous works [5], the high selectivity is showed by the manganese(III) mixed-ligand complexes with two acetylacetone ligands and one maleate ligand and its hydroxylamine derivative. The catalytic ability of a complex is determined by its composition and it depends on the nature of a ligand. It gives a possibility to change the complex structure and its selective catalytic activity by changing the ligands [6]. The synergistic action of the complex Mn(III)-acetylacetone with acid leads to the ligands exchange and to the formation of mixed Mn(III)-diacetyl acetonecarboxylate helate [7]. The replacement of the acetylacetone with the carboxylate ligand increases the helate activity in the catalytic reaction. Catalyses usually go over splitting ligand and oxidation of Mn(II) into Mn(III). The increased activity of the complex is connected with the

helate electronic structure change [8,9,10]. In order to explain the lower selectivity of Mn(III)-diacetylacetonehydroxylaminmaleate in comparison to Mn(III)-diacetylacetonemaleate, as well as the different impact of inductive time on film hardness [11,12], the UV and ESR spectroscopy have been used to determine the kinetics of the complex decomposition of the manganese(III) mixed-ligand.

Experimental

Instrumental measurements

The carbon, hydrogen and nitrogen analyses have been performed using a CHN 24000 Perkin-Elmer analyzer. The manganese content has been determined by the spectrophotometric method, at 525 nm. The Fourier-transform infrared (FTIR) spectra were recorded using a Michaelson Bomem MB-series spectrophotometer and the KBr pellet (1 mg/100 mg) technique. Magnetic susceptibilities have been determined at room temperature employing the MSB-MKI magnetic susceptibility balance (Sherwood Scientific Ltd., Cambridge, England). The electronic spectra (UV/VIS) have been recorded on a Varian Cary-100 spectrophotometer using 10^{-4} moldm^{-3} solutions in ethanol in quartz cuvettes. The electron spin resonance (ESR) measurements of water samples have been recorded at 20°C on the X-band microwave frequency on a Bruker 300E spectrometer utilizing 25.0 kHz magnetic field modulation. The TGA/DTA curves of the complexes have been studied in the air atmosphere at the heating rate of 10°C·min^{-1}, at the temperatures ranged 20-550°C, using the Bomen TGS+ Thermogravimetric system.

Synthesis of the complexes

All the used chemicals have been of the p.a. grade purity. The starting complex [Mn(C$_5$H$_7$O$_2$)$_3$] has been obtained from commercial sources and has been utilized without further purification.

Synthesis of Mn(III) diacetylacetonemaleate (I). Maleic anhydride and methanol (1:1) have been refluxed for 120 min. The [Mn(C$_5$H$_7$O$_2$)$_3$] has been dissolved in benzene. The reaction mixture has been cooled and the equimolar amounts of [Mn(C$_5$H$_7$O$_2$)$_3$] and monomethylmaleate have been mixed. The mixture has been held at 10-25°C for about 10-20 min. The dark-green product (insoluble in benzene) has been filtered under vacuum, washed with solvent and dried at room temperature, the yield being 90%.

Synthesis of Mn(III) diacetylacetonehydroxylaminmaleate (II). In order to synthetize these complexes, the maleic anhydride and methanol (1:1) have been refluxed for 120 min, and hydroxylamine hydrochloride in ethanol (0.5 mol dm^{-3}) has been added in an equimolar amount, the refluxing lasting about 15 min. To cool the redistilled solution, the Mn(III)-acetylacetone complex (previously dissolved in a minimal volume of benzene) has been added. The green product has been filtered under vacuum, washed with the solvent and dried at room temperature, the yield being 80%.

Results and Discussion

The results of the microanalysis of carbon, hydrogen and nitrogen in the investigated compounds are given in Table 1. The complexes have been synthesized applying the Mn(III)-acetylacetone and the

acid ligand in the 1:1 mole ratio. The results in Table 1 indicate the replacement of the acetylacetone ligand by the corresponding acid ligand. The complexes are soluble in water, tetrahydrofurane, propylene glycol, metoxypropylacetate and other polar solvents.

Table 1. Data of the basic analysis of the investigated compounds (L^1 = -OCO-CH=CH-COOH, L^2 = -OCO-CH=CH-CONHOH).

Compounds	Molecular Formula	Yield (in %)	Colour	Carbon (in %)		Hydrogen (in %)		Nitrogen (in %)		Manganese (in %)	
				found	calcd	found	calcd	found	calcd	found	calcd
I	$[Mn(C_5H_7O_2)_2L^1]$	90	dark-green	44.33	45.61	4.57	4.62	-	-	15.3	14.9
II	$[Mn(C_5H_7O_2)_2L^2]$	80	green	42.51	43.82	4.59	4.70	3.51	3.65	13.6	14.3

Infrared spectra

The band at ~3564 cm^{-1} (-OH stretching vibration) indicate the acetylacetone ligand's replacement with the maleic acid in the compound (I). The bands at 1708 cm^{-1} and ~1338 cm^{-1} have been assigned to the asymmetric and symmetric stretching vibrations of the COOH-group [7]. The two bands of the ionized carboxylic group have been detected, too: the first at 1615 cm^{-1} of the asymmetric vibrations and the second at 1458 cm^{-1} from the symmetric vibrations (Figure 1).
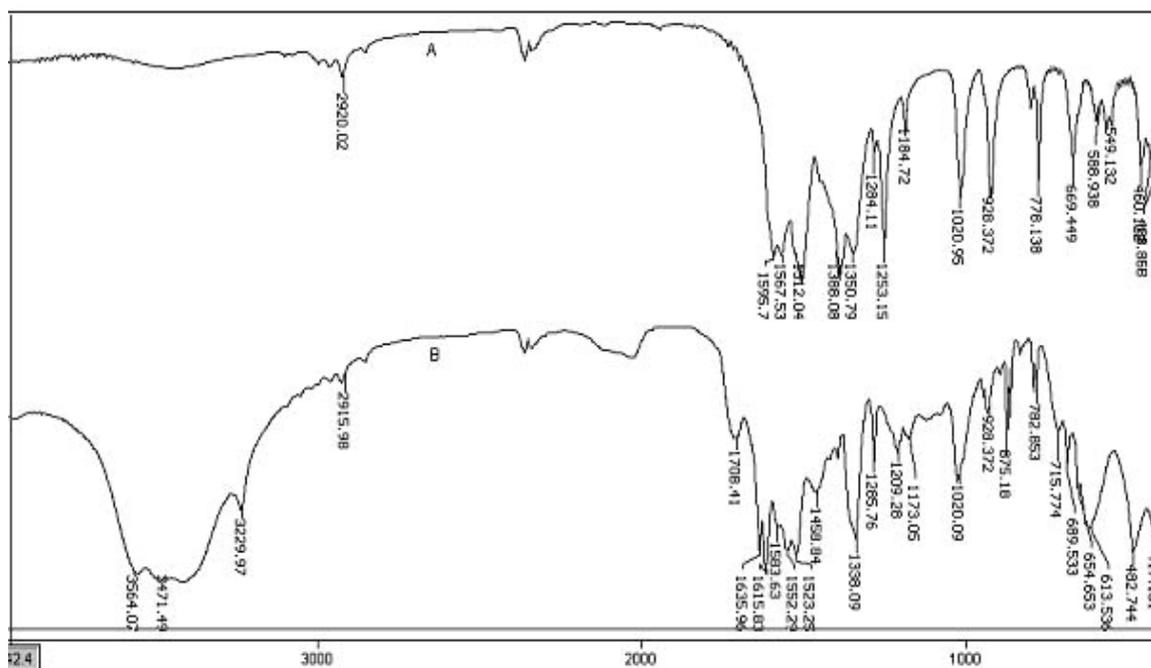

Figure 1. Comparative FTIR spectra: A) the complex of Mn(III)-acetylacetone,
B) the complex of Mn(III)-diacetylacetonemaleate.

The complex with the hydroxylamine derivative of the maleic acid has showed vibrations only of the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at 1595 cm^{-1} and 1407 cm^{-1}.

The bands at 417, 482, 613, 654, 689 cm^{-1}, assigned to Mn-O vibrations, as well as the bands at 928 and 1020 cm^{-1} show that the Mn(III) is bonded to two acetylacetone ligands. The band at 1312 cm^{-1} attributed to the coupling of the $\nu(C-N)$ and $\delta(N-H)$ vibrations and $\delta(N-H)$ deformation band at 717 cm^{-1} confirm this suggestion (Table 2).

Table 2. The FTIR spectral data of the compounds [frequency (cm^{-1})].

[Mn(C$_5$H$_7$O$_2$)$_3$]	[Mn(C$_5$H$_7$O$_2$)$_2$L^1]	[Mn(C$_5$H$_7$O$_2$)$_2$L^2]	Assigment of bands [a]
430 m	417 m	425 m	ν(Mn-O), δ(Mn-O=C)
460 m	482 m	487 m	ν(Mn-O), ν(C-CH$_3$), ν(C=C)
550 m	613 m	575 m[b]	π_{ring}+ ν(Mn-O)
588 s	654 s	633 m	ν(Mn-O), δ(Mn-O=C, CH$_3$-C=O)
669 ms	689 m	689 m	ν(C-CH$_3$), ν(Mn-O), δ(O=C-CH$_3$)
		771 m	γ(N-H).
778 s	782 s	778 w[c]	π(C-H)
	875 m	876 m	δ(COO)
928 s	928 m	927 m	ν(C-CH$_3$)
1020 s	1020 s	1023 s	γ(CH$_3$)
1185 w	1173 w	1180 w	δ(C=CH)
1253 s	1285 s	1281 m	ν(C=C), ν(C-CH$_3$)
		1312 m	ν(C-N), δ(N-H)
	1338 s		ν_sCOOH)
1350 s		1361 s	δ(CH$_3$)
1388 s	1388 w		δ(CH$_3$)
	1458 m	1407	ν_s(COO)
		1462 m	δ(=CH)
1512 s	1523 s	1514 s	ν(C=C), δ(C=CH)
1567 s	1552 s	1551 s	ν(C=C), δ(C=CH)
1595 s	1615 s	1595 s	ν_{as}(COO)
	1635 s		ν(C=C)
		1651 m	ν(C=O)
	1708 m		ν_{as}(COOH)
2920 w	2915 w	2920 w	ν(C-H)
	3229 m	3213 m	ν(=CH)
		3559 m	ν(N-H)
	3564 s	3400 s	ν(O-H)

Notes: [a] Relative intesity: s-strong, m-medium, w-weak and [b]π_{ring}, ring deformation out-of-plane that includes torsions τO-C- C- C, τO- C- C- H, τCH$_3$-C-C-H; [c]π(C- H), C-C-C-H out-of-plane vibration.

The two major bands have appeared in the complex (II): NH stretching vibrations at ~3559 cm^{-1} and the band attributed to the vibration of the carbonyl C=O group (1651cm^{-1}) indicating the replacement of the acetylacetone ligand by the hydroxylaminmaleate ligand [7].

The bands at 417, 482, 613, 654, 689 cm^{-1}, assigned to Mn-O vibrations, as well as the bands at 927 and 1023 cm^{-1} show that Mn(III) is coordinated to two acetylacetone ligands (Figure 2).

The main frequencies and their assignments are presented in Table 2.

Thus, the data (Table 2) from the infrared spectra provide the clear evidence that the ligands of the maleic acid and its hydroxylamine derivative are bonded with two acetylacetone ligands in the Mn(III) mixed-ligand complexes.
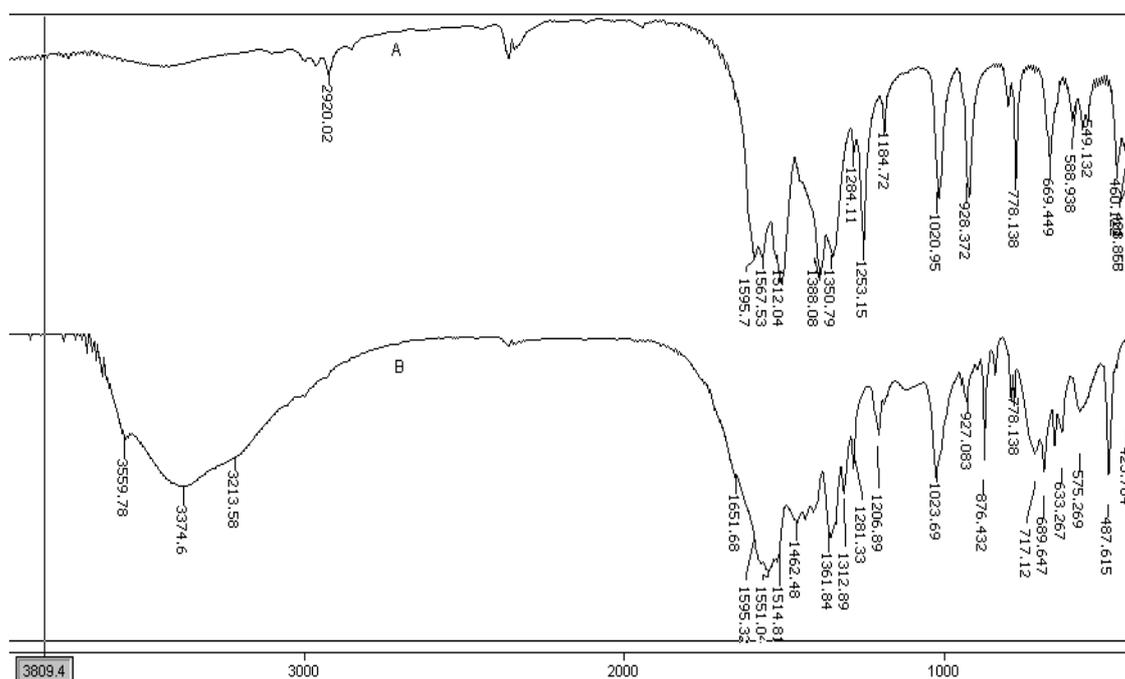

Figure 2. Comparative FTIR spectra:
    A) the complex of Mn(III)-acetylacetone
    B) the complex of Mn(III)-diacetylacetonehydroxylaminmaleate.

Electronic spectra

The spectral data and magnetic moments of the compounds are presented in Table 3. In the complex Mn(III)-acetylacetone [6], there are two absorption bands, assigned to $\pi\rightarrow\pi^*$ transitions and one apsorption band assigned to $\pi^*\rightarrow d$ transition. These transitions have also been found in the spectra of the synthesized complexes, but they are shifted towards lower and higher frequencies, depending on the ligands structures.

Table 3. The electronic spectral data of the complexes recorded in ethanol [frequency (cm^{-1})/ ε_{max} (mol^{-1} dm^3 cm^{-1})].

Complex	μ_{eff}/μ_B	$\pi\rightarrow\pi^*$	$\pi\rightarrow\pi^*$	$\pi^*\rightarrow d$	$d\rightarrow d^*$	$d\rightarrow d^*$
				$v(10^4$ $cm^{-1})/$ ε		
[Mn(C$_5$H$_7$O$_2$)$_3$]	4.90	40.8/17 500	36.4/24 000	30.7/9 500	24.8/950	17.5/100
[Mn(C$_5$H$_7$O$_2$)$_2$L^1]	4.76	41.6/31 000	35.2/12 000	30.2/17 500	24.3/1 000	17.6/70
[Mn(C$_5$H$_7$O$_2$)$_2$L^2]	4.81	42.0/22 500	35.9/14 500	30.3/11 000	24.8/1 500	17.5/170

In the VIS electronic absorption spectrum there are two absorption bands assigned to $d\rightarrow d^*$ transitions in the complexes (I, II). These bands could be attributed to a changed transfer transition, or even to the $d\rightarrow d^*$ transition. The color of the complexes is probably due to these transitions. The color

of the transition metal complexes has originated from d-orbitals. It is known that a ligand splits d-orbitals of the central ion into two groups. This splitting is weak and the excitation of an electron from t_{2g} to e_g orbitals is always observed in the visible electronic absorption spectra.

Magnetic properties

An indication of the most probable stereochemistry of the synthesized manganese(III) complexes is given by its color and a magnetic moment. Namely, the black Mn(III)-acetylacetone complex usually has an octahedral configuration. The room temperature effective magnetic moments of the manganese(III) complexes with mixed ligands are in the range of 4.76-4.9 μ_B, which corresponds to four unpaired electrons typical of the d^4 system.

It is supposed that in the mixed-ligand complexes the ligands have localized π-bonds and do not favor the electron-pairing. The Jahn-Teller effect, due to an unequal filling up of t_{2g} and e_g orbitals, yields a distorted octahedral geometry in complexes. These complexes have a dark green to green colour [13].

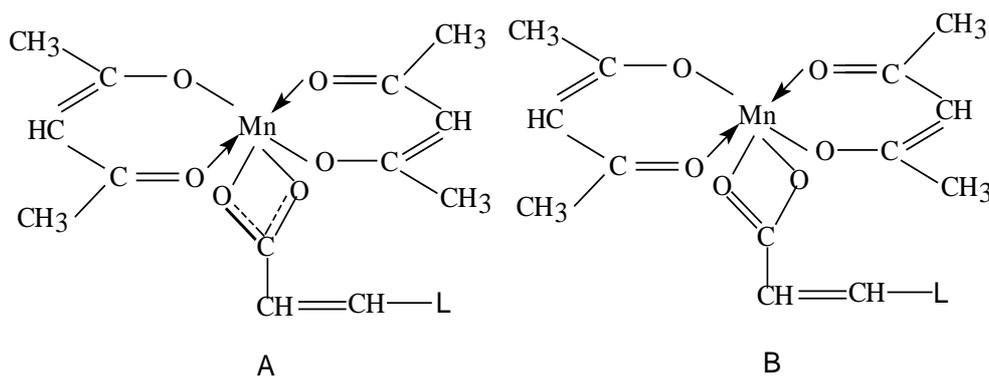The proposed structures of the complexes shown in Figure 3 are consistent with the related data [6].

Figure 3. The proposed structure of the complexes with mixed ligands

      L = -COOH, Mn(III)-diacetylacetonemaleate

      L = -CONHOH, Mn(III)-diacetylacetonehydroxylaminmaleate.

Decomposition of the complex with the mixed ligand

In the complex Mn(III)-diacetylacetonemaleate, there are two absorption bands at 240 nm and 280 nm assigned to the $\pi \rightarrow \pi^*$ transitions, and one absorption band at 325 nm assigned to the $\pi^* \rightarrow d$ transitions. These bands have significant maximums and their overlapping is less than for Mn(III)-acetylacetone, which is consistent with the already known data for the similar manganese(III) mixed-ligand complexes.

In the previous researches [14,15], the rate of the ligand exchange in Mn(III)-acetylacetone with the other (acid one) in the methanol solution has been investigated. The addition of Mn(II)-acetylacetone decreases the rate of ligands exchange, supposing the formation of the mixed complex $Mn^{3+}(C_5H_7O_2)_x$ Mn^{2+} that does not undergo homolysis. Similar results are found for the $Cu^{1+}Cu^{2+}$ mixed complex [16].

As it is shown (Figure 4), the decomposition of the Mn(III)-diacetylacetonemaleate complex decreases in time with the intensity of the band at 240 nm due to the $\pi \rightarrow \pi^*$ transition in the ligand. It can also be seen, that the already mentioned band at 325 nm, which is consistent with $\pi^* \rightarrow d$, also decreases in intensity during the same period. In contrast to this, the intensity of the band at 280 nm increases.
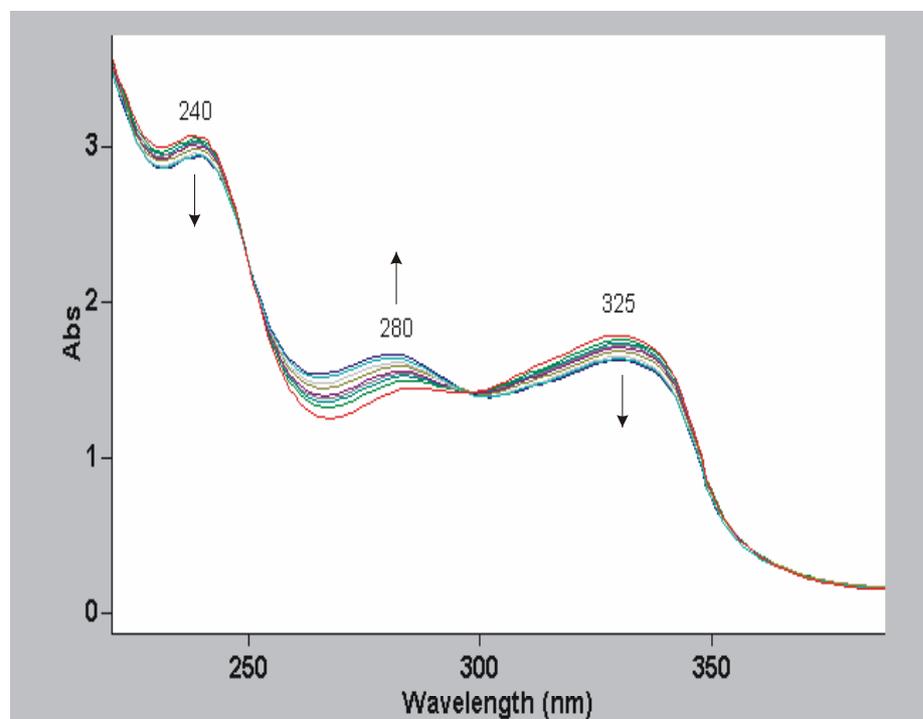

Figure 4. The UV spectra of the decomposition of the complex of Mn(III)-diacetylacetonemaleate in ethanol with time (30 min.).

The parallel changing of the band intensity at 280 and 325 nm for the Mn(III)-acetylacetone and Mn(III)-diacetylacetonemaleate complexes, shows that the reduction is faster with Mn(III)-acetylacetone, reaching the balance in 10 min. It suggests that the once established Mn^{3+}/Mn^{2+} balance does not permit further transition Mn^{3+} in Mn^{2+}.

The decomposition of the complex with the mixed ligands is slower and the balance is established after 30 min. The spectra have been recorded periodically every 3 min. In the complex Mn(III)-diacetylacetonemaleate, the balance has been established after 9 times (27 min), but there has been no change in the UV spectra of Mn(III)-acetylacetone after 9 min (Figure 5).
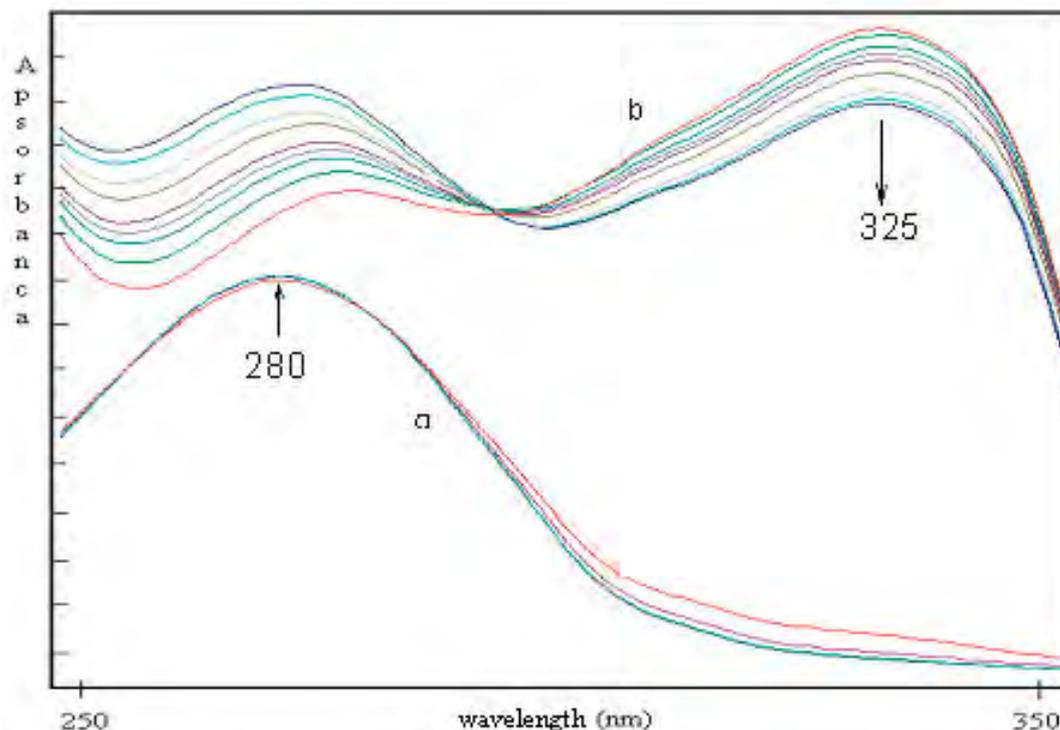
Figure 5. The comparison of the UV spectra
   a) of Mn(III)-acetylacetone and
   b) of Mn(III)-diacetylacetonemaleate in ethanol with respect to time.

In the Mn(III)-diacetylacetonehydroxylaminmaleate, the balance Mn^{3+}/Mn^{2+} is established very fast, in 15 min, and does not permit further transition manganese(III) in manganese(II). The concentration of the acid ligand in the solution is somewhat less, compared to other complexes where the balance is established a little bit slowlier (Figure 6).

The ESR spectroscopy is used to observe the concentration of Mn^{2+}, obtained as a product of the Mn^{3+} reduction [17]. It is shown that once the balance has been established in the solution, the coordinated acid ligand (hydroxylamine derivative of the maleic acid) decreases the effect of the positive charge of the Mn^{3+} ion making the reduction difficult. When the balance is established in the solution, the concentration of the Mn^{2+} ion is higher in the complex with the maleic acid ligand (Figure 7a), than in the complex with the ligand consisting of the hydroxylamine derivative of the maleic acid (Figure 7b).
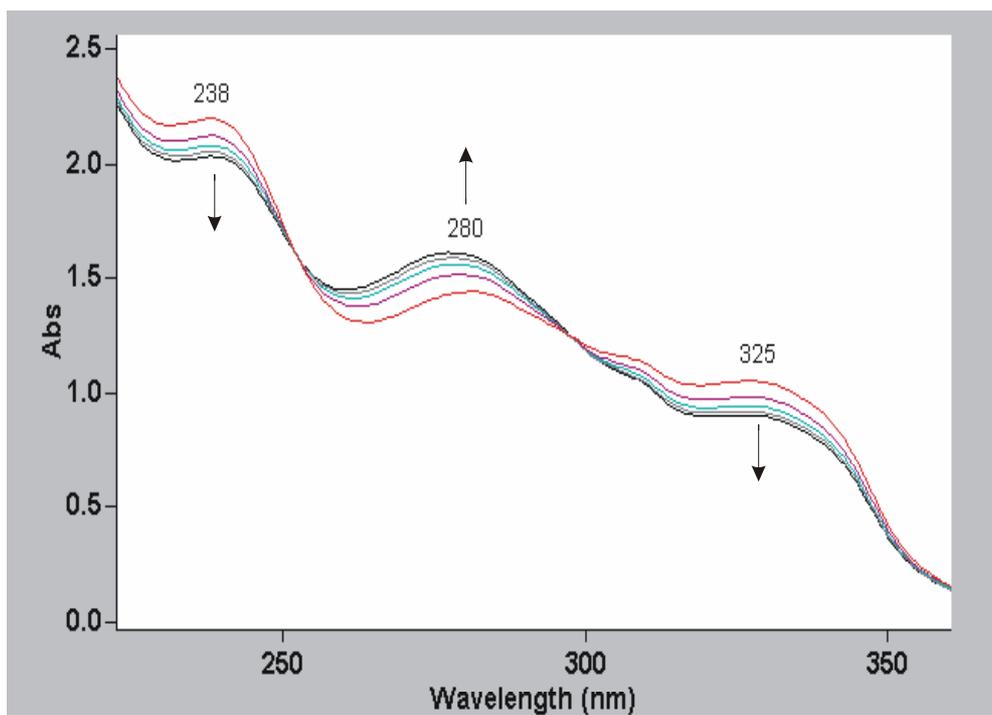
Figure 6. The UV spectra of the decomposition of the complex of Mn(III)-diacetylacetonehydroxylaminmaleate in ethanol with respect to time (15 min).
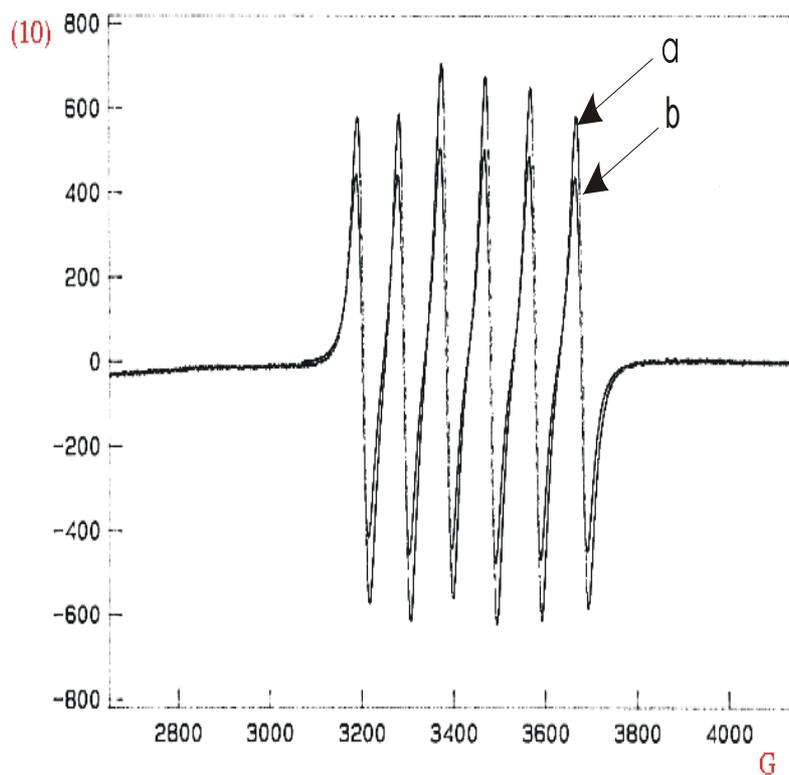

Figure 7. The comparison of the ESR spectra after the balance has been established of Mn^{3+}/Mn^{2+}
      a) of Mn(III)-diacetylacetonemaleate, and
      b) of Mn(III)-diacetylacetonehydroxylaminmaleate.

The reduction of the pH of water, as a result of the dissolution of the manganese(III) complex, confirms the removal of the acid ligand out of the complex. However, the removal of the acetyl acetone ligand will increase the pH since the ligand receives a proton from the solution and transforms into acetylacetone [16].

The thermal analysis of the Mn(III)-acetylacetone complex suggests that the acetyl acetone ligand is released. The weight loss of 28% at 160°C, is in accordance with splitting the acetylacetone ligand. This is in good relation with the theoretical weight loss of 31.3%. The TG and DTG curves in Mn(III)-diacetylacetonemaleate show the first weight loss at 160°C. The starting weight loss of 31% shows that the decomposition of this complex begins with the loss of the maleic ligand. The complex with the hydroxylaminmaleate ligand shows less thermal stability, since the pyrolysis starts at 120°C. The weight loss of 34% suggests the loss of hydroxylaminmaleic ligand [17].
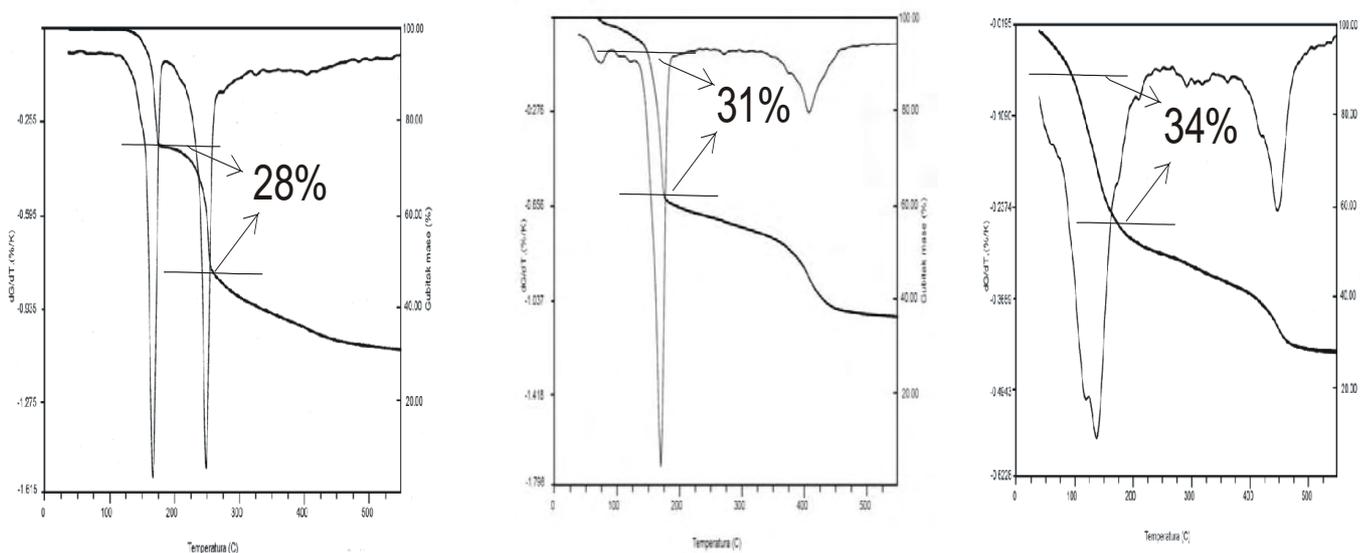

Figure 8. The TG and DTG curves
         a) of Mn(III)-acetylacetone,
         b) of Mn(III)-diacetylacetonemaleate and
         c) of Mn(III)-diacetylacetonehydroxylaminmaleate.

Conclusions

The ligands of the maleic acid (L^1) and its hydroxylamine derivative (L^2), formed with the Mn(III)-acetylacetone complex the mixed-ligand complexes of the general formula [Mn(C$_5$H$_7$O$_2$)$_2$L]. The complexes have been synthetized and characterized by means of the basic analyses, the magnetic susceptibility measurements, the IR and UV/VIS spectra. The replacement of the acetylacetone ligand by the corresponding acid ligand has been confirmed in Mn(III)-acetylacetone. Based on the obtained experimental data and the literature indications, the structural formulae have been assigned to these compounds.

The impact of the acid ligand on the Mn^{3+}/Mn^{2+} balance, as well as the nature of the ligand itself, is the main factor in the selective catalysis of the aqueous two-component polyurethane formulations.

The results obtained in this work could explain the lower hardness [12], and the reduction of the activation energy [18], of the formed films by using the Mn(III)-diacetylacetonehydroxylaminmaleate compared to the Mn(III)-diacetylacetonemaleate.

Acknowledgements

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