

SEPARATION OF ALKALINE-EARTH RADIONUCLIDES IN THE PRESENCE OF IRON

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ABSTRACT

For the separation of alkaline-earth radionuclides out of the liquid radioactive wastes resulted from the American TRIGA 14MW Reactor, one of the best chemical treatment methods has been found.

Starting from inactive simulated solutions there have been obtained ten complex combinations containing maleat ($O_4C_4H_2$)²⁻ presenting the following general types:

- $Fe_2ML_2(OH)_4 \cdot xH_2O$ (M = Ca, Sr, Ba; L = $O_4C_4H_2$ ²⁻; x = 5)
- $Fe_2ML_4 \cdot xH_2O$ (M = Sr, Ba; L = $O_4C_4H_2$ ²⁻; x = 4.6)
- $Fe_3ML_2(OH)_7 \cdot xH_2O$ (M = Sr, Ba; L = $O_4C_4H_2$ ²⁻; x = 3)
- $Fe_3ML_4(OH)_3 \cdot xH_2O$ (M = Ca, Sr, Ba; L = $O_4C_4H_2$ ²⁻; x = 3.6)

The syntheses have been performed in the well definite conditions depending on: pH of reaction medium, molar ratio of components, anion nature, temperature.

For characterization of the compound we have recorded the vibration, Mössbauer, and electronic spectra and both the thermic analyses and molecular electric conductivity have been performed.

From the vibration spectra, on the Δ parameter criterium it results that the maleat ions have worked as chelating agent and as bridging ligand. The electronic spectra have presented in the high energies range (380 nm) bands assigned to the transitions L→Fe and in the lower energies range as bands assigned to a superexchange between iron ions Fe(III)→Fe(III). From the Mössbauer spectra we have measured: isomer shift, quadrupolar splitting and relative area. Based on obtained results, taking into account the tabulated values of these parameters it results that the iron ion presented as Fe(III) has an octahedral symmetry.

The thermic analyses effected in specific testing conditions have confirmed that the assigned formulae are the most probable.

Molecular electric conductivity measurements, confirmed the nature of electrolytes 1:1 of these combinations.

INTRODUCTION

In connection with the development of Nuclear Energy in Romania the problem of liquid radioactive wastes that have resulted at the Nuclear Research Institute of Pitesti - Romania, has been raised.

The very saline radioactive wastes from ionic resin regeneration mixed with detergents from decontamination made them unsuitable for direct evaporation without prior chemical treatment. At the same time, owing to lack of a proper evaporation station the treatment of these radioactive wastes by chemical methods has been considered only for a couple of years. Since among the chemical methods, the complexation presents the best advantages regarding the selective separation, a study has been effected in order to select the best treatment method in Romania's specific conditions (1). The diversity of ion types from wastes excludes the possibility of using a sole complexing agent for eliminating all the radionuclides.

Among the radionuclides which are presented in solution Cs-137 of the first group and Sr-89, Sr-90 and Ba-140 of the second group the most difficult problems occurred. Taking into consideration the oxygen affinity of these elements several carboxylic acid have been tested among which, the maleic acid was suitable to most requirements for the elements of the second group.

Starting from these results, a systematic investigation has been initiated in establishing the Ca, Sr and Ba behavior in the presence of iron an indispensable element in modern techniques always present in the working fluids both in classical and nuclear power plants, as well as in liquid radioactive wastes, simultaneously (2).

THE SYNTHESSES OF THE COMPOUNDS

The studies effected for characterizing the compounds involved in the liquid radioactive waste treatment were started from simulated solutions. There have been obtained ten combinations containing maleat ions ($O_4C_4H_2$)²⁻ constituting part of the following general types:

- $\text{Fe}_2\text{ML}_2(\text{OH})_4 \cdot x\text{H}_2\text{O}$ ($M = \text{Ca, Sr, Ba; L} = \text{O}_4\text{C}_4\text{H}_2^-$; $x = 5$)
- $\text{Fe}_2\text{ML}_4 \cdot x\text{H}_2\text{O}$ ($M = \text{Sr, Ba; L} = \text{O}_4\text{C}_4\text{H}_2^-$; $x = 4.6$)
- $\text{Fe}_3\text{ML}_2(\text{OH})_7 \cdot x\text{H}_2\text{O}$ ($M = \text{Sr, Ba; L} = \text{O}_4\text{C}_4\text{H}_2^-$; $x = 3$)
- $\text{Fe}_3\text{ML}_4(\text{OH})_3 \cdot x\text{H}_2\text{O}$ ($M = \text{Ca, Sr, Ba; L} = \text{O}_4\text{C}_4\text{H}_2^-$; $x = 3.6$)

The studies have been effected in the following stages:

- establishing the conditions for obtaining and characterizing the combinations with alkaline-earth elements and iron formed with maleat ions;
- testing of the separation features of the formed combinations.

The synthesis of the studied combinations was achieved in different conditions regarding: molar ratio of components, nature of present anion, temperature and the pH of reaction medium. The composition of compounds was determined by the analysis of atomic absorption spectrophotometry and a carbon analysis.

In order to characterize these compounds, we have recorded vibration, electronic and Mössbauer spectra, thermic analysis and measurements of molecular electric conductivity.

VIBRATION SPECTRA

The vibration spectra in infrared have been recorded with a Karl Zeiss UR 10 Type spectrophotometer using the KBr pelleting technique.

Out of the analysis of the vibration spectra of the above mentioned compounds specific bands have been determined shifted in comparison to the free ligand bands (see Table I and Fig. 1) as follows:

- The band at 1210 cm^{-1} from free ligand spectrum assigned to symmetric stretching of OCO group ($\nu_{\text{sym OCO}}$) is recovered shifted in the studied combinations spectra in the range $1290 + 1550 \text{ cm}^{-1}$ obtaining information of the mode of coordination of the maleat anion.

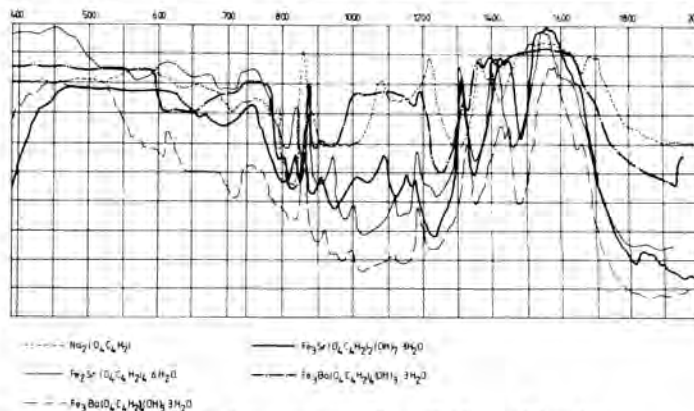


Fig. 1. Vibration spectra of studied combinations.

- The intense frequencies at 1520 cm^{-1} , 1560 cm^{-1} , 1560 cm^{-1} from free ligand spectrum assigned to asymmetric stretching frequencies of OCO group ($\nu_{\text{asym OCO}}$) are recovered shifted in the range $1530-1605 \text{ cm}^{-1}$ of studied combinations spectra.

On the basis of the obtained data, taking into account the criterium ($\nu_{\text{asym OCO}} - \nu_{\text{sym OCO}}$) and a greater value of the $\nu_{\text{sym OCO}}$ group (3) it has been deduced that the ligands worked as chelating agent and/or as bridging ligands. Thus, there have resulted the most probable formulae as presented on the following page.

ELECTRONIC SPECTRA

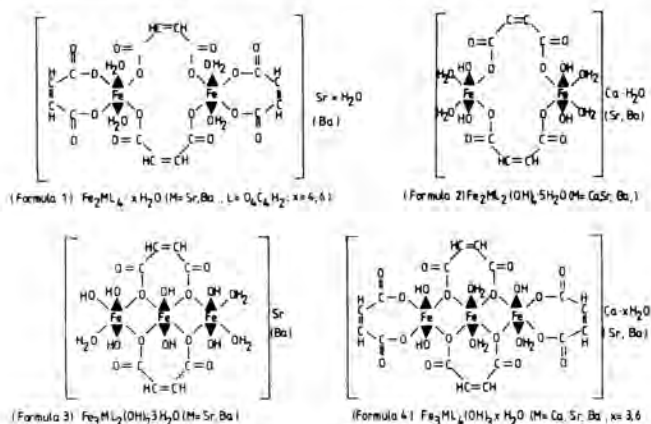
The electronic spectra have been recorded at room temperature by means of a Carl Zeiss Jena YSV-28 Type spectrophotometer, by the reflexing technique with MgO reference.

On the basis of the Tanabe-Sugano diagram it has resulted for the case of ion Fe(III) in the crystalline field of octahedral symmetry that all electronic transition are forbidden by the selection of spin rule. However the presence in the recorded spectra comes out of the studied combinations of some bands more intensively that would have been expected by the application of that selection rule.

In the range of higher frequencies at the limit of detection of the apparatus (380 nm) it has been observed a wide band

TABLE I
Assignment of Frequencies From the Studied Combinations Vibration Spectra

Vibration Mode/ Compound	$\nu_{\text{sym OCO}}$	$\nu_{\text{asym OCO}}$	$\Delta = \nu_{\text{asym OCO}} - \nu_{\text{asym oco}}$
$\text{Na}(\text{O}_4\text{C}_4\text{H}_2)^{-2}$	1210	1520;1560;1585	310;350;375
$\text{Fe}_3\text{Ca}(\text{O}_4\text{C}_4\text{H}_2)_4(\text{OH})_3 \cdot 6\text{H}_2\text{O}$	1300	1555;1580	255;280
$\text{Fe}_2\text{Ca}(\text{O}_4\text{C}_4\text{H}_2)_2(\text{OH})_4 \cdot 5\text{H}_2\text{O}$	1315	1530;1570	215;255
$\text{Fe}_2\text{Sr}(\text{O}_4\text{C}_4\text{H}_2)_4 \cdot 6\text{H}_2\text{O}$	1310	1550;1565	240;255
$\text{Fe}_3\text{Sr}(\text{O}_4\text{C}_4\text{H}_2)_2(\text{OH})_4 \cdot 5\text{H}_2\text{O}$	1350	1530;1555;1580	180;205;230
$\text{Fe}_3\text{Sr}(\text{O}_4\text{C}_4\text{H}_2)_4(\text{OH})_3 \cdot 3\text{H}_2\text{O}$	1290	1570;1595	280;305
$\text{Fe}_3\text{Sr}(\text{O}_4\text{C}_4\text{H}_2)_2(\text{OH})_7 \cdot 3\text{H}_2\text{O}$	1310	1560;1590	250;280
$\text{Fe}_2\text{Ba}(\text{O}_4\text{C}_4\text{H}_2)_4 \cdot 4\text{H}_2\text{O}$	1315	1522;1543;1573;1598	207;228;258;283
$\text{Fe}_3\text{Ba}(\text{O}_4\text{C}_4\text{H}_2)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$	1322	1540;1590;1630	218;268;308
$\text{Fe}_3\text{Ba}(\text{O}_4\text{C}_4\text{H}_2)_4(\text{OH})_3 \cdot 3\text{H}_2\text{O}$	1320	1530;1558;1575;1595	210;238;202;275
$\text{Fe}_3\text{Ba}(\text{O}_4\text{C}_4\text{H}_2)_2(\text{OH})_7 \cdot 3\text{H}_2\text{O}$	1318	1520;1540;1605	202;222;287



Formula 1-4.

on the spectra of these combinations assigned to a charge transfer $L \rightarrow Fe(III)$ (4).

In the spectra of these combinations it has been also determined bands of reduced intensity assigned to a mechanism of a superexchange between iron ions from bis and trisnuclear units ($Fe(III) \rightarrow Fe(III)$).

Figure 2 some electronic spectra of these combinations have been presented.

MÖSSBAUER SPECTRA

Mössbauer spectra of some representative samples from the series of studied combinations have been recorded using an ELRON type Mössbauer spectrometer in constant acceleration mode. The calibration was made by using the standard absorbers for the selected velocity of 4.5mm/s, with Co-57 Mössbauer source. In order to establish the iron valence in the studied combinations and for ascertaining nuclear electronic neighborhood, Mössbauer spectra of some combinations have been recorded as they are presented in Fig. 3.

By the computer processing of Mössbauer spectra of outstanding combinations the following parameters have been calculated: isomer shift (I.S.), quadrupolar splitting (ΔE_Q) and relative area (5).

From the analysis of the obtained values of these parameters, it results that in the studied combinations the iron ion is

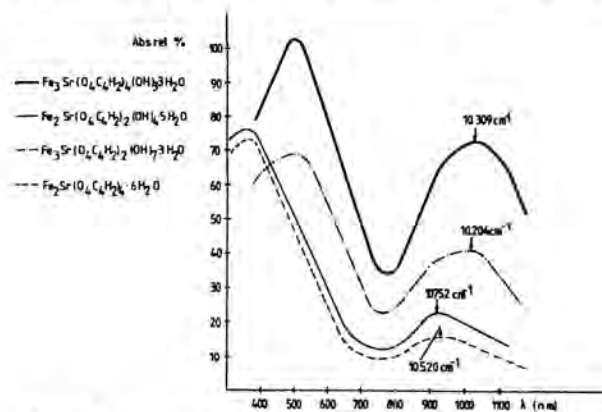


Fig. 2. Electronic spectra of studied combinations.

present as $Fe(III)$ in an octahedral symmetry. The best computer fit was obtained by assuming the presence of two iron species in the samples (denoted a) and b)).

This fact may be explained by the existence of some bisnuclear and trisnuclear units in the system.

We can notice (see Table II) that ΔE_Q values of a) species are greater than those of corresponding b) species.

One can conclude that in the studied combinations the iron ion with the alkaline-earth ion neighborhood is found in a strongly disturbed octahedral environment.

THERMIC ANALYSES

Derivatograms of the studied combinations have been recorded by using a derivatograph type 102-568 from Hungary. The quantities of the analyzed substances have been chosen taking into account both the molecular weights of these substances and the apparatus sensitivity. For each case two factors which strongly affect both thermic decomposition and the shape of the decomposition curves have been chosen. Experimental conditions have been fixed up in conformity with ICTA recommendations. In Table II some thermic results have been presented.

MOLECULAR ELECTRIC CONDUCTIBILITY

Molecular electric conductivity measurements in DMSO have presented values in the range 60+90

TABLE II
Mössbauer Parametra of Some Studied Combinations

Mössbauer Parameter/Combinations	Isomer Shift (mm/s) \pm (0.01)	Quadrupolar splitting (mm/s) $(\pm 0.05)\Delta E_Q$	Relative Area ($\pm 1\%$)
$Fe_2CaL_2(OH)_4 \cdot 5H_2O$ a)	0.38	0.89	44
b)	0.37	0.58	56
$Fe_3CaL_2(OH)_3 \cdot 6H_2O$ a)	0.33	0.65	35
b)	0.35	0.39	65
$Fe_2SrL_2(OH)_4 \cdot 5H_2O$ a)	0.37	0.81	48
b)	0.35	0.56	52
$Fe_2BaL_2(OH)_4 \cdot 5H_2O$ a)	0.36	0.87	47
b)	0.37	0.51	53

$L = O_4C_4H_2^{2-}$

a) = $Fe(III)$ in A-E neighborhood

b) = $Fe(III)$ without A-E neighborhood

TABLE III
Results of Thermic Analyses

Parameter/Combination	Σ oxyde (mg) exp/theor	Σ liguand (mg) exp/theor	Σ OH (mg) exp/theor	Σ H ₂ O (mg) exp/theor
Fe ₂ CaL ₂ (OH) ₄ ·5H ₂ O	112.00/109.32	142.62/135.62	40.00/40.45	48.00/53.56
Fe ₃ CaL ₄ (OH) ₃ ·6H ₂ O	110.00/104.88	156.75/159.66	16.00/17.86	38.00/37.81
Fe ₂ SrL ₂ ·6H ₂ O	94.00/92.45	156.85/160.10	-	40.00/37.92
Fe ₂ SrL ₂ (OH) ₄ ·5H ₂ O	148.00/145.75	125.21/126.21	36.00/37.64	50.00/49.85
Fe ₃ SrL ₄ (OH) ₃ ·3H ₂ O	110.00/104.86	134.21/139.34	16.00/15.58	18.00/16.50
Fe ₃ SrL ₂ (OH) ₇ ·3H ₂ O	164.00/162.12	106.06/107.72	54.00/56.22	28.00/25.51
Fe ₂ BaL ₄ ·4H ₂ O	114.00/112.79	165.31/164.32	-	24.00/25.95
Fe ₂ BaL ₂ (OH) ₃ ·5H ₂ O	136.00/135.55	102.81/98.74	28.00/29.45	36.00/38.98
Fe ₃ BaL ₄ (OH) ₃ ·3H ₂ O	144.00/141.56	162.26/164.31	18.00/18.36	20.00/19.46
Fe ₃ BaL ₂ (OH) ₇ ·3H ₂ O	206.00/208.16	124.12/120.80	62.00/63.06	28.00/28.61

L = O₄C₄H₂₂.

CONCLUSIONS

In order to characterize the compounds resulted from the selective separation of the alkaline - earth radionuclides in presence of iron with maleic acid from radioactive wastes the vibration, electronic and Mössbauer spectra, thermic analyses and molecular electric conductivity measurements have been recorded.

On the basis of the obtained results from vibration spectra, taking into account the Δ parameter criterium, it was deduced that maleat ions have worked as chelating agents and/or as bridging ligands and the compounds are, in fact, complex combinations.

Electronic spectra have shown the presence of the bounds assigned to the L→Fe transitions and to the super-exchanges between iron ions Fe(III) - Fe(III).

From Mössbauer spectra it was deduced that iron as Fe³⁺ ions have an octahedral symmetry and are in a perturbed field due to the presence of the alkaline - earth ions adjoining to the formed bis and tris nuclear units of the complex combinations.

The thermic analyses and the molecular electric conductivity measurements have confirmed that the assigned formulae are the most probable.

At the same time as were tested, the crystalline features assure the good separation property of these complex combinations.

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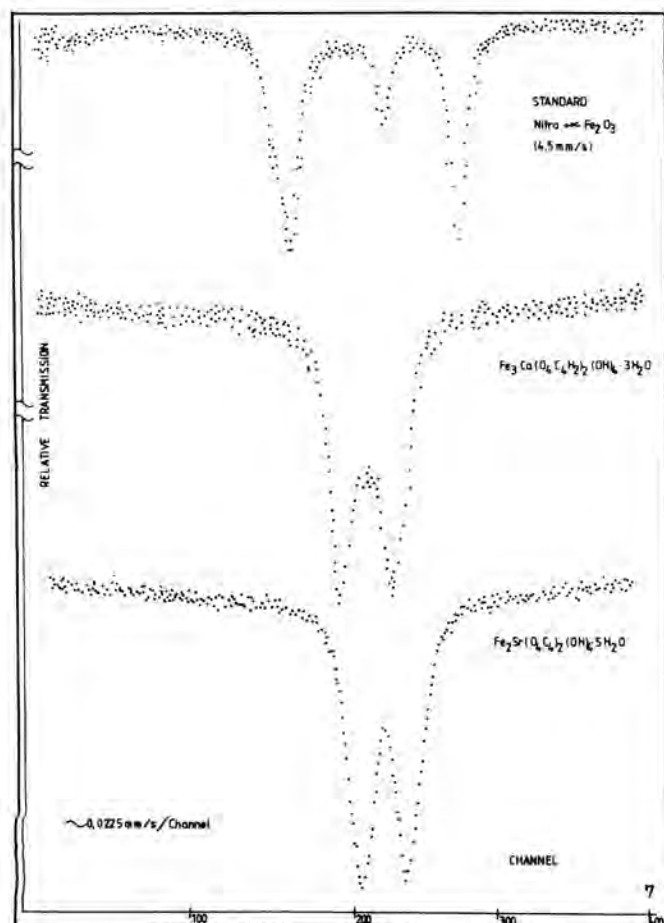


Fig. 3. Mössbauer spectra.

$\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ confirming the nature of electrolytes 1:1 of these combinations and previous assignments referring to structure of these combinations (7).

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