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CONTENTS / CONTEÚDO

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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COSTIN D. NENITZESCU (1902 -1970)
100 th ANNIVERSARY OF HIS BIRTH

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ABSTRACT

Costin D. Nenitzescu was born in Bucharest in 1902 and passed away in Busteni, Romania in 1970. He obtained primary and secondary education in Romania and began university studies at the Swiss Federal Polytechnic Institute in Zürich. Later, he moved to the Technische Hochschule in München (Munich) where he worked with Hans Fischer and obtained the Doctor of Engineering Degree in 1925. During the same year he returned to Romania where he spent the rest of his life working, first at the University of Bucharest (1925-1935) and then at the Polytechnic Institute (1935-1970). Costin D. Nenitzescu is considered the founder of the School of Modern Organic Chemistry in Romania. He has published approximately 300 (three hundred) scientific articles, twenty books and treatises dealing mainly with organic chemistry and authored about forty patents.Several organic reactions bear his name. Costin D. Nenitzescu's work includes the chemistry of indole and pyrrole, Romanian petroleum, nitroderivatives, reactions catalyzed by aluminum chloride, pyrylium salts, aromatic alkylation, cyclobutadiene, cyclooctatetraene, annulenes, carbonium ion reactions, eliminations, oxidations and additions.

KEYWORDS History of Chemistry. Aliphatic and Aromatic Alkylation. Nenitzescu Indole Synthesis. Naphthenic Acids. Mechanistic Organic Chemistry.

RESUMO

Costin D. Nenitzescu nasceu em Bucareste em 1902 e faleceu em Busteni, Romênia em 1970. Fez os estudos primários e secundários na Romênia e começou os estudos universitários na Escola Politécnica Federal de Zurique. Mais tarde transferiu-se para a Technische Hochschule München (Munique) onde trabalhou com Hans Fischer o obteve o grau de Doutor em Engenharia em 1925. No mesmo ano voltou para Romênia, onde passou o resto de sua vida trabalhando, primeiramente na Universidade de Bucareste (1925-35) e depois na Escola Politécnica de Bucareste (1935-1970). Costin D. Nenitzescu é considerado o fundador da Escola Moderna de Química Orgânica na Romênia. Publicou aproximadamente 300 (trezentos) artigos científicos, aproximadamente vinte livros e tratados, principalmente sobre química orgânica e foi o inventor de aproximadamente quarenta patentes. Várias reações orgânicas levam seu nome. O trabalho de Costin D. Nenitzescu inclui a química do indol e pirol, petróleo romeno, nitroderivados, reações catalizadas por cloreto de alumínio, sais de pirílio, alquilação aromática, ciclobutadieno, ciclooctatetraeno, anulenos, reações do íon carbônio, eliminações, oxidações e adições.

Costin D. Nenitescu (Nenitzescu in languages other than Romanian) was born in Bucharest on July 15, 1902 and passed away in Busteni, Romania on July 28, 1970.

He was a member of a prominent Romanian family from the Galati Region. His uncle , Ioan Nenitescu (1854-1901) studied at the University of Iasi and in Germany, was mayor of Tulcea and a well known poet and patriot. His father, Dimitrie Nenitescu (1865-1930) followed a military career, later studied law at the University of Louvain, Belgium and published an important work entitled *"The Danube and International Law"*. As Minister of Industry and Commerce he was fundamental in the promulgation of the first law dealing with workers insurance, benefits, social security and regulation of professions in Romanis.

Costin D. Nenitzescu received a very good primary and secondary education and graduated from the *Gh. Lazar Lyceum*, the most prestigious secondary school in Bucharest. In the fall of 1920 he travelled to Switzerland and enrolled as a student at the Swiss Federal Polytechnic Institute in Zürich. Among his teachers in Zürich were Peter Debye *(Nobel Prize 1936)* and Hermann Staudinger *(Nobel Prize 1953)*. In 1922, Costin D. Nenitzescu moved to Munich to study with Hans Fischer, a chemist, physician and biochemist at the Technische Hochschule. He was fascinated by Hans Fischer's work with blood, bile and leaf pigments. Munich, at the time could be considered one of the world's centers for organic chemistry with Richard Willstätter (1872-1942;*Nobel Prize 1915*), Heinrich Wieland (1877-1957; *Nobel Prize 1927*) and Hans Fischer (1881-1945; *Nobel Prize 1930*).

He obtained the Doctor of Engineering Degree in 1925 and his thesis dealt with the synthesis of degradation products of blood pigments. During the same year he returned to Romania, where he spent the rest of his life working, first at the University of Bucharest (1925-1935) and then at the Polytechnic Institute of Bucharest (1935-1970).

Costin D. Nenitzescu is considered the Founder of the School of Modern Organic Chemistry in Romania. He has published approximately three hundred (300) scientific articles, twenty books or treatises dealing mainly with organic chemistry and authored about forty patents.

His research work includes indole and pyrrole derivatives, nitroderivatives, Romanian petroleum, reactions catalyzed by aluminum chloride, synthesis and reactions of pyrylium salts, mechanism of aromatic alkylation, cyclobutadiene, cyclooctatetraene, annulenes, carbonium ion reactions, eliminations, oxidations and additions. Several organic reactions bear his name.

Costin D. Nenitzescu believed that applied research was an important part of the work of a scientist. His more than forty patents include industrial production of thiodiglycol, benzene, toluene, xylene, organic compounds of arsenic, polymerization of ethylene, chlorination of cyclohexane and

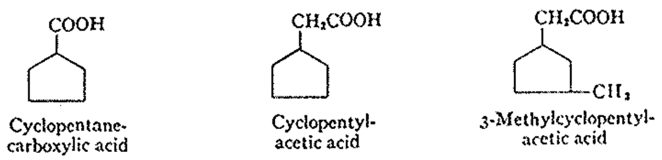
C D Nenitescu

COSTIN D. NENITESCU (1902 – 1970)

benzene, production of chloroprene, terephthalate and bicycloheptadiene. He worked with nerve gases and was instrumental in the industrial production of many drugs in Romania during the difficult years following World War II.

He held many positions in various agencies of the Ministry of Petroleum and Mines and the Ministry of Chemistry that dealt with industrial and technological development in Romania including INCT (Institutul National de Cercetari Tehnologice - 1947), ICEPS (Intreprinderile pentru Cercetari si Productie Semiindustriala - 1948), ICECHIM (Institutul de Cercetari Chimice - 1950) and IPROCHIM (Institutul de Proiectari Chimice - 1950).

Costin D. Nenitzescu studied the chemistry of coal from the Petrosani Region, but a more important contribution was the discovery and isolation of several naphthenic acids, tetramethylbenzene and dimethylnaphthalenes in Romaniam petroleum. Naphthenic acids have many technical uses, including mildew proofing of sandbags, rope for use at sea, wood, cotton, jute and hemp, compounding of special lubricants for high pressure and NAPALM, employed widely for incendiary bombs.



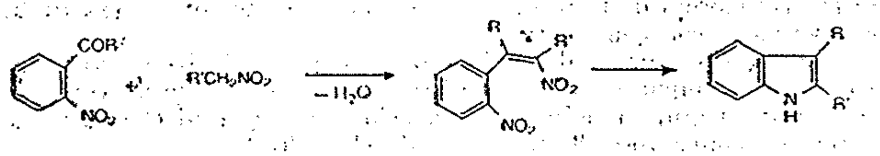
Cyclopentanecarboxylic acid

Cyclopentylacetic acid

3-Methylcyclopentylacetic acid

SOME OF THE NAPHTHENIC ACIDS DISCOVERED BY COSTIN D. NENITZESCU IN ROMANIAN PETROLEUM.

Several organic reactions were named after Costin D. Nenitzescu. In 1925 he published in *Berichte der Deutschen Chemischen Gessellschaft* a new reaction for the synthesis of indole (Nenitzescu Indole Synthesis).

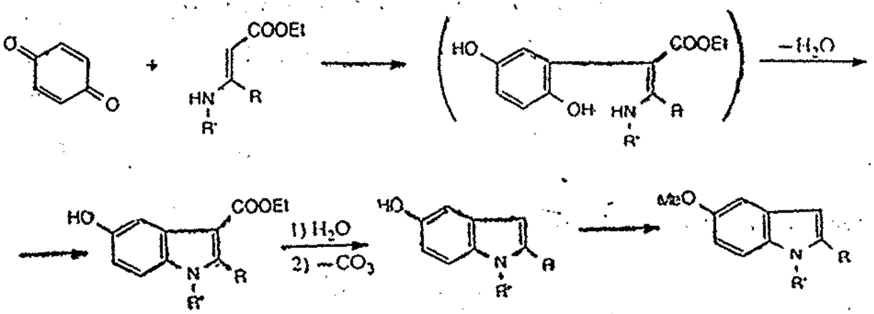


NENITZESCU INDOLE SYNTHESIS.

AUGUST WILHELM VON HOFMANN GOLD MEDAL AWARDED BY THE GERMAN CHEMICAL SOCIETY.

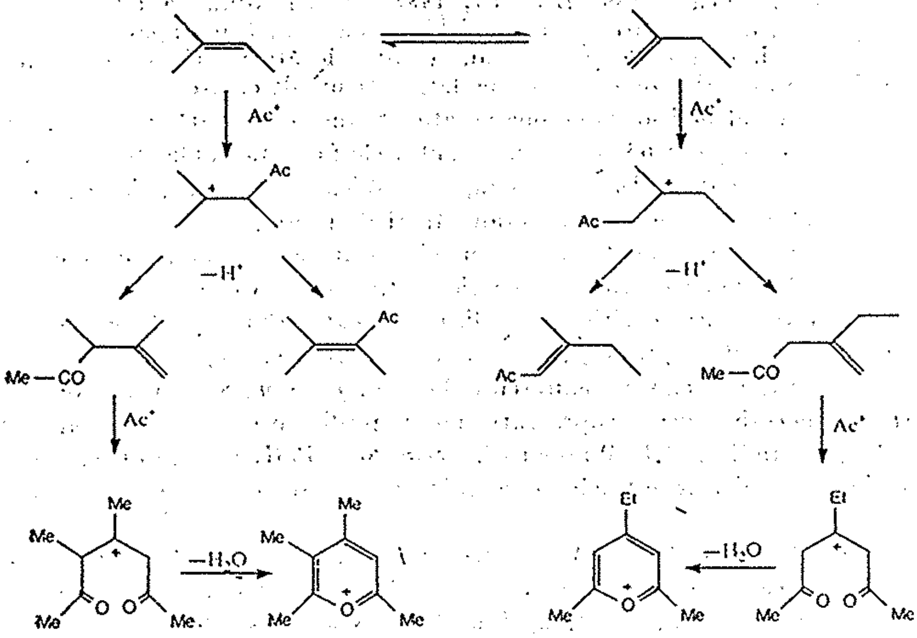
ROMANIAN POSTAGE STAMPS HONORING C.D. NENITESCU

Four years later he developed an improved synthesis for 5-hydroxyindole (*Cf. Bull. Soc. Chim. Rom.,11,37, 1929*). Both reactions are still widely used today to obtain biologically active compounds. The second reaction is more important and is used to prepare tryptamine, serotonin and indoleacetic acid.



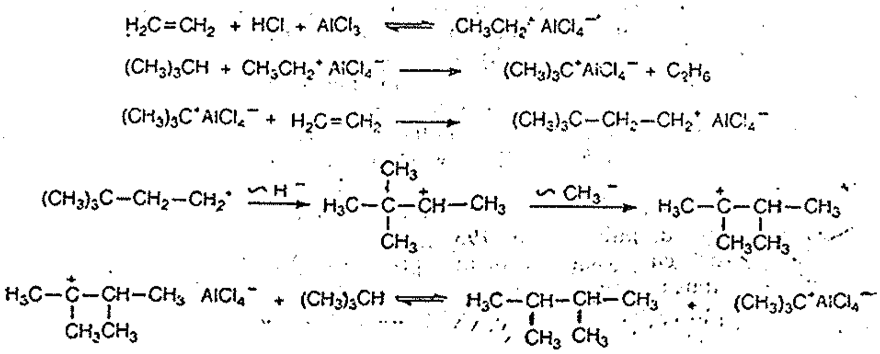
NENITZESCU 5-HYDROXYINDOLE SYNTHESIS.

The work of C.D. Nenitzescu and A.T. Balaban on the synthesis of pyrylium salts was published simultaneously with P.F.G. Praill of Queen Elizabeth College, London (*Cf. J. Chem. Soc.,1961,3553-3573*) and the reaction is generally known as the Balaban-Nenitzescu-Praill Pyrylium Salts Synthesis.



BALABAN-NENITZESCU-PRAILL PYRYLIUM SALTS SYNTHESIS.

Hydride Transfer Reactions during Friedel-Crafts Catalysis were studied by Nenitzescu and his collaborators during War War II and were first described in 1945 (*Cf. Acad. Roum. Bull. Section Scientifique, XXVII (10),1, 1945*). Today this reaction is known as the Bartlett-Nenitzescu-Schmerling Migration.



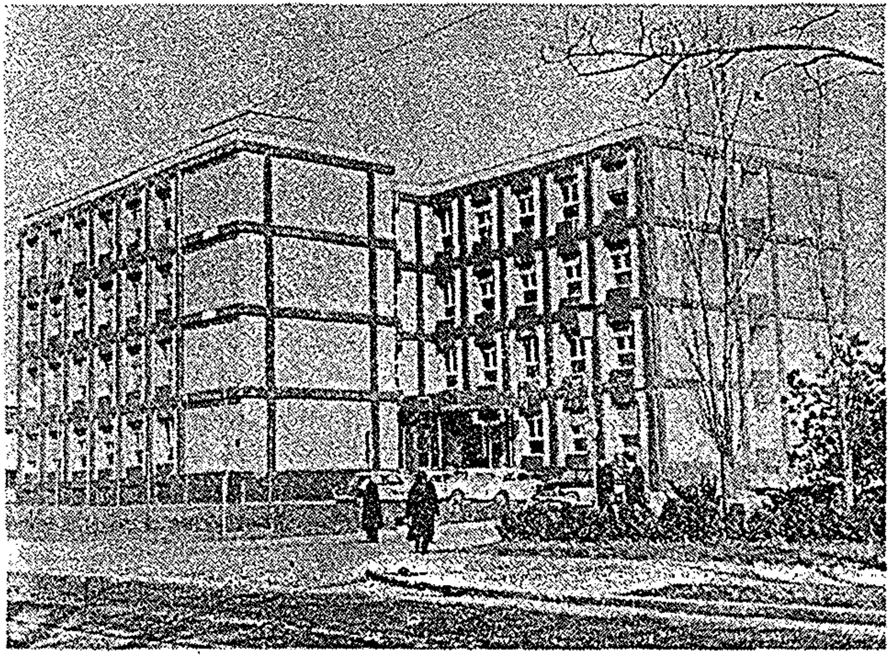
BARTLETT-NENITZESCU-SCHMERLING MIGRATION.

Costin D. Nenitzescu has published more than twenty books at all levels, dealing mostly with organic chemistry, but including topics such as nerve gases, technical dictionaries in many languages and chemical engineering. His book on advanced organic chemistry was translated to many languages.

He was a member of many scientific societies and received many prizes and awards. Among them we cite the *August Wilhelm vonHofmann Gold Medal*, the highest award of the German Chemical Society. He was distinguished by Scientific Academies in Romania, Germany, Russia, Poland, Czechoslovakia and Hungary.

We met Professor Nenitzescu and his wife Ecaterina Cioranescu-Nenitzescu in Bucharest in 1965. At the time we visited him at his home on Strada Scoalei. As a young, aspiring chemist we presented him with a copy of our Master's Thesis on Liquid Scintillators, work done at the University of New Mexico and the Los Alamos Scientific Laboratory under the supervision of G.H. Daub and F. Newton Hayes. Costin D. Nenitzescu was a kind, warm hearted person. He had a noble bearing and implied respect. We remember a large desk in his study full of books on organic chemistry. We recognized most of the treatises and manuals that were in use in the United States.

At the time, one of Costin D. Nenitzescu's major preoccupations was the construction of the new Research Center of Organic Chemistry of the Romanian Academy. It was eventually inaugurated in 1968 and it still functions today.



NEW BUILDING OF THE CENTER OF ORGANIC CHEMISTRY IN BUCHAREST INAUGURATED IN 1968.

One of his best friends was Horia Hulubei, a Romanian physicist and co-discoverer of francium. They served together on many scientific commisions and both enjoyed mountain climbing in the Carpathians around Sinaia and Busteni.

Costin D. Nenitzescu firmly believed in the importance of resaerch. He was convinced that the person that transmits science must be a researcher, a creator of science, or at least should try to be one. Some of his former students are today renowned scientists working in Romania, United States, Germany, Moldavia, Israel and other countries.

He was preoccupied with both pure and applied research. In fact, his last address before the Academy of Science of the Socialist Republic of Romania in July 1970, a few weeks before his death, was entitled *"Meditations on the Relation between Science and Technology"*. Costin D. Nenitzescu thought that both pure and applied research were important. His thinking was based on the analysis of science and technology from antiquity to the present time and on the role that scientists played throughout history. According to him, activity in science should never be directed or controlled. In fact, liberty or the freedom to search the truth is the most important aspect of science.

Some representative publications of Costin D. Nenitzescu (after ref. 1) are listed on the following pages.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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NATURAL PYRRHOTITE DISSOLUTION IN AQUEOUS SOLUTION

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ABSTRACT

The effects of some metal (II) ions on the natural pyrrhotite dissolution in hydrochloric acid solutions were studied. Our results suggest that the rate of pyrrhotite dissolution increases in the presence of Sn^{2+} *ion. Ions like* Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} *do not appear to have any effect on pyrrhotite dissolution in hydrochloric acid solutions. The magnitude of the activation energy (23.31 kJ* mol^{-1}*) is in agreement with a mechanism controlled by a diffusion process.*

RESUMO

Foram estudados os efeitos de vários íons metálicos (II) sobre a dissolução do mineral pirrohotita em soluções aquosas de ácido clorídrico. Os resultados experimentais indicam que a presença de íons de Sn^{2+} aumenta a dissolução deste mineral de ferro. Po outro lado, íons como Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} não tem nenhum efeito sobre a dissolução. A magnitude da energia de ativação (23.31 kJ mol^{-1}) está de acordo com um mecanismo controlado por processos de difusão.

KEYWORDS: pyrrhotite, nonoxidative dissolution, activation energy, iron minerals

INTRODUCTION

Pyrrhotite is an nonstoichiometric[1] compound, with the general formula $Fe_{1-x}S$, based on Fe(II) and S^{2-} ions. Values of x vary within the range $0<x<0.125$. The forms of the hexagonal pyrrhotite most commonly found in natural samples arise from vacancy ordering with numerous hexagonal and orthorhombic superstructures across Fe_9S_{10}, $Fe_{10}S_{11}$, - - - (or $Fe_{1-x}S$).

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There have been numerous studies on pyrrhotite dissolution in the literature[2-8]. Literature values for activation energy of pyrrhotite dissolution in acidic condition vary widely. On the basis of iron release, Janzen et al.[5] reported that the activation energies for pyrrhotite oxidation by oxygen and ferric iron ranged from 47 to 63 kJ mol^{-1}. Ingrham et al.[8] reported 29 kJ ·mol^{-1} for dissolution in oxygen free condition at a pH less than one. This value is in the energy range for diffusion control. In addition to temperature, the crystal structure, trace metal content and specific surface area have also been reported to be controlling factors in the reaction kinetics of pyrrhotite dissolution.[9] Pyrrhotite dissolution mechanism and its dependence on aqueous solution composition is of fundamental importance in understanding mineral processing and the treatment of resulting waste mineral. Recovery of copper, nickel, gold and platinum often involves the processing of an iron sulfide rich matrix. Waste from the processing of sulfide ores are typically rich in pyrrhotite and other iron sulfides. These materials are a major contributor to acidic run off, commonly at pH 3 or lower.

The objective of this study is to compare the dissolution behavior of pyrrhotite as function of temperature and dissolved metal concentration. From these experiments we expect to improve the understanding of the mechanism of pyrrhotite dissolution in acidic solutions.

EXPERIMENTAL

Reagent grade tin (II) chloride ($SnCl_2 \cdot 2H_2O$), cobalt (II) chloride ($CoCl_2 \cdot 6H_2O$), nickel (II) chloride ($NiCl_2 \cdot 6H_2O$), cupric chloride ($CuCl_2 \cdot 2H_2O$) and zinc chloride ($ZnCl_2$) were obtained from Aldrich. The stock solutions of metal (II) chloride with a concentration of 0.1 mol L^{-1} were prepared by dissolving appropriate metal chloride in water containing 0.1 mol L^{-1} HCl. These solutions were diluted further with 0.1 mol L^{-1} HCl solution to obtain the required concentrations. The deoxygenated solutions were prepared by bubbling nitrogen for at least 2 hours.

The pyrrhotite was crushed and the particles ranging in size from 50 to 80 μm were recovered by sieving. This size fraction was used for the experiments.

Dissolution experiments were performed in a reaction vessel immersed in a controlled temperature bath. The vessel consisted of glass to minimize adsorption of pyrrhotite particles on the walls. The cap of the reaction vessel contained borings for sampling and for the stirrer. An agitation rate of 600 revolutions per minute (rpm) was chosen as a standard condition for the experiments. The experiments used 0.25 g pyrrhotite in 250 mL 0.1 mol L^{-1} HCl solutions with different metal (II) clorides.

The dissolution rate was monitored by determining the amount of total iron in solution. Periodically, 10 mL samples were extracted via a filter unit, to remove fine particles. The concentration of total Fe in solution was determined by Atomic Absorption Spectroscopy (AAS) with a Perkin Elmer AAS 3100 spectrometer. Reaction rates were measured experimentally by determining the slopes of concentration-time curves.

Identification of pyrrhotite by X-ray powder diffraction analysis was performed using an Inel Compteur Courbe X-ray diffractometer, with Co X-rays generated at 40 kV and 25 mA. The related X-ray diffractogram is shown in Figure 1; peak positions are consistent with reported ASTM data of hexagonal pyrrhotite. This sample composition was characterized by electron microprobe beam techniques (accelerating voltage of 25 kV and beam current 20.130 nA). The results gave a composition of $Fe_{1-0.11}S$. Trace elements content (Co, Zn and As) in the pyrrhotite matrix was below 0.32 %.

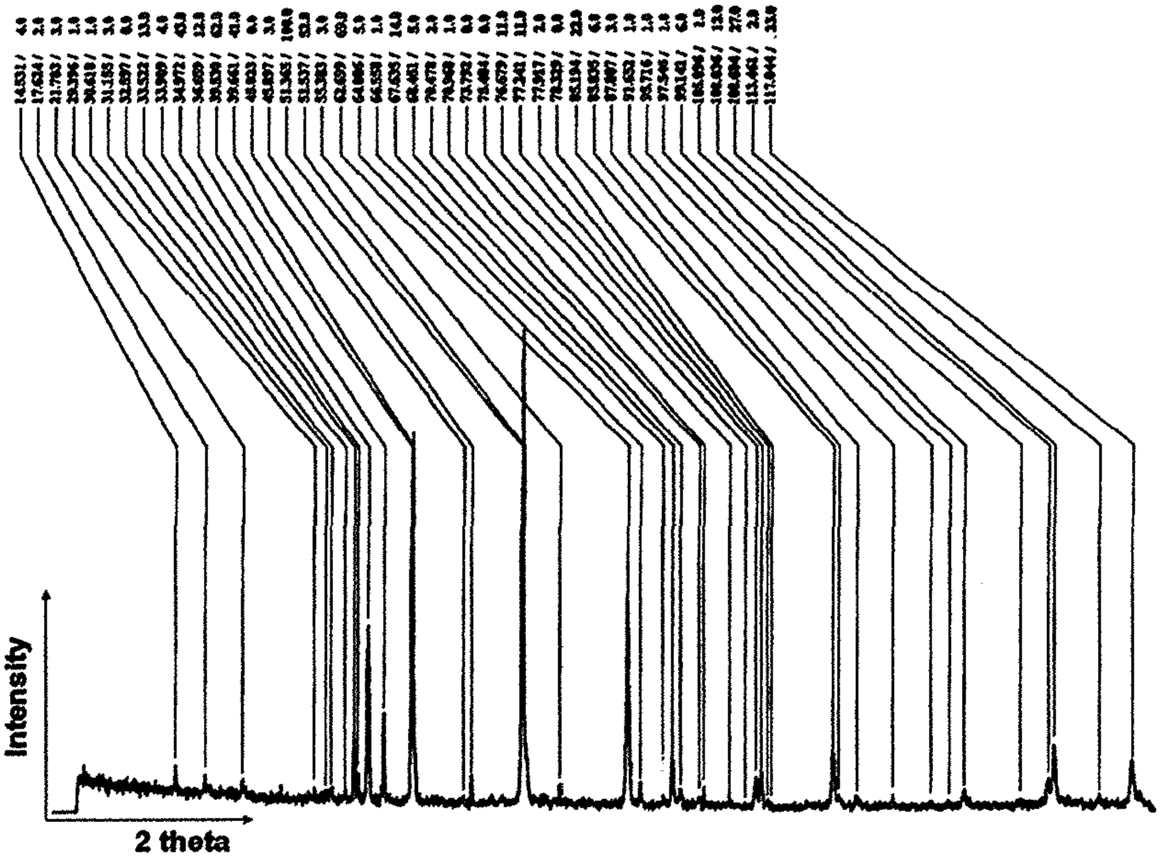

Figure 1. X-ray diffractogram of the pyrrhotite sample.

RESULTS AND DISCUSSION

Typical results of the dissolution experiments are shown in Figure 2. These results exhibit high iron fluxes during early times, with a decline to more consistent rates over short periods of time. The time over which rates were calculated for each experiment corresponds to intervals containing relatively consistent rate values. The initially high iron concentrations appear to be the result of preexperimental oxidation of the pyrrhotite surfaces that is difficult, if not impossible to avoid. This is the reason that the rate data was ignored prior to about 600 s into experimental runs.

The pyrrhotite dissolution rate in acidic conditions and in presence of Sn^{2+} ions is affected by changes in temperature (Table 1). A plot of the - ln Rate against 1/T yields a straight line in temperature range 30-65°C and an activation energy of 23.31 $kJ \cdot mol^{-1}$. This value of activation energy point to diffusion controlled mechanism. The activation energy is much closed from value obtained by Ingrahmm et al.[7] than others values from literature.

Table 1. Data for rate dependence on temperature for pyrrhotite dissolution in the presence of $SnCl_2$.

$[Sn^{2}]$ (mol L^{-1})	T (°C)	d* (μm)	Rate (mol s^{-1} g^{-1})
5×10^{-3}	65	50-80	1.733×10^{-7}
5×10^{-3}	50	50-80	1.218×10^{-7}
5×10^{-3}	40	50-80	1.017×10^{-7}
5×10^{-3}	30	50-80	6.402×10^{-8}
0	65	50-80	1.180×10^{-8}

*d = diameter of pyrrhotite particles.

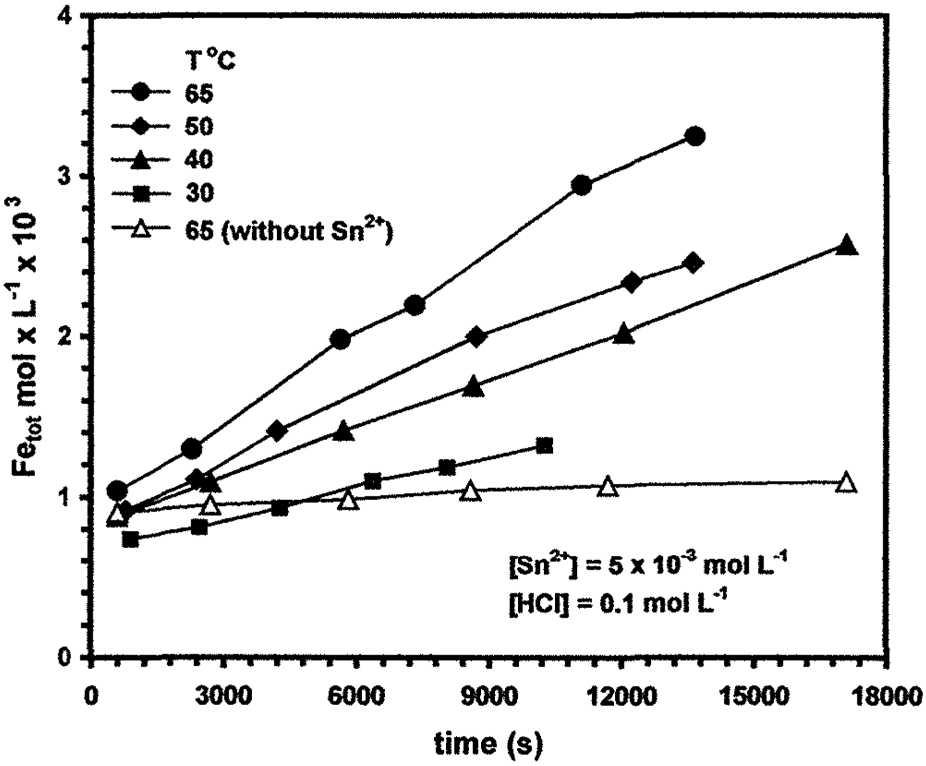

Figure 2. Effect of temperature on pyrrhotite dissolution in hydrochloric acid solution.

The addition of $SnCl_2$ with initial concentrations ranging from 2×10^{-4} to 5×10^{-3} mol L^{-1} causes an asympthotical increase of the pyrrhotite dissolution rate by a factor ~ 8 (Figure 3).

The release rates of iron indicate that the presence of the Sn^{2+} ions influences the dissolution of natural pyrrhotite. The results show that the Sn^{2+} is indeed able to increase the dissolution rate of pyrrhotite. The conclusion seems therefore obvious that the observed increase of dissolution rate of pyrrhotite in presence of Sn^{2+} is related to the reduction of ferric iron by Sn^{2+}.

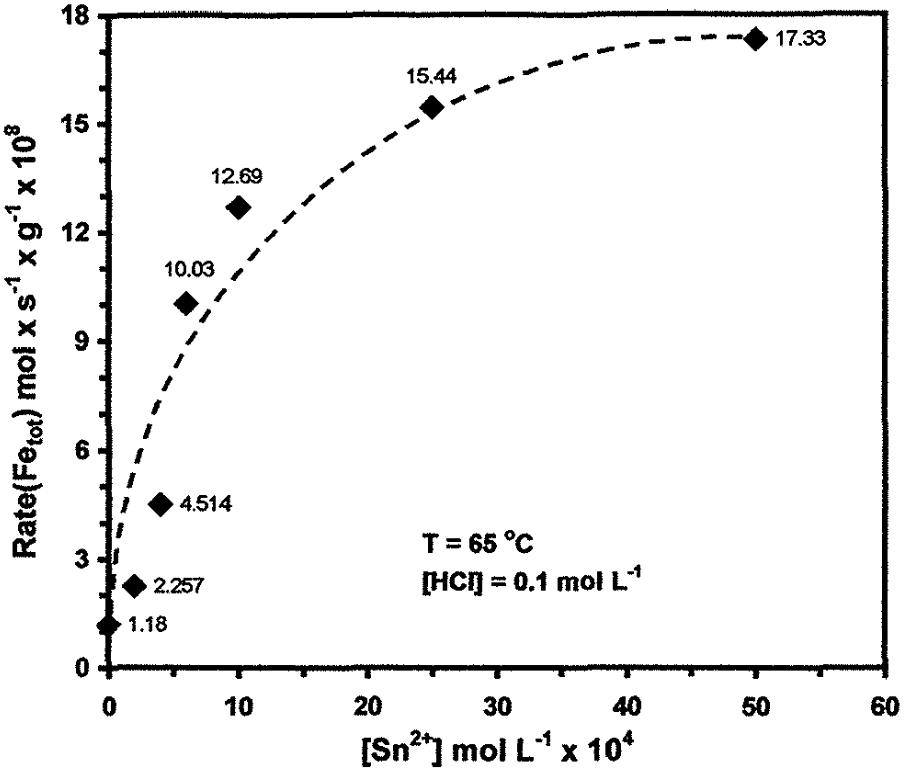

Figure 3. Rate for the dissolution of natural pyrrhotite in acidic solutions at various initial concentration of Sn^{2+}.

In order to understand this pattern one has to recapitulate the mechanism for dissolution of pyrrhotite proposed in the literature. Unlike pyrite, pyrrhotite can dissolve both oxidatively and nonoxidatively. Any oxidative dissolution which occurs increases the iron deficiency of the pyrrhotite structure and thus decreases the probability of H_2S production and rapid release of Fe.[4]

It is generally accepted that ferric iron has an oxidant effect on pyrrhotite. Fe^{3+} may be directly released into solution from the pyrrhotite surface during the first stage of dissolution. Pratt et al.[10] and Mycroft et al.[11] have shown that when exposed to air, pyrrhotite surface oxidized rapidly to form a superficial layer of iron (III) oxyhydroxides, and later iron sulfate.

Partial oxidation of pyrrhotite by ferric iron may produce either elemental sulfur or increasingly sulfur-rich pyrrhotite:

$$Fe_{1-x}S + 2yFe^{3+} \rightarrow 3yFe^{2+} + Fe_{1-x-y}S \qquad (1)$$

Nonoxidative dissolution can occur in acidic conditions whenever there is exposed S^{2-} on the surface of a iron sulfide. The reaction which occurs is

$$FeS + 2H^{+} \rightarrow Fe^{2+} + H_2S \qquad (2)$$

Under these conditions the extra sulfur rich layer on the pyrrhotite is absent or is thin, and dissolution of pyrrhotite will be more rapid.

Any interference of Sn^{2+} on the pyrrhotite dissolution must be related to this model. In the presence of the Sn^{2+}, which reduce Fe^{3+}, the concentration of the iron species in solution and at the pyrrhotite surface will be altered. The reduction of the ferric iron will affect the oxidation of pyrrhotite, which is equivalent to avoid the extra sulfur rich layer formation on the pyrrhotite surface (Eq. 1). The activation energy value suggests that the rate-controlling step is a diffusive process rather than chemical reaction. The $Fe_{1-0.11}S$ can be considered like sulfur rich iron sulfide. Therefore, it is possible that in this experiment the release of Fe into solution may be influenced by the diffusion rate of iron through pyrrhotite.

Nicol and Scott[12] showed that nonstoichiometric iron-deficient sulfides dissolved spontaneously via nonoxidative dissolution once reduction to stoichiometric FeS had occurred via cathodic potential. The results shown here are in agreement with their observations.

The effect of some metals (Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}) on the pyrrhotite dissolution rate was also examined. The experiments were conducted in 0.1 mol L^{-1} HCl solutions with 5×10^{-3} mol L^{-1} metal (II) concentration at 65°C. Runs made in these solutions showed little or no effect on the pyrrhotite dissolution rates (Table 2). The addition of these metals ions to the aqueous solution will not result in a change in the iron species present in solution and on the pyrrhotite surface. Addition of Sn^{2+} ions to a pyrrhotite suspension may results in the conversion of a ferric iron to ferrous iron.

Table 2. Effect of metals on the dissolution rates of natural pyrrhotite in 0.1 mol L^{-1} HCl at 65 °C.

Metal	$[M^{2+}]$ mol L^{-1}	Rate (mol s^{-1} g^{-1})
Ni^{2+}	5×10^{-3}	2.017×10^{-8}
Co^{2+}	5×10^{-3}	1.094×10^{-8}
Cu^{2+}	5×10^{-3}	3.952×10^{-8}
Zn^{2+}	5×10^{-3}	2.108×10^{-8}

As can be seen, attempts to fit our experimental results with the general mechanism remain somewhat speculative. Since laboratory work gave quite contrasting results on the rates of the oxidation of pyrrhotite with ferric iron,[5] the proposed mechanism needs further experimental confirmation. Future studies should therefore be designed to explain the interaction between the surface states and the solution composition.

CONCLUSIONS

The results of pyrrhotite dissolution experiments presented here indicate that the presence of Sn^{2+} affects its dissolution behaviour. The dissolution rates increased in the presence of Sn^{2+} ions in solution. This implies that in presence of reducing species the rate of pyrrhotite dissolution can be enhanced. On the other hand, ions like Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} do not appear to have any effect on pyrrhotite dissolution in hydrochloric acid solutions.

The activation energy (23.31 kJ·mol^{-1}) points to a diffusion controlled mechanism.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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LIQUID-LIQUID EQUILIBRIA OF THE WATER+ETHANOL+DIMETHYL ADIPATE TERNARY SYSTEM

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ABSTRACT

Liquid-liquid equilibrium data for the ternary system water+ethanol+dimethyl adipate (dibasic ester) have been determined experimentally at 298.15±0.20, 308.15±0.20 and 318.15±0.20 K. Tie-line compositions were correlated by Othmer-Tobias method. The UNIFAC method was used to predict the phase equilibrium in the system using the interaction parameters determined from experimental data between the CH_3, CH_2, OH, CH_3COO *and* H_2O *groups. Distribution coefficients and separation factors were evaluated for the immiscibility region.*

KEYWORDS: ethanol, dimethyl adipate, liquid-liquid extraction, ternary systems

RESUMO

Dados experimentais de equilíbrio foram determinados experimentalmente para o sistema ternário água-etanol -dimetiladipato a 298.15 , 308.15 e 318.15 K . As composições das linhas de união foram correladas com o método de Othmer-Tobias. O método UNIFAC foi usado para predizer equilíbrio entre fases para o sistema, usando parâmetros de interação determinados experimentalmente de dados considerando os grupos CH_3, CH_2, OH, CH_3COO *e* H_2O. *Coeficientes de distribuição e fatores de separação foram avaliados na região de imiscibilidade.*

INTRODUCTION

In the scope of investigating more benign solvents as potential replacements for chlorocarbons or aromatic hydrocarbons and as new solvents for separations, we have concentrated on the dibasic esters (dimethyl adipate, dimethyl glutarate, dimethyl succinate and mixture these three esters) which have excellent properties for industrial applications. They are powerful solvents, and as such they are already widely used in the paint, coating, and polymer industry and as industrial cleaners. They have low toxicity, great stability, rather high boiling points (463-573 K), and viscosity and density that are close to those of water. The dibasic esters also be used as novel solvents in separation techniques[1].

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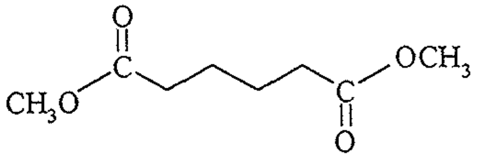
Dimethyl adipate is a colourless liquid, produced from adipic acid esterification. Its formulae is as follows:



dimethyl adipate

The properties of dimethyl adipate are excellent solvency, high boiling point, high flash point, low miscibility with water (beneficial for waste water treatment), high miscibility with organic solvents (safe diluent for classified solvents) and readily biodegradable. Dimethyl adipate is used in paint, lacquers, varnishes, in plasticizers for cellulose type resins, and in paint strippers. It is offer as an alternative to hazardous solvents[2].

In order to separate the ethanol from fermentation product, traditional distillation processes are frequently used, but these processes are very energy intensive. On the other hand, liquid-liquid extraction is a technique known to separate the ethanol from water mixtures and it is an alternative to distillation. In addition, liquid-liquid extraction allows to obtain high-standard ethanol. This also lowers the energy cost of the process in comparison to distillation[3-10].

The real behaviour of fluid mixtures can be calculated with the help of activity coefficients. The correct description of the dependence on temperature, pressure and composition in multicomponent systems requires reliable thermodynamic models, which allow the calculation of these properties from available experimental data[3,6]. The UNIFAC method (UNIFAC Functional Group Activity Coefficient) was developed by Fredenslund et al.[11]. It is one of the best methods in the estimating activity coefficient that has been established to date. The UNIFAC method for estimation of activity coefficients is based on the concept that a liquid mixture may be considered a solution of structural units from which the molecules are formed rather than a solution of the molecules themselves. This type of procedure is known as group contribution method. It has the advantage of being able to form a very large number of molecules from a relatively small set of structural units. The structural units in the calculation method are called subgroups. The mole fractions, X_i^E and X_i^R of liquid-liquid equilibrium phase can be calculated using the following equations.

$$\gamma_i^E X_i^E = \gamma_i^R X_i^R \tag{1}$$

In this study, the predicted interaction parameters between CH$_3$, CH$_2$, OH, CH$_3$COO and H$_2$O groups were used to estimate the activity coefficients by the UNIFAC method.

This study is part of a research program on the recovery of ethanol from dilute aqueous solutions using solvents with high boiling points. In this study, in order to evaluate dimethyl adipate as an agent for the extraction of ethanol from dilute aqueous solutions, we reported liquid-liquid equilibrium results at temperatures 298.15, 303.15 and 318.15 K for the ternary system water+ethanol+dimethyl adipate. Dependence on temperature was studied by evaluating distribution coefficients and separation factors for each case.

EXPERIMENTAL PROCEDURE

Materials. Ethanol and dimethyl adipate were purchased from Merck Co. with purities of 99.98 % (W/W) and 99 % (W/W). Ethanol and dimethyl adipate were used without further purification. Deionized water was further distilled before use. The measured physical properties are listed in Table I, along with literature values[12].

Table I. Densities (d), refractive indices (n_D) and boiling points (B.P.) of the pure compounds.

	d (298.15 K) g.cm^{-3}		n_D (298.15 K)		B.P. (101.325 kPa/K)	
Compound	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Water	1.0000	0.99704	1.3324	1.3325	373.18	373.21
Ethanol	0.7851	0.78493	1.3593	1.3594	351.16	351.17
Dimethyl adipate	1.0610	1.06301	1.4278	1.4285	505.23	505.15

Procedure. Three different temperatures were fixed to study the ternary equilibrium system in order to observe the evolution of the tie lines. At each temperature, (298.15±0.20, 308.15±0.20 and 318.15±0.20 K) tie-line data were obtained by preparing ternary mixtures (water+ethanol+dimethyl adipate) of known overall compositions lying within the two phase region after being stirred vigorously and allowed to reach equilibrium in the isothermal conditions at constant temperatures at the Figure 1.

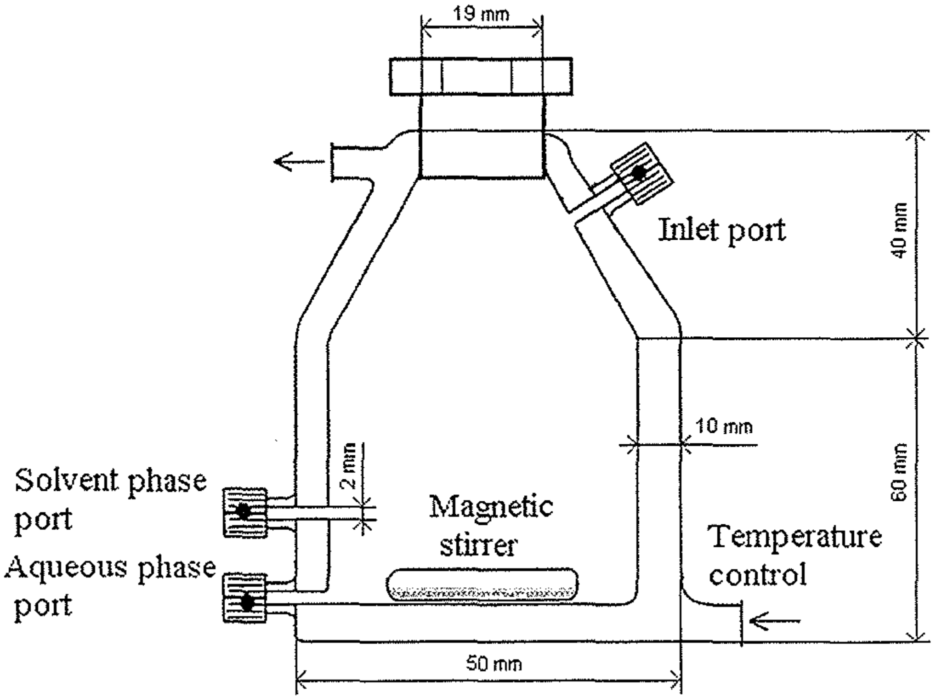


Figure 1. Liquid-liquid equilibrium cell.

The suitable stirring time for the attainment of equilibrium was 4 hours. After the stirrer was turned off, the contents were immediately allowed to enter the vertical settler also equipped with an isothermal jacket. After the complete separation of the phases, a suitable amount of each layer was removed for analysis. Temperature was controlled using a Proportional-Integral-Derivative (PID) controlled thermostat with a precision of 0.02 K. All mixtures were prepared by weighing with a Mettler balance with an accuracy of ± 0.0001 g.

Analysis. The liquid samples were analysed using a Gas Chromatograph (Hewlett Packard GC, Model 6890 Series), equipped with a Thermal Conductivity Detector (TCD) for the quantitative determination of water, ethanol and dimethyl adipate. A 15-m long HP-Plot Q column (320-micrometer diameter with a 20-micrometer film thickness) was used with a temperature programmed analysis. The oven temperature was fixed at 523.15 K. The detector temperature was kept 523.15 K, while injection-port temperature was held at 473.15 K. The flow rate of carrier gas, nitrogen was kept 6 mL/min. Samples of single phase with known compositions were used to calibrate the instrument in the composition range of interest.

RESULTS AND DISCUSSION

The experimental tie line data of water+ethanol+dimethyl adipate ternaries at temperatures 298.15, 303.15 and 318.15 K, are given in Table II.

It was found that dimethyl adipate was only slightly soluble in water but miscible with ethanol. The experimental and predicted tie-lines for the system at each temperature were plotted and shown in Figures 2-4.

Table II. Experimental Tie-Line Data of Water (1)+Ethanol (2)+Dimethyl adipate (3) at temperatures of 298.15, 308.15 and 318.15 K.

	water-rich phase (W/W, %)			solvent-rich phase (W/W, %)		
Temp. (K)	water	ethanol	dimethyl adipate	water	ethanol	dimethyl adipate
298.15	88.91	7.08	4.01	3.66	1.88	94.46
	86.21	9.42	4.37	4.22	2.66	93.12
	82.20	13.15	4.65	4.73	4.05	91.22
	78.48	16.15	5.37	6.37	5.81	87.82
	77.71	17.50	5.49	6.42	6.69	86.89
	73.66	19.65	6.69	7.78	8.63	83.59
308.15	88.96	7.11	3.83	3.96	2.11	93.93
	86.25	9.42	4.33	4.43	2.91	92.66
	82.81	12.87	4.32	5.02	4.32	90.66
	78.84	15.65	5.51	6.18	5.95	87.87
	75.99	17.81	6.20	7.28	7.46	85.26
	72.78	19.55	7.67	8.53	8.94	82.53
318.15	88.68	6.72	4.60	4.10	2.14	93.76
	86.73	9.05	4.22	4.30	3.11	92.59
	82.87	12.41	4.72	5.16	4.55	90.29
	79.60	15.51	4.89	6.19	6.11	87.70
	77.13	17.47	5.40	7.26	7.46	85.28
	74.22	19.32	6.46	8.85	9.05	82.10

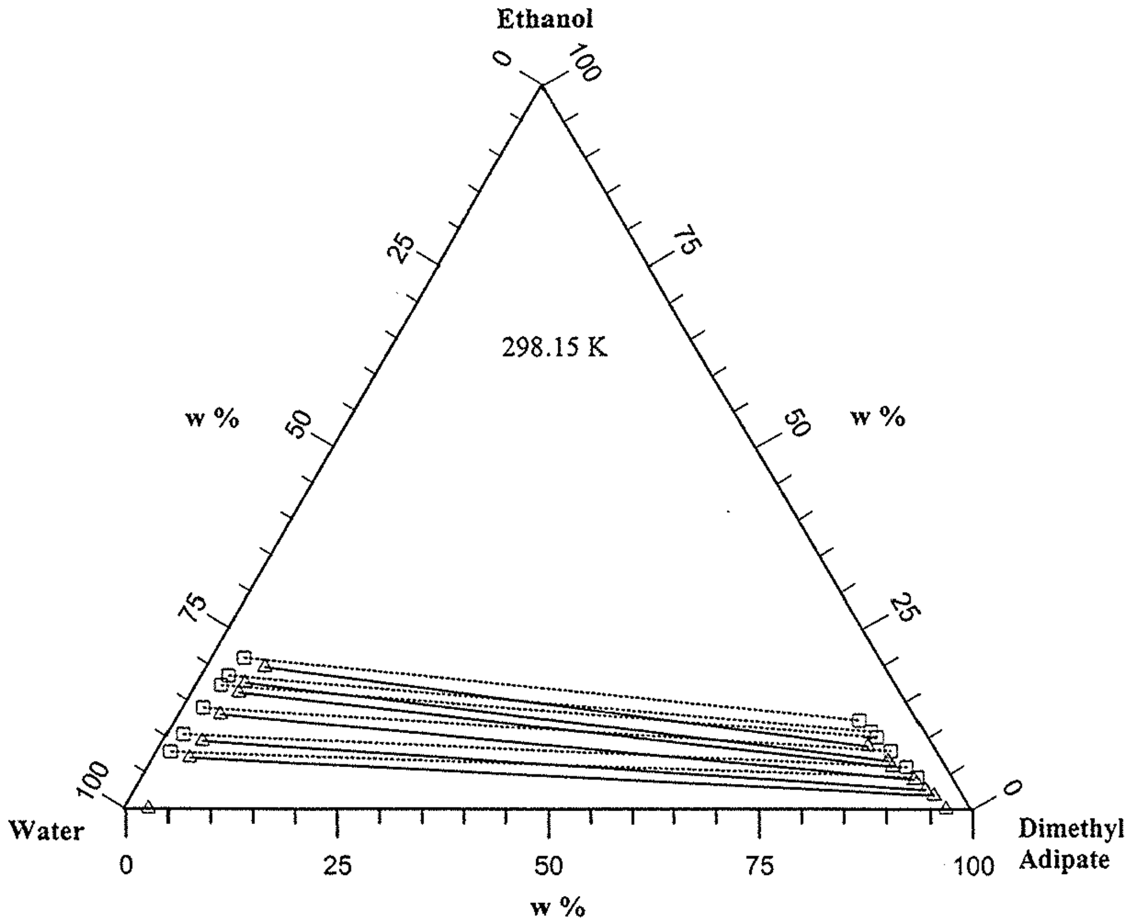


Figure 2. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dimethyl adipate (3) at 298.15 K; –Δ– experimental tie-line data, --□-- calculated (UNIFAC) tie-line data.

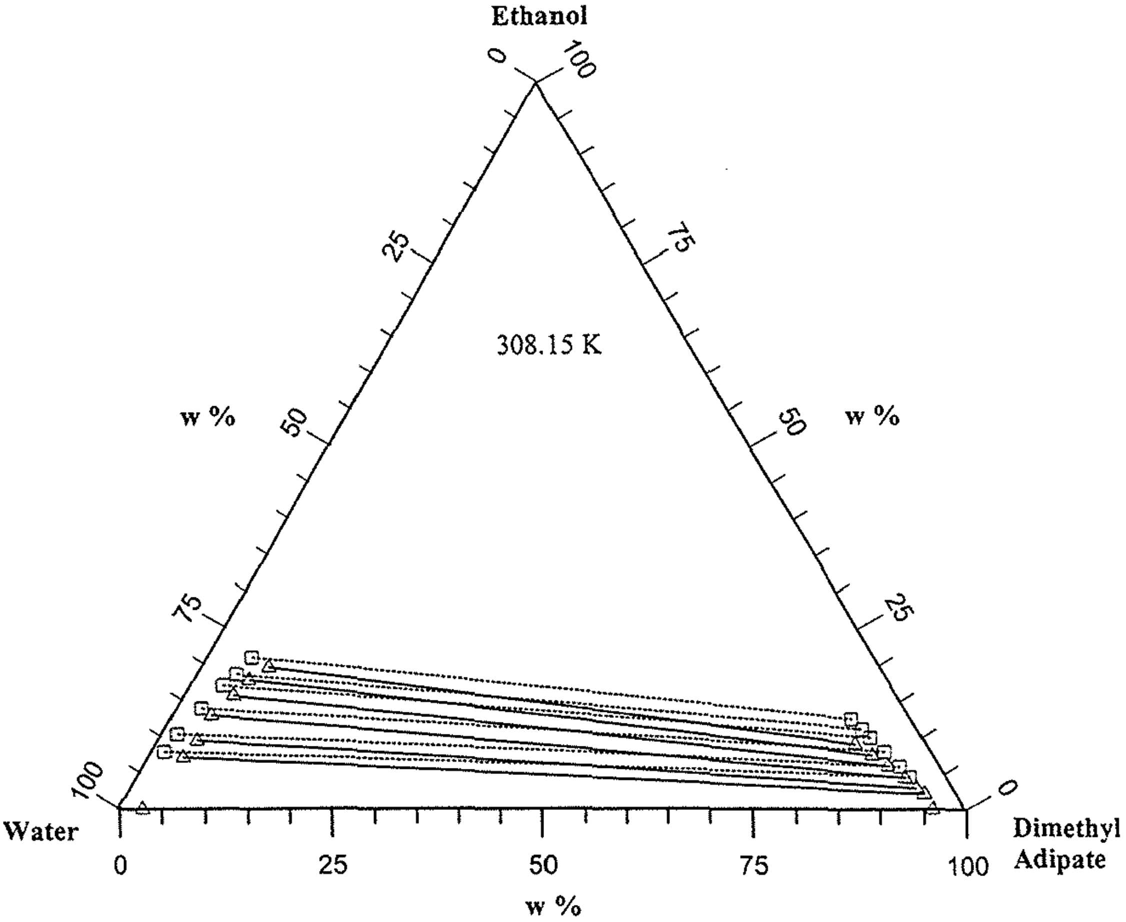


Figure 3. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dimethyl adipate (3) at 308.15 K; –Δ– experimental tie-line data, --□-- calculated (UNIFAC) tie-line data.

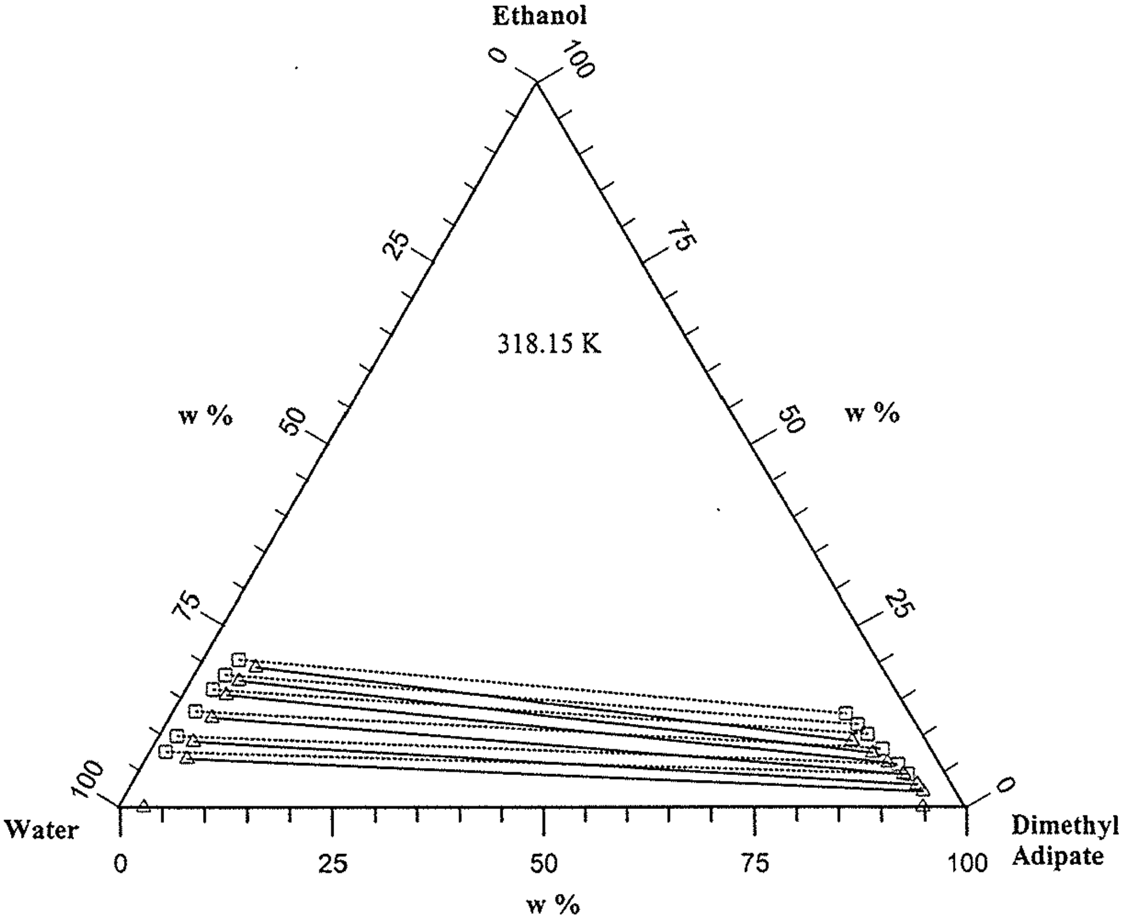


Figure 4. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dimethyl adipate (3) at 318.15 K; –Δ– experimental tie-line data, --□-- calculated (UNIFAC) tie-line data.

Distribution coefficients, D_i, for ethanol (i=2) and water (i=1) and separation factors, S, were determined as follows:

$$D_i = \frac{\text{Weight fraction in solvent phase } (W_{i3})}{\text{Weight fraction in aqueous phase } (W_{i1})} \tag{2}$$

$$S = \frac{D_2}{D_1} \tag{3}$$

The distribution coefficient, D_2 of ethanol was calculated according to the Equation 2. The distribution coefficients and separation factors for the each temperature are given in Table III.

Table III. Distribution Coefficients, D_i of Water (1)-Ethanol (2) and Separation Factors at 298.15, 308.15 and 318.15 K.

Temperature, (K)	D_1	D_2	S
298.15	0.0412	0.2655	6.4505
	0.0490	0.2824	5.7687
	0.0575	0.3080	5.3523
	0.0812	0.3598	4.4322
	0.0834	0.3823	4.5856
308.15	0.0445	0.2968	6.6667
	0.0514	0.3089	6.0145
	0.0606	0.3357	5.5371
	0.0784	0.3802	4.8502
	0.0958	0.4189	4.3722
318.15	0.0462	0.3185	6.8879
	0.0496	0.3436	6.9313
	0.0623	0.3666	5.8883
	0.0778	0.3939	5.0658
	0.0941	0.4270	4.5366

The separation factor (S) is greater than unity for all temperatures reported. This means extraction of ethanol using dimethyl adipate is possible. Hovewer, it is not constant over the whole two-phase region. The extracting power of the solvent at each temperature, plots of D_2 *vs.* W_{21} and S *vs.* W_{21} are given in Figure 5 and 6, respectively.

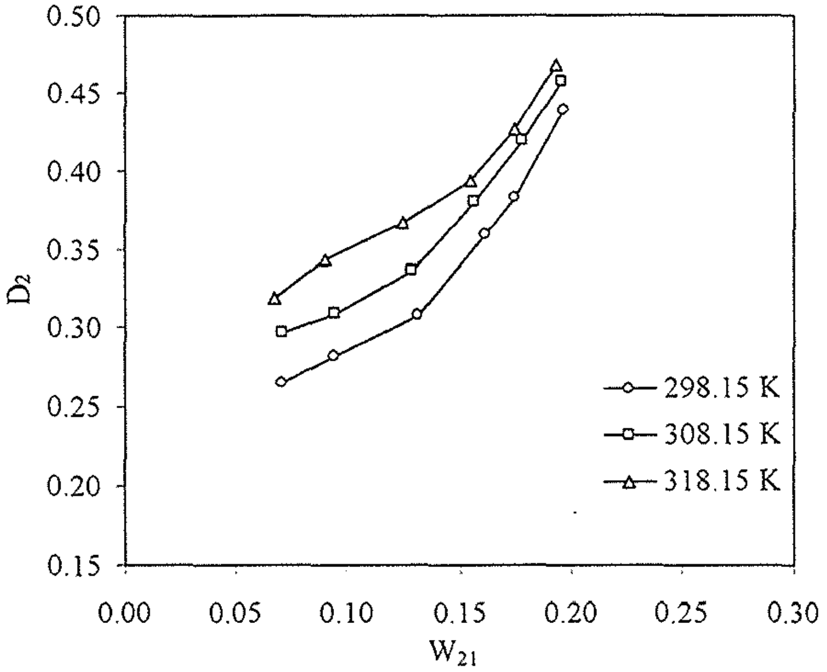


Figure 5. Distribution coefficient, D_2 of ethanol as a function of the mass fraction W_{21} of ethanol in aqueous phase.

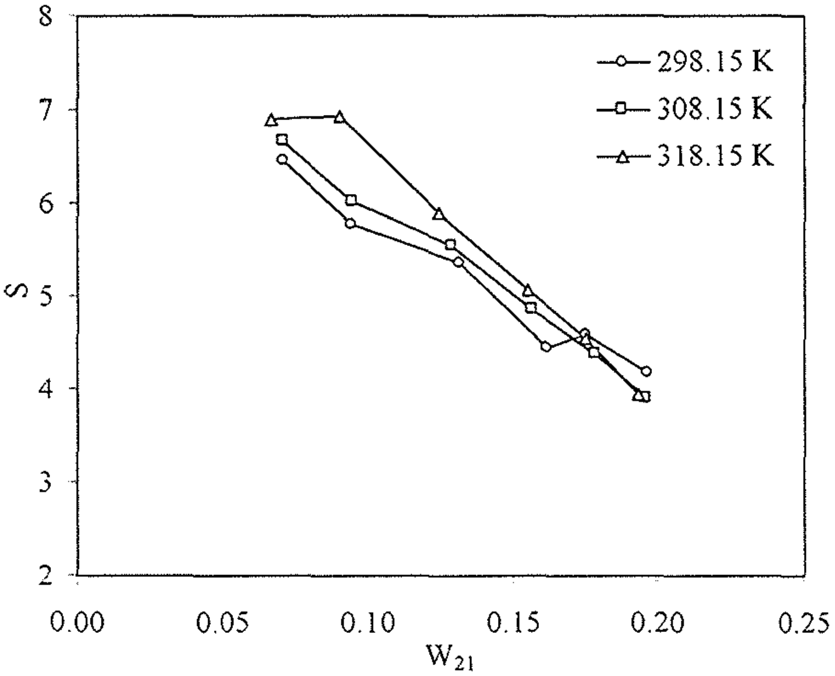


Figure 6. Separation factor, S as a function of the mass fraction W_{21} of ethanol in the aqueous phase.

The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer-Tobias correlation Equation 4 at each temperature[13].

$$\ln\left(\frac{1-W_{33}}{W_{33}}\right) = a + b\ln\left(\frac{1-W_{11}}{W_{11}}\right) \tag{4}$$

The linearity of the plot indicates the degree of consistency of the data. Othmer-Tobias plots were made of the $\ln((1-W_{33})/W_{33})$ *vs.* $\ln((1-W_{11})/W_{11})$. The parameters of the Othmer-Tobias correlation are in Table IV.

Table IV. Othmer-Tobias Equation Constants for Water + Ethanol + Dimethyl Adipate System.

Temperature, (K)	a	b	R^2
298.15	0.4137	0.8630	0.9880
308.15	0.4633	0.9135	0.9931
318.15	0.2736	0.8489	0.9928

Prediction of Equilibria by the UNIFAC Method. The equilibrium data of the ternary mixture were predicted by UNIFAC method[11] using the interaction parameters between CH_3, CH_2, OH, CH_3COO and H_2O obtained by Magnussen et al.[14]. UNIFAC parameters for LLE prediction are summarised in Table V.

Table V. UNIFAC group parameters for prediction tie lines data[14].

	CH_3	CH_2	OH	CH_3COO	H_2O	R_k	Q_k
CH_3	0	0	156.4	114.8	300	0.9011	0.848
CH_2	0	0	156.4	114.8	300	0.6744	0.54
OH	986.5	986.5	0	245.4	-229.1	1	1.2
CH_3COO	232.1	232.1	101.1	0	72.87	1.9031	1.728
H_2O	1318	1318	353.5	200.8	0	0.92	1.4

We observe, in Figures 2-4, how the UNIFAC method predicts the equilibrium data (dashed lines in Figures 2-4). The discrepancy between the experimental and predicted solubilities do not change with temperature because the predicted and experimental data are practically independent of temperature.

The temperature effect on the distribution coefficients was found to be slightly positive. The experimental and UNIFAC model predictions were fitted according to the following equation.

$$D_2 = A\exp(-E_A / RT) \tag{5}$$

The experimental and predicted UNIFAC values are shown in Figure 7.

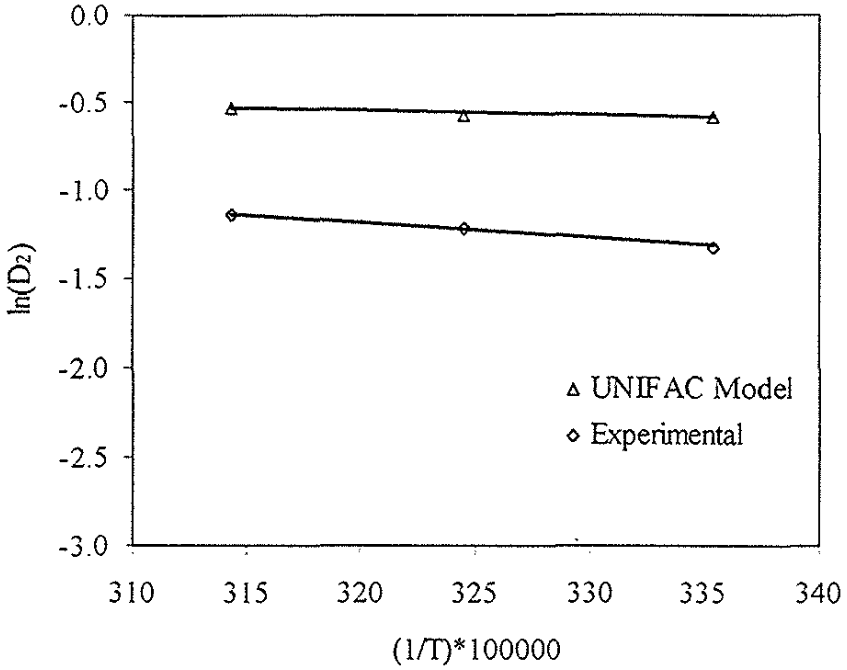


Figure 7. Temperature effect on the distribution coefficient, D_2 of ethanol.

The experimental activation energy (E_A) and the frequency factor (A) were found as -0.0715 J.mol^{-1} and 1.5763, respectively. The calculated (UNIFAC) activation energy (E_A) and the frequency factor (A) were found as -0.0216 J.mol^{-1} and 1.3306, respectively.

Selectivity. Selectivity diagrams on a solvent-free basis are obtained by plotting $W_{23}/(W_{23}+W_{13})$ *vs.* $W_{21}/(W_{21}+W_{11})$ for 298.15, 308.15 and 318.15 K in Figure 8. The effect of temperature change on the selectivity values was found to be insignificant.

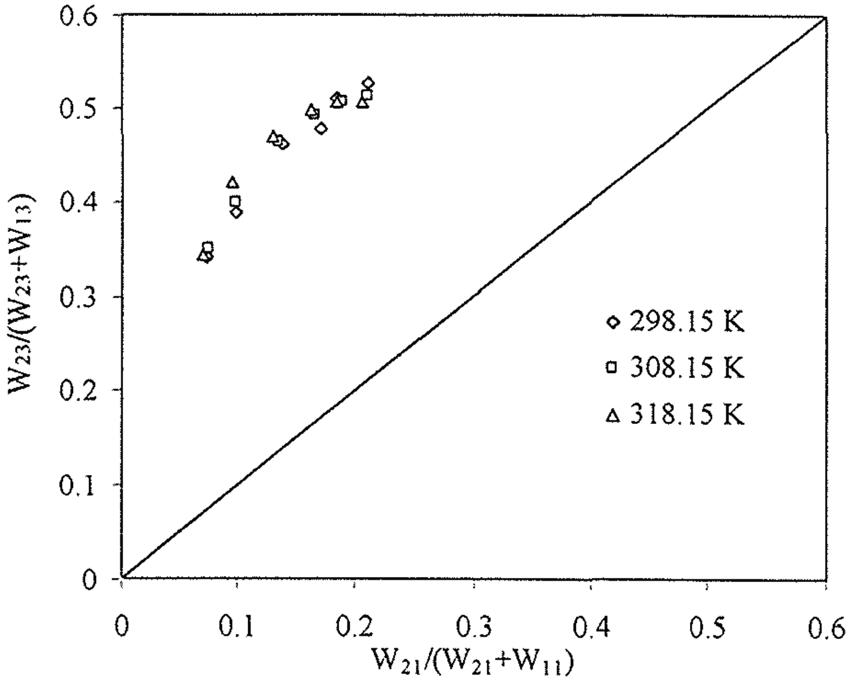


Figure 8. Selectivity diagram at investigated temperatures (free-solvent basis)

CONCLUSION

Dimethyl adipate was chosen on the basis of its suitability for industrial applications. It is concluded that because dimethyl adipate shows low solubility in water it may serve as an adequate solvent to extract ethanol from dilute aqueous solutions. The tie-lines in Figures 2-4 show, as was expected, that ethanol is more readily soluble in the water phase than in the dimethyl adipate phase. It was found the UNIFAC method predictions were satisfactory and agreed qualitatively with the experimental data.

ACKNOWLEDGEMENT

The authors would like to thank to Emel Keskinocak for the gas chromatography analysis.

NOMENCLATURE

A	: frequency factor, Equation 6
d	: density, (g.cm^{-3})
D_i	: distribution coefficient of the ith component, Equation 2
E	: extract (solvent) phase
E_A	: activation energy, J.mol^{-1}
I	: component number of water (1), ethanol (2) and solvent (dimethyl adipate) (3)
R	: raffinate (aqueous) phase and universal gas constant, Equation 6
S	: separation factor, Equation 3
T	: temperature, K
W_i	: weight fraction of the ith component

W_{11} : weight fraction of water (1) in the aqueous phase
W_{21} : weight fraction of ethanol (2) in the aqueous phase
W_{31} : weight fraction of dimethyl adipate (3) in the aqueous phase
W_{13} : weight fraction of water (1) in the solvent-rich phase
W_{23} : weight fraction of ethanol (2) in the solvent-rich phase
W_{33} : weight fraction of dimethyl adipate (3) in the solvent-rich phase
X : mole fraction of the component
n_D : refractive index
γ : activity coefficients of the component

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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TRANSITION METAL COMPLEXES OF HETEROCYCLIC LIGANDS. PART VI. COMPLEXES OF 5- HYDROXY – 6- MERCAPTO-BENZO[a]PHENAZINE WITH Co(II), Ni(II), Cu(II), Zn (II) AND Cd(II)

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ABSTRACT

The paper reports the conclusions about the structure of five new complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with the heterocyclic ligand, 5- hydroxy –6- mercapto – benzo[a] phenazine (H_2L). These were obtained by elemental analysis, IR, UV-VIS and EPR spectral analysis, conductivity and magnetic susceptibility measurements and thermal analysis. Bacteriological studies revealed that the ligand and the complexes possess moderate antimicrobial activity.

KEYWORDS : heterocyclic ligand; antibacterial activity; thermal decomposition; activated energies; transition metal complexes

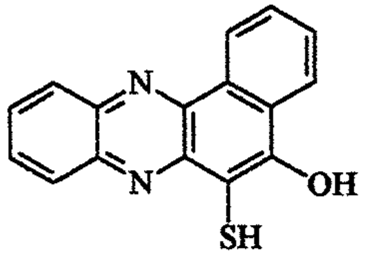
RESUMO

Foi determinada a estrutura de cinco complexos novos do ligante heterocíclico 5-hidroxi-6-mercapto-benzo(a)fenazina (H_2L) com Co(II), Ni(II), Zn(II), Cu(II) e Cd(II). Foram usadas técnicas de análise elementar, infravermelho, ultravioleta-visível, RPE, condutividade, susceptibilidade magnética e análise térmica. Estudos bacteriológicos indicaram que o ligante e os complexos possuem atividade antimicrobial.

INTRODUCTION

Metallic complexes of heterocyclic ligands are of considerable interest from the structural point of view and, also, as a consequence of their applications *e.g.* in analytical chemistry, in polymer industry and, specially, in medical-biological systems, where their bacteriostatic and cytostatic properties are useful [1].

In continuation of our earlier studies on the study of such complexes [2], we report here the synthesis and characterization of the products obtained by the reaction of 5- hydroxy –6- mercapto – benzo[a]phenazine (H_2L) [3], with Co(II), Ni(II), Cu(II), Zn (II) and Cd(II).



H_2L

The bacteriostatic activity of the ligand and its complexes was determined against selected bacteria.

EXPERIMENTAL PROCEDURE

All chemical used were of analytical grade: $Co(OAc)_2\cdot 4H_2O$ (Merck, p.a.); $Ni(OAc)_2\cdot 4H_2O$ (Merck, p.a.); $Cu(OAc)_2\cdot H_2O$ (Merck, p.a.); $Zn(OAc)_2\cdot 2H_2O$ (Merck, p.a.) and $Cd(OAc)_2$ (Merck, p.a.).

The ligand was doubly recrystallized from ethanol.

The IR spectra were recorded on a BIO RAD FTS 135 instrument in anhydrous KBr pellets in the range 400-4000 cm^{-1}. An Unicam UV2-300 spectrometer was used to obtain electronic spectra. The molar conductivities were determined using an OK - 102 Radelkis conductivity meter. The magnetic susceptibility measurement was made with a Faraday balance at room temperature. The thermogravimetric curves were traced with derivatograph MOM 1500-D (10°C/min). The EPR spectrum was registered on a Art –5 – Ifin Bucharest spectrometer, that operates in the X band, the modulation of magnetic field being 100 kHz, using Mn^{2+} as an internal standard.

The complexes were prepared by mixing ethanolic solutions of metal acetate with 5-hydroxy –6- mercapto – benzo[a]phenazine in a 1:1 molar ratio and an adequate pH. The resulting solution was gently refluxed for one hour at 100°C. The reaction mixture was left at room temperature for six hours. Then, the corresponding metal complexes precipited. They were filtered, washed with ethanol and dried in an oven at 100-110°C.

RESULTS AND DISCUSSIONS

The complexes obtained were microcrystalline colored powders. They are stable at room temperature and their solubilities in common inorganic and organic solvents are medium.

The elemental analysis data for C, H, N and S showed that the complexes prepared are of the type $[M(HL)_2]\cdot EtOH$ where M=Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) and HL=the mono-anion of the ligand. The molar electric conductivities are in the range λ=10.0-15.2 Ω^{-1} cm^2mol^{-1} in DMF (10^{-3}M) solutions at room temperature, which means that all the complexes are non-electrolytes.

The important bands (cm^{-1}) observed in the infrared spectra of the ligand and the metal complexes were as follows:the ligand shows absorption band at 3400 cm^{-1} characteristic for ν_{OH} which appears in complexes at lower frequencies (3435-3440 cm^{-1}). This decrease indicates the coordination of the oxygen atom with the metal ion. The absorption band observed at 2550 cm^{-1} in the spectrum of the ligand due to ν_{SH}, disappeared in the complexes, indicating the deprotonation of thiol group and coordination of the sulphur atom with the metal ion. Another significant change in the IR spectra of metal complexes was the appearance of $\nu_{C\text{-}OH}$ band between 1125-1130 cm^{-1} as compared to 1140 in the ligand, thus showing a shift towards lower region by 10-15 cm^{-1}. This decrease indicated the existence of hydroxyl group and the coordination of oxygen atom. The metal complexes were also characterized by the appearance of some new bands of medium and low intensity at 440-450 cm^{-1}, which could be assigned to $\nu_{M\text{-}O}$ stretching frequencies. The absorption band observed at 685 cm^{-1} in the spectrum of ligand appeared at 655-662cm^{-1}, thus showing a shift towards lower regions. This band was characteristic of $\nu_{C\text{-}S}$, and its shift supported the coordination of sulphur atom.

In conclusion, 5-hydroxy-6-mercapto-benzo[a]phenazine acts as a monoanionic bidentate ligand in the complex compounds investigated.

The information referring to the geometry of the complexes was obtained from the electronic spectra in solution and from values of the magnetic moments.

The UV spectrum of the ligand reveals two bands assigned to the transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. These transitions were also found in the spectra of the complexes but shifted to lower frequencies ($\Delta\nu$=1500-3000 cm^{-1}), confirming the coordination of the ligand to the metal ions.

The magnetic moment value of the Co (II) complex is 3.08 MB. Its electronic spectrum displays two bands at 16400 and 21200 cm^{-1}, which may be assigned to $^2A_{1g} \rightarrow {}^2B_{2g}$ and $^2A_{1g} \rightarrow {}^2E_g$ transitions, respectively, in a square-planar configuration around Co(II) [4].

The Ni(II) complex is diamagnetic. The electronic spectrum of this chelate exhibited two bands at 18700 (ν_1), 20900 (ν_2), which are assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively. These transitions are characteristic of compounds with a square - planar geometry for the Ni (II) ion [5].

The magnetic moment for the Cu(II) complex is 1.83 B.M. (close to the spin - only value of d^9 ion). The electronic spectrum displays two weak and broad bands around 21700 and 16800 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively in a square- planar symmetry [4].

The EPR spectrum of the compound $[Cu(HL)_2] \cdot EtOH$ presents values for the anisotropic parameters as follows: $g_{\parallel}$=2.2014 and $g_{\perp}$=2.0102. Because $g_{\parallel} > g_{\perp}$ the line shape suggests a tetragonal geometry specific for Cu(II) in a square planar configuration[6].

The Zn (II) and Cd (II) complexes are diamagnetic. The electronic spectra exhibit two peaks in the UV domain due to $L \rightarrow L^*$ transitions only.

Thermal analyses were carried out for the Co(II), Ni(II) and Cu(II) complexes and the results are presented in Table 1. The agreement between experimental and theoretical mass loss for each of the complexes is within experimental error (±2%) and confirms the formula of the complexes.

Table 1. Thermal analysis data for the complexes.

Step	T_i (°C)	T_f (°C)	T^a (°C)	Δm^b (%)	T_V^c (°C)
$[Co(HL)_2]\cdot EtOH$					
1	58.3	102	78.5(+)	6.9	78.5
2	102	185.6	175(+)	22.76	125
3	185.6	340	260.8(-)	52.17	254.6
4	340	480.8	-	37.63	-
5	480.8	580.2	506.6(-)	50.48	506.6
6	580.2	665.3	-	51.2	-
7	665.3	780	-	56	-
8	780	995	-	67.2	-
$[Ni(HL)_2]\cdot EtOH$					
1	70.8	90.7	78.5(-)	6.83	78.5
2	90.7	175.7	-	7.12	-
3	175.7	240	240(+)	8.21	-
4	240	325	306.6(-)	12.83	300.4
5	325	373.4	370(-)	20.12	370
6	430	890	-	61.6	454.4
$[Cu(HL)_2]\cdot EtOH$					
1	73.5	82.8	78.5(+)	6.51	78.5
2	82.8	182.3	170(+)	32.15	154.08
3	182.3	240	-	34.42	233.6
4	240	313.6	-	36.17	299.2
5	313.6	479.4	320.6(+)	46.35	-
6	479.4	673.8	-	66.21	538.3
7	673.8	980	748.3(-)	73	-

[a] Endothermic (+) or exothermic (-) process
[b] Total mass losses
[c] The temperature when the speed of decomposition is maximum

The thermogravimetric curves proved again the existence of one molecule of ethanol in the structure of the complexes. The loss of this molecule takes place at 78.5°C which means that the ethanol is not chemically bound.

The mass losses of the TG and DTG curves indicate that the ligand is lost in two steps as a radical which is then stabilized through dimerization. Confirmation of this process has been obtained for case of the Ni(II) complex at room temperature by IR analysis of the evolved heterocycles of the cooled melt initially obtained at about 300°C, by collection.

The two steps in which are lost the two molecules of ligand have maximum of temperatures which are specified for each complex. In table 2 are presented these temperatures ΔT_1 and ΔT_2 and the activated energies of the thermal decomposition [7].

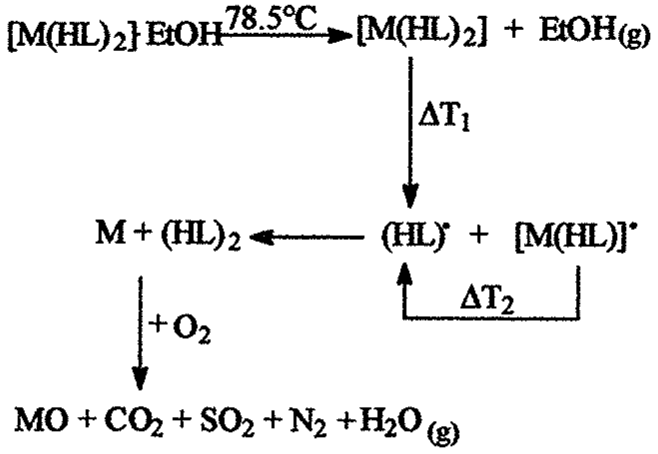
The activation energies have comparable values for the three complexes, but the temperatures are different, which means that the strength metal – ligand is not the same in these complexes. The bond is stronger in nickel complex (ΔT_1=300.4°C) but in radical complex $[Ni(HL)]^{\bullet}$, the breaking of the metal – ligand bond is achieved easier (ΔT_2=370°C) than in the case of $[Co(HL)]^{\bullet}$ and $[Cu(HL)]^{\bullet}$ complexes (ΔT_2=538.3°C, ΔT_2=500.6°C, respectively).

Table 2. The maximum of the temperatures ΔT_1 and ΔT_2 and the activation energies.

Complex	ΔT_1 (°C)	E'_a (kJ/mol)	ΔT_2 (°C)	E''_a (kJ/mol)
$[Co(HL)_2]\cdot EtOH$	125	98.12	506.6	50.2
$[Ni(HL)_2]\cdot EtOH$	300.4	94.24	370	40.96
$[Cu(HL)_2]\cdot EtOH$	154.08	87.97	538.3	42.19

The chemical analysis of the black final residue in each case, gave no indication of carbon, nitrogen, sulphur and hydrogen being present in the composition, and it was mainly identified as MO (where M=Co(II), Ni(II) and Cu(II)).

The general mechanism proposed for the thermal decomposition of the three complexes is one radicalic:



Base on the above observations, a structure in which metal ions in the complexes prepared with the sulphur and oxygen donating ligand have coordination number equal to 4, may be proposed.

Bacteriological Studies

Antibacterial activity of the ligand and its complexes was studied against S. aureus and E. coli by employing the diffusion method using streptomycin as control [8]. The ligand does not exhibit any remarkable activity (zone of inhibition < 8mm) while the complexes showed moderate activities (zone of inhibition 10-20 mm). The antibacterial activity was found to increase in the order: Ni>Co>Cu.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 10 , N° 11, 2002

NEW MIXED TETRADENTATE CHELATES OF Co(III) WITH ETHYLENDIIMINO- BIS – DIBENZOYLMETHANE

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ABSTRACT

Five new chelates of Co(III) of the $[Co(dibenzec)(amine)_2]^+$ *type (dibenzec.*H_2 *– ethylenediimino-bis- dibenzoylmethane:* $C_{32}H_{28}N_2O_2$*, amine=aniline, o-anisidine, p-toluidine, m- xilidine, α- naphtilamine) were synthetized and characterized by isolation of thirty-four new complex salts by means of the double decomposition reactions. The thermal stability of the complexes was studied by means of differential thermal analysis. The structural properties were discussed on the basis of IR and UV spectra.*

KEYWORDS : Co(III), chelates, complex salts, structure chromium (III)

RESUMO

Cinco quelatos novos de Co(III) do tipo $[Co(dibenzec)(amina)_2]^+$ *foram sintetizados e caracterizados através da isolação de trinta e quatro sais complexos usando reações de decomposição dupla. (dibenzec.*H_2*-etilenodiimino-bis-dibenzoilmetano :* $C_{32}H_{28}N_2O_2$*, amina=anilina, o-anisidina, p-toluidina, m-xilidina, α-naftilamina). A estabilidade térmica dos complexos foi estudada com análise térmica diferencial. As propriedades estruturais foram discutidas em termos de espectros na região infravermelha e ultravioleta.*

INTRODUCTION

The β- diketones (e.g. acetylacetone, benzoylacetone, dibenzoylmethane) react easily with 1,2- and 1,3- aliphatic diamines and aromatic ortho – diamines. The formed bis – Schiff's bases act as tetradentate chelating agents towards bi and trivalent transition metal ions. Various complex salts and non-electrolytes of this class were obtained and characterized. Some derivatives were also used for analytical purposes [1-4].

The synthesis of ethylendiimino – bis – acetylacetone (ec.H_2) and some non – electrolytic complexes: Ni (ec.), Cu (ec), Pd (ec) was reported by Combers [5]. Mixed chelates of Co(lll) with ammonia $[Co(ec)(NH_3)_2]X$ were obtained by Morgan and Smith [6]. In our previous papers [7-9] a series of new mixed complexes of the type: $[Co(ec)(amine)_2]^+$ (aromatic and heterocyclic amines) were described.

Zsakó, Várhelyi and co-workers described in a previous paper new chelates of the ethylenediimino – bis – benzoylacetone (benzec.H_2: $C_{22}H_{24}N_2O_2$) [10].

In the present paper instead dibenzoylmethane was used for condensation with ethylendiamine. The bis Schiff's base formed: ethylendiimino – bis – dibenzoylmethane (dibenzec.H_2: $C_{32}H_{28}N_2O_2$) provides a series of new chelate cations with Co(lll) in the presence of organic N-bases.

EXPERIMENTAL PROCEDDURE

Ethylendiimine – bis- dibenzoylmethane (dibenzec.H_2): A sample of 0.2 mole of dibenzoylmethane and 0.1 mole of ethylenediamine in 250 mL methanol were refluxed on a water bath. After 2-3 hours boiling the Schiff base that separated was filtered off and washed with dilute methanol. Silky, irregular needles were obtained.

[Co(dibenzec)] ($C_{32}H_{28}N_2O_2$) : Dark yellow microcrystals were obtained by refluxing 0.1 mole cobalt acetate and 0.1 mole dibenzec.H_2 in 250 mL methanol for 30-40 minutes (Co calcd. 11.13%, found 11.08%).

$[Co(dibenzec)(amine)_2]$- acetate – solutions :

Method l.

Fifty mmoles of cobalt acetate and 50 mmole of dibenzec.H_2 in 400 mL ethanol were refluxed on a water bath for 30-40 minutes, subsequently 120-130 mmoles of different aromatic amines, pyridine or alkyl-pyridine derivatives were added. The mixture was oxidized by adding dropwise an excess of 30% (aprox. 10-12 mL) H_2O_2. The scarlet yellow microcrystals [Co(dibenzec)] formed dissolved slowly and a dark brown (from dark yellow a reddish brown depending on the nature of amine component). $[Co(dibenzec)(amine)_2]$- acetate – solution was formed. After cooling the solutions were filtered and used for double decomposition reactions.

Method ll.

The suspension of 50 mmoles of [Co(dibenzec)] and 5g of sodium acetate in 400 mL ethanol was treated with 120-130 mmole of amine and oxidezed with 10-12 mL of 30% H_2O_2 added dropwise under refluxing conditions and the cooled. The filtered solutions were used for double decompositions reactions.

$[Co(dibenzec)(amine)_2]X$ complex salts: A sample of 10 mmoles of $[Co(dibenzec)(amine)_2]$ acetate in 100 mL alcoholic solutions was treated with an excess of 2-10% aqueous KI, $NaClO_4$, $NH_4[Co(NH_3)_2(NO_2)_4]$, $[Cr(NCS)_4(amine)_2]NH_4$

in 3% aqueous-alcoholic solutions. The obtained crystalline products were filtered off after 15-30 minutes, washed with dilute ethanol and dried in air.

Analytical Determinations

The cobalt content of the samples was determined complexometrically after decomposing 80-100 mg of the substance with boiling conc. sulphuric acid and some crystals of KNO_3.

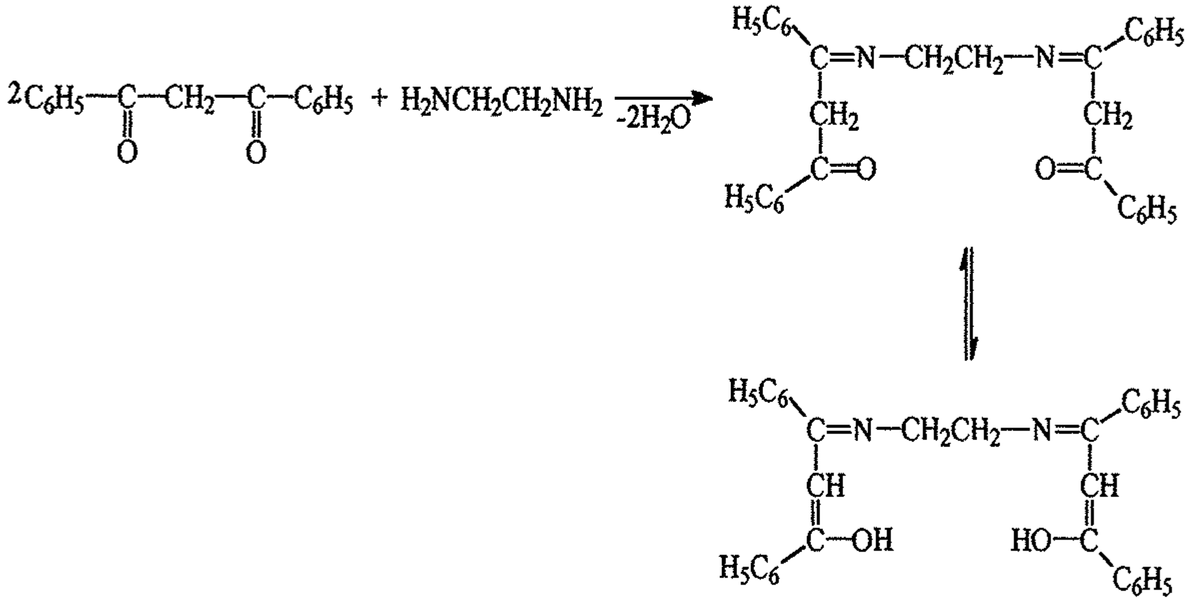
After dilution with water the solution was neutralized with sodium acetate. The N contents were determined by usual microanalytical methods.

The electronic spectra were recorded in methanol with a Specord recording spectrophotometer (Carl Zeiss Jena).

The infrared spectra were registered in KBr tablet on a IR Perkin-Elmer 1600 apparatus.

RESULTS AND DISCUSSIONS

The condensation reaction take place according to the following equation:

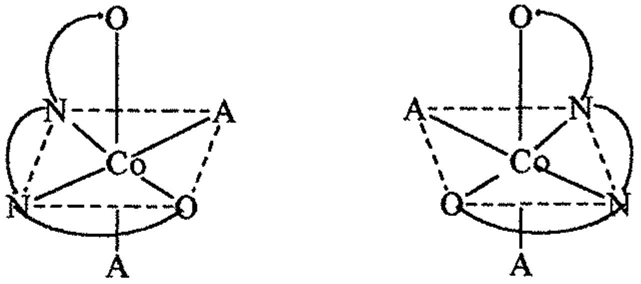


The enolic form of this bis Schiff's base exhibits chelating properties towards transitions metal ions. Of the analogous derivatives of the higher homologues of the diamines only 1,2- and 1,3-propanediamine are suitable for chelation. The condensation products with 1,4-, 1,5-, 1,6- diamines do not present complexing properties.

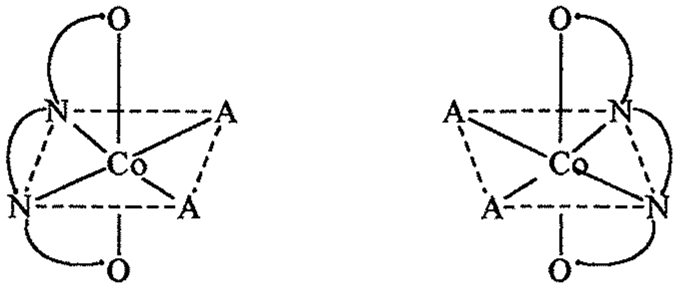
Some bivalent transition metals form well defined, non-electrolytic type chelates with the above mentioned reagent, e.g. Cu(dibenzec), Co(dibenzec), Pd(dibenzec), Pt(dibenzec). From these M(dibenzec) type compounds the Co(II) derivative can be oxidized easily to mixed electrolytic chelates of cobalt (II), in the presence of monodentate ligands. For this purpose perhydrol, chlorine and bromine can be used in the presence of amines, phosphines, arsines, e.g.:

$$2Co^{2+} + 2dibenzecH_2 + 4amine + H_2O_2 \rightarrow 2[Co(dibenzec)(amine)_2]^+ + 2H^+ + 2H_2O$$

In this paper five new chelate cations [Co(dibenzec)(amine)$_2$]$^+$ (amine=aniline, o-anisidine, p- toluidine, m- xilidine, α- naphthylamine, pyridine, γ- picoline) were prepared. These new chelate cations were characterized by isolation of 34 salts by means of double decomposition reaction from the alcoholic solutions of the acetates with alkaline salts of the halides, pseudohalides and complex acids of Co(lll) and Cr(lll), respectively. The [Co(dibenzec)(amine)$_2$]$^+$ type chelate cations exhibit five stereoisomeric modifications, viz. two optical antipode pairs and an inactive, symmetrical "*trans*" form (Fig.1).



Active



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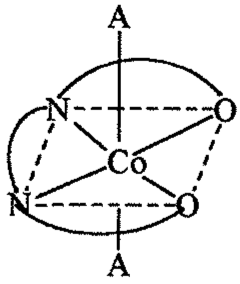

Inactive

Figure 1. The stereoisomers of the [Co(dibenzec)(amine)$_2$]$^+$ type chelate cations.

The new complex salts obtained are characterised in Table 1.

Table 1. New complex salts of the type [Co(dibenzec)(amine)$_2$]X.

No	Formula	Molecular Weight calc.	Yield (%)	Aspect	Analysis (%)	
					calc.	found
I	II	III	IV	V	VI	VII
1	[Co(dibenzec)(pyridine)$_2$]I	814.48	72	sparkling, red-brown prisms	Co 7.23 N 6.87	7.19 6.73
2	[Co(dibenzec)(pyridine)$_2$]ClO$_4$	787.03	76	sparkling, dark brown spears	Co 7.48 N 7.11	7.30 4.06
3	[Co(dibenzec)(pyridine)$_2$]NCS	745.66	40	brown square plates	Co 7.90 N 9.38	7.77 9.21
4	[Co(dibenzec)(pyridine)$_2$] [Co(NO$_2$)$_4$(NH$_3$)$_2$]	964.61	75	brown needles	Co 12.22 N 14.51	12.10 14.43
5	[Co(dibenzec)(pyridine)$_2$] [Cr(NCS)$_4$(NH$_3$)$_2$]	1006,01	86	reddish brown microcrystals	Co+Cr 11.02 N 13.91	10.93 13.83
6	[Co(dibenzec)(pyridine)$_2$] [Co(NCS)$_4$(aniline)$_2$]	1158.01	90	Brown needles	Co+Cr 9.58 N 12.09	9.47 11.94
7	[Co(dibenzec)(γ-picoline)$_2$]I	842.50	52	Brown irregular crystals	Co 6.99 N 6.64	6.92 6.58
8	[Co(dibenzec)(γ-picoline)$_2$]ClO$_4$	815.05	60	orange-brown short prisms	Co 7.23 N 6.87	7.15 6.71
9	[Co(dibenzec)(γ-picoline)$_2$]NCS	773.68	38	thick, dark brown disks	Co 7.61 N 6.46	7.55 6.34
10	[Co(dibenzec)(γ-picoline)$_2$] [Co(NO$_2$)$_4$(NH$_3$)$_2$]	992.63	82	short, brown irreg. prisms	Co 11.87 N 14.10	11.78 14.00
11	[Co(dibenzec)(γ-picoline)$_2$] [Cr(NCS)$_4$(aniline)$_2$]	1185.03	88	reddish brown microcrystals	Co+Cr 9.36 N 11.81	9.22 11.74
12	[Co(dibenzec)(o-anisidine)$_2$]I	902.66	53	dark brown square prisms	Co 6.52 N 6.20	6.44 6.12
13	[Co(dibenzec)(o-anisidine)$_2$]ClO$_4$	875.21	58	square thin brown plates	Co 6.73 N 6.39	6.65 6.20
14	[Co(dibenzec)(o-anisidinc)$_2$]SCN	817.77	47	thick, dark brown disks	Co 7.20 N 8.55	7.17 8.43
15	[Co(dibenzec)(o-anisidine)$_2$] [Cr(NCS)$_4$(NH$_3$)$_2$]	1094.19	94	brown irreg. cryst.	Co+Cr 10.14 N 12.79	10.06 12.69
16	[Co(dibenzec)(o-anisidine)$_2$]I	870.54	73	sparkling brown prisms	Co 6.77 N 6.43	6.71 6.33
17	[Co(dibenzec)(p-toluidine)$_2$]ClO$_4$	843.09	82	brown disks plates	Co 6.99 N 6.64	6.85 6.57
18	[Co(dibenzec)(p-toluidine)$_2$]SCN	801.72	50	brown square	Co 7.35 N 8.73	7.19 8.62
19	[Co(dibenzec)(p-toluidine)$_2$] [Co(NO$_2$)$_4$(NH$_3$)$_2$]	1020.67	84	light brown microcrystals	Co 11.54 N 13.71	11.43 13.60
20	[Co(dibenzec)(p-toluidine)$_2$] [Cr(NCS)$_4$(NH$_3$)$_2$]	1062.07	94	reddish – brown micro-crystals	Co+Cr 10.44 N 13.18	10.31 13.10
21	[Co(dibenzec)(p-toluidine)$_2$] [Cr(NCS)$_4$(aniline)$_2$]	1214.07	87	reddish – brown micro-crystals	Co+Cr 9.13 N 11.53	9.06 11.40
22	[Co(dibenzec)(α-naphtylamine)$_2$]I	942.54	83	brown disk	Co 6.25 N 5.94	6.18 5.82

I	II	III	IV	V	VI	VII
23	[Co(dibenzec)(α-naphtylamine)$_2$]ClO_4	915.09	86	red-brown microcrystals	Co 6.25 N 5.94	6.18 5.82
24	[Co(dibenzec)(α-naphtylamine)$_2$]NCS	873.72	73	reddish-brown microcrystals	Co 6.74 N 8.01	6.71 7.95
25	[Co(dibenzec)(α-naphtylamine)$_2$] [Cr(NCS)$_4$(NH_3)$_2$]	1134.07	94	red-brown microcrystals	Co+Cr 9.78 N 12.34	9.66 12.21
26	[Co(dibenzec)(α-naphtylamine)$_2$] [Cr(NCS)$_4$(aniline)$_2$]	1286.07	96	red-brown microcrystals	Co+Cr 8.62 N 10.88	8.55 10.79
27	[Co(dibenzec)(m-bromoaniline)$_2$]I	972.40	74	dark brown irreg. prisms	Co 6.06 N 5.75	6.00 5.63
28	[Co(dibenzec)(m-bromoaniline)$_2$]ClO_4	944.95	80	sparkling, short brown prisms	Co 6.23 N 6.87	6.20 6.77
29	[Co(dibenzec)(aniline)$_2$]I	842.50	51	sparkling, thin brown prisms	Co 6.99 N 6.64	7.02 6.51
30	[Co(dibenzec)(aniline)$_2$]ClO_4	815.05	62	sparkling, brown rhomb. plates	Co 7.23 N 6.87	7.26 6.79
31	[Co(dibenzec)(aniline)$_2$] [Cr(NCS)$_4$(aniline)$_2$]	1186.03	84	brown dendrites	Co+Cr 9.35 N 11.80	9.20 11.69
32	[Co(dibenzec)(m-xylidine)$_2$]I	898.74	53	dark brown plates	Co 6.55 N 6.23	6.44 6.19
33	[Co(dibenzec)(m-xylidine)$_2$]ClO_4	871.29	62	sparkling brown plates	Co 6.76 N 6.42	6.70 6.33
34	[Co(dibenzec)(m-xylidine)$_2$] [Cr(NO_2)$_4$(aniline)$_2$]	1242.27	92	reddish-brown microcrystals	Co+Cr 8.89 N 11.26	8.77 11.11

When compared to the analogous ethylendiimino – bis- acetylacetone derivatives, [Co(ec)(amine)$_2$]X, the [Co(dibenzec)(amine)$_2$]X salts are more sparingly soluble in water and dilute alcohol.

The salts with [Co(NCS)$_4$(amine)]$^-$ are insoluble in water and alcohol, and easily soluble in ketones, e.g. acetone, acetylacetone, dimethylformamide and dimethylsulfoxide, respectively.

Thermal Stability

The thermal stability of some [Co(dibenzec)(amine)$_2$]X type complexes was studied by means of differential thermal analysis. The complicated thermal degradation processes begins at 140-180°C in the case of the [Co(dibenzec)(amine)$_2$]X derivatives as a function of the nature of the amine component and of the external anion. The nitrates, perchlorates, periodates (not analysed) decompose suddenly, generally with explosion. The halides, pseudohalides and the corresponding salts with complex acids liberate free amines, N_2, CO, CO_2 and other decomposition and oxidation products in non stoichiometric ratios, during a slower pyrolysis process under the static air atmosphere of the furnace. The final product at 800-850°C is Co_3O_4 or $Co_3O_4 + Cr_2O_3$.

The thermal behaviour of the [Co(dibenzec)(amine)$_2$]X type complexes is analogous with that of the [Co(ec)(amine)$_2$]X derivatives, the latter having a higher thermal stability.

The exo- and endothermal peaks in the temperature range of 150-550°C show these complicated decomposition and oxidation processes.

The first not well formed inflection point on the thermograms of some derivatives with X=Br, I, NCS corresponds to a partial deamination reaction.

$[Co(dibenzec)(amine)_2]X \rightarrow [Co(dibenzec)(amine)X] + amine$

This endothermal process (DTA- peak at 150-180°C is not so evident as in the case of the dimethylglioximino complexes $[Co(DH)(amine)_2]X$ which were reported in our earlier papers [11-12], also from the kinetic point of view:

$[Co(DH)_2(amine)_2]X \rightarrow [Co(DH)_2(amine)X] + amine$

Electronic Spectra

The spectrum of dibenzec.H_2 has a similar feature to that of benzec.H_2 and ec.H_2 respectively, but its characteristic double bond, situated at about 30800 and 32700 cm^{-1} in case of the latter, is strongly shifted towards the visible region and appears at 28400 cm^{-1} and 29400 cm^{-1} for the former. This important shift is due to the effect of the phenyl group, extending the π-bond system of the molecule. Presumably, the above mentioned bands correspond to a π-π^* transition.

Table 2. IR spectral data of some $[Co(dibenzec)(amine)_2]X$ type complexes and free dibenzec.H_2.

Substance vibration	I	II	III	IV	V	VI
νN-H	-	3220- 3180m 3125m	3220- 3160m 3130m	3200- 3160m 3120m	3200m 3130 3080	3260m 3170m 3085m
νC-H	2960m 2880m	2960w 2860w	2970m 2880w	2960m 2870w	2980m 2860m	2985w 2880w
νC_{Ar}-C_{Ar}	1620vs	1605vs	1605vs	1605vs	1610vs	16020vs
$\delta_{as}NH_2$	-	1580m	1585m	1580m	1590w	1540vs
νC-N	1555vs	1530vs	1535vs	1535vs	1540vs	1540vs
$\delta_{as}CH_3$	1451s	1495vs 1470s	1470s	1470s	1475m 1450s	1485s 1435s
$\delta_s CH_2$	1355vs	1350m	1360m	1360m	1370m	1365m
δNH_2	-	1310s	1310s	1310s	1318s	1310vs
νC-O	1180w 1160w	1130s	1134s	1145s	1145w 1135w	1340m
γNH_2	-	845m	850m	850m	825m	865m
γC_{Ar}-C_{Ar}	770vs	770vs	765vs	765vs	760vs	760m
γC_{Ar}-H	715vs	720s	720s	720s	715s	720vs

I. Dibenzec.H_2; II $[Co(dibenzec)(aniline)_2]I$; III $[Co(dibenzec(m\text{-}toluidine)_2]I$; IV $[Co(dibenzec)(o\text{-}Br\text{-}aniline)_2]I$; V $[Co(dibenzec)(m\text{-}xylidine)_2]I$; VI $[Co(dibenzec)(\alpha\text{-}naphtylamine_2]I$

The coordination of both ec.H_2 and dibenzec.H_2 gives rise to the formation of larger delocalized π-bond systems, involving also the π type d_{xy} and d_{yz} orbitals of the Co atom. In this case the π-π^* absorption bands may be expected to be shifted toward lower wave number values. In the case of the analogous ec and pec (pec.H_2=1,3-propylenediimino-bis-acetylacetone) complexes of Co(III) two absorption bands appear indeed at about 2300 and 2960 cm^{-1}, respectively.

Freshly prepared solutions of the [Co(II)dibenzec] complex exhibit several d-d transition bands, viz. at 13600, 1490 and 16500cm^{-1}. In the UV region two main bands appear, at 24100 and 30200 cm^{-1}, respectively, as well as three inflection points at 21000, 23000 and 28000 cm^{-1}. Upon contact with air, the spectrum changes gradually in 48 hours, the d-d bands disappear and there remains a single strong band at 2800 cm^{-1} and two inflection points at 17000 and 29000 cm^{-1}. Presumably, this transformation is due to the oxidation of Co(II) to Co(III) and the strong band may correspond to the π-π^* transition in the conjugated π-bond system of the resulting $[Co(dibenzec)(H_2O)_2]^+$ complex ion. Generally, in the visible and UV region, the amine containing dibenzec complex of Co(III), ($[Co(dibenzec)(amine)_2]^+$), exhibits five absorption bands, as the corresponding ec and pec derivatives. Sometimes, besides them inflection points between 13800 and 15000 cm^{-1} also appear, indicating weak d-d transitions.

The absorption bands of the dibenzec complexes studied are summarized in Table III.

Table III. Wave numbers(in cm^{-1}) and molar absorptivity (ε) of the absorption bands in the electronic spectrum of $[Co(dibenzec)(amine)_2]X$ type complexes.

No	Amine	X	Bands				
			A	B	C	D	E
1	NH_3*	I	21800	27300	34000	43500	49300
			1700	23000	20000	32000	74000
2	aniline	I	22000	27000	35500	43000	49000
3	m-toluidine	I	21500	27300	34200	40600	48800
4	p-toluidine	ClO_4	22000	27400	35600	40300	49000
5	pyridine*	ClO_4	22700	27400	-	50000	74000
			1500	11600		39300	46500
6	γ-picoline	ClO_4	22700	27400	-	39500	45300
7	α-naphtylamine	Ac	21500	29200	36100	41500	46600
8	m-xylidine	I	21200	27100	35400	28500	37600
9	o-anisidine	I	22000	27200	35200	38500	48500
10	m-bromoaniline	I	22000	27500	35500	44500	48500
11	p-bromoaniline	I	22200	27300	35000	37800	48000
12	β-picoline	Ac	22600	27400	-	39500	45300

Ac=CH_3COO^-; *Ref. 13.

Obviously, both bands A and B have lower wave numbers as compared to the absorption bands of dibenzec.H_2 exactly as with the analogous ec. complexes, suggesting that these might be due to π-π^* transitions. As far as the influence of the amine ligands is concerned, in the case of ec and pec complexes of Co(III), a difference has been observed [7] between the behaviour of the amine ligands forming only σ-bands with Co and those forming also π-bonds. The former situation appears in the case of complexes 1-9 in Table III, the latter one with complexes 10-12.

The mean values of the wave numbers of the five absorption bands obtained for the dibenzec complexes studied, are presented in Table IV, separately for σ- bond forming amine derivatives (δ), and π-bond forming ones (π).

Table IV. Mean wave numbers (in cm^{-1}) of the absorption bands for dibenzec and ec. complexes of Co(III) containing only σ- bond forming amine ligands (δ), also π-bond forming ones (π) and general mean values(g).

Bond		A	B	C	D	E
dibenzec	σ	21720	27400	34900	41920	48500
	π	22000	27700	36100	39000	47000
	g	21850	27500	35300	40800	48000
ec	σ	23600	29700	35400	42000	45700
	π	22900	29600	35000	38900	45300
	g	23300	29700	35200	40500	45600

For the sake of comparison besides the general mean value (g) the analogous data reported earlier for ec. complexes are also given in the same Table.

By comparing the mean wave numbers one can see, that substitution of ec with dibenzec entails the shift of bands A and B towards lower values; bands C and D are practically not affected and band E exhibits an important shift towards higher wave numbers. Therefore we presume that bands A and B might be due to π-π* transitions as shown above, bands C and D besides the Co atom might be involved the amine ligands and with band E the ec and dibenzec ligands, respectively.

Concerning the influence of the σ or π type of the amine ligands, practically, the bands B and C are not affected at all. In the case of band D, and in a smaller extent also band E, the π type amine ligands give rise to a shift towards lower wave numbers, both with ec and dibenzec derivatives. The behaviour of band A is more complicated. It is also shifted towards lower wave number by π type amines in the case of ec-complexes, but the opposite is observed with dibenzec ones, these effects however are not important and might be due to experimental artifacts.

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PHYSICAL AND CHEMICAL PROPERTIES OF CONVENTIONAL PATTERN WAX AND REFORMULATED PATTERN WAX USED IN INVESTMENT METAL CASTING.

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ABSTRACT

The present study reports experimental results obtained for the physical and chemical properties of conventional or standard pattern wax and reformulated pattern wax blended in order to obtain maximum efficiency for possible recycling in the investment metal casting industry. Some of the properties determined included melting point, flash point, water content, ash content, volumetric expansion, hardness, refractive index, infrared and ultraviolet spectra, thermal behavior, curves obtained by DSC, DTA and TGA. The reformulated wax was shown to be relatively stable and good for industrial use after twelve simulated recycling steps.

RESUMO

O presente trabalho apresenta resultados experimentais obtidos para cera padrão para modelos, convencionalmente utilizada pela indústria, e cera reformulada visando sua reciclabilidade quando utilizada no processo de microfusão. Algumas das propriedades determinadas foram: temperaturas de fusão e de volatilização, teores de água (voláteis), cinzas, dureza, módulo de elasticidade, Índice de refração, expansão volumétrica, espéctros característicos no infravermelho e ultravioleta e as curvas térmicas: DSC, DTA, TGA ou DTG. Os resultados obtidos mostram que a cera reformulada permanece relativamente estável depois de doze ciclos simulados de utilização e que ela é satisfatória para processos industriais de microfusão.

KEY WORDS: Pattern Wax, Metal Casting, Dewaxing, Recycling of Pattern Wax.

INTRODUCTION

Pure beewax or common waxes modified with fats and resins have been used since ancient times in Europe, Asia end Africa, to make models that were invested with clays to give ceramic moulds from which metal casting especially bronze, were made. Art objects of high quality were manufactured in Italy during the 16th century, but the lost-wax process only became of industrial importance with the development of dental metallurgy and particularly the advent of the turbine engine in the years preceeding World War II.[1-4]

The investment casting process is characterized by the manufacturing of parts of high metallurgic quality, especially with respect to complexity of design, dimensional aspects and surface finshing. In addition, investment casting is able to achieve the tolerance necessary to eliminate difficult or impossible machining operations. [4-10]

Waxes used for patterns are complex mixtures composed of selected, high-priced ingredients that have been formulated and blended by a wax supplier in order to make the best wax patterns possible.

Pattern wax is a very valuable raw material and represents the starting point for the production of investment casting. Obviously, the better the quality of the wax patterns prepared, the higher will be the quality of investment castings produced.

Waxes are generally classified into three cathegories: natural waxes, modified natural waxes and fully synthetic waxes. [11,12.] Natural waxes, widely distributed in nature, are usually classified into fossil and nonfossil or recent waxes. Among the more common fossil waxes are petroleum waxes that consist of long chain hydrocarbons and *monton* waxes that contain oxygen functional groups in the molecules. [12,13] Nonfossil or recent waxes include animal and plant waxes. By far, the most widely known is beewax produced by Apis mellifera and other bees of the Apis especies, but there are other insect waxes used on a large scale produced by bugs at the Coccidae family, the Chinese insect wax, being the most widely commecialized. Animal waxes come from land animals (e.g, wool wax) and marine animals (e.g. sperm whale or spermaceti wax). Among plant waxes the more common ones are carnaúba, an exudate of the carnaúba palm leaves produced commercially in Northern Brazil in the states Of Ceará and Piauí and candelilla wax obtained from a desert shrub, produced on a large scale in Mexico, in the states of Sonora and Chihuahua.[13]

Modified natural waxes are obtained from crude oil by physical refining methods or chemical processes involving paraffin or monton waxes [14].

Fully synthetic waxes may be hydrocarbon waxes or nonhydrocarbon waxes including amides, ethers alcohols, acids, polyethylene and Fischer – Tropsch waxes[15]. .

A wide majority of the pattern waxes available commercially are usually a blend of waxes, resins and additives selected to impart the necessary characteristics [16]. Among the desired features are strength, hardness, melting point, viscosity, surface smootheness, ash content, dimensional stability, shrinkage, toughness, mold release, injection temperature and compatibility with mold materials.

The purpose of the present study was to analyze physical and chemical properties of a typical pattern wax used by the regional investment casting industries in the State of Rio Grande do Sul, Brazil and evaluate the possibility of recyclinig, making the necessary adjustment in the formulation of the pattern wax blend.

Some of the properties determined included melting point, flash point, water content, ash content, volumetric expansion, hardness, refractive index, elastic modulus, viscous modulus, viscosity, complex viscosity, infrared and ultraviolet spectra and thermal behavior curves obtained by a differential scanning calorimetry (DSC) and a differential thermal analysis (TGA).

MATERIAL AND METHODS

The two model pattern waxes used in this study were prepared from commercial products. One model, the conventional or standard pattern wax, used by the regional investment casting industries in the State of Rio Grande do Sul, Brazil, consists of 48% by weight pitch, 20% mineral wax, 5% carnaúba palm wax and 2% ethylene vinyl acetate (EVA). The second model, a reformulated pattern wax, consisted of 38% pitch, 40% paraffin, 27% synthetic wax, 2% ethylene vinyl acetate (EVA) and 1% butylated hydroxytoluene (BHT)

The model waxes were prepared in a container equipped with heating and paddle stirring and a hot filtering system. The fusion processes were a performed as follows: a) melting of paraffin and mineral wax (120°c). b) addition and melting of EVA and pitch under continuous stirring until the temperature reached 90°c. c) addition and fusion of carnaúba palm wax. d) stirring for 30 minutes and e) warm filtration followed by cooling.

The microfusion process was simulated starting with 15 kg of pattern wax, dewaxing in an autoclave under the same conditions used by the investment casting industries 7,4 to 7,6 kg/cm^2 of pressure, 170 to 175 °C; 10 minutes dewaxing time followed by cooling and testing under environmental conditions for 24 hours. The reformulated pattern wax was subject to twelve (12) recycling processes.

The infrared spectra were obtained using KBr pellets with a Perkin-Elmer FT-IR Spectrum 1000 Spectrophotometer and the ultraviolet spectra were determined in cyclohexane solution containing 3mg/L of solute using a Shimadzu Model 160 /PC UV-VIS Spectrophotometer.

Thermal and termogravimetric analyses were performed using a TA instrument Model DSC-2010, with inert atmosphere, closed capsule and a heating rate of 10 °C/min and a Netzch Instrument Model STA-409 with an open capsule, an oxidizing atmosphere (a flow of 150 ml of air per minute) and a heating rate of 2,5 °C/min.

The water content of the wax was determined employing a Sartorius Model MA 30 Eletronic Humidity Analyzer at 105 °C for 5 minutes keeping the sample in equilibrium with a hygroscopic environment (60% humidity and –24 °C).

The characterization and monitoring during the successive cycles was done measuring the refractive index (Abbé refractometer at 80 °C with a precision of ± 0,0015); Young Elasticity Modulus (EMIC DL500 Apparatus at 24°C, 85% deformation of 10mm and a rate of 20 mm/min); Shore D Hardness; volumetric expansion (IBER-P-092 Technical Norm) and melting and Flash points using Differential Scanning Calorimetry DSC.

RESULTS AND DISCUSSION

Figure 1 shows the physical appearance of conventional pattern wax-(a) and (c) and reformulated pattern wax (b) and (d).

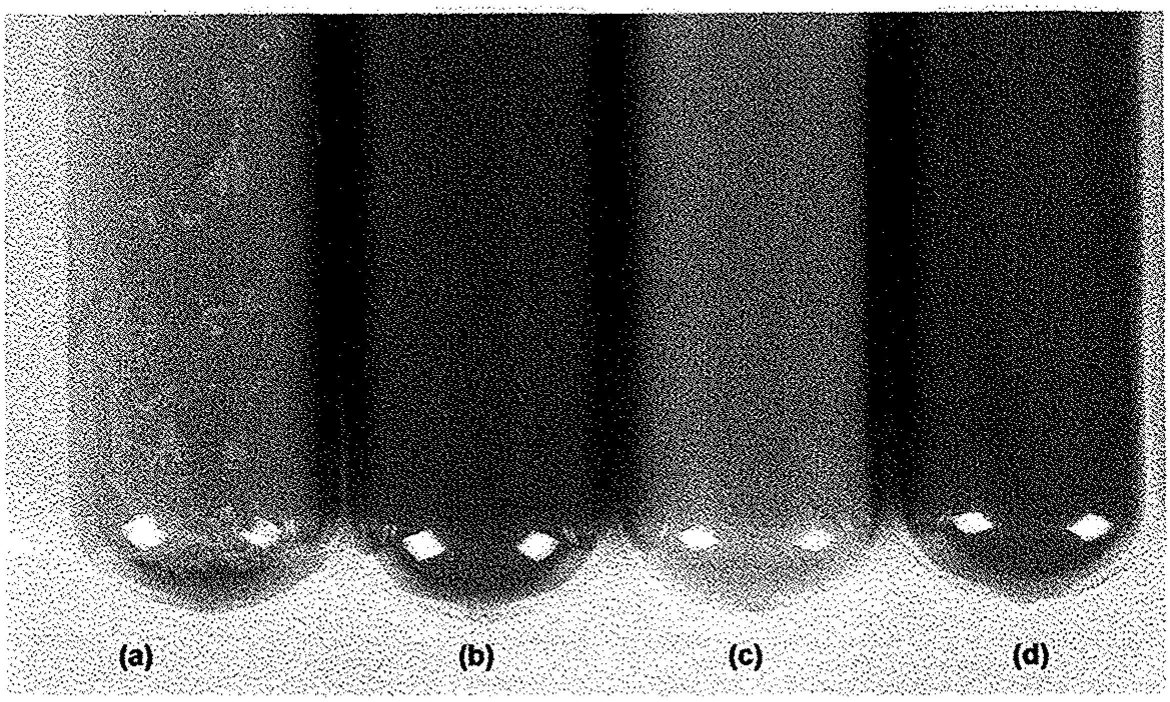

Figure 1. Physical Aspect of Conventional Pattern Wax a) Fused at Rest and c) Fused with stirring and Reformulated pattern Wax b) Fused at Rest and d)Melted with Stirring

The reformulated pattern wax shows no phase separations indicating that the desired structural stability has been achieved.

Figure 2 illustrates the infrared spectra of the standard or conventional pattern wax and the reformulated pattern wax. Absorption bands at 2907, 1469 and 717 cm^{-1} are characteristic ox waxes containing hydrocarbons (paraffins and mineral waxes). The bands at 2907, 1694 and 1277cm^{-1} are typical of acid waxes and the peaks at 3426, 1694 and 1181 cm^{-1} indicative of waxes that contain esters. It is worthwhile to note that no absorption bands occur about 1500 cm^{-1}, indicating the absence of saponificated carboxyl groups.

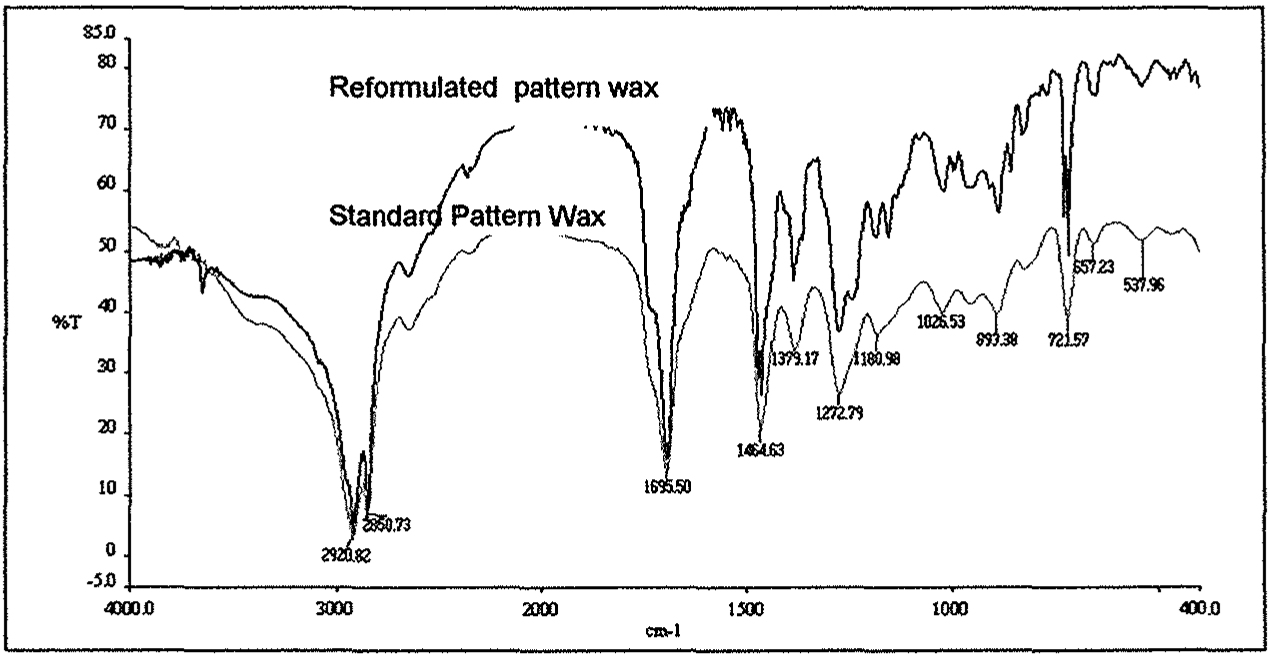

Figure 2. Infrared Spectrum of Standard of Conventional Pattern Wax and Reformulated Pattern Wax.

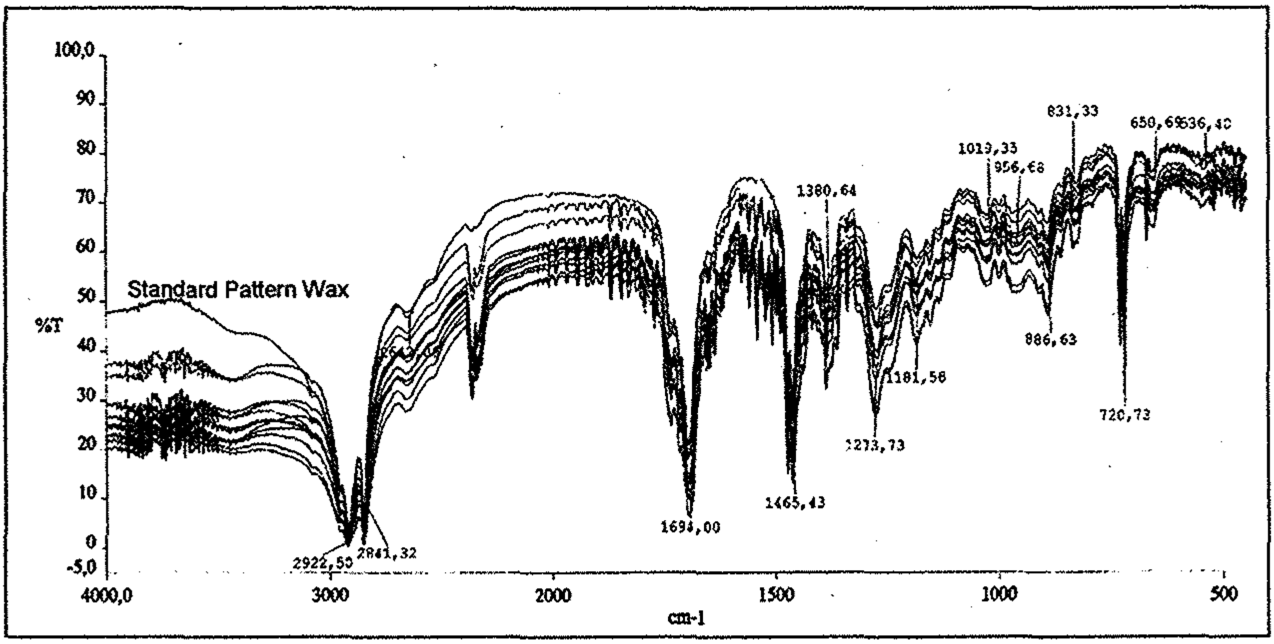

Figure 3. Infrared Spectrum of Reformulated Pattern Wax followed by Spectrum of Simulated Recycled Samples (Odd Numbers).

As can be seen in Figure 3 the recycling of the reformulated pattern wax (cycles 1,3,5,7,9 and 11) has little effect on the IR Spectrum as a whole, indicating the relative stability of the reformulated wax. It should be noted that the spectra were obtained after drying and filtering the recycled sample and removing the dark paticles from the dewaxed waxes.

Figure 4. shows the ultraviolet absorption spectra obtained for the conventional or standard wax and even – numbered recycled samples of reformulated wax.

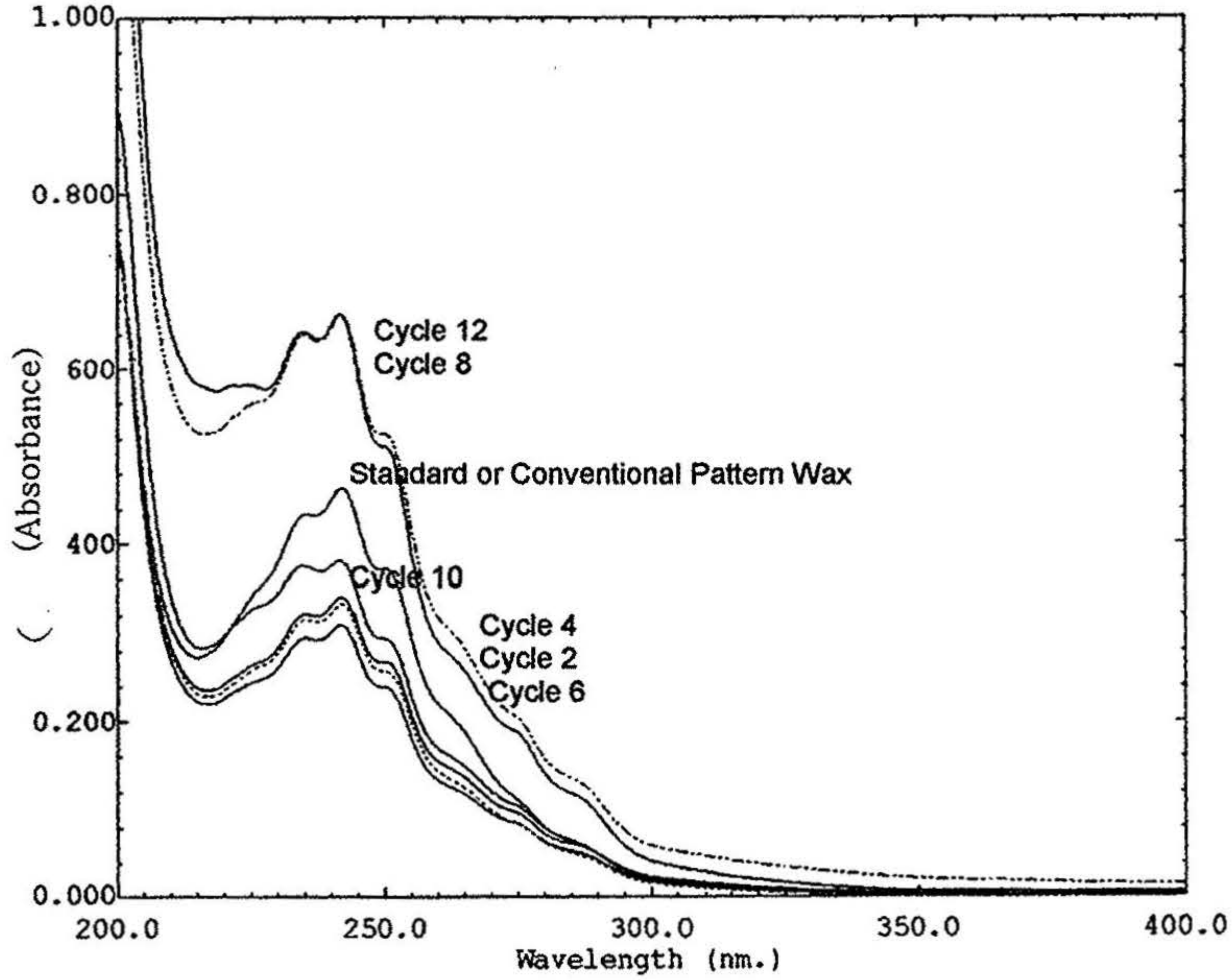

Figure 4. Ultraviolet Absorpition Spectra of Standard or Conventional Pattern Wax and Recycled Sample of Reformulated Pattern Wax (Even – Numbered Cycles).

Some changes in the spectra of the recycled sample are to be noted in the region of 215 to 220 mm. They are however, difficult to interpret, On the whole, it may be concluded that the dewaxing process leads to little oxidation of double bonds of the abietic acid ring, and apparenty no cyclo-additions of the Diels – Alder type, ring condensations and polymerizations take place[17, 18].

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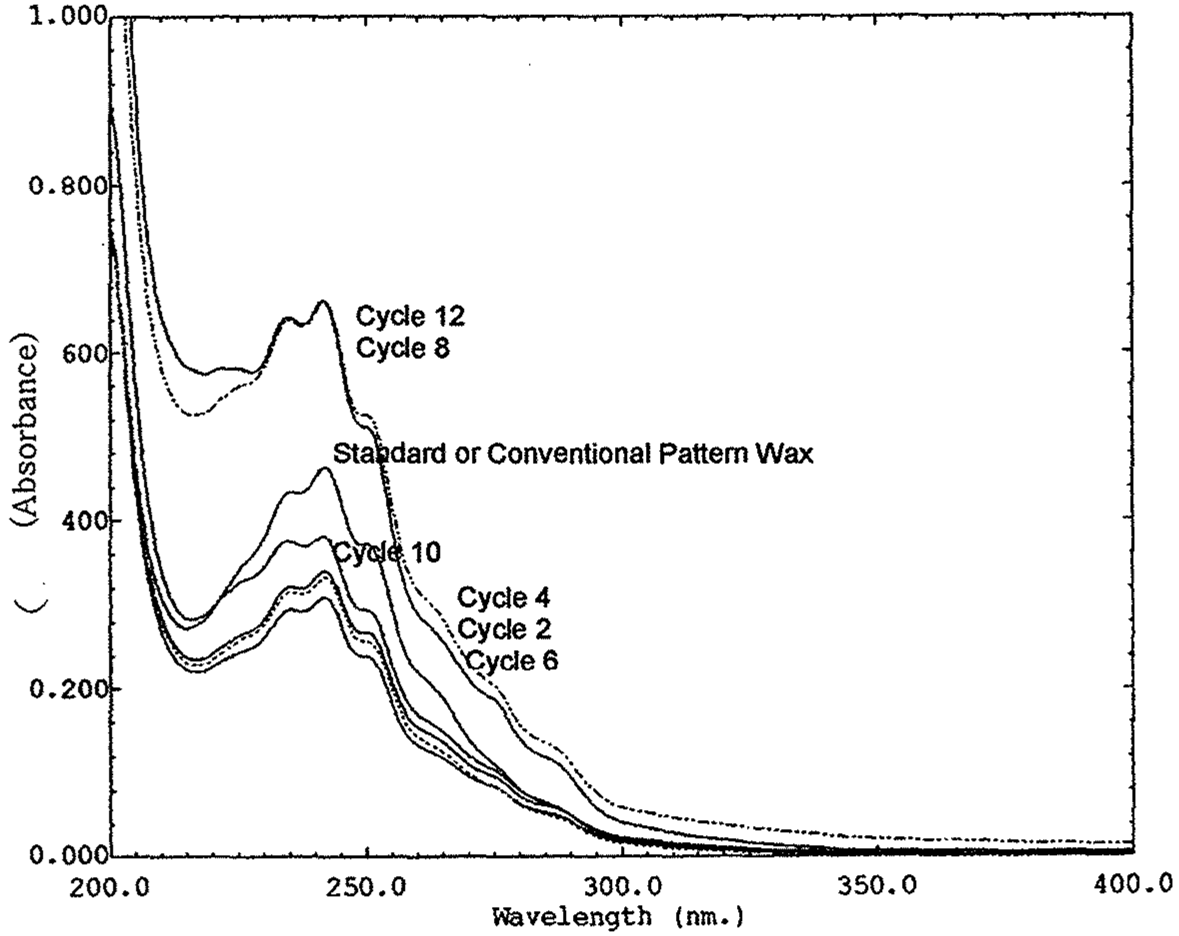

Figure 4. Ultraviolet Absorpition Spectra of Standard or Conventional Pattern Wax and Recycled Sample of Reformulated Pattern Wax (Even – Numbered Cycles).

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Figure 5. ilustrates a typical differential scanning calorimetry (DSC) curve for a conventional pattern wax. The two transitions, melting point at 56,2 °C and the flash point at 253,3 are very distinct.

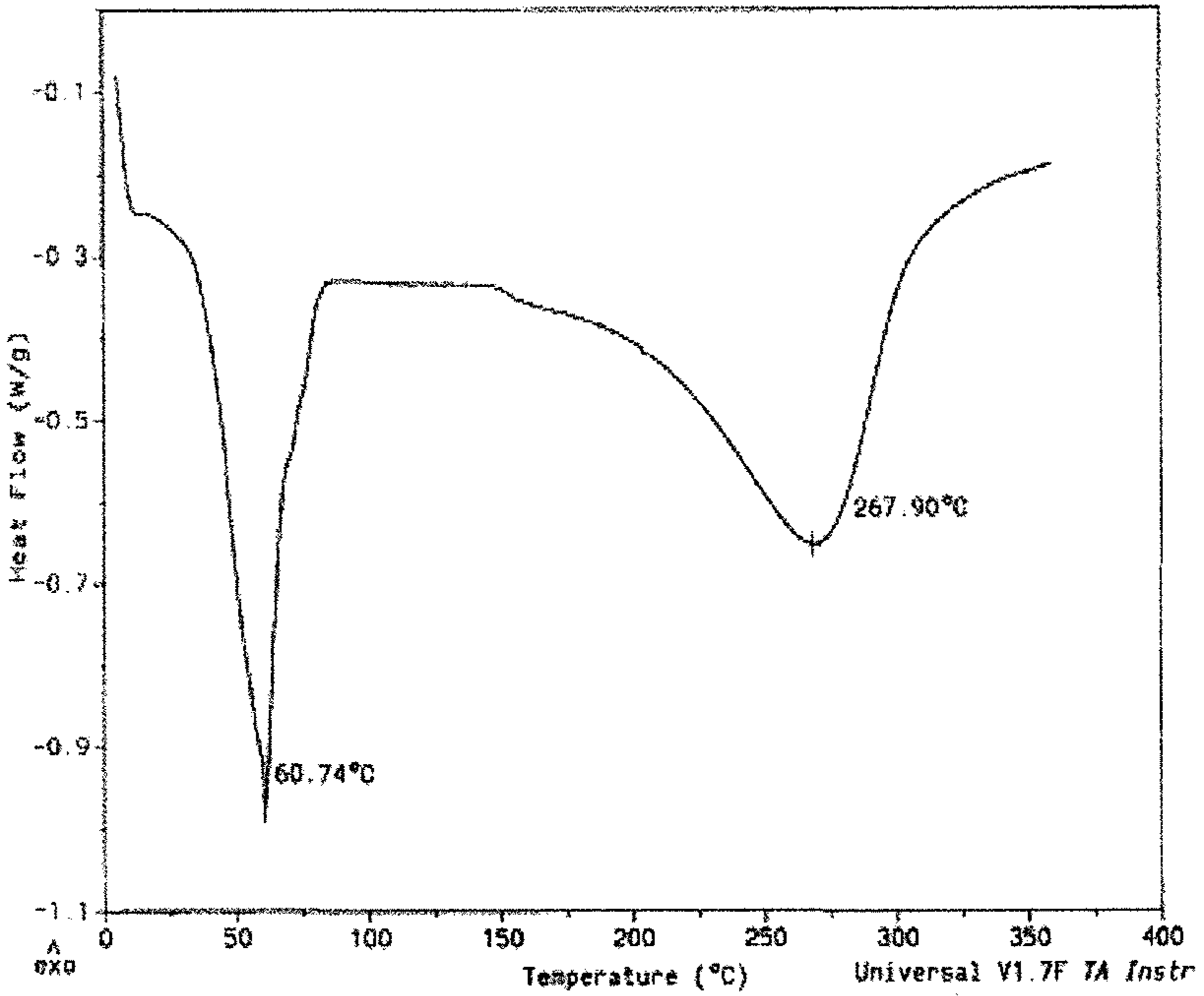

Figure 5. DSC Curve for a Standard Pattern Wax (10 °C/min under N_2 Atmosphere)

Figure 6. shows DSC curves a virgin pattern wax, a dewaxed pattern wax and a dewaxed and dried pattern wax corresponding to the first dried recycling process. Again, the melting and flash points are clearly distinct in all three cases and exhibit essentially the same values. It is interesting to note the presence of a large number of minor peaks for the case of the dewaxed pattern wax indicating the presence of water, essentially in the emulsified and occluded forms. These peaks are absent in the other two cases. Differential Scanning Calorimetry thus appears to be a sensible technique for detecting the presence of water in waxes.

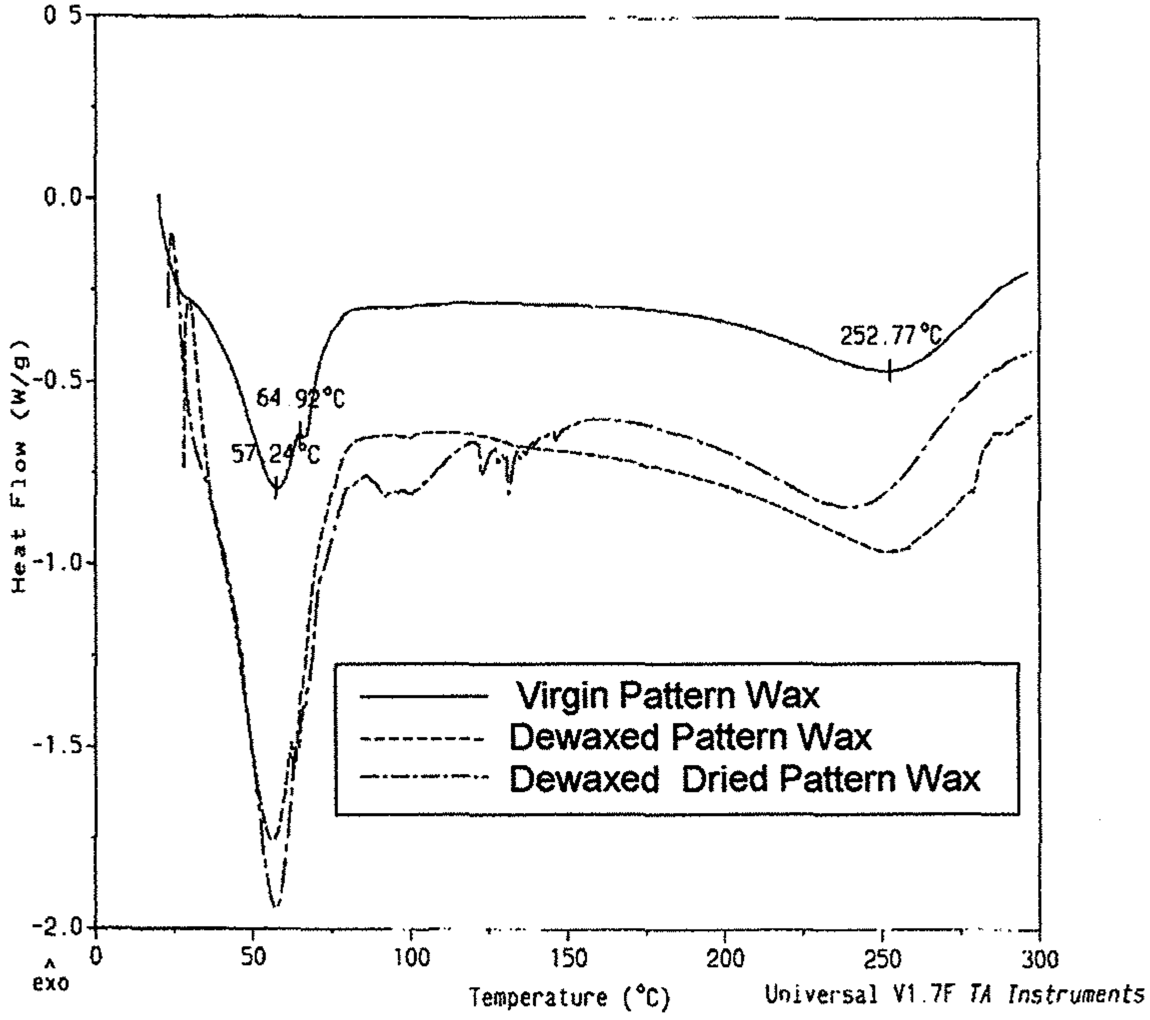

Figure 6. DSC Curves for Virgin Pattern Wax, a Dewaxed Patern Wax and Dewaxed Dried Patern Wax

TG and TGA curves studied the total thermal degradation of pattern wax and representative results are illustrated in Figure 7. The interpretation of the results in terms of TGA and DTA curves leads to three distinct steps. During the first step, below 340 °C (interval A – B) the pattern wax is thermally stable the only processes occurring are melting and loss of humidity. The second step between 340 °C and 470 °C (interval C) involves volatilization and combustion of the fraction of the wax with lower molecular weight. The third step, between 470 °C and 580 °C (interval D) corresponds to the volatilization and combustion of the high molecular weight fraction. The process ends about 600 °C (point E) with total combustion of the wax resulting in an inorganic residue (ashes).

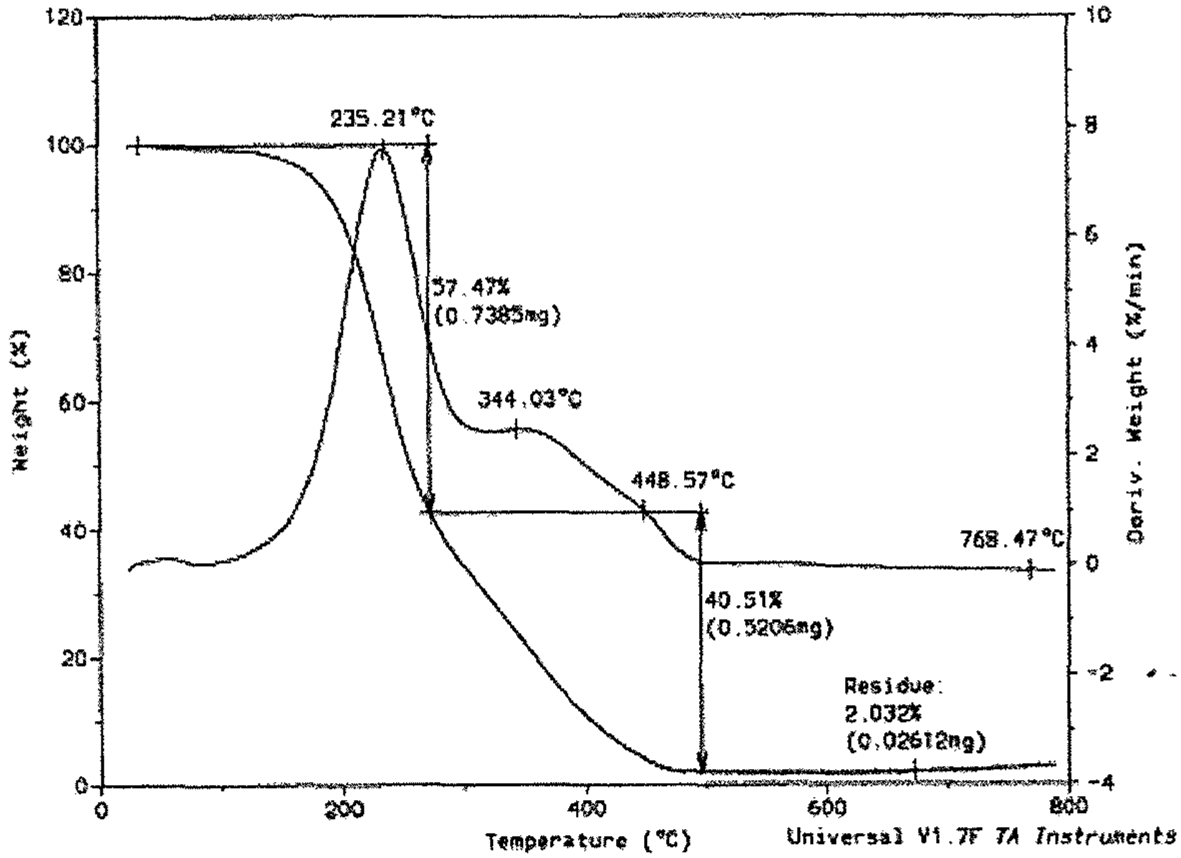

Figure 7. TGA Curve and Its Derivative for a Pattern Wax (Heating Rate 10 °C/min, under Nitrogen Atmosphere).

Table I summarizes the mass loss in percent by weight at different temperatures in the presence of air for pattern wax and some of its components.

Table I. Mass Loss for the Pattern Wax and its Components (%mg) and the Corresponding Temperature in the Presence of Air (40mL/min).

MATERIAL	*Step 1*		*Step 2*		*Step3*	
	°C	Δ%mg	°C	Δ%mg	°C	Δ%mg
Pitch	258,31	83,01		5,98	521,39	10,67
Parafin	263,49	92,63	491,00	7,52	534,75	10,73
Mineral Wax	296,76	77,9	441,57	13,37		
Carnaúba	307,19	64,61	416,94	21,83	495,42	13,62
EVA*	*no mass loss					
Patern Wax	235,21	57,47		40,51		2,03

Analysis of the data in Table I shows that for all the components the preponderant weight loss occurs below 300 °C by volatilization (fumigation) and subsequent combustion of the vapors. The rate of mass loss is an indication of the ease of volatilization and may also show which materials are carried during autoclaving and which may be removed with water. For example, mineral wax is the first to disappear and leaves no residue and thus is easily eliminated and alters the composition and structure of the recycled wax, Carnaúba, on the other hand, volatilized and decomposed more slowly and leaves a lot of residue.

The behavior of pattern wax is different when compared to its components, showing that it is really a blend. The study of the degradation process under oxidizing atmosphere may provide a wealth of information about the reactivity, heats of reaction, kinetics and activation energy of the steps involved.

Figure 8 illustrates some typical Shore D Hardness values obtained for standard pattern wax and the corresponding 12 cycles simulated with and without the presence of ceramic investment at 23 °C.

Similar results are presented in Figure 9 for reformulated pattern wax at 23 °C for the odd numbered cycles simulated.

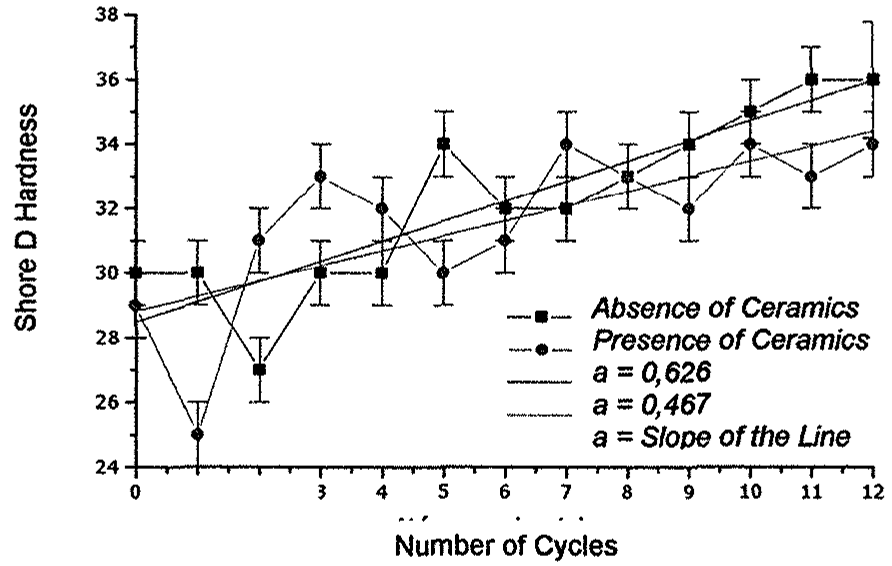

Figure 8. Shore D Hardness for Patter Wax in the Presence and Absence of Ceramics for Twelve Simulated Cycles.

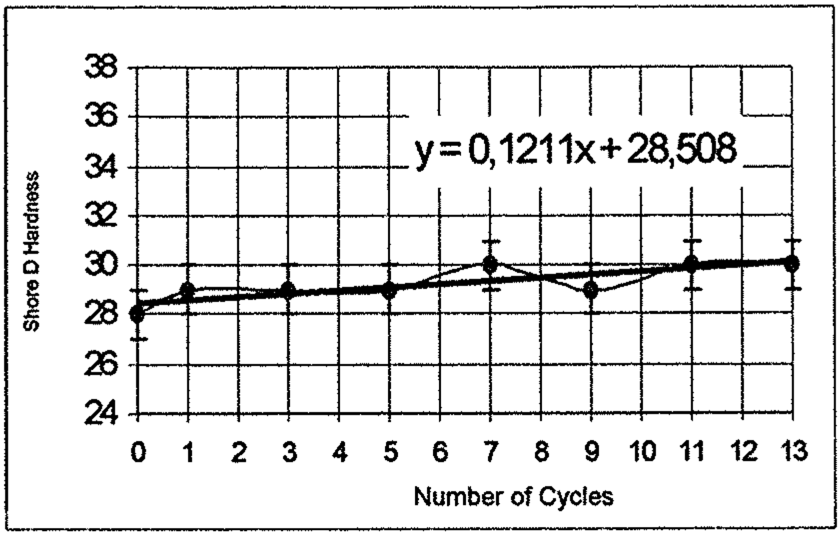

Figure 9. Shore D Hardness for Reformulated Pattern Wax at 23°C for Odd-numbered Cycles Simulated.

The hardness increases in a linear form for samples with or without the presence of ceramics. The slope "a" of the line in Figure 8 may be considered a measure of the degradation of the wax during recycling. The experimental results in all cases sugest a relative small degradation rate and relative structural instability for each cycle.

Similar results are presented for the refractive index of the pattern wax and reformulated pattern wax in Figures 10 and 11, respectively, at 80 °C. As can be seen, the refractive index increases both in the presence and absence of ceramics.

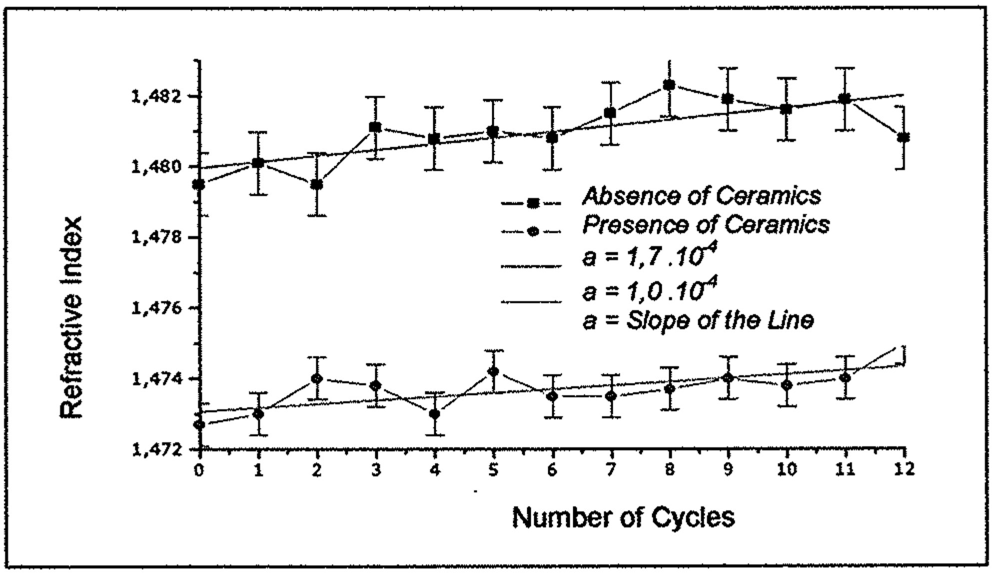

Figure 10. Refractive of Pattern Wax and 80 °C in the Presence and Absence of Ceramics.

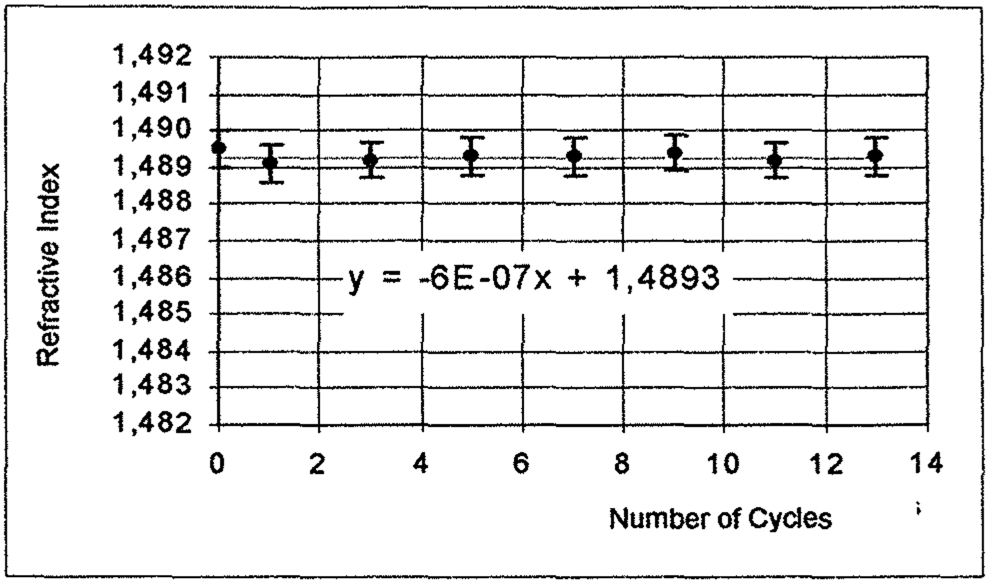

Figure 11. Refractive Index of Reformulated Pattern Wax at 80 °C for Odd-Numbered Simulated Cycles.

The presence of fine ceramic particles decreases as a whole the refractive index as can be seen in Figure 10. Again, the gradual increase of the refractive index as a function of recycling is indicative of a slow and linear degradation of the wax and its structural instability, since the refractive index is directly related to molecular composition.[20]

Volumetric expansion, water content and the modulus of elasticity are not good parameters for determining degradation or decomposition of the wax. On the other hand, they are very sensitive to structural instability, as can be deduced from the results of the recycling processes.

In conclusion it may be stated that the original standard pattern wax and the reformulated pattern wax are heterogeneous dispersions. Pitch added in a high concentration tends to segregate the system causing instability of the mixture.

Wax has typical and reproductive spectra that may be used for its characterization. In the infrared (IR), bands at 2907, 1469 and 717 cm^{-1} are characteristic of paraffin and mineral waxes due to hydrocarbons, the acid fraction has bands at 2907, 1694 and 1277 cm^{-1} and the ester fraction exhibits strong peaks at 3426, 1694 and 1181 cm^{-1}. In the ultraviolet (UV) region there is a strong band at 241 mm characteristc of abietic acid present in pitch.

Differential Scanning Calorimetry (DSC) termal curves for pattern wax are typical and show that the processes occurring below 300 °C are loss of humidity and volatile materials, fusion, fumigation (volatization of inflammable vapors and incipient oxidations. The thermogravimetric (CTG) curves obtained for total thermal degradation indicate that wax contains two characteristic molecular fractions, one that volatilizes and oxidizes between 340 and 470 °C and a second one that undergoes similar processes between 470 and 580 °C. The hot water present in the autoclave mixes with the wax and upon solidification most of it remains occluded in the mixture and the rest is emulsified, beeing associated with polar groups of the wax.

The experimental results obtained for the analysis of sample of pattern wax subject to the simulated recycling show that the main change is random and of a structural nature and that the extent of degradation is very small and can be measured by the refractive index, hardness, viscosity and other dynamical and mechanical parameters.

The shift of the base line of DSC curves indicates that the thermal properties of the wax are changed during the recycling. The change may be due to oxidations and elimination of components by volatilization and carriage.

The infrared spectra show the possible occurrence of cleavage of molecules, oxidations, dehydrogenations, reactions involving functional groups, ring condensations and formation of a new products. Similar processes appear to take place with pitch during dewaxing especially involving dimerization of acid isomers, ring condesantions and double bond oxidations.

The higher homogeneity of the dewaxed wax samples containing ceramics is due to the successive processing steps (filtration, dewaxing and removal of the water during each cycle) that eliminate the incompatible fractions and due to the presence of fine ceramic particles, that improve the structural stability of the wax.

The reformulated pattern wax presented all the prerequisites necessary for sucessful recycling and possible industrial use or application.

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SOLVATION OF THE $[Cr(NCS)_4(IMIDAZOLE)_2]^-$ ION IN ETHANOL - WATER MIXTURES

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ABSTRACT

Solvation kinetics of $[Cr(NCS)_4(imidazole)_2]^-$ has been studied in ethanol-water mixtures at different temperatures. The first stage of the solvation consists of two competitive reactions: two NCS^- ions are exchanged, presumably, by water molecules and simultaneously an imidazole molecule by ethanol, the latter in a second-order reaction, accelerated by hydrogen ions. The exchange of the amine is followed by the substitution of the first two NCS^- ions. The third and fourth NCS^- ions are substituted only in neutral and slightly acidic solutions. Kinetic parameters have been determined for reactions (1), (2) and (4). The influence of the solvent composition and acidity is discussed.

KEYWORDS: complexes of chromium, competitive reactions, mechanism, kinetic parameters, water-ethanol solution.

RESUMO

A cinética de solvatação do íon $[Cr(NCS)_4(imidazol)_2]^-$ foi estudada a várias temperaturas em soluções aquosas de etanol. A primeira etapa de solvatação consiste de duas reações competitivas: dois íons NCS^- são substituidos por moleculas de água e simultâneamente uma molécula de imidazol é substituida por etanol. A segunda reação, que é de segunda ordem, é acelerada por íons de hidrogênio. O intercâmbio da amina é seguido pela substituição dos primeiros dois íons NCS^-. O terceiro e o quarto íon NCS^- são substituidos somente em soluções neutras ou levemente ácidas. Foram determinados parametros cinéticos para as reações (1), (2) e (4). Os efeitos da composição do meio e da acidez do mesmo são discutidas.

INTRODUCTION

In our previous papers [1-7] we described the solvation kinetics of some $[Cr(NCS)_4(amine)_2]^-$ type complexes that have been studied in ethanol-water mixtures, with the following amines: aniline, p-toluidine, p-ethylaniline, p-anisidine and p-phenetidine.

The first stage of solvation consists of two competitive reactions, viz. of the exchange of the first NCS^- ion or of an amine molecule A by the solvent molecules ROH, i.e.

$$[Cr(NCS)_4A_2]^- + ROH = [Cr(NCS)_3(A)_2ROH] + NCS^- \qquad (1)$$
$$[Cr(NCS)_4A_2]^- + ROH = [Cr(NCS)_4(A)ROH]^- + A \qquad (2)$$

Reaction (1) proceeds by a S_{N1} mechanism and is followed presumably by the practically instantaneous reaction:

$$[Cr(NCS)_3(A)_2ROH]^- + ROH = [Cr(NCS)_2(A)_2(ROH)_2]^+ + NCS^- \qquad (3)$$

Reaction (2) seems to be of S_{N2} mechanism. It is accelerated by the presence of mineral acids and is followed by the reactions:

$$[Cr(NCS)_4(A)ROH]^- + ROH = [Cr(NCS)_3(A)(ROH)_2] + NCS^- \qquad (4)$$
$$[Cr(NCS)_3(A)(ROH)_2] + ROH = [Cr(NCS)_2(A)(ROH)_3]^+ + NCS^- \qquad (5)$$

Reaction (4) is analogous with reaction (1). It's kinetic parameters are very close to those characteristic of reaction (1) and reaction (5) is presumably also instantaneous.

In neutral solutions the third and the fourth NCS^- ions are also substituted, according to the equations:

$$[Cr(NCS)_2(A)_2(ROH)_2]^+ + ROH \rightarrow [Cr(NCS)(A)_2(ROH)_3]^{2+} + NCS^- \qquad (6)$$
$$[Cr(NCS)_2(A)(ROH)_3]^+ + ROH \rightarrow [Cr(NCS)(A)(ROH)_4]^{2+} + NCS^- \qquad (7)$$
$$[Cr(NCS)(A)(ROH)_3]^{2+} + ROH \rightarrow [Cr(A)_2(ROH)_4]^{3+} + NCS^- \qquad (8)$$
$$[Cr(NCS)(A)(ROH)_4]^{2+} + ROH \rightarrow [CrA(ROH)_5]^+ + NCS^- \qquad (9)$$

On cannot exclude the possibility that the second amine molecule may be exchanged. Thus, other reactions may also by involved.

Kinetic parameters of reactions (1) and (4) are not influenced sensibly by the nature of the amine molecule, but the rate of reaction (2) depends on the nucleophilic character of the amine, viz. it has lower values if A is p-anisidine or p-phenetidine, when compared to the other amines studied.

EXPERIMENTAL

The synthesis of the imidazole·$H[Cr(NCS)_4(imidazole)_2]$ complex salt been described in our previous paper [10,11].

Kinetic measurements have been carried out in the same way as described earlier in the literature [5].

RESULTS AND DISCUSSION

In the present paper the solvation of the complex ion with A=imidazole has been studied at different temperatures and in ethanol-water mixtures containing 37.7, 48.5, 72.7 and 97.0 percent by volume in ethanol. The concentration of the non-transformed complex ion and the NCS⁻ ions liberated has been followed with time. The concentration of the non-transformed complex ion has been determined colorimetrically and since the validity of Beer's law been observed, the plot of *log A* versus time was used to determine the rate constants. This graphical plot gives very good straight lines, and shows the overall reaction to be of first order. Some examples are given in Figure 1.

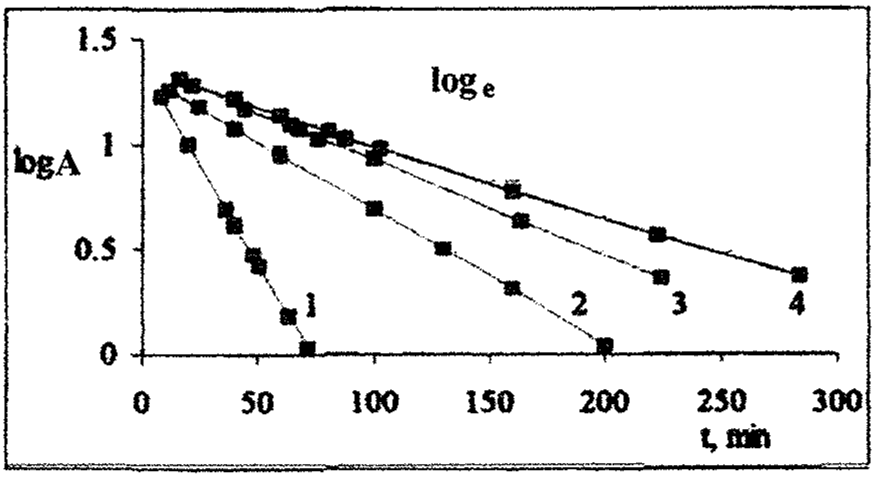

Fig.1 Determination of overall first order rate constants k 1. 48.5% EtOH, 40°C; 2. 72.7% EtOH, 40°C; 3. 97.0% EtOH, 40°C; 4. 48.5% EtOH, 40°C.

Rate constants derived from the slope of these straight lines are presented in Table 1. The graphical plot of log_e *k/T* values versus *1/T* enabled us to calculate the apparent activation energy and entropy values. Both decrease systematically with increasing ethanol content of the solvent, as is seen from Table 1.

Table 1 Kinetic parameters of the overall process

EtOH content (%Vol.)	$k \cdot 10^3 sec^{-1}$				$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ e.u.
	40°C	45°C	50°C	55°C		
37.7	0.098	0.236	0.541	1.18	33.3	29.2
48.5	0.136	0.309	0.698	1.46	31.7	24.5
72.7	0.177	0.381	0.803	1.74	30.2	21.2
97.0	0.242	0.513	1.082	2.23	29.5	19.1

In order to find the fraction of reactions (1) and (2) in the overall reaction, the ratio between the concentration C_1 of NCS⁻ ions liberated and the complex transformed,

$r=C_1/(C_0-C)$ has been determined (C_0 and C stand for the initial and actual concentration of the complex ion studied). As in the case of the complexes investigated earlier, a finite zero-time NCS^--ion concentration has been found and in order to estimate the concentration NCS^- liberated, C_1-values have been corrected with the zero-time values, obtained by means of extrapolation of experimental data.

Similarly to the analogous complexes, the ratio has a practically constant value at the beginning of the solvation process and it depends only on the ethanol content of the solvent and not on the temperature. The plot of r versus transformation degree of the complex is shown in Figure 2.

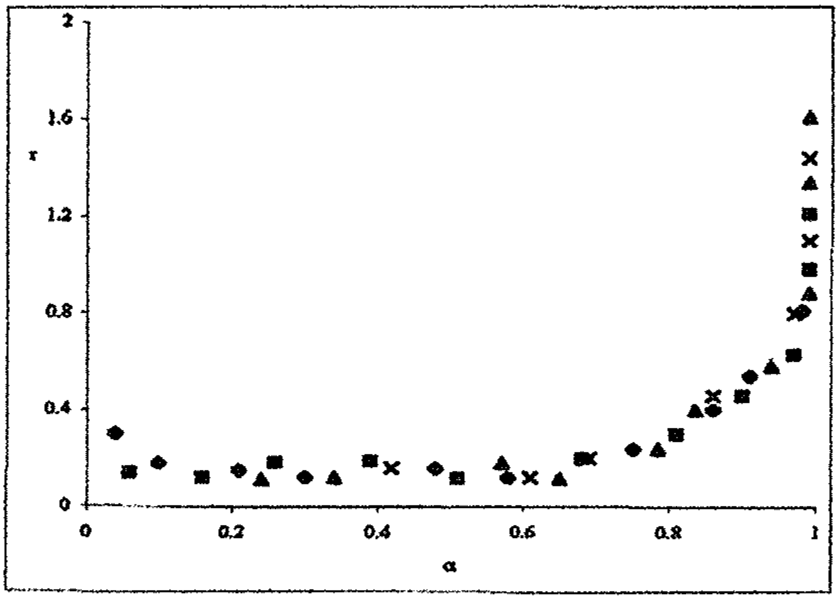

Fig.2 Ratio $r=C_1/(Co-C)$ as function of transformation degree α. 48.5% EtOH;
♦ 40°C; ■ 45°C; ▲ 50°C; x 65°C.

The shape of the r - α curves is also similar for other ethanol concentrations. The nearly constant initial r values, which are referred to as r_0, are the following:

Ethanol content (Vol. %)	37.7	48.5	72.7	97.0
r_0	0.26	0.17	0.091	0.052

The small r_0 values show that reaction (2) plays an important part in the overall process. By using the above given r_0 values, the rate constants k_1 and k_2 of reactions (1) and (2) can be derived from the overall first-order rate constant k. In order to diminish the influence of experimental errors, calculations have been carried out by using corrected k values, derived from $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values given in Table 1, instead of the experimentally determined ones. In these calculations reaction (3) has been presumed to be instantaneous.

This presumption seems to be sound, since in the case of the Reinecke salt, with $A=NH_3$ [8] and also in the case of the analogous benzylamine derivative [9], where the amine molecules are not substituted, $r_0 \approx 2$ has been observed, which means the practically simultaneous exchange of the first two NCS⁻ ligands. By adopting this reaction scheme, the individual first-order rate constants k_1 and k_2 can be calculated according to the following formulae:

$$k_1 = kr_0/2 \text{ and } k_2 = k(1-r_0/2) \qquad (10)$$

The results are given in Table 2.

Rate constants k_1 are a little larger than for the analogous complexes studied earlier and show a systematic decrease with increasing ethanol content. This variation is much larger than previously observed. The first order rate constants k_2 increase simultaneously with the ethanol content and the ratio k_2 to molar concentration of ethanol is practically constant for a given temperature. One may presume the amine molecules to be substituted only by ethanol by an S_{N2} pathway. The corresponding second-order constants k'_2 are given in Table 2. These values are close to k'_2 obtained for the analogous complexes when A-p-toluidine and p-ethylaniline [4,5].

Table 2. Rate constants of reactions (1) and (2)

EtOH content (%Vol.)	Rate const.	Temperature			
		40°C	45°C	50°C	52°C
37.7	$K_1 \cdot 10^5 sec^{-1}$	1.34	3.15	7.28	16.1
48.5		1.11	2.46	5.44	11.8
72.7		0.781	1.70	3.65	7.75
97.0		0.602	1.27	2.66	5.53
37.7	$K_2 \cdot 10^4 sec^{-1}$	0.864	2.01	4.63	10.3
48.5		1.25	2.86	6.25	13.6
72.7		1.67	3.64	7.83	16.4
97.0		2.36	5.04	10.52	21.6
37.7	$K'_2 \cdot 10^4 sec^{-1}$	1.133	0.319	0.726	1.64
48.5		0.152	0.344	0.765	1.65
72.7		0.131	0.297	0.634	1.32
97.0		0.140	0.306	0.639	1.30

The influence of acidity upon the solvation kinetics has been studied in solution with 37.7 percent ethanol, by adding various amounts of perchloric acid. The results obtained are given in Table 3.

The general picture is the same as observed in our previous papers: k_1, r_0, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ decrease with increasing in perchloric acid concentration, i.e. reaction (1) is hindered and reaction (2) is, on the contrary, enhanced. At concentration higher than 10^{-2} M, the rate constant k_1 is practically not influenced by the acidity. Generally, increasing acidity and increasing ethanol content make k_1 and k_2 vary in the some direction, but a partial reaction order can be found only in the case of k_2 and only for ethanol. The order effects involve presumably different pre-equilibria.

Table 3. Influence of perchloric acid on the kinetic parameters. (37.7% EtOH)

$[HClO_4]$ (mole/l)	Rate const.	Temperature				$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ e.u.	r_0
		40°C	45°C	50°C	55°C			
10^{-4}	$k \cdot 10^3 sec^{-1}$	0.112	0.245	0.535	1.38	31.1	22.6	0.141
10^{-3}		0.134	0.301	0.642	1.30	30.4	21.4	0.092
10^{-2}		0.164	0.343	0.767	1.55	31.3	21.5	0.034
10^{-1}		0.193	0.422	0.871	1.81	29.3	18.6	0.023
10^{-4}	$k_1 \cdot 10^5 sec^{-1}$	0.786	1.76	3.82	8.09			
10^{-3}		0.601	1.31	2.87	5.97			
10^{-2}		0.281	0.611	1.33	2.74			
10^{-1}		0.244	0.521	1.11	2.22			
10^{-4}	$k_2 \cdot 10^4 sec^{-1}$	0.103	0.230	0.507	1.06			
10^{-3}		0.129	0.281	0.606	1.29			
10^{-2}		0.156	0.346	0.735	1.56			
10^{-1}		0.193	0.411	0.864	1.74			

The kinetic parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the overall reaction decrease when the part played by reaction (2) increases. This suggest the idea, that both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of reaction (1) are higher than the same parameters for reaction (2). We could not obtain individual values, since our experimental data were too scattered to evidence the influence of temperature upon the initial ratio r_0.

In order to obtain additional information concerning the second stage of the solvation process, i.e. reactions (4) – (9), the excess concentration C_{ex} of NCS^- ions has been calculated by subtracting from the experimental free NCS^- concentrations the theoretical C_1, calculated from k_1 values, taking also in to account the instantaneous reaction (3).

Results expressing the influence of temperature, ethanol content and of the acidity on this excess concentration are given in Figs. 3-5.

From these figures it is apparent, that the third and fourth NCS^- ions are also substituted in neutral and in slightly acidic solution.

However, the rate of this reaction decreases considerably with increasing ethanol content. The NCS^- ions are presumably exchanged by water molecules, which may be involved in the reaction mechanism too.

Fig. 5 shows reactions (6) – (7) to be entirely hindered in highly acidic solutions and the excess NCS^- ion concentration to be due only to reactions (4) and (5). By using a curve fitting method, described earlier [4-7] rate constants k_4 of reaction (4) can be derived from the C_{ex}-time curves for concentration of $HClO_4 = 10^{-2}$ and 10^{-1} M, on the presumption that reaction (5) was instantaneous. The procedure is illustrated by Fig. 6, showing several theoretical curves calculated for different k_4 values, as well as experimental data.

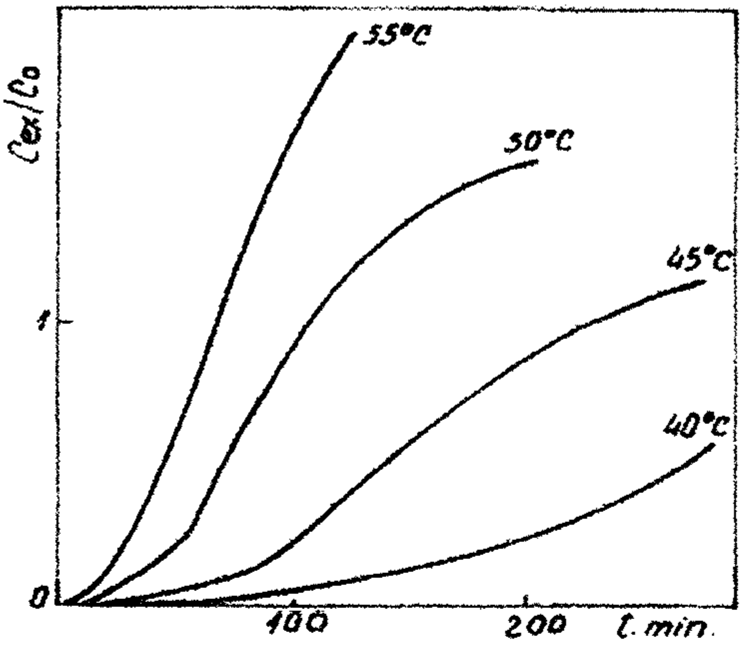

Fig. 3 Influence of temperature on the excess NCS⁻ concentration.
(37.7% ethanol by volume)

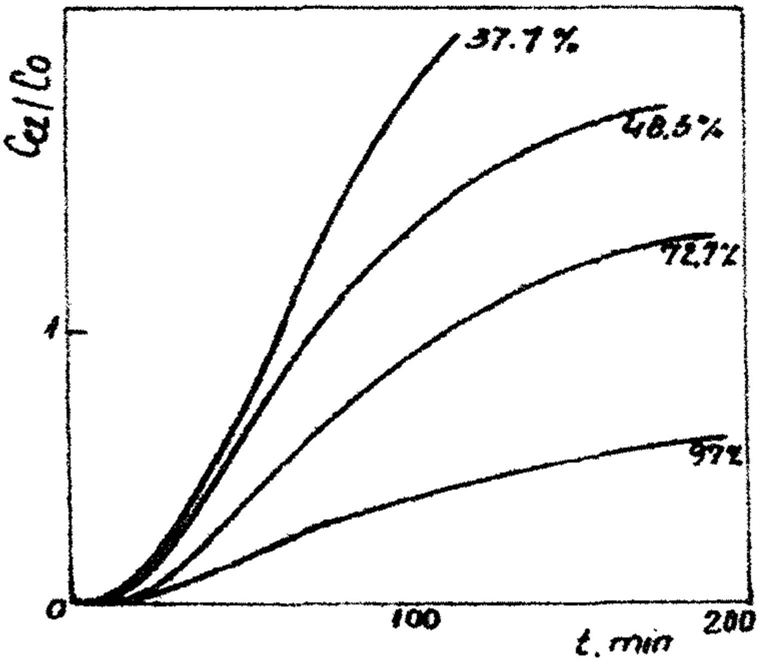

Fig. 4 Influence of the ethanol content on the excess NCS⁻ concentration. 55°C

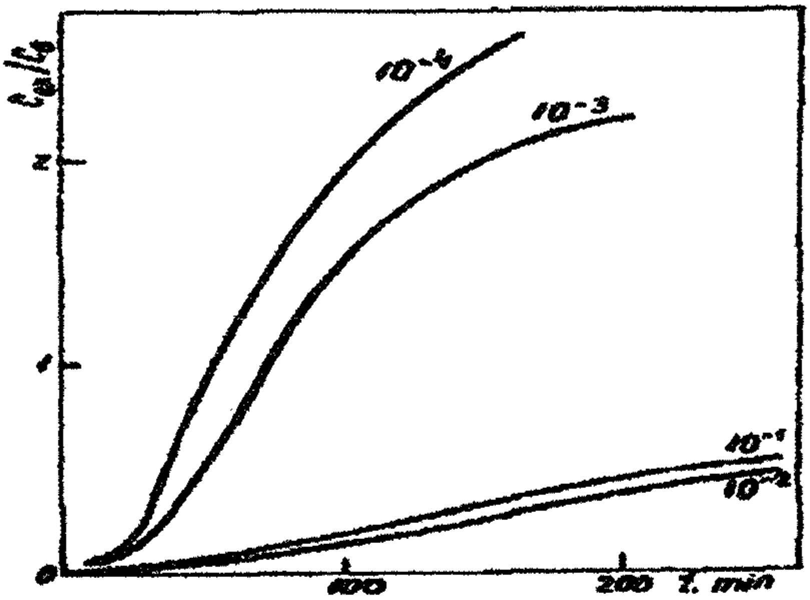

Fig. 5 Influence of perchloric acid concentration (in mole/1) on the excess NCS^- concentration. (37.7% EtOH, 55°C.)

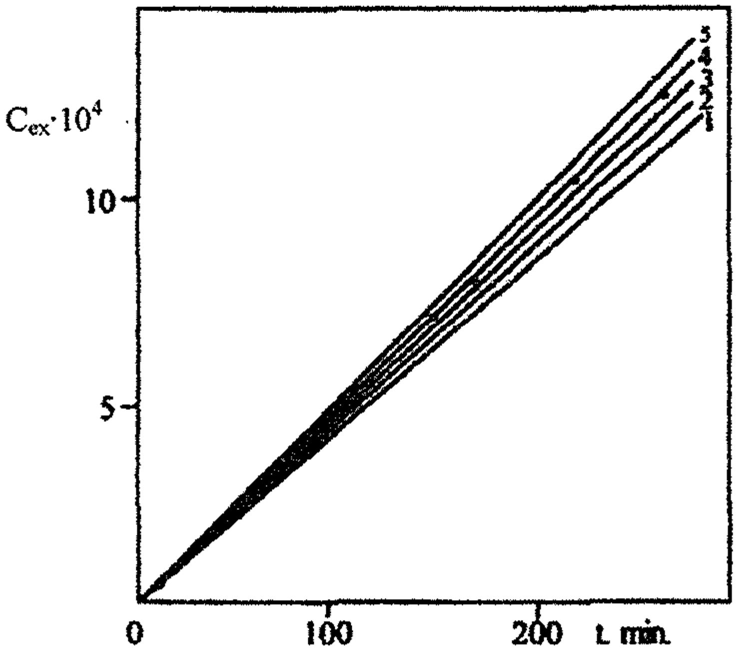

Fig. 6 Determination of k_4 by means of the curve fitting method. (37.7% EtOH. 55°C.)
Conc. of $HClO_4 = 10^{-1}$ M. Presumed $k_4 \cdot 10^5$ values:
1 and 2.0; 2 and 2.1; 3 and 2.2; 4 and 2.3; 5 and 2.4

Rate constants k_4 determined by means of this procedure are presented in Table 4.

Table 4. Rate constants of reaction (4) in acid solutions $k_4 \cdot 10^5 sec^{-1}$, (37.7% ethanol by volume)

t°C	$[HClO_4]$, (mole/l)	
	10^{-1}	10^{-2}
40	0.28	0.29
45	0.58	0.58
50	1.17	1.13
55	2.28	2.32

Values obtained are very close to k_4 values for analogous complexes studied earlier [4-7].

The plot of $\log(k_4/T)$ versus $1/T$, given in Fig.7, shows a good linearity and enabled us to calculate, by means of the least square method, the following kinetic parameters of reaction (4). $\Delta H^{\neq} = 27.6 \pm 0.6$ kcal/mole, $\Delta S^{\neq} = 3.6 \pm 2.0$ e.u.

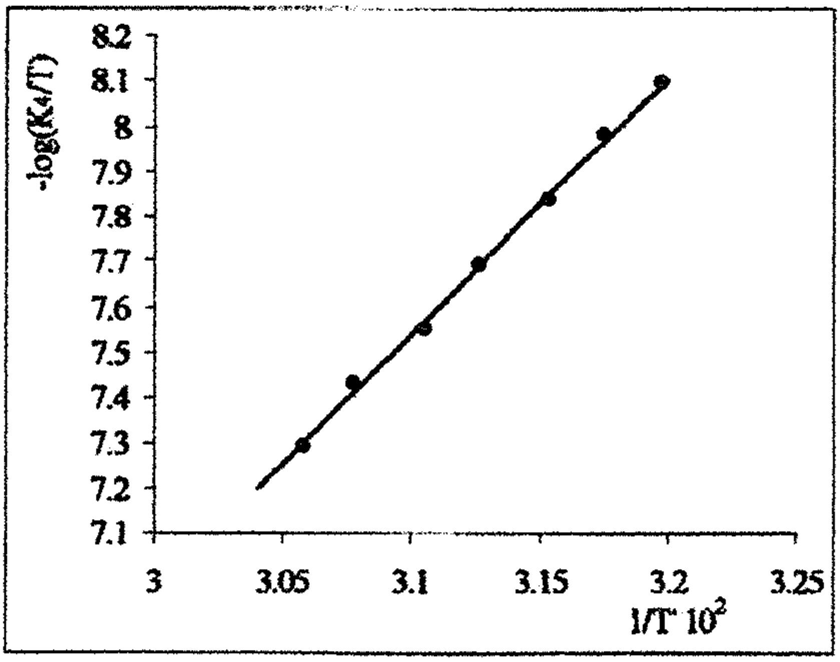

Fig.7 Determination of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in acid solution.(37.7% ethanol by volume)

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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A STUDY OF PARAMETERS RELATED TO ANALYSIS OF TRANSITION TEMPERATURES AND ENTHALPIES OF POLYPROPYLENE BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

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ABSTRACT

Polypropylene is a thermoplastic polymer, widely employed by converter industries to produce different plastic objects. In order to control and optimize the final properties of the polypropylene material, the evaluation of transition temperatures and enthalpies by Differential Scanning Calorimetry (DSC) has a very important role. Therefore, it is fundamental to know how the analytical conditions influence the results. In this study heating and cooling rates, 10°C/min and 20°C/min, and two different rates of nitrogen flow, 20 mL/min and 50 mL/min, were investigated. It was concluded that thermal properties are influenced by rates of heating and rates of nitrogen flow. Best precision was obtained with the low heating rate, 10°C/min, and high flow rate, 50 mL/min. These conditions are being used with the DSC method for polyolefin quality control and material characterization.

KEY WORDS: Polypropylene, Differential Scanning Calorimetry, Thermal Analysis.

RESUMO

O polipropileno é uma resina termoplástica largamente utilizada por transformadores na produção de diferentes artefatos plásticos e a determinação das temperaturas de transição e das entalpias por Calorimetria Exploratória Diferencial (DSC) é extremamente importante no sentido de controlar e otimizar as propriedades finais do polímero. Assim, é fundamental conhecer a influência das condições analíticas nos resultados, sendo que neste trabalho foram avaliados os efeitos das taxas de aquecimento e resfriamento de 10°C/min e 20°C/min, e dos fluxos de nitrogênio de 20 mL/min e 50 mL/min. Foi possível concluir que as propriedades térmicas são influenciadas pelas taxas de aquecimento e resfriamento e pelos fluxos de nitrogênio. A maior precisão nas determinações foi obtida com taxa de aquecimento de 10°C/min e com fluxo de nitrogênio de 50 mL/min. Estas condições foram adotadas no método de DSC para controle de qualidade e de caracterização de poliolefinas.

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INTRODUCTION

Polypropylene is a thermoplastic polymer widely employed by converter industries for different applications such as fibers (carpets, tape, cordage, nonwoven fabrics,...), injection molded products (rigid packaging, home appliances, ...), films, automotive parts and others.

The growing use of polypropylene (PP) for the plastic compounders and processors can be related to both low cost and thermal and mechanical properties of the material. They allow its use in the production of fibers, films, parts molded by injection, etc[1]. The final properties of the PP product depends on polymerization conditions, stabilization recipies and other variables. In order to design the performance of the compound, the evaluation of melting temperature (Tm), crystallization temperature (Tc), enthalpies of fusion (ΔHf) and crystallization (ΔHc) by Differential Scanning Calorimetry (DSC) are very helpful[2]. Therefore, it is important to improve the analytical conditions and this study represents an effort to understand the effect of variables such as heating and cooling rates and nitrogen flow.

METHODOLOGY

In this work samples of PP random copolymer and PP homopolymer produced by the bulk polymerization according to the Spheripol process were analyzed. The DSC equipment used was the DSC 2920 from T.A. Instruments previously calibrated with In and Sn. Approximately 6 mg of the sample was weighed and placed inside an aluminum pan. In order to get the results, every experimental measurement was evaluated ten times. The analytical conditions follow ASTM standards[3,4] and the variables evaluated are presented in Table 1.

Table 1. Variables Studied

Variable Description*	Heating and Cooling Rate (°C/min)	Nitrogen Flow (mL/min)
R10F20	10	20
R20F20	20	20
R20F50	20	50

*** R means rate, 10°C/min or 20°C/min, and F means flow, 20 mL/min or 50 mL/min;**

RESULTS AND DISCUSSION

Figure 1 illustrates typical results obtained for the melting temperature (Tm) and Figure 2 shows a representative result measured for the crystallization temperature (Tc).

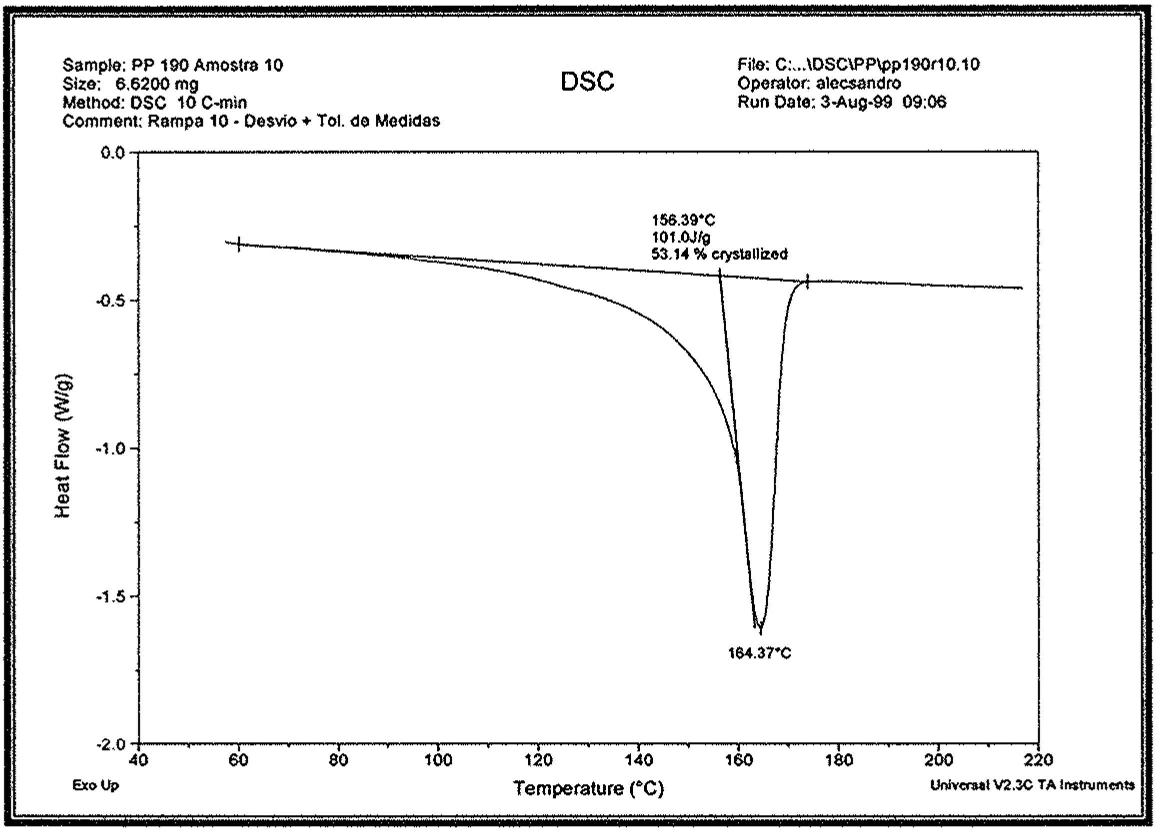

Figure 1. Determination of Melting Temperature of a Polypropylene (PP) Sample by DSC

Table 2 presents the results for the analysis keeping the nitrogen flow at 20 mL/min and changing the heating/cooling rates. In the calculation of the crystallinity, it was considered that PP (100% crystalline) releases 190 J/g. The statistical values are related to 95% confidence level and the Dixon test was done to exclude outliers.

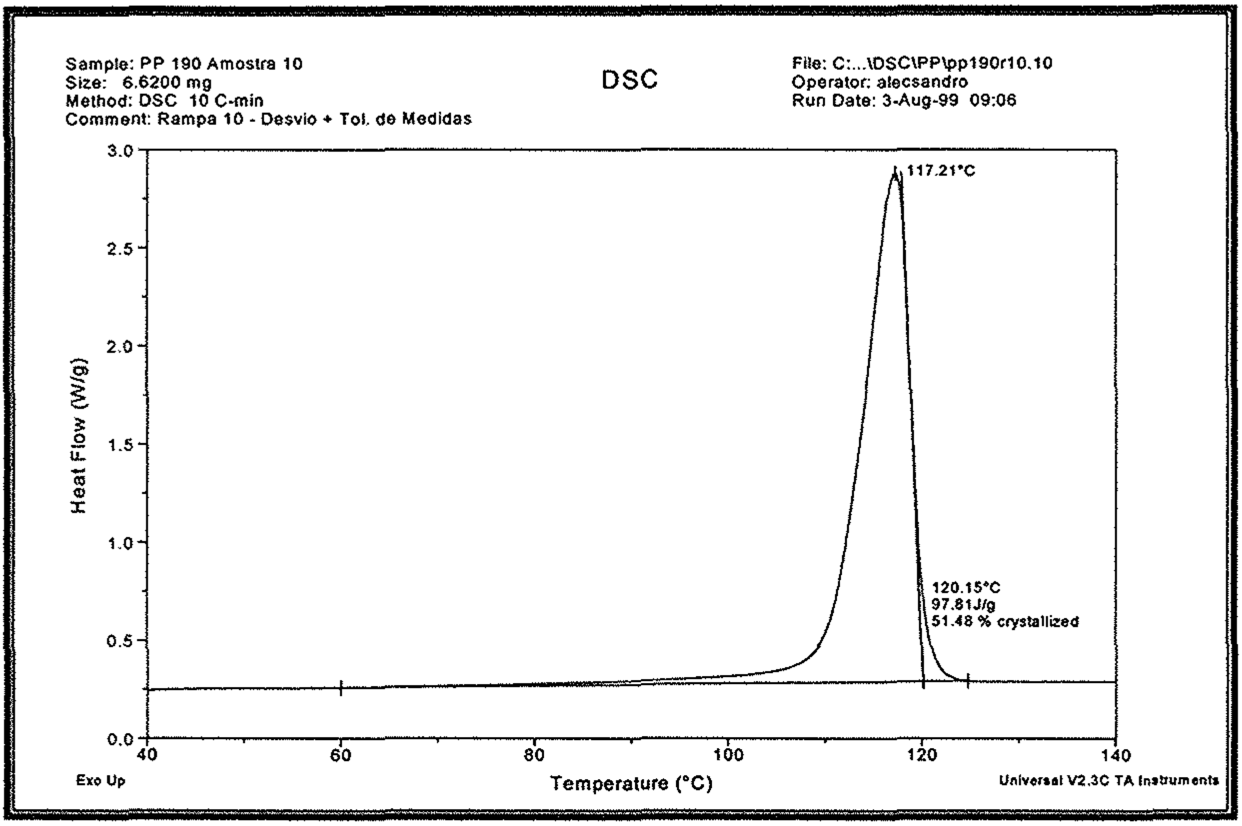

Figure 2. Evaluation of the Crystallization Temperature Tc for a Polypropylene (PP) Sample by DSC

Table 2. Results of Properties of PP Obtained Changing Heating Rates and Constant Flow

Property	Tm (°C)		Tc (°C)		ΔHf (J/g)		ΔHc (J/g)	
Condition*	R10F20	R20F20	R10F20	R20F20	R10F20	R20F20	R10F20	R20F20
Results	164,44	163,56	117,16	113,41	107,93	101,87	99,15	97,76
Crystallinity (%)	-	-	-	-	57 ± 1	54 ± 1	52 ± 1	51 ± 1
CL (±)	0,16	0,36	0,29	0,35	1,73	2,07	1,30	1,66
CV (%)	0,14	0,30	0,34	0,41	2,25	2,41	1,83	2,64
R	0,72	1,55	1,28	1,53	7,75	8,02	5,80	7,42

* R means rate, 10°C/min or 20°C/min, and F means flow, 20 mL/min or 50 mL/min;

Significance tests were used to decide if there were differences between the conditions. The results are shown on Table 3.

Table 3. Significance Test Results

Test	Method Precision (Variance)		Average Comparison
Item	F Snedecor Test	Cochran Test	t Test
Tm	Rate 10°C/min and flow 20 mL/min has better precision	Rate 10°C/min and flow 20 mL/min has better precision	Averages are different
Tc	No differences	-	Averages are different
ΔHf	No differences	No differences	Averages are different
ΔHc	No differences	No differences	Averages are different

The following equations were applied:

$$CL = \frac{ts}{\sqrt{n}}$$

$$CV = \frac{s.100}{X}$$

$$R = ts\sqrt{2}$$

where,

CL = confidence limits,
t = coefficient from t Student distribution,
s = standard deviation of a sample,
n = sample size,
CV = coefficient of variation or relative standard deviation,
X = arithmetic mean of a sample,
R = repeatability.

It is possible to conclude that the analytical procedure with the low heating rate has better precision in the Tm determination than the condition using 20°C/min. No precision differences were noticed in the other evaluations but the methods are really different.

Tests were carried out keeping the heating/cooling rate at 20°C/min and changing the nitrogen flow from 20 mL/min to 50 mL/min. The results and the statistical interpretation of the analysis are presented on Tables 4 and 5.

Table 4. Property Results Changing Flow Rate and Keeping the Heating Rate Constant

Temperature	Tm (°C)		Tc (°C)	
Condition*	R20F50	R20F20	R20F50	R20F20
Average Value	163,92	163,56	112,91	113,41
Nitrogen Flow (mL/min)	50	20	50	20
CL (±)	0,22	0,35	0,22	0,36
CV (%)	0,19	0,30	0,28	0,41
R	0,97	1,55	1,00	1,53

* R means rate, 10°C/min or 20°C/min, and F means flow, 20 mL/min or 50 mL/min;

Table 5. Significance Test Results

Test	Method Precision (Variance)		Average Comparison
Item	F Snedecor Test	Cochran Test	t Test
Tm	No differences	No differences	No differences
Tc	No differences	-	Averages different

No significative differences between the precision and methods averages were noticed but there is a tendency that the better precision is obtained using the high flow.

CONCLUSIONS

The heating/cooling rate alter the results and the best precision is obtained using 10°C/min rate. Anyway, the differences are not big. Changing the nitrogen flow from 20 mL/min to 50 mL/min seems optimize the precision a little bit.

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METAL COMPLEX TETRAIZOINDOLES AS SENSOR MATERIALS

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ABSTRACT

The paper presents the synthetic routes for obtaining of some organic semiconductors and their characterization in order to use in thin film deposition for gas sensing devices.

An original technique was used to control the molecular weight of polymeric phthalocyanine.

We have fabricated devices consisting of evaporated thin films of copper, nickel and iron phthalocyanines onto interdigital electrodes and estimated the electrical conductivity by in-situ measurements. The films were evaporated onto substrates (gold or aluminum) which were entirely integrated in the standard CMOS (capacitor metal oxide semiconductor) technology.

The objectives of this work were to improve the synthesis methods of organic metal-complex tetraizoindoles and their polymers and to evaluate their electrical response and thermal stability as evaporated thin films. We have also investigated the variation of polymers conductivity and sublimation yield with the average molecular weight. We found that for polymeric phthalocyanines, the thermal stability was higher than for Pcs monomers. The stability of polymers increased with the average molecular weight.

Keywords: organic semiconductors, phthalocyanine, polymers, electrical measurement, thermal stability.

RESUMO

Este trabalho trata da síntese e propriedades de películas finas de ftalocianinas de Cu, Ni e Fe. Em particular, foram determinadas propriedades tais como peso molecular, estabilidade térmica de ftalocianinas poliméricas, condutividade in- situ. As películas foram evaporadas sobre substratos de Au ou Al completamente integrados na teconologia CMOS. A condutividade elétrica está relacionada ao tamando do sistema conjugado de eletrons -π e os gases adsorvidos sobre os filmes finos.

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1. Introduction

Monomeric and polymeric compounds of metallic phthalocyanines (MePcs) are of great interest in material science because of their electronic and photophysical properties. The use of these materials is expected to significantly increase the performance of gas detection devices for NO, NO_2, CO, NH_3, and other gases. MePcs are proved to be organic semiconductors; the majority of carriers in double sublimated CuPc are p-types carriers [1].

One of the best-known molecules in cell signaling is nitric oxide (NO). It has a wide range of functions including regulation of blood pressure and neurotransmission. Since its half-life is very short (in range of seconds), devices detecting small amounts of NO have to be enough sensitive to overcome such difficulties. Solid MePc (Me=Mn, Co, Cu, and Fe) have been reported to axial coordinate NO [2]. The coordination between the central metal and the NO molecule was accompanied by some electron transfer phenomena.

Thin films of PbPc (lead phthalocyanine) have been shown particularly sensitive to NO_2, with useful response to Cl_2 and very low sensitivity to electron donor gases. For reversibility and minimized effects of water vapor, most of the work on these devices has been carried out at 100^0C. The film sensitivity decreases with the increasing of temperature above 160^0C, because of strong adsorption and reaction of oxygen with the lead atom.

In metal-free, NiPc or FePc there is no evidence of a similar process[3]. PbPc, NiPc and CuPc show significant changes in IR adsorption spectra following high-temperature (>300^0C) treatment. These changes are consistent with the modification in polymorphism of Pcs from the α-phase to the β-phase (for CuPc and NiPc). For PbPc, which has no α or β polymorphism, the observed properties seem to be due to the non-planar structure the single crystal.

Evaporated thin films of CuPc exhibit reversible changes of conductance in the presence of very small (ppb) concentrations of oxidizing gases: NO, O_3, SO_2, etc. The conductance of films didn't change after exposing them to reducing gases as CO [4].

2. Materials and Methods

We succeeded in synthesizing several MePc, monomers and polymers. The synthesis procedures for monomers were previously presented in detail[5]. The MePc monomers were obtained either by classical synthesis methods (in solvent, at high temperature), or by using a better method (without solvent, in a microwave field).

We prepared MePcs (Me = Cu, Co, Ni and Fe (II) in a microwave field by heating phthalonitrile with metal salts and urea (using a molar ratio 5:1:5) for 15 minutes at 220^0C. The magnetron power was 500-600W.

A new method was used for purifying the monomers. The crude solid product was added into 40ml acetonitrile and the suspension was heated under reflux for 30 minutes. After cooling the solid is filtered off, washed with distilled water and purified again with HCl 2% solution and NaOH 2% solution.

The second technique has been shown to be faster and more efficient than the classical techniques.

The polymers were prepared by the reaction of pyromellitic anhydride, urea and metal salts (using a molar ratio of 1:20:1.5) at 180-200^{0}C for 5 minutes.

An original method was applied to obtain polymeric MePcs with variable average molecular weight (MW). The structure is presented in figure 1. In order to stop the polymerization, variable amounts of phthalic anhydride were added to the usual reaction mixture. The molar ratio between pyromellitic dianhydride and phthalic anhydride was in the range of 1:0 to 1:0.9.

We obtained a variation of the average molecular weight between 4.000D and 80.000D.

Characterization of the Pcs

The elemental analysis of the Pcs confirmed a high purity degree of synthesized compounds. The results, including IR and UV-VIS analysis, are reported in tables 1 and 2. The polymers are dark blue-green to black powders with fair thermal stability and show the visible and infrared absorption bands, characteristic of phthalocyanines.

The thermal behavior of Pc products appears to be the key for their use in evaporated thin films (stability to high-temperature treatment, sublimation capacity, etc.).

The thermogravimetrical analysis (TGA) was carried out on TGA-V5-1A Du Pont 2000 equipment. Thermal evaporation was carried out at 200-400^{0}C and $2x10^{-5}$ mbar for 60-90nm thickness of monomers Pcs. For polymeric Pcs, higher temperatures were required (>1000K), with a step rate of 200K/min. The layer to be obtained was about 30 times thicker (300nm).

The SEM pictures of the evaporated thin films were obtained using a scanning electron microscope Philips XL 20.

The thin film preparation

All of the Pc thin films were obtained by vacuum evaporation, using a Bal-Tech Med 020-Modular high vacuum coating system. Each of tested Pcs was deposited onto an electronic device using a mask. For each deposition, approximately 2g of Pc powder was evaporated from a molybdenum boat, at high temperature (300-400^{0}C), under a vacuum pressure of $8.7x10^{-5}$mbar. The geometry of the films was determined by the mask pattern.

Using a deposition rate of 0.20nm/s for all the Pcs (NiPc, FePc and CuPc), films of 20-40nm thickness were obtained. The deposition was controlled with a film thickness and rate monitor **QSG 060, BAL-TEC** type (Liechtenstein). For polymeric Pc higher temperatures were required (>630^{0}C).

Phthalocyanine films were evaporated onto the substrates of the interdigital electrodes in order to analyze their sheet resistivities. The Pc film temperature was accurately controlled by the integrated heating element and thermoresistor. For an accurate deposition of phthalocyanine in the active area of the device, the lift off technique was used. The active area of the sensor contained the metal electrodes. The thickness of the metal layer (Cr-Au) was 400nm.

The process for obtaining the interdigital integrated sensor was presented in detail elsewhere[6].

Table 1. **Metallic Phthalocyanine characterization**

Nr. crt	Pcs	Elemental analysis								IR values (KBr)	UV-VIZ values (DMF)	
		C%		H%		N%		Metal %		-cm^{-1}-	λ_{max} (nm)	lg ε
		requires	found	requires	found	requires	found	requires	found			
1	CuPc	66.74	66.69	2.78	2.72	19.45	19.41	11.03	11.00	728, 754, 779, 874, 894, 1048, 1081, 1114, 1157, 1277, 1324, 1409, 1452, 1495, 1602, 3025	662	0.495
2	CoPc	67.28	67.30	2.80	2.79	19.61	19.57	10.32	10.28	733, 736, 756, 780, 870, 910, 1056, 1089, 1118, 1157, 1283, 1327, 1419, 1458, 1515, 1591, 3040	646	0.628
3	NiPc	67.30	67.27	2.80	2.75	19.61	19.57	10.27	10.25	727, 752, 771, 861, 907, 1055, 1084, 1114, 1157, 1277, 1320, 1415, 1457, 1517, 1596, 3025	655	0.775
4	FePc (II)	67.64	67.59	2.82	2.78	19.71	19.67	9.83	9.78	734, 56, 780, 871, 904, 1076, 1117, 1156,1279, 1327, 1411, 1456, 1501, 1598, 3035	587 645	0.507 1.407

Table 2. Copper polyphthalocyanine characterization and mean molecular weight variation

Polymer no.	Molar ratio pyromellitic anhydride: phthalic anhydride	% CuFt* monomer	Elemental analysis				VIS		
			N%		Cu%		λ_{max} (nm)	Solubility (g/100ml DMF)	Viscosity
			requires	found	requires	found			
1	1:0	0	20.41	19.13	11.56	3.84	667, 641, 603	0.003	1.84
2	1:0.1	0.5	20.41	15.09	11.56	3.84	692, 685, 658	0.003	0.19
3	1:0.3	2	20.41	17.52	11.56	13.66	667, 640, 602	0.007	0.38
4	1:0.5	2.6	20.41	18.5	11.56	3.8	698, 650, 610	0.006	0.56
5	1:0.6	4	20.41	15.02	11.56	4.32	670, 650, 603	0.007	0.507
6	1:0.7	8	20.41	19.35	11.56	15.21	667, 639, 602	0.009	0.83
7	1:0.8	11	20.41	22.25	11.56	14.77	668, 639, 602	0.014	0.65
8	1:0.9	14	20.41	17.81	11.56	9.2	668, 639, 601	0.1	1.58

* *found by extraction of polymer in basically solution (DMF-water)*

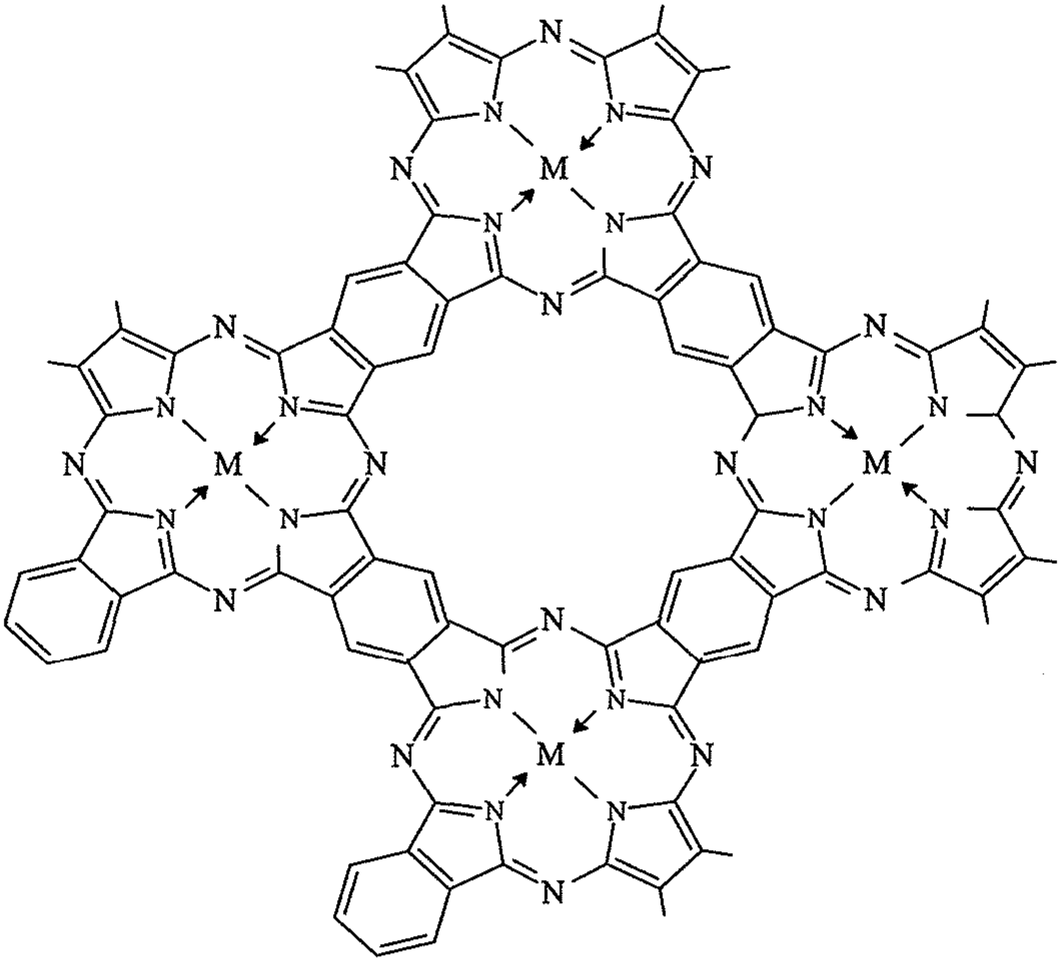

Fig.1. Metallic phthalocyanine polymer structure

3. Results and Discussion

CuPc monomer exhibited a remarkable thermal stability up to 300^{0}C. After this point, the sublimation process was very fast with a constant rate of evaporation (0.16nm/s.) and a minimal decomposition of the CuPc (<1%).

For the polymeric phthalocyanines, the thermal stability was higher than for Pcs monomers. The stability increased with the average molecular weight (350^{0}C for MW = 20.000D and more than 600^{0}C for MW = 80.000D). The polymeric pigment stability was not dependent on observed temperatures between 125-400^{0}C. The molecular weight decrease up to 125^{0}C was due to the humidity loss.

Electrical conductibility was determined for CuPc ($10^{-12}\Omega^{-1}cm^{-1}$) and for polymeric Pcs ($5x10^{-2}\,\Omega^{-1}cm^{-1}$ when MW = 80.000D).

For a variation of molecular weight in the range of 4.000D and 80.000D, the specific resistivity was $\rho=10^{-9}$- $5x10^{-2}\Omega^{-1}cm^{-1}$ as shown in figure 2.

The ρ variation with the temperature is exponential:

$$\rho = \rho_0 \cdot e^{\varepsilon/2kT}$$

where: ρ_0 - specific resistance at very high temperature (infinite), ε - width of restricted band, k - Boltzmann constant.

$$\ln\rho = \ln\rho_0 + \varepsilon/2kT$$

The Pcs films deposited onto microsensor electrodes had high resistance values: 10MΩ for CuPc, 15MΩ for NiPc and 30MΩ for FePc. It is important to study the uniformity of the resulting layers in order to prevent degradation by clustering of the contact metal. The electrode strips were thicker than the Pc film deposited on the top. A relative bad covering of the strips and a relative high number of cracks caused by the edges of the capacitor strips were expected. Pcs did not form a continuous film over the edge of the electrode strips.

During the evaporation, the incident angle of the Pc molecules was not normal to the surface and, therefore, the strip edge formed a kind of shadow on one side. The cracks can be observed in SEM picture of the electrodes covered with MePc layer (figure 3).

In very aggressive environments, MePc films were very stable and still sensitive to gases. The films were evaporated on interdigital electrode substrates (gold or aluminum) which were entirely integrated in the standard CMOS (capacitor metal oxide semiconductor) technology for detection of NO, NO_2 in the air.

4. Conclusions

The conductance of very thin films allowed resistance measurements without any contact problems. The electrical conductivity dependence to the adsorbed gas nature was correlated with the size of the π electron-conjugated system in the polymeric molecules.

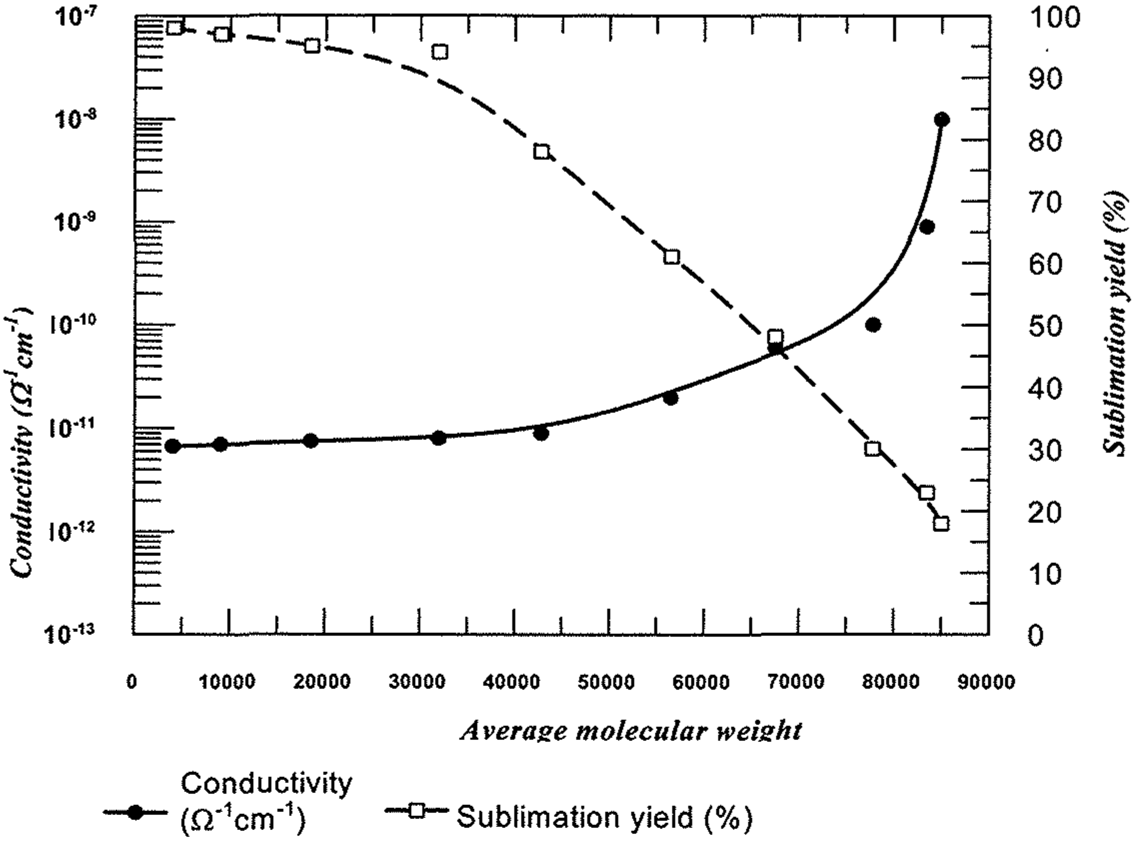

Fig.2. Variation of polymers conductivity and sublimation yield with the average molecular weight

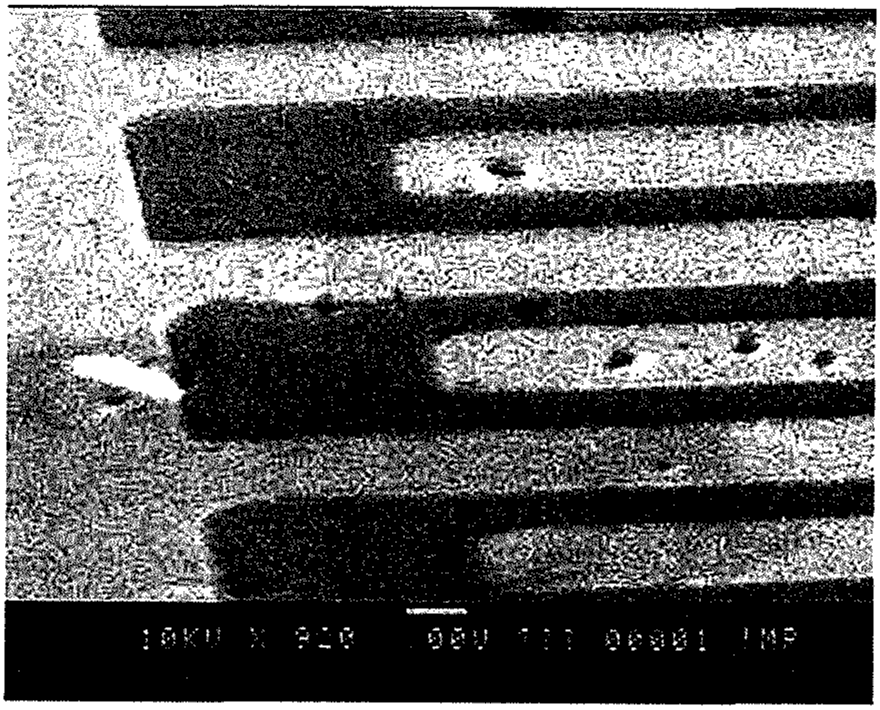

Fig 3. SEM picture of electrodes covered with 20nm FePc thin film

However, resistance to sublimation decreased with the increasing of the average molecular weight. The decrease was more significant under molecular weights of 50.000D.

This behavior of Pc requires further research in order to achieve a more reproducible technology for producing highly sensitive detecting layers, in gas sensors.

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SPECTROPHOTOMETRIC STUDY ON THE FORMATION AND ANALYTICAL APPLICATION OF THE RHODIUM (III) CHELATE WITH 2-THIOXO-4-THIAZOLIDINONE

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ABSTRACT

The paper presents a spectrophotometric study of the binary system Rh(III) -2- thioxo - 4 -thiazolidinone. The formation conditions and the analytical application of the formed complex for spectrophotometric determination of Rh(III) were studied. The composition of the Rh(III) chelate with this particular ligand was determined by the continous variation method,its instability constant being $K_{inst} = 1,61 \cdot 10^{-8}\ mol^2 L^{-2}$.

KEYWORDS : rhodium (III), 2-thioxo-4-thiazolidinone, spectrophotometric study

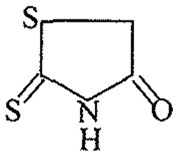
RESUMO

O presente trabalho trata do estudo espectrofotométrico do sistema binário Rh(III)-2-tioxo-4-tiazolidinona. Foram estudadas as condições de formação e as aplicações do complexo para determinação analítica de Rh(III). A composição do quelato do Rh(III) com este ligante foi determinada usando o método de variação contínua e a constante de instabilidade, K_{inst}, *foi* $1,61x10^{-8} mol^{2}L^{-2}$.

INTRODUCTION

Among all platinum metals, rhodium has the greatest number of oxidation states, namely eight positives and two negatives ones. The oxidation state for which the greatest diversity of complexes is found is (III). Ligands which are good σ-donors, but which have marked π-donor or π-acceptor properties are often associated with the oxidation state Rh (III). The methods based on the complex combinations formation with N-donor ligands (oxime, α-substituted dioxime, hydrazone) or S-donor ligands (NCS^-, thiokethone, thioamide) are much more used[1-6].

The present paper reports the study on the formation, the optical properties and the structure of the Rh (III) chelate with 2-thioxo-4-thiazolidinone (L). The chemical bond implies the participation of both a sulphur atom and a nitrogen of the ligand in coordination to the metal. This chelate was proposed for spectrophotometric determination of Rh (III).



(L)

EXPRIMENTAL PROCEDURE

All the chemicals we used were of analytical grade: $RhCl_3 \cdot 3H_2O$ (Merk p.a.), 2-thioxo-4-thiazolidinone (L) (recrystallized).

The electronic spectra were performed in aqueous solutions using an Ocean Optics spectrometer(USA).

Experiments were done with an aqueous solution of $RhCl_3$ ($1 \cdot 10^{-3}$M, $1/2 \cdot 10^{-3}$M, $1/3 \cdot 10^{-3}$M) with the aqueous solution of L ($1 \cdot 10^{-3}$M, $1/2 \cdot 10^{-3}$M, $1/3 \cdot 10^{-3}$M) by solving the ligand. As a consequence of the reaction taking place between Rh (III) and the ligand L, yellow coloured complex compound was obtained, then the samples were heated for 10 minutes. The solutions were cooled and brought to 25 ml in calibrated fasks.

RESULTS AND DISCUSSIONS

Rh (III) reacts with 2-thioxo-4-thiazolidinone (L) at high temperature to form yellow complex compound.

The factors influencing the formation of the new compound are: the time period in which the colour of the new product stabilizes is about 10 minutes and the optimum pH for the formation is 5,5. The other pH values do not certify the formation in the studied system of the other more stable coloured compounds.

The electronic spectrum of the complex compound is presented in Figure 1. From the obtained data one can see that the most favourable wavelength in 460 nm (corresponding to 21739 cm^{-1}).

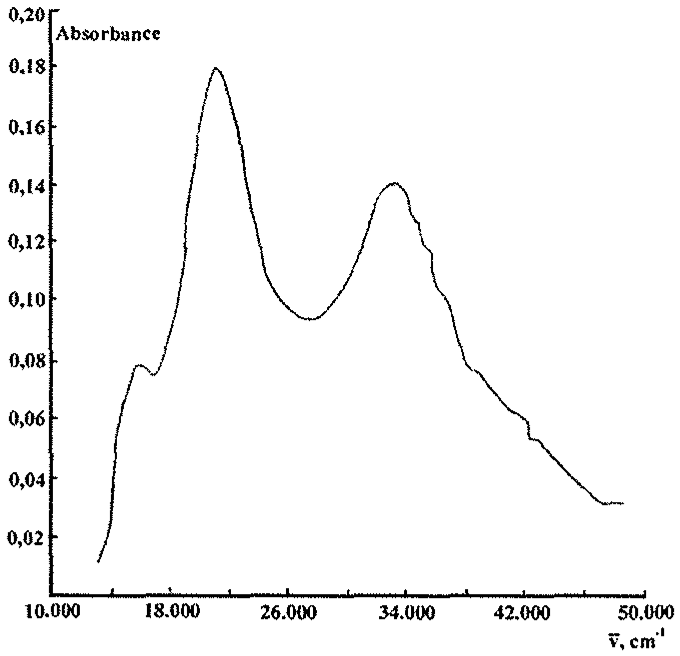


Figure 1. Electronic spectrum of the $RhCl_3$-L system at pH=5,5

The composition of the Rh (III) chelate was determined by the continous variation method. Figure 2 presents the results of the Job's method application for the three isomolar solution series ($1 \cdot 10^{-3}$M, $1/2 \cdot 10^{-3}$M, $1/3 \cdot 10^{-3}$M) at pH=5,5 and λ=460 nm. One can notice that each of the three curves reaches a single maximum value corresponding to the same molar ratio, which proves that a single complex compound was formed in the binary system and that its molar ratio is Rh (III):L = 1:2.

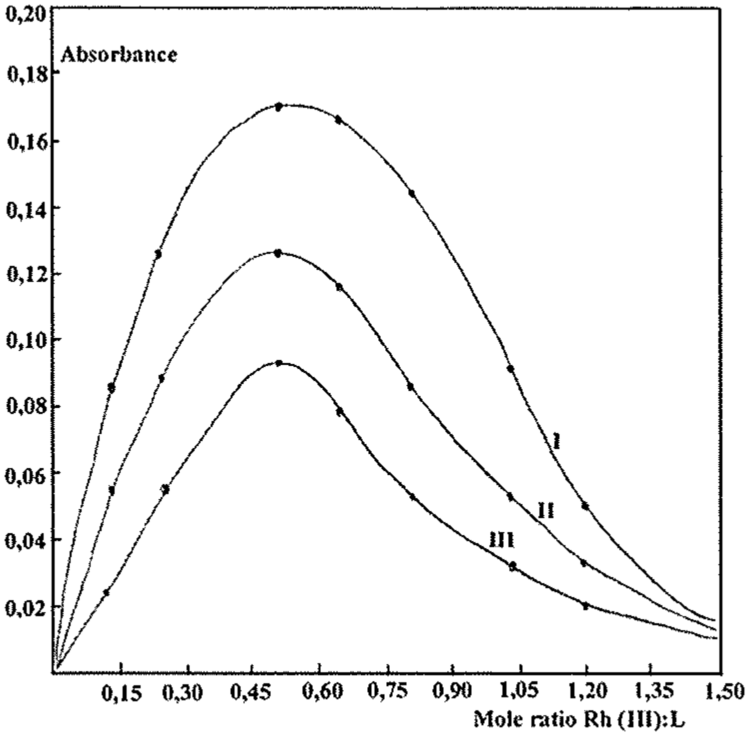


Figure 2. Variation of the absorbance for isomolar series.: I-$1 \cdot 10^{-3}$M, II-$1/2 \cdot 10^{-3}$M, III-$1/3 \cdot 10^{-3}$M

To calculate the instability constant of the complex one has made use of the nonisomolar series method.

The general expression of the instability constant for equilibrium

$$mA + nB \rightleftharpoons A_mB_n \qquad (1)$$

is:

$$K_{inst} = \frac{C^{m+n-1}\, p^{n-1}[(pm+n)x-n]^{m+n}}{[m^{n-1}n^{m-1}(p-1)^{m+n-1}][n-(m+n)x]} \qquad (2)$$

in which m and n are molar index, C = the molar concentration of A, p = the molar concentration ratio of B and A, x = the mole ratio corresponding to maximum absorbance.

For the studied system, the molar index being m = 1 and n = 2 we obtain the following simplified expression:

$$K_{inst} = \frac{C^2\, p[(p+2)x-2]^3}{(p-1)^2(2-3x)} \qquad (3)$$

Two series of nonisomolar solutions were prepared:

- the solution $RhCl_3$ ($1/2 \cdot 10^{-3}$M) – L (10^{-3}M);
- the solution $RhCl_3$ ($1/3 \cdot 10^{-3}$M) – L (10^{-3}M).

The results obtained are given in Figure 3.

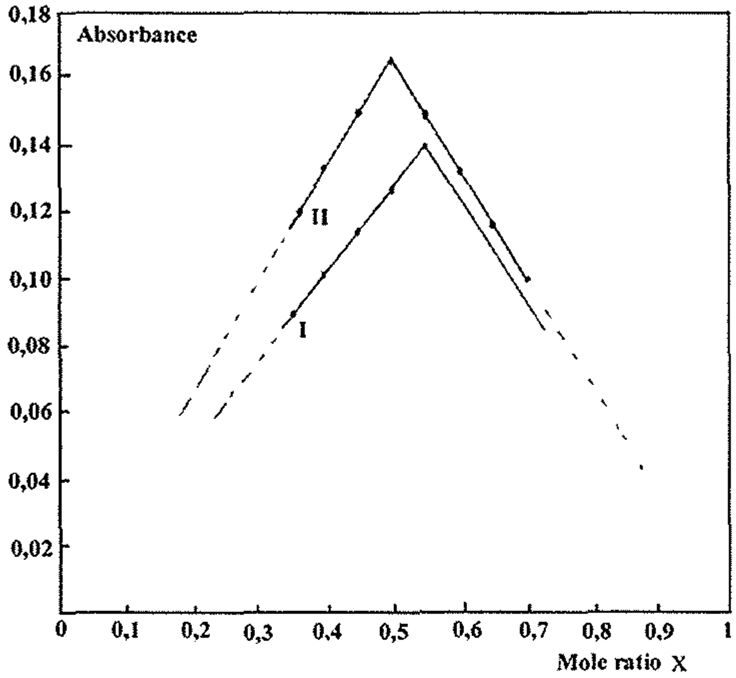


Figure 3. Variation of the absorbance in the nonisomolar series: I= Rh (III) ($1/2 \cdot 10^{-3}$M) – L (10^{-3}M); II= Rh (III) ($1/3 \cdot 10^{-3}$M) – L (10^{-3}M).

By introducing the practical results into the expression of the instability constant we obtain the values enclosed in Table 1.

Table 1
Values of the instability constant

C ($mol \cdot L^{-1}$)	p	x	K_{inst} ($mol^2 \cdot L^{-2}$)	$K_{m,inst}$ ($mol^2 \cdot L^{-2}$)
$1/2 \cdot 10^{-3}$	3	0,55	$1,14 \cdot 10^{-8}$	$1,61 \cdot 10^{-8}$
$1/3 \cdot 10^{-3}$	2	0,50	$2,07 \cdot 10^{-8}$	

The charge determination of the complex ion has been achieved by means of the electrophoretic migration method in presence of a weak solution of potassium nitrate. A small quantity of urea was introduced into the solution containing the complex compound corresponding to the molar ratio 1:2. After 15 minutes the displacement of the coloured complex ion towards the catode could be observed, thus proving the existence of its positive charge.

The results prove the following formula: $[RhL_2Cl_2]^+$, in which L acts as a bidentate ligand, using both a sulphur atom and a nitrogen in coordination to the metal.

In order to establish the coordination geometry and the symmetry for the new complex compound, a spectral analysis in the visible and UV range has been done. The correspondence between the absorption band occurring at 21739 cm^{-1} (460 nm) and 33335 cm^{-1} (299 nm) in the investigated complex $[RhL_2Cl_2]^+$ (Figure 1) and the ones found for the trans octahedral complexes of the type t-$[Rh(N_2S_2)Cl_2]^+$[7-9], leads us the conclusion that the coordinative compound that appears from the binary system Rh (III)-2- thioxo-4-thiazolidinone is stabilized by 2 L in equatorial plan and the monodentate Cl^- ligands are situated in trans to each other, so that $[RhL_2Cl_2]^+$ has an octahedral coordination geometry and a tetragonal symmetry, belonging to the $\mathbf{D_{2h}}$ point group[10] consequently (actually, the point group is either $\mathbf{C_{2h}}$ or $\mathbf{C_{2v}}$, but the internal structure of the ligand may be neglected).

Taking into account the results of the study above, which confirm high enough stability of this complex compound, it has been used for analytical purposes, namely for establishing a method of spectrometric determination of Rh (III).

The experimental results of the absorbance variation versus Rh (III) concentration are presented in Figure 4. The Beer's law was respected over the concentration range 0,2-20,6 µg Rh (III)/mL.

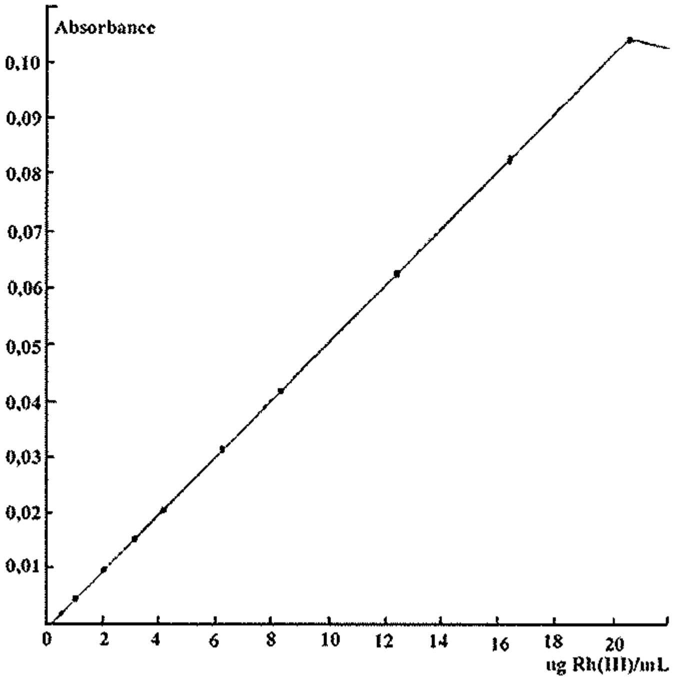


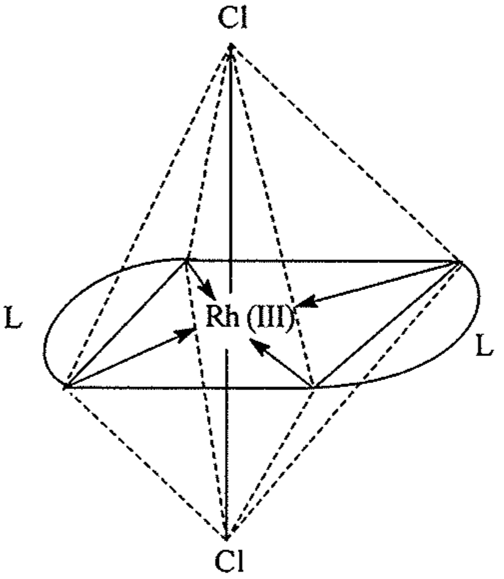
Figure 4. Variation of the absorbance versus Rh (III) concentration

In order to test the validity of the method, the experimental data were statistically interpreted. The error corresponding to eight determinations ($t_{0,95}$ = 2,447) is m = $(30.414 \pm 0,2334)\cdot 10^{-4}$, meaning that the proposed method is reproducible and accurate and it is not affected by systematic errors, so that $[RhL_2Cl_2]^+$ can be used indeed for the spectrometric determination of Rh (III).

Other platinum metals (M = Pd, Pt) do not interfere in the spectrometric determination of rhodium in the $[RhL_2Cl_2]^+$ form. From the reaction`s feature between Rh (III) and L it has been ascertained that it is possible to recognize the Rh (III) in ruthenium`s presence up to the ratio Rh (III): Ru (III) = 1:18 and in gold`s presence up to the ratio Rh (III): Au (III) = 1:20.

CONCLUSIONS

On the basis of all the results obtained by this study, the following structure is proposed for the new complex compound, trans-$[RhL_2Cl_2]^+$:



It also has been proved that trans-$[RhL_2Cl_2]^+$ may be used for analytical purposes, namely for establishing a reproducible and accurate method of spectrometric determination of Rh (III).

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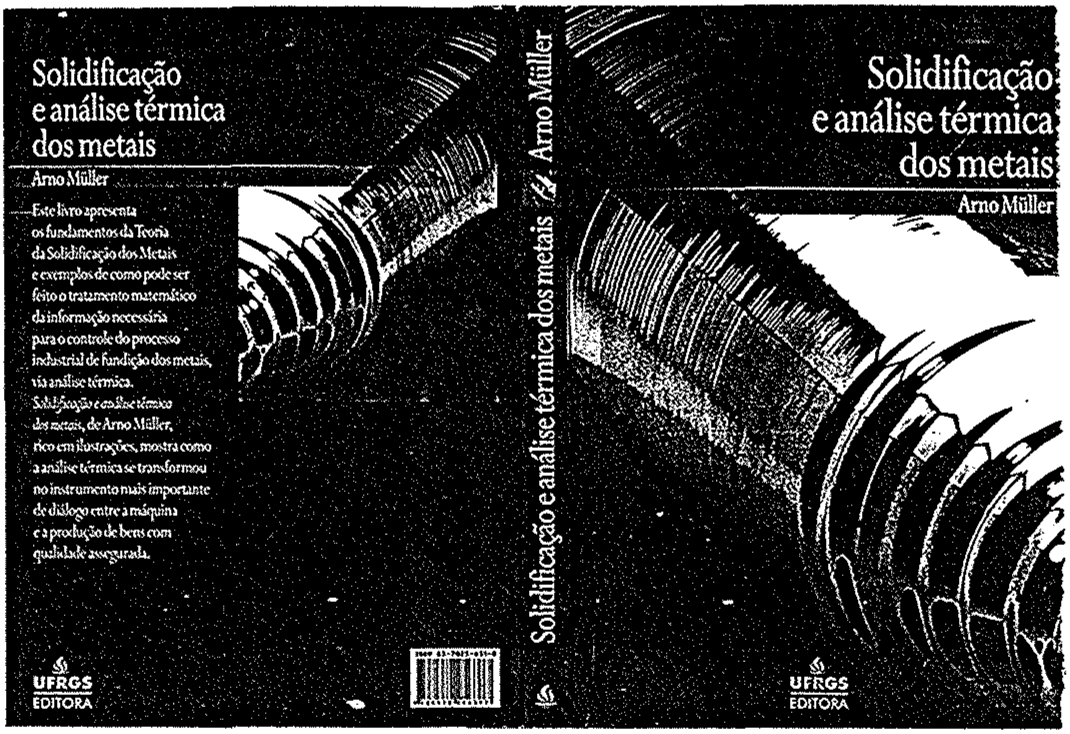
BOOKS / LIVROS

LIVROS

ARNO MÜLLER, *Solidificação e Análise Térmica dos Metais,* Editora da UFRGS, Porto Alegre, RS, Brasil, 2002, 278p.

Solidificação e Análise Térmica dos Metais trata de conceitos fundamentais que constituem a base para o entendimento dos processo e mecanismos de fabricação de bens industriais pelo uso da fundição. Por um lado a solidificação garante a qualidade das peças metálicas eliminando defeitos e a análise térmica, medindo as reações térmicas durante a solidificação assegura a qualidade e as propriedades mecânicas do produto da fundição.

O livro contém sete capítulos e um apêndice com anexos ricos em dados de interesse na metalurgia e apresenta a solidificação e a análise térmica da forma mais quantificada possível. O processo de solidificação, incluindo embriogênese de metais, termodinâmica, transformação e nucleação são tratados de maneira exemplar no Capítulo 1. A transferência de calor e a difusão de massa durante a solidificação são analisados nos Capítulos 2 e 3, respectivamente. O Capítulo 4 trata da estrutura de lingotes, o Capítulo 5 de defeitos de solidificação. Os fundamentos de análise térmica dos metais são apresentados no Capítulo 6 e as aplicações industriais são discutidas de maneira clara no Capítulo 7.



Solidificação
e análise térmica
dos metais

Arno Müller

Este livro apresenta
os fundamentos da Teoria
da Solidificação dos Metais
e exemplos de como pode ser
feito o tratamento matemático
da informação necessária
para o controle do processo
industrial de fundição dos metais,
via análise térmica.
Solidificação e análise térmica
dos metais, de Arno Müller,
rico em ilustrações, mostra como
a análise térmica se transformou
no instrumento mais importante
de diálogo entre a máquina
e a produção de bens com
qualidade assegurada.

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Solidificação e análise térmica dos metais
Arno Müller

Solidificação
e análise térmica
dos metais

Arno Müller

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De certa forma, o livro reflete a personalidade, caráter e filosofia de vida do Professor Arno Müller. Ele é Engenheiro Metalúrgico formado pela UFRGS, Mestre em Ciência dos Materiais pelo Instituto Tecnológico da Aeronáutica (ITA) de São José dos Campos, São Paulo e Doutor em Engenharia pela Universidad Nacional de Rosário, República Argentina. Foi Professor Titular de Metalurgia da UFRGS, fundador do Laboratório de Fundição do Centro de Tecnologia da UFRGS e Diretor da Escola de Engenharia da mesma universidade.

Junto com outros pioneiros visionários e bandeirantes desbravadores, o Prof. Dr. Arno Müller foi também um dos fundadores do Programa de Doutorado em Engenharia Metalúrgica e dos Materiais da Escola de Engenharia da Universidade Federal do Rio Grande do Sul.

Atualmente ele ocupa os cargos de Professor e Coordenador do Programa de Pós-Graduação em Engenharia: Energia, Ambiente e Materiais da ULBRA – Universidade Luterana do Brasil.

Reproduzimos *ad integra* o frontispício do livro do Prof. Arno Müller.

"Duas visões do mundo tive comigo como engenheiro e pesquisador.

A primeira:
Fac quod in te est, ou faz aquilo que está ao teu alcance,
lema da Escola de Engenharia da UFRGS.

A segunda, a frase de Kant:
Alles Wissen stammt aus der Erfahrung
Ou seja, todo o conhecimento é proveniente da experiência.

Dedico este livro ao sofrido povo brasileiro, que custeou minha educação
universitária em todos os níveis."

Recomendamos altamente este livro para todos os interessados em propriedades e uso de metais, incluindo alunos de graduação e pós-graduação em engenharia, física, química, mineralogia e ciência dos materiais. A sua tradução em outras línguas seria muito salutar.

Lavinel G. Ionescu, B.S., M.S., Ph.D. (Físico-Química)

ARNO MÜLLER, *Solidificação e Análise Térmica dos Metais*, Editora da UFRGS, Porto Alegre, RS, Brasil, 2002, 287p.

Solidification and Thermal Analysis of Metals (in Portuguese) treats fundamental concepts necessary for the understanding of metal casting and manufacturing of industrial metal products. The book consist of seven chapters and an appendix with physical data.

It includes solidification embryogenesis of metals, nucleation, solidification defects, thermodynamics, heat and mass difusion, thermal analysis and industrial applications. The book is the result of experience, reflection and practice of many decades of teaching and research in metallurgy. We recommend its translation to English and other languages.

Lavinel G. Ionescu, B.S., M.S., Ph.D.

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AUTHOR INDEX / ÍNDICE DE AUTORES

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