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INFORMATION FOR AUTHORS

The Southern Brazilian Journal of Chemistry - SBJC will publish review articles, original research papers and short communications dealing with chemistry and interdisciplinary areas such as materials science, biotechnology, bioengineering and other multidisciplinary fields.

Articles report the results of a complete study. They should include an Abstract, Introduction describing the known art in the field Experimental or Materials and Methods, Results and Discussion, Acknowledgments (when appropriate) and References.

Short Communications should be limited to 1500 words, including the equivalent space for figures and/or tables and should include an Abstract and concise Experimental.

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2. K. L. Mittal, Ed., "*Solution Chemistry of Surfactants*", Plenum Press, New York (1984), Vols. 1-3, pp. 1-2173.

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EDITORIAL

THE SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY COMPLETES 20 YEARS OF PUBLICATION

With this issue, THE SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY completes twenty (20) years of continuous, uninterrupted publication. The printed version of the JOURNAL has been distributed in more than fifty (50) countries of the globe, covering all continents.

We are well aware that at the present time, when globalization and centralization of information and control of many other human activities are in vogue, we may be appearing to go against the main stream, or even in the opposite direction. As we stated in the first issue of the SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY twenty years ago (see *The Birth of a Journal*, on the next page) we are still open for the debate and discussion of chemical education, history and philosophy of science and still hope, in a modest way to contribute to the analysis and solution of the crisis of moral and ethical values and standards that affects science and education all over the world.

We publicly thank all the members of the Editorial Board that includes distinguished scientists from all continents for the assistance and advice given during the last 20 years.

Special thanks are due to Prof. Dr. Joseph A. Schufle of Las Vegas, N.M., United States of America and Prof. Dr. Cristofor I. Simionescu of Iasi, Romania. Both of them have left us and now continue their activity on higher planes of the Universe.

We also thank SARMISEGETUSA Research Group, Santa Fe, New Mexico, United States of America for the financial support that made this endeavor possible and real for 20 years.

We finally thank, Dr. Luis Alcides Brandini de Boni , Assistant Editor of this Journal for the help with informatization and the preparation of the home site.

We continue open to any questions, suggestions and contributions and will maintain this international forum open for the dissemination of high quality research in chemistry and other areas of science.

Lavinel G. Ionescu, A.A., B.S., M.S., Ph.D. (*Physical Chemistry/Astrophysics*)

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
Vol.1, No. 1, 1993

THE BIRTH OF A JOURNAL

It is with great pleasure and satisfaction that we bring to light the premier issue of *THE SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY*.

This Journal was founded to provide an open international forum for the discussion and publication of theoretical and applied aspects dealing with chemistry and related interdisciplinary, multidisciplinacry and transdiciplinary areas of science and to fill a gap and lacuna in terms of scientific literature for Southern Brazil.

This Journal is also open for the debate and discussion of chemical education and history and philosophy of science and hopes, in a modest way, to contribute to the analysis and solution of the present crisis of moral and ethical values and standards that affects science and education all over the world.

The idea of a NEW JOURNAL first arose during 1978, soon after our arrival in Florianópolis, Santa Catarina at the invitation of the Brazilian Ministry of Education and Culture to help establish the graduate program in Physical Chemistry at the Federal University of Santa Catarina.

It gained new impetus during our tenure as Secretary of the Rio Grande do Sul Section of the Brazilian Chemical Society (1986-1990). Fortunately, now, after tackling some serious aberrations and irregularities in the Federal University System, we can devote the due attention to this Journal.

The main purpose of *THE SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY* is to publish original research articles and short communications, but occasionally, it will include invited review papers and state of the art overviews by experts in their areas.

THE SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY will be published mainly in English with abstracts in English and Portuguese. Occasionally, we will consider the publication of articles in other languages.

We publicly thank all the illustrious members of the EDITORIAL BOARD of *THE SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY*, that includes distinguished scientists from all continents, who have thus far given us invaluable assistance, advice and suggestions, and who with their cumulative wisdom and experience will help chart the future of this JOURNAL.

We also thank *SARMISEGETUSA RESEARCH GROUP* of Santa Fe, New Mexico, United States of America, for the financial support that made this endeavor possible and real.

We hope that this JOURNAL will provide an open international forum for the dissemination of high quality research in chemistry and related areas and are open to any questions and suggestions.

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

EDITOR

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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OTTO RICHARD GOTTLIEB, FATHER OF BRAZILIAN PHYTOCHEMISTRY

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ABSTRACT

Otto R. Gottlieb was born in Brno, Czechoslovakia on August 31, 1920 and passed away in Rio de Janeiro, Brazil on June 19, 2011. He immigrated to Brazil in 1939 and did his undergraduate studies at the Universidade do Brasil, where he obtained a degree in industrial chemistry in 1945. He was awarded a doctorate in chemistry by the Universidade Federal Rural do Rio de Janeiro in 1966. He worked in industry and held positions at several institutes and universities in Brazil. His research work dealt mainly with phytochemistry, natural and medicinal products and biodiversity. He was research advisor of approximately 150 students and is responsible for approximately 700 scientific publications. Otto R. Gottlieb may be considered the father of Brazilian Phytochemistry.

KEY WORDS: Phytochemistry, Natural Products, Chemistry in Brazil, History of Science

RESUMO

Otto R. Gottlieb nasceu em Brno, Checoslováquia em 31 de Agosto de 1920 e faleceu no Rio de Janeiro em 19 de Junho de 2011. Ele veio para o Brasil em 1939 e formou-se em Química Industrial pela Universidade do Brasil em 1945. Obteve o doutorado em química em 1966 na Universidade Federal Rural do Rio de Janeiro. Trabalhou na indústria e ocupou cargos em vários institutos e universidades no Brasil. Seu trabalho de pesquisa tratou principalmente de fitoquímica, produtos naturais e medicinais e biodiversidade. Orientou mais de 150 alunos de mestrado e doutorado e publicou aproximadamente 700 trabalhos científicos. Otto R. Gottlieb pode ser considerado o paia da Fitoquímica Brasileira.

PALAVRAS CHAVE: Fitoquímica, Produtos Naturais, Química no Brasil, História da Ciência

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Otto Richard Gottlieb was born on August 31, 1920 in Brno, Moravia, Czechoslovakia (present day Czech Republic) and passed away in Rio de Janeiro, Brazil on June 19, 2011. He was buried in the Jewish Cemetery of Caju, Rio de Janeiro.

He lived in Brno up to the age of 16, completed primary school and began secondary school in Czechoslovakia and in 1936 when his family came to Brazil, he went to England together with his brother where they attended Badingham College. In 1939, sensing the coming of World War II, Otto R. Gottlieb came to Brazil and at the age of 21 opted for the Brazilian Citizenship. His maternal grandfather was exporting coffee from Rio de Janeiro and Vitoria since 1880 and his mother was from Petropólis, sate of Rio de Janeiro.

His paternal grandfather was the owner of a porcelain factory in Czechoslovakia and his father was the factory chemist. In 1936, his father immigrated to Brazil and founded an industrial plant for the extraction of essential oils and raw materials for the perfume industry. Chemistry was really part of a family tradition.

In Brazil, he studied for two years at the Colégio Universitário, the best preparatory school of Rio de Janeiro and subsequently enrolled in the Escola Nacional de Química of the Universidade do Brasil. He obtained the Degree in Inustrial Chemistry in 1945. For the following ten years he worked in the factory helping his father and performing all kinds of duties.

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OTTO R. GOTTLIEB (1920-2011)

In 1955 Otto R. Gottlieb obtained a research grant from CNPq (Brazilian National Research Council) to pursue studies at the Instituto de Química Agricola (Institute of Agricultural Chemistry) in Rio de Janeiro. It is there that Otto R. Gottlieb developed a strong interest for research in natural products chemistry, plant metabolism , medicinal chemistry and biodiversity. After his father closed his industrial plant in 1959, he began to dedicate himself almost exclusively to research. He gained important research experience at the Weizman Institute, Rehovot, Israel, University of Sheffield in England and the University of Indiana in the United States.

He obtained the Doctorate in Chemistry from the Universidade Federal Rural do Rio de Janeiro (Federal Rural University of Rio de Janeiro) in 1966.

Dr. Otto Richard Gottlieb held many positions at research institutes and universities all over Brazil. We shall mention only some of them. His former doctoral students and collaborators are to be found in practically all of the states of Brazil, most of them being involved in research and graduate programs in chemistry and pharmacy dealing mainly with natural products and medicinal chemistry. Otto R. Gottlieb himself was directly responsible for the establishment of a large number of graduate programs in chemistry and pharmacy throughout Brazil.

Among the research institutes, we mention the Instituto Nacional de Pesquisas da Amazònia (INPA) in Manaus and Fundação Instituto Oswaldo Cruz (FIOCRUZ), Rio de Janeiro.

Among the universities we mention Federal Rural University of Rio de Janeiro, University of Brasília,University of São Paulo, Federal University of Minas Gerais, Federal University of Pernambuco , Fluminense Federal University and the Universty of Hamburg, Germany.

Otto Richard Gottlieb was research advisor of approximately 150 graduate students. As we mentioned above, about half were at the master and the other half at the doctoral level. His research interests dealt mainly with phytochemistry, natural products, medicinal chemistry, plant metabolism, biodiversity and the development of new drugs.

Later in his life he began to devote much time, effort and attention to sustainability and preservation of the environment. Prof. Dr. Otto R. Gottlieb was fascinated by the chemical richness, biodiversity and ecosystems of the Amazon Forest. The accelerated destruction of the Amazon Rain Forest was for him comparable to the fire of Alexandria, Egypt and was destroying and burning the most valuable "library" of the world before it was read and its contents were known. For those that may be interested in the subject we mention a book in English: ("*CHEMISTRY OF THE AMAZON –Biodiversity, Natural Products and Environmental Issues", Peter R. Seidl, M.A. Kaplan and Otto R. Gottlieb, Eds., ACS Symposium Series 588, Washington, D.C., USA, 1995).*

Prof. Dr. Otto Gottlieb is the author of approximately 700 scientific publications, holds two patents and is the author of five books, dealing with chemistry, ecology, plant metabolism, micromolecular evolution and biodiversity.

During his life, Prof. Dr. Otto Richard Gottlieb received a large number of prizes, medals and awards. He was the recipient of practically all awards given in science and chemistry in Brazil. We shall mention only a few: National Order of the Big Cross for Scientific Merit from the President of Brazil (1999), Pergamon Phytochemistry Prize (1992), Almirante Álvaro Alberto Prize of the Brazilian

National Research Council (CNPq-1990), Fritz Feigl Prize in 1977 and the Freitas Machado Prize of the Escola Nacional de Química in 1943.

Otto Richard Gottlieb received the *Doctor Honoris Causa Degree* from more than a dozen Brazilian universities and from the University of Hamburg, Germany in 1988. He has been a member of the Brazilian Academy of Sciences (1966), Latin American Academy of Sciences (1983), New York Academy of Science (1984), International Academy of Wood Science (1989) and Third World Academy of Science (1999).

Prof. Dr. Otto Richard Gottlieb was indicated for the Nobel Prize in Chemistry on three occasions, in 1998,1999 and 2000. Roald Hoffmann (Nobel Prize in Chemistry in 1981) was one of his nominees and made this comment "*Otto was a great scientist and is responsible for the formation of the school of natural products in Brazil. He had a great influence over Brazilian science*".

We first met Prof. Dr. Otto R. Gottlieb in 1978, a short time after our arrival in Brazil, coming at the invitation of the Brazilian Ministry of Education and Culture to help establish the Graduate Program in Physical Chemistry at the Federal University of Santa Catarina in Florianópolis.

Prior to our coming top Brazil, we asked a famous chemist with whom we had the privilege to collaborate et the University of California about chemists and the state of chemistry in this country of continental dimensions. He told us that he knew of two great and good chemists in Brazil. One of them was Ernesto Giesbrecht [Cf. L. G. Ionescu, "*Ernesto Giesbrecht, Great Chemical Educator and Father of Brazilian Inorganic Chemistry, South. Braz. J. Chem, 4(4), 1-8,1996*].

The other was Otto Richard Gottlieb. At our personal invitation Prof. Dr. Otto R. Gottlieb visited and gave seminars at the new graduate programs in chemistry at the Federal University of SantaCatarina, Florianóplis and the Federal University of Rio Grande do Sul, Porto Alegre. We remember him as a somewhat formal and reserved person.

At the time of his visit in Florianópolis, Prof. Dr. Otto Gottlieb held faculty positions at the University of São Paulo, Federal Rural University of Rio de Janeiro and also worked in Manaus, Amazonas. During the second day of his visit we created courage and asked him why he worked in so many places. He looked at us seriously gave us a tap on the shoulder and said: *"Meu filho, no Brasil em quantos mais lugares você trabalha, melhor!"*(My son, in Brazil, the more places you work, the better). With our youthful enthusiasm and experience we thought for ourselves *" crazy old man"*. About ten years later when we were working and faced widespread embezzlement of public funds and ecologic crimes at the Federal University of Rio Grande do Sul we remembered Professor Otto's advice and appreciated his wisdom.

Prof. Dr. Otto R. Gottlieb was a very influential person in scientific circles. When some members of the Chemistry Department in Florianópolis were contrary to hiring a chemist from a nearby Latin American country in order to help establish Research Program in medicinal chemistry in the College of Pharmacy, the message from Prof. Otto (via Brasília) was more like an ultimatum-either the organic chemist will be hired or the project funds will not be liberated. The chemist was hired and the medicinal chemistry program, under the leadership of Professor Calixto is today one of the best in the country.

Otto R. Gottlieb, Father of Brazilian Phytochemistry

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During the years that followed we met with Prof. Dr. Otto R. Gottlieb mostly at the National Meetings of Associação Brasileira de Química (ABQ). He tried to be always present, for it was his original contact with ABQ the eventually led to his brilliant academic career. In the last years of his life he suffered from Parkinson's disease, but even so, he was there whenever possible.

Prof. Dr. Otto Richard Gottlieb may be truly considered the Father of Brazilian Phytochemistry.

For those that may want to learn more about Otto R. Gottlieb, we suggest reading his interview with Vera Rita da Costa "Na Torre de Marfim" published in *Ciência Hoje* in October of 1988.

REPRESENTATIVE PUBLICATIONS

For a complete list we suggest http://lattes.cnpq.br/8174445528014427

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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES ON CERTAIN SUBSTITUTED ARYLAZO IMIDAZOLE CONTAINING OXADIAZOLES

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ABSTRACT

A series of novel substituted 1-[5-(2-methyl-5-nitro-4phenyl-imidazol-1yl methyl)-2-phenyl-(1,3,4)oxadiazol-3-yl]-ethanones have been synthesized. Formation of 1,3,4-oxadiazole ring was accomplished by the reaction of corresponding hydrazide with acetic anhydride. The structure determination of these compounds has been made on the basis of IR, ^{1}H NMR, and elemental analysis. All the compounds were screened for their antibacterial activity. The antimicrobial activity of title compounds were examined against two gram-negative (Staphylococcus aureus and Bacillus subtilis), two gram-negative bacteria (Escherichia coli and Pseudomonas aeruginosa) and antifungal activity was carried out against Candida albicans. The MIC values for the newly synthesized compounds have been assessed by serial dilution method All the compounds demonstrated potent antibacterial activity.

KEYWORDS: Imidazole, 1,3,4-Oxadiazole, Characterization, Antimicrobial activity

RESUMO

Uma série nova de etanonas substituídas, 1-{5-2(-metil-5-nitro-4-fenil(1,3,4)oxadiazol-3-il}-etanonas, foram sintetizadas. A formação do anel do 1,3,4-oxadiazol foi obtida através da reação da hidrazida correspondente com anhidrido acético. As estruturas dos compostos foi determinada usando técnicas de IV, RMN e análise elementar. Os compostos mostraram atividade antimicrobiana contra várias bactérias e Cândida albicans,

PALAVRAS CHAVE: Imidazol, 1,3,4-Oxadiazol, Atividade antimicrobians

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INTRODUCTION

N and O containing heterocylces have been reported to be associated with a wide range of biological activity. 1, 3, 4- Oxadiazoles are five membered ring compounds with two nitrogen atoms and one oxygen atoms. 1, 3, 4- Oxadiazoles are the class of compounds which have demonstrated immense biological activity due to the presence of –N=C-O- linkage. The wide spread use of 1, 3, 4- oxadiazole moiety as a scaffold in medicinal chemistry establishes it as an important bioactive class of heterocycles. Molecules containing 1, 3, 4-oxadiazoles moiety have shown broad spectrum of biological activities including antifungal[1], antibacterial[2], antiviral[3], anti tubercular[4], cytotoxic[5], anticancer[6], anti-inflamatory[7]. Hence 1, 3, 4-oxadiazole moiety serve as a versatile building block for experimental drug design.

On the other hand, imidazole moiety has occupied a unique place in the field of medicinal chemistry. Being a polar and ionisable aromatic compound, it improves pharmacokinetic characteristics of lead molecules. Imidazole and its derivatives are reported to be physiologically and pharmacologically active and find applications in the treatment of diseases including antibacterial[8], antifungal[9], antitubercular[10], antiviral[11], anticancer[12] etc. Hence the incorporation of the imidazole nucleus is an important synthetic strategy in drug discovery.

From the above discussion it is evident that imidazole and 1,3,4- oxadiazoles have become important components of many pharmaceuticals. With a view to broaden the scope in chemotherapy and to integrate the high therapeutic characteristics of both these moieties, the authors have made an attempt to incorporate above mentioned moieties, in a single entity.

MATERIALS AND METHODS

The starting material 2-methyl-5-nitro-imidazole (1) employed in the preparation of hydrazide (3) was obtained as a gift sample from Arathi Drugs company, Mumbai. Ethyl chloroacetate was procured from Ranbaxy, India. All the reagents and chemicals used were analytical grade obtained from Merck, India.

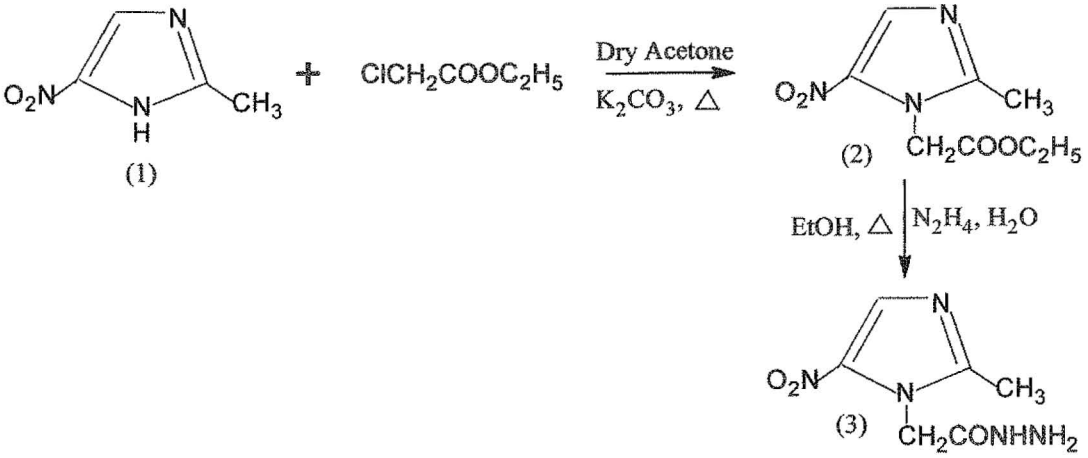
The melting points of the newly synthesized compounds were determined in open capillaries and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 983 IR spectrophotometer in KBr pellet. The ^{1}H-NMR spectra were recorded on a Bruker AC 300F (200 MHz) NMR spectrometer using DMSO – d_6 as solvent and TMS as an internal standard. All chemical shift values are expressed in δ scale downfield from TMS. The purity of all the compounds was confirmed by TLC.

GENERAL PROCEDURES FOR THE SYNTHESIS

Synthesis of (2-Methyl-5-nitro-imidazole-1-yl)-acetic acid hydrazide[13]

The mixture of 1 (0.1 mol), ethylchloroacetate (0.1 mol) and potassium carbonate (0.2 mol) in dry acetone was refluxed for about 10 hours to get 2-methyl-5-nitro-1-imidazo-ethyl acetate (2). The reaction mixture was filtered and ester so obtained was recrystalised from ethanol.

A mixture of 2-methyl-5-nitro-1-imidazo-ethyl acetate (2) (0.5 mol) and hydrazine hydrate (0.5 mol) in ethanol (100 mL) was refluxed for 8 hours. The solutions was cooled, filtered and recrystallized from ethanol to get imidazole hydrazide (3). The two steps involved in the synthesis are shown in Scheme 1.



Scheme 1. Synthesis of (2-Methyl-5-nitro-imidazole-1-yl)-acetic acid hydrazide

GENERAL PROCEDURE FOR THE SYNTHESIS OF SUBSTITUTED 1-[5-(2-METHYL-5-NITRO-4PHENYL-IMIDAZOL-1YL METHYL)-2-PHENYL-(1,3,4)OXADIAZOL-3-YL]-ETHANONE (7).

Synthesis of [4-(4-substituted-phenyl azo)-2-methyl-5-nitro-imidazole-1-yl]-acetic acid hydrazide (5)

The required benzene azo diazonium chlorides (4 a-f) were synthesized according to literature methods[14-16].

To a mixture of sodium acetate (1.0 g) in 100 mL of aqueous alcohol (50%) and 2-methyl-5-nitro-1-imidazo-acethydrazide (0.1 mol) (3) in 50 mL of ethanol cooled to 0^0C, corresponding diazonium chloride (4) was added slowly to get reddish brown crystals. The crystals (5a–f) were filtered, washed with water and dried.

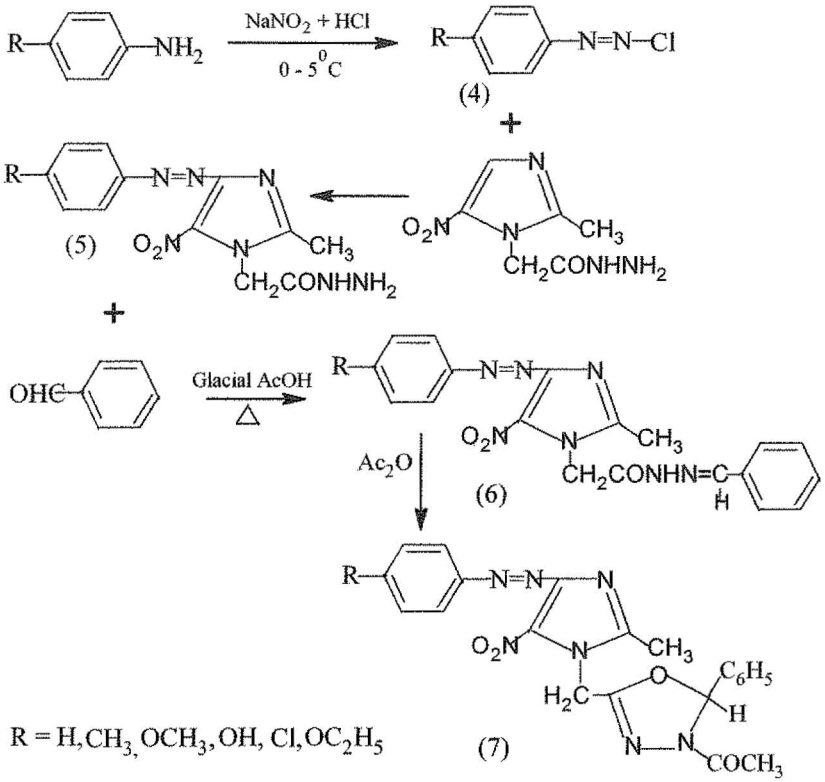
Synthesis of substituted (2-methyl-5-nitro-4-phenyl azo-imidazol-1-yl)-acetic acid benzylidene-hydrazide (6).

A mixture of 5 (0.1 mol) and benzaldehyde (0.1 mol) in glacial acetic acid (50 mL) was refluxed for one hour. The reaction mixture was cooled to room temperature and the contents were

poured into ice-cold water. The solid separated was filtered, dried and recrystallized from a mixture of ethanol-DMF to give **6a-f.**

Synthesis of substituted 1-[5-(2-methyl-5-nitro-4phenyl-imidazol-1yl methyl)-2-phenyl-(1,3,4)oxadiazol-3-yl]-ethanone (7).

A mixture of 6 (0.05 mol) and acetic anhydride (30 mL) was refluxed for 4 hours. The excess acetic anhydride was distilled off and the residue was poured into ice-cold water. The solid separated was filtered, dried and recrystallized from a mixture of ethanol-DMF. Different steps involved in the synthesis are shown in Scheme 2.



Scheme 2. Synthesis of substituted 1-[5-(2-methyl-5-nitro-4phenyl-imidazol-1yl methyl)-2-phenyl-(1,3,4)oxadiazol-3-yl]-ethanone

RESULTS AND DISCUSSION

The elemental and analysis data, spectral data and the respective assignments of **5** are given below.

Table 1. Characterization data of (2-methyl-5-nitro-4-phenylazo-imidazol-1-yl)-aceticacid hydrazide (5 a-f)

Compound No.	-R	Molecular formula	Yield (%) m.p. (^{0}c)	(Calculated) Found %			
				C	H	N	Cl
5a	H	$C_{12}H_{13}N_7O_3$	84 193-194	(47.52) 46.92	(4.32) 4.07	(32.33) 32.83	--
5b	CH_3	$C_{13}H_{15}N_7O_3$	68 207-209	(49.21 48.71	(4.76) 4.51	(30.90) 31.50	--
5c	OCH_3	$C_{13}H_{15}N_7O_4$	72 196-198	(46.85 46.15	(4.54) 4.29	(29.42) 29.92	--
5d	OH	$C_{12}H_{13}N_7O_4$	63 229-221	(45.14 44.64	(4.10) 3.85	(30.71) 31.31	--
5e	Cl	$C_{12}H_{12}ClN_7O_3$	76 236-238	(42.68 42.08	(3.58) 3.33	(29.03) 29.53	(10.50) 10.96
5f	OC_2H_5	$C_{14}H_{17}N_7O_4$	58 221-223	(48.41 47.71	(4.93) 4.68	(28.23) 28.83	--

IR (KBr) Spectral data (ν_{max} in cm^{-1})

5a: 3295 (NH), 3440 and 3420 (NH_2), 2932 (CH_3), 1665 (C=O), 1544 and 1355 (NO_2), 1625 (N=N), 3040 (C_6H_5)

5b: 3285 (NH), 3436 and 3416 (NH_2), 2930 (CH_3), 1655 (C=O), 1556 and 1310 (NO_2), 1620 (N=N), 3035 (C_6H_5)

5c: 3328 (NH), 3435 and 3415 (NH_2), 2934 (CH_3), 1668 (C=O), 154 and 1325 (NO_2), 1635 (N=N), 3031 (C_6H_5)

5d: 3292 (NH), 3434 and 3414 (NH_2), 2938 (CH_3), 1659 (C=O), 1545 and 1335 (NO_2), 1638 (N=N), 3038 (C_6H_5)

5e: 3306 (NH), 3432 and 3412 (NH_2), 2932 (CH_3), 1666 (C=O), 1540 and 1332 (NO_2), 1632 (N=N), 3033 (C_6H_5)

5f: 3275 (NH), 3416 and 3396 (NH_2), 2936 (CH_3), 1676 (C=O), 1546 and 1322 (NO_2), 1638 (N=N), 3029 (C_6H_5)

^{1}H NMR Spectral data

The ^{1}H NMR spectra (200MHz) of [4-(4-substituted-phenyl azo)-2-methyl-5-nitro-imidazole-1-yl]-acetic acid hydrazide : **5 a-f** : were recorded using DMSO-d_6 as a solvent and TMS as an internal standard. ^{1}H NMR spectrum of **5a** contains a signal due to the methyl group δ 1.35 integrating for 3 protons. The N-CH_2CO group protons came into resonance at δ 7.27. The aromatic protons of the phenyl group appeared as singlet at δ 7.52. The NH proton appeared as a broad singlet at δ 10.92, while the NH_2 proton appeared as singlet at δ 2.1.

^{1}H NMR (DMSO – d_6) Spectral data (δ in ppm)

5a: 1.35(s, 3H, CH_3), 7.27 (s, 2H, NCH_2), 10.92 (s, H, CONH), 2.10 (s, 2H, NH_2), 7.52 (s, 5H, C_6H_5)

5b: 1.30 (s, 3H, CH_3), 7.22 (s, 2H, NCH_2), 10.87 (s, H, CONH), 2.05 (s, 2H, NH_2), 7.25-7.35 (m, 4H, C_6H_4)

5c: 1.22 (s, 3H, CH_3), 3.65 (s, OCH_3), 7.32 (s, 2H, NCH_2), 10.97 (s, H, CONH), 2.20 (s, 2H, NH_2), 6.80-7.20 (m, 4H, C_6H_4)

5d: 1.18 (s, 3H, CH_3), 4.85 (s, H, OH), 7.42(s, 2H, NCH_2), 11.07 (s, H, CONH), 2.30 (s, 2H, NH_2), 6.90-7.30 (m, 4H, C_6H_4)

5e: 1.13 (s, 3H, CH_3), 7.47 (s, 2H, NCH_2), 11.12 (s, H, CONH), 2.35 (s, 2NH, NH_2), 6.95-7.35 (m, 4H, C_6H_4)

5f: 1.21 (s, 3H, CH_3), 3.90 (q, 2H, OCH_2), 1.30 (t, 3H, CH_3), 7.57 (s, 2H, NCH_2), 11.19 (s, H, CONH), 2.42 (s, 2H, NH_2), 7.02-7.42 (m, 4H, C_6H_4)

Table 2. Characterization data of (2-methyl-5-nitro-4-phenyl azo-imidazol-1-yl)-aceticacid benzylidene - hydrazide (6 a-f)

Compound No	-R	Molecular formula	Yield (%) m.p. (^{0}C)	(Calculated) Found %			
				C	H	N	Cl
6a	H	$C_{19}H_{17}N_7O_3$	72 212-215	(58.31) 57.71	(4.38) 4.06	(25.05) 25.65	--
6b	CH_3	$C_{20}H_{19}N_7O_3$	83 226-228	(59.25) 58.75	(4.72) 4.32	(24.18) 24.88	--
6c	OCH_3	$C_{20}H_{19}N_7O_4$	78 184-186	(57.00) 56.40	(4.54) 4.22	(23.27) 23.87	--
6d	OH	$C_{19}H_{17}N_7O_4$	75 204-206	(56.02) 55.52	(4.21) 3.81	(24.07) 24.77	--
6e	Cl	$C_{19}H_{16}Cl\ N_7O_3$	74 191-194	(53.59) 52.99	(3.79) 3.47	(23.03) 23.63	(8.33) 8.03
6f	OC_2H_5	$C_{21}H_{21}N_7\ O_4$	69 242-244	(57.92) 57.42	(4.86) 4.46	(22.52) 23.22	--

IR (KBr) Spectral data (ν_{max} in cm^{-1})

6a: 3285 (NH), 2927 (CH_3), 1675 (C=O), 1534 and 1390 (NO_2), 1615 (N=N), 3030 (C_6H_5), 1625 (C=N)

6b: 3275 (NH), 2925 (CH_3), 1665 (C=O), 1546 and 1350 (NO_2), 1595 (N=N), 3025 (C_6H_5), 1610 (C=N)

6c: 3318 (NH), 2934 (CH_3), 1668 (C=O), 1535 and 1335 (NO_2), 1615 (N=N), 3021 (C_6H_5), 1630 (C=N)

6d: 3282 (NH), 2938 (CH_3), 1659 (C=O), 1535 and 1365 (NO_2), 1623 (N=N), 3028 (C_6H_5), 1613 (C=N)

6e: 3303 (NH), 2927 (CH_3), 1690 (C=O), 1556 and 1398 (NO_2), 1620 (N=N), 3023 (C_6H_5), 1620 (C=N)

6f: 3265 (NH), 2936 (CH_3), 1676 (C=O), 1536 and 1312 (NO_2), 1630 (N=N), 3019 (C_6H_5), 1620(C=N)

^{1}H NMR spectral data

The ^{1}HNMR (200MHz) spectrum of 6a contains a singlet at δ 1.45 integrating for 3 protons. due to methyl group. The N-CH_2CO protons were appeared at δ 7.35. The aromatic protons of phenyl group directly attached to N=N group were noticed at δ7.56 and the other phenyl group linked to –N=CH- was observed at δ7.74. The NH proton has appeared as a broad singled at δ 10.96, while N=CH proton came into resonance at δ 11.2 as a singlet.

^{1}H NMR (DMSO – d_6) Spectral data (δ in ppm)

6a: 1.45(s, 3H, CH_3), 6.90 (s, 2H, NCH_2), 10.96 (s, H, CONH), 11.2 (s, H, N=CH), 7.33 (m, 5H), 7.56 (s, 5H)

6b:1.41 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 7.00 (s, 2H, NCH_2), 11.06 (s, H, CONH), 11.30 (s, H, N=CH), 7.43 (m, 5H) , 7.66 (s, 4H)

6c: 1.49 (s, 3H, CH_3), 3.75 (s, OCH_3), 7.10 (s, 2H, NCH_2), 11.16 (s, H, CONH), 11.40 (s, H, N=CH), 7.53 (m, 5H) , 7.40 (m, 4H)

6d: 1.52 (s, 3H, CH_3), 4.85 (s, H, OH), 7.20 (s, 2H, NCH_2), 11.26 (s, H, CONH), 11.30 (s, H, N=CH), 7.63 (m, 5H) , 7.86 (m, 4H)

6e: 1.58 (s, 3H, CH_3), 7.27 (s, 2H, NCH_2), 10.94 (s, H, CONH), 11.11 (s, H, N=CH), 7.74 (m, 4H, Ar-H), 7.5-7.7(m, 5H, Ar-H)

6f: 1.41 (s, 3H, CH_3), 7.25 (s, 2H, NCH_2), 11.01 (s, H, CONH), 11.05 (s, H, N=CH), 7.38 (m, 5H), 7.61 (m, 4H) 3.90 (q, 2H, OCH_2) 1.30 (t, 3H, CH_3)

Table 3. Characterization data of 1-[5-(2-methyl-5-nitro-4-phenyl azo-imidazol-1-yl)-2-phenyl-[1,3,4]oxadiazol-3-yl]-ethanone (7 a-f)

Compound No.	-R	Molecular formula	Yield (%) m.p. (0C)	(Calculated) Found %			
				C	H	N	Cl
7a	H	$C_{21}H_{19}N_7O_4$	86 201-204	(58.19) 57.59	(4.42) 4.06	(22.62) 23.12	--
7b	CH_3	$C_{22}H_{21}N_7O_4$	65 188-191	(59.05) 58.55	(4.73) 4.47	(21.91) 22.41	--
7c	OCH_3	$C_{22}H_{21}N_7O_5$	72 211-214	(57.02) 56.42	(4.57) 4.21	(21.16) 21.76	--
7d	OH	$C_{21}H_{19}N_7O_5$	66 216-218	(56.12) 55.62	(4.26) 4.00	(21.82) 28.32	--
7e	Cl	$C_{21}H_{18}ClN_7O_4$	71 222-224	(53.91) 53.31	(3.88) 3.52	(20.96) 21.56	(7.58) 7.38
7f	OC_2H_5	$C_{23}H_{23}N_7O_5$	72 208-211	(57.86) 57.36	(4.86) 4.60	(20.53) 20.03	--

IR (KBr) Spectral data (ν_{max} in cm^{-1})

7a: 1630 (N=N), 1556 and 1373 (NO_2), 2929 (CH_3), 1685 (C=O), 3034 (C_6H_5)

7b: 1625 (N=N), 1551 and 1305 (NO_2), 2927 (CH_3), 1650 (C=O), 3029 (C_6H_5)

7c: 1640 (N=N), 1540 and 1320 (NO_2), 2931 (CH_3), 1663 (C=O), 3025 (C_6H_5)

7d: 1643 (N=N), 1540 and 1330 (NO_2), 2935 (CH_3), 1654 (C=O), 3032 (C_6H_5)

7e: 1637 (N=N), 1535 and 1335 (NO_2), 2931 (CH_3), 1666 (C=O), 3025 (C_6H_5)

7f: 1643 (N=N), 1541 and 1317 (NO_2), 2933 (CH_3), 1675 (C=O), 3023 (C_6H_5)

^{1}H NMR spectral data

The ^{1}H NMR (200MHz) spectrum of 7a contains a singlet integrating for three protons of methyl group was observed at δ2.22. The singlet integrating for three protons of the acetyl group was observed at δ 2.46. The NCH_2 protons came into resonance at δ 5.26. The oxadiazole protons (5H) appeared as a singlet at δ 6.86. The aromatic protons were noticed at δ 7.3 and δ 7.5 as multiplets. The ^{1}H NMR data of 36a-f are presented below.

^{1}H NMR (DMSO – d_6) Spectral data (δ in ppm)

7a: 2.22(s, 3H, CH_3), 2.46 (s, 3H, $COCH_3$), 5.26 (s, 2H, NCH_2), 6.86 (Oxadiazole 5H proton), 7.30(m, 5H), 7.50 (s, 5H)

7b: 2.20 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.6 (s, 3H, $COCH_3$), 5.24 (s, 2H, NCH_2), 6.83 (s, Oxadiazole 5H proton), 7.26 (d, 2H, Ar-H), 7.83 (d, 2H, Ar-H)

7c: 2.18 (s, 3H, CH_3), 2.8 (s, 3H, $COCH_3$), 5.24 (s, 2H, NCH_2), 2.43 (s, OCH_3), 7.0 (s, Oxadiazole 5H proton), 7.2 (d, 2H, Ar-H), 7.5 (d, 2H, Ar-H), 7.7 (m, 5H, Ar-H)

7d: 2.12 (s, 3H, CH_3), 2.32(s, 3H, $COCH_3$), 5.18 (s, 2H, NCH_2), 6.73-7.13 (m, 4H), 7.43 (s, 5H), 4.80 (s, H, OH), 6.82(s, Oxadiazole 5H proton)

7e: 2.09 (s, 3H, CH_3), 2.29 (s, 3H, $COCH_3$), 5.15 (s, 2H, NCH_2), 6.70-7.10 (m, 4H), 7.40 (s, 5H), 6.83 (s, Oxadiazole 5H proton)

7f: 2.16 (s, 3H, CH_3), 2.36 (s, 3H, $COCH_3$), 5.22 (s, 2H, NCH_2), 6.77-7.17 (m, 4H), 7.47 (s, 5H), 3.90 (q, 2H, OCH_2), 1.30 (t, 3H, CH_3) 6.82 (s, Oxadiazole 5H proton)

Anti-microbial activity

The newly synthesized 1, 3, 4 – oxadiazoles were screened for antibacterial and antifungal activity. Antibacterial activity was carried out against four different pathogenic organisms, two of them were gram-negative namely *Staphylococcus aureus* and *Bacillus subtilis* and two of them were gram-negative namely *Escherichia coli* and *Pseudomonas aeruginosa.* Antifungal activity was carried out against *Candida albicans.* The MIC values for the newly synthesized compounds in the present investigation have been assessed by serial dilution method.

Table 4. Antibacterial and Antifungal activity data of compounds

Compd No.	Antibacterial activity (MIC in μg/mL)				Antifungal activity (MIC in μg/mL)
	S. aureus	*P.aeruginosa*	*E.coli*	*B.subtilis*	*C. albicans*
7a	0.25	0.25	0.25	0.50	0.20
7b	0.25	0.25	0.25	0.25	0.20
7c	0.40	0.25	0.25	0.40	0.20
7d	0.25	0.25	0.25	0.25	0.20
7e	0.25	0.25	0.25	0.50	0.20
7f	0.25	0.25	0.25	0.25	0.20
Standard Furacin	0.25	0.25	0.25	0.50	---
Standard Flucanazole	---	---	---	---	0.25
Control : (DMF)	---	---	---	---	---

It is evident from the Table 4 that all the compounds demonstrated significant antimicrobial activity and was comparable with that of the standards.

CONCLUSION

A series of 6 novel imidazole containing oxadiazoles were synthesized and characterized. The antimicrobial activity all the newly synthesized compounds was evaluated and reported. Form the present study, it can be concluded that by varying the substituents in the heterocycles, these compounds can be developed in to potential antimicrobial agents.

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SELECTIVE CAPTURE AND ENCAPSULATION OF METALLIC CATIONS BY HYDROGELS CONSISTING OF COPOLY(N-ISOPROPYLACRYLAMIDE/FUNCTIONAL MONOMER) NETWORKS

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ABSTRACT

Under the U.S. Department of Energy Waste Treatment Baseline and Integrated Waste Management Strategy the recycling of spent nuclear fuel to minimize waste, to assure maximum energy recovery and to pursue science-based R&D to possibly eliminate the need for geologic waste repositories, are programmatic goals. We have developed both polymer gel and porous materials for separation and adsorption of targeted contaminants. Here, we have investigated capture and encapsulation capabilities of hydrogels consisting of thermally-sensitive copoly[*N*-isopropylacrylamide(1-*x*)/*functional* monomer(x)] networks, where *functional* denotes carboxylic, hydroxyl, or cyanide group (mol fraction *x*); the captured and encapsulated species were: Cr^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Eu^{3+},Ho^{3+} and Tb^{3+} present in aqueous medium. Natural diffusions of cations into gel phase and the physico-chemical affinity of functional groups for cations played a major role in capturing cations. Encapsulation of cations trapped in hydrogels was achieved by loss of water and conformational transformation of networks through a volumetric phase transition. Experimental determinations of cation amounts (mass) and copolymer composition were carried out by atomic absorption and elemental analyses of carbon, nitrogen and hydrogen, respectively. We developed two approaches for determination of efficiency and selectivity metrics describing capture and encapsulation of cations by functional groups using two theories: 1) mean field theory and 2) first-order thermodynamic perturbation theory. The integrated results thus obtained show that: Cu^{2+} and Co^{2+} were selectively encapsulated by carboxylic and cyanide groups, respectively. Carboxylic and hydroxyl groups were superior extractants for Cr^{3+}, Eu^{3+} and Ho^{3+}. Further the cyanide group was also effective for Eu^{3}+ and Ho^{3+}. However, all functional groups examined here were ineffective in capture and encapsulation of Ni^{2+}. (259)

KEYWORDS: hydrogels, networks, capture, metallic cations, N-isopropylacrylamide, functional monomer, waste remediation, lanthanides, rare earths

RESUMO

Foram investigadas as capabilidades de redes de hidrogeis termicamente sensitivos de copoli[N-isopropilacrilamida(1-x)/monómero funcional(x)] para capturar seletivamente e encapsular cátions metálicos provenientes de combústivel nuclear. Os grupos funcionais foram o carboxílico, hidroxila e cianeto. As espécies capturadas e encapsuladas foram cátions trivalentes de Cr,Eu, Ho, Tb e bivalentes de Co, Cu e Ni.. Os resultados experimentais foram avaliados usando a Teoria do Campo Médio (MFT) e a Teoria de Perturbação Termodinâmica de Primeira Ordem (FOTHPER)

PALAVRAS CHAVE: hidrogeis. redes, captura, cátions metálicos,monómero funcional, N-isopropilacrilamida, remediação de resíduos, lantanídeos, terras raras

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I. INTRODUCTION

Under the U.S. Department of Energy (DOE)Waste Treatment Baseline and Integrated Waste Management Strategy (WTB-IWMS) reported by Gombert,[1,2] an important aspect toward minimizing or even eliminating the need for long-term geologic waste storage is the shedding the country's dependence on fossil fuels, while concurrently minimizing/reducing the recycling of spent nuclear fuel such as to minimize waste and to assure maximum energy recovery (high burn-up) of fuel. It is self-evident that science-based R&D is needed to achieve this objective. Tokuhiro, Bertino, Leventis and co-workers, over past 5-7 years, developed various polymer gel and porous materials for separation and adsorption; many have relevant application in processing of waste-based contaminants. For example, Bertino, Tokuhiro and Leventis have developed sol-gel materials with high mechanical strength, tunable porosity and tunable surface chemistry[3,4].

Radioactive waste, whether as high or low-level, contains a variety of elements as cations in water or similar solutions. Within the management of radioactive waste, we sought to consider new approaches for radioactive hazardous waste processing in aqueous or similar forms and in fact, 'contaminants of concern(CoC)' often stored as diluted aqueous solutions of radioactive (or non-radioactive) elements and contained in storage containers. The CoC, for example are generated from 'washing', as noted in Figure 1.

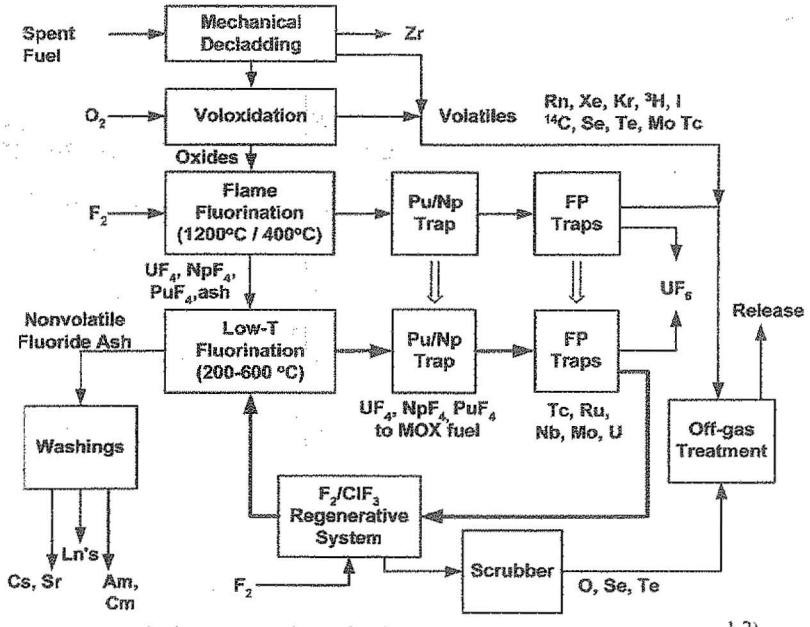

Figure 1. Spent nuclear fuel treatment process overview[1,2]

One of the general problems associated with mixed liquid waste is the lack of an efficient, effective, and inexpensive means of processing (separating) its constituents. Two of the objectives in processing solid-containing radioactive low-level liquid waste, LLW, are as follows: 1) to separate or extract radioisotopes from the rest of the mixed constituents, and 2) to produce stable solidified forms encapsulating radioactive elements. Recent R&D in the physical chemistry of gel materials, have identified promising approach to simultaneously achieve the above objectives.By utilizing and manipulating the physico-chemical properties of various silica- and polymer-based gels at the nanoscale, we have demonstrated a process by which specific chemical species are encapsulated[5,6a,6b]. Here, we limit our discussion to hydrogels of thermally-responsive poly[*N*-isopropylacrylamide (NIPA)] networks that reversibly exhibit contraction-expansion of gel volume with increasing-decreasing temperature. This change is highlighted by a transition from the swollen (sw) to shrunken(sh) state at just above ambient temperature; here for NIPA at the transition temperature, T_{tr} = 33.4°C. The total volume of gels per single polymeric residue and associated water in this transition changes in order from several to several tenths cubic nanometers [nm^3]. This volume change is caused by loss/gain of water molecules accompanied by a change in conformation of polymer networks, i.e., from an expanded to a contracted form[3, 4]. We note that replacement of NIPA, in part by polymeric residues containing other polar or ionizable groups, shifts T_{tr} to higher temperature[7-9,10-21] and simultaneously contributes chemically different characteristics to the overall polymer networks (functionalization). Moreover, we emphasize that all hydrogels form a phase independent of the liquid phase and thus, are amenable to simple physical filtration.

If a polymer component containing functional group is capable of capturing metallic cations in aqueous medium, hydrogels of copoly[NIPA(1-*x*)/functional-monomer] (where x stands for mol fraction) may retain cations in gels. Such gels can potentially serve as (candidate) extractant material for separation of radioactive metallic cations from waste streams in a simple manner.

Here, we investigated such possibility by studying the metal binding capability/retainability of hydrogels consisting of copoly[NIPA(1-*x*)/functional-monomer]. Functional groups were amide group in NIPA, carboxylic, hydroxyl and cyanide groups. We examined cations of transition metals (Cr^{3+}, Co^{2+}, Cu^{2+}, and Ni^{2+}) and of rare-earth elements (Eu^{3+}, Tb^{3+} and Ho^{3+}) dissolved in water. We particularly focused on analysis of data to find quantitative relationship between numbers of cations caught in gels and those of functional groups at the molecular level. We developed two analytical approaches.: 1) mean field theory and 2) first order thermodynamic perturbation theory. By applying two approaches, we will express the results as efficiency and selectivity of functional groups *versus* cations.

II. EXPERIMENTAL

1. Synthesis of copoly[NIPA(1-*x*)/functional-monomer] networks

Syntheses of copoly[NIPA(1-*x*)/functional-monomer] networks and gelation were carried out at 5°C as described in the literature.[3-6, 7-18]. In aqueous pre-gel solutions, the concentrations of total monomers, a functional-monomer and, cross-linker [methylene-bis-*N*-acrylamide (BIS)] were kept constant at 700 mM, 175 mM (x = 0.25) and 8.6 mM, respectively. Hydrogels thus synthesized were washed with a large amount of water by replacing the aqueous medium with fresh O_2/CO_2 free de-ionized water, at least once per day over a week at room temperature.

Copolymer networks were obtained by lyophilizing hydrogel pieces using a freeze-drying method [7-10] over 36 hours.

2. Determination of chemical composition of copolymer networks

Chemical composition of lyophilized gel pieces was determined experimentally by performing elemental analysis for hydrogen, carbon and nitrogen[5,6]. Accuracy of the Perkin Elmer Model 2400 Elemental Analyzer was checked by using re-crystallized NIPA. The results showed that experimental values for all atomic species expressed in atomic weight percent agree with theoretical values with less than 1.0% error. On this basis, we[5,6] determined the stoichiometric ratio of functional-monomer (x) namely, sodium carboxylate, allyl alcohol or allyl cyanide versus the major component, NIPA. The calculation of atomic weight percent for hydrogen, carbon and nitrogen was repeated by varying the stoichiometric ratio (x) in an iterative procedure until all atomic percentages reached less than 2% error.

3. Determination of amounts of cations caught in hydogels by atomic absorption flame photometry (AA)

(a) Calibration with standard solutions

Digitized values of absorption intensity obtained by the spectrometer (Perkin Elmer Model 2380) were calibrated with standard solutions. Original standard solutions were obtained from commercial sources[20]. Since bottles were individually labeled with the absolute concentration, all diluted solutions used for calibration were prepared accordingly. We found all absorption intensities I_{abs} basically followed Lambert-Beer's law over low concentration of ions [C]. However, we showed experimentally that I_{abs} covering wider [C] range is well represented by a continuous but somewhat non-linear curve without any peaks. Therefore, we expressed I_{abs} by a power series expansion of [C] (in units of mg of metal/L of solutions). Here, Greek letters stand for coefficients and are experimentally determined for all cations examined in this study. We found that Eq. [1] exhibits a good convergence character.

$$I_{abs} = \alpha + \beta[C] + \gamma[C]^2 + \delta[C]^3 + \varepsilon[C]^4, \quad [1]$$

Table 1 summarizes wavelength, flame environment, and coefficients for all cations examined. In practice, we thus used Eq. [1] for determination of [C] in unknown samples by solving Eq. [1] as the general solutions for quadratic, cubic and quartic equations are available.

Table 1. Wavelength, flame environment in AA method, and coefficients in Eq. (1) for all cations examined

Cation	λ (nm)	Environment	α	β	γ	δ
Cr3+	357.90	Air-Acetylene	-6.00E+06	6.65E+03	-1.20E-03	0.00E+00
Co2+	240.70	ditto	1.00E+13	-5.00E+08	1.82E+04	3.20E-03
Ni2+	232.00	ditto	9.00E+12	-5.00E+08	1.95E+04	1.02E-02
Cu2+	324.80	ditto	-3.00E+08	2.58E+04	4.80E-03	0.00E+00
Eu3+	459.40	NO-acetylene	9.02E-03	6.53E-04	2.27E-05	-7.74E-08
Tb3+	432.60	ditto	1.99E-05	2.25E-04	1.56E-07	0.00E+00
Ho3+	410.40	ditto	-5.66E-03	1.20E-03	0.00E+00	0.00E+00
Na+	589.00	Air-acetylene	4.71E-02	4.09E+03	0.00E+00	0.00E+00

(b) Preparation of samples for AA Measurement

All gel pieces were digested by gently boiling concentrated nitric acid in a Kjeldahl flask for 24 – 36 hours. Digested solutions (about 2 mL) were transferred to a 50 or 25 mL volumetric flask, washed flask with deionized water a few times and filled up to a fiducial mark. These solutions were used for AA determination. The amount of cations, as determined by AA method, is expressed in units of g/mL (solution), by the AA photometer. Then, the total amount of cations present in a sample was calculated in units of gram. For determination of the ratio of the number of cations per a single functional group, this was eventually expressed as the number of mols by knowing the atomic mass for the respective cations.

4. Capture and encapsulation of cations

In order to assess the anticipated dynamic phenomena that could be encountered in *in-situ* waste processing, a static condition must be established and taken as the reference case. This permits us to evaluate the effects introduced by dynamic processing measures, such as mechanical stirring. The term static implies the absence of any macroscopic motions such as convective currents in contrast to inherent molecular motions. To determine the quantitative relationship between the number of functional groups and the number of cations captured and encapsulated in polymer gel pieces, the following capturing and encapsulating processes were performed. Step 1) was to determine the metal binding capability of functional groups. Swollen gel pieces (in the sw state) were left in aqueous solutions of various cations for 7 days at 30°±1°C. The amount of cations caught in the gels was determined by AA-method. Step 2) was to evaluate the retainability of functional groups. We determined the quantity of cations remaining in gel pieces (by AA method), after transforming the polymer networks from the sw(swollen) to sh(shrunken) state. This is the encapsulation process in brief.

In practice, the actual experiments were conducted as follows: Step 1) Pieces of lyophilized polymer gels were weighed and left in deionized water for more than a week at room temperature. After discarding the water, aqueous solutions (100 mL) of 100 mM nitrates of Cr (III), Co (II), Cu (II), or Nil (II) and also acetates of Eu (III), Tb (III) or Ho(III) were added to now swollen gel pieces. Amounts of cations caught in gel pieces were indirectly determined (AA method) by monitoring decreasing concentration of cations in solution by taking 1.0 mL solution samples every day. As drop in concentration for all cations in solutions reached plateaus within one full week (see Fig. 2), solutions were removed from all (28) samples on the 7th day and 14 samples were subjected for determination of cations caught in gel pieces The other 14 samples were used in Step 2).

In Step 1), the samples, which were now colored gel pieces were transferred carefully without touching them to another small vial. The vials were then immersed in a small, thermo-regulated water bath whose temperature was adjusted to slightly above the respective T_{tr}. As the vial temperature rose rapidly above the respective T_{tr}, the small gel pieces shrank in volume within a matter of a few minutes. Water released from the gel pieces was quickly removed and vials were transferred in a large thermo-regulated water bath (65°C ± 0.1°C). All vials were left closed for 3 full days. Further shrinkage of gel pieces produced additional water. After carefully removing the residual solution while maintaining the same bath temperature, the closed vials were quickly removed tightly capped and left to acclimate to room temperature. This process completed the encapsulation of cations in gel pieces. The shrunken small gel pieces so produced were deeply colored as compared to gel pieces produced by step 1) . Colors of Co^{2}+, Cr^{3+}, Cu^{2+}, and Ni^{2+} were pink, purple, blue, and green, respectively, as shown in Fig. 3. Then, each vial was weighed and the mass of a gel piece was recorded.

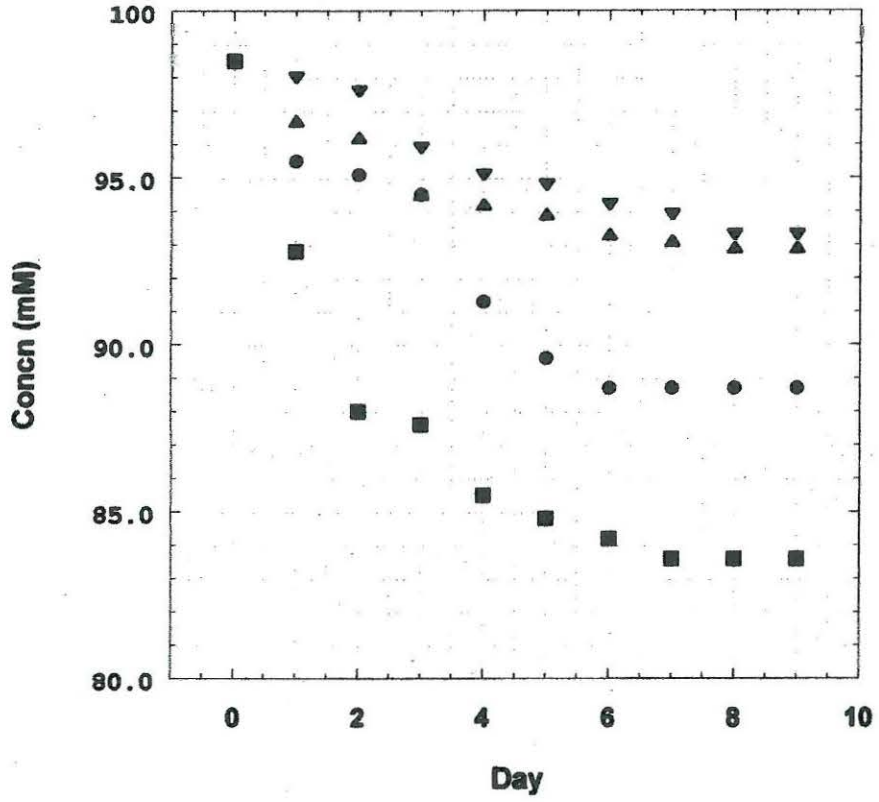

Figure 2. Capture of Ni^{2+} by hydrogels consisting of copoy[NIPA(1-x)/ functional monomer(x)] networks at 303.0 *K* Legend: circle: NIPA; square: NaAc; triangle: Allyl alcohol; inverted triangle: allyl cyanide

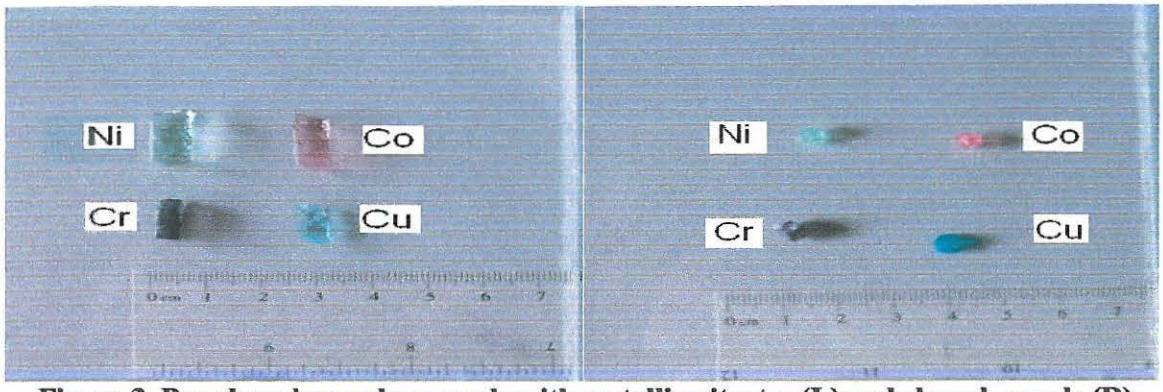

Figure 3. Pre-shrunken polymer gels with metallic nitrates (L) and shrunken gels (R)

III. RESULTS AND DISCUSSION

1. Chemical composition of copolymer networks

The final stoichiomeric ratios for copolymers are shown in **Table 2** The results indicated that mol fractions for functional-monomer x were smaller than the original value (0.25) used in pre-gel solutions for all functional groups. If the original value for x was materialized in real synthesis and, if all functional groups are assumed to be randomly distributed in networks, this would mean that all functional groups were directly bonded to one NIPA molecule on one side and two NIPA residues on the other side. However, the actual values implied that all functional groups are well separated by the major NIPA residues.

Table 2. Chemical composition of copoly[NIPA(1-x)/functional-monomer(x)] networks. x denotes mol fraction of functional component

Copolymer Composition		
NIPA(1-x)/minor(x)	x	mean F. M.
minor group		
Sodium Acrylate (NaAc)	0.154	110.216
Allyl Alcohol (A Al)	0.097	107.817
Allyl Cyanide (A Cn)	0.060	110.395

It is a good approximation to assume that the mass of dried polymer networks m_p (g) consists of many multiples of the polymeric residues[3-6]. Thus, m_p (g) = n_p x [formula mass (F.M.) of polymeric residue] where n_p stands for the number of mols. This concept for polymer networks consisting of mono-polymer component, poly(NIPA), has experimentally been verified within the experimental error range in the elemental analysis . On this basis, the mean mass of networks consisting of copoly[NIPA(1-x)/functional-monomer(x)] was defined as,

$$\text{mean F. M.} = \text{F.M.(NIPA)}\cdot(1-x) + \text{F.M.(functional-monomer)}\cdot(x) \quad [2]$$

Table2 lists the experimental results for three functional monomers obtained by the procedure presented in Section II-2 and Eq. [2].

2. Physical property of hydrogels consisting of copoly[NIPA(1-x)/functional-monomer(x)] networks

A summary of stoichiometry of all gels for transition metal cations is tabulated in **Table 3.**. Amounts of the respective polymer networks were calculated by using Eq. (2) and x values listed in **Table 2**. The results are expressed in units of number of μmol (column 7). Differences in the state of hydration between the sw and sh states are well represented by the number of water molecules per a single mean polymeric residue N_s(gel)[3] (column 9),the ratio of water vs. networks. These varied rather extensively with kinds of cations and of functional groups. N_s(gel) in the sw state were merely several to more than one hundred times the value in the corresponding sh state.

Table 3. Physical property of hydrogels consisting of copoy[NIPA(1-*x*)/ functional-monomer (*x*)] networks in the swollen and shrunken states

(Swollen State)								
			Experimental				calculated	
	Polymer	mass of	mass of	mass of	mass of	amount of	amount of	ratio
Cation	networks	networks	gels	cations	water	networks	water	water vs.
		mg	mg	µg	mg	µmol	mmol	networks
	NIPA	15.1	423.2	1954.0	406.1	133.0	22.6	169.0
Cr3+	NIPA/NaAc	12.0	212.3	1785.0	198.5	105.0	11.0	105.0
	NIPA/AAL	6.7	245.3	1816.0	236.8	63.0	13.2	210.0
	NIPA/ACN	11.2	297.1	2091.0	283.8	101.0	15.8	155.0
	NIPA	15.3	476.6	1365.0	459.9	135.0	25.6	189.0
Co2+	NIPA/NaAc	10.9	552.7	1530.0	540.3	96.0	30.0	314.0
	NIPA/AAL	6.6	384.9	1256.0	377.0	62.0	21.0	339.0
	NIPA/ACN	6.4	342.0	1191.0	334.4	58.0	18.6	321.0
	NIPA	13.5	396.3	1116.0	381.7	119.0	21.2	178.0
Cu2+	NIPA/NaAc	10.9	370.2	1061.0	358.2	96.0	19.9	208.0
	NIPA/AAL	5.4	217.3	187.0	211.7	50.0	11.8	233.0
	NIPA/ACN	8.0	201.1	223.0	192.9	72.0	10.7	148.0
	NIPA	12.2	410.8	18.0	398.6	108.0	22.1	205.0
Ni2+	NIPA/NaAc	16.6	498.9	25.0	482.3	146.0	26.8	184.0
	NIPA/AAL	7.0	205.9	18.0	198.9	65.0	11.1	169.0
	NIPA/ACN	7.1	228.1	18.0	221.0	64.0	12.3	191.0

(Shrunken State)								
			Experimental				calculated	
	Polymer	mass of	mass of	mass of	mass of	amount of	amount of	ratio
Cation	networks	networks	gels	cations	water	networks	water	water vs.
		mg	mg	µg	mg	µmol	mmol	networks
	NIPA	15.1	25.7	1675.0	8.9	133.0	500.0	3.7
Cr3+	NIPA/NaAc	6.1	24.7	649.0	18.0	53.0	1000.0	18.6
	NIPA/AAL	2.5	33.6	477.0	30.6	23.0	1700.0	72.9
	NIPA/ACN	8.6	91.6	905.0	82.1	78.0	4560.0	58.5
	NIPA	14.1	38.5	779.0	23.6	125.0	1310.0	10.5
Co2+	NIPA/NaAc	4.5	45.6	209.0	40.9	39.0	2270.0	57.6
	NIPA/AAL	6.6	8.1	192.0	1.0	62.0	70.0	1.2
	NIPA/ACN	12.5	28.2	1375.0	14.3	113.0	800.0	7.0
	NIPA	13.5	55.3	632.0	41.2	119.0	2290.0	19.2
Cu2+	NIPA/NaAc	2.7	11.2	270.0	8.2	24.0	460.0	19.3
	NIPA/AAL	6.9	57.3	83.0	50.3	64.0	2800.0	43.4
	NIPA/ACN	11.5	75.5	268.0	63.7	104.0	3540.0	34.0
	NIPA	13.0	25.3	2.0	12.3	115.0	680.0	5.9
Ni2+	NIPA/NaAc	6.4	13.9	10.0	7.5	56.0	420.0	7.4
	NIPA/AAL	3.6	11.5	15.0	7.9	34.0	440.0	13.0
	NIPA/ACN	13.3	34.4	18	21.1	120.0	1170.0	9.7

3. Data analysis of cations captured in swollen gels and encapsulated in shrunken states

Further understanding of the qualitative nature of the process in Step 1) was achieved by reversing the process itself. Namely, all colored (shrunken) gels obtained were re-immersed in pure deionized water and left intact at 31°C for one full week. The result was that the colored gel pieces returned to their transparent, uncolored state (judged by visual inspection) and the water became colored. This reversible infusion of cations into hydrogel pieces is thus a simple diffusion of cations in and out of the gel phase, and is likely driven by the concentration gradient of cations. However, differences in time dependences of process (see Fig. 1) and in amounts of cations caught in gels indicated that physical-chemical interactions between cations and functional groups also played an important role. The gels thus serve as a filter that extracts targeted species[20].

The capturing processes for Ni^{2+} by hydrogels consisting of copoly[NIPA(1-x)/functional-monomer(x)] is plotted using concentration and time in Fig. 2.
Experiments showed that: 1) all hydrogel pieces in the sw-state reached equilibrium within 6-7 days, and 2) the time dependence of uptake of the different respective cations varied significantly among different copolymer networks before reaching eventual equilibrium. These semi-quantitative results will serve as the reference with respect to evaluation of effects from possible dynamic method(s) introduced in actual processing of waste streams.

Previous studies[24-31)] for adsorption of metallic cations present in aqueous media have mostly focused on identifying suitable functional groups, determining the adsorption process in the time domain, and determining the nature of chemical adsorption for the functional groups in a semi-quantitative manner. Experimental methods for determination of the amount of cations bound to functional groups were indirectly carried out by spectrometric measurements (in UV and visible region) of cations remaining under aqueous solutions. Direct determinations of bound cations were not implemented. These past studies were at the macroscopic level. On the other hand, we have carried out direct determination as described in the preceding section and developed two different analytical approaches for determination of effectiveness of capture and encapsulation of cations at the molecular level. That is, we utilized both mean field theory, MFT, and first-order thermodynamic perturbation theory, FOTPER. The primary focus of our analysis was to express the efficiency and selectivity of capture and encapsulation of cations by functional groups in a quantitative manner.

(a) Mean field (MFT) theory

Mean Field Theory, MFT, was applied to determine the following: 1) metal binding capability of functional groups exhibited in the sw state (**Table 4**) ; and 2) retainability of metallic cations manifested in the sh state (**Table 5**) . We could easily calculate the number of polymeric residues needed for capturing a single cation (5^{th} column) from the number of mol of metallic cations determined by AA (3^{rd} column) and a number of mols of polymeric residues in gel piece (4^{th} column) on the basis of Eq. (2). Taking values thus obtained or poly(NIPA) networks (5^{th} column) as a reference, values listed in 5th column for other copoly[(NIPA(1-

Table 4. Captured cations in hydrogels consisting of copoy[NIPA(1-*x*)/ functional-monomer (*x*)] networks (swollen state)

				Mean Field	Field	Perturbation	
ion	polymer	cation	Amount	Number	Efficiency	Number	Ratio
	netorks	in gels	of polymer		versus	of minor	minor vs
		µmol	µmol	per cation	NIPA	per cation	NIPA
	NIPA	37.40	133.00	3.57	1.00	0.00	1.00
Cr3+	NIPA/NaAc	33.80	109.00	3.22	1.11	0.50	0.32
	NIPA/Aal	0.00	62.10	18000	0.00	3.17	1.20
	NIPA/Acn	39.90	102.00	2.54	1.41	2.19	0.50
	NIPA	23.80	135.00	5.68	1.00	0.00	1.00
Co2+	NIPA/NaAc	26.90	98.90	3.68	1.54	0.76	0.81
	NIPA/Aal	21.80	61.20	2.81	2.02	1.99	1.30
	NIPA/Acn	20.60	58.10	2.81	2.02	3.10	1.20
	NIPA	17.40	119.00	6.86	1.00	0.00	1.00
Cu2+	NIPA/NaAc	16.50	98.90	5.98	1.14	0.29	0.36
	NIPA/Aal	2.94	50.10	17.00	0.40	~ 0	~ 0
	NIPA/Acn	4.83	72.50	20.80	0.33	~ 0	~ 0
	NIPA	0.30	108.00	360.00	1.00	0.00	1.00
Ni2+	NIPA/NaAc	0.47	151.00	321.00	1.12	0.00	0.22
	NIPA/Aal	0.30	64.90	217.00	1.66	0.02	0.84
	NIPA/Acn	0.30	64.30	215.00	1.67	0.03	0.78
	NIPA	15.90	124.00	7.80	1.00	0.00	1.00
Eu3+	NIPA/NaAc	11.20	65.30	5.84	1.30	0.41	0.58
	NIPA/Aal	6.73	39.90	5.92	1.30	0.55	0.46
	NIPA/Acn	13.40	114.00	8.52	0.92	~ 0	1.00
	NIPA	12.50	190.00	15.20	1.00	0.00	1.00
Tb3+	NIPA/NaAc	6.77	72.60	10.70	1.40	0.24	0.68
	NIPA/Aal	15.00	39.00	25.90	0.59	~ 0	1.00
	NIPA/Acn	10.60	125.00	11.80	1.30	0.38	0.37
	NIPA	12.70	213.00	16.80	1.00	0.00	1.00
Ho3+	NIPA/NaAc	9.81	113.00	11.60	1.50	0.23	0.71
	NIPA/Aal	3.12	29.70	9.53	1.80	0.53	0.95
	NIPA/Acn	10.60	139.00	13.10	1.30	0.34	0.40

Table 5. Encapsulated cations in hydrogels consisting of copoy[NIPA(1x)/ functional-monomer(x)] networks (shrunken state)

				Mean Field	Field	Perturbation	
ion	polymer	cation	Amount	Number	Efficiency	Number	Ratio
	netorks	in gels	of polymer		versus	of minor	minor vs.
		µmol	µmol	per cation	NIPA	per cation	NIPA
	NIPA	31.70	133.00	4.22	1.00	0.00	1.00
Cr3+	NIPA/NaAc	11.90	55.30	4.66	0.91	0.14	0.10
	NIPA/Aal	8.78	23.20	2.66	1.60	1.80	0.82
	NIPA/Acn	18.30	77.90	4.26	0.99	0.00	----
	NIPA	13.70	125.00	9.10	1.00	0.00	1.00
Co2+	NIPA/NaAc	3.54	40.80	11.50	0.79	0.00	----
	NIPA/Aal	3.25	61.20	18.80	0.48	0.00	----
	NIPA/Acn	24.00	113.00	4.72	1.93	1.80	1.10
	NIPA	9.82	119.00	12.10	1.00	0.00	1.00
Cu2+	NIPA/NaAc	4.21	24.50	5.82	2.08	0.67	1.50
	NIPA/Aal	1.31	64.00	48.70	0.25	~ 0	~ 0
	NIPA/Acn	3.96	104.00	26.30	0.46	~ 0	~ 0
	NIPA	0.04	115.00	3291.00	1.00	0.00	1.00
Ni2+	NIPA/NaAc	0.17	58.10	348.00	9.46	0.02	11.00
	NIPA/Aal	0.26	33.40	131.00	25.10	0.08	2.80
	NIPA/Acn	0.30	121.00	403.00	8.17	0.04	7.90
	NIPA	2.90	120.00	41.50	1.00	0.00	1.00
Eu3+	NIPA/NaAc	17.30	156.00	9.00	4.61	0.59	4.50
	NIPA/Aal	11.30	88.10	7.83	5.30	1.09	4.90
	NIPA/Acn	7.78	95.10	12.20	3.40	0.99	2.00
	NIPA	5.68	101.00	17.80	1.00	~ 0	1.00
Tb3+	NIPA/NaAc	4.35	107.00	24.60	0.72	~ 0	~ 1.0
	NIPA/Aal	0.33	51.00	156.00	0.11	~ 0	~ 1.0
	NIPA/Acn	1.67	87.00	52.00	0.34	~ 0	~ 1.0
	NIPA	1.00	92.80	93.00	1.00	0.00	1.00
Ho3+	NIPA/NaAc	3.80	130.00	34.10	2.72	1.84	21.00
	NIPA/Aal	1.15	60.30	52.40	1.77	0.10	1.00
	NIPA/Acn	3.41	69.70	20.50	4.54	0.73	4.30

x)/functional-monomer(x)] network systems are evaluated. The results are summarized in 1st column through 6th in **Tables 4** and **5**, respectively. They were interpreted as follows. If values listed in 6th column are less than unity, the specific functional groups were more efficient than the amide group for capturing or encapsulating cations. Thus, the use of Eq. (2) was correct in expressing amount of polymer networks with a given composition x. However, there is the implication that copoly[NIPA(1-x)/functional-monomer (x)] networks are made of *mean* residues. Namely, every polymeric residue is a NIPA residue, but somewhat modified by the character of the functional-polymeric residue, by the amount x. This is the interpretation based on mean field theory. These *'mean'* polymeric networks are different from possible real network structures where NIPA and functional-polymeric residues are randomly bonded in 3D space; in reality, individual NIPA and functional group residues are recognized. As the major polymeric component, NIPA, also participates in capture and encapsulation of cations, the number of functional-polymeric residues per a single cation (5th column) cannot purely be assigned to a functional-group. In fact, it includes contributions from NIPA residues near a functional-residue. Thus the difference between that calculated by MF theory and possibly the *bona fide* value assigned exclusively to the respective functional group arises from the following: 1) one assumes a completely random distribution of functional groups made in MFT, 2) a non-crystalline nature of polymer networks, and 3) the absence of cooperative behavior of two different functional groups. In other words, the configuration of networks is not the same in all cases. We must thus exercise caution in consideration of differences.

(b) First-order thermodynamic perturbation theory (FOTHPER)

As the major NIPA component is not extensively replaced by functional groups (**Table 2**), it is a good approximation to regard the functional-polymeric groups as a perturbing element of the unperturbed poly(NIPA) networks. We could then directly apply the fundamental principles of FOTHPER[9, 10, 32] theory to evaluate both metal binding capability and retainability of respective functional groups. The difference in the experimental values for cation amounts, between perturbed and unperturbed systems, logically arise from the contribution from functional-polymeric residues (7th column). As we have presented in our previous works[9, 10], the cation amounts solely captured or encapsulated per a single NIPA residue in the unperturbed poly(NIPA) networks were easily obtained by using values listed in 3rd and 4th columns. Cation amounts caught by all NIPA residues in copoly[NIPA(1-x)/functional-monomer(x)] (the perturbed system) were evaluated by applying the difference in respective chemical compositions. Values listed in the 8th column were obtained by taking the ratio of these values in perturbed systems *versus* to those in unperturbed systems with respect to specific cations. Therefore, this value may be regarded as describing the efficiency of capture and retention apability of the respective functional group, in reference to the amide group in the NIPA residue. The same argument described for MFT should be applied to the physical meaning of number of functional-polymeric residues per a single cation (7th column). In FOTHPER theory, the interactions of cations and functional groups occur as if functional groups occupy (randomly) the non-interacting NIPA residues. In contradt to MFT, the values in 7th column do not contain contributions from neighboring NIPA residues, if cooperative influence of captured/encapsulated cations by functional and amide groups exist. Again, the calculated results must be considered as a virtual situation.

4. Metal binding capability of functional groups for transition metal cations

A total of sixteen (16) gel samples were subjected to Step 1) experiments. The results for cations are tabulated in **Table 4**. Here, we focused on the relationship between the amount of cation and that of minor polymer component, as indicated in the 3rd and 4th columns. The results obtained from MFT are shown in the 5th and 6th columns. In considering the scientific significance expressed under MF Theory, we can state that: values in the 5th column indicated that the amide group for NIPA residue was quite effective in the capture of Cr^{3+}, Co^{2+} and Cu^{2+}; but not Ni^{2+}. Further all functional groups were relatively ineffective in capture of Ni^{2+}. This is well supported by the FOTHPER approach. The hydroxyl group was totally ineffective for capturing Cr^{3+}, while other groups were effective for Cr^{3+} in the increasing order of amide, carboxylic, and cyanide groups (values noted in 6th column). All functional groups were marginally effective in capturing Co^{2+} and Cu^{2+}. However, the results for cyanide group for both Cr^{3+} and Co^{2+}, as well as hydroxyl group for Co^{2+} suggested another important factor; namely, the proximity of functional groups. In considering the arguments developed in consideration of MF and FOTHPER approaches, the values shown in the 5th and 7th columns reflected the ineffectiveness of cation capture if multiple functional groups are available.

5. Retaining capability of functional groups: Encapsulation of transition metal cations

The results shown in **Table 5** exhibited substantial differences from the corresponding trends found for capturing cations. All functional groups were ineffective in capturing and encapsulating Ni^{2+}. The results from both MFT and FOTHPER approaches indicated that both carboxylic and hydroxyl groups effectively encapsulated Cr^{3+} and the former, selectively encapsulated Cu^{2+}. The cyanide group is the only functional group that successfully encapsulated Co^{+}, even though all functional groups effectively capture Co^{2+}. Chromium tri-valent cation offered an important case that reveals the difference between capture and encapsulation processes. The proximity of multiple functional groups seemed to play an important role in the latter process as exemplified by the hydroxyl group.

6. Metal binding capability of functional groups for rare-earth cations

Experimental results for three lanthanide, tri-valent cations, Eu^{3+}, Tb^{3+}, and Ho^{3+} are given in **Table 4**. In contrast to transition metal cations, the amide group was in general ineffective in capturing lanthanide cations. The carboxylic group was basically a good extractant for all lanthanide cations; however, the hydroxyl group acted selectively, being best for Eu^{3+}. Further, the cyanide group was quite effective in capturing both Tb^{3+} and Ho^{3+} but, not Eu^{3+}. As the functional group was well separated (**Table 2**) and surrounded by NIPA residues, the smaller values shown for the functional group of NIPA residue (7th column of **Table 4**) reflected high affinity *via* the sole functional group rather than 'collective affinity', as exhibited by NIPA groups. This suggests that increase of mol fraction (minor group) was also an important factor for effective capture of lanthanide cations.

7. Retaining capability of functional groups: Encapsulation of rare-earth cations

Experimental results for encapsulation are given in **Table 5**. The results by MF Theory clearly showed selective encapsulation of cations by specific functional groups. Namely, all functional groups were ineffective for Tb^{3+}. In contrast, carboxylic, hydroxyl, and cyanide groups were relatively more effective for Eu^{3+} and Ho^{3+}. This result was also supported by the results obtained by FOTHPER. Terbium cation distinctly exhibited a difference between the capture and encapsulation processes.

It is worthwhile to briefly compare the preceding results with hard-soft acid-base theory[34] which is more qualitative than quantitative in nature. Among the cations we examined Cr^{3+} is regarded as a hard acid and Co^{2+} lies at the border. Among functional groups, carboxylic acid is referred to as a hard base. On the basis of hard-soft acid-base theory, hard acids react faster and form stronger bonds with hard bases. This assertion seemed to hold very well between Cr^{3+} (as well as Co^{2+}) and carboxylic acid, as supported by both MFT and FOTHPER approaches. As well, it seemed correct for the cyanide group.

It is well known that rare earth tri-valent ions form salts with oxalic acid. According to hard-soft acid-base theory, all rare earth tri-valent ions must be regarded as hard acids and this concorded with their observed affinity for hard base. However, another hard base, the hydroxyl showed selective affinity for the three cations as revealed by both MFT and FOTHPER approaches..

IV. CONCLUSION

Although the long-term storage of spent nuclear fuel in the U.S. is again under reconsideration, three constant objectives are that the U.S. recycle spent nuclear fuel in order to minimize waste. while concurrently assuring the maximum energy recovery via longer burn-up of fuel. Science-based R&D to possibly eliminate the need for geologic waste repositories continues to be needed. Here, we investigated the selective capture and encapsulation of metallic cations dissolved in water by hydrogels, consisting of functionalized, thermo-sensitive copoly[*N*-isopropylacrylamide(1-*x*)/*functional-monomer(x)*]. It is a feasible means for cation removal from aqueous medium. The *functional-monomer (x)* stands for carboxylic, hydroxyl, and cyanide groups with the corresponding mol fraction x = 0.154, 0.097 and 0.060, respectively. Our results indicated mildly selective process; the amide group's associative property was noticeable for all cations examined in this study. The carboxylic group also acted as a good extractant for Cr^{3+}, Cu^{2+}, Eu^{3+}, and Ho^{3+}. Significant selective numbers of encapsulations are primarily noted for Cr^{3+}, Cu^{2+}, and Co^{2+} by hydroxyl, carboxylic and cyanide groups, respectively. Finally, among functional groups examined for three representative lanthanide cations, the hydroxyl group exhibited the highest selectivity for Eu^{3+}.

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CONDUCTOMETRIC STUDY OF COMPLEX FORMATION BETWEEN 2,3-PYRAZINEDICARBOXYLIC ACID AND SOME TRANSITION METAL IONS IN METHANOL

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ABSTRACT

The complexation reactions between $CuCl_2$, $CoCl_2$ and $NiCl_2$ with 2,3-Pyrazinedicarboxylic acid in methanol (MeOH) at 313.15 K were studied by conductometric methods. The association constants, formation constants and Gibbs free energies were calculated from the conductometric titration curves. On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines were obtained indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes. The formation constants and Gibbs free energies of different complexes in absolute Methanol at 313.15 K follow the order:)

$K_f(2:1)>K_f(1:1)$for (M:L) and $\triangle G_f(2:1)>\triangle Gf(1:1)$ for (M:L)

KEY WORDS: Association constants; formation constants; Gibbs free energies of association; Gibbs free energies of complex formation.

RESUMO

A formação de complexos entre $CuCl_2$, $CoCl_2$, $NiCl_2$ e ácido 2,3-pirazinodicarboxílico em metanol á 313.15 K foi estudada usando métodos de condutividade. As constantes de associação e formação e as energias livres de Gibbs foram calculadas a partir de curvas de titulação condutimétrica. A relação entre a condutância molar e a proporção das concentrações metal-ligante levou a linhas retas indicando a formação de complexos estequiométricos (M:L) 1:1 e 2:1. As constantes de formação e as energias livres de Gibbs dos vários complexos em metanol à 313.15 K seguem a ordem:

$K_f(2:l)>K_f(1:1)$ para (M:L) e $\triangle Gf(2:1)>\triangle G_f(1:1)$ para (M:L)

PALAVRAS CHAVE: Constantes de associação. Constantes de formação,Energias livres de Gibbs de associação, energias livres de Gibbs para formação de complexos.

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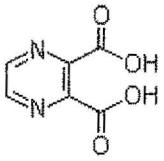
INTRODUCTION

The long range ion – ion interactions due to screened columbic forces are the most important features of electrolyte in solutions. These act together with shorter – ranged forces between the solvent molecules and between the solvent molecules and ion. Electrical conductivity (EC) is a measure measure of solvent to conduct electric current and depends on: concentration of the ions, ligand and temperature in solutions. Current is carried out by both cations and anions, but to different degree. The conductivity due to divalent cations is more than that of mono-valet cations, it is not true for anions. Metal cations with d^0 noble gas electron configuration (alkali and alkaline earth) metal ions together with the inert molecular ions like tetraalkylammonium,-phosphonium,-arsonium , and trialkylsulfonium ions exhibit properties mainly determined by their charge and size [1].Solvation of such cations in protic and polar solvents is due essentially to electrostatic ion-dipole and ion induced dipole interactions. Metal cations with filled d - orbitals, the d^{10} cations, exhibit partially covalent character in their interactions; their properties depend on the charge and size and partially on their electro negativity. Cations with incomplete d- orbitals called d^n-cations .With these cations protic and polar solvent molecules are strongly bound in complexes to a central cation through p-d orbital overlap and exchange only slowly with the bulk solvent. The formation of complexes becomes more important at high concentration of the complex ion and is likely to be more extensive in non-aqueous solvents, particularly in dipolar aprotic solvents, whereas the salvation of anions is weaker, leading to stronger complexation. Therefore conductivity study is valuable on using transition metal cations [2-7]. This work provides the analytical analyst and the biological analyst data can help him for deterring the concentration of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in blood and different solutions.

2,3-Pyrazinedicarboxylic acid

Identification

Name	2,3-Pyrazinedicarboxylic acid
Synonyms	Pyrazine-2,3-dicarboxylic acid
Molecular Structure	
Molecular Formula	$C_6H_4N_2O_4$
Molecular Weight	168.11
CAS Registry Number	89-01-0
EINECS	201-875-3

Properties

Melting point	185-188 °C
Water solubility	Soluble

EXPERIMENTAL

The chemicals used 2, 3-pyrazine dicarboxylic acid and methanol were provided from Merck Co. and used directly without purification.

The experimental procedure to obtain the formation constant of complexes of 2,3-Pyrazinedicarboxylic acid with $CuCl_2$, $CoCl_2$ and $NiCl_2$ by conductometric procedure was as follows : -

A solution of metal chloride ($1x10^{-3}$ M) was placed in a titration cell, at a const temperature (313.15) K , and the conductance of the solution was measured . The ligand (1×10^{-2} M) was transferred step-by-step to the titration cell using a precalibrated micropipette and the conductance of the solution was measured after each transfer. Addition of the ligand solution was continued until the total concentration of the (2, 3-Pyrazinedicarboxylic acid) was approximately four times higher than that of metal ions. The conductance of the solution was measured after each addition. The complex formation constant, K_f, and the molar conductance of the complex, ML, were evaluated by computer fitting to the molar conductance mole ratio data.

RESULTS AND DISCUSSIOIN

- The stability of a transition metal complex with a polydentate chelate ligand depends on a range of factors including: number and type of the donor atoms present, the number and size of the chelate rings formed on complexation. In addition, the stability and selectivity of complexities strongly depend on the donor ability and dielectric constant of the solvent and shape and size of the solvent molecules.

- 2, 3-Pyrazinedicarboxylic acid is a polydentate ligand which tends to be completely coordinated to a metal ion. This reagent is soluble in water and soluble in most organic solvents

- The specific conductance values (Ks) of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in absolute (MeOH) were measured experimentally in absence and in the presence of ligand at 313.15 K.

The molar conductance (Λ_m) values were calculated [8] using equation (1):

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \quad (1)$$

Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively; K_{cell} is the cell constant and C is the molar concentration of the $CuCl_2$, $CoCl_2$ and $NiCl_2$ solutions.

- The limiting molar conductances (Λ_o) at infinite dilutions were estimated $CuCl_2$, $CoCl_2$ and $NiCl_2$ in absolute methanol (MeOH) alone and in the presence of the ligand by extrapolating the relation between Λ_m and $C_m^{1/2}$ to zero concentration (Fig.1). By drawing the relation between molar conductance (Λ_m) and the molar ratio of metal to ligand (M/L) concentrations , different lines are obtained with sharp breaks indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes (Fig.2).

- The experimental data of (Λ_m) and (Λ_o) were analyzed for the determination of association and formation constants for each type of the stoichiometric complexes.

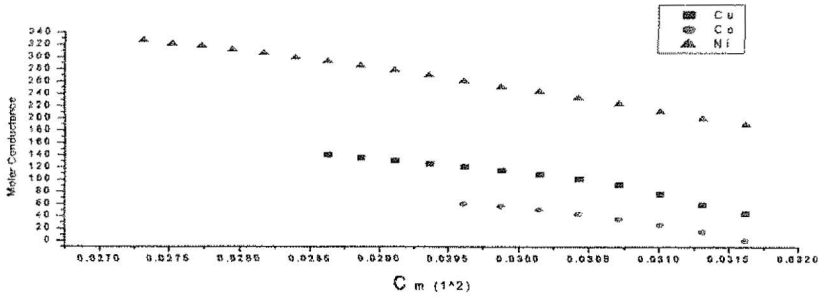


Figure 1. The relation between molar conductance (Λ_m) and ($\sqrt{C}$) of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the presence of H_2L in absolute methanol at 313.15 K.

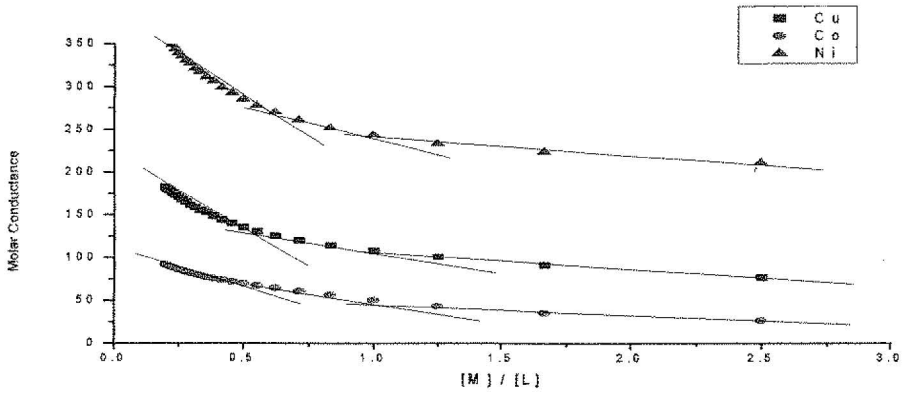


Figure 2. The relation between molar conductance (Λ_M) and the molar ratio (M/L) of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the presence of H_2L in absolute methanol at 313.15 K indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes.

- The association constants of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the presence of ligand in absolute MeOH at 313.15 K for 1:2 asymmetric electrolytes were calculated [9, 10] by using equation (2):

$$K_A = \frac{\Lambda_0^2(\Lambda_0 - \Lambda_m)}{4C_m^2 + \Lambda^3 S(z)} \qquad (2)$$

Where (Λ_m, Λ_0) are the molar and limiting molar conductance, respectively of $CuCl_2$, $CoCl_2$ and $NiCl_2$, C_m is molar concentration of $CuCl_2$, $CoCl_2$ and $NiCl_2$, S(Z) is Fuoss-Shedlovsky factor , equal one for strong electrolytes [11]. The calculated association constants are shown in Table 1.

- The Gibbs free energies of association (ΔG_A) were calculated from the association constant [12,13] by applying equation (3) :

$$\Delta G_A = -R\,T \ln K_A \qquad (3)$$

Where R is the gas constant (8.341 J) and T is the absolute temperature (313.15 K). The calculated Gibbs free energies were presented in Table 1.

Table 1. Association constants and Gibbs free energies of association for $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the presence of ligand in absolute MeOH at 313.15 K .

C	Λ_m			Λ_0^2 (Λ_0-Λ_m)			$4C^2+\Lambda^3_m$			K_A			ΔG_A (k J/mol)		
	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni
0.001	44.2365	1.5347	190.1071	4153605	409822.3	35726553	7828.18	3.614689	6870605	530.622	113404.6	5.199913	-16.3877	-30.4001	-4.30623
0.00098	58.78107	14.99206	199.8977	3698561	334627.6	34109455	13820.86	3369.845	7987726	267.6072	99.30655	4.270234	-14.5997	-12.0105	-3.78174
0.000962	76.43012	26.64074	211.637	3146071	269453	32170481	23366.25	16907.72	9479266	134.6416	14.25095	3.393774	-12.8056	-6.93958	-3.19169
0.000943	91.21989	35.77829	224.4413	2683089	218328.1	30055600	33264.27	45799.27	11305987	80.6113	4.767064	2.658379	-11.4657	-4.07922	-2.55378
0.000926	100.9503	43.57271	234.2381	2378486	174717.9	28437481	40763.85	82726.31	12852051	58.34791	2.112	2.21268	-10.6214	-1.95281	-2.07445

- The association free energies evaluated for CuCl2, CoCl2 and NiCl2 -ligand complexes are small and spontaneous indicating electrostatic attraction.
- The formation constants (K_f) for $CuCl_2$, $CoCl_2$ and $NiCl_2$ complexes were calculated for each type of complexes (1:1) and (2:1) (M:L) by using equation (4) [14,15] :

$$K_f = \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]} \qquad (4)$$

Where Λ_m is the molar conductance of the CuCl2, CoCl2 and NiCl2 alone, Λ_{obs} is the molar conductance of solution during titration and Λ_{ML} is the molar conductance of the complex.

- The obtained values (K_f) for $CuCl_2$, $CoCl_2$ and $NiCl_2$ -ligand stoichiometric complexes are presented in Table 2, 3. The Gibbs free energies of formation for each stoichiometric complexes were calculated by using the equation :

$$\Delta G_f = -R\ T \ln K_f \qquad (5)$$

- The calculated ΔG_f values are presented in Tables 2, 3.

Table 2. Formation constants and Gibbs free energies of formation for 1: 1 (M/L) , $CuCl_2$, $CoCl_2$ and $NiCl_2$-H_2L in absolute MeOH at 313.15 K .

[L]	Λ_{obs}			$(\Lambda_{obs}-\Lambda_{ML})/[L]$			$(\Lambda_m-\Lambda_{obs})$			K_f			ΔG_f (k J/mol)		
	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni
0.001525	130.5947	70.41492	279.0194	0.03436	0.026712	0.054091	381.4053	422.3387	170.9806	11100.35	15810.72	3161.006	-24.3299	-25.2538	-21.0491
0.001379	125.2748	67.66132	270.7058	0.023731	0.020429	0.037443	386.7252	425.0387	179.2942	16296.39	20805.3	4788.516	-25.3328	-25.9709	-22.1339
0.001228	120.062	64.96128	261.3417	0.014727	0.013209	0.021837	391.9381	429.0942	188.6583	26613.65	32485.43	8639.321	-26.514	-27.1347	-23.6752
0.001071	114.3794	60.90575	252.1424	0.00676	0.007413	0.009195	397.6206	432.9314	197.8576	58818.62	58403.4	21517.08	-28.6654	-28.6669	-26.0587
0.000909	108.2582	57.08869	244.2408	0.000171	0.000831	0.000619	403.7419	438.9357	205.7592	2360436	528080.5	332449.7	-36.3292	-34.4181	-33.2094

Table 3. Formation constants and Gibbs free energies of formation for 2:1 (M/L) $CuCl_2$, $CoCl_2$ and $NiCl_2$-H_2L in absolute MeOH at 313.15 K.

[L]	Λ_{obs}			$(\Lambda_{obs}-\Lambda_{ML})/[L]$			$(\Lambda_M-\Lambda_{obs})$			K_f			ΔG_f (k J/mol)		
	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni
0.002186	153.0003	77.87709	311.6939	0.03931	0.016292	0.05883	359.9997	412.1221	136.1061	9132.511	26295.58	2347.531	-23.8202	-26.4813	-20.2719
0.002063	148.7928	76.53127	307.0205	0.028399	0.01259	0.045439	363.2072	413.4687	142.9795	12789.27	32841.27	3146.609	-24.6999	-27.1632	-21.0371
0.001935	144.3875	74.42244	299.5928	0.018111	0.007727	0.028044	367.6125	415.5776	150.4072	20297.51	53760.36	5325.254	-25.9063	-28.4515	-22.4114
0.001803	140.1737	72.46812	293.5041	0.009276	0.003675	0.015335	371.8263	417.5319	156.4959	40066.58	113604.8	10205.02	-27.6839	-30.4048	-24.1103
0.001667	135.4038		286.2205	0.000623		0.002034	376.5962		163.7795	504488.3		80512.97	-34.7711		-29.5054

- The association free energies evaluated for CuCl2, CoCl2 and NiCl2 -1igand complexes indicating a spontaneous electrostatic attraction.

- The formation constants and Gibbs free energies of different complexes in absolute methanol at 313.15 K follow the order: K_f (2:1) › K_f (1:1) for (M:L), and ΔG_f(2:1) › ΔG_f(1:1) for (M:L) .

CONCLUSION

This work concentrated on the behavior of $CuCl_2$, $CoCl_2$ and $NiCl_2$ with the ligand conductometrically .The main target is to discuss the complexation between the metal and ligand for evaluating different concentrations from the metal ion in different solutions

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SYNTHESIS OF NEW SPIRO- HETEROCYCLES CONTAINING DIHYDROTETRAZINE MOIETY

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ABSTRACT

The reaction of nitrilimines with hydrazones of alkanones and cycloalkanones led to the formation of acyclic electrophilic addition products, which upon treatment with C/S/Zn cyclized to 1,6-dihydro-1,2,4,5-tetrazine derivatives. The structures of the synthesized compounds have been established by their elemental analyses and spectroscopical data.

KEYWORDS

Nitrilimines, Hydrazones, Cyclization, Synthesis, 1,6-dihydro-1,2,4,5-tetrazine

RESUMO

A reação de nitriliminas com hidrazonas de alcanonas e cicloalcanonas levou à formação de produtos acíclicos de adição eletrofílica. Depóis de tratamento com C/S/Zn eles levaram a derivados cíclicos de 1,6-dihidro-1,2,4,5-tetrazinas.As estruturas dos compostos sintetizados foram comprovadas com análise elementar e dados especroscópicos.

PALAVRAS CHAVE

Nitriliminas, Hidrazonas, Ciclização, Síntese de 1,6-dihidro-1,2.4,5-tetrazina

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GRAPHICAL ABSTRACT

Synthesis of New Spiro-Heterocycles Containing Dihydrotetrazine moiety

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III V-IX

V, Ar = Ph; VI, Ar = PhNH; VII, Ar = 2-Furyl;
VIII, Ar = 2-Tienyl; IX, Ar = 2-Naphthyl

1. INTRODUCTION

Previous publications, showed that the simple hydrazones derived from aliphatic aldehydes and ketones react with nitrilimines at ambient temperature to give acyclic addition products, which undergo oxidative cyclization upon refluxing with active charcoal to yield the corresponding 1,6-dihydro-s-tetrazines [1] or amidrazones [2,3]. On the other hand, methyl hydrazones of alkanals and alkanones furnish 1,2,3,4-tetrahydro-s-tetrazines [3,4].

Recently, we found that nitrilimines react with 1-methyl, 1-phenyl, 1-acetyl, 1-formyl and 1-ethoxycarbonyl-1-methylhydrazines at room temperature afforded acyclic electrophilic addition products, which cyclized intramolecularly to the corresponding 1,2,3,4-tetrahydro-1,2,4,5-tetrazines by heating them with activated charcoal or lithium hydride in refluxing benzene or toluene [5.]

Quite recently, we described the synthesis of 1,2,3,4-tetrahydro-1,2,4,5-tetrazin-3-ones by the reaction of acetylhydrazone pyridinium chloride (Girard-reagent P) with different nitrilimines [6]. Several methods have been reported for the synthesis of tetrazine derivatives, and the most frequently used method for the preparation of 1,2,3,4-tetrahydro-1,2,4,5-tetrazines is the cyclization of alkylformazanes by heating or base treatment [7].

In the present study, the synthesis of a series of new substituted 1,2,4,5-tetrazines **5-9** were performed (Scheme 1) and their structures were characterized by ^{1}H NMR ^{13}C NMR, IR spectroscopy and elemental analysis.

2. RESULTS AND DISCUSSION

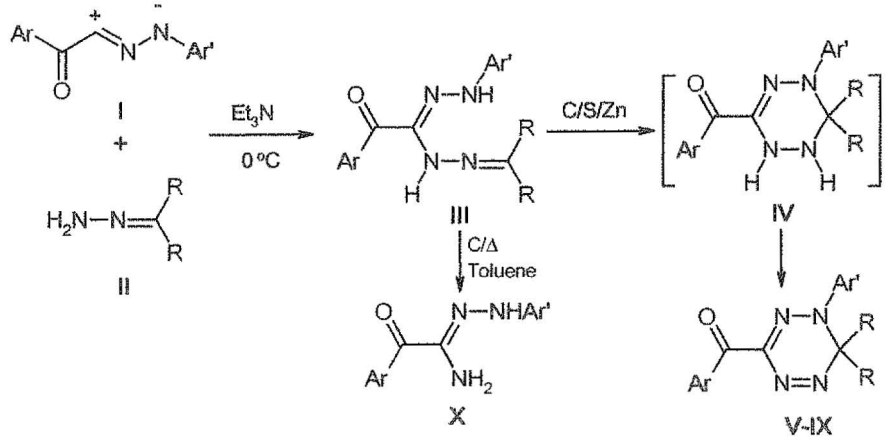
The formazans (acyclic adducts) **III** were synthesized via reaction of nitrilimines **I** with alkanones and cycloalkanone hydrazones **II** as shown in Scheme 1. Attempts to cyclize the acyclic adducts **III** (Ar = Me or OMe) by heating in tetrahydrofuran or ethanol were unsuccessful. However, treatment of solution of later adducts **III** (Ar = Me or OMe) with palladium-carbon brought about oxidative cyclization to the 1,6-dihydro-1,2,4,5-tetrazines [1].

On the other hand, cyclization of acyclic compounds **III** (Ar = Ph, PhNH, 2-furyl, 2-theinyl, 2-naphthyl) using active charcoal in refluxing toluene give complicated mixture of products as indicated by TLC, among which amidrazones **X** were separated, rather than the expected 1,6-dihydro-1,2,4,5-tetrazines [2,3] (Figure 1).

Treatment of solution of formazans **III** (Ar = Ph, PhNH, 2-furyl, 2-theinyl, 2-naphthyl) with new catalyst containing (C/S/Zn), developed in our laboratory by our colleague of physical chemistry, at room temperature in benzene or toluene give directly 1,6-dihydro-1,2,4,5-tetrazines **V-IX** (Figure 1) in excellent yields. (Table 1). It is suggested that the conversion of acyclic compounds **III** into s-tetrazines **V-IX** involves the non isolable intermediate formation of the tetrahydro-s-tetrazines **IV** (Figure 1).

2.1 Spectral data analysis

The assignment of structures of compounds **V-IX** is based on their analytical and spectroscopic data. Physical properties and microanalysis are presented in Table 1. These compounds gave satisfactory combustion analysis for the proposed structures which are confirmed on the basis of their spectroscopic data.



V, Ar = Ph; VI, Ar = PhNH; VII, Ar = 2-Furyl;
VIII, Ar = 2-Tienyl; IX, Ar = 2-Naphthyl

Ar' = 4-X-C_6H_4-

Entery	a	b	c	d	e	f	g	h	i	j	k	l
X	Cl	Cl	Cl	Cl	Cl	H	H	H	H	H	H	H
R R	Me Me					Me Me						

Figure 1. Synthetic pathway for the preparation of compounds **V-IX**.

In the IR spectra of compounds **V-IX**, showed the disappearance of NH signals and the C=O bond stretching of the carbonyl group at C-3 occurs at higher frequency (1665-1655 cm^{-1}) than it dose in the acyclic precursors **III** (1650-1635 cm^{-1}). This implies that conjugation of this exocyclic group with the hetero-ring π–system is decreased as a consequence of homoaromaticity and the slightly non-planar arrangement of the N-2, N-4 and C-3 plane with the substituents at C-3 [8-9] Compounds **V-IX** revealed strong absorption at about 1620-1600 cm^{-1} assigned to C=N bond stretching.

^{1}H and ^{13}C NMR spectra of obtained compounds **V-IX** provide strong evidence in support of the proposed structures. Their ^{1}H NMR spectra showed the disappearance of 2NH signals, in addition to aromatic protons signals, a characteristic signal due to amide NH proton for compounds **VI** resonating as singlet at 9.10-8.80 ppm. For compounds **Va,VIa,VIf,IXa** tow signals for the

methyl groups ($2CH_3$) protons appeared as singlet at 1.41-1.34 ppm and the signals of the cycloalkane protons in other compounds appeared in the range of 2.53-1.51 ppm.

The dihydrotetrazines **V-IX** exhibited a characteristic ^{13}C NMR signal at 68-87 ppm assigned to the C-6. This is similar to reported values of quaternary or spiro carbon flanked by tow nitrogens in six-membered heterocycles [2,3]. In the acyclic analogues **III**, this carbon resonates at 140-155 ppm [2,3]. This provides a strong evidence in support of cyclic structure of compounds **V-IX**. The ^1H and ^{13}C NMR spectral data of the synthesized compounds are presented in the experimental part.

3. EXPERIMENTAL SECTION

3.1. Reagents and Instrumentation

Triethylamine (TEA), tetrahydrofuran (THF), acetone, cyclohexanone, 4-methylcyclohexanone, 4-t-butylcyclohexanone, cyclopentanone, cycloheptanone, cyclooctanone and toluene were purchased from Avocado Chemical Company, England, and used as purchased. All melting points were determined on a Stuart Electrothermal Apparatus and are uncorrected.

The IR spectra were obtained by using Perkin-Elmer 737 infrared spectrophotometer in potassium bromide pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400.13 MHz) at room temperature in $CDCl_3$ and DMSO-d_6, using tetramethylsilane (TMS) as an internal reference. All chemical shifts were reported as δ values in parts per million (ppm) downfield from internal TMS.

Electron impact (EI) mass spectra were measured on Shimadzu GCMS-QP1000 EX Mass spectrometers at 70 eV. Elemental analysis are performed at Cairo University, Egypt, and the results agreed with the calculated values within experimental errors. Nitrilimines **1** and hydrazones **2** used in this study, were prepared according to described procedures [1,10,11].

3.2. Synthesis of 1,6-dihydro-s-tetrazines V-IX

3.2.1 Reaction of nitrilimines I with hydrazones II

To a stirred mixture of the appropriate hydrazonoyl halide [nitrilimines **I** precursors] (0.01 mol) and hydrazones **II** (0.02 mol) in dry THF (100 mL), triethylamine (5 mL, 0.05 mol) in THF (20 mL) was dropwise added at -5 to 0 °C and the reaction mixture was controlled by TLC. The reaction temperature was allowed to rise slowly to room temperature and stirring was continued until the starting substrates were completely consumed (4-6 hours). The precipitated triethylammonium chloride salt was filtered off, the solvent was removed under reduced pressure. The residue was washed with water (3x50 mL), then triturated with ethanol (10 mL), the crude solid product was collected and recrystallized from aqueous ethanol to give the desired compounds **III**.

Table 1. Physical data and elemental analysis for compounds (V-IX).

Comp.	Molecular Formula (MW)	Yield (%)	mp (°C)	Analysis (%) Calculated / (Found)		
				C	H	N
Va	$C_{17}H_{15}ClN_4O$ (326.79)	82	173-5	62.48 (62.70)	4.63 (4.50)	17.14 (17.25)
Vb	$C_{19}H_{17}ClN_4O$ (352.83)	86	166-8	64.68 (64.45)	4.86 (4.75)	15.88 (16.05)
Vc	$C_{20}H_{19}ClN_4O$ (366.85)	89	184-6	65.48 (65.75)	5.22 (5.35)	15.27 (15.10)
Vd	$C_{21}H_{21}ClN_4O$ (380.88)	91	167-9	66.22 (61.95)	5.56 (5.70)	14.71 (14.60)
Ve	$C_{22}H_{23}ClN_4O$ (394.91)	87	175-7	66.91 (67.10)	5.87 (5.00)	14.19 (14.30)
VIa	$C_{17}H_{16}ClN_5O$ (341.80)	81	182-4	59.74 (60.00)	4.72 (7.65)	20.49 20.30)
VIc	$C_{20}H_{20}ClN_5O$ (381.87)	86	191-3	62.91 (63.15)	5.28 (5.35)	18.43 (18.60)
VIe	$C_{22}H_{24}ClN_5O$ (409.92)	84	187-9	64.46 (64.20)	5.90 (6.05)	17.08 (16.95)
VIf	$C_{17}H_{17}N_5O$ (307.36)	88	194-6	66.43 (66.65)	5.58 (5.40)	22.79 (22.90)
VIg	$C_{19}H_{19}N_5O$ (333.40)	92	201-3	68.45 (68.25)	5.74 (5.90)	21.01 (20.85)
VIh	$C_{20}H_{21}N_5O$ (347.42)	90	181-3	69.14 (68.90)	6.09 (5.95)	20.16 (20.30)
VIi	$C_{21}H_{32}N_5O$ (361.45)	87	196-8	69.78 (69.55)	6.41 (6.25)	19.38 (19.55)
VIj	$C_{24}H_{29}N_5O$ (403.53)	83	167-9	71.44 (71.15)	7.24 (7.35)	17.36 (17.20)
VIk	$C_{21}H_{23}N_5O$ (361.45)	94	177-9	69.78 (69.95)	6.41 (6.55)	19.38 (19.25)
VIl	$C_{22}H_{25}N_5O$ (375.48)	91	183-5	70.38 (70.10)	6.71 (6.55)	18.65 (18.80)
VIIb	$C_{17}H_{15}ClN_4O_2$ (342.74)	93	153-5	59.57 (59.80)	4.41 (4.30)	16.34 (16.20)
VIIc	$C_{18}H_{17}ClN_4O_2$ (356.81)	90	148-50	60.59 (60.35)	4.80 (4.95)	15.70 (15.85)
VIIIb	$C_{17}H_{15}ClN_4O_2S$ (358.85)	85	163-5	56.90 (57.15)	4.21 (4.40)	15.61 (15.50)
VIIId	$C_{19}H_{19}ClN_4O_2S$ (386.91)	89	146-8	58.98 (59.25)	4.95 (5.10)	14.48 (14.35)
IXa	$C_{21}H_{17}ClN_4O$ (376.85)	83	190-2	66.93 (67.20)	4.55 (4.40)	14.87 (15.00)
IXb	$C_{23}H_{19}ClN_4O$ (402.89)	91	176-8	68.57 (68.80)	4.75 (4.65)	13.91 (14.05)
IXc	$C_{24}H_{21}ClN_4O$ (416.91)	87	189-91	69.14 (68.90)	5.08 (4.95)	13.44 (13.60)
IXd	$C_{25}H_{23}ClN_4O$ (430.94)	84	168-70	69.68 (69.90)	5.38 (5.50)	13.00 (12.85)
IXe	$C_{26}H_{25}ClN_4O$ (444.97)	89	184-6	70.18 (69.95)	5.66 (5.80)	12.59 (12.45)

3.2.2 Cyclization of compounds (III):

Acyclic compounds III (0.005 mol) and C/S/Zn (0.1 w/w%) in benzene or toluene were stirred at room temperature for 1-2 hours and monitored by TLC. The reaction mixture was cooled, then filtered and the solvent was minimized and petroleum ether (bp. 40-60 °C) was slowly added to effect complete crystallization of the desired cyclic compounds V.
The following compounds were prepared using this method:

3-Benzoyl-1-(4-chlorophenyl)-6,6-dimethyl-1,6-dihydro-1,2,4,5-tetrazine (Va): ^{1}H NMR ($CDCl_3$) δ: 7.92-7.03 (m, 9H, Ar-CH), 1.39 (s, 3H, CH_3), 1.37 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 187.4 (C=O), 171.6 (COOH), 143.7 (C=N), 144.3-126.6 (Ar-C), 68.6 (quaternary carbon), 22.5 (CH_3). IR (KBr) *v*/cm^{-1}: 1660 (C=O), 159.2 (C=N).

8-Benzoyl-6-(4-chlorophenyl)-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (Vb): ^{1}H NMR ($CDCl_3$) δ: 8.02-7.11 (m, 9H, Ar-CH), 1.90-1.68 (m, 8H, cyclopentane protons). ^{13}C NMR ($CDCl_3$) δ: 185.7 (C=O), 143.9 (C=N), 144.9-126.1 (Ar-C), 86.7 (spiro carbon), 32.1, 23.7 (cyclopentane carbons). IR (KBr) *v*/cm^{-1}: 1655 (C=O), 1594 (C=N).

3-Benzoyl-1-(4-chlorophenyl)-1,2,4,5-tetraazaspiro[5.5]undec-2,4-diene (Vc): ^{1}H NMR (DMSO-d_6) δ: 7.97-7.06 (m, 9H, Ar-CH), 1.86-1.66 (m, 10H, cyclohexane protons). ^{13}C NMR (DMSO-d_6) δ: 185.5 (C=O), 143.9 (C=N), 144.4-126.2 (Ar-C), 84.3 (spiro carbon), 32.1, 24.7, 23.4 (cyclohexane carbons). IR (KBr) *v*/cm^{-1}: 1655 (C=O), 1593 (C=N).

3-Benzoyl-1-(4-chlorophenyl)-1,2,4,5-tetraazaspiro[5.6]dodec-2,4-diene (Vd): ^{1}H NMR ($CDCl_3$) δ: 8.27-7.00 (m, 9H, Ar-CH), 2.53-1.56 (m, 12H, cycloheptane protons). ^{13}C NMR ($CDCl_3$) δ: 185.6 (C=O), 143.4 (C=N), 142.7-119.6 (Ar-C), 87.5 (spiro carbon), 39.5, 28.7, 22.3 (cycloheptane carbons). IR (KBr) *v*/cm^{-1}: 1660 (C=O), 1597 (C=N).

3-Benzoyl-1-(4-chlorophenyl)-1,2,4,5-tetraazaspiro[5.7]tridec-2,4-diene (Ve): ^{1}H NMR ($CDCl_3$) δ: 7.99-6.96 (m, 9H, Ar-CH), 2.46-1.36 (m, 14H, cyclooctane protons). ^{13}C NMR ($CDCl_3$) δ: 185.6 (C=O), 143.9 (C=N), 145.0-114.8 (Ar-C), 86.6 (spiro carbon), 34.4, 27.2, 25.2, 23.1 (cyclooctane carbons). IR (KBr) *v*/cm^{-1}: 1650 (C=O), 1594 (C=N).

1-(4-Chlorophenyl)-3-phenylaminocarbonyl-6,6-dimethyl-1,6-dihydro-1,2,4,5-tetrazine (VIa): ^{1}H NMR (DMSO-d_6) δ: 9.12 (s, 1H, NH), 7.61-7.18 (m, 10H, Ar-CH), 1.41 (s, 3H, CH_3), 1.38 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ: 159.2 (C=O amide), 136.7 (C=N), 142.4-126.6 (Ar-C), 68.7 (spiro carbon), 22.5 (CH_3). IR (KBr) *v*/cm^{-1}: 1650 (C=O), 1594 (C=N).

1-(4-Chlorophenyl)-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.5]-undec-2,4-diene (VIc): ^{1}H NMR (DMSO-d_6) δ: 9.10 (s, 1H, NH), 7.63-7.20 (m, 10H, Ar-CH), 1.86-1.60 (m, 10H, cyclohexane protons). ^{13}C NMR (DMSO-d_6) δ: 159.3 (C=O amide), 136.9 (C=N), 141.9-125.8 (Ar-C), 84.8 (spiro carbon), 31.4, 25.7, 22.6 (cyclohexane carbons). IR (KBr) *v*/cm^{-1}: 1655 (C=O), 1598 (C=N).

1-(4-Chlorophenyl)-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.7]-tridec-2,4-diene (VIe): ^{1}H NMR (DMSO-d_6) δ: 9.12 (s, 1H, NH), 7.60-7.20 (m, 14H, Ar-CH), 2.53-1.44 (m, 10H, cyclooctane protons). ^{13}C NMR (DMSO-d_6) δ: 159.4 (C=O amide), 136.8 (C=N), 141.7-126.0 (Ar-C), 86.5 (spiro carbon), 34.5,

30.7, 28.4, 23.2 (cyclooctane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1596 (C=N).

1-Phenyl-3-phenylaminocarbonyl-6,6-dimethyl-1,6-dihydro-1,2,4,5-tetrazine (VIf): ^{1}H NMR (DMSO-d_6) δ: 9.00 (s, 1H, NH), 7.63-7.23 (m, 10H, Ar-CH), 1.37 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ: 158.9 (C=O amide), 136.7 (C=N), 143.7-124.4 (Ar-C), 68.7 (spiro carbon), 22.7 (CH_3). IR (KBr) ν/cm^{-1}: 1650 (C=O), 1598 (C=N).

6-Phenyl-8-phenylaminocarbonyl-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (VIg): ^{1}H NMR (DMSO-d_6) δ: 9.10 (s, 1H, NH), 7.60-7.19 (m, 10H, Ar-CH), 1.95-1.70 (m, 8H, cyclopentane protons). ^{13}C NMR (DMSO-d_6) δ: 158.8 (C=O), 136.4 (C=N), 142.3-126.2 (Ar-C), 86.6 (spiro carbon), 32.3, 23.4 (cyclopentane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1596 (C=N).

1-Phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.5]undec-2,4-diene (VIh): ^{1}H NMR (DMSO-d_6) δ: 9.00 (s, 1H, NH), 7.58-7.16 (m, 10H, Ar-CH), 1.85-1.63 (m, 10H, cyclohexane protons). ^{13}C NMR (DMSO-d_6) δ: 158.5 (C=O amide), 136.7 (C=N), 141.7-124.6 (Ar-C), 80.6 (spiro carbon), 32.0, 24.8, 23.1 (cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1595 (C=N).

9-Methyl-1-phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.5]-undec-2,4-diene (VIi): ^{1}H NMR (DMSO-d_6) δ: 9.05 (s, 1H, NH), 7.62-7.17 (m, 10H, Ar-CH), 2.05-1.22 (m, 9H, cyclohexane protons), 0.94 (s, 3H, CH_3 at cyclohexane). ^{13}C NMR (DMSO-d_6) δ: 158.6 (C=O amide), 136.6 (C=N), 141.5-125.0 (Ar-C), 84.5 (spiro carbon), 33.8, 31.4, 28.4, 22.7 (methyl-cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1598 (C=N).

9-tert-Butyl-1-phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro-[5.5]undec-2,4-diene (VIj): ^{1}H NMR (DMSO-d_6) δ: 9.10 (s, 1H, NH), 7.66-7.21 (m, 10H, Ar-CH), 2.05-1.10 (m, 9H, cyclohexane protons), 0.88 (s, 9H, tert-butyl group) . ^{13}C NMR (DMSO-d_6) δ: 158.7 (C=O amide), 136.5 (C=N), 141.6-124.3 (Ar-C), 84.9 (spiro carbon), 47.1, 35.8, 32.4, 27.6, 24.1 (tert-butyl-cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1650 (C=O), 1594 (C=N).

1-Phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.6]dodec-2,4-diene (VIk): ^{1}H NMR (DMSO-d_6) δ: 8.95 (s, 1H, NH), 7.65-7.20 (m, 10H, Ar-CH), 2.45-1.62 (m, 12H, cycloheptane protons). ^{13}C NMR (DMSO-d_6) δ: 158.5 (C=O amide), 136.7 (C=N), 141.7-124.6 (Ar-C), 87.7 (spiro carbon), 39.6, 28.4, 22.3 (cycloheptane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1596 (C=N).

1-Phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.7]tridec-2,4-diene (VIl): ^{1}H NMR (DMSO-d_6) δ: 9.10 (s, 1H, NH), 7.60-7.20 (m, 10H, Ar-CH), 2.52-1.43 (m, 14H, cyclooctane protons). ^{13}C NMR (DMSO-d_6) δ: 158.4 (C=O amide), 136.5 (C=N), 139.7-126.6 (Ar-C), 86.9 (spiro carbon), 34.8, 31.1, 28.7, 23.2 (cyclooctane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1593 (C=N).

6-(4-Chlorophenyl)-8-(2-furoyl)-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (VIIb): ^{1}H NMR ($CDCl_3$) δ: 7.87-7.26 (m, 7H, Ar-CH), 1.95-1.70 (m, 8H, cyclopentane protons). ^{13}C NMR (DMSO-d_6) δ: 174.7 (C=O), 143.3 (C=N), 136.8-115.9 (Ar-C), 86.6 (spiro carbon), 34.5 32.2, 23.2 (cyclopentane carbons). IR (KBr) ν/cm^{-1}: 1665 (C=O), 1594 (C=N).

1-(4-Chlorophenyl)-3-(2-furoyl)-1,2,4,5-tetraazaspiro[5.5]undec-2,4-diene (VIIc): ^{1}H NMR ($CDCl_3$) δ: 8.26-7.21 (m, 7H, Ar-CH), 1.84-1.61 (m, 10H, cyclohexane protons). ^{13}C NMR (DMSO-d_6) δ: 174.6 (C=O), 143.1 (C=N), 136.7-

116.1 (Ar-C), 80.6 (spiro carbon), 32.6, 24.8, 23.3 (cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1660 (C=O), 1595 (C=N).

6-(4-Chlorophenyl)-8-(2-thenoyl)-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (VIIIb): ^{1}H NMR ($CDCl_3$) δ: 8.23-7.18 (m, 7H, Ar-CH), 1.92-1.67 (m, 8H, cyclopentane protons). ^{13}C NMR (DMSO-d_6) δ: 174.6 (C=O), 143.4 (C=N), 136.7-115.0 (Ar-C), 86.8 (spiro carbon), 32.4 23.7 (cyclopentane carbons). IR (KBr) ν/cm^{-1}: 1665 (C=O), 1598 (C=N).

1-(4-Chlorophenyl)-3-(2-thenoyl)-1,2,4,5-tetraazaspiro[5.6]dodec-2,4-diene (VIIId): ^{1}H NMR ($CDCl_3$) δ: 8.21-7.16 (m, 7H, Ar-CH), 2.42-1.60 (m, 12H, cycloheptane protons). ^{13}C NMR (DMSO-d_6) δ: 174.6 (C=O), 143.2 (C=N), 136.6-114.6 (Ar-C), 87.5 (spiro carbon), 39.5 28.2, 22.5 (cycloheptane carbons). IR (KBr) ν/cm^{-1}: 1665 (C=O), 1596 (C=N).

1-(4-Chlorophenyl)-6,6-dimethyl-3-(2-naphthoyl)-1,6-dihydro-1,2,4,5-tetrazine (IXa): ^{1}H NMR ($CDCl_3$) δ: 8.59-7.16 (m, 11H, Ar-CH), 1.41 (s, 3H, CH_3), 1.39 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ: 187.5 (C=O), 135.5 (C=N), 144.2-125.9 (Ar-C), 68.6 (spiro carbon), 22.6 (CH_3). IR (KBr) ν/cm^{-1}: 1645 (C=O), 1595 (C=N).

6-(4-Chlorophenyl)-8-(2-napthoyl)-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (IXb): ^{1}H NMR ($CDCl_3$) δ: 8.57-7.12 (m, 11H, Ar-CH), 2.10-1.67 (m, 8H, cyclopentane protons). ^{13}C NMR (DMSO-d_6) δ: 187.4 (C=O), 135.4 (C=N), 144.0-115.3 (Ar-C), 80.7 (spiro carbon), 31.9, 23.5 (cyclopentane carbons). IR (KBr) ν/cm^{-1}: 1646 (C=O), 1598 (C=N).

1-(4-Chlorophenyl)-3-(2-naphthoyl)-1,2,4,5-tetraazaspiro[5.5]undec-2,4-diene (IXc): ^{1}H NMR ($CDCl_3$) δ: 8.56-7.13 (m, 11H, Ar-CH), 2.15-1.58 (m, 10H, cyclohexane protons). ^{13}C NMR ($CDCl_3$) δ: 187.5 (C=O), 135.5 (C=N), 143.9-126.0 (Ar-C), 70.9 (spiro carbon), 30.8, 25.8, 22.6 (cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1648 (C=O), 1597 (C=N).

1-(4-Chlorophenyl)-3-(2-naphthoyl)-1,2,4,5-tetraazaspiro[5.6]dodec-2,4-diene (IXd): ^{1}H NMR ($CDCl_3$) δ: 8.58-7.24 (m, 11H, Ar-CH), 2.35-1.65 (m, 12H, cycloheptane protons). ^{13}C NMR ($CDCl_3$) δ: 187.1 (C=O), 135.6 (C=N), 144.5-119.6 (Ar-C), 85.3 (spiro carbon), 39.4, 31.2, 28.3, 22.6 (cycloheptane carbons). IR (KBr) ν/cm^{-1}: 1645 (C=O), 1593 (C=N).

1-(4-Chlorophenyl)-3-(2-naphthoyl)-1,2,4,5-tetraazaspiro[5.7]tridec-2,4-diene (IXe): ^{1}H NMR ($CDCl_3$) δ: 8.56-6.98 (m, 11H, Ar-CH), 2.48-1.37 (m, 14H, cyclooctane protons). ^{13}C NMR ($CDCl_3$) δ: 187.2 (C=O), 135.7 (C=N), 142.1-114.7 (Ar-C), 84.9 (spiro carbon), 34.6, 30.8, 28.7, 23.4 (cyclooctane carbons). IR (KBr) ν/cm^{-1}: 1645 (C=O), 1594 (C=N).

4. CONCLUSION

In conclusion, the results demonstrate that the nitrilimines react with hydrazone of aliphatic alkanones and cycloalkanone to give an acyclic addition product, which upon treatment with new catalyst (C/S/Zn) yielded the spiro heterocyclic compounds containing tetrazine moiety.

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SYNTHESIS AND ANTIMICROBIAL PROFILE OF SOME NEWER HETEROCYCLES BEARING THIAZOLE MOIETY

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ABSTRACT

Various substituted acetophenones on treatment with iodine and thiourea yielded 2-amino-4-(substituted-phenyl)-thiazole, which on further treatment with acetic anhydride generated *N*-(4-(substitutedphenyl)thiazol-2-yl)acetamide (1-5). All the synthesized compounds were characterized by their respective FTIR, ^{1}H NMR and mass data. Synthesized compounds (1, 2, 3, 4, 5) when subjected to investigation for their antimicrobial activities i.e. antibacterial and antifungal studies against *Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, Candida albicans, Asperigillus flavus and Asperigillus fumigatus* by disk diffusion method, revealed that compound 2 deemed to be most potent with largest zone of inhibition.

KEYWORDS: Thiazole, Acetophenones, Antimicrobial, Substituted Aldehydes.

RESUMO

Tratamento de acetofenonas substituídas com iodo e tiouréia levou a formação de vários 2-amino tiazóis -4- (fenilsubstituidos) . O tratamento destes com anihidrido acético gerou N-(4-fenilsubstituido)tiazol-2-il) acetamidas (1-5). Todos os compostos sintetizados foram caracterizados com técnicas de infravermelho com transformadas de Fourier, RMN de ^{1}H e espectrometria de massa. .As propriedades frmacêuticas dos compostos 1,2,3,4 e 5 foram avaliadas com *Staphylococcus aureus, Eschericia coli, Pseudomonas aeruginosa, Cândida albicans. Aspergillus flavus e Aspergillus fumigatus.* O composto 2 foi o mais potente.

PALAVRAS CHAVE: Tiazol, Acetofenonas, Aldeídos Substituídos, Atividade Antimicrobiana.

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INTRODUCTION

Thiazole derivatives have attracted a great deal of interest owing to their anticancer activity[1-3], antibacterial activity[4], antifungal activity[4], anti-inflammatory activity[4], antitubercular activity[5], cardiotonic activity[6], antidegenerative activity on cartilage[7] etc. Thiazoles are known to be allosteric enhancer of A_1 adenosine receptors[8] whereas other analogs are known to be inhibitors of protein phosphatases[9]. Heterocycle-bearing substrates are particularly desirable structures for screening and are prevalent in drugs that have reached the market place.

The development of simple and general synthetic routes for widely used organic compounds from readily available reagents is one of the major challenges in organic chemistry. Therefore to meet the facile results of these tough challenges thiazole nucleus was being considered. Among the wide variety of heterocycles that have been explored for developing pharmaceutically molecules, thiazole derivatives have played a vital role in the medicinal chemistry. There are large numbers of synthetic compounds with thiazole nucleus used for anticancer activities when properly substituted at 2-position. In view of these observations and in continuation to develop better and potent anticancer agents, some newer thiazole derivatives were synthesized.

MATERIALS AND METHODS

Melting points were taken in open capillaries and are uncorrected. IR spectrum of compounds in KBr pellets were recorded on a FTIR-8400S spectrophotometer (SHIMADZU). ^{1}HNMR spectra of the compounds were recorded on Bruker DRX 300 NMR spectrophotometer in DMSO-d_6 using TMS as internal standard. Mass spectra of the compounds were recorded on MSN-9629 mass spectrometer. Elemental analysis was carried out on Elemental Vario EL III Carlo Erba 1108. The purity of compounds was monitored by thin layer chromatography. Thin layer chromatographic analysis of the compounds were performed on silica gel G coated glass plates using Chloroform: Methanol: Pet.Ether (9:1:0.5) as mobile phase. The spots were visualized by exposure to iodine vapours.

General method for the synthesis of 2-amino-4-(substituted-phenyl)-thiazole

Various substituted acetophenones (0.01mol) were refluxed with iodine (0.01mol) and thiourea (0.02mol) for 9 hrs to get 2-amino-4-(substituted-phenyl)thiazole. The solid obtained was washed with diethyl ether, after which it was washed with sodium thiosulfate. Finally, it was washed with water and the residue was filtered, dried and recrystallized from distilled water.

General method for the synthesis of (1-5)

Then, 2-amino-4-(substituted-phenyl)thiazole (0.01mol) was refluxed with acetic anhydride (0.01mol) for 2hrs. This led to the formation of N-(4-(substituted-phenyl)thiazol-2-yl)acetamide (1-5). The final products were purified by recrystallization from ethanol. Physical data of compounds synthesized are summarized in Table-1.

Table-1. Physical data of compounds (1-5)

Compound	R	Molecular Formula	Mol. Wt.	Yield (%)	m.p. (°C)
1	H	$C_{11}H_{10}N_2OS$	218.27	61	98-99
2	*p*-chloro	$C_{11}H_9ClN_2OS$	252.72	69	209-210
3	*p*-bromo	$C_{11}H_9BrN_2OS$	297.17	65	202-203
4	*p*-hydroxy	$C_{11}H_{10}N_2O_2S$	234.27	65	141-142
5	*o*-hydroxy	$C_{11}H_{10}N_2O_2S$	234.27	70	115-116

***N*-(4-phenylthiazol-2-yl)acetamide (1):** UV λ_{max} (Methanol): 232 nm. FTIR (KBr): 3392.55 (N-H stretching), 2977.89 (aromatic C-H stretching), 2931.6 (C-H stretching of methyl), 1622.02 (C=O stretching), 1569.95 (C=N stretching), 1498.59 (aromatic C-C stretching), 690.47 cm^{-1} (C-S stretching of thiazole). ^{1}HNMR (DMSO-d_6) δ: 2.142 (s, 3H, CH_3), 7.117 (s, 1H, =C-H of thiazole), 7.273-7.854 (m, 5H, Ar-H), 8.854 ppm (s, 1H, NH, D_2O exchangeable). ESI-MS: m/z (%) 219 (8) $[M+1]^+$, 218 (43) $[M]^+$, 203 (40), 175 (100), 134 (43), 133 (23). Elemental Analysis: Calcd for $C_{11}H_{10}N_2OS$: C, 60.53; H, 4.62; N, 12.83; S, 14.69. Found: C, 60.50; H, 4.63; N, 12.81; S, 14.68 %.

***N*-(4-(4-chlorophenyl)thiazol-2-yl)acetamide (2):** UV λ_{max} (Methanol): 224 nm. FTIR (KBr): 3394.48 (N-H stretching), 2981.74 (aromatic C-H stretching), 2947.03 (C-H stretching of methyl), 1623.95 (C=O stretching), 1564.16 (C=N stretching), 1492.8 (aromatic C-C stretching), 746.4 (C-Cl stretching), 651.03 cm^{-1} (C-S stretching of thiazole). ^{1}HNMR (DMSO-d_6) δ : 2.466 (s, 3H, CH_3), 6.545 (s, 1H, =C-H of thiazole), 7.116-7.625 (m, 4H, Ar-H), 9.154 ppm (s, 1H, NH, D_2O exchangeable). ESI-MS: m/z (%) 254 (17) $[M+2]^+$, 253 (6) $[M+1]^+$, 252 (46) $[M]^+$, 237 (32), 209 (100), 168 (42), 167 (22). Elemental Analysis: Calcd for $C_{11}H_9ClN_2OS$: C, 52.28; H, 3.59; Cl, 14.03; N, 11.08; S, 12.69. Found: C, 52.27; H, 3.57; Cl, 14.02; N, 11.06; S, 12.71 %.

***N*-(4-(4-bromophenyl)thiazol-2-yl)acetamide (3):** UV λ_{max} (Methanol): 225 nm. FTIR (KBr): 3417.63 (N-H stretching), 3029.33 (aromatic C-H stretching), 2993.32 (C-H stretching of methyl), 1672.17 (C=O stretching), 1598.88 (C=N stretching), 1488.94 (aromatic C-C stretching), 693.26 (C-S stretching of thiazole), 570.89 cm^{-1} (C-Br stretching). ^{1}HNMR (DMSO-d_6) δ : 2.763 (s, 3H, CH_3), 6.967 (s, 1H, =C-H of thiazole), 7.317-7.825 (m, 4H, Ar-H), 8.778 ppm (s, 1H, NH, D_2O exchangeable). ESI-MS: m/z (%) 299 (43) $[M+2]^+$, 298 (8) $[M+1]^+$, 297 (42) $[M]^+$, 282 (40), 254 (100), 213 (32), 212 (27). Elemental Analysis: Calcd for $C_{11}H_9BrN_2OS$: C, 44.46; H, 3.05; Br, 26.89; N, 9.43; S, 10.79. Found: C, 44.45; H, 3.01; Br, 26.87; N, 9.46; S, 10.80 %.

***N*-(4-(4-hydroxyphenyl)thiazol-2-yl)acetamide (4):** UV λ_{max} (Methanol): 242 nm. FTIR (KBr): 3558.42 (O-H stretching), 3406.05 (N-H stretching), 3048.29 (aromatic C-H stretching), 2923.88 (C-H stretching of methyl), 1631.67 (C=O stretching), 1554.52 (C=N

stretching), 1526.93 (aromatic C-C stretching), 675.04 cm^{-1} (C-S stretching of thiazole). ^{1}HNMR (DMSO-d_6) δ: 2.228 (s, 3H, CH_3), 4.955 (s, 1H, OH, D_2O exchangeable), 6.369 (s, 1H, =C-H of thiazole), 7.296-7.658 (m, 4H, Ar-H), 8.564 ppm (s, 1H, NH, D_2O exchangeable). ESI-MS: m/z (%) 235 (6) $[M+1]^+$, 234 (28) $[M]^+$, 219 (22), 191 (100), 150 (20), 149 (14). Elemental Analysis: Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.39; H, 4.30; N, 11.96; S, 13.69. Found: C, 56.40; H, 4.33; N, 11.98; S, 13.65 %.

***N*-(4-(2-hydroxyphenyl)thiazol-2-yl)acetamide (5):** UV λ_{max} (Methanol): 267 nm. FTIR (KBr): 3555.6 (O-H stretching), 3408.42 (N-H stretching), 3046.05 (aromatic C-H stretching), 2926.05 (C-H stretching of methyl), 1633.88 (C=O stretching), 1554.07 (C=N stretching), 1523.96 (aromatic C-C stretching), 1291.67 (C-O stretching), 673.68 cm^{-1} (C-S stretching of thiazole). ^{1}HNMR (DMSO-d_6) δ: 2.156 (s, 3H, CH_3), 4.702 (s, 1H, OH, D_2O exchangeable), 6.911 (s, 1H, =C-H of thiazole), 7.316-7.625 (m, 4H, Ar-H), 8.778 ppm (s, 1H, NH, D_2O exchangeable). ESI-MS: m/z (%) 235 (6) $[M+1]^+$, 234 (28) $[M]^+$, 219 (22), 191 (100), 150 (20), 149 (14). Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.39; H, 4.30; N, 11.96; S, 13.69. Found: C, 56.37; H, 4.33; N, 11.98; S, 13.67 %.

Antimicrobial activity

The synthesized compounds 1-5 were screened for antibacterial (*S. aureus, E. coli, P. aeruginosa*) and antifungal (*C. albicans, A. flavus, A. fumigatus*) activities by disk diffusion method at a concentration of 2 mg/mL using DMF as a solvent. The results were recorded in duplicate using Ciprofloxacin and Fluconazole as standards and are given in Table 2 & 3.

Table-2: Antibacterial Activity of compounds (1-5)

Compounds	Zone of Inhibition (mm)		
	S. aureus	*E. coli*	*P. aeruginosa*
1.	15.5 ± 0.00	17 ± 0.33	16 ± 0.00
2.	21.5 ± 0.33	20.5 ± 0.00	19.3 ± 0.00
3.	19.7 ± 0.67	20.3 ± 0.33	20.3 ± 0.33
4.	16.4 ± 0.00	15 ± 0.00	15.5 ± 0.00
5.	17.3 ± 0.00	17 ± 0.33	17 ± 0.67
Ciprofloxacin	27 ± 0.00	28 ± 0.00	27 ± 0.00
DMF	-	-	-

Table 3. Antifungal Activity of Compounds (1-5)

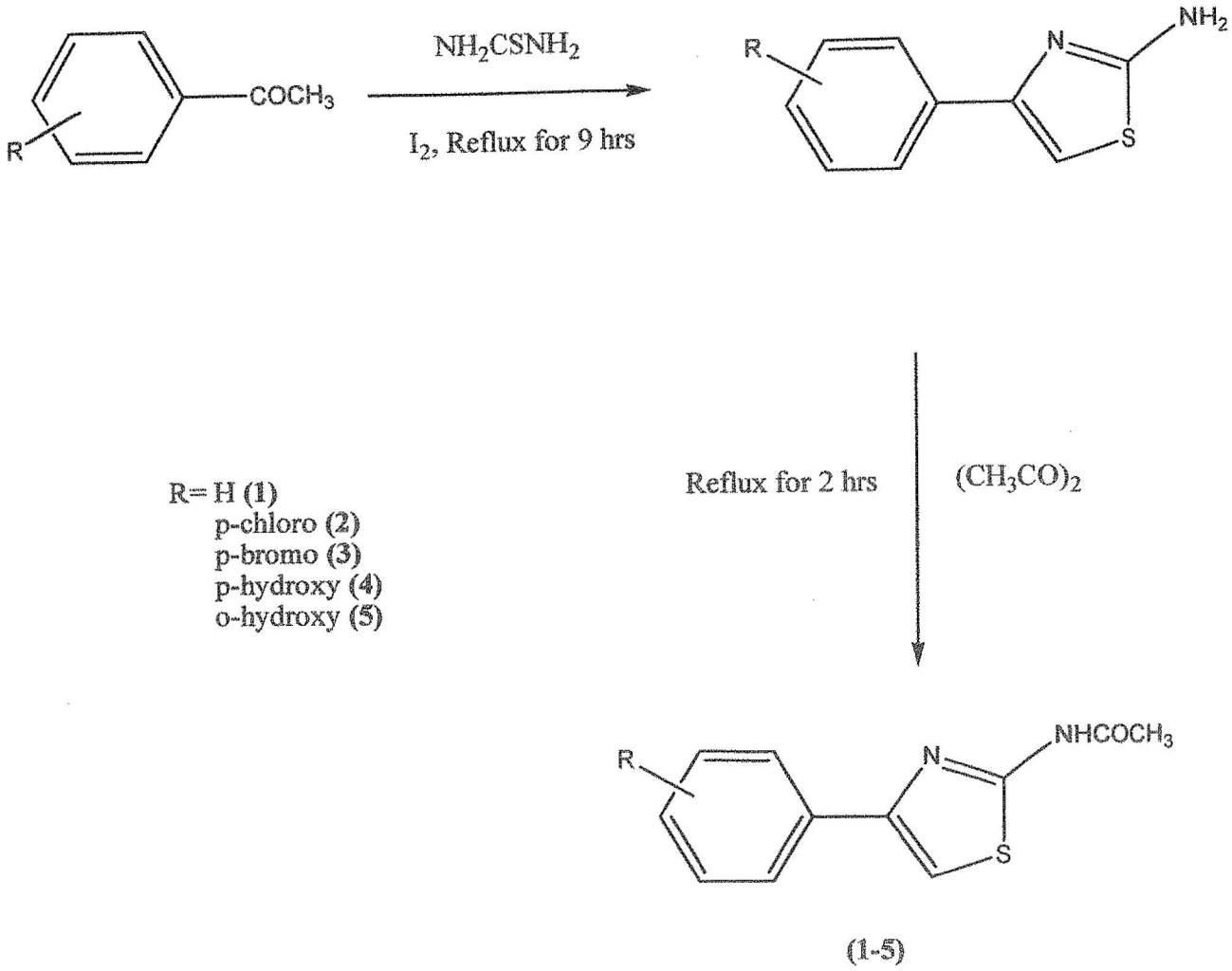
Compounds	Zone of Inhibition (mm)		
	C. albicans	*A. flavus*	*A. fumigatus*
1.	5.4 ± 0.00	5.0 ± 0.00	6.5 ± 0.00
2.	11.3 ± 0.33	12.5 ± 0.00	11 ± 0.00
3.	10.7 ± 0.67	9.3 ± 0.33	8.3 ± 0.33
4.	8.2 ± 0.00	7.4 ± 0.00	8.0 ± 0.00
5.	8.3 ± 0.00	7.8 ± 0.00	8.7 ± 0.67
Fluconazole	17 ± 0.00	16 ± 0.00	17 ± 0.00
DMF	-	-	-

RESULTS AND DISCUSSION

Various substituted acetophenones reacted with iodine and thiourea to get 2-Amino-4-(substituted-phenyl)-thiazole[10]. Nextly, the 2-amino group of 2-Amino-4-(substituted-phenyl)-thiazole was acetylated with acetic anhydride, which led to the formation of *N*-(4-(substitutedphenyl)thiazol-2-yl)acetamide (**1-5**) in moderate to good yields (Scheme-1). The FTIR spectra of compounds **1-5** exhibited bands in the region of 3344.12-3417.23 cm^{-1} due to N-H stretching and in the region 1622.02-1672.46 cm^{-1} due to C=O stretching of amide. In ^1H NMR spectra of compounds **1-5**, one proton singlet appeared between δ 8.85-9.15 ppm was assigned to N-H proton which disappeared on D_2O exchange.

The structures of the synthesized compounds were assigned on the basis of elemental analysis, ^1H NMR, FTIR and mass spectral data and physical data. The synthesized compounds 1-5 were screened for antibacterial (*S. aureus, E. coli, P. aeruginosa*) and antifungal (*C. albicans, A. flavus, A. fumigatus*) activities by disk diffusion method at a concentration of 2 mg/mL using DMF as a solvent. This revealed that compound **2** deemed to be most potent with the largest zone of inhibition for both i.e. antibacterial activity and antifungal Activity.

SCHEME 1:



(1-5)

Where R = H, *p*-chloro, *p*-bromo, *p*-hydroxy and *o*-hydroxy- group

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SYNTHESIS, CHARACTERIZATION AND COMPARATIVE SCREENING OF SOME NEWER 2-PHENYL INDOLE AND 5-CHLORO-2-PHENYL INDOLE DERIVATIVES

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ABSTRACT
Biologically active phenyl indole and chloro phenyl indole derivatives were efficiently synthesized. The reaction of 2-phenyl-1H-indole **A** and 5-chloro-2-phenyl-1H-indole **B**, with chloroacetylchloride yielded 2-chloro-1-(2-phenyl-1H-indol-1yl)ethanone **1** and 2-chloro-1-(5-chloro-2-phenyl-1H-indol-1-yl)ethanone **4** respectively. Compound **1** and **4** on Friedal Crafts cyclization in presence of aluminium chloride and nitrobenzene yielded indolo[2,1-α]isoquinolin-6(5H)-one **2** and 10-chloroindolo [2,1-α]isoquinolin-6(5H)-one **5** respectively, which upon hydrolysis afforded 2-(2-(1H-indol-2-yl)phenyl)acetic acid **3** and 2-(2-(5-chloro-1H-indol-2-yl) phenyl) acetic acid **6** respectively. The newly designed compounds were characterized on the basis of spectral studies and screened for anti-inflammatory and anti-microbial activities.
KEYWORDS: 2-phenyl-indole, 5-chloro-2-phenyl-indole, Friedal Crafts cyclization.

RESUMO
Derivados de fenil indol e clorofenil indol, biologicamente ativos, foram sintetizados de maneira eficiente. A reação de 2-fenil- 1H-indol e 5-cloro-2-fenil-1H-indole com cloreto de cloroacetila seguida por ciclização Friedel Crafts levou aos compostos **2** e **5**, respectivamnete, os quais depois de hidrólise formaram 2-(2-(1H-indol-2-il)ácido fenilacético,3, e 2-(2-(5-cloro-1H-indol-2-il) ácido fenilacético, **6**. Os compostos foram caracterizados e a atividade antiinflamatória e antimicrobial foram avaliadas.
PALAVRAS CHAVE: 2-Fenil indol, 5-Cloro-2-fenil indol, Ciclização Friedel Crafts

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INTRODUCTION

The statistical data provided that the global pharmaceutical market *grew to 712 billion* US dollars *in 2007* at a rate of *10.7% and is* expected to grow to 929 billion US dollars by 2012, which consists of 25.5 billion dollars of NSAIDS market. The global anti-infective market is currently valued at 66.5 *billion* US dollars with antibacterial agents accounting for over 50% of sales. Indole and phenyl acetic acid derivatives are known to have potent anti –inflammatory (1), anti-microbial (2) and analgesic (3) activities. As per prospects of NSAIDS in global pharmaceutical market and literary evidences for activities associated with indoles, an attempt was made to generate novel potent anti-inflammatory and anti-microbial drugs by converting a 2-phenyl indole moiety **A** and 5-chloro-2- phenyl indole moiety **B** into some novel 2-(2-(1H-indol-2-yl)phenyl)acetic acid **3** and 2-(2-(5-chloro-1H-indol-2-yl) phenyl) acetic acid **6.** During this pathway of synthesis of 2-chloro-1-(2-phenyl-1H-indol-1yl)ethanone **1**, indolo[2,1-α]isoquinolin-6(5H)-one **2**, 2-chloro-1-(5-chloro-2-phenyl-1H-indol-1yl)ethanone **4** and10-chloroindolo [2,1-α]isoquinolin-6(5H)-one **5** were obtained as key intermediates. All the newly designed compounds were further characterized and evaluated for anti-inflammatory and anti-microbial activities.

EXPERIMENTAL

Melting points of newly designed compounds were determined in open capillary tubes. IR spectra were recorded (in KBr) on Perkin Elmer and 1HNMR spectra on Bruker, SF 300 instruments. Purity of designed compounds was checked by TLC on aluminium sheets with silica gel 60 F254 (0.2 mm).

2-chloro-1-(2-phenyl-1H-indol-1yl)ethanone (1)
To a solution of 2-phenyl-1H-indole **A** (0.01 mol) in methyl ethyl ketone, a solution of chloro acetyl chloride (in methyl ethyl ketone) was added dropwise on a magnetic stirrer. During the reaction to maintain the pH 8-9 a solution of sodium carbonate (in distilled water) was also added dropwise. The stirring was continued for further 75 min. From the resultant mixture the organic layer was separated and subjected for distillation under reduced pressure. The obtained crude product was recrystallized from methanol to yield compound **1**.
IR (KBr, cm^{-1}): 2916 (C-H of CH_2), 3020 (C-H of aromatic ring), 1662 (C=O of amide)
^{1}HNMR (CDCl3, ppm): 4.88 (2H; s; CH_2), 6.53 (1H; s; H_3), 7.05-7.29 (3H; m; H_5, H_6 & H_4'), 7.31-7.46 (5H; m; H_7, H_2', H_3', H_5', H_6'), 7.6 (1H; m; H_4)
MS (m/z): 269 (M^+), 233, 76, 51

indolo[2,1-α]isoquinolin-6(5H)-one (2)
To a solution of 2-chloro-1-(2-phenyl-1H-indol-1yl)ethanone **1** in nitrobenzene, 1g of powdered aluminium chloride was added in small portions with simultaneous stirring for 15 min. The reaction mixture was further stirred continuously for 1 hr. The resultant mixture was transferred onto crushed ice to form a semisolid mass, which was subjected to distillation to remove nitrobenzene to get a solid product. The obtained crude product was recrystallized from methanol to yield compound **2**

IR (KBr, cm-1): 2922 (C-H of CH_2), 3045 (C-H of aromatic ring), 1668 (C=O of amide)
^{1}HNMR (CDCl3, ppm): 3.66 (2H, s, CH_2), 6.61 (1H; s; H_3), 6.8-7.24 (5H; m; H_5, H_6 H_3', H_4', & H_5'), 7.29-7.67 (3H; m; H_4, H_5, H_2')
MS (m/z): 233 (M^+), 76, 51

2-(2-(1H-indol-2-yl)phenyl)acetic acid (3)
A mixture of indolo[2,1-α]isoquinolin-6(5H)-one **2** in ethanol and sodium hydroxide solution was refluxed for 6 hrs. The resultant reaction mixture was filtered and to the filtrate HCl was added drop wise to yield a solid mass. The crude product so obtained was filtered and recrystallized from methanol to yield 2-(2-(1H-indol-2-yl)phenyl)acetic acid **3**.
IR (KBr, cm-1): 3447 (O-H of COOH), 3021 (C-H of aromatic ring), 2930 (C-H of methylene), 1721 (C=O of COOH),
^{1}HNMR (CDCl3, ppm): 8.52 (1H, s, N-H), 3.42 (2H, s, CH_2), 6.51 (1H, s, H_3), 6.82-7.19 (5H; m; H_5, H_6, H_3', H_4', H_5'), 7.29-7.64 (3H, m; H_2', H_7, H_4), 11.2 (1H, s, O-H)
MS (m/z): 251 (M^+), 234, 233, 224, 206, 91, 76, 51, 45

2-chloro-1-(5-chloro-2-phenyl-1H-indol-1yl)ethanone (4)
To a solution of 5-chloro-2-phenyl-1H-indole A (0.01 mol) in methyl ethyl ketone, a solution of chloro acetyl chloride (in methyl ethyl ketone) was added dropwise on a magnetic stirrer. During the reaction to maintain the pH 8-9 a solution of sodium carbonate (in distilled water) was also added drop wise. The stirring was continued for further 75 min. From the resultant mixture the organic layer was separated and subjected for distillation under reduced pressure. The obtained crude product was recrystallized from methanol to yield compound **4**.
IR (KBr, cm-1): 2919 (C-H of CH_2), 3028 (C-H of aromatic ring), 1664 (C=O of amide)
^{1}HNMR (CDCl3, ppm): 4.92 (2H; s; CH_2), 6.59 (1H; s; H_3), 7.14-7.34 (3H; m; H_5, H_6 & H_4'), 7.39-7.49 (5H; m; H_7, H_2', H_3', H_5', H_6'), 7.54 (1H; d; j=2.7, H_4)
MS (m/z): 303 (M^+), 267, 76, 51

10-chloroindolo [2,1-α]isoquinolin-6(5H)-one (5)
To a solution of 2-chloro-1-(5-chloro-2-phenyl-1H-indol-1yl)ethanone **4** in nitrobenzene, 1g of powdered aluminium chloride was added in small portions with simultaneous stirring for 15 min. The reaction mixture was further stirred continuously for 1 hr. The resultant mixture was transferred onto crushed ice to form a semisolid mass, which was subjected to distillation to remove nitrobenzene to get a solid product. The obtained crude product was recrystallized from methanol to yield compound **5**.
IR (KBr, cm-1): 2930 (C-H of CH_2), 3049 (C-H of aromatic ring), 1674 (C=O of amide)
^{1}HNMR (CDCl3, ppm): 3.72 (2H, s, CH_2), 6.68 (1H; s; H_3), 6.94-7.28 (5H; m; H_5, H_6 H_3', H_4', & H_5'), 7.36-7.48 (2H; m; H_5, H_2'), 7.56 (1H; d; j=2.6, H_4)
MS (m/z): 267 (M^+), 231, 91, 76, 51

2-(2-(5-chloro-1H-indol-2-yl) phenyl) acetic acid (6)
A mixture of 10-chloroindolo [2,1-α]isoquinolin-6(5H)-one **5** in ethanol and sodium hydroxide solution was refluxed for 6 hrs. The resultant reaction mixture was filtered

and to the filtrate HCl was added drop wise to yield a solid mass. The crude product so obtained was filtered and recrystallized from methanol to yield 2-(2-(5-chloro-1H-indol-2-yl) phenyl) acetic acid **6**.

IR (KBr, cm-1): 3458 (O-H of COOH), 3028 (C-H of aromatic ring), 2942 (C-H of methylene), 1716 (C=O of COOH)

^{1}HNMR (CDCl3, ppm): 8.65 (1H, s, N-H), 3.52 (2H, s, CH_2), 6.47 (1H, s, H_3), 6.93-7.14 (4H; m; H_6, H_3', H_4', H_5') 7.32-7.38 (2H; m; H_7, H_2') 7.62 (1H; d; J = 2.8, H_4), 11.35 (1H; s, O-H)

MS (m/z): 285 (M^+), 268, 267, 258, 249, 240, 91, 76, 51, 45

Biological activity

The designed compounds **1, 2, 3, 4, 5, 6** were screened for anti-inflammatory activity by carageenan induced paw oedema method using distilled water as solvent. The results were recorded using indomethacin as standard drug and are given in table-II. The designed compounds **1-6** were also were screened for antibacterial and antifungal activity using disk diffusion method. The results were recorded using amoxicillin and egriseofulvin as standard drugs respectively and are given in Table-III and Table-IV.

RESULTS AND DISCUSSION

2-chloro-1-(2-phenyl-1H-indol-1yl)ethanone **1** and 2-chloro-1-(5-chloro-2-phenyl-1H-indol-1-yl)ethanone **4**, prepared from 2-phenyl-1H-indole **A** and 5-chloro-2-phenyl-1H-indole **B** respectively. The obtained compounds **1** and **4** when cyclized with aluminium chloride yielded indolo[2,1-α]isoquinolin-6(5H)-one **2** and 10-chloroindolo [2,1-α]isoquinolin-6(5H)-one **5** respectively, which on hydrolysis lead to potent anti-inflammatory 2-(2-(1H-indol-2-yl)phenyl)acetic acid **3** and 2-(2-(1H-indol-2-yl)phenyl)acetic acid **6** respectively. The synthetic procedure for conversion of compound **A to 3** and **B to 6** is suggested in Scheme 1 and 2. Physical data of **1-6** are given in Table I. The assigned structure, molecular formulae and the anomeric configuration of the newly designed compounds **1-3** and **4- 6** were further confirmed and supported by mass, 1H-NMR and IR spectral data, based on occurrence of molecular ion peak of the assigned structures, downfield shifting of protons and different stretching bands of the compounds. The resultant compounds 1, 2, 3, 4, 5 and 6 after characterizations were further screened for anti-inflammatory and anti-microbial activity (data given in Table-II, III and IV).

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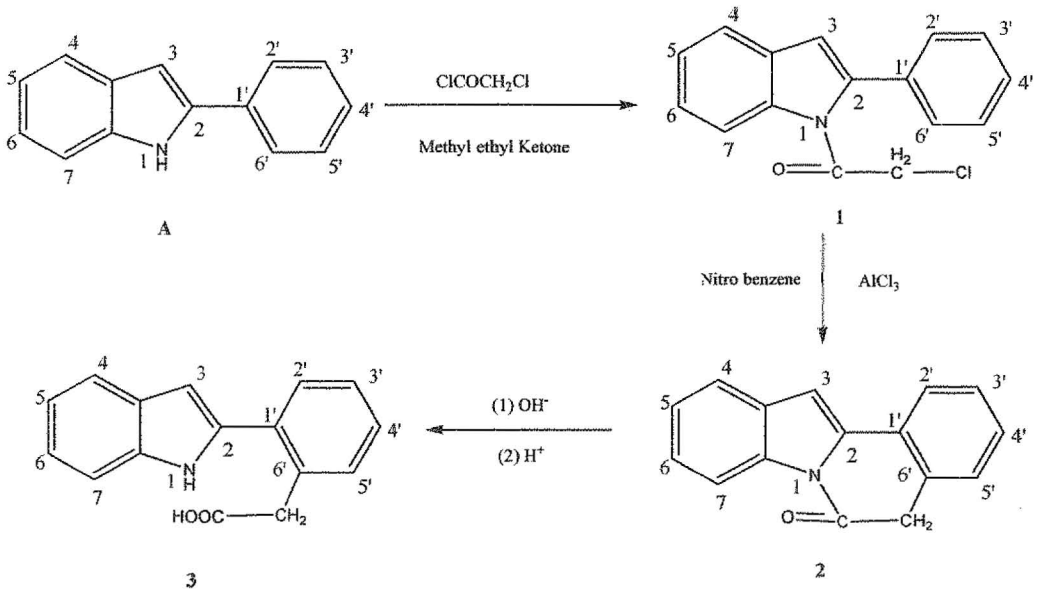
Scheme1



Scheme 2

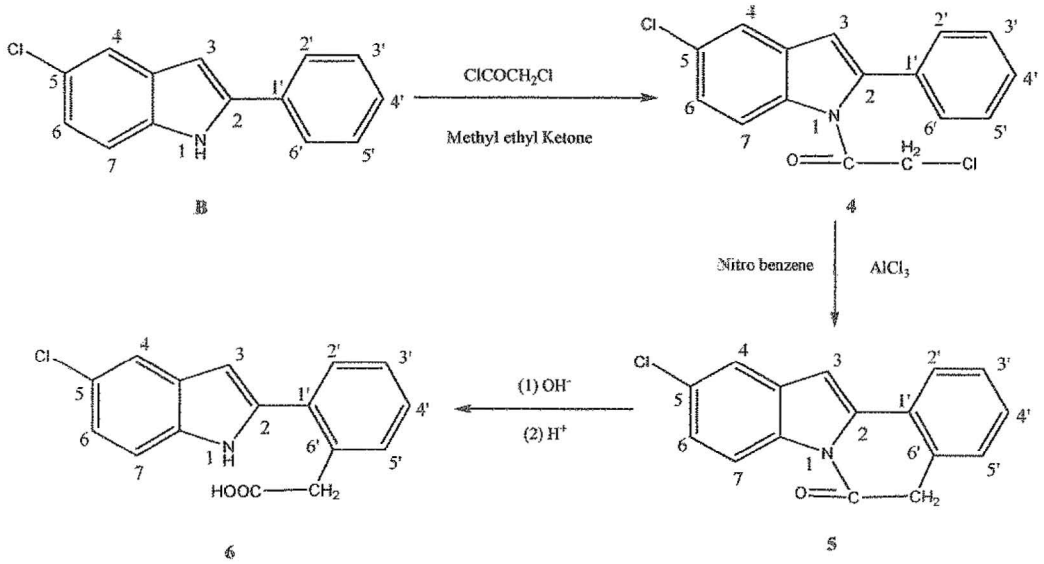


Table I. Physical data of compounds

Compound No.	Physical characteristics	Yield (%)	Molecular formula	Mol. Wt.	M.P. (°C)	R_f Value
1	White crystals	82	$C_{16}H_{12}ClNO$	269.73	205-206	0.56
2	White crystals	76	$C_{16}H_{11}NO$	233.26	212-213	0.42
3	White crystals	73	$C_{16}H_{13}NO_2$	251.28	228-229	0.38
4	White crystals	74	$C_{16}H_{11}Cl_2NO$	304.17	217-218	0.52
5	White crystals	68	$C_{16}H_{10}ClNO$	267.71	223-224	0.46
6	White crystals	64	$C_{16}H_{12}ClNO_2$	285.72	231-232	0.34

TABLE II- Anti-inflammatory activity of 2-phenyl indole and 5-chloro-2-phenyl indole derivatives on carrageenan-induced paw oedema in rats.

Compd 20mg/po	Paw volume in ml, mean ±SD(% inhibition of paw edema)			
	After 1hr	After 2hr	After 3hr	After 4hr
Control	0.880±0.0179	0.886±0.0163	0.897±0.0151	0.885±0.0242
Indomethacin	0.368±0.0197 (58.18%)*	0.326±0.0163 (63.2%)*	0.290±0.0219 (67.67)*	0.265±0.0350 (70.05%)*
1	0.847±0.0242 (3.75%)	0.833±0.0273 (5.98%)	0.803±0.029 (10.47%)	0.790±0.0452 (10.73%)
2	0.840±0.0219 (4.45%)	0.817±0.0151 (7.78%)	0.787±0.0350 (12.26%)	0.757±0.0234 (14.46%)
3	0.583±0.0408 (33.75%)*	0.557±0.0197 (37.13%)*	0.527±0.0350 (41.24%)*	0.503±0.067 (43.16%)*
4	0.817±0.0388 (7.15%)	0.793±0.0273 (10.4%)	0.773±0.0350 (13.8%)	0.737±0.0151 (16.7%)
5	0.663±0.0344 (25.79%)*	0.647±0.0266 (27.2%)*	0.615±0.0253 (31.43%)*	0.595±0.0179 (32.95%)*
6	0.540±0.057** (38.63%)	0.515±0.0210** (41.8%)	0.395±0.0283** (55.96%)	0.325±0.0266** (63.27%)

*p<0.05 vs control, **p<0.01 vs control (n=6)

Table: III – Antibacterial-sensitivity testing of 1-6.

Compd. No.	Antibacterial Activity		
	Zone of Inhibition (mm)		
	S. aureus	***E. coli***	***P. aeruginosa***
1	14.3 ± 0.33	18.3 ± 0.33	14.3 ± 0.33
2	20.7 ± 0.67	12 ± 0.00	16.7 ± 0.33
3	21.7 ± 0.67	16 ± 0.00	17.7 ± 0.33
4	16.7 ± 0.67	18 ± 0.00	14.7 ± 0.67
5	22.3 ± 0.67	17.7 ± 0.33	12 ± 0.00
6	23 ± 0.00	18.3 ± 0.33	20.7 ± 0.33
Amoxicillin	26 ± 0.54	25 ± 0.68	26 ± 2.4
DMF	-	-	-

- All the values are expressed as mean ± SEM of triplicates

Table: IV– Antifungal-sensitivity testing of 1-6.

Compd. No.	Antifungal Activity		
	Zone of Inhibition (mm)		
	C. albicans	***A. flavus***	***A. fumigates***
1	10.3 ± 0.33	8 ± 0.00	9 ± 0.00
2	9 ± 0.00	11 ± 0.00	10 ± 0.00
3	10 ± 0.00	11 ± 0.00	8 ± 0.00
4	8 ± 0.00	11.7 ± 0.67	9 ± 0.00
5	10.3 ± 0.33	12 ± 0.00	9.3 ± 0.33
6	14 ± 0.00	13 ± 0.00	9 ± 0.00
Griseofulvin	24± 0.00	25 ± 0.00	23 ± 0.00
DMF	-	-	-

- All the values are expressed as mean ± SEM of triplicates

CONCLUSIONS

After screening the designed compounds for anti-inflammatory and anti-microbial (anti-bacterial and anti-fungal) studies it was found that each compound **1-3** and **4-6** possesses anti-inflammatory activity and anti-microbial activity to certain extent. Among the newly synthesized derivatives, compound **6** have shown significant ($p<0.01$) anti-inflammatory activity and was found to be almost equipotent to indomethacin when tested on rats. The compounds **3** and **5** have also shown significant ($p<0.05$) results. The other tested compounds **1, 2 and 4** have also shown anti-inflammatory activity to certain extent. Anti-microbial (anti-bacterial and anti-fungal) screening revealed that among the newly synthesized derivatives, compound **6** have shown the most significant anti-microbial activity when compared to standard drugs. Compound **5, 3 and 2** were found to have moderate activity while compound **1** and **4** were found to have mild activity among the tested compounds. After comparing the anti-inflammatory activity, anti-microbial activity and structural configuration of compounds **1-3** and **4-6**, it was concluded that the incorporation of chlorine in derived compounds enhances their activity.

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GREEN INHIBITORS FOR CORROSION PROTECTION OF N80 CARBON STEEL IN 1M HCl AQUEOUS SOLUTIONS

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ABSTRACT

The inhibitive action of Saponinic extract of both Zygophyllum album and Zygophyllum aegyptium leafs which could serve as eco-friendly materials was investigated on the corrosion of N80 carbon steel in 1M HCl solution .The techniques employed for study were weight loss measurements, potentiodynamic polarization, electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS). The results obtained show that these extracts could serve as effective inhibitor for N80 carbon steel. The percentage inhibition increases with increasing concentration of the inhibitor at 25 °C. The percentage inhibitor efficiency above 90% was obtained at concentration of 700 ppm for both extracts. The corrosion rates of steel and inhibitive efficiencies obtained from impedance and polarization measurements were in good agreement with those obtained from weight loss measurements. Potentiodynamic polarization studies clearly reveal that both extracts act as mixed type inhibitor. The study shows that the inhibition efficiency decreased with temperature rise of the medium. Heat of adsorption (ΔH_{ads}) and thermodynamic parameters (ΔG) and (ΔS) indicated that the adsorption process is mainly controlled by physical adsorption process.

KEYWORDS

Green Inhibitors, N80 Carbon steel, Corrosion Protection

RESUMO

A inibição da corrosão do aço carbono N80 foi estudada na presença de extratos saponínicos de folhas de Zygophyllum álbum e Zygophyllum aegyptium em solução aquosa de HCl. Foram usadas técnicas de perda de peso, polarização potenciodinâmica, modulação da freqüência eletroquímica e espectroscopia de impedância eletroquímica, Os resultados experimentais mostraram que os extratos são eficientes na inibição da corrosão. O processo de inibição depende da concentração de extrato e da temperatura.

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Inibidores Verdes, Aço Carbono N80, Proteção da Corrosão

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1-INTRODUCTION

Chemical inhibitors play an important role in the protection and mitigation strategies for retarding corrosion (1). Most acid inhibitors are organic compounds containing nitrogen, oxygen and/or sulpher. These compounds are adsorbed on the metallic surface, blocking the active corrosion sites (2-5). Due to the negative effects of these compounds caused in the environment (6), the development of novel corrosion inhibitors of natural sources and non-toxic type has been considered to be more important and desirable (7). Some investigations have been made recently on the corrosion inhibition properties of naturally occurring plant extracts, which have been reported to have generally good inhibition efficiencies for carbon steel (8-16) and for other metals like tin (17), copper (18), aluminum (19-20) and zinc (21). The aqueous extract of one of the plants under investigation (Zygophyllum album) has been formerly investigated for X52 Mild Steel in sulfuric acid (22). However, the constituents that provide inhibitive action, the mechanisms and the best condition for inhibition are still unclear.

As a contribution to the current interest on eco- friendly, green, corrosion inhibitors, the present study investigates the inhibiting effect of saponin extracts of the leafs of Zygophyllum aegyptium, which grows in the deltaic Mediterranean coast of Egypt (23) and Zygophyllum album on N80 carbon steel corrosion in 1 M HCl .

2. EXPERIMENTAL

2-1. Preparation of plant extracts

Zygophyllum album and Zygophyllum aegyptium leaves which grow in the deltaic Mediterranean coast of Egypt were collected. These were crushed and extracted using methanol. The methanol crude extracts were partitioned against several solvents like petroleum ether , ethyl acetate and dichloromethane using a separatory funnel to get a high polar compound crude extract and passed through a diion column using methanol to get a moderate polar compound crude extract followed by the addition of acetone in order to get the crude saponien fraction . Plant extracts test solutions were prepared at concentrations of 50, 100, 300, 500 and 700 mg/L.

2.2. Specimen preparation

Al metal was provided from the pipeline Casing of "Mansoura Petroleum Company, Mansoura Fields" . Its chemical composition is (0.42%) C, (0.20%) Si, (1.03%) Mn, (0.012%) P, (0.007%) S, (0.019%) Cr, (0.002%) Ni, (0.005%) Ti, (0.04%) Cu and Fe balance. Coupons

were cut into 2 × 2 × 1 cm dimensions used for weight loss measurements, whereas specimens with 1 × 1 × 1 cm dimensions, sealed by polyester resin, leaving a surface area of 1 cm^2, were used as working electrode for polarization , EFM and EIS measurements. The surfaces of the sample were mechanically polished by grit silicon carbide paper progressively up to 1200 mesh, rinsed with acetone washed with bidistilled water and then dried before each experiment.

2.3. Solutions preparation

All chemicals and reagents were of analytical grade. A 1 M HCl stock solution was prepared by dilution of 37% HCl using distilled water. The concentration range of the employed extracts was varied from 50 to 700 mg/l.

2.4. Weight loss measurements

Weight loss study was carried out at 25, 35 & 45 °C for 3 hours time duration in HCl solution. The inhibition efficiency (IE) is determined by following equation:

$$IE = (1 - [Wi / W0]) \times 100 \qquad (1)$$

Where W_0 and W_i are the weight loss values in absence and in presence of inhibitor.

2.5. Polarization measurements

Potentiostatic polarization studies were carried out using a typical three-compartment glass cell consisted of the iron specimen as working electrode with an exposed working area of 1.0 cm2 , saturated calomel electrode (SCE) as a reference electrode and a platinum foil (1.0 cm^2) as a counter electrode. The reference electrode was connected to a Luggin capillary to minimize IR drop. The cells were under athmospheric conditions without stirring and at the room temperature. All potential values were reported versus SCE. Prior to every experiment, Tafel polarization curves were obtained by changing the electrode potential automatically from -500 to 500 mVSCE at open circuit potential with a scan rate of 5 mVs-1. Stern-Geary method used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines of charge transfer controlled corrosion reactions to a point which gives log(i_{corr}) and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each concentration of the used inhibitors. Then (i_{corr}) was used for calculation of inhibition efficiency and surface coverage (θ) as below:

$$\%IE = (1 - [i_{corr\ (inh)} / i_{corr\ (free)}]) \times 100 \qquad (2)$$

$$\theta = 1 - [i_{corr\ (inh)} / i_{corr\ (free)}] \qquad (3)$$

Where $i_{corr\ (free)}$ and $i_{corr\ (inh)}$ are the corrosion current densities in the absence and presence of inhibitor

2.6. Electrochemical impedance spectroscopy (EIS)

Impedance measurements were carried out in frequency range from 100000 Hz to 0.5 Hz with amplitude of 10 mV peak-to-peak using Ac signals at open circuit potential. The experimental impedance were analyzed and interpreted on the basis of the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer R_{ct} (diameter of high frequency loop) and the capacity of double layer C_{dl} which is defined as:

$$Cdl = 1/ (2 \pi fmax\ Rct) \quad (4)$$

Where *fmax*, is the frequency at which the imaginary component of the impedance is maximal

The inhibition efficiencies and the surface coverage (θ) obtained from the impedance measurements are defined by the following relations:

$$\%IE = (1- [R^{\circ}_{ct}/R_{ct}]) \times 100 \quad (5)$$

$$\square\theta = 1-[R^{\circ}_{ct}/R_{ct}] \quad (6)$$

where R°_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor,

2.7. Electrochemical frequency modulation (EFM)

Electrochemical frequency modulation, EFM, was carried out using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1 s. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. The Intermodulation spectra contain current responses assigned for harmonical and Intermodulation current peaks. The larger peaks were used to calculate the corrosion current density (I_{corr}), the Tafel slopes (β_c and β_a) and the causality factors CF2& CF3

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements:

The corrosion rate and inhibition efficiency for N80 carbon steel in 1M HCl Solution at 25 °C, 35 °C and 45 °C in the absence and presence of the Zygophyllum album and Zygophyllum Aegyptium extracts are given in Table (1) and Table (2). It is indicated that inhibitions efficiency for N80 carbon steel increases with the increase of the inhibitor concentration up to 89.32% for both Zygophyllum album and Zygophyllum Aegyptium at 25°C. As the temperature increases the inhibition efficiency decreases. At 35 and 45 °C maximum inhibition efficiencies of 73.90% and 66.53% is observed for Zygophyllum album , but for Zygophyllum Aegyptium extract the maximum inhibition efficiencies were 85.29% and 73.93% obtained in 1M HCl solution containing 700 ppm for both plants extracts. This indicates that Zygophyllum Aegyptium extract as a corrosion inhibitor has

more resistance for temperature changes than Zygophyllum album extract. Figures (1) and (2) represent the relation between weight loss and time in absence and presence of different concentrations of Zygophyllum album and Zygophyllum Aegyptium extracts.

Conc. (ppm)	Temperature								
	25°C			35°C			45°C		
	Corrosion rate (mg/cm2 h)	□	IE (%)	Corrosion rate (mg/cm2 h)	□	IE (%)	Corrosion rate (mg/cm2 h)	□	IE (%)
blank	0.0206	0	0	0.02525	0	0	0.04592	0	0
50	0.0089	0.56796	56.796	0.01336	0.47089	47.089	0.02672	0.41811	41.811
100	0.0077	0.62621	62.621	0.01285	0.49108	49.108	0.02313	0.49629	49.629
300	0.00451	0.78106	78.106	0.01028	0.59287	59.287	0.02028	0.55836	55.836
500	0.00211	0.89757	89.757	0.00846	0.66495	66.495	0.01691	0.63175	63.175
700	0.0022	0.89320	89.320	0.00659	0.73900	73.900	0.01537	0.66528	66.528

Table 1. Calculated values of corrosion rate, inhibition efficiency, Surface Coverage for N80 Carbon steel coupons in 1M HCl solutions containing Various Conc. n of Zygophyllum album.

Conc. (ppm)	Temperature								
	25°C			35°C			45°C		
	Corrosion rate (mg/cm2 h)	□	IE (%)	Corrosion rate (mg/cm2 h)	□	IE (%)	Corrosion rate (mg/cm2 h)	□	IE (%)
blank	0.02066	0	0	0.02985	0	0	0.05051	0	0
50	0.01113	0.46135	46.135	0.01336	0.55242	55.242	0.02227	0.55909	55.909
100	0.01028	0.50249	50.249	0.01285	0.56951	56.951	0.02056	0.59295	59.295
300	0.00676	0.67284	67.284	0.00901	0.69815	69.815	0.01803	0.64304	64.304
500	0.00423	0.79528	79.528	0.00634	0.78760	78.760	0.0148	0.70698	70.698
700	0.00220	0.89352	89.352	0.00439	0.85293	85.293	0.01317	0.73925	73.925

Table 2. Calculated values of corrosion rate, inhibition efficiency, Surface Coverage for N80 Carbon steel coupons in 1M HCl solutions containing Various Conc. of Zygophyllum Aegyptium.

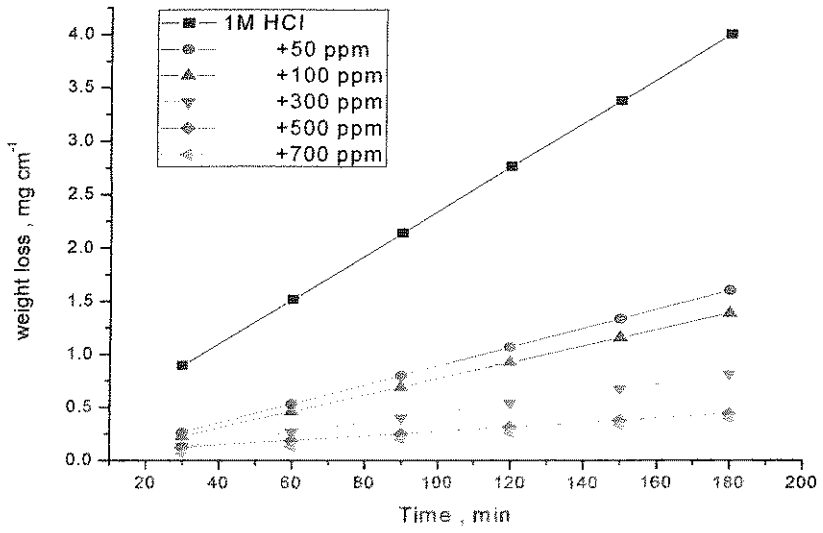

Fig. 1. Weight loss-time curves for the dissolution of N80 Carbon steel in the absence and presence of different concentrations of Zygophllum album at 25 °C

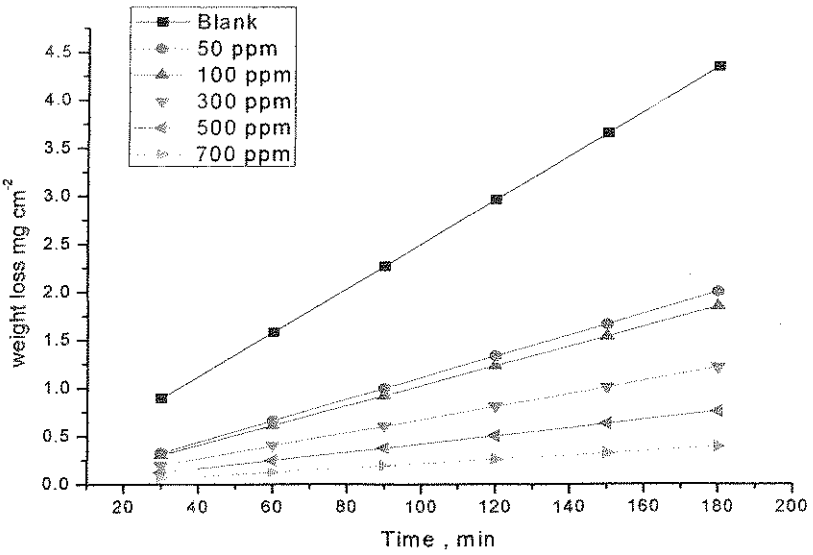

Fig. 2. Weight loss-time curves for the dissolution of N80 Carbon steel in the absence and presence of different concentrations of Zygophllum aegyptium at 25 °C

3.2 Potentiodynamic polarization

The potentiodynamic polarization curves for Carbon steel (N80) in 1 M HCl solutions containing different concentrations plant extracts at 20 °C are shown in Figure 3 and 4. The intersection of Tafel regions of cathodic and anodic branches gives the corrosion current density (icorr) and the corrosion potential (Ecorr). Tables 3 and 4 show the electrochemical parameters (Ecorr, anodic and cathodic Tafel slopes, βa, βc, and icorr,) obtained from Tafel plots for the Carbon Steel (N80) alloy electrode in 1 M HCl solution in the absence and presence of different concentrations of investigated plant extracts.

Inspection of Figures 3 and 4 show that the addition of plant extracts has an inhibitive effect in both anodic and cathodic parts of the polarization curves and the addition of plant extracts generally has no effect on the Ecorr value and also decreases icorr value compared to the uninhibited Carbon Steel alloy. Thus, addition of these inhibitors reduces the Carbon Steel alloy dissolution as well as retards the hydrogen evolution reaction. In addition, parallel cathodic Tafel curves in Figures 3 and 4 show that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of the inhibitor [24]. The anodic curves of N80 Carbon Steel in

1 M HCl in the presence of plant extract show that the tested compounds have no effect at potential higher than Ecorr, This behavior may be the result of significant Carbon Steel alloy dissolution leading to a desorption of the inhibiting layer. In this case, the desorption rate of the inhibitor is higher than its adsorption rate [25]. So, it could be concluded that these compounds are of the mixed-type but dominantly act as a cathodic inhibitor (βc>βa) for Carbon Steel alloy in 1 M HCl medium, which may be adsorbed on the cathodic sites of the Carbon Steel alloy and reduce the evolution of hydrogen. This limitation of inhibitory action on cathodic domain is found by different researchers [26, 27]. The data of Tables 3 and 4 revealed that icorr decreases considerably with increasing inhibitor concentration, while no definite trend was observed in the shift of Ecorr values. The Tafel slopes show slight changes with addition of inhibitors, which suggests that the inhibiting action occurred by simple blocking of the available cathodic and anodic sites on Carbon Steel alloy surfaces. The dependence of % IE versus inhibitor concentration is also presented in Tables 3 and 4. The obtained efficiencies indicate these investigated plant extracts act as effective inhibitor.
The order of decreasing inhibition efficiency of the investigated compounds was found to be: for Zygophllum extract: Aegyptium >Album.

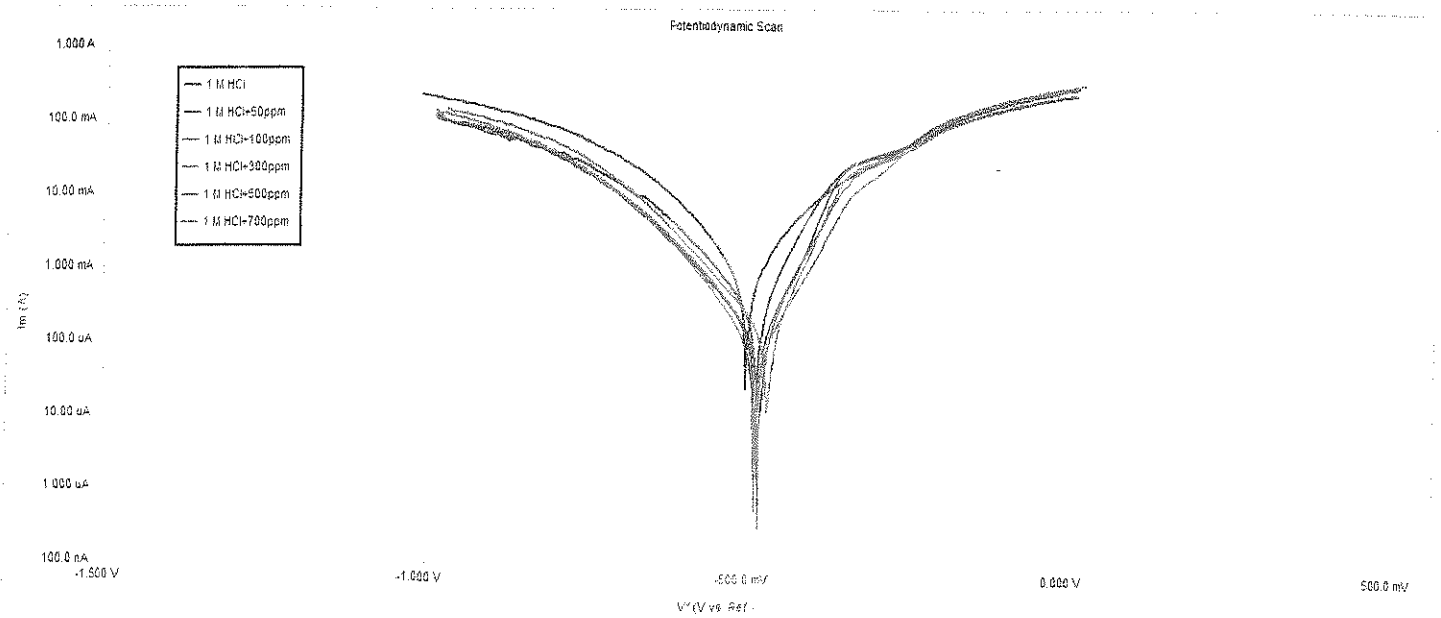

Figure 3. Potentiodynamic polarization curves for Carbon Steel in 1M HCl solution without and with various concentrations (50-700 PPM) of Zygophllum album at 20°C.

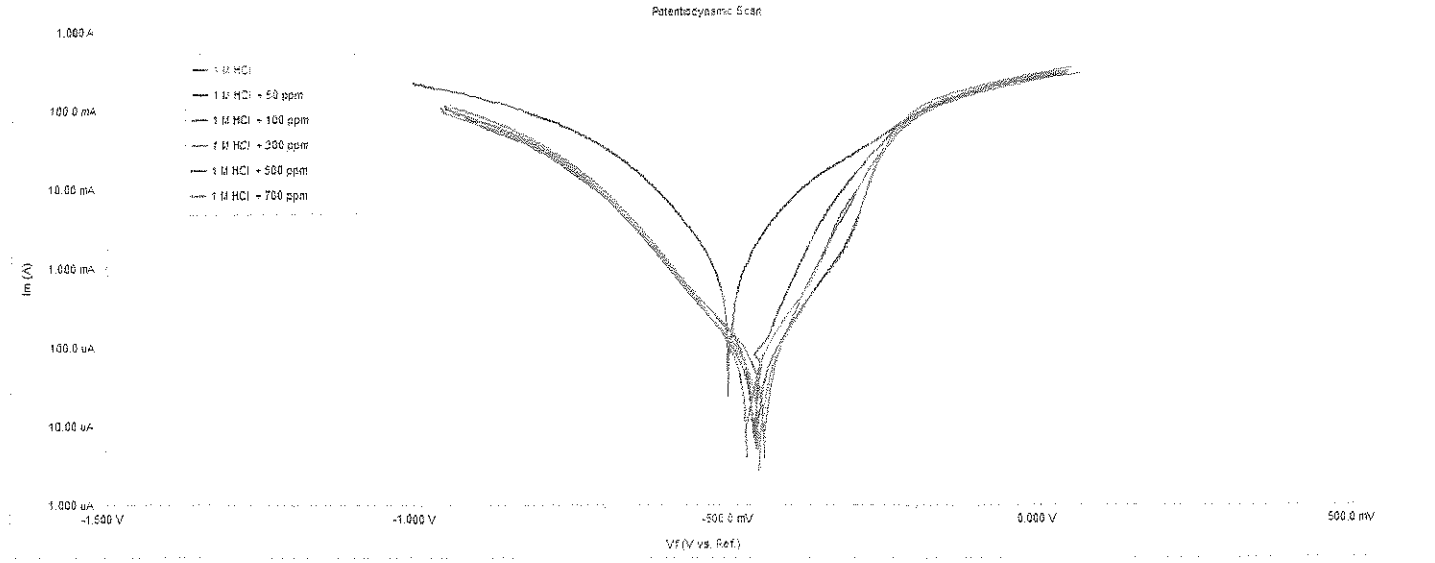

Figure 4. Potentiodynamic polarization curves for Carbon Steel in 1M HCl solution without and with various concentrations (50-700 PPM) of Zygophllum Aegyptium at 20°C.

Concentration, PPM	icorr, A cm-2	Ecorr, V vs.SCE	βa, VSCE dec-1	βc, VSCE dec-1	θ	% IE
1M HCl	1.74E-03	-5.02E-01	0.1691	0.1686	--	--
50	6.72E-04	-4.85E-01	0.1196	0.1813	0.613793	61.37931
100	2.69E-04	-4.86E-01	0.1031	0.15	0.845402	84.54023
300	2.55E-04	-4.68E-01	0.0918	0.144	0.853448	85.344828
500	2.36E-04	-4.80E-01	0.094	0.1509	0.864368	86.436782
700	1.49E-04	-4.86E-01	0.0933	0.1306	0.914368	91.436782

Table 3. The effect of concentration of the investigated Zygophllum Album on the free corrosion current density (icorr), corrosion potential (Ecorr) , Tafel slopes (βa& βc), corrosion rate ,degree of surface coverage (θ) and inhibition efficiency (% IE)for the corrosion of Carbon Steel in 1 M HCl at 20°

Concentration, PPM	icorr, A cm-2	Ecorr, V vs.SCE	βa, VSCE dec-1	βc, VSCE dec-1	θ	% IE
1M HCl	1.62E-03	-5.02E-01	0.1768	0.2012	--	--
50	11.50E-05	-4.62E-01	0.0781	0.1399	0.613793	61.37931
100	7.41E-05	-4.43E-01	0.0732	0.133	0.845402	84.54023
300	5.89E-05	-4.50E-01	0.0844	0.126	0.853448	85.344828
500	5.92E-05	-4.59E-01	0.0896	0.1216	0.864368	86.436782
700	5.88E-05	-4.71E-01	0.0827	0.1112	0.914368	91.436782

Table 4. The effect of concentration of the investigated Zygophllum Aegyptium on the free corrosion current density (icorr), corrosion potential (Ecorr) , Tafel slopes (βa& βc), corrosion rate ,degree of surface coverage (θ) and inhibition efficiency (% IE)for the corrosion of Carbon Steel in 1 M HCl at 20°

3.3. Electrochemical impedance spectroscopy measurements:

Electrochemical impedance spectroscopy provides a new method to characterize the film coverage on the electrode, which is related to charge transfer resistance (Rct). The interface capacitance can also be used to determine the film quality [28-32]. It is known that the coverage of an organic substance on the metal surface depends not only on the structure of the organic substance and the nature of the metal, but also on the experimental conditions such as immersion time and concentration of adsorbent.

Figures 5 and 6 show the Nyquist plots for Carbon steel (N80) in 1M HCl solution in the absence and presence of different concentrations of plant extracts at 25 ° C. All the impedance spectra were measured at the corresponding open-circuit potentials. The fact that impedance diagrams have an approximately semi-circular appearance shows that the corrosion of Carbon steel (N80) in 1M HCl is controlled by a charge-transfer resistance process. Small distortion was observed in some diagrams. This distortion has been attributed to frequency dispersion as a result of surface roughness, impurities, dislocations, grain boundaries, and adsorption of inhibitors, formation of porous layers and in homogenates of the electrode surface. Inspections of the data reveal that each impedance diagram consists of a large capacitive loop with one capacitive time constant in the Bode phase plots -Figures (5-1&6-1)-which was assigned to presence of oxide film on the surface of Carbon Steel (N80) and its dielectric properties. The diameter of the capacitive loop increases with increasing concentration and were indicative of the degree of inhibition of the corrosion process. In addition to the high frequency capacitive loop, the semi-circles rolled over and extended to the fourth quadrant, and a pseudo-inductive loop at low frequency end was observed, indicating that Faradic process is taking place on the free electrode sites. This inductive loop is generally attributed to the adsorption of species resulting from the Carbon steel dissolution and the adsorption of hydrogen [33].

The electrical equivalent circuit model (Randles circuit) shown in Figure 7 was used to analyze the obtained impedance data. The circuit consists of the solution resistance (Rs), the charge-transfer resistance of the interfacial corrosion reaction (Rct) and the double layer capacitance (Cdl). Excellent fit with this model was obtained with our experimental data.

EIS data (Tables 5 and 6) show that the Rct values increases and the Cdl values decreases with increasing the inhibitor concentrations. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, decreasing the extent of dissolution reaction. The high (Rct) values, are generally associated with slower corroding system. The decrease in the Cdl can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [34], suggested that the inhibitor molecules function by adsorption at the metal/solution interface.

The % IE obtained from EIS measurements are close to those deduced from polarization. It can be seen that the inhibition efficiency decreases in the order: Aegyptium> Album.

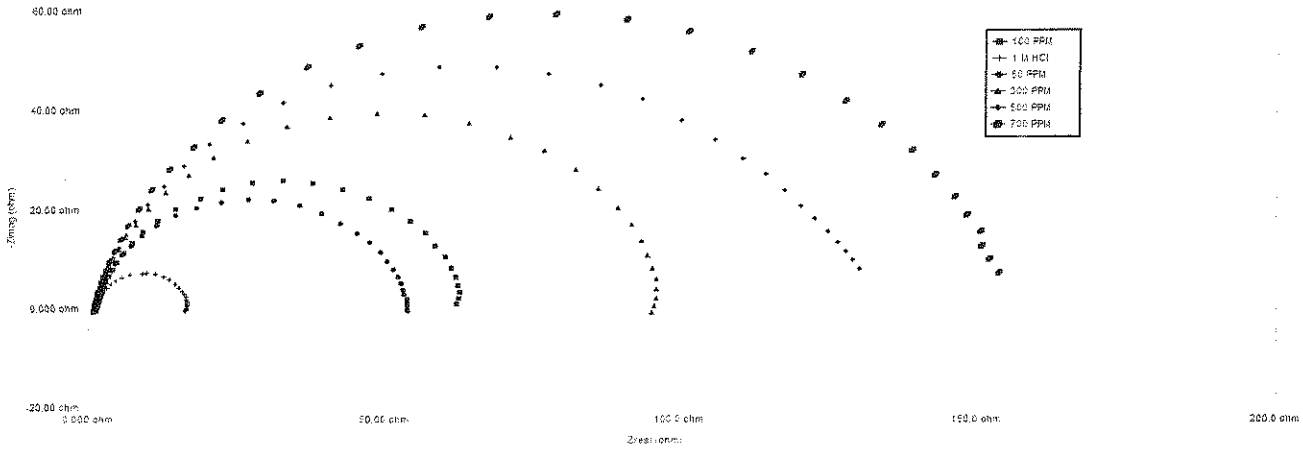

Figure 5. Nyquist plots recorded for Carbon Steel in 1M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Album at the respective corrosion potentials and 20°C.

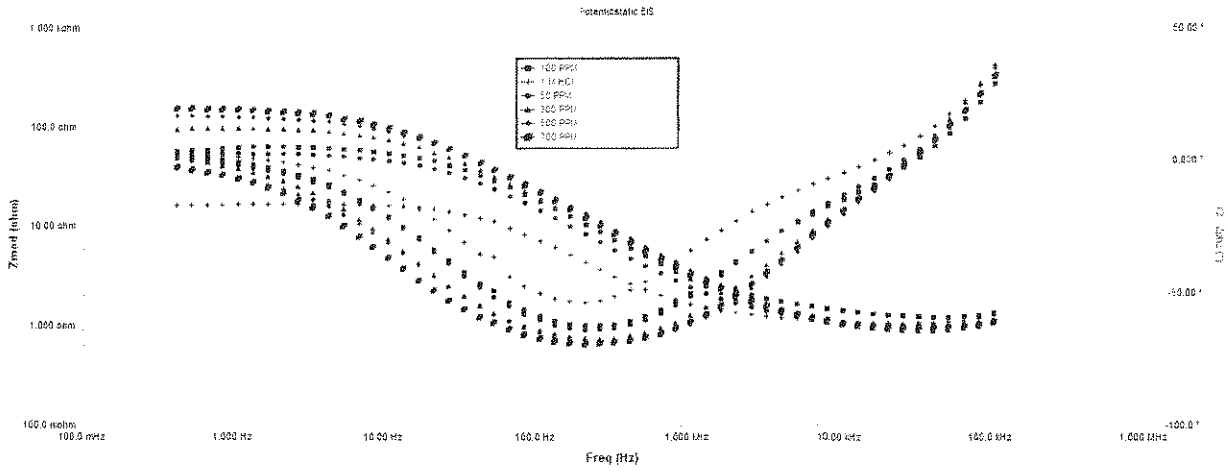

Figure (5-1). Bode plots recorded for Carbon Steel in 1M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Album at the respective corrosion potentials and 20°C.

Concentration, PPM	Rct, Ω cm2	Ru, Ω cm2	Cdl, F cm-2	θ	% IE
1M HCl	15.59	1.077	2.23E-04	--	--
50	52.84	1.004	1.25E-04	0.704958	70.49584
100	61.18	1.259	1.00E-04	0.745178	74.51782
300	96.06	8.82E-01	1.03E-04	0.837706	83.77056
500	124.5	9.26E-01	8.66E-05	0.874779	87.47791
700	149.7	9.17E-01	9.70E-05	0.895858	89.58584

Table 5.Electrochemical kinetic parameters obtained by EIS technique for Carbon steel in 1MHCl solution containing various concentrations of the investigated Zygophillum Album Extract at 20°C.

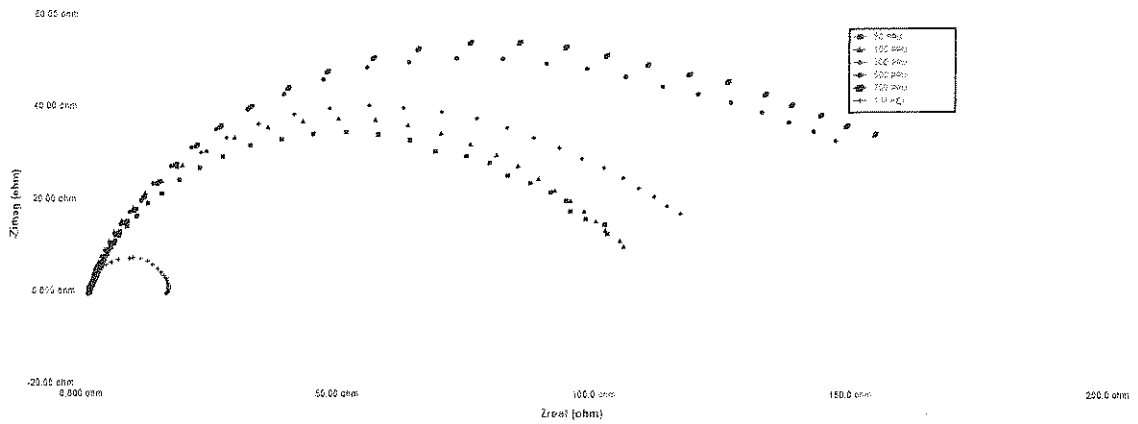

Figure 6. Nyquist plots recorded for Carbon Steel in 1M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Aegyptium at the respective corrosion potentials and 25°C.

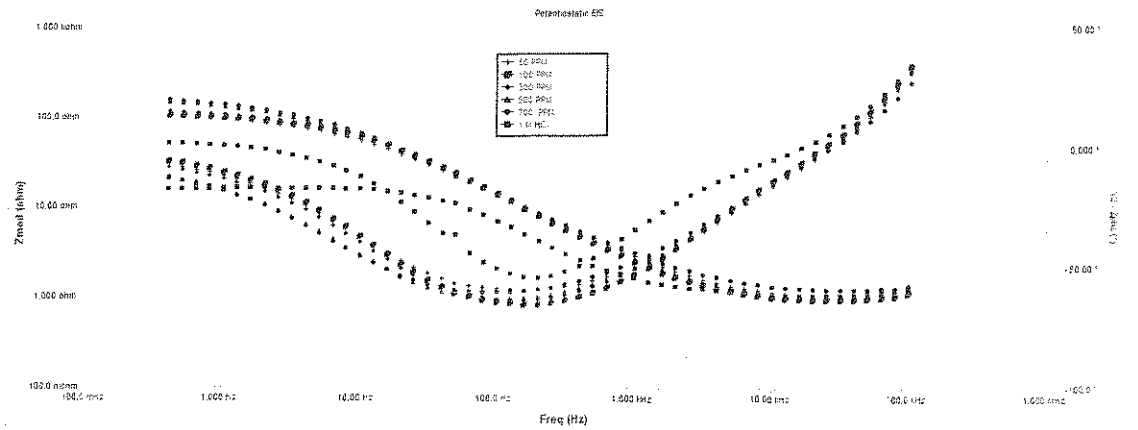

Figure (6-1): Bode plots recorded for Carbon Steel in 1M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Aegyptium at the respective corrosion potentials and 25°C.

Concentration, PPM	Rct, Ω cm2	Ru, Ω cm2	Cdl, F cm-2	θ	% IE
1M HCl	15.59	1.077	2.23E-04	--	--
50	100.6	9.73E-01	1.97E-04	0.84503	84.50298
100	100.7	9.19E-01	1.63E-04	0.845184	84.51837
300	113	9.70E+02	1.86E-04	0.862035	86.20354
500	147.4	9.49E-01	2.21E-04	0.894233	89.42334
700	159.6	1.17E+00	2.29E-04	0.902318	90.23183

Table 5. Electrochemical kinetic parameters obtained by EIS technique for Carbon steel in 1MHCl solution containing various concentrations of the investigated Zygophllum Aegyptium Extract at 25°C.

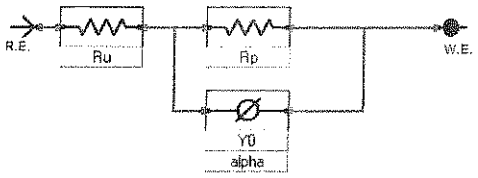

Figure 7. Electrical equivalent circuit used to fit the impedance data.

3.4. Electrochemical frequency modulation measurements (EFM)

The EFM is a nondestructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Like EIS, it is a small signal ac technique. Unlike EIS, However, two sine waves (at different frequencies) are applied to the cell simultaneously.

Studying effect of addition of Zygophllum album and Zygophllum Aegyptium plant extracts on the Corrosion of (N80) Carbon steel. ,Intermodulation spectra obtained from EFM measurements are presented in Figure 8 and 9 are examples of alloy in aerated 1 M HCl solutions devoid of and containing different concentrations of plant extracts at 25°C. Each spectrum is a current response as a function of frequency. The two large peaks are

the response to the 2 Hz and 5Hz excitation frequencies. These peaks are used by the EFM 140 software package to calculate the corrosion current and Tafel constants.

The calculated corrosion kinetic parameters at different concentrations of the investigated extracts in 1 M HCl at 25 °C (icorr, βa, βc, CF-2, CF-3 and % IE) are given in Tables 7 and 8.

From Tables (7,8), the corrosion current densities decrease by increasing the concentration of investigated plant extracts and the inhibition efficiencies increase by increasing investigated plant extracts concentrations. The causality factors in Tables (7,8)are very close to theoretical values which according to EFM theory should guarantee the validity of Tafel slopes and corrosion current densities. Values of causality factors in Tables (7,8) indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The deviation of causality factors from their ideal values might due to the perturbation amplitude was too small or the resolution of the frequency spectrum is not high enough also another possible explanation that the inhibitor is not performing very well. It can be seen that the inhibition efficiency slightly decreases in the order: Aegyptium > Album. The obtained results showed good agreement of inhibition efficiency obtained with the Potentiodynamic polarization, EIS and EFM methods.

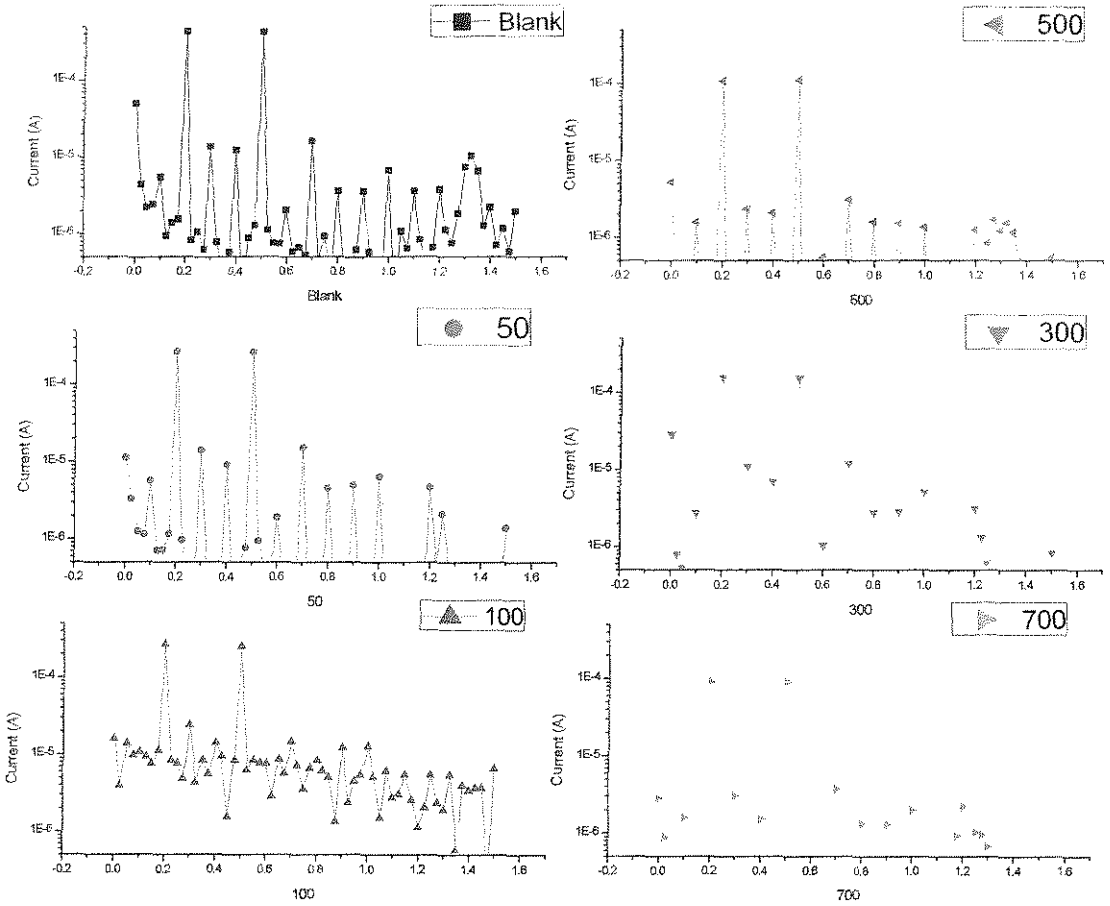

Figure 8. Intermodulation spectrum for Carbon steel in 1 M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Album at 25°C.

Concentration, PPM	i_{corr}, $\mu A\ cm^{-2}$	β_a, $mV_{SCE}\ dec^{-1}$	β_c, $mV_{SCE}\ dec^{-1}$	Causality Factor (2)	Causality Factor (3)	C.R. mpy	θ	% IE
1 M HCl	799.4	0.1072	0.1388	1.559	2.074	365.3	--	--
50	361.8	0.0761	0.1022	1.874	2.978	165.3	0.547	54.7
100	274.3	0.0585	0.0798	1.439	1.155	125.3	0.657	65.7
300	215.1	0.0746	0.1127	1.891	3.067	98.31	0.731	73.1
500	172	0.0935	0.1087	1.592	2.685	78.6	0.785	78.5
700	126.5	0.0806	0.0984	1.926	4.218	57.8	0.842	84.2

Table 7. Electrochemical kinetic parameters obtained by EFM technique for Carbon Steel in 1M HCl solutions containing various concentrations of the investigated Zygophyllum album plant extract at 25°C.

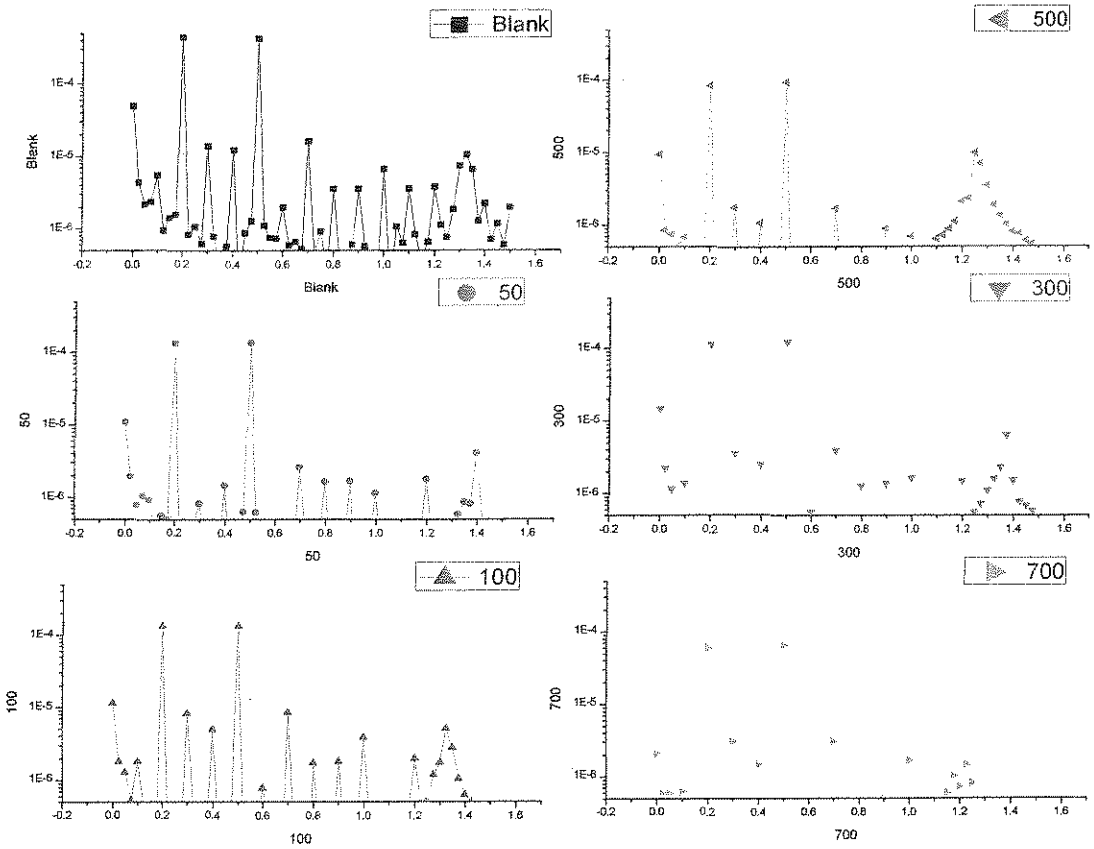

Figure 9. Intermodulation spectrum for Carbon steel in 1 M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum aegyptium at 25°C.

Concentration, PPM	i_{corr}, $\mu A\ cm^{-2}$	β_a, $mV_{SCE}\ dec^{-1}$	β_c, $mV_{SCE}\ dec^{-1}$	Causality Factor (2)	Causality Factor (3)	C.R. mpy	θ	% IE
1 M HCl	799.4	0.1072	0.1388	1.559	2.074	365.3	--	--
50	222.9	0.1039	0.1132	1.292	6.254	101.8	0.7212	72.12
100	218.9	0.0871	0.1312	1.914	3.142	100	0.7262	72.62
300	200.8	0.0987	0.1220	1.807	3.071	91.75	0.7488	74.88
500	151.3	0.1021	0.1161	1.957	3.235	69.14	0.8107	81.07
700	123.6	0.1077	0.1599	1.932	3.97	56.47	0.8454	84.54

Table 8.Electrochemical kinetic parameters obtained by EFM technique for Carbon Steel in 1M HCl solutions containing various concentrations of the investigated Zygophyllum aegyptium plant extract at 25°C.

3.5. Adsorption isotherms:

(It is generally assumed that the adsorption of the inhibitors on the metal surface is the essential step in the inhibition mechanism [49]. To determine the adsorption mode, various isotherms were tested and the Langmuir mode was the best Fitted, given by Eq. (7) [35]:

$$\theta/ 1- \theta = Ka\ C \qquad (7)$$

where θ is the surface coverage, C is the inhibitor concentration (g/L) and Ka is the equilibrium constant of adsorption process and is related to the standard free energy of adsorption $\Delta G°_{ads}$ by the equation:

$$Ka= 1/55.5 \exp (-\Delta G°_{ads}/RT) \qquad (8)$$

The value of 55.5 is the concentration of water in solution expressed in mole per liter, R is the universal gas constant and T is the absolute temperature. The Weight loss results were used to calculate the adsorption isotherm parameters. The surface coverage θ data are very useful while discussing the adsorption characteristics. The plot of C/ θ vs. C for all investigated Compounds gave a straight line (Figure 10) characteristic of the Langmuir adsorption isotherm. The calculated ΔG°ads values, using 8), were also given in Table (9). ΔG expressed in kJ mol-1 adsorbed. The negative values of $\Delta G°_{ads}$ ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the N80 carbon steel surface. It is well known that values of ΔG°ads of the order of 40 kJ mol-1 or

higher involve charge sharing or transfer from the inhibitor molecules to metal surface to form coordinate type of bond (chemisorptions); those of order of 20 kJ mol-1 or lower indicate a physisorption. [36-39].

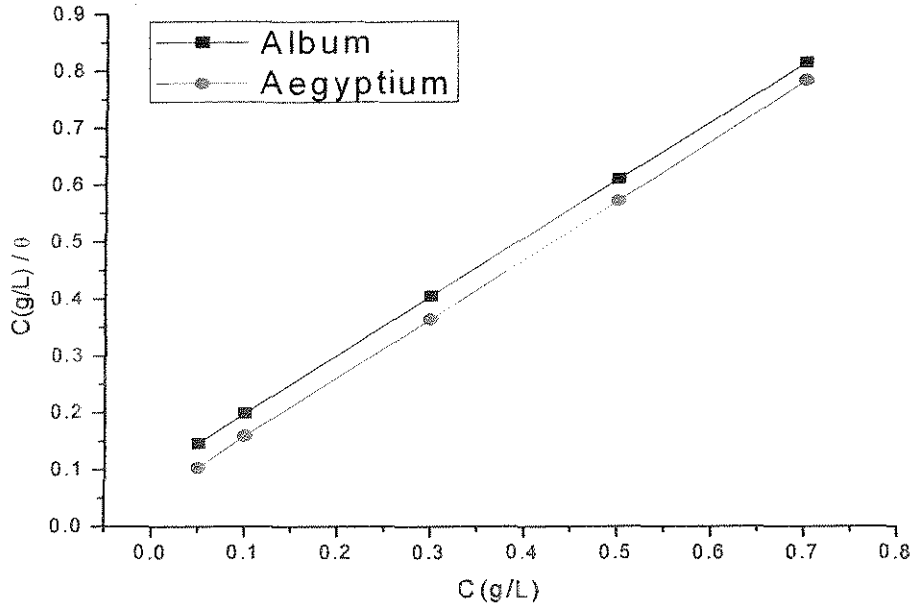

Figure 10 . Curve fitting of corrosion data for N80 carbon steel in 1M HCl in the presence of different concentrations of Zygophyllum album and Zygophyllum aegyptium extracts to Langmuir adsorption isotherm at 25° C.

Inhibitor	Langmuir Isotherm		
	i	K	$-\Delta G°_{ads}$
Zygophyllum album	0.0493	20.2968	17.0272
Zygophyllum aegyptium	0.0928	10.7721	15.4922

Table 9. Equilibrium constant and adsorption free energy of the investigated compounds adsorbed on N80 carbon steel surface.

The calculated $\Delta G°_{ads}$ values (Table 9) are less negative than -20 kJmol-1 indicate, therefore, that the adsorption mechanism of the investigated extract on N80 carbon steel in 1 M HCl solution is typical of physisorption.

3.6. Effect of temperature and activation parameters of inhibition process:

The influence of temperature on the corrosion rate of N80 carbon steel in 1 M HCl in the absence and presence of a various range of the tested plant extracts was investigated by the Weight loss technique in temperature range 25, 35 and 45 °C
The dependence of corrosion current density on the temperature can be expressed by Arrhenius equation:

$i_{corr} = A \exp(-E_a^* / RT)$ (9)

Where A is the pre-exponential factor and E_a^* is the apparent activation energy of the corrosion process. Tables (10&11) showed that the value of E_a^* for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of Al is slow in the presence of inhibitor. It is known from Eq. (9) that the higher E_a^* values lead to the lower corrosion rate.

Enthalpy and entropy of activation (ΔH^*, ΔS^*) of the corrosion process were calculated from the transition state theory -Tables (10&11):

Rate (i_{corr}) = (RT/ Nh) exp ($\Delta S^*/R$) exp ($-\Delta H^*/RT$) (10)

where h is Planck's constant and N is Avogadro's number. A plot of log (icorr/ T) vs. 1/ T for Al in 1 M HCl for the investigated extracts , gives straight lines as shown in Figure (12&14). Values of ΔH^* are positive. This indicates that the corrosion process is endothermic one .The entropy of activation is large and negative. This implies that the activated complex represents association rather than dissociation step , indicating that a decrease in disorder takes place, going from reactants to the activated complex [57].

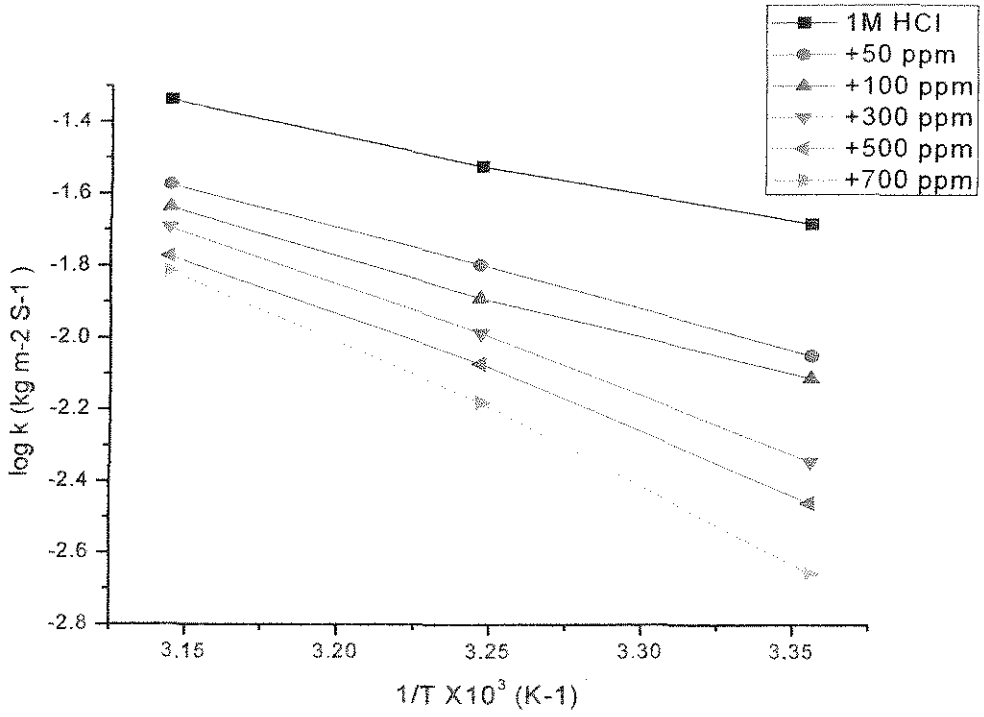

Figure 11 . log k (corrosion rate) – 1/T curves for N80 carbon steel dissolution in 1 M HCl in the absence and presence of Various conc. Range of Zygophyllum album extract.

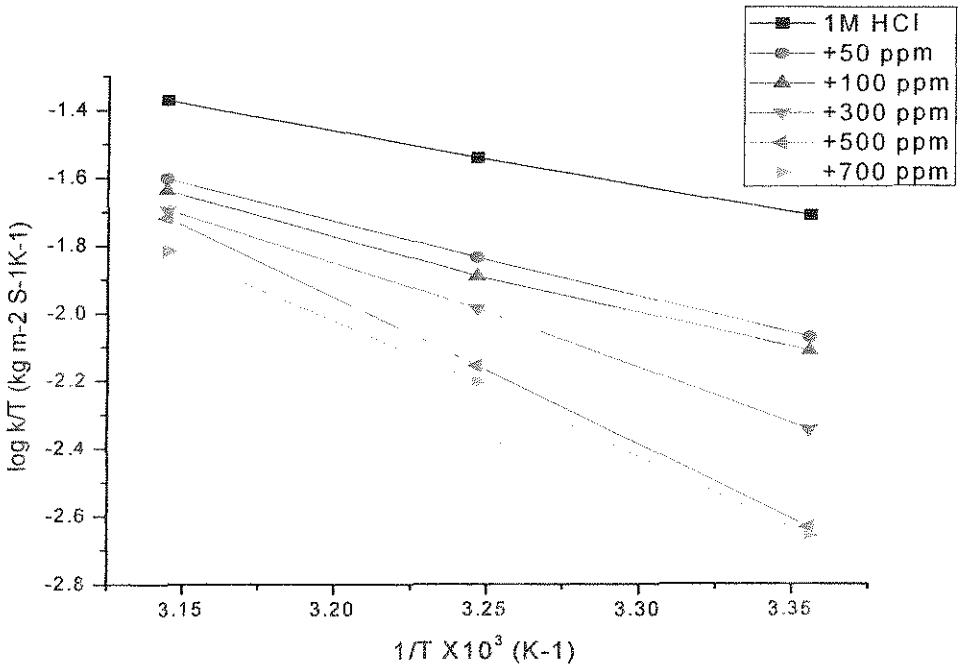

Figure 12 . log k (corrosion rate)/T – 1/T curves for N80 carbon steel dissolution in 1 M HCl in the absence and presence of Various conc. Range of Zygophyllum album extract.

conc.	Species : Zygophyllum album		
	E_a^* , kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
1M HCl	5.92	3.56	40.16
50 ppm	5.42	4.94	36.69
100 ppm	5.33	4.84	37.17
300 ppm	7.17	6.68	31.62
500 ppm	9.69	9.21	23.96
700 ppm	9.24	8.75	25.61

Table 10 . Activation parameters of the corrosion of N80 carbon steel in 1M HCl at various concentration ranges of Zygophyllum album extract.

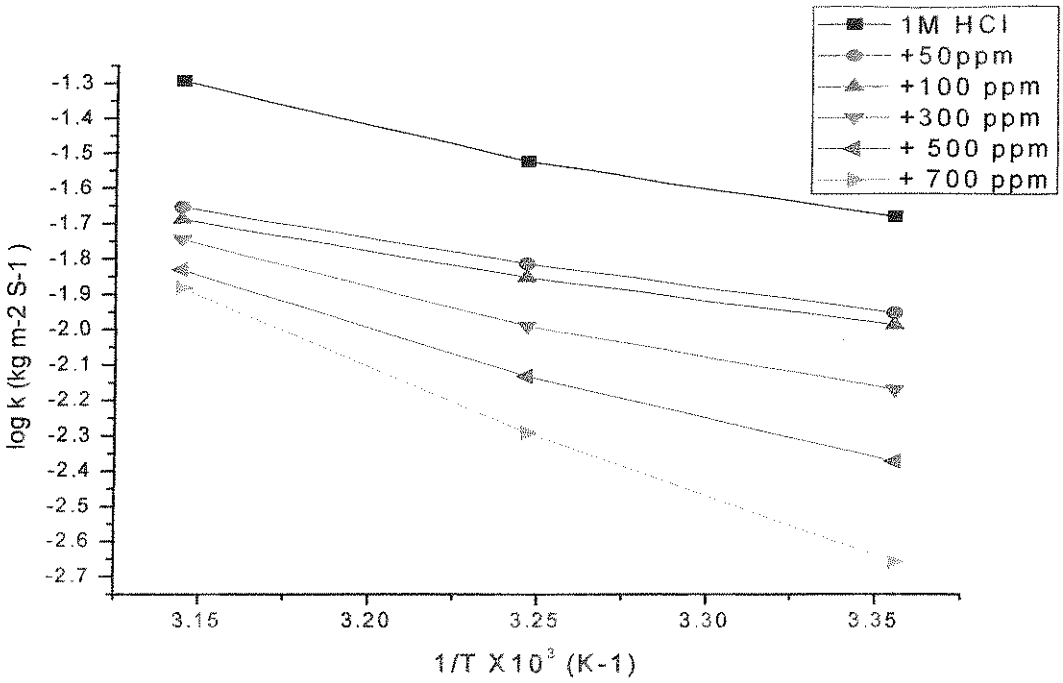

Figure 13 . log k (corrosion rate) – 1/T curves for N80 carbon steel dissolution in 1 M HCl in the absence and presence of Various conc. Range of Zygophyllum Aegyptium extract.

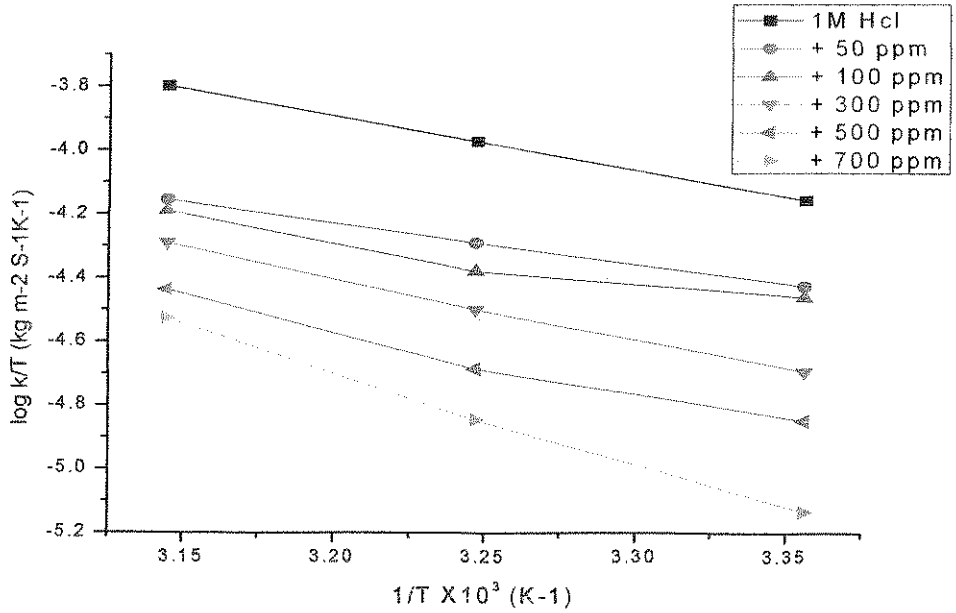

Figure 14 . log k (corrosion rate)/T – 1/T curves for N80 carbon steel dissolution in 1 M HCl in the absence and presence of Various conc. Range of Zygophyllum Aegyptium extract.

conc.	Species : Zygophyllum Aegyptium		
	E_a^* , kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
1M HCl	5.92	3.56	40.16
50 ppm	3.49	3.01	42.99
100 ppm	3.45	2.97	43.22
300 ppm	4.91	4.43	38.93
500 ppm	6.23	5.75	35.13
700 ppm	8.80	8.32	27.33

Table 11 . Activation parameters of the corrosion of N80 carbon steel in 1M HCl at various concentration ranges of Zygophyllum Aegyptium extract.

4. GENERAL CONCLUSIONS

Zygophyllum album and Zygophyllum aegyptium extracts acts as inhibitors for N80 carbon steel corrosion in 1M HCl solution. The corrosion process is inhibited by adsorption of the extract species on the N80 carbon steel surface following the Langmuir isotherm. The results suggested the use of Zygophyllum Aegyptium as a corrosion inhibitor because it has more resistance for temperature changes than Zygophyllum album extract.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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OS MINERAIS DE BERÍLIO (*BERYLLIUM MINERALS*)

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RESUMO

O berílio é um elemento componente do Grupo 2 da Tabela Periódica dos Elementos, não cristaliza como um sólido natural e exibe concentração geoquímica de 2,8 ppm na crosta terrestre, sendo considerado um elemento traço de baixa representatividade, juntamente com érbio e bromo. Apresenta alta reatividade química, muito embora apareça com pouca freqüência nas substâncias minerais, ocorrendo na composição química de apenas 96 espécies. Os principais minerais fonte do elemento, para a indústria, são berilo, bertrandita e, secundariamente helvita, crisoberilo, euclásio, berilonita e fenaquita. Este artigo apresenta uma sinopse dos minerais em que berílio está presente, constituindo uma contribuição à divulgação do conhecimento científico desses compostos.

PALAVRAS-CHAVE: berílio, minerais de berílio, usos do berílio.

ABSTRACT

Beryllium is a chemical element component of the Group 2 of the Periodic Table of Chemical Elements. Its does not crystallize as a natural solid, and exhibits crustal abundance of 2.8 ppm. It is a chemical element among the trace elements with low representativity, together with erbium and bromine. It shows a high chemical reactivity, and a low abundance in the chemical composition of minerals (only 96 minerals have beryllium in their chemical compositions). The principal beryllium-bearing minerals for industrial usages are beryl and bertrandite, and secondary sources are helvite, chrysoberyl, euclase, beryllonite, and phenakite. This review presents a synopsis of the beryllium-bearing minerals as a contribution to the scientific knowledge of these substances.

KEY-WORDS: beryllium, beryllium-bearing minerals, uses of beryllium.

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1. INTRODUÇÃO

A mineralogia descritiva, como ciência geológica básica, vem sendo relegada nos últimos anos a um plano secundário dentro das próprias universidades. Isso se deve, principalmente, ao fato de que as agências de fomento exigem rápidos resultados e preocupam-se majoritariamente com a ciência aplicada, levando a ciência pura a certo esquecimento[1]. Assim, minerais com pouco volume na natureza, mas importantes do ponto de vista científico, pela possibilidade de síntese de correspondentes industriais, ficam pouco conhecidos pela comunidade farmacêutica, química e geológica[2].

Didaticamente, é de suma importância viabilizar, aos discentes de ciências da Terra, uma visão ampla dos compostos químicos que naturalmente apresentam cada um dos elementos químicos em suas composições. Isto pode ser sintetizado pela famosa frase do grande geocientista norte-americano Frederick H. Pough, ex-curador do *American Museum of Natural History*, que apregoou que apenas a mineralogia pode funcionar como um verdadeiro passatempo educacional, por relacionar geografia, física, química e matemática em suas análises[3].

Este artigo é uma continuação dos trabalhos descritivos sobre a mineralogia associada aos elementos da Tabela Periódica dos Elementos Químicos. Já foi publicada a mineralogia do hidrogênio, prata, cobre, ouro, chumbo, platina, lítio, urânio, elementos terras raras e arsenatos[3–12].

O trabalho visa a divulgação científica das espécies minerais que contêm berílio em suas composições químicas, com informações mais detalhadas sobre aquelas que apresentam interesse industrial, além do teor do elemento e os sistemas cristalinos nos quais cristalizam as demais espécies. Observa-se que são informações que geralmente encontram-se dispersas em bibliografia especializada e, muitas, de difícil acesso. Também é abordada a nomenclatura química destes compostos pela sistemática de Strunz e Nickel[13].

2. BERÍLIO E SUAS PROPRIEDADES

Berílio (do Grego: [βερυλλος] = *beryllos* ou [γλυκυς] = *glykys* (doce), devido ao sabor adocicado de seus sais), cujo símbolo químico é Be, é o metal alcalino-terroso (juntamente com magnésio, cálcio, estrôncio, bário e rádio) de menor raio atômico e o de menor caráter metálico. Apresenta coloração cinza, é duro, leve, quebradiço e sólido à temperatura ambiente, formando cátions divalentes. O berílio, na forma de fumos e pó, é bastante tóxico. Quando inalado, pode desenvolver uma patologia chamada berilose, que se caracteriza por pneumocomioses e granuloses de vários tipos. Muitos compostos de berílio também apresentam altos índices de toxicidade e devem ser manuseados com muito cuidado[14].

Apesar de pertencer ao Grupo 2, assemelha-se diagonalmente ao alumínio (Grupo 3), em função das semelhanças nos tamanhos dos átomos e íons. O berílio, ao contrário dos outros elementos alcalino-terrosos, forma uma série de complexos, com números de coordenação quatro[14,15].

É o quarto elemento da classificação periódica (Z = 4), tendo se formado juntamente com o lítio, no resfriamento havido após o *Big Bang*, pela fragmentação dos núcleos de átomos maiores, a partir de raios cósmicos, no processo de espalação. Assim como o lítio, não ocorre na matéria do Universo, pois os núcleos de seus átomos são muito frágeis não podendo resistir às altas temperaturas estelares[16-38]. Apresenta três isótopos (um estável e dois instáveis). O estável é o ^{9}Be (abundância de 100% e massa atômica de 9,012 u). Os instáveis são o ^{7}Be (meia-vida de 53,28 dias e massa atômica de 7,017 u) e o ^{10}Be (meia-vida de $2,6x10^{6}$ anos e massa atômica de 10,013 u)[19].

Na crosta terrestre apresenta abundância geoquímica de 2,8 ppm, sendo considerado, entre os elementos-traço, como de baixa representatividade, juntamente com érbio e o bromo[20].

Não ocorre livre na Terra, sendo encontrado principalmente na composição de minerais silicatados como berilo ($Be_3Al_2Si_6O_{18}$), crisoberilo ($BeAl_2O_4$), fenaquita (Be_2SiO_4), bertrandita ($Be_4Si_2O_7(OH)_2$), helvita ($Mn^{2+}{}_4Be_3(SiO_4)_3$) e berilonita ($NaBe_3PO_4$). As maiores reservas mundiais desses minerais encontram-se no Cazaquistão, Rússia, Estados Unidos da América, República Popular da China, Alemanha, Canadá e Brasil[21-22].

O berílio foi descoberto pelo farmacêutico e químico Louis Nicolas Vauquelin[113] (Figure 1), ao estudar óxido de berilo e a variedade mineralógica esmeralda ($Be_3Al_2Si_6O_{18}$, com impurezas de crômio, em 1787.

Figur1 1 - Louis Nicolas Vauquelin (☼16.05.1763, Saint-André d'Hébertot – †14.11.1829, Saint-André d'Hébertot).

Entretanto, só foi isolado em 1828, pelo pedagogo e químico alemão Friedrich Wöhler[114] (Figure 2), precursor da química orgânica, a partir da reação de potássio e cloreto de berílio. Em homenagem aos mesmos foram validados os minerais vauquelinite ($Pb_2Cu^{2+}(CrO_4)PO_4(OH)$)[133], em 1818 e wöhlerite ($Na_2Ca_4Zr(Nb,Ti)(Si_2O_7)_2(O,F)_4$)[134], em 1843

Figure 2 – Friedrich Wöhler (☼31.07.1800, Eschersheim – †23.09.1882, Göttingen).

Suas propriedades físicas são: número atômico (Z) = 4; massa atômica = 9,012182(3) u; cor: cinza-prateado; ponto de fusão: 1.560,00 K (1.296,85°C); ponto de ebulição = 2.744,00 K (2.470,85°C); eletronegatividade de Pauling = 1,57; configuração do átomo no estado fundamental = $[He]2s^2$; estado físico a 25°C e 1 atm: sólido; estado de oxidação: 2^+; composição isotópica: 100% de ^9Be, ^7Be, ^{10}Be; raio atômico = 105 pm, raio covalente = 90 pm, raio iônico = 41 pm (para NC = 4); densidade: 1,848 $Kg.m^{-3}$; volume molar = 4,85 x 10^{-6} $m^3.mol^{-1}$; estrutura cristalina: hexagonal de empacotamento compacto; primeira energia de ionização = 898,80 $KJ.mol^{-1}$; segunda energia de ionização = 1.757,10 $KJ.mol^{-1}$; terceira energia de ionização = 14.848,70 $KJ.mol^{-1}$; calor específico = 1.825 $J.Kg^{-1}K$; entalpia de fusão = 12,20 $KJ.mol^{-1}$; entalpia de vaporização = 292,40 $KJ.mol^{-1}$; pressão de vapor = 4.180 Pa; velocidade do som = 13.000 $m.s^{-1}$; condutividade térmica = 201 W. $m^{-1}.K$; condutividade elétrica = 31,6 x $10^6.m^{-1}$ ohm[14,15,19,25].

3. MINERAIS EM QUE BERÍLIO OCORRE E SUA SISTEMÁTICA

Até 2008 (Back e Mandarino[26]), apenas 86 minerais contendo berílio em suas composições químicas encontravam-se validadas pela *IMA* (*International Mineralogical Association*), sistematizadas nas seguintes Classes mineralógicas: silicatos 55 (9 ciclossilicatos, 4 filossilicatos, 12 inossilicatos, 14 nesossilicatos, 8 sorossilicatos e 8 tectossilicatos), fosfatos e arseniatos (22), óxidos e hidróxidos (8) e boratos (3), perfazendo aproximadamente 2% do universo mineral. Após 2008, foram validadas pela *IMA*, outras cinco espécies: o carbonato niveolanita (*niveolanite*) $NaBe(CO_3)(OH).2H_2O$[26], e os silicatos bussyíta-(Ce) (*bussyite-(Ce)*) $((Ce,ETR)_2(Na,H_2O)_6MnSi_9Be_5(O,OH)_{30}(F)_4$ e eirikita (*eirikite*) $(KNa_6Be_2(Si_{15}A_2)O_{39}F_2)$ (filossilicatos), friedrichbeckeíta (*freiderichbeckeite*)

(K(□Na)(Mg_2)(Be_2Mg)$Si_{12}O_{30}$) (ciclossilicato) e alflarsenita (*alflasernite*) ($NaCa_2Be_3Si_{14}O_{13}(OH).2H_2O$) [47-51] (tectossilicato), totalizando assim 91 espécies.

3.1. Sistemática

Segue Strunz e Nickel[13] e, serão tecidas informações mais detalhadas apenas àquelas substâncias mais importantes do ponto de vista industrial.

a) Óxidos e Hidróxidos – aos óxidos correspondem compostos com configurações estruturais variáveis, desde coordenação 2 até 10, com os poliedros apresentando ligação com um cátion metálico. Aos hidróxidos correspondem à presença de OH^-, com ou sem H_2O, ligado a um cátion metálico.
Os minerais portadores de berílio nesta Classe são:

1. Crisoberilo (*Chrysoberyl*) $BeAl_2O_4$ – sistema ortorrômbico, massa molar = 126,97 $g.mol^{-1}$, com 7,10% de Be. Aspecto dos cristais: esverdeados a verdes-esmeralda, amarelos, castanhos; tabulares, prismáticos. Ocorrências: pegmatitos graníticos. Associação mineralógica: quartzo, muscovita, albita, schorlita, berilo, topázio, albita, fluorita e fenaquita. Principais jazimentos: mina do Bode, Campo Formoso, Bahia e pegmatito de Padre Paraíso, Minas Gerais, Brasil; pedreira Oxford, Maine, Estados Unidos da América; mina Nyanda, Zimbábue. Usos: fonte secundária de Be e material gemológico (variedades alexandrita e olho-de-gato), fonte industrial de berílio. É um mineral-tipo do Brasil (Araçuaí, Minas Gerais).[22,32,33]

2. Bromellita (*Bromellite*) BeO – sistema hexagonal, massa molar = 26,01 $g.mol^{-1}$, com 36,03% de Be. Aspecto dos cristais: incolores, brancos a amarelo-claros; prismáticos, tabulares, agregados rosetiformes. Ocorrências: veios hidrotermais (escarnitos e pegmatitos)[34].

3. Ferrotaaffeíta-2N'2S (*Ferrotaaffeite-2N'3S*) $(Fe^{2+},Mg,Zn)_3Al_8BeO_{18}$ – sistema trigonal, massa molar = 470,24 $g.mol^{-1}$, com 1,72% de Be. Aspecto dos cristais: verde-claros; tabulares; Ocorrências: pegmatitos[35].

4. Magnesiotaaffeíta-6N'3S (*Magnesiotaaffeite-6N'3S*) $Mg_2BeAl_6O_{12}$ – sistema hexagonal, massa molar = 426,60 $g.mol^{-1}$, com 1,90% de Be. Aspecto dos cristais: verde-oliva-claros; maciços, platiformes. Ocorrências: pegmatitos[36].

5. Magnesiotaaffeíta-2N'3S (*Magnesiotaaffeite-2N'2S*) $Mg_3BeAl_8O_{16}$ – sistema hexagonal, massa molar = 529,47 $g.mol^{-1}$, com 1,63% de Be. Aspecto dos cristais: púrpura a esverdeados; arredondados. Ocorrências: pláceres aluviais[37].

6. Swedenborgita (*Swedenborgite*) $NaBe_4Sb^{5+}O_7$ – sistema hexagonal, massa molar = 292,78 $g.mol^{-1}$, com 12,31% de Be. Aspecto dos cristais: amarelo-acastanhados, incolores, amarelo-mel; prismáticos. Ocorrências: escarnitos[38].

7. Behoíta (*Behoite*) $Be(OH)_2$ – sistema ortorrômbico, massa molar = 43,03 $g.mol^{-1}$, com 20,95% Be. Aspecto dos cristais: incolores, brancos, castanho-pálidos; esfenoidais, pseudo-octaédricos, granulares. Ocorrências: pegmatitos e tufos[39].

8. Clinobehoíta (*Clinobehoite*) $Be(OH)_2$ – sistema monoclínico, massa molar = 43,03 $g.mol^{-1}$, com 20,95% Be. Aspecto dos cristais: incolores, brancos; agregados radiais, cuneiformes, platiformes. Ocorrências: pegmatitos[40].

b) Carbonatos – são caracterizados por conterem complexos planares $[CO_3]^{=}$, ligados a cátions metálicos.
O único mineral portador de berílio nesta Classe é:

9. Niveolanita (*Niveolanite*) $NaBe(CO_3)(OH).2H_2O$ – sistema tetragonal, massa molar = 143,07 $g.mol^{-1}$, com 6,17% Be. Aspecto dos cristais: branco-nevados a branco-perláceos; fibrosos. Ocorrências: produto de alteração da eudidymite ($NaBeSi_3O_7(OH)$)[27].

c) Boratos – são caracterizados com base na química do grupo, levando em consideração o número de íons borato presentes na fórmula química (mono, di, tri, tetra-boratos e, assim por diante.
Os minerais portadores de berílio nesta Classe são:

10. Berborita (*Berborite*) $Be_2(BeO_3)(OH).H_2O$ (monoborato) – sistema monoclínico, massa molar = 112,35 $g.mol^{-1}$, com 16,04% Be. Aspecto dos cristais: incolores; cubos euédricos. Ocorrências: escarnitos[41].

11. Londonita (*Londonite*) $(CsBe_4Al_4(B_{11},Be)O_{28}$ (megaborato) – sistema cúbico, massa molar = 808,60 $g.mol^{-1}$, com 5,57% Be. Aspecto dos cristais: incolores, brancos, amarelos; cubos euédricos. Ocorrências: cavidades miarolíticas em pegmatitos[42].

12. Rodizita (*Rhodizite*) $(K\ Be_4Al_4(B_{11}Be)O_{28}$ (megaborato) – sistema cúbico, massa molar = 778,83 $g.mol^{-1}$, com 8,10% Be. Aspecto dos cristais: incolores, acinzentados, amarelos, branco-amarelados, brancos; dodecaédricos, tetraédricos. Ocorrências: pegmatitos graníticos[42].

d) Fosfatos – são caracterizados por apresentarem ânions $[PO4]^{3-}$ isolados, com cátions pequenos com NC = 4, médios com NC = 6 e grandes com NC = 8, ou maior.

13. Atencioíta (*Atencioite*) $Ca_2(Fe^{2+})_3Mg_2Be_4(PO_4)_6(OH)_4.6H_2O$ – sistema trigonal, massa molar = 1.060,05 $g.mol^{-1}$, com 3,34% Be. Aspecto dos cristais: castanho-esverdeados; concreções esféricas. Ocorrências: pegmatitos graníticos. É um mineral-tipo do Brasil[43].

14. Babeffita (*Babefphte*) $BaBePO_4F$ – sistema trigonal, massa molar = 259,56 $g.mol^{-1}$, com 3,34% Be. Aspecto dos cristais: brancos; grãos anédricos achatados. Ocorrências: pláceres aluviais de regiões escarníticas[44].

15. Berilonita (*Beryllonite*) $NaBe(PO_4)$ – sistema monoclínico, massa molar = 126,97 $g.mol^{-1}$, com 7,10% de Be. Aspecto dos cristais: incolores, brancos a amarelo pálidos; maciços, esféricos, fibrosos. Ocorrências: pegmatitos graníticos

alcalinos. Associação mineralógica: albita, berilo, herderita, lepidolita, ortoclásio, petalita, pollucita, quartzo e triplita. Principais jazimentos: montanhas Sugarloaf, Maine, Estados Unidos da América; Mont Saint-Hilaire, Quebec, Canadá; lavras do Ênio, em Galiléia, da Ilha, em Taquaral e mina do Almerindo, em Linópolis, Minas Gerais, Brasil. Usos: fonte secundária de berílio e material gemológico[22,33].

16. Ehrleíta (*Ehrleite*) $Ca_2ZnBe(PO_4)_2(PO_3OH).4H_2O$ – sistema triclínico, massa molar = 480,04 g.mol^{-1}, com 1,88% Be. Aspecto dos cristais: incolores, brancos; tabulares. Ocorrências: pegmatitos graníticos[45].

17. Faheyíta (*Faheyite*) $BeMn^{2+}(Fe^{3+})_2(PO_4)_4.6H_2O$ – sistema hexagonal, massa molar = 664,98 g.mol^{-1}, com 2,71% Be. Aspecto dos cristais: branco-azulados, branco-acastanhados, brancos; fibrosos, rosetiformes, massas botrioidais. Ocorrências: pegmatitos graníticos. É um minera-tipo do Brasil (Sapucaia, Minas Gerais)[32,46].

18. Fransoletita (*Fransoletite*) $Ca_3Be_2(PO_4)_2(PO_3OH)_2.4H_2O$ – sistema monoclínico, massa molar = 592,22 g.mol^{-1}, com 3,42% Be. Aspecto dos cristais: incolores, brancos; agregados setiformes. Ocorrências: pegmatitos graníticos[47].

19. Glucina (*Glucine*) $CaBe_4(PO_4)_2(OH)_4.0,5H_2O$ – sistema monoclínico, massa molar = 343,11 g.mol^{-1}, com 10,51% Be. Aspecto dos cristais: incolores, brancos, amarelo claros; concreções maciças, arredondadas. Ocorrências: depósitos de fluorita[48].

20. Greifensteinita (*Greifensteinite*) $Ca_2Be_4(Fe^{2+})_5(PO_4)_6(OH)_4.6H_2O$ – sistema monoclínico, massa molar = 343,11 g.mol^{-1}, com 3,31% Be. Aspecto dos cristais: incolores, brancos, amarelo claros; concreções maciças, arredondadas. Ocorrências: pegmatitos graníticos[49].

21. Guimarãesita (*Guimarãesite*) $Ca_2Be_4Zn_5(PO_4)_6(OH)_4.6H_2O$ – sistema monoclínico, massa molar = 1.107,66 g.mol^{-1}, com 3,25% Be. Aspecto dos cristais: castanhos; prismáticos, agregados botrioidais. Ocorrências: pegmatitos graníticos. É um mineral-tipo do Brasil (Itinga, Minas Gerais)[32,40].

22. Herderita (*Herderite*) $CaBePO_4$] – sistema monoclínico, massa molar = 163,06 g.mol^{-1}, com 5,53% Be. Aspecto dos cristais: brancos, amarelo-esbranquiçados, branco-esverdeados; prismáticos, tabulares, fibrorradiados, botrioidais. Ocorrências: pegmatitos graníticos[51].

23. Hurlbutita (*Hurlbutite*) $CaBe_2(PO_4)_2$ – sistema monoclínico, massa molar = 248,05 g.mol^{-1}, com 7,27% Be. Aspecto dos cristais: incolores, branco-esverdeados, amarelos; prismáticos. Ocorrências: pegmatitos graníticos[52].

24. Mccrillisita (*Mccrillisite*) $NaCs(Be,Li)Zr_2(PO_4)_4.1\text{-}2H_2O$ – sistema tetragonal, massa molar = 753,75 g.mol^{-1}, com 0,90% Be. Aspecto dos cristais: incolores, branco-esverdeados, amarelos; bipiramidados. Ocorrências: pegmatitos graníticos[53].

25. Moraesita (*Moraesite*) $Be_2(PO_4)(OH).4H_2O$ – sistema monoclínico, massa molar = 202,06 g.mol^{-1}, com 8,92% Be. Aspecto dos cristais: brancos; agregados crustiformes, aciculares, tabulares. Ocorrências: pegmatitos graníticos. É um mineral tipo do Brasil (Galiléia, Minas Gerais)[32,46].

26. Pahasapaíta (*Pahasapaite*) $Li_8(Ca,Li,K)Be_{24}(PO_4)_{24}.38H_2O$ – sistema cúbico, massa molar = 3.532,65 $g.mol^{-1}$, com 6,12% Be. Aspecto dos cristais: incolores, verde-amarelados, rosa claro; cúbicos euédricos. Ocorrências: pegmatitos graníticos[46].

27. Parafransoletita (*Parafransoletite*) $Ca_3Be_2(PO_4)_2(PO_3OH)_2.4H_2O$ – sistema triclínico, massa molar = 592,22 $g.mol^{-1}$, com 3,42% Be. Aspecto dos cristais: incolores, brancos; lanciformes. Ocorrências: pegmatitos graníticos[54].

28. Roscherita (*Roscherite*) $Ca_2(Mn^{2+})_5Be_4(PO_4)_6(OH)_4.6H_2O$– sistemas monoclínico/triclínico, massa molar = 1.097,90 $g.mol^{-1}$, com 3,55% Be. Aspecto dos cristais: castanho claros, castanho-escuros, verde-olivas, vermelho-alaranjados, vermelhos; agregados psolíticos. Ocorrências: cavidades miarolíticas em pegmatitos graníticos[55,111].

29. Ruifrancoíta (*Ruifrancoite*) $Ca_2(\square Mn)_2(Fe^{3+},Mn,Mg)_4(Be_4(PO_4)_6.4H_2O$– sistema cúbico, massa molar = 1.075,85 $g.mol^{-1}$, com 6,12% Be. Aspecto dos cristais: castanho-avermelhados; aciculares, agulhiformes, botrioidais. Ocorrências: pegmatitos graníticos. É um mineral-tipo do Brasil[33].

30.Selwynita (*Selwynite*) $NaKBeZr_2(PO_4)_4.2H_2O$ – sistema tetragonal, massa molar = 673,96 $g.mol^{-1}$, com 1,0% Be. Aspecto dos cristais: azul purpúreos; radiais, esteliformes. Ocorrências: pegmatitos graníticos. É um mineral-tipo do Brasil[36].

31. Uralolita (*Uralolite*) $Ca_2Be_4(PO_4)_3(OH)_3.5H_2O$ – sistema monoclínico, massa molar = 542,22 $g.mol^{-1}$, com 6,65% Be. Aspecto dos cristais: incolores, brancos, branco-acastanhados; concreções maciças arredondadas. Ocorrências: produto de alteração da berilonita em pegmatitos[37].

32. Väyrynenita (*Väyrynenite*) $BeMn^{2+}PO_4(OH)$ – sistema monoclínico, massa molar = 176,43 $g.mol^{-1}$, com 5,11% Be. Aspecto dos cristais: rosas, vermelho rosados; prismáticos, agregados granulares finos. Ocorrências: produto de alteração do berilo e da trifilita em pegmatitos[38].

d) Silicatos – Classe mineralógica estruturada à base de tetraedros de sílica $[SiO_4]^{4-}$, sendo as estruturas classificadas segundo o grau de polimerização, com o compartilhamento dos tetraedros através dos vértices.

d_1) Nesossilicatos – nessas estruturas os tetraedros de $[SiO_4]^{4-}$ encontram-se isolados e encontram-se ligados uns aos outros por ligações iônicas através de cátions intersticiais.

33.Esferobertrandita (*Sphaerobertrandite*) $Be_3SiO_4(OH)_2$ – sistema monoclínico, massa molar = 152,62 $g.mol^{-1}$, com 17,07% Be. Aspecto dos cristais: amarelos, branco-acastanhados, brancos, cinzas; platiformes, achatados, esféricos, agregados arredondados. Ocorrências: pegmatitos alcalinos e greisens[39].

34. Euclásio (*Euclase*) $BeAlSiO_4(OH)$ – sistema monoclínico, massa molar = 145,08 $g.mol^{-1}$, com 6,21% Be. Aspecto dos cristais: azuis, incolores, brancos, azuis claros, verde claros; prismáticos. Ocorrências: produto de alteração de berilo em

pegmatitos. Associação mineralógica: quartzo, feldspatos, micas, topázio, berilo, calcita, ankerita e cloritas. Principais jazimentos: rio Sanarka, Montes Urais, Rússia; Las Cruces, Chivor, Colômbia; Ouro Preto, Minas Gerais e Brumado, Bahia, Brasil; Usos: material gemológico (variedade alexandrita), fonte industrial de berílio. É um mineral-tipo do Brasil (Araçuaí, Minas Gerais)[32,33,60].

35. Fenaquita (*Phenakite*) Be_2SiO_4 – sistema trigonal, massa molar = 110,11 $g.mol^{-1}$, com 16,937% Be. Aspecto dos cristais: incolores, amarelo-grenás, amarelos, rosas, vermelho rosados; prismáticos, granulares, maciços, fibrosos. Ocorrências: pegmatitos e pláceres aluviais. Associação mineralógica: berilo, crisoberilo, quartzo e apatitas. Principais jazimentos: Mount Antero, Chafee, Colorado, Estados Unidos da América; Mina Tokowaja, Miask, Montes Urais, Rússia; Mina de Socotó, Campo Formoso, Bahia e depósitos de São Miguel de Piracicaba, Minas Gerais, Brasil; Usos: material gemológico, fonte industrial secundária de berílio [22,33,61].

36. Gadolinita-(Ce) (*Gadolinite-(Ce)*) $(Ce_2Fe^{2+}Be_2O_2(SiO_4)_2)$– sistema monoclínico, massa molar = 571,37 $g.mol^{-1}$, com 5,98% Be. Aspecto dos cristais: pretos, castanhos; prismáticos. Ocorrências: pegmatitos sieníticos na zona de contato com basaltos e monzonitos[62].

37. Gadolinita-(Y) (*Gadolinite-(Y)*) $(Y_2Fe^{2+}Be_2O_2(SiO_4)_2)$ – – sistema monoclínico, massa molar = 467,85 $g.mol^{-1}$, com 3,85% Be. Aspecto dos cristais: castanhos, verdes, preto-esverdeados, verde claros, pretos; maciços. Ocorrências: pegmatitos ricos em elementos terras raras[63].

38. Hingganita-(Ce) (*Hingganite-(Ce)*) $BeCe(SiO_4)(OH)$ – sistema monoclínico, massa molar = 460,63 $g.mol^{-1}$, com 3,95% Be. Aspecto dos cristais: castanho-avermelhados pálidos; dipiramidados euédricos. Ocorrências: cavidades miarolíticas em pegmatitos graníticos[64].

39. Hingganita-(Y) (*Hingganite-(Y)*) $BeY(SiO_4)(OH)$ – sistema monoclínico, massa molar = 433,65 $g.mol^{-1}$, com 4,30% Be. Aspecto dos cristais: verdes, castanho-amarelos, brancos, azul claros, amarelo claros; agregados que lembram feixes de trigo. Ocorrências: granófiros[65].

40. Hingganita-(Yb) (*Hingganite-(Yb)*) $BeYb(SiO_4)(OH)$ – sistema monoclínico, massa molar = 453,70 $g.mol^{-1}$, com 3,97% Be. Aspecto dos cristais: incolores; agregados esféricos, aciculares. Ocorrências: pegmatitos amazoníticos[66].

41. Liberita (*Liberite*) Li_2BeSiO_4 – sistema monoclínico, massa molar = 114,98 $g.mol^{-1}$, com 7,84% Be. Aspecto dos cristais: castanhos, amarelo claros; agregados diminutos, às vezes com múltiplos pinacoides. Ocorrências: tactitos[67].

42. Melifanita (*Meliphanite*) $Ca_4(Na,Ca)_4Be_4AlSi_7O_{24}(F,O)_4$ – sistema tetragonal, massa molar = 241,15 $g.mol^{-1}$, com 3,74% Be. Aspecto dos cristais:.incolores, amarelos, vermelho-amarelados, vermelhos; prismáticos. Ocorrências: pegmatitos nefelina-sieníticos[68,112].

43. Minasgeraisita-(Y) (*Minasgeraisite-(Y)*) $CaBe_2Y_2Si_2O_{10}$ – sistema monoclínico, massa molar = 452,08 $g.mol^{-1}$, com 3,99% Be. Aspecto dos cristais: violetas, lilases, púrpuras; agregados lanciformes que lembram feixes de trigo.

Ocorrências: pegmatitos graníticos. É um mineral-tipo do Brasil (pedreira do José Pinto, Jaguaruçu, Minas Gerais)[32,69].

44. Surinamita (*Surinamite*) $Mg_3Al_3O(Si_3BeAlO_{15})$ – sistema monoclínico, massa molar = 553,76 g.mol^{-1}, com 1,63% Be. Aspecto dos cristais: azuis, verde-azulados; platiformes. Ocorrências: gnaisses milonitizados[70].

45. Sverigeíta (*Sverigeite*) $NaBe_2(Mn^{2+})_2SnSi_3O_{12}(OH)$ – sistema ortorrômbico, massa molar = 532,22 g.mol^{-1}, com 3,39% Be. Aspecto dos cristais: amarelos; anédricos. Ocorrências: rejeito de minerações[71].

46. Trimerita (*Trimerite*) $CaBe_3(Mn^{2+})_2(SiO_4)_3$ – sistema monoclínico, massa molar = 453,24 g.mol^{-1}, com 5,97% Be. Aspecto dos cristais: incolores, vermelho-amarelados, rosas; prismáticos. Ocorrências: veios hidrotermais associados a metamorfismo de contato e metassomatismo[72].

d_2) Sorossilicatos – nessas estruturas os tetraedros de $[SiO_4]^{4-}$ encontram-se dispostos principalmente em pares isolados, onde cada par é conectado ao outro por um átomo de oxigênio através dos seus ápices. Nesta Subclasse a relação Si:O é de 2:7.

47. Aminoffita (*Aminoffite*) $Ca_3(BeOH)_2Si_3O_{10}$ – sistema tetragonal, massa molar = 416,52 g.mol^{-1}, com 4,33% Be. Aspecto dos cristais: incolores, vermelho-amarelados, rosas; prismáticos. Ocorrências: veios hidrotermais associados a metamorfismo de contato e metassomatismo[72].

48. Barilita (*Barylite*) $BaBe_2Si_2O_7$ – sistema ortorrômbico, massa molar = 323,52 g.mol^{-1}, com 5,57% Be. Aspecto dos cristais: incolores, brancos, azulados; prismáticos, tabulares. Ocorrências: cavidades miarolíticas de pegmatitos alcalinos; nefelina sienitos[73].

49. Bertrandita (*Bertrandite*) $Be_4Si_2O_7(OH)_2$ – sistema ortorrômbico, massa molar = 238,23 g.mol^{-1}, com 15,13% Be. Aspecto dos cristais: incolores, amarelo pálidos; prismáticos. Ocorrências: produto de alteração de berilo em cavidades miarolíticas de pegmatitos graníticos. Associação mineralógica: berilo, fenaquita, herderita, turmalina, muscovita, fluorita e quartzo. Principais jazimentos: pedreira Barbin, Loire, França; Val Vigezzo, Piedmont, Itália; pedreira Strickland, Middlesex, Connecticut, Estados Unidos da América; Mica creek, Queensland, Austrália; Lavra da Golconda, Governador Valadares, Minas Gerais, Brasil. Usos: fonte industrial primária de berílio[74].

50. Clinobarilita (*Clinobarylite*) $BaBe_2Si_2O_7$ – sistema monoclínico, massa molar = 327,37 g.mol^{-1}, com 5,42% Be. Aspecto dos cristais: incolores; agregados radias, platiformes a prismáticos. Ocorrências: pegmatitos alcalinos[75].

51. Gugiaíta (*Gugiaite*) $Ca_2BeSi_2O_7$ – sistema tetragonal, massa molar = 257,33 g.mol^{-1}, com 3,50% Be. Aspecto dos cristais: incolores; prismáticos. Ocorrências: escarnitos e melanitos[76].

52. Harstigita (*Harstigite*) $Ca_6Be_4Mn^{2+}(Si_2O_4)_2(Si_2O_7)_2(OH)_2$ - sistema ortorrômbico, massa molar = 885,97 g.mol^{-1}, com 4,07% Be. Aspecto dos cristais:

incolores, brancos; prismáticos. Ocorrências: veios hidrotermais de depósitos manganesíferos[77].

53.Jeffreyíta (*Jeffreyite*) $(Ca,Na)_2(Be,Al)Si_2(O,OH)_7$ - sistema ortorrômbico, massa molar = 255,30 g.mol^{-1}, com 2,65% Be. Aspecto dos cristais: incolores; platiformes. Ocorrências: granitóides[78].

54. Samfowlerita (*Samfowlerite*) $Ca_{14}(Mn^{3+})_3Zn_3Be_2Be_6Si_{14}O_{52}$ $(OH)_6$ - sistema monoclínico, massa molar = 2.271,52 g.mol^{-1}, com 2,02% Be. Aspecto dos cristais: incolores, brancos; Ocorrências: mineral de metamorfismo em depósitos zincíferos[79].

d_3) Ciclossilicatos – nessas estruturas os tetraedros de $[SiO]^{4-}$ encontram-se conectados. Apresentam configurações fechadas (cíclicas) do tipo Si_2O_9, Si_2O_{12} e Si_4O_{18}. Nesta Subclasse a relação Si:O é de 1:3.

55. Almarudita (*Almarudite*) $K(\square,Na)_2(Mn,Fe,Mg)_2[(Be,Al)_3Si_{12}]O_{30}$ - sistema hexagonal, massa molar = 1.000,32 g.mol^{-1}, com 1,86% Be. Aspecto dos cristais: amarelos, laranjas; dipiramidados. Ocorrências: xenólitos em nefelina tefritos[80].

56. Asbecasita (*Asbecasite*) $Ca_3(Be,B,Al)_2((Ti,Sn,Fe)(As,Sb)_6Si_2O_{20}$ - sistema trigonal, massa molar = 1.057,85 g.mol^{-1}, com 1,70% Be. Aspecto dos cristais: castanhos; romboédricos. Ocorrências: ortognaisses[81].

57. Bazzita (*Bazzite*) $Be_3(Sc,Fe^{3+},Mg)_2Si_{618}$ $.Na_{0,32}.nH_2O$ - sistema hexagonal, massa molar = 564,46 g.mol^{-1}, com 4,79% Be. Aspecto dos cristais: azuis, azul escuros; prismáticos. Ocorrências: pegmatitos[82].

58. Berilo (*Beryl*) $Be_3Al_2Si_6O_{18}$ – sistema hexagonal, massa molar = 537,50 g.mol^{-1}, com 5,03% Be. Aspecto dos cristais: verdes, azuis, amarelos, incolores e rosas; prismáticos, colunares, tabulares, granulares. Ocorrências: pegmatitos graníticos e nefelina sienitos. Associação mineralógica: ambligonita, cassiterita, columbita, espodumênio, feldspatos, muscovita, lepidolita, quartzo, tantalita, topázio e turmalina. Principais jazimentos: Nuristan, Laghman, Afeganistão; minas de Muzo, Chivor, Boyacá e Coscuez, Colômbia; depósitos do Monte Antero, Colorado, Estados Unidos da América; Distrito Pegmatítico de Governador Valadares, Minas Gerais, Depósito de Esmeralda de Santa Terezinha, Goiás, depósitos de Carnaíba e Socotó, Campo Formoso, Bahia, Brasil. Usos: fonte industrial primária de berílio e material gemológico (variedades esmeralda, goshenita, bisbita, morganita, heliodoro e água-marinha[22,33,83].

59. Friedrichbeckeíta (*Friedrichbeckeite*) $(K(\square Na)(Mg_2)(Be_2Mg)Si_{12}O_{30})$ - sistema hexagonal, massa molar = 982,67 g.mol^{-1}, com 1,68% Be. Aspecto dos cristais: amarelo claros; tabulares. Ocorrências: xenólitos em rochas efusivas[30].

60. Hialotequita (*Hyalotekite*) $(Ba,Pb,K)_4(Ca,Y)_2Si_8(B,Be)_2(Si,B)_2O_{28}F_2$ - sistema triclínico, massa molar = 1.474,06 g.mol^{-1}, com 0,27% Be. Aspecto dos cristais: brancos, cinza perláceos; maciços, granulares. Ocorrências: pegmatitos alcalinos[84].

61. Milarita (*Milarite*) $KCa_2(Be_2AlSi_{12})O_{30}.H_2O_2$ - sistema hexagonal, massa molar = 1.980,55 g.mol^{-1}, com 1,82% Be. Aspecto dos cristais: incolores, brancos,

branco-esverdeados, branco-amarelados; prismáticos. Ocorrências: pegmatitos graníticos, aplitos e sienitos[85].

62. Odintsovita (*Odintsovite*) $K_2Na_4Ca_3Ti_2Be_4Si_{12}O_{38}$ - sistema hexagonal, massa molar = 1.367,20 g.mol^{-1}, com 2,64% Be. Aspecto dos cristais: incolores, rosa claros, rosa-acastanhados; granulares. Ocorrências: pegmatitos sieníticos alcalinos e kalsilita sienitos[86].

63. Pezzottaíta (*Pezzottaite*) $CsLiBe_2Al_2Si_6O_{18}$ - sistema hexagonal, massa molar = 658,80 g.mol^{-1}, com 4,19% Be. Aspecto dos cristais: vermelhos, rosas; prismáticos. Ocorrências: pegmatitos graníticos[87].

64. Stoppaniíta (*Stoppaniite*) $(Fe^{3+})_2(Be_3Si_6O_{18}).H_2O$ - sistema hexagonal, massa molar = 1.190,23 g.mol^{-1}, com 4,54% Be. Aspecto dos cristais: azul claros; dipiramidados. Ocorrências: cavidades miarolíticas de ejetólitos vulcânicos[88].

d_4) Inossilicatos – nessas estruturas os tetraedros de $[SiO]^{4-}$ encontram-se conectados em cadeias, compartilhando oxigênios com os tetraedros adjacentes. Essas cadeias simples unem-se lateralmente formando cadeias duplas. Nas cadeias simples a relação Si:O é de 1:3 e nas cadeias duplas de 4:11.

65. Bavenita (*Bavenite*) $Ca_4Be_2Al_2Si_9O_{26}(OH)_2$ - sistema ortorrômbico, massa molar = 931,22 g.mol^{-1}, com 2,81% Be. Aspecto dos cristais: brancos, verdes, rosas, castanhos; maciços, lamelares, fibrorradiados. Ocorrências: drusas em pegmatitos[89].

66.Chkalovita (*Chkalovite*) $Na_2BeSi_2O_6$ - sistema ortorrômbico, massa molar = 207,16 g.mol^{-1}, com 4,35% Be. Aspecto dos cristais: incolores, brancos; granulares. Ocorrências: pegmatitos alcalinos[90].

67. Epididimita (*Epididymite*) $NaBe_2Si_3O_7(OH)$ - sistema ortorrômbico, massa molar = 245,26 g.mol^{-1}, com 3,67% Be. Aspecto dos cristais: incolores, brancos, cinzas, amarelos, azuis; tabulares, maciços, granulares, esferulíticos. Ocorrências: pegmatitos nefelina sieníticos[91].

68. Eudidimita (*Eudidymite*) $Na_2Be_3Si_6O_{15}.H_2O$ - sistema monoclínico, massa molar = 245,26 g.mol^{-1}, com 3,67% Be. Aspecto dos cristais: azuis, cinzas, amarelos, violetas; tabulares, maciços, granulares, esferulíticos. Ocorrências: pegmatitos nefelina sieníticos[92].

69. Hogtuvaíta (*Hogtuvaite*) $Ca_4[(Fe^{2+})_6](Fe^{3+})_6]O_4[Si_8Be_2Al_2O_{36}]$ - sistema monoclínico, massa molar = 837,17 g.mol^{-1}, com 1,94% Be. Aspecto dos cristais: pretos; prismáticos. Ocorrências: gnaisses graníticos e pegmatitos máficos: pegmatitos nefelina sieníticos[92].

70. Khmaralita (*Khmaralite*) $Mg_4(Mg_3Al_9)O_4[Si_5Be_2Al_5O_{36}]$ - sistema monoclínico, massa molar = 1.401,96 g.mol^{-1}, com 1,03% Be. Aspecto dos cristais: verde-escuros; agregados drusiformes. Ocorrências: pegmatitos nefelina sieníticos[93].

71. Leucofanita (*Leucophanite*) $NaCaBeSi_2O_6F$ - sistema ortorrômbico, massa molar = 235,92 g.mol^{-1}, com 3,82% Be. Aspecto dos cristais: brancos, amarelo-

esverdeados, amarelos, verdes claros; prismáticos, tabulares. Ocorrências: pegmatitos alcalinos[68].

72. Makarochkinita (*Makarochkinite*) $Ca_4[(Fe^{2+})_8(Fe^{3+})_2Ti_2]O_4[Si_8Be_2Al_2O_{36}]$ - sistema trigonal, massa molar = 235,92 g.mol^{-1}, com 0,94% Be. Aspecto dos cristais: pretos; granulares. Ocorrências: pegmatitos graníticos[94].

73. Mottanaíta-(Ce) (*Mottanaite-(Ce)*) $(CeCa)_2AlBe_2(Si_4B_4O_{22})O_2$ - sistema monoclínico, massa molar = 1.007,13 g.mol^{-1}, com 0,72% Be. Aspecto dos cristais: castanho pálidos; granulares. Ocorrências: cavidades miarolíticas em sienitos alcalinos[95].

74. Piergorita-(Ce) – (*Piergorite-(Ce)*) $Ca_8Ce_2AlLiSi_6B_8O_{36}(OH)_2$ - sistema monoclínico, massa molar = 1.498,89 g.mol^{-1}, com 0,22% Be. Aspecto dos cristais: incolores, amarelo pálidos; aciculares. Ocorrências: cavidades miarolíticas em ejetólitos vulcânicos[96].

75. Sorensenita (*Sorensenite*) $Na_4Be_2Sn(Si_3B_9)_2.2H_2O$ - sistema monoclínico, massa molar = 721,23 g.mol^{-1}, com 2,50% Be. Aspecto dos cristais: incolores, branco leitosos, rosados; prismáticos, aciculares. Ocorrências: nefelina sienitos[44].

76. Tvedalita (*Tvedalite*) $Ca_4Be_3Si_6O_{17}(OH)_4.3H_2O$ - sistema ortorrômbico, massa molar = 764,79 g.mol^{-1}, com 3,54% Be. Aspecto dos cristais: brancos, cinza pálidos, beges; aciculares, esferulíticos. Ocorrências: pegmatitos nefelina sieníticos[97]

d_5) Filossilicatos – nessas estruturas os três dos quatro oxigênios existentes em cada um dos tetraedros de $[SiO]^{4-}$, são compartilhados com os tetraedros vizinhos, numa relação Si:O de 2:5. Quase que todos os minerais desta Classe contêm OH em suas estruturas.

77. Bityíta (*Bityite*) $CaLiAl_2(Si_2BeAl)O_{10}(OH)_2$ - sistema monoclínico, massa molar = 387,16 g.mol^{-1}, com 2,33% Be. Aspecto dos cristais: branco-acastanhados, incolores, amarelos, branco perláceos; platiformes, incrustrações. Ocorrências: pegmatitos litiníferos[98].

78. Bussyíta-(Ce) (*Bussyite-(Ce)*) $(Ce,ETR,Ca)_3(Na,H_2O)_6MnSi_9Be_5(O,OH)_{30}F_4$ - sistema monoclínico, massa molar = 1.329,21 g.mol^{-1}, com 3,12% Be. Aspecto dos cristais: laranja rosado pálidos; aciculares. Ocorrências: pegmatitos nefelina sieníticos[99].

79. Eurikita (*Eirikite*) $KNa_6Be_2(Si_{15}Al_3).O_{39}F_2$- sistema hexagonal, massa molar = 1.359,26 g.mol^{-1}, com 1,33% Be. Aspecto dos cristais: brancos, cinza pálidos, beges; agregados radiais. Ocorrências: pegmatitos nefelina sieníticos[39].

80. Leifita (*Leifite*) $Na_7Be_2(Si_{15}Al_3)O_{39}(F,OH)_2$ - sistema trigonal, massa molar = 425,47 g.mol^{-1}, com 1,48% Be. Aspecto dos cristais: brancos, incolores, brancos; prismáticos, aciculares. Ocorrências: cavidades miarolíticas em pegmatitos alcalinos[100].

81. Nabesita (*Nabesite*) $NaBeSi_4O_{10}.4H_2O$ - sistema ortorrômbico, massa molar = 391,94 g.mol^{-1}, com 2,30% Be. Aspecto dos cristais: incolores, brancos; platiformes. Ocorrências: cavidade miarolíticas em albititos[101].

82. Telyushenkoíta (*Telyushenkoite*) $CsNa_6Be_2Al_3Si_{15}O_{39}F_2$ - sistema trigonal, massa molar = 1.433,11 $g.mol^{-1}$, com 1,28% Be. Aspecto dos cristais: incolores, brancos: granulares. Ocorrências: morenas glaciais[102].

d_6) Tectossilicatos – nessas estruturas todos os oxigênios existentes em cada tetraedro de $[SiO]^{4-}$, são compartilhados com os tetraedros vizinhos, numa relação Si:O de 1:2.

83. Alflarsenita (*Alflarsenite*) $NaCa_2Be_3Si_4O_{13}(OH).2H_2O$ - sistema monoclínico, massa molar = 503,55 $g.mol^{-1}$, com 5,37% Be. Aspecto dos cristais: incolores; agregados. Ocorrências: pegmatitos sieníticos[31].

84. Chiavennita (*Chiavennite*) $CaMn[Be_2Si_5O_{13}(OH)_2].2H_2O$ - sistema ortorrômbico, massa molar = 531,51 $g.mol^{-1}$, com 3,39% Be. Aspecto dos cristais: amarelos, laranjas, laranja-avermelhados; piramidados, agregados esferulíticos. Ocorrências: pegmatitos sieníticos[31].

85. Danalita (*Danalite*) $Be_3(Fe^{2+})_4(SiO_4)_3S$ - sistema cúbico, massa molar = 558,74 $g.mol^{-1}$, com 4,84% Be. Aspecto dos cristais: castanhos, preto-acastanhados, amarelo-acinzentados, rosas, castanho rosados; maciços. Ocorrências: granitos, pegmatitos graníticos, escarnitos, gnaisses e cornubianitos[103].

86. Genthelvita (*Genthelvite*) $Be_3Zn_4(SiO_4)_3S$ - sistema cúbico, massa molar = 596,91 $g.mol^{-1}$, com 4,53% Be. Aspecto dos cristais: verde-azulados, castanhos, incolores, verdes, amarelos, brancos; maciços; tetraedros e tritetraedros. Ocorrências: granitos alcalinos, cavidades miarolíticas de pegmatitos graníticos e sieníticos, escarnitos e greisens[104].

87. Helvina (*Helvine*) $Be_3(Mn^{2+})_4)SiO_4)_3S$ - sistema cúbico, massa molar = 555,10 $g.mol^{-1}$, com 4,87% Be. Aspecto dos cristais: castanhos, amarelo-acastanhados, cinzas, verde-amarelados; maciços, piramidados. Ocorrências: pegmatitos e escarnitos[105].

88. Hsianghualita (*Hsianghualite*) $Li_2Ca_3Be_3(SiO_4]_3F_2$ - sistema ortorrômbico, massa molar = 475,40 $g.mol^{-1}$, com 5,69% Be. Aspecto dos cristais: brancos, incolores; trioctaédricos, dodecaédricos. Ocorrências: granitos e ardósias[106].

89. Lovdarita (*Lovdarite*) $K_2\ Na_6Be_4Si_{14}O_{36}.9H_2O$ - sistema ortorrômbico, massa molar = 1.466,77 $g.mol^{-1}$, com 2,39% Be. Aspecto dos cristais: incolores, amarelos, branco-amarelados, brancos; prismáticos, radiados, esteliformes. Ocorrências: pegmatitos alcalinos[107].

90. Roggianita (*Roggianite*) $Ca_2BeAl_2Si_4O_{13}(OH)_2.nH_2O$ - sistema tetragonal, massa molar = 540,72 $g.mol^{-1}$, com 1,67% Be. Aspecto dos cristais: amarelos, branco-amarelados, brancos; prismáticos, fibrosos, fibrorradiados. Ocorrências: albititos[108].

91. Tugtupita (*Tugtupite*) $Na_4BeAlSi_4O_{12}Cl$ - sistema tetragonal, massa molar = 467,74 $g.mol^{-1}$, com 1,93% Be. Aspecto dos cristais: brancos, rosas, vermelho carmesins, verdes, azuis; prismáticos, piramidados, esfenoédricos, biesfenoédricos, maciços. Ocorrências: sienitos e sodalita sienitos. Associação mineralógica: albita, analcima, egirina, natrolita, chkalovite, epistolite, niobofilita, monazita,

rabdofânio, gerasimovskita, berilita, nenadkeviquite e micas litiníferas. Principais jazimentos: Tugtup, intrusão Ilímaussaq, Groenlândia, Território Ultramarino da Dinamarca; Monte Sengischorr, Lovozero, Península de Kola, Rússia; Mount Saint-Hilaire, Quebec, Canadá. Usos: material gemológico[33,109].

4. OCORRÊNCIAS E USOS DE BERÍLIO

Os minerais de berílio são encontrados majoritariamente em rochas alcalinas insaturadas em sílica e em produtos residuais de magmas graníticos, principalmente em cavidades miarolíticas de corpos pegmatíticos.

Seus principais minerais-fonte são berilo e bertrandita e, secundariamente, helvita, danalita, crisoberilo, berilonita e fenaquita. Como materiais gemológicos, devido às cores e perfeições de seus cristais, destacam-se a fenaquita – incolor, rosa, amarelo, azul, castanho; tugtupita – branco, rosa, vermelho carmesim, verde, azul; berilo (variedades: goshenita – laranja, roxo, castanho, cinza, preto e incolor; bisbita – vermelho; morganita – rosa; heliodoro – amarelo; esmeralda – verde; água-marinha - azul), berilonita – incolor, amarelo claro; crisoberilo (variedades: alexandrita – verde, violeta; olho-de-gato – verde, amarelo, cinza, com *chatoyance*), euclásio – incolor, amarelo, verde, azul; rodizita – incolor, branco, cinza, verde, vermelho, amarelo; taaffeíta - incolor, vermelho, rosa, azul, violeta, roxo[33, 110].

No Brasil, as principais ocorrências de minerais contendo berílio encontram-se nos estados de Minas Gerais (Almenara, Aracuaí, Belmonte, Capelinha, Caraí, Itabira, Conselheiro Pena, Coronel Murta, Galiléia, Golconda, Governador Valadares, Hematita, Itinga, Jequitinhonha, Marambaia, Medina, Minas Novas, Salinas, Mucuri, Nova Era, Padre Paraíso, Pavão, Pomarolli, Rio Doce, Rubelita, Sabinópolis, Santa Maria do Itabira, Santa Maria do Saçuí, Santana dos Ferros, Santa Rita do Passaquatro, São Miguel de Piracicaba, Serro, Teófilo Otoni, Três Barras, Urucum e Virgem da Lapa), Bahia (Brumado, Campo Formoso, Carnaíba, Encruzilhadas, Itambé, Macarani, Marota, Medeiros Neto, Prado, Salininha (Pilão do Arcado), Socotó, Teixeira de Freitas e Vitória da Conquista), Paraíba (Alagoa Grande, Cristal, Juazeirinho, Picuí e Soledade), Rio Grande do Norte (Carnaúba dos Dantas, Cerro Corá, Currais Novos, Equador, Jardim do Seridó, Parelhas, Santo Antônio, São Tomé e Tenente Ananias), Ceará (Cachoeira, Quixeramobim, Solonópole e Tauá), Goiás (Campos Verdes, Itaberaí, Pirenópolis e Santa Terezinha), São Paulo (Itapecerica da Serra e Patrocínio Paulista) e Amazonas (Presidente Figueiredo). No mundo, as principais ocorrências encontram-se nos Estados Unidos da América, Colômbia, Afeganistão, Namíbia, Moçambique, Paquistão, República da África do Sul, República Popular da China, Madagascar, Áustria, Noruega, União de Myanmar, Itália, República Tcheca, Rússia, Sri Lanka e Zimbábue[21,22,110].

5. CONCLUSÕES

Até o momento existem 96 espécies mineralógicas contendo berílio em suas composições químicas validadas pela *IMA*. A bromellita é a que apresenta a maior massa do elemento com 36,03%. Em sua grande maioria pertencem à Classe mineralógica dos silicatos (59 espécies), seguida dos fosfatos e arseniatos (22 espécies), óxidos e hidróxidos (8 espécies), boratos (3 espécies) e carbonatos (somente uma espécie), estando relacionados, em sua grande maioria, a zonas de granitóides e pegmatitos alcalinos.

O berílio é um importante elemento de aplicabilidade industrial (desacelerador neutrônico em reatores nucleares, janelas para tubos de raios X, aumenta a resistência em ligas metálicas, componente de giroscópios, liga para molas de relógios e ferramentas antifaiscantes). Seus principais minerais-fonte são berilo, bertrandita, helvita, danalita, crisoberilo, berilonita e fenaquita. Um grupo significativo serve como material gemológico (berilo, crisoberilo, berilonita, euclásio, tugtupita, fenaquita, rodizita e taaffeíta), além de belas peças para acervo de museus. Os demais servem apenas como material de interesse científico e museológico.

Entre os maiores portadores em massa do elemento temos a bromellita com 36,03%, behoíta e clinobehoíta com 20,95% e a esferobertrandita com 17,07%. Muito embora contenham mais Be do que os minerais-fonte não apresentam interesse devido à distribuição pontual de seus depósitos.

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