SCIENCO

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-5431

AN INTERNATIONAL FORUM FOR THE RAPID PUBLICATION
OF ORIGINAL SCIENTIFIC ARTICLES DEALING WITH CHEMISTRY AND
RELATED INTERDISCIPLINARY AREAS

VOLUME ONE, NUMBER ONE

DECEMBER 1993

EDITOR

LAVINEL G. IONESCU, SCIENCO Scientific Consulting Services. Huntington Beach, California, USA

EDITORIAL BOARD

FARUK NOME AGUILERA, Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, Brasil
D. BALASUBRAMANIAN, Centre for Cellular and Molecular Biology, Hyderabad, INDIA
HÉCTOR E. BERTORELLO, Departamento de Quimica Organica, Facultad de Ciencias Quimicas, Universidad Nacional de Cordoba, Cordoba, ARGENTINA
AÉCIO P. CHAGAS, Instituto de Química, UNICAMP, Campinas, SP, BRASIL
JUAN JOSÉ COSA, Departamento de Quimica y Fisica, Facultad de Ciencias Exactas, Universidad Nacional de Rio Cuarto, Rio Cuarto, ARGENTINA
GLENN A. CROSBY, Department of Chemistry, Washington State University, Pullman, WA, USA
VITTORIO DEGIORGIO, Dipartimento di Elettronica, Sezione di Fisica Applicata, Università di Pavia, Pavia, ITALIA
JOSÉ C. TEIXEIRA DIAS, Departamento de Química, Universidade de Coimbra, Coimbra, PORTUGAL
OMAR A. EL SEOUD, Instituto de Química, Universidade de São Paulo, São Paulo, SP, BRASIL
FERNANDO GALEMBECK, Instituto de Química, UNICAMP, Campinas, SP, BRASIL
NISSIM GARTI, Casali Institute of Applied Science, Hebrew University of Jerusalem, Jerusalem, ISRAEL
GASPAR GONZALEZ, Centro de Pesquisa, CENPES-PETROBRAS, Ilha do Fundão, Rio de Janeiro, RJ, BRASIL
YOSHITAKA GUSHIKEM, Instituto de Química, UNICAMP, Campinas, SP, BRASIL
WILLIAM HASE, Department of Chemistry, Wayne State University, Detroit, MI, USA
I. B. IVANOV, Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, Sofia, BULGARIA
IVAN IZQUIERDO, Departamento de Bioquímica, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, BRASIL
V.A. KAMINSKY, Karpov Institute of Physical Chemistry, Moscow, RUSSIA
MICHAEL LAING, Department of Chemistry, University of Natal, Durban, SOUTH AFRICA
EDUARDO LISSI, Departamento de Quimica, Universidad de Santiago de Chile, Santiago, CHILE
WALTER LWOWSKI, Department of Chemistry, New Mexico State University, Las Cruces, N.M., USA
CRISTINA MANDRAVEL, Catedra de Chimie Fizica, Facultatea de Chimie, Universitatea din Bucuresti, Bucuresti, Romania
C. MANOHAR, Bhabha Atomic Research Centre, Chemistry Division, Bombay, INDIA
AYRTON FIGUEIREDO MARTINS, Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS, BRASIL
FRED MENGER, Department of Chemistry, Emory University, Atlanta, GA, USA
KASHMIRI LAL MITTAL, Private Consultant, Hopewell Junction, N.Y., USA
ARNO MÜLLER, Escola de Engeharia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, BRASIL
JOSE MIGUEL PARERA, Instituto de Investigaciones en Catalisis y Petroquimica, Universidad Nacional del Litoral, Santa Fe, ARGENTINA
LARRY ROMSTED, Department of Chemistry, Rutgers University, Piscataway N.J., USA
GILBERTO FERNANDES DE SÁ, Departamento de Quimica Fundamental, Universidade Federal de Pernambuco, Recife, PE, BRASIL
DIMITRIOS SAMIOS, Instituto de Quimica, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, BRASIL
DIOGENES DOS SANTOS, Department of Molecular Biology, Oxford University, Oxford, ENGLAND
JOSEPH A. SCHUFLE, Department of Chemistry, New Mexico Highlands University, Las Vegas, N.M., USA
BEN K. SELINGER, Department of Chemistry, Australian National University, Canberra, AUSTRALIA
KOZO SHINODA, Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama, JAPAN
CRISTOFOR I. SIMIONESCU, Academia Româna, Filiala Iasi, Iasi, ROMANIA
BRUNO SZPOGANICZ, Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, Brasil
UMBERTO TONELLATO, Dipartimento di Chimica Organica, Università degli Studi di Padova, Padova, ITALIA
DIETER VOLLHARDT, Max Planck Institut für Kolloid und Grenzflächenforscung, Berlin, GERMANY
RAOUL ZANA, Institut Charles Sadron, CRM-EAHP, Strassbourg, FRANCE

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.

Manuscripts may be submitted on-line or in triplicate (original and two copies by registered mail) and are received with the understanding that the original has not been submitted for publication elsewhere. It is implicit that all the persons listed as authors have given their approval for the submission of the paper and that permission has also been granted by the employer, when necessary.

Manuscripts must be written in American or British English, single spaced, on A4 sheets (21 cm x 29.5 cm) and one side only and should be numbered beginning with the title page. Type must be 12 Arial or Times New Roman.

Margins of at least 3 cm should be left at the top and bottom and both sides of each page. The first page of the paper should contain only the title of the paper, the name(s) and addressees) of the author(s), an abstract of not more than 250 words and 4-8 keywords. We reserve the right to translate the abstract in Portuguese. Abstracts are required of all papers including reviews and short communications.

Figures and Tables with short explanatory titles, each on a separate sheet, should be adequate for direct reproduction and identified in pencil on the back of each page by Arabic numerals, corresponding to the order they appear in the manuscript. Tables and Figures (BMP or JPG format) may also be included directly in the text when convenient and the article may submitted in a quasi-final form in order to facilitate editorial work.

References should be numbered in the sequence they appear in the text, cited by superior numbers and listed at the end of the paper in the reference section in the numerical order they appear in the text. The style for references is shown below:

1. L. G. Ionescu and D. S. Fung, *J. Chem. Soc. Faraday Trans. I*, *77*, 2907-2912 (1981).
2. K. L. Mittal, Ed., "*Solution Chemistry of Surfactants*", Plenum Press, New York (1984), Vols. 1-3, pp. 1-2173.

IUPAC Rules should be used for the name of chemical compounds and preference should be given to 51 units.

Authors are invited to send manuscripts by registered air mail to the EDITOR - SBJC, C.P. 15032, Agronomia, Porto Alegre, RS BRASIL 91501, or by e-mail to **lavinel@ibest.com.br** or **lavinel@pop.com.br**.

VISIT OUR SITE: http://www.sbjchem.he.com.br

SCIENCO

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-5431

The *SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY - SCIENCO* publishes original research articles in chemistry and related interdisciplinary areas and is intended to fill a gap in terms of scientific information for Southern Brazil.

Occasionally the journal will include review papers and articles dealing with chemical education and philosophy and history of science. It will be published mainly in English, with abstracts in Portuguese and only occasional papers in other languages. At the present there are no page charges and the authors will receive twenty five reprints of their papers free of charge.

We have set high standards for the articles to be published by ensuring strong but fair refereeing by at least two reviewers. We hope that this journal will provide a forum for dissemination of high quality research in chemistry and related areas and are open to any questions and suggestions.

The Editor

SUBSCRIPTION INFORMATION

Brazil and Latin America:
US$ 35.00 per issue,

Other Countries: US$ 50.00 per issue, including air mail delivery. Persons or institutions outside Brazil should send subscription fee payable to Dr. L. G. Ionescu, c/o SBJC, 8532 Howard Circle, Huntington Beach, California, USA 92647

MAILING ADDRESS

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
Lavinel G. Ionescu, B.S., M.S., Ph.D., Editor
C.P. 15032, Agronomia
Porto Alegre, RE, BRASIL 91501-970
Tel. 055 51 3485-1620 / 051 55 3485-1711 / 055 51 995-26616
E-Mail lavinel@ibest.com.br lavinel@pop.com.br
VISIT OUR SITE: http://www.sbjchem.he.com.br

FINANCIAL SUPPORT

SARMISEGETUSA RESEARCH GROUP

SANTA FE, NEW MEXICO, U.S.A.

Endless Column, 1937, cast iron
CONSTANTIN BRANCUSI

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-5431

VOLUME ONE , NUMBER ONE DECEMBER 1993

CONTENTS / CONTEÚDO

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 puropse 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

DOI:10.48141/SBJCHEM.v1.n1.1993.6_1993.pdf
The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com.
This text was introduced in this file in 2021 for compliance reasons.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

Vol. 1, No. 1, 1993

ILIE G. MURGULESCU, A PROMINENT SCIENTIST AND EDUCATOR

Ilie G. Murgulescu was born on January 27, 1902 in Cornu, County of Dolj,(*Judetul Dolj*), Oltenia, Romania and passed away in Bucharest on October 28, 1991.

He completed elementary school in his native village and attended secondary school at the Carol Lyceum in Craiova. He later enrolled in the Faculty of Science of the University of Cluj, where he had distinguished teachers such as Gheorghe Spacu, Adrián Ostrogovich and Dan Radulescu.He obtained the Ph.D. Degree in Chemistry form the same University in 1930. His doctoral dissertation entitled "*Copper Thiosulfate Complexes*" was approved "Magna Cum Laude".

During 1932 and 1933 he was a collaborator of F. Weigert at the Physical Chemistry Institute of the University of Leipzig, working in photochemistry and chemical kinetics.

Ilie G. Murgulescu held faculty positions first at his *Alma Mater*, the University of Cluj (1928-1932), then the Polytechnic Institute of Timisoara (1934-1949) and subsequently at the University of Bucharest (1949-1972).

In 1948 he was elected Member of the Romamian Academy. Prof. Acad. I. G. Murgulescu held many important administrative positions including Rector of the Polytechnic Institute of Timisoara (1947-1949), Rector of the University of Bucharest (1949-1950), Deputy Minister and Minister of Education (1950-1956), again Minister of Education (1960-1963), Vice-President (1959-1963) and President of the Romanian Academy (1963-1966).

Prof. Academician Ilie G. Murgulescu was elected to many public offices, including Member of the Romanian Parliament, Grand National Assemby, (1948-1965), Vice-President of the Council of State (1965-1967) and Vice-President of the Grand National Assembly (1967-1975).

In 1963 he founded the *Centre of Physical Chemistry* in Bucharest and served as its Director until 1977. During this period, the Centre provided a stimulating environment for research in physical chemistry to many young scientists and graduate students from Romania and abroad.He organized a series of international conferences on physical chemistry and established exchange programs with scientists from all over the world.

Professor's Murgulescu research work covers a variety of fields including photochemistry, chemical kinetics, thermodynamics, electrochemistry, spectroscopy, inorganic and analytical chemistry and molten salts chemistry. Approximately forty young scientists obtained their Ph.D. Degree having Professor I.G. Murgulescu as thesis advisor.

He published over 250 scientific articles.We would like to highlight his contributions in photochemistry dealing with the mechanism and quantum efficiency of the decomposition of potassium cobaltic oxalate and diphenyldiazomethane , anodic passivation of metals and alloys, electrochemical behavior of

DOI: 10.48141/SBJCHEM.v1.n1.1993.7_1993.pdf

thin films, electrode kinetics, new analytical methods for mercury, physical chemical properties of molten salts and adsorption of gases on solid surfaces.

Besides being an outstanding researcher, Professor I. G. Murgulescu was a great teacher. During his tenure as Minister of Education and Member of Parliament,in spite of a plethora of responsibilities, he continued to teach physical chemistry at the University of Bucharest. On many occasions, late at night he used to prepare his lectures for the following day. Routinely,he used to update and improve the physical chemistry laboratory experiments.

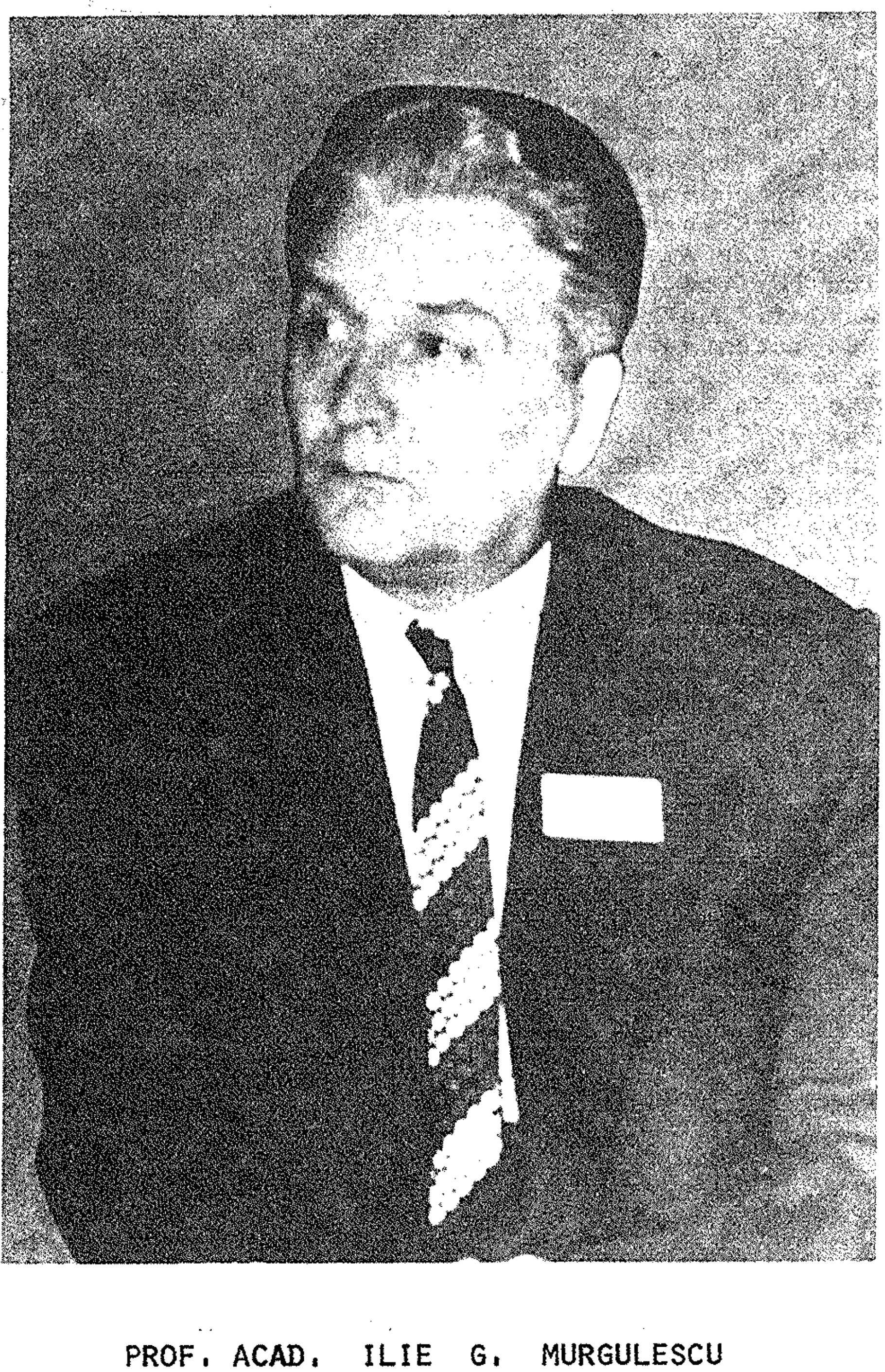
His monumental treatise "*Introduction to Physical Chemistry*", that he began publishing in 1976 (Editura Academiei Republicii Socialiste România, Bucuresti, 1976) represents the lectures given by him to students of chemistry and chemical engineering for almost a quarter of a century. This great and monumental work spans thousands of pages and consists of four volumes divided into seven parts:*I,1 Atoms, Molecules, Chemical Bond; I,2 Structure and Properries of Molecules; I,3 Atomic Nucleus. Nuclear Reactions. Elementary Particles; II,1 Molecular Theory of the States of Matter: Gas, Solid, Liquid and Solutions; II,2 Chemical Kinetics. Catalysis; III, Chemical Thermodynamics; IV, Electrochemistry.* It is undoubtedly one of the most comprehensive textbooks ever written on physical chemistry.

Professor I. G. Murgulescu firmly believed that the true scientist has a social responsibility and that a teacher can teach the most by his example. He knew that the main purpose of the true scientist was the search for truth and its application to the improvement of the conditions of man. He was convinced that education was the cornerstone in the building and forging of any just society.

During his tenure as Minister of Education, Prof. Ilie G. Murgulescu was always preoccupied with instruction at all levels. He introduced an experimental program involving teaching by subjects in 500 elementary schools. Elementary, secondary, professional, trade schools, university instruction and research institutes were all part of a total effort. He visited hundreds of educational estabilshments and often solved problems and took decisions on the spot. In this he followed the footsteps of other great Romanian educators, like Vasile Conta and Spiru Haret. Conta, the philosopher, known for his Theory of Universal Ondulation and Theory of Fatalism, during his short term as Minister of Public Instruction, almost a century earlier, had introduced trade and technical schools.

In spite of the many important positions that he held during his life, Prof. I. G. Murgulescu was a modest person and never lost contact with his roots . As Minister and Member of Parliament, he continued to visit his native village, where he had spent his childhood and during the summer months had helped his parents in the fields or at the mill.

Vol. 1, No. 1, 1993



PROF. ACAD. ILIE G. MURGULESCU

He became a legendary figure among the peasants of the village of Cornu and they used to say "Mr. Professor, the one with the black lamb hat, is one of ours, from Cornu!"*("Domnu Profesor, ăla cu căciula neagră de miel, e de-al nostru, de la Cornu!")*

Prof. Acad. Ilie G. Murgulescu was widely esteemed and respected in Romania and abroad. He was a member of many erudite societies and academies, including the Academy of Sciences of the USSR, the Czechoslovak Academy of Sciences, Hungarian Academy of Sciences, Bulgarian Academy of Sciences, the New York Academy of Sciences and others. He was also a member of the American Chemical Society, the American Association for the Advancement of Science and the International Society of Electrochemistry.

He received many prizes, medals awards and distinctions. Among them we cite the Romanian State Prize (1963), Gold Medal of the 39th International Congress of Industrial Chemistry (1970) and Hero of Socialist Labor (1971).

He was a Member of the Editorial Board of *Electrochimica Acta* and *Corrosion Science* and Editor in Chief of *Revue Roumaine de Chimie* and *Studii si Cercetări de Chimie - Academia Republicii Socialiste România.*

Prof. Acad. Ilie G. Murgulescu was also a Member of the Editorial Board of the *Southern Brazilian Journal of Chemistry* and he gave us invaluable advice and encouragement during the initial stages of this Journal.

Lavinel G. Ionescu

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

Vol. 1, No. 1, 1993

CARBON-13 NMR OF SOME S-METHYLTHIOLESTERS

Paulo Irajara Borba Carneiro*
Instituto de Química
Universidade Federal do Paraná - UFPR
Caixa Postal 19081
81.521-970 Curitiba, Paraná, BRASIL
&
Roberto Rittner and Rogério Custódio
Instituto de Química
Universidade Estadual de Campinas - UNICAMP
Caixa Postal 6154
13.081-970 Campinas, São Paulo, BRASIL

ABSTRACT

H-1 and C-13 NMR chemical shifts for some alkyl-S-methylthiolesters (RCOSMe) are reported. The α-methylene and carbonyl carbons show lower field shifts when compared to analogous carboxylic acid derivatives. This behavior was explained by using charge densities and separation energies calculated by the AM1 MO-SCF semiempirical method.

KEYWORDS: C-13 NMR, Chemical Shifts, Alkyl-S-methylthiolesters.

RESUMO

O presente trabalho apresenta deslocamentos químicos de RMN de H-1 e C-13 para alguns ésteres de alquil-S-metiltiol (RCOSMe). Os carbonos do grupo α-metileno e carbonila exibem um deslocamento para campo mais baixo, quando comparados com derivados análogos de ácidos carboxílicos. Este comportamento foi explicado usando densidades de carga e energias de separação calculadas através do método semi-empírico AM1 MO-SCF.

INTRODUCTION

Although thiolesters (RCOSMe) are important starting materials for condensation and transference reactions of the acyl group in biological systems[1], there is a lack of NMR data in the literature for this type of compounds, particularly when R is a nonbranched alkyl group. The electronic structure of these compounds is well known.

C-13 NMR chemical shifts for the α-methylene and carbonyl carbons have been reported to show a lower field chemical shift in relation to analogous carboxylic acid derivatives.

This work describes the study of a closely related series of four alkyl-S-methylthiolesters that has also been investigated using the semiempirical AM1 MO-SCF calculations in order to check the generality of the observed behavior.

---

* *Author to whom correspondence should be addressed.*

DOI: 10.48141/SBJCHEM.v1.n1.1993.11_1993.pdf

EXPERIMENTAL PROCEDURE

Materials.

Solvente were of spectroscopic quality and were used without further purification. All compounds were prepared according to procedures described in the literature[9,10].

Spectra.

The C-13 NMR spectra of 1,0 M solutions in $CHCl_3$, with 5% TMS as an internal reference in 10 mm o.d. sample tubes , were recorded at 25,2 MHz using a Varian XL-100 spectrometer in the FT mode. The conditions were as follows: pulse width, 20 µs; acquisition time , 0,67 s; spectral width, 6150 Hz; pulse repetition time , 0,4 s; temperature, 30º C; internal lock, D_2O; angle tumbling, 45º; number of transients, 6000; and number of data points, 8192. The C-13 NMR spectra were recorded in both the proton-noise decoupled and coupled modes. The H-1 NMR spectra of the various solutions investigated , in 5 mm o.d. sample tubes, were recorded at 80 MHz using a Bruker Aw-80 spectrometer in the FT mode.

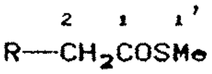
Computations.

Net charge densities and energy separations were obtained through the AM1 SCF-MO semiempirical method on an IBM computer with the AMPAC program.

RESULTS AND DISCUSSION

Table I summarizes the experimental C-13 chemical shifts obtained for the four alkyl-S-methylthiolesters studied.

TABLE I. C-13 NMR CHEMICAL SHIFTS[a] FOR ALKYL-S-METHYLTHIOLESTERS[b].



$R\text{---}\overset{2}{C}H_2\overset{1}{C}OS\overset{1'}{Me}$

Compounds		C-1	C-2	C-3	C-4	C-5	C-6	C-1'
1	CH_3CH_2COSMe	198.1	36.6	9.1				10.7
2	$CH_3CH_2CH_2COSMe$	196.5	44.6	18.3	12.4			10.0
3	$CH_3CH_2CH_2CH_2COSMe$	197.6	42.8	27.1	21.5	13.0		10.5
4	$CH_3CH_2CH_2CH_2CH_2COSMe$	198.1	43.3	24.9	30.7	21.9	13.3	10.8

a: in ppm relative to TMS. b: Ref. 6 in $HCCl_3$ solutions.

Table II presents the boiling points and experimental H-1 NMR data obtained. The physical constants of compounds 1-4 agree with data published in the literature[1-4].

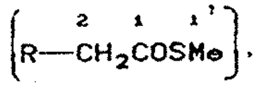
TABLE II. PHYSICAL AND SPECTRAL DATA FOR ALKYL-S-METHYLTHIOLESTERS[a].

Compound	bp (°C/Torr)	H-2[b]	H-3	H-4	H-5	H-6	H-1'
1	60/110	2.60^{q}	1.20^{t}				2.30^{s}
2	55/40	2.50^{t}	1.70^{st}	0.95^{t}			2.25^{s}
3	70/30	2.55^{t}	$1.10\text{-}1.90^{m}$		0.90^{t}		2.25^{s}
4	70/20	2.50^{t}	1.65^{m}	$1.10\text{-}1.45^{m}$		0.90^{t}	2.25^{s}

a: ppm relative to TMS, in deuterated chloroform solutions. b: s = singlet; t = triplet; q = quartet; st = sextet and m = multiplet

The signals of these compounds were assigned by single-frequency off-resonance decoupling (SFORD), proton noise decoupled (DFL) spectra and known chemical shift rules[5].

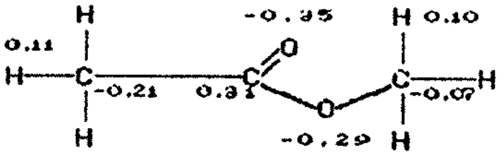
The chemical shifts of the carbonyl carbon were found in the 197,30± 0,80 ppm band, next to analogous aldehydes and ketones. This values is about 15-20 ppm higher, when compared to analogous carboxylic acid derivatives.

In the alkyl-S-methylthiolesters  $\left(R—\overset{2}{C}H_2\overset{1}{C}OS\overset{1'}{Me}\right)$, C-1 and C-2 show paramagnetic chemical shifts. On the other hand, the C-1' carbon showed diamagnetic chemical shifts, when compared to analogous carboxylic acid derivatives.

Comparison between the thiolesters and analogous carboxylic acid derivatives showed that the C—O bond length is shorter than the C—S bond. This is the case because the oxygen atom is more electronegative than the sulfur atom. The magnitude of the pπ-pπ or pπ-dπ conjugation is inversely proportional to the core length and is more pronounced in the C—O bond. This reduces the carbonyl withdrawing effect in the alpha carbon. In the oxygenated esters the carbonyl carbon is more shielded than in the thiolesters analogues.

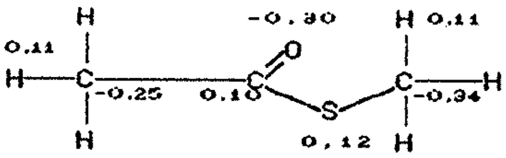
The inductive effect of the oxygen atom deshields the methyl carbon (C-1') and its resonance appears in a lower field. The chemical shift differences between these compounds is thus caused by the differences in size between the two heteroatoms and the differences in their electronegativities, polarizabilities and energy of the atomic lone pair orbitals[7].

Making use of the AM1 MO-SCF semiempirical calculations, we computed the charge densities of the carbon atoms in compounds 5 and 6 and also determined the energy separation (ΔE).



5

ΔE = 12,51 ev



6

ΔE = 10,37 ev

According to Equation (I) the paramagnetic constant, derived by Karplus and Pople[8], shows that the higher ΔE and Q_i, the higher the shielding observed in the carbon atom. Our experimental results and the values computed for ΔE and Q_i are in agreement with these observations.

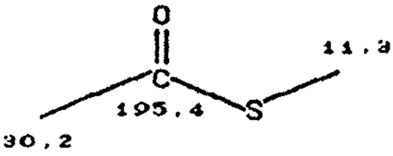
$$\sigma_p = -\frac{e^2 h^2}{m^2 c^2} \Delta E^{-1} \langle r^{-3} \rangle_{2p} \left[Q_i + \Sigma Q_{ij} \right] \qquad \text{(I)}$$

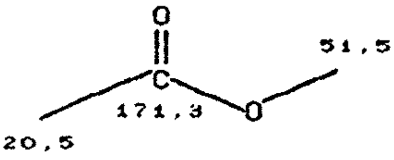
The charge densities show that in the methyl ester (C-1) the carbonyl carbon is more shielded (Q_{C-1} = 0,31) than in the thiolester analogue (Q_{C-1} = 0,10).

Our calculations show that that the energy separation and charge of the C-1 of the thiolester are smaller. This corresponds to higher polarizability and chemical shifts of the alpha and carbonyl carbons of these sompounds.

These observations can explain the principal properties of the thiolesters: C-1 and C-2 have resonance in a lower field when compared to analogous oxygenated esters (C-1$\Delta\delta \approx$15-20 ppm, C-2 $\Delta\delta \approx$10 ppm). They also expalin the higher reactivity of thiolacetates to alkaline hydrolysis when compared to analogous acetates[2]. The lower electronegativity of the sulfur atom results in a lower inductive effect in C-1'. In fact, C-1' is more shielded in these compounds in the C-13 NMR spectra. C-1' appears in an even higher field ($\Delta\delta \approx$ 40 ppm) when compared to alkyl esters analogues.

These observations are confirmed by the chemical shifts of S-methylethanethioate and methyl acetate shown on the following page.





Acknowledgements. The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support of this research and for a grant to R.R and R.C., and Coordenação e Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for a grant to P.I.B.C.

REFERENCES

1. C. M. Hall and J. Wemple, *J. Org. Chem.*, *42*, 2118-2123 (1977).
2. J. P. Idoux, P. T. R. Hwang and C. K. Hancock, *J. Org. Chem.*, *38*, 4239-4243 (1973).
3. J. Obermeyer, *Ber.*, *20*, 2918-2928 (1887).
4. V. A. Vinkurov and E. G. Gaevoi, *J. Org. Chem. USSR*, *23*, 1990-1991 (1987).
5. E. Breitmeier and W. Voelter, *"Carbon-13 NMR Spectroscopy"*, 3rd edition, Weinheim, New York, USA, 1987.
6. P. I. B. Carneiro, *"Tese de Doutoramento"*, UNICAMP, Campinas, São Paulo, 1991.
7. F. Bernardi, I. G. Csizmadia, H. B. Schlegel and S. Wolfe, *Can. J. Chem.*, *53*, 1144-1153 (1975).
8. M. Karplus and J. A. Pople, *J. Chem. Phys.*, *38*, 2803 (1963).
9. D. J. Dagli, P. S. Yu and J. Wemple, *J. Org. Chem.*, *40*, 3173-3178 (1975).
10. P. N. Rylander and S. Tarbell, *J. Amer. Chem. Soc.*, *72*, 3021-3025 (1950).

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

FLAVONOIDS IN CULTIVARS OF SOYBEAN: ANTIOXIDANT ACTION

Tanus Jorge Nagem*, Tânia Toledo de Oliveira e Albuquerque,
Luiz Carlos Guedes de Miranda
Departamento de Química
Universidade Federal de Viçosa
Avenida P. H. Rolphs, s/n
Viçosa, Minas Gerais, BRASIL 36570-000
&
Marilda Conceição da Silva
Departamento de Química
Universidade Federal de Minas Gerais
Pampulha, Cidade Universitária
Belo Horizonte, Minas Gerais, BRASIL 30161

ABSTRACT

The purpose of this investigation was the identification, quantification and determination of antioxidant activity of flavonoids of soybean. Examination of nine cultivars was carried out. All of them had the same stage of maturity and were grown on the same soil. The results showed the presence of genistein, genistin, daidzein, daidzin, naringenin, kaempherol, formonometin and biochanin A in all cultivars. In terms of antioxidant activity, the best results were obtained with genistein and genistin.

KEYWORDS: Flavonoids, soybean, antioxidant action.

RESUMO

O propósito do presente estudo foi a identificação, quantificação e determinação da ação antioxidante de compostos flavonóidicos em sementes de soja. Foram examinados nove cultivares, todos no mesmo estágio de desenvolvimento e cultivados no mesmo solo. Os resultados experimentais mostraram a presença de genisteína, genistina, daidzeiona, daidzina, naringenina, kaempherol, formonometina e biochanina A em todos os cultivares. Os melhores resultados de ação antioxidante foram obtidos com genisteína e genistina.

INTRODUCTION

Flavonoid compounds have been studied for many years, particularly because of their use in a variety of areas including food industry[1-3], mycology and plant physiology[4], phytopathology[4-6], microbiology[7], biochemical ecology[7-10], entomology[8] and chemistry[11].

We decided to identify and study this type of compounds and consider some of their applications, because of their world wide economic importance. The use of flavonoid compounds

---

* *Author to whom correspondence should be addressed.*

DOI: 10.48141/SBJCHEM.v1.n1.1993.16_1993.pdf

as antioxidant agents[1-3], antifungal[4-6], antibacterial agents[7], as well as insect repellents[8], sweeteners[9], estrogenics[10,11] and phytoalexins[4] has been described in the literature. The purpose of this work was to isolate, identify, quantify and above all test these secondary matabolites as antioxidizing agents.

MATERIALS AND METHODS

Flavonoid compounds were extracted from soybean seeds obtained from nine cultivars at the same stage of maturity and grown on the same soil. The procedure described by Naim[12] was used for genistein (I), genistin (II), daidzein(III) and daidzin (IV). The soybean seeds, ground (40 mesh),were extracted exhaustively with hexane and 60% ethanol. After evaporation of the solvent, the extract was treated with acetone (2 to 1) and filtered. After evaporation of the solvent, the soluble portion was adsorbed on silica gel 200 G, followed by exhaustive extraction with acetone for three days. The residue obtained after evaporation of the solvent was crystallized from 80% ethanol and washed with chloroform.

The compounds naringenin (V), kaempherol (VI), formonometin (VII) and biochanin A (VIII) were extracted according to the method described by Murphy[13]. The sample was heated in acetic acid for 10 minutes using a water bath. The filtered product, after 1 hour hydrolysis with 1,00 N HCl was extracted with anhydrous diethyl ether and the solvent was evaporated.

The flavonoid compounds genistein, genistin, daidzein, daidzin, kaempherol, formonometin, biochanin A were isolated by thin layer chromatography and identified by ultraviolet and infrared spectroscopy, proton nuclear magnetic resonance and melting point. Comparison with standars available in our laboratory was also done.

The quantification was done by HPLC according to the method described by Eldrige[16]. A Corasil C-18 30cm x 30mm ID column was employed.Polar eluents such as water-methanol (25-50%) for 20 min and a flux ratio of 1 ml/min (with N-butyrophenone as internal standard) were used.

The antioxidant activity of the flavonoid compounds mixed with soybean oil was obtained by determining the acidity, iodine and peroxide indexes using the method described by Pregnolatto[14]. The determination of the acidity index involved the titration with 0,1 N NaOH using phenolphthalein as an indicator. The iodine index was determined by thiosulfate titration of the excess iodine of the sample, previously dissolved in chloroform and treated with fresh 15% KI solution.

The peroxide index was determined by dissolving the sample in acetic acid-chloroform solution (3to2), addition of 1% starch solution (0,5 ml) , titration of the excess iodine with 0,01 N sodium thiosulfate and comparison to a blank solution under the same conditions.

The quantification of the protein in the soybean seeds was performed using the method of Bradford[15] and the determination of lipid content was done according to the procedure described by Pregnolatto[14].

RESULTS AND DISCUSSION

The identification of the flavonoid compounds was done using ultraviolet, infrared and proton nuclear magnetic resonance spectroscopy and comparison to standard samples available in the laboratory. Tables I,II,III and IV sumarize the experimental results obtained by the different tecnhiques. Figure 1 illustrates the chemical structures of the flavonoids studied.

Table V shows the average values obtained for protein, oil and flavonoid compounds extracted from the nine cultivars studied. As can be seen, Cultivar UFV-5' showed the highest contents for all the parameters determined.

It is well known that great part of the phenolic compounds is found in plants bound to proteins[17]. In fact, in *Cicer arietanum*, member of the Leguminosae, the vast majority of protein is found along with a large quantity and a variety of flavonoid compounds[17].

These results are wholly justifiable, if one considers that flavonoid compounds are involved in nitrogen fixation in plants[23-26]. This process, that begins with the capture of nitrogen,involves the synthesis of phenylalanine and thyrosine in one of the metabolic pathways. Both amino acids are precursors of flavonoid compounds in plants. Of course, the fixation of nitrogen also leads to the biosynthesis of proteins.

Analysis of the results shown in Table IV also shows that the average values obtained for daidzin (IV) are higher than those for daidzein (III) and that the values obtained for genistin (II) are higher than those of genistein (I). This is in acoordance with the results described by Farmalidis[18]. This may be attributed to the need of glucose/sulfate/glucuronate incorporation in the detoxification process of these secondary metabolites in plants. The presence of glucose units in genistin (II) and daidzin (IV) is supposed to facilitate hydrosolubility and transport by water during the elimination[9].

The results obtained in this experiment also point out that the differences observed in all parameters studied for genetically different cultivars are in agreement with results described by other workers with genetically different cultivars of *Trifolium subterraneum*[11,20] *and Ononis Spinosa L.*[19].

Further analysis of Table V also permits the identification of the cultivar with the highest concentration of flavonoid compounds. This may facilitate future studies.

Table VI points out the high antioxidizing power of flavonoid compounds. As can be seen, genistein (I) and genistin (II) exhibited the best acidity, iodine and peroxide indexes, when compared to normal values-CNNPA (ABIA)[21]. These values point an acidity index of ± 0,423 percent oleic acid; iodine index of 188-198 in mg/100g and a peroxide index of 20 meq/kg.

It is interesting to note that results similar to those obtained by us with soybean oil have also been observed by other

TABLE I. SOME PHYSICAL PROPERTIES OF THE FLAVONOID COMPOUNDS STUDIED.

COMMON NAME	OFFICIAL NAME	Molecular Weight	Literature m.p. ºC	Melting Point Found ºC
Genistein	4',5,7-trihydroxy-isoflavone	270,25	302	300 - 302
Genistin	4',5-dihydroxy-7-O-glucosil isoflavone	-	253	251 - 253
Daidzein	4',7-dihydroxy-isoflavone	254,25	323	321 - 323
Daidzin	4'-hydroxy-7-O-glucosil isoflavone	-	238	236 - 238
Naringenin	4',5,7-trihydroxy-flavonone	272,25	251	249 - 251
Kaempherol	3,4',5,7-tetrahydroxy-flavone	286,23	277	274 - 276
Formonometin	7-hydroxy-4'-methoxy-isoflavone	268,26	212	210 - 212
Biochanin A	5,7-dihydroxy-4'-methoxy-isoflavone	284,3	284	281 - 283

TABLE II. ULTRAVIOLET SPECTRA OF FLAVONOID COMPOUNDS (WAVELENGTH IN NANOMETERS).

COMPOUND	MeOH	NaOMe	$AlCl_3$
Genistein	260, 327	275, 328	271, 307, 372
Genistin	260, 330	270, 353	270, 306, 374
Daidzein	238, 248, 257 309	253, 271, 333	236, 248, 260, 300
Daidzina	255, 312	255, 270, 319	257, 302
Naringenin	289, 325	242, 320	310, 373
Kaempherol	251, 262, 293 322, 367	278, 318, 415	260, 265, 302 349, 423
Formonometin	236, 247, 258, 301	258, 288, 327	240, 248, 259, 300
Biochanin A	259, 329	248, 272, 326	270, 309, 371

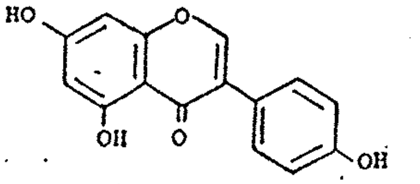
COMPOUND	$AlCl_3$/HCl	NaOAc	NaOAc/H_3BO_3
Genistein	270, 308, 371	270, 323	260, 336
Genistin	271, 305, 371	260, 329	260, 326
Daidzein	239, 248, 260, 301	253, 310, 332	260, 301
Daidzina	255, 301, 260	256, 320	254, 316
Naringenin	309, 370	284, 321	290, 331
Kaempferol	256, 269, 303 348, 423	271, 302, 387	266, 298, 320, 371
Formonometin	241, 247, 260 300	253, 272, 309 329	261, 303
Biochanin A	273, 309, 374	271, 326	261, 331

TABLE III. INFRARED SPECTRA OF FLAVONOID COMPOUNDS.

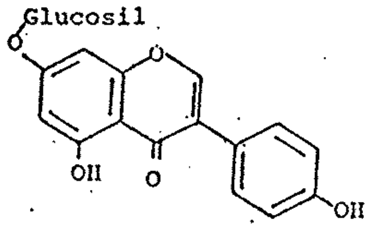
COMPOUND	WAVELENGTH (cm^{-1})
Genistein	3650-3000,1650,1620,1570,1520,1500,1420,1360,1320,1280,1260,1210,1180,1150,1050
Genistin	3600-3000,1640,1620,1500,1360,1280,1260,1210,1200,1180,1150,1100,1050
Daidzein	3550-3000,1640,1620,1600,1530,1470,1390,1310,1280,1240,1200,1100,1050,890,850
Daidzin	3500-3000,1640,1600,1530,1480,1390,1300,1280,1240,1220,1200,1150,1130,1050
Naringenin	3500-3000,1640,1600,1520,1500,1460,1380,1330,1320,1250,1180,1150,1080,1060,890,830
Kaempherol	3500-3000,1640,1600,1520,1500,1460,1300,1250,1150,1100,1050
Formonometin	3500-3000,1640,1600,1570,1515,1460,1390,1320,1290,1270,1250,1200,1180,1100,1040,880
Biochanin A	3400-3000,1650,1620,1570,1520,1440,1360,1290,1250,1190,1150,1050,1030,830

TABLE IV. PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF FLAVONOID COMPOUNDS (CHEMICAL SHIFTS IN PPM).

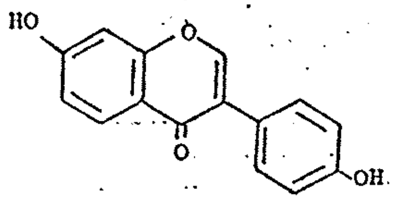
COMPOUND		SOLVENT	H-2	H-3	H-5	H-6	H-7	H-8'	H-2'	H-3'	H-5'	H-6	CH' OCH$_3$	Glucosil
Genistein	δ	CCl_4	7,60	-	-	5,8	-	6,85	7,50	6,85	6,85	7,50	-	
Genistin	δ	CCl_4	7,80	-	-	6,3	-	7,10	7,50	6,85	6,85	7,50	-	H1-Glucosil 5,0/3,90-3,3 (6H)
Daidzein	δ	CCl_4	7,70	-	8,0	6,50	-	6,75	7,50	6,85	-	6,85	7,50	
Daidzin	δ	CCl_4	7,90	-	8,2	7,1	-	7,0	7,50	6,85	-	6,85	7,50	H-Glucosil 5,0/3,85-3,20 (6H)
Naringenin	δ	CCl_4	5,20	2,50-2,90	-	5,85	-	6,0	7,25	6,75	6,75	7,25	-	
Kaempherol	δ	CCl_4	-	-	-	6,15	-	6,45	8,0	6,85	-	6,85	8,0	
Formonometin	δ	CCl_4	7,70	-	8,0	6,50	-	6,75	7,35	6,65	6,85	7,35	3,90	
Biochanin A	δ	CCl_4	7,65	-	-	6,15	-	6,40	7,35	6,85	6,85	7,35	3,8	



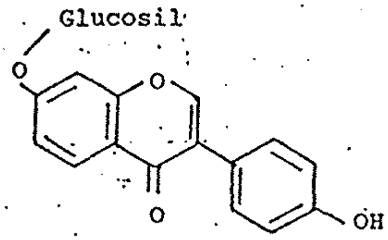
[I] Genistein



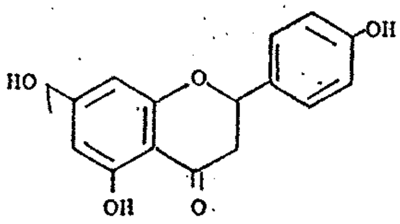
[II] Genistin



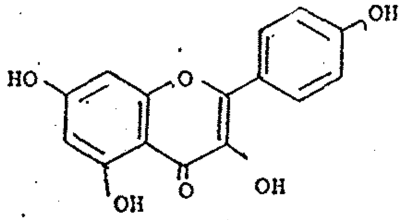
[III] Daidzein



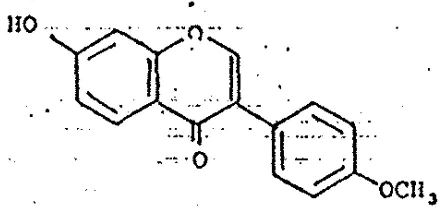
[IV] Daidzin



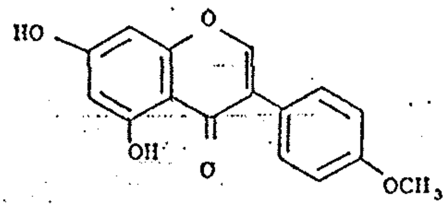
[V] Naringenin



[VI] Kaempferol



[VII] Formonometin



[VIII] Biochanin A

FIGURE 1. CHEMICAL STRUCTURES OF THE FLAVONOID COMPOUNDS STUDIED.

TABLE V. AVERAGE VALUES OBTAINED FOR THE CONTENTS OF FLAVONOID COMPOUNDS IN NINE CULTIVARS OF SOYBEAN.

Cultivars of Soya	Protein (%)	Oil (%)	Genistein (mg/100g)	Genistin (mg/100g)	Daidzein (mg/100g)	Daidzin (mg/100g)	Formononetin (mg/100g)	BiochaninA (mg/100g)
Doko	34,76 G	20,93 CD	28,16 F	112,00 D	34,16 F	38,16 F	34,26 G	66,26 G
IAC-8	37,86 F	23,76 A	32,16 E	114,00 CD	39,16 B	50,26 E	35,23 F	68,26 F
FT-Cristalina	38,10 EF	23,10 AB	32,00 E	113,33 CD	39,00 D	50,20 E	35,20 F	68,06 F
UFV-1'	40,13 D	20,36 D	33,16 D	116,66 C	41,50 C	52,23 D	39,40 D	71,33 CD
UFV-5'	45,20 A	23,80 A	38,23 A	123,00 AB	48,16 A	60,13 A	43,23 A	77,86 A
UFV-7'	39,36 DE	21,40 C	33,23 D	120,33 B	36,50 F	52,16 D	38,00 E	70,40 E
UFV-9'	42,20 B	21,40 C	36,00 B	124,00 A	45,23 B	57,30 B	41,16 B	75,30 B
UFV-10'	40,50 CD	22,40 B	33,23 D	122,00 AB	41,13 C	52,40 D	39,26 D	71,16 DE
UFV-15'	41,66 BC	22,40 B	34,33 C	124,00 A	44,33 B	55,16 C	40,23 C	72,20 C

* The values followed by at least one equal letter do not differ statistically by Tuckey's Test (5% probability level).

TABLE VI. ANTIOXIDANT ACTION OF FLAVONOID COMPOUNDS. AVERAGE EXPERIMENTAL VALUES OF ACIDITY, IODINE AND PEROXIDE INDEXES.

Mixture of Soybean Oil with	Acidity Index % Oleic Acid	Iodine Index (mg/100g)	Peroxide Index (mEq/kg)
Genistein	0,42 CD	187,66 E	20,33 D
Genistin	0,41 CD	187,66 E	20,33 D
Daidzein	0,40 CD	186,00 F	18,33 E
Daidzin	0,40 CD	186,00 F	18,33 F
Naringenin	0,43 C	192,33 D	23,00 BC
Kaempherol	0,40 CD	186,00 F	18,33 E
Formonometin	0,45 C	193,00 A	24,00 B
Biochanin A	0,38 D	190,66 C	22,00 C
Soybean Oil without Antioxidant	3,55 A	54,00 G	36,33 A
Refined Soybean Oil with Antioxidant	0,54 B	188,33 D	20,00 D

* The values followed by at least one equal letter do not differ statistically by Tuckey's Test (5% probability level).

workers studying other flavonoids in various plants[1-3,22].

In conclusion we can firmly state that the analysis of nuclear magnetic resonance, ultraviolet and infrared spectra led to the identification of flavonoid compounds in nine cultivars of soya. The quantification results permit us to conclude that the leguminosa (soybean) is rich in flavonoid compounds and also rich in proteins, the highest values being obtained for Cultivar UFV-5'.

The efficiency of flavonoid compounds as antioxidants was verified by acidity, iodine and peroxide indexes. The best results were obtained for genistein (I) and genistin (II).

REFERENCES

1. R. A. Larson, *Phytochem.*, *27*, 969-978 (1988).
2. G. A. Richardson and M. L. El-Rafey, *J. Dairy Sci.*, *30*, 397-413 (1974).
3. J. A. Araújo and D. E. Pratt, *Cienc. Tecnol. Aliment.*, *5*, 22-30 (1985).
4. D. A. Smith and W. B. Stephen, *Phytochem.*, *25*, 979-995 (1986).
5. G. B. Russel , G. J. Shaw, P. E. Christmas, M. B. Yates, R.W. Oliver and O. R. W. Sutherland, *Phytochem.*, *23*, 1417-1420 (1984).
6. P. J. Kuhn, D. A. Smith and D. F. Ewing, *Phytochem.*, *16*, 296-297 (1977).
7. S. K. Waage and P. A. Hedin, *Phytochem.*, *23*, 2509-2511 (1984).
8. P. A. Hedin, J. N. Jenkins, D. H. Collum, W. H. White and W. L. Parrot, in *"Plant Resistance to Insects"*, *ACS Symposium Series Nº 257*, P. A. Hedin, Editor, American Chemical Society, Washington, D.C., USA, 1984, p. 171.
9. R. M. Horwitz, in *"Biochemistry of Phenolic Compounds"*, J. B. Harborne, Editor, Academic Press, London, 1964, pp. 545-572.
10. R. B. Bradbury and D. E. White, *Vitamins and Hormones*, *12*, 207-233 (1954).
11. J. J. Patroni, W. J. Collins and W. R. Stern, *J. Chromat.*, *247*, 366-368 (1982).
12. M. Naim, B. Gestetner, I. Kirson and A. Bondi, *Phytochem.*, *12*, 169-170 (1973).
13. J. B. Murphy and C. A. Stutte, *Analyt. Biochem.*, *86*, 220-228 (1978).
14. W. Pregnolatto and N. P. Pregnolatto, in *"Normas Analíticas do Instituto Adolfo Lutz"*, São Paulo, 1985, Vol. I, pp. 245-261.
15. M. N. Bradford, *Analyt. Biochem.*, *72*, 248-254 (1976).
16. A. C. Eldridge, *J. Chromat.*, *234*, 494-497 (1982).
17. K.S. Mathur, S.S. Singhal and R. D. Sharma, *J. Nutrit.*, *84*, 164 (1964).
18. E. Farmalidis and P. A. Murphy, *J. Chromat.*, *295*, 513-515 (1984).
19. G. F. Nicollier and A. C. Thompson, *J. Chromat.*, *249*, 399-402 (1982).
20. P. Piergiorgio and C. Zio, *J. Chromat.*, *260*, 497-501 (1983).

21. CNNPA - Associação Brasileira das Indústrias de Alimentação, São Paulo, 1969, VI, pp. 245-246.

22. D. E. Pratt and P. M. Birac, *J. Food Sci.*, *44*, 1720-1749 (1979).

23. J. L. Firmin, K. E. Wilson, L. Rossen and A. W. B. Johnston, *Nature*, *324*, 90 (1986).

24. N. K. Peters, J. W. Frost and S. R. Long, *Science*, *233*, 977 (1986).

25. J. W. Redmond, M. Batley, M. A. Djordjevic, R. W. Imnes, P. L. Kuempel and B. G. Rolfe, *Nature*, *323*, 632 (1986).

26. H. P. Spaink, C. A. Wijffelman, E. Pees, R. J. H. Okker and B. J. J. Lugtemberg, *Nature*, *328*, 337 (1987).

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

ELASTOMERIC COMPOSITIONS FOR THE PRODUCTION OF RUBBER ARTIFACTS USED IN SHOE MANUFACTURING AND CIVIL CONSTRUCTION

José Cláudio Del Pino*, Anildo Bristoti and Mário Pinheiro
Departamento de Química Inorgânica, Instituto de Química
Universidade Federal do Rio Grande do Sul
Av. Bento Gonçalves 9500
91540-000 Porto Alegre, RS BRASIL

ABSTRACT

Sugar cane bagasse is a common byproduct of the alcohol and sugar industries. In the present work we describe the preparation of elastomeric agglomerates containing SBR [poly(styrene-butadiene)] and bagasse or kaolin as inert filler. The experimental results and a series of laboratory and field tests show that the sugar cane bagasse agglomerate can be very appropriate and useful for practical applications, especially in the manufacture of shoe soles.

RESUMO

O bagaço de cana-de-açúcar é um subproduto comum da indústria açucareira e do álcool. O presente estudo descreve a preparação de aglomerados elastoméricos contendo SBR [poli(estireno-butadieno)] e bagaço de cana ou caulim como carga inerte. Os resultados experimentais e uma série de ensaios de laboratório e de campo mostram que o aglomerado com bagaço de cana-de-açúcar pode ter várias aplicações práticas, especialmente na fabricação de solas de sapatos.

KEYWORDS: Sugar Cane Bagasse, Elastomeric Composites, Agglomerates.

INTRODUCTION

Sugar cane bagasse has been used in many countries of the world for the manufacturing of composite agglomerated materials employed on a large scale in buildings, furniture and means of transportation[1]. It is a byproduct of the sugar and alcohol industries with a chemical composition consisting mainly of lignin and cellulose[2]. It represents about 25% of the milled or ground sugar cane and at times there is a surplus of up to 30%, since its use as fuel depends upon the energy requirements of the industrial complex[3,4,5].

Because of its physical and chemical properties, sugar cane bagasse can be used as an inert filler for elastomeric composites employed for the manufacture of rubber artifacts in the place of kaolin and carbonates[6,7]. When added to plastifying materials such as phenolic resins, it facilitates the industrial processing of the vulcanizate and improves mechanic properties such as hardeness, resistance to abrasion and to heat[7,8].

The purpose of this work is to use finely divided bagasse

---

* *Author to whom correspondence should be addressed.*

DOI: 10.48141/SBJCHEM.v1.n1.1993.28_1993.pdf

mixed with phenolic resin and incorporate it into elastomers in varying proportions. The study of the physical and mechanical properties of the different rubber composites should give some clues for the possible use of some of these new materials for the production of rubber artifacts for the shoe , furniture and construction industries.

MATERIALS AND METHODS

Sugar cane bagasse (SCB) was ground, dried and sifted to obtain fractions that were 35/60 and 60/100 Mesh. These were subsequently added to SBR elastomers of [poly(styrene-butadiene)] together with other ingredients whose composition is expressed in "parts per hundred parts of rubber" (phr). The formulations are described in Tables I and II.

TABLE I. FORMULATIONS OF RUBBER COMPOSITES.

	I (phr)	II (phr)	III (phr)
SBR 1502	100,0	100,0	100,0
Stearic Acid	2,0	2,0	2,0
Zinc Oxide	5,0	5,0	5,0
Vulkanox HS	1,0	1,0	1,0
Sicosil 45	30,0	30,0	-
Polyethylene Glycol (PEG-4000)	3,0	3,0	-
Mercaptobenzothiazol (MBT)	1,5	1,5	1,0
Diphenylguanidine (DPG)	1,5	1,5	1,0
Sulfur	2,0	2,0	2,0
Phenolic Resin	5,0	5,0	20,0
Sugar Cane Bagasse (SCB 35/60)	-	-	200,0
Sugar Cane Bagasse (SCB 60/100)	25,0	-	-
Kaolin	-	25,0	-
TOTAL	176,0	176,0	332,0

Samples of kaolin (pH=6,3 and 0,4% residue of 325 Mesh) were added to the elastomer under the same conditions as bagasse. Formulations I and II, using 25 phr of filling and 5 phr of phenolic resin, Thor MD 278, were intended for the manufacture of rubber artifacts for the shoe industry, since they gave better properties according to results already described[9,10].

Formulation III was intended for the production of new materials to be used as wood substitutes. The ingredients were homogenized in an open blender or mixer. The test samples were vulcanized at 165ºC and their mechanical and physical properties were determined using the following tests: D 2240-75 for Hardness Shore A and D,D 412-75 for Tension at Break and Elongation, D 297-77 for Hydrostatic Density, 55516 for Abrasion, 53.507 for Progressive Tear, 53.543 for Flexion and MB 26 for Tension of Flexion and the PFI Method was used for Special Abrasion. These tests have been described by ASTM/DIN. The density of the filler was determined by using a pycnometer and the determination of the volatile material was performed using the D 1817 method, described in the literature[11,12].

TABLE II. CHARACTERIZATION OF FILLERS.

Property/ Filler	Density (25°C)	Humidity (%)
SCB 35/60 Mesh	1,40	6,34
SCB 60/100 Mesh	1,40	6,12
Kaolin 200/ 325 Mesh	2,60	0,30

Field tests were performed using rubber composites in the soles of shoes used by mailmen during their regular working schedule for 25 days. Comparisons were done between soles made from sugar cane bagasse and kaolin, fiberboard, agglomerate industrially available and elastomeric agglomerate with sugar cane bagasse.

RESULTS AND DISCUSSION

As can be seen in Table II, kaolin has a density 85% higher than sugar cane bagasse. This leads to a higher hydrostatic density and lesser efficiency in volume (bulk) in terms of material processing. This means that for the same mass of composites, one containing sugar cane bagasse and the other kaolin, that with bagasse will produce a greater number of parts.

Analysis of the results summarized in Tables III and IV, compared to the compositions containing kaolin, indicates that the rubber compositions with sugar cane bagasse have a higher hardness and resistance to progressive tear.

On the other hand, hydrostatic density and abrasion exhibit lower values as does resistance to flexion. This means that rubber compositions with sugar cane bagasse have the characteristics necessary for the use in shoe soles production. The field tests showed that soles of shoes used by mailmen and made with elastomeric compositions containing sugar cane bagasse met the requirements. These results are in agreement with previous studies described by our group[10] and show that the blending of phenolic resins and sugar cane bagasse is satisfactory and reinforces the desired properties of the compositions.

TABLE III. MECHANICAL PROPERTIES OF RUBBER COMPOSITES.

Property	Composition	Value Obtained
Hardness Shore A	SCB	75
	Kaolin	68
Elongetion(%)	SCB	520
	Kaolin	600
Tension at Break (MPa)	SCB	9,3
	Kaolin	13,6
Hydrostatic Density (g/cm^3)	SCB	1,15
	Kaolin	1,21
Abrasion (mm^3/40m)	SCB	232
	Kaolin	262

TABLE IV. SPECIFIC PROPERTIES EVALUATED FOR SHOE MANUFACTURING.

Test	Especification	Composition	Value Obtained
Progressive Tear	8,0 N/mm	SCB	14,4 N/mm
		Kaolin	10,2 N/mm
Flexion	Maximum Progression 4 mm	SCB	passes test
		Kaolin	passes test
Special Abrasion PFI	Parameter for outdoor shoes 0,8 mm	SCB	0,33 mm
		Kaolin	0,42 mm

Ther are specific interactions at the elastomer-filler interface such as covalent and hydrogen bonds and these are well known. The effect of vulcanizing agents such as sulfur or phenolic resins on these interactions have also been described[7,13]. These compounds, as well as the reinforcing filler tend to form cross-linking between the polymer chains. Figure 1 illustrates the relationship between the density of crosslinking or reticulation, nature of polymer and filler, and some properties of the vulcanizate[7].

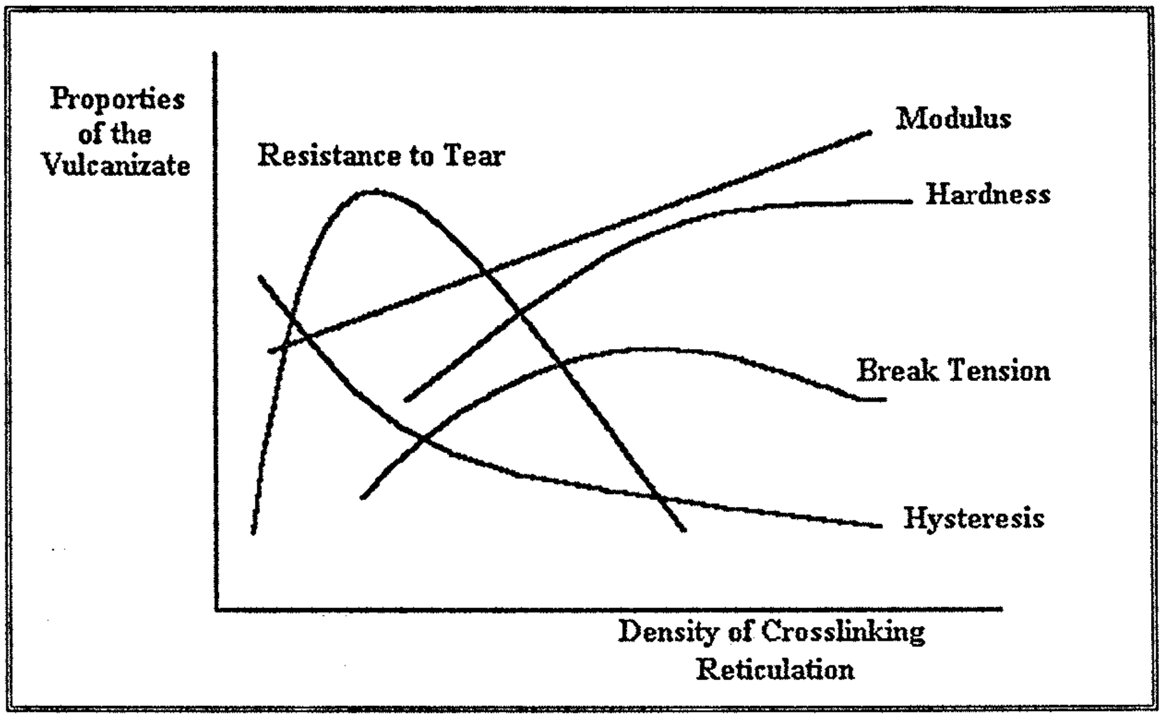


FIGURE 1. RELATIONSHIP BETWEEN PROPERTIES OF THE VULCANIZATE AND INTENSITY OF RETICULATION.

When compared to fiberboard and agglomerates commercially available, the agglomerated elastomer containing sugar cane bagasse has a higher flexibility. It deforms under a flexion tension of 1,5 MPa without tear and it returns to the original position at the end of the test. The other materials used in this study break under the flexion tension conditions described in Table V. The elastomeric agglomerate may be cut, nailed or secured with screws with a performance similar to that of wood. Its hardness depends on the amount of phenolic resin and of sugar cane bagasse present in the composition and it may reach Hardness Shore 40 values similar to those of agglomerate and fiberboard.

TABLE V. MECHANICAL PROPERTIES OF AGGLOMERATE.

Test	Commercial Fiberboard	Commercial Agglomerate	Sugar Cane Bagasse Elastomers
Flexion Tension (MPa)	6,1	2,0	1,5
Hardness Shore D	60	60	40

REFERENCES

1. V. Nagy, *Silvae Cultura Tropica et Subtropica, 5,* 127-134 (1976).
2. T. J. B. Menezes, *"Etanol. O Combustível do Brasil",* Editora Agronômica Ceres, Ltda., São Paulo, 1980, 233pp.
3. Sociedade de Produtores de Açúcar e Álcool-SOPRAL, *"Avaliação do Bagaço de Cana-de-Açúcar",* São Paulo, 1983, 101 pp.
4. M. T. Tolmasquim,*"Anais IV Congresso Brasileiro de Energia",* Rio de Janeiro, 1987, pp. 1159-1166.
5. J. G. Silva, G. E. Serra, J. R. Moreira and J. C. Gonçalves, *Brasil Açucareiro (Piracicaba), 6,* 452-465 (1976).
6. R. O Babbit, *"The Vanderbilt Rubber Handbook",* R. T. Vanderbilt Company, Inc., Los Angeles, 1978, 950 pp.
7. F. R. Eirich, *"Science and Technology of Rubber",* Academic Press, Inc., New York, 1978, 670 pp.
8. P. O. Powers, *Rubber Chemistry and Technology, 36(5),* 1558-1570 (1963).
9. J. C. Del Pino, H. R. Soares and A. Bristoti, *"Anais XXVIII Congresso Brasileiro de Química",* Porto Alegre, RS, 1988.
10. J. C. Del Pino, M. Pinheiro and E. Forte, *"Anais XXXI Congresso Brasileiro de Química",*Recife, PE, 1991.
11. American Society for Testing Materials-ASTM,*"Annual Book of ASTM Standards. Part 37",* Philadelphia, Pa., 1979, 888 pp.
12. Superintendência da Borracha- MIC, *"Polígrafos do Curso de Tecnologia dos Elastômeros",* Porto Alegre, RS, 1987.
13. R. D. Deanin, *"Polymer Structure, Properties and Applications",* Cahners Publishing Company, Inc. Boston, Mass., USA, 1972, 496 pp.

The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com. This text was introduced in this file in 2021 for compliance reasons.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

Vol.1, No. 1, 1993

AN INTERESTING CASE OF CONSECUTIVE REACTIONS

José Schifino
Departamento de Físico-Química
Instituto de Química
Universidade Federal do Rio Grande do Sul
91.540-000 Porto Alegre, RS BRASIL

ABSTRACT

This paper deals with a special case of two consecutive first order reactions where the two rate constants are equal. This peculiar situation, that may not exist in real systems, has an interesting mathematical solution.

RESUMO

Este trabalho trata do caso especial de duas reações consecutivas de primeira ordem quando as duas constantes de velocidade são iguais. Nesta situação peculiar, que pode não existir em sistema reais, a solução matemática é muito interessante.

Considering a system of first order consecutive reactions of the type

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \qquad (1)$$

and starting with pure A it is possible to solve a set of three differential equations finding the temporal dependence of the concentrations of A, R and S[1].

$$C_A = (C_A)_o \exp(-k_1 t) \qquad (2)$$

$$C_R = \frac{k_1 (C_A)_o}{k_2 - k_1} \left[\exp(-k_1 t) - \exp(-k_2 t)\right] \qquad (3)$$

$$C_S = (C_A)_o + \frac{(C_A)_o}{k_2 - k_1} \left[k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)\right] \qquad (4)$$

boundary conditions being at t=0, $C_A=(C_A)_o$, $(C_R)_o=(C_S)_o=0$

DOI: 10.48141/SBJCHEM.v1.n1.1993.34_1993.pdf

Equations (3) and (4) may be used whenever $k_1 \neq k_2$ but not in the particular case when $k_1 = k_2$. A closer look at this very peculiar situation becomes a quite interesting kinetic exercise although it may not have real existence.

Supposing $k_1 = k_2 = k$ in system (1) we may write, in differential form

$$-\frac{dC_A}{dt} = kC_A \qquad (5)$$

$$\frac{dC_R}{dt} = kC_A - kC_R \qquad (6)$$

Equation (5) integrates to the usual first order decay expression $C_A = (C_A)_o \exp(-kt)$. On the other hand, eq.(6) may be written

$$\frac{dC_R}{dt} + kC_R = k(C_A)_o \exp(-kt) \qquad (7)$$

Solving eq.(7) for boundary conditions $t=0$, $(C_R)_o = 0$, the time dependence of C_R is given by

$$C_R = k(C_A)_o t \exp(-kt) \qquad (8)$$

The maximum concentration of R in the system and the time necessary to reach it can be calculated by equating to zero the time derivative of eq.(8).

$$(C_A)_o t^2 \exp(-kt) = 0 \qquad (9)$$

which gives

$$t_{max} = 1/k \qquad (10)$$

$$(C_R)_{max} = (C_A)_o \exp(-1) \qquad (11)$$

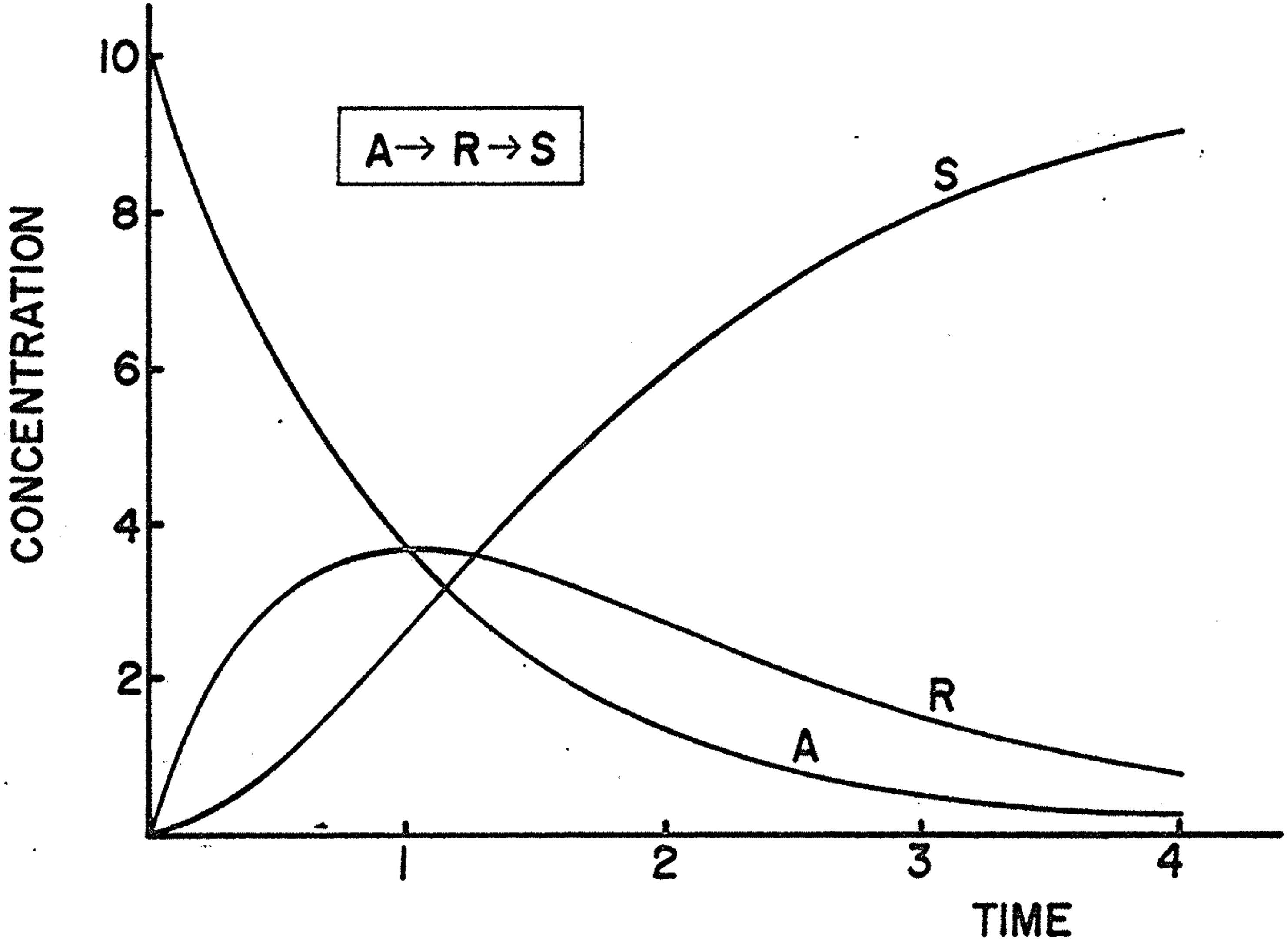


FIGURE 1. CONCENTRATION VERSUS TIME CURVES FOR THE FIRST ORDER SYTEM $A \rightarrow R \rightarrow S$, WITH IDENTICAL RATE CONSTANTS, STARTING WITH PURE A. ARBITRAY UNITS WERE USED FOR CONCENTRATION AND TIME.

Equations (10) and (11) show that t_{max} is the mean life of A and the maximum value of C_R is 1/e or about 37% of the initial amount of A present in the system.

Figure 1 is a graphical representation of the case in study. Concentrations of A, R and S can be easily calculated with the help of a pocket calculator and the curves may be either drawn by hand or displayed in a microcomputer making use of a quite simple BASIC program.

Note that, according to the derived equations, the maximum of the curve which gives C_R coincides with the curve C_A in the point where the concentration of A is reduced to 1/e or 37% (see Fig. 1).

REFERENCES

1. Benson, S.W. "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960, p.33.

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

THE KNIGHT'S MOVE IN THE PERIODIC TABLE:

a regularity amongst the d^{10} metals on the lower right-hand side

Michael Laing, University of Natal
DURBAN, South Africa.

ABSTRACT

This article describes a pattern of reactivity and properties of the d^{10} metals in the bottom right-hand side of the periodic table. Pairs of metals such as Zn-Sn, Cu-In, Ag-Tl, Cd-Pb and Sn-Po, all related by the knight's move, are discussed taking into consideration their properties, electronic configuration and metallic state.

RESUMO

Este trabalho descreve um padrão ou protótipo de comportamento das propriedades e reatividade dos metais com configuração d^{10} na parte inferior da direita da Tabela Periódica. Pares de metais tais como Zn-Sn, Cu-In, Ag-Tl, Cd-Pb e Sn-Po, todos relacionados com o movimento do cavalo no jogo de xadrez, são discutidos em termos das suas propriedades, configuração eletrônica e estado metálico.

All teachers of inorganic chemistry are familiar with the various patterns of regularities in the periodic table. There are the Triads of Dobereiner (1). For example, the properties of bromine are intermediate between those of chlorine and iodine. This applies to colour, physical state and atomic weight . Mendeleyeff based his predictions on this type of regularity when he predicted in detail the properties of the element eka-silicon, i.e., germanium (2). The chemical properties of an element were seen to be the "mean" of those of the elements above and below and to left and right of it.

On the top left of the periodic table there is yet another regularity, the so-called Diagonal Relationship. Here the chemical properties of an element are similar to those of an element one place to the right and one below it (3). For example, beryllium and aluminum and titanium have many properties

DOI: 10.48141/SBJCHEM.v1.n1.1993.38_1993.pdf

in common, particularly their solution chemistry and the behaviour of their oxides. This relationship is ascribed to a similarity in "ionic potential", the ratio of the charge to the ionic radius, of the two elements (3d).

The elements of Period 6 in the lower right hand side of the periodic table display the Inert Pair effect where the heaviest element in a group exhibits a stable oxidation state two less than the group number (4). The best known example is group IV where both tin and lead are found in oxidation states 2+ and 4+, but tin 2+ is a reducing agent and tin 4+ is inert, while lead in the 4+ state is an oxidiser and lead 2+ is inert. This effect is usually ascribed to the 6s pair of electrons being very firmly held to the nucleus.

Some time ago I was assigned the task of teaching descriptive inorganic chemistry to the freshman engineering students as a foundation for their course on materials. I covered the common trends in the periodic table and then, in an effort to emphasise the uses of the elements, I mentioned the common metals used for plating steel: tin plate used in cans for foodstuffs, and zinc plating to make galvanised iron for corrugated roofing and water tanks on farms (5).

I asked myself - why should these two metals so effectively plate steel? What is the link between them? I could not answer this question immediately except to say that tin is one down and two to the right from zinc in the periodic table. I wondered, was this Knight's Move a general regularity for the metallic elements on this side of the periodic table?

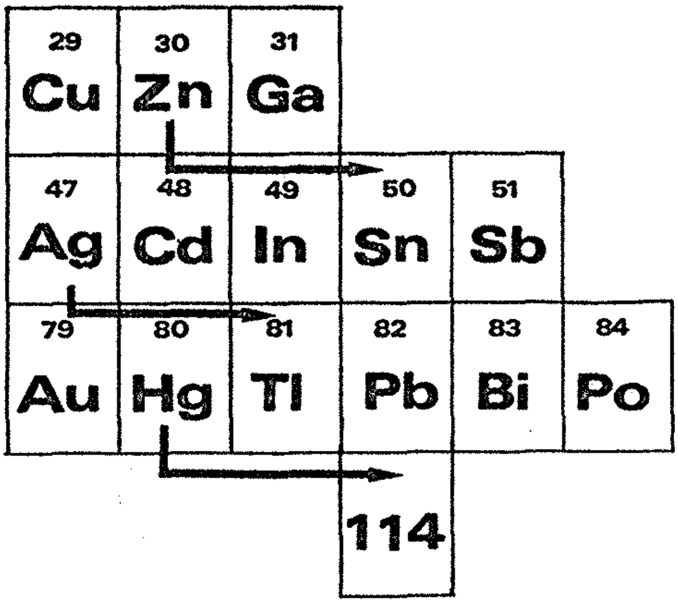


Figure 1. These metallic elements with d^{10} electron configurations show the Knight's Move relationship.

I suddenly remembered my lecturer of 30 years ago talking of thallium and saying that its stable oxidation state was +1, that its chloride was insoluble in water, and that it was photo-sensitive like silver chloride (6). Thallium and silver also were related by the Knight's Move!

Could the Knight's Move predict the properties of a rare element such as polonium? For example, what would be its melting point? That of tin is 232°C; if the pattern is true then the melting point of polonium might be similar. To my amazement it turned out to be 254°C, almost too good to be true (7). Now I asked myself the question - Why should these similarities be? What are they trying to tell us?.

The similarity in melting point for tin and polonium implies that the forces between the atoms in the solids must be comparable in magnitude. Examination of the crystal structures shows that both metals have the same coordination number of six and a similar pattern of M-M bonds (ideally octahedral in polonium, but distorted in tin) (8), in spite of the electron configuration of tin being $d^{10}s^2p^2$ while that of polonium is $d^{10}s^2p^4$. (But do these electron configurations have any reality in the metallic state? They were, after all, deduced from atomic spectra at infinite dilution in the gas phase). The s^2 pair on the polonium atom seems to be acting as an "Inert Pair", leaving the four p electrons to participate in the bonding; while the s^2 pair on tin seems to be promoted and joins with the p^2 electrons in the bonding.

I returned to the metals zinc and tin; what other similarities were there? Of course: brass is an alloy of zinc and copper, while bronze is an alloy of tin and copper (9). Both alloys have been known since antiquity. The relationship was there again. To be sure there are also intermetallic compounds with well-defined atom ratios such as CuZn and Cu_3Sn (10) whose bonding fits the Hume-Rothery ratios (11). But these Hume-Rothery rules require that the zinc contribute two electrons while the tin has to be a four-electron donor. I checked another book about alloys. Although miscible as liquids, zinc and tin are insoluble in each other as solids (12)! They form neither alloys nor intermetallic compounds; yet they are mutually soluble in copper to give the alloy of approximate compsoition 96 Cu, 2 Sn, 2 Zn which is used in British bronze 1p coins.

As may be expected, their crystal structures differ greatly (13). Zinc is distorted hexagonal close-packed with a $^c/a$ ratio of 1.856 compared with 1.633 for an ideal HCP structure. This gives the Zn atom a total coordination number of 12, with 6 atoms at 2.64 A^0 in a close-packed layer, and a further six, three above and three below, at 2.91 A^0. On the other hand, tin has the unusual structure with coordination number 6 mentioned above.

The atomic volume of zinc is 15.2 $Å^3$ while that of tin is almost double, 27.0 $Å^3$. Nevertheless, iron with its body-centered cubic sturcture senses something similar about the two solid metals that allows them to plate onto iron so successfully. Copper also feels some similarity in the individual zinc and tin atoms as they dissolve into it to form brass and bronze. Yet the atoms of the pure metals will not interact enough to give mutual solubility (14): a puzzlement. The only faint ray of light is that both iron and copper have the identical atomic volume of 11.8 $Å^3$.

I looked at other properties. Zinc and tin are non-poisonous. Zinc occurs in many enzymes necessary for biochemical processes in the human body, and it is commonly taken by mouth as a trace element supplement (15). Tin is used in medicines and is taken orally as both metal and oxide (in Metinox) for the treatment of acne. The harmless nature of tin can easily be deduced from its ubiquitous presence as stannous fluoride in toothpaste to combat caries.

Compare this with their congeners, the pair cadmium and lead, both of which are poisonous if ingested. Generally speaking, the heavy metals that form insoluble sulphides are toxic e.g. mercury, thallium, lead, cadmium.

It is interesting to note that bismuth is not toxic, and that each year over 100 tons are used in the manufacture of phar- maceuticals (16). Bismuth is taken orally in the form of the basic nitrate (in Bisodol) for minor digestive problems, and the oxide and subgallate are used in suppositories (such as Anusol and Anugesic) for the treatment of haemorrhoids. Antimony also is used as a medicant in the form of the well-known compound tartar emetic.

Stepping back the Knight's Move from bismuth and antimony, one comes to indium and gallium, about which toxicological information is rather sparse (17). However, gallium appears to be innocuous, while indium is less toxic than cadmium, thallium and lead.

I looked at the melting and boiling points of some pairs of metal halides (18): see Table 1.

These values showed that the Knight's Move pattern of regularity was more widespread than I had originally thought. Similarities of melting point will occur if the crystal structures and intermolecular forces in both solid and liquid are similar. This suggests that there will be similarities between pairs of chlorides and bromides which are mainly covalently bonded and therefore are molecular in nature. On the other hand, the picture must change for fluorides because the bonding in these compounds is predominantly

TABLE 1

Melting and Boiling Points of Metal Chlorides and Bromides

	Melting Point °C		Boiling Point °C
AgCl	445	$CdCl_2$	980
TlCl	429	$PbCl_2$	954
AgBr	430	$GaCl_3$	200
TlBr	456	$SbCl_3$	221
CdI_2	385	$GaBr_3$	279
PbI_2	412	$SbBr_3$	280
$ZnCl_2$	275	$ZnBr_2$	650
$SnCl_2$	247	$SnBr_2$	619
$GaCl_3$	77	$CdBr_2$	863
$SbCl_3$	73	$PbBr_2$	916

ionic in character, with structures (and therefore lattice energies) strongly dependent on the ionic radius of the metal cation as well as on its charge (19). For example, the melting point of CdF_2 is 1110°C, while that of PbF_2 is 822°C, in line with the radii of 0.92 Å for Cd^{2+} and 1.21 Å for Pb^{2+}.

I returned to the behaviour of thallium. That TlCl should be insoluble in water indicates that the lattice energy must be similar to the analogous value for silver chloride. However, AgCl will dissolve in ammonia while TlCl is insoluble. This is easily explained by the formation of the $[Ag(NH_3)_2]^+$ cation, in which the bonding picture invokes the use of two collinear sp orbitals (20). This is impossible for Tl^+ because the cation already has a pair of tightly held (presumably) s electrons. However, an analogous linear species $[TlL_2]^+$ should exist in which the two L groups are one-electron donors. Such cations do exist: e.,g. $[Tl(CN)_2]^+$ and the stable linear complex $[Tl(CH_3)_2]^+$, formal derivatives of Tl(III), which are isoelectronic with the other wellknown linear species $Hg(CN)_2$ and $[Au(CN)_2]^-$ (21).

Applying the Knight's Move to copper suggests that indium should be in various ways similar to it. The melting point of indium is only 157°C, in keeping with its crystal structure which is not close packed and very different from the crystal structure of copper (22).

However, In(I) with its $d^{10}s^2$ electron configuration may be expected to form compounds analogous to those of the d^{10} Cu(I) species. These compounds exist, e.g. InI and $InClO_4$, and, like those of Cu(I), are easily synthesised in CH_3CN as solvent (23). A conventional examination of the periodic table would not have led to such a prediction.

The same approach can be used in the qualitative analysis scheme (24). $PbCrO_4$ is a yellow insoluble species, therefore (a Knight's Move away) $CdCrO_4$ should also be yellow and insoluble in water, and now a classical Mendeleyevian approach requires that $ZnCrO_4$ will be similar. It is, and $ZnCrO_4$ is the corrosion inhibitor in the paint used as an undercoat on steel (25), which was of interest to my engineers who started all this!

Sb_2S_3 is wellknown as the bright orange sulphide precipate in Group II of the qualitative analysis scheme. The Knight's Move suggests that Ga_2S_3 should be in some way similar. Ga_2S_3 is a yellow solid, but it hydrolyses in water as Al_2S_3 does. The similarity between the compounds Ga_2S_3 and Sb_2S_3 turns out to be in the complexity of their crystal structures, neither of which is as simple as the stoichiometry would suggest. That of Ga_2S_3 is a derivative of the Wurtzite structure but with vacancies at the metal positions, while the structure of Sb_2S_3 is unique and quite complex (26).

By the same token, the structures of ZnS and SnS should be related. They are, in the sense that the metal atoms in both cases have coordination number four, despite the two extra electrons on the Sn(II) (27).

Similarly, the structures of ZnO and SnO are expected to be related. Once again, the common factor is a coordination number of 4 for the metal but, as might be predicted, the coordination about Sn is distorted with four short Sn-O contacts in a square on one side, and no close contacts on the other side. The Pb(II) cation in PbO has the same environment. (Figure 2, below). This in turn is almost identical with the coordination geometry around the Sb(III) cation in tartar emetic which is non-spherical, being coordinated to four oxygen atoms in a square on one side of the cation (28). The two non-bonded electrons on the antimony atom seem to have the steric attributes more closely associated with an orbital of p-character. The distortion of the Pb(II) cation from sphericity is not the behavior expected from a cation with a spherically symmetrical "inert lone pair" of electrons! Simarly, in Pb_3O_4 the coorindation about the Pb(IV) cation is nicely octahedral, while that about the Pb(II) ion is very irregular. The Pb(II) ion is clearly not "spherical". This is hardly what one would expect for a cation with a spherically symmetrical inert s-pair.

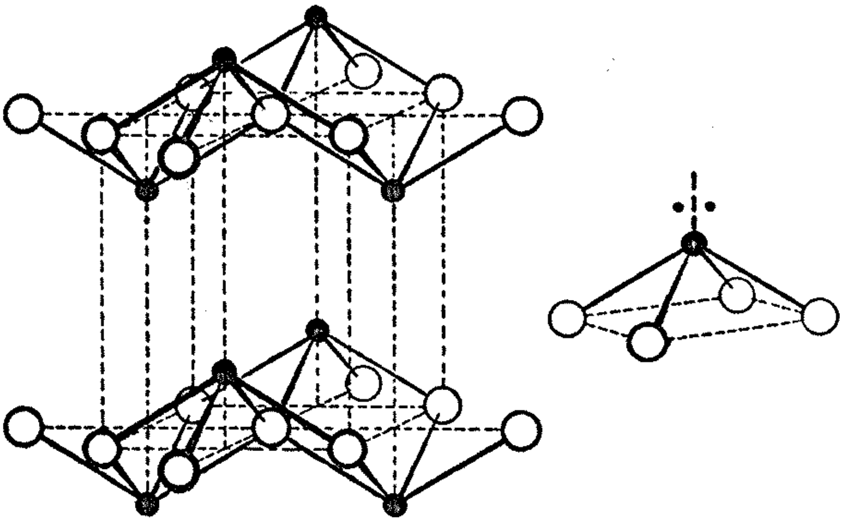


Figure 2. The crystal structure of PbO (and SnO). The solid circles represent the metal cations. The arrangement of the four close M-O contacts is shown on the right hand side; the two dots represent the "inert" pair of electrons.

The "lone" pair of electrons on Pb(II) seems also to be sterically "active" in various xanthate and thioate complexes (29), where the coordination sphere is an irregular pentagonal bipyramid with the "lone pair" occupying an equatorial position. Nevertheless, the mean Pb-S bond length in the thioate complex is little different from the Pb-S distance of 2.97 Å found in cubic galena (30).

Is the Knight's Move merely a special case of the Inert Pair effect applied to metals with a d^{10} electron configuration? The electron configuration of the metal at the upper left is $d^{10}p^{X}$ or $d^{10}s^{2}p^{X}$ while that at the end of the move is $d^{10}s^{2}p^{X}$ or $d^{10}s^{2}p^{X+2}$. But to invoke an inert s^2 pair is too facile. In fact the lower right-hand metals of the linked pairs often behave as if the electron pairs were not inert s^2 but rather p^2 i.e. a sterically active "inert lone pair" with p-character! e.g. the non-spherical nature of the Pb(II) cation. There is more behind the Knight's Move than meets the eye.

We are dealing here with an extremely complex phenomenon, not easy to explain. The macroscopic observable is the result of a complicated balance of factors including: covalent bonding within the species; intermolecular forces between the species in the solid as well as in the liquid state; the size of the metal cation; the ratio of charge to cationic radius; and the stability of the $6s^2$ pair of electrons (arising from relativistic effects) (31). Or as Dr. Johnson might have said: "I have found you an argument; it is a little more difficult to find you an under-standing" (32).

Nevertheless, application of the idea of the Knight's Move amongst the metals with d^{10} electron configurations on the bottom right hand side of the periodic table leads to many correct predictions that would not be made easily by the conventional application of the usually accepted trends in the Periodic Table. The Knight's Move also acts as a useful aide-memoire when dealing with the chemistry of these heavy metals.

As a final exercise in prediction I asked the question : which of the superheavy yet-to-be-discovered elements has the best chance of being found in isolable amounts? The answer is element 114, eka-lead (33). And what will be its physical and chemical properties? Apply the Knight's Move and the element on which to base prediction is Mercury. One concludes then that element 114 will be a metal of moderate density, about 16, having a very low melting point, possibly liquid at room temperature. Its stable oxidation states will be 0 and +2. Its chloride will have the formula MCl_2 and its oxide, MO, will be thermally unstable (34). We must now await the production of macroscopic amounts of element 114 to test these predictions which could have been made by any undergraduate with the aid of the Knight's Move in the Periodic Table.

REFERENCES

1. Weeks, M. E. Discovery of the Elements, 6th ed.; J. Chemical Education: Easton, 1956; pp. 653 and 747.

2(a) Moeller, T. Inorganic Chemistry; J. Wiley : New York, 1982; p.107.

(b) Nekrasov, B.V. Osnovy Obshchei Xhimii; Xhimiya: Moscow, 1969; Vol. 1, p.217.

3(a) Huheey, J. E. Inorganic Chemistry; Harper and Row : New York, 1972; pp. 87 and 604.

(b) Hanusa, T. P. J. Chem. Educ. 1987, 64, 686.

(c) Ref. 2, p.247.

(d) Cartlege, G.H., J. Amer. Chem. Soc., 1928, 50, 2855; 1930, 52, 3076.

4(a) Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 4th ed.; J. Wiley : New York, 1980; pp. 327 and 380.

(b) Ref. 3(a), p. 620-622.

5. Street, A.; Alexander, W. Metals in the Service of Man, 8th edition; Penguin: Harmondsowrth, U.K., 1982; p.191 (Tin plating), p.196 (Zinc plating).

6. Partington, J.R. A Text-book of Inorganic Chenmistry, 5th edition; Macmillan: London, 1947; p.887, 888. (Dumas called thallium the "platypus" among the elements).

7. Bagnall, K. W. Chemistry of The Rare Radioelements; Butterworths : London, 1957; p.47.

8. Donohue, J. The Structures of the Elements; J. Wiley: New York, 1974; pp. 274-276, 391.

9. Van Vlack, L.H. Elements of Material Science, 2nd edition; Addison-Wesley: Reading, MS, 1970; pp.266, 269.

10(a) Hume-Rothery, W. Electrons, Atoms, Metals and Alloys, 3rd edition; Dover: New York, 1963; pp.205, 206 (inert pair), pp.276, p.315 (brass), p.300 (bronze).

(b) Remy, H. Treatise on Inorganic Chemistry; Elsevier: Amsterdam, 1956; Vol. 1, p.574; Vol. 2, pp.16-22, 372.

11(a) Evans, R.C. Crystal Chemistry, 2nd edition; C.U.P.: Cambridge, 1964; p.328.

(b) Seitz, F. The Modern Theory of Solids; McGraw-Hill: New York, 1940; pp.30-32.

(c) Barret, C.; Massalski, T.B. Structure of Metals, 3rd edition; Pergamon: Oxford, 1980; p.159 (brass), pp.249-252 (Hume-Rothery ratios).

12(a) See ref. 5, p.187.

(b) Metals Handbook; Anmerican Society for Metals; Cleveland, 1948; p.1240 (Sn/Zn phase diagram), p.1265 (Cu, Sn, Zn phase diagram).

13. See ref. 8, p.225.

14. Further details of the phase diagrams and solubility characteristics are available in:

(a) ref. 12b. pp.1217, 1218 (Fe/Sn); pp.1220, 1221 (Fe/Zn).

(b) Metals Handbook, 8th edition; American Society for Metals: Ohio, 1973; Vol. 8 p.293 (Cu/Fe), p.299 (Cu/Sn), p.301 (Cu/Zn), p.306 (Fe/Sn), p.308 (Fe/Zn), p.336 (Sn/Zn), p.431 (Cu/Sn/Zn).

(c) Hansen, M. Constitution of Binary Alloys, 2nd edition; McGraw-Hill: New York, 1958; pp.580-582 (Cu/Fe), pp.633-636 (Cu/Sn), pp.649-653 (Cu/Zn), pp.718-719 (Fe/Sn), pp.737-740 (Fe/Zn), pp.1217-1218 (Sn/Zn).

15(a) Hughes, M.N. The Inorganic Chemistry of Biological Processes; J. Wiley: Chichester, 1984; pp.89-115, 297.

(b) Stryer, L. Biochemistry, 2nd edition; Freeman: New York, 1981; pp.148-153.

16. Greenwood, N.N.; Earnshaw, A. Chemistry of the Elements; Pergamon: Oxford, 1984; p.640.

17. Sax, N.I. Dangerous Properties of Industrial Materials; Van Nostrand Reinhold: New York, 1975; p.504 (cadmium), p.783 (gallium), p.829 (indium), p.861 (lead), p.1160 (thallium).

18. Sanderson, R. T. Inorganic Chemistry; van Nostrand Reinhold : New York, 1967; pp. 318, 319, 344 and 357.

19. Parish, R.V. The Metallic Elements; Longmans: London, 1977; p.184.

20. Huheey, J.E. Inorganic Chemistry; Harper and Row: New York, 1972; pp.371, 372.

21(a) Greenwood, N.N.; Earnshaw, A. Chemistry of the Elements; Pergamon: Oxford, 1984; p.293.

(b) Ford-Smith, M.H. The Chemistry of Complex Cyanides; H.M.S.O.: London, 1964; pp.48, 64, 66, 68, 69.

22. See ref. 8, pp.220, 244, 245.

23. Cotton, F.A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th edition; J. Wiley: New York, 1988; p.230.

24. Brady, J.E.; Holum, J.R. Fundamentals of Chemistry, 3rd edition; J. Wiley: New York, 1988; pp.1076, 1078.

25(a) Thompson, R., Editor, Speciality Inorganic Chemicals, Special Publication No. 40; Royal Society of Chemistry: London, 1981; pp.333, 334.

(b) Austin, G.T. Shreve's Chemical Process Industries, 5th edition, McGraw-Hill: New York, 1984; p.436.

26. Naray-Szabo, I. Inorganic Crystal Chemistry; Akademiai Kiado: Budapest, 1969, pp.179, 180, 284, 285.

27(a) Bokii, G.B. Introduction to Crystal Chemistry; USAEC: Washington, 1960 (English translation), Moscow, 1954 (Russian original), Vol. 2, pp.375, 382.

(b) Krebs, H. Fundamentals of Inorganic Crystal Chemistry; McGraw-Hill: London, 1968; pp.198, 204.

28. Cotton, F.A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th edition; J. Wiley: New York, 1988; p.421.

29. Lawton, S.L.; Kokotailo, G.T. Inorg. Chem. 1972, 11, 363.

30. Wells, A.F. Structural Inorganic Chemistry, 5th edition; O.U.P.: Oxford, 1984; pp.752, 1186; see also pp. 557 to 559.

31(a) McKelvey, D.R. J.Chem. Educ. 1983, 60, 112.
(b) Pitzer, K.S. Acc. Chem. Res. 1979, 12, 271.
(c) Pyykko, P.; Deslaux, J.P. Acc. Chem. Res. 1979, 12, 276.

32(a) Bartlett, J. Familiar Quotations, 15th edition; Macmillan: New York, 1980; p.357.
(b) Cohen, J.M.; Cohen, M.J. The Penguin Dictionary of Quotations; Penguin: 1960; p.210.

33. Ref. 2, p.114.

34. Fricke, B. Superheavy Elements in Structure and Bonding; Springer-Verlag : New York, 1975; Vol. 21, p.89.

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

TORNBERN BERGMAN'S THUNDERSTORM LECTURES

Joseph A. Schufle
Professor of Chemistry (Emeritus)
New Mexico Highlands University
Las Vegas, New Mexico USA

ABSTRACT

This article describes and analyzes the importance of Tornbern Bergman's inaugural lecture given to the Swedish Royal Society in 1764 on preventing the destructive effects of thunderstorms.

RERSUMO

Este trabalho descreve e analisa a importância da conferência inaugural de Tornbern Bergman perante a Acadêmia Real da Suécia em 1764 sobre a prevenção e efeitos destrutivos dos trovões.

In the process of preparing a translation from Swedish of Torbern Bergman's Inaugural Lecture to the Swedish Royal Socity on "Preventing the Destructive Effects of Thunderstorms" (1), I became very much aware of the international nature of research on lightning and other effects of thunderstorms in this period over two centuries ago. Benjamin Franklin was publishing his famous experiment with the kite in 1752 (2), at about the same time that Bergman began his own experiments on electricity that resulted in his inaugural lecture on the occasion of his being taken into the Swedish Royal Society in 1764. And at about the same time in Russia, Georg Wilhelm Richman (1711-1753) was undertaking his experiments on natural electricity that resulted in his dramatic death by electrocution while he was carrying out such an experiment.

We can get the best description of Franklin's kite experiment in his own words, from his letter to Peter Collinson, Esq., F.R.S. (2):

> "Make a small cross of two light strips of cedar, the arms so long as to reach to the four corners of a large thin silk handkerchief when extended: tie the corners of the handkerchief to the extremities of the cross, so you have the body of the kite; which being properly accomodated with a tail, loop, and string, will rise in the air, like those made of paper; but this being of silk is fitter to bear the wet and wind of a thunder-gust without tearing. To the top of the upright stick of the cross is to be fixed a very sharp pointed wire, rising a foot or more above the wood. To the end of the string, next to the hand, is to be tied a silk ribbon, and where the silk and twine join, a key must be fastened. This kite is to be raised when a thunder-gust appears to be coming on, and the person who holds the string must stand within a door or window, or under some cover, so that the silk ribbon

DOI: 10.48141/SBJCHEM.v1.n1.1993.54_1993.pdf

> may not be wet; and care must be taken that the twine does not touch the frame of the door or window. As soon as any of the thunder clouds come over the kite, the pointed wire will draw the electric fire from them, and the kite, with all the twine, will be electrified, and loose filaments of the twine will stand out every way, and be attracted by an approaching finger. And when the rain has wet the kite and twine, so that they can conduct the electric fire freely, you will find it stream out plentifully from the key on the approach of your knuckle. At this key the phial may be charged; and from electric fire thus obtained, spirits may be kindled, and all the other electric experiments be performed, which are usually done by the help of a rubbed glass globe or tube, and thereby the sameness of the electric matter with that of lightning be completely demonstrated."

We can only marvel at Franklin's good fortune in carrying out this experiment, in which he exposed himself to the same extreme danger of lightning stroke that caused the death of Richman.

Since Richman was not around to describe his fatal experiment, we have to depend on the deposition of an engraver for the Royal Society, I. Sokolov, who was present at the time (see Ref. 1, Note (n)):

> "Professor Richman in Petersburg in the previous year (1752) had prepared for the start of his investigations, and he was especially engaged with them in measuring artificial and meteoritic electricity and comparing them with each other. On 9 Aug 1752 all his equipment became so electrified that he trembled as from cold, and the spark moved backwards up his arm. On 31 May 1753 the electricity crackled so loudly that those in the third room from his could hear it. Alone on the 6th of Auygust (1753), he came to his unfortunate hour, when his investigations and his life ended at the same time, as we were informed in detail (see Note (bb) (1))...
>
> "Note (bb) Professor G.W. Richman belongs under the first [category] which Dalibord's experiments imitated. He knocked a hole in the bottom of a bottle and inserted an iron rod, which was fastened in the neck [of the bottle] with a cork. After this a roof tile was removed on the north side of the house, and the bottle was fixed in its place, and held by the tile lying on top of it; and all was arranged so that the point of the [iron] rod reached four to five feet above the roof. The lower end of the rod did not touch any grounded body, since it was fastened to the same iron chain which, supported by silk cords, was led into his [Richman's] chamber. The window of the room faced

toward the south, and against the window stood a table, four feet high, on which the electric detector (gnomon) [electrometer] was placed. The detector stood on a small iron rod, which was supported on a glass base filled with iron filings as detectors. A twine cord, one and one-half feet long, with a grain of lead at the end, was fastened to the small rod at the top. This hanging piece hung at right angles, or nearly so, as long as it was not electrified. A quadrant divided into degrees, which were two lines [2 Linien = 4 mm] in size, lay against the twine cord, and in such a way that the midpoint of the curve rested against the cord. Since the chain was connected to this small rod, one could immediately detect if the rod were electrified; for then the cord of the plumb line was driven up [the scale], and the stronger the charge the farther it was driven. Mr. Richman compared the strength of meteoritic electricity with artificial [electricity] and found the latter to be greater; for the cord could be driven 55 degrees up [the scale] by it [artificial], whereas the former [meteoritic] never more than 30 degrees. Sometimes he even used a detector which was connected to the inside of a Leiden flask [jar], and a second detector connected to the outside of the same flask. On 6 August 1753 his installation was again electrified, and with it he used only one detector, with which he could observe to what degree the cord was driven up; but at that very instant a fire-ball, as large as a fist, was led by the small iron chain towards his head, which was one foot away from it, and struck him dead to the ground. The explosion was like a small cannon shot. An iron wire, which connected the chain to the iron rod, exploded, and a piece of it burned the clothes of your Academy's engraver, Sokolora, who stood nearby. Richman had in his pocket 70 Rubel, which were not damaged. See Winkler's Programma, and Lomonosov's Orat. de Meteor., vi electr. ortis.

> Richmanni funus multa cavere jubet.
> Dum tangit ferrum rapitur super aethera
>   doctor
> Ac inter Physices sidera latus erat.

> [The death of Richman shows us much that should be avoided. When he touched iron the doctor was snatched to heaven. And at the same time, Physics was related to the stars.]

> "The mistake in his installation was this, that the lightning was carried into the room, with no off-conductor provided beforehand in the event of violent danger. If a chain leading out from the installation, even one quarter the size of that chain which brought the electricity inside, had been prepared, then the spark would hit the out-conducting chain as soon as it became at all dangerous, and in no way would such a diligent investigator have been killed."

Bergman described the effects of lightning strokes very vividly in his lecture:

> "The strongest towers and walls are very often shattered in an instant (c); our churches and dwellings are set afire, destroyed, and quite often changed into an ash-heap (d); the floating habitations of sea-farers are also sometimes struck, whereupon the self-same inhabitant must cast his lot either with fire or water (e); if the ship is undamaged, yet still is that direction indicator, namely the compass, destroyed or made unruly (f); the best and longest ropes are broken into pieces, or torn into countless parts (g); animals are slain (h), friends and next of kin are injured, and often, close beside us, fall lifeless to the ground (i); and we count ourselves very lucky if our own body escapes uninjured from this danger which threatens us...
>
> "... then Doctor Franklin proposed a means by which to ascertain fully the truth of these things (m). A trustworthy experiment had taught him that a metal point, held at a fixed distance from an electrified body, attracted to itself more or less of the [electrical] power; from which it was evident that if this rubbed point were isolated from electrically conducting bodies adjacent to it by means of glass, sealing wax, silk, and the like, then because of this the electricity would hardly allow itself to be conducted away. If we now erected [such] pointed iron rods provided with glass supports on high places, and thunderclouds passed over them, then if this parcel of air were electrified and not too high above, the same force must collect itself in the rod and would then reveal itself through sparks, etc."

The letters in parentheses refer to Bergman's Notes appended to his lecture proper (see Ref. 1).

Bergman then described the difference between non-conducting substances such as glass, sealing wax, pitch, and silk, and conducting substances such as metals, water, and animal bodies. He described an experiment he made to determine the speed with which electricity was conducted through metals:

> "An attempt has been made at measurement, in which this electrical force was conducted forwards for more than 900 Swedish fathoms [5400 feet] without the slightest difference in time being noted between the moments when the force showed itself at the nearest end and at the farthest end. Metals conduct this force most perfectly of all substances, insofar as we know up to now; and I have, in a paper submitted to the Royal Society, shown that a cylinder of water of three decimal lines diameter [9 mm] does not have the capacity to conduct away the entire charge on a small electrified glass [globe?], while in comparison a small strip of gold leaf of the same width does it perfectly. In addition it may be added that lightning matter is not as abundant as was once thought; that the point [of a rod] attracts it [electrical matter] from a long distance before the clouds reach it [the rod] and come to stand over it midway, which [clouds] will then largely discharge through it before they come to their zenith, or to the point where danger is the greatest; and finally that the conducting power of metals exceeds all known limits; and so it becomes possible for us to believe that the thunderstorm can be averted to a considerable extent.
>
> "If the bank or side of a stream could be provided with a channel in which water could be sucked and carried away with a velocity such as that with which a metal rod carries electricity, it is my conviction that floods would cause no particular damage in surrounding regions. We must not however overlook the reasonable conclusion that this is derived from some already known and accepted principles; in particular, we should proceed to investigate whether we have not already learned something from experience, namely if we can find any conclusive evidence that the thunderstorm may actually be turned away sometimes without doing any damage; and then under what circumstances this occurs."

He then described Franklin's experiments with lightning rods in Philadelphia. Then he asked a crucial quuestion:

Bergman's Thunderstorm Lecture.

"If we now ask: 'Why do thunderbolts not spare the churches and castles that are now armed with iron points?', then we can answer reasonably: the cause is the lack of an adequate conductor attached to it. For example, if a quantity of metal roof ornaments are fastened to a [dry] wall, then that electricity which they collect cannot be lost because a dry brick wall will not conduct away the electrical power: and, as so often happens, if the power is increased sufficiently, the sparks can jump to the nearest metal or conducting body, and also at the same time setting fire to anything inflammable lying in the way (a). If now this new conductor is itself detached [from the ground], then fire can occur in a third place, and so on. In this way it happens that one stroke starts fires in several places at the same time. The fate of Professor Richman in Petersburg (bb) testifies sufficiently about this (cc), as to what we risk if we lack a conductor.

"I had occasion a year ago to be convinced of this fact in a similar incident. The Marienstadt Church is tall, and in addition is situated very conspicuously by itself: the new roof and likewise the new steeple are covered with sheets of iron, and the latter [the steeple] is now provided with five high-standing iron rods which have stars on the ends. We expected from all this that the steeple would attract to itself some lightning material from thunderclouds passing by, which would strike so much more dangerously because the great church roof and the roof of the steeple had no metal connector [to the ground]. In the summer of the year 1762, I expressed to the church authorities my concern about this. But they seemed to attach little importance to this, and especially in this case because the new steeple was constructed much lower than the old one had been, and such was also the case with the rafters of the roof. But lightning struck four days afterwards, and the stroke took exactly the path that I had predicted, namely from the steeple it led down to the great roof, from which it passed down to the inside of the wall, which workmen were still cementing with lime, and from there it passed from the wall on the north side down to the earth. If the mortar had had more time to dry, the stroke would have found no conductor down from the great church roof, and would undoubtedly have set fire then to something in the steeple. Moreover, it is especially worthy of attention, that that side of the church wall which faced particularly towards the north, and thus was divested less of its moisture by

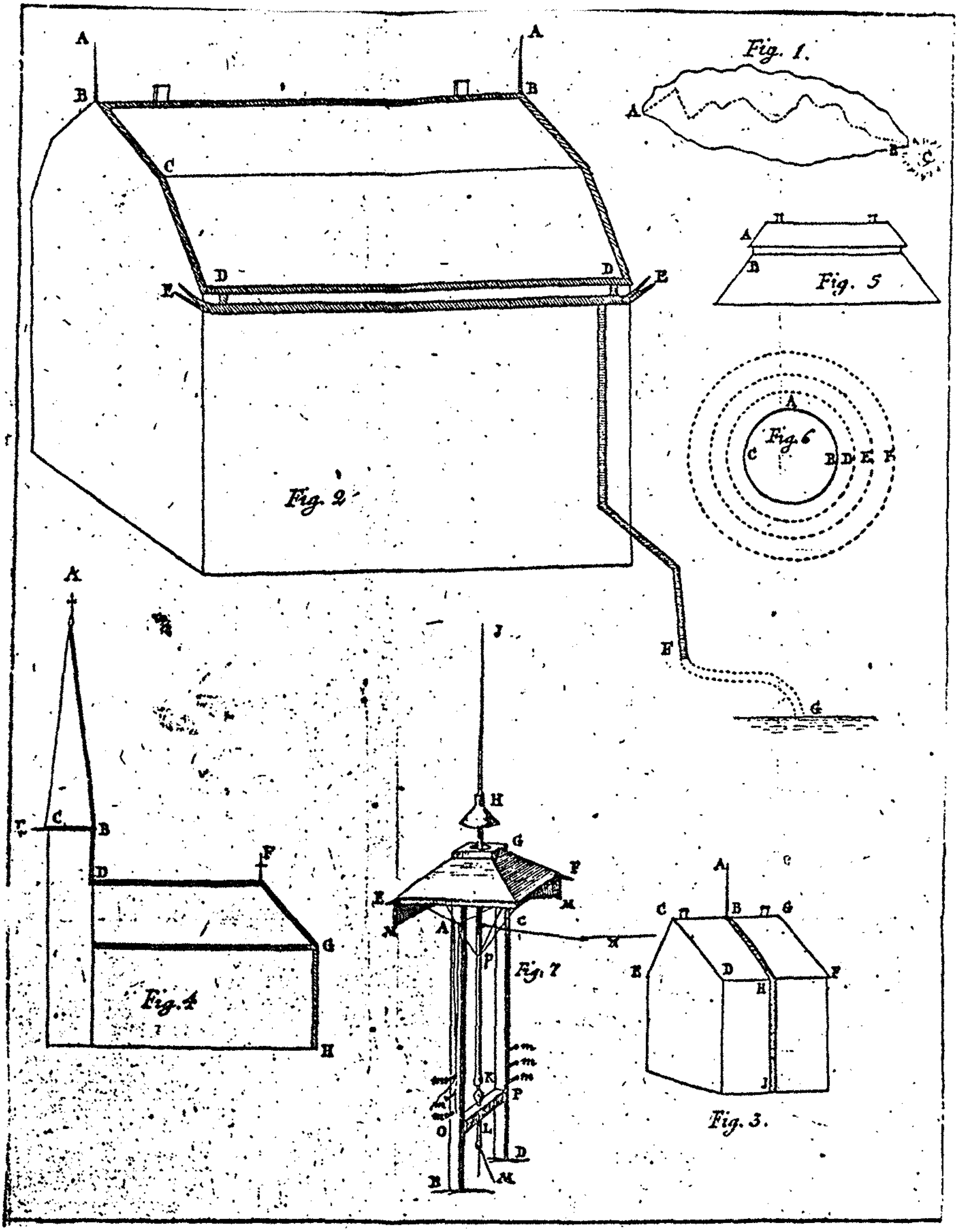
> the sun, conducted away completely the fire of the stroke from the roof, and thereby prevented any further damage (y)."

Bergman then discussed the moral implications of erecting protective devices against the thunderstorm:

> "It is not physics, but has to do with legality, how to justify it, if we are going to do this as things now stand. Some would put the defense against the thunderstorm in the same class with innoculation against chicken pox, and consider it to be impious, mistaken, and not for mere mortals; like a council of ogres wishing to attack the heavens. The innate corruption of men condemns them to be unworthy of doing good, and their lack of gratitude toward the Omnipotent God is such that, with fearful hearts, they ought to regard the perils hanging over their heads as being the well-deserved consequences of the evil they have committed. The Lord of Nature has himself ordained the lightning for His own purposes, in order to threaten and punish thereby the earth's inhabitants; so it would be unthinkable if now thunder and lightning could not occur in the very places where the greatest sin had been committed. This is undoubtedly the correct attitude, the right direction and the best ultimate purpose of physics, in addition to the ethics common to all other fields which, in view of the lowly nature of man, can best describe the omnipotence of the Creator. But, on the other hand, I have never heard that anybody has yet refused to protect themselves against infectious diseases, or earthquakes, or typhoons or other similar hazardous occurrences. So, if this kind of thing is permitted, why then could we not also seek to protect our property, our health, and our lives against the thunderstorm, if we can find the means to do so? Now enough of this one particular subject!"

He then described a proper installation for protection against lightning strokes, and a conductor connected to it to carry the charge to the ground:

> "On each end of the beam which forms the ridge or point of the roof, and to which all rafters of the roof are attached, is fastened a flat or round iron rod, a few ells in length, with a gilded point; or if we wish, we can equip the end of this iron rod with a metallic sphere, which has spikes or barbs protruding outwards



FIGURES 1-7. FIGURES THAT APPEARED IN BERGMAN'S PUBLISHED LECTURE TO ILLUSTRATE VARIOUS TYPES OF LIGHTNING ROD INSTALLATIONS.[1]

all around it, upon which the electricity can spurt from all sides. (Many springs flow fuller and easier than a few.) In order to prevent rust on these spikes and the rod, they must ne gilded, for it has been found that rust obstructs the passage of the electrical material.

"If the roof is covered completely with metal plates, it is necessary to provide only a metallic connection between the roof and the ground and soil. A similar connection may be provided for a tiled roof which is covered with iron plates at the points and ridges, the edges and the foot of the gables; and where such metallic facings are missing they must be constructed.

"In order to conduct the lightning matter down on the walls of buildings, we must sheath the main corners, or at least two corners situated diagonally opposite to each other, with a facing of tinned sheet-iron, which must be connected to the roof plates. If there are sheet-metal gutters under the roof, then these should be connected to the roof plates, and no facing of sheet-iron is then needed over the edges of the walls in such a case. If possible, everything which is of metal on the outside of the bilding must be connected together, so that a continuous conductor is provided.

"If the building is very tall so that the clouds can occasionally touch the battlements, for the sake of greater security, one or more points are erected at the bottom of the roof, which points must project at the edges of the roof. On the whole it must be stated that metal points must never be lacking on the outer trimming of churches and other important buildings. Earth and sand are substances which, taken by themselves alone, are too dry to conduct the electricity. Thus it is not sufficient to provide a connection between the endangered object and the earth; for still more [attention] is required here. In this case one or more tinned pipes should be prepared, which are connected to the water-spouting, or with the sheet-metal roof facing at the corners, and which [pipes] must be long enough so that they can reach to the water lying closest at hand, it may be a brook, a trench, or a river, in which the lightning material can be carried away, if the clouds are active (jakada), or [the kind] from which enough moderated (blikande) matter can be obtained if they are inactive (nekada) (kk). Plates and pipes are most suitable for this contrivance, because experience teaches us that the

> larger the surface is the more electrical matter it can accomodate."

Bergman even described how you could protect yourself in an open field:

> "If one finds himself in an open field it is not advisable for him to continue on his way (ll); nor should he seek refuge under high trees (g). If he can reach a house, which is protected in the aforesaid manner, then he obtains the greatest degree of safety; for the advantage which one gains from wet clothing, is obtained very easily at the same time, though often against our will; worst of all is the inconvenience that we can never free ourselves from peril because our body is at least as good a conductor as wet clothes. It is somewhat different with houses and buildings of stone, whose walls in themselves are not serviceable as conductors; for a heavier rain can make the walls at times conducting, and the building is in this way preserved instead of being destroyed by the event. A naked sword or small iron spike held over the head is likewise a means which can bring not only advantage but also harm; for if the lightning strikes upward or downward through the sword, then a limb of the human body will be in the path or course of the lightning material, and perhaps for the last time. More trustworthy, even though inconvenient to carry with you, would be a properly adapted umbrella (mm)."

Note (mm) referred to reads as follows:

> "(mm) Mr. Franklin believes that we would be sufficiently protected against lightning in an open field if we would make our clothes wet or moist; and the reason for this is that no wet rats have ever lost their lives from electrical stroke. I have indeed, up to now, never thought about making an investigation of this [theory]; however it is known that fish die in a tank if the water in which they are held is made part of an [electrical] conducting circuit. If any such fish cannot survive when surrounded by water, what can we expect from such a small amount of water that it only moistens our clothes? I am certainly convinced that Mr. Franklin has made a mistake of one kind or another in this."

Bergman's Thunderstorm Lecture.

Bergman ended his lecture, and appended notes, as he often did, with a Latin quotation:

> "Interea Physici studio non cedite
> vestro,
> Spes ut res ultro promoveatur adest.
> Quam natura suis monstrat cultoribus
> artem,
> Fructibus eximiis accumulare sciet."

Which I translate:

> Meanwhile our study of Physics never
> ceases,
> The search for knowledge is known to
> progress of its own accord.
> It is as if Nature wants to show its
> secrets to the searchers,
> So they learn to gather uncommon
> fruits.

REFERENCES

1. "Preventing the Destructive Effects of Thunderstorms", Torbern Bergman, Uppsala, Sweden, 1764. Translated into English by J.A. Schufle, Meadow Press, Las Vegas, New Mexico, 1993.

2. "Letter to Peter Collinson", Benjamin Franklin. Transactions of the Royal Society (London), Vol. 47, pp. 565-567 (1752).

*****

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

USE OF POLLUTION BIOINDICATORS FOR FLUORIDE IN THE VICINITY OF COAL THERMOELECTRIC POWER PLANTS

Érico M. M. Flores and Ayrton F. Martins*
Departamento de Química
Universidade Federal de Santa Maria
Santa Maria, RS, BRASIL 97119-900

ABSTRACT

Determination of fluoride in environmental samples of pasture and honey lead to the conclusion that these materials may be used as pollution bioindicators in areas of industrial activity. Concentrations of fluoride determined in recent times are above reference values. This observation is reinforced by the occurrence of various cases of bone deformation (fluorosis) and dental problems of ruminants in the area. A synergetic effect of fluoride on the abrasion of coal ash deposited on graze lands is also observed.

KEYWORDS: Fluoride, Pollution Bioindicators,Pasture, Honey.

RESUMO

A determinação de fluoreto em amostras de pastagem e mel permite concluir que estas matrizes podem ser utilizadas como bioindicadores de poluição em zonas de atividade industrial. Valores determinados em épocas mais recentes encontram-se acima de valores de referência. Esta constatação é reforçada pela ocorrência de diversos casos de deformação óssea (fluorose) e acentuado desgaste dentário em ruminantes nas imediações. Verificou-se, também, um efeito sinergético da abrasão da cinza de carvão depositada com a ação do fluoreto sorvido na pastagem.

INTRODUCTION

Among the common air contaminants, fluoride is generally considered the most dangerous phytotoxic agent, even when polluting in trace amounts[1]. Plants grown in areas contaminated by fluoride show a series of physiologic injuries caused by the absorption of fluoride [2,3,4].

The intensive use of coal in the generation of thermoelectricity is along with the processing of phosphate minerals a very important source of fluorine dispersion in the environment[5,6,7]. Fluoride concentrations above 100 ppm are common in mineral coal[8,9]. During combustion, this air pollutant is volatilized and expelled through the chimney along with fly ash and gases[10].

---

* *Author to whom correspondence should be addressed.*

DOI: 10.48141/SBJCHEM.v1.n1.1993.65_1993.pdf

Under the influence of climactic factors, the emitted fluorine returns to the soil in the form of fluoride, it is deposited and interacts with the components of the biosphere (water, soil, vegetation, fauna, etc.)[11].

The concentration of fluoride in environmental materials can be an indicator of the degree of environmental contamination. It is a function of regional climactic factors and the distance from the source of the emission [12,13].

This paper deals with the determination of fluoride concentration in samples of pasture and honey collected for a period of three years (1987-90) using ion-selective electrode tecnhiques. Samples were collected in the vicinity of two thermoelectric power plants located in Southern Brazil. One is Usina Termoelétrica Presidente Medici (UTPM/446 MW), located at Candiota, Bagé, Rio Grande do Sul. The other is Usina Termoelétrica de Charqueadas (UTC/72 MW), situated at Charqueadas, Rio Grande do Sul. In both areas, besides the generation of thermoelectricity, coal mining is also practiced - in open pits in Candiota and 300 m deep mines in Charqueadas.

The experimental results obtained by the analysis of the environmental samples were submitted to statistical treatment in order to verify the behavior of concentration (dependent variable) as a function of three factors: distance from the plant, time of collection of samples and direction of collection of samples.

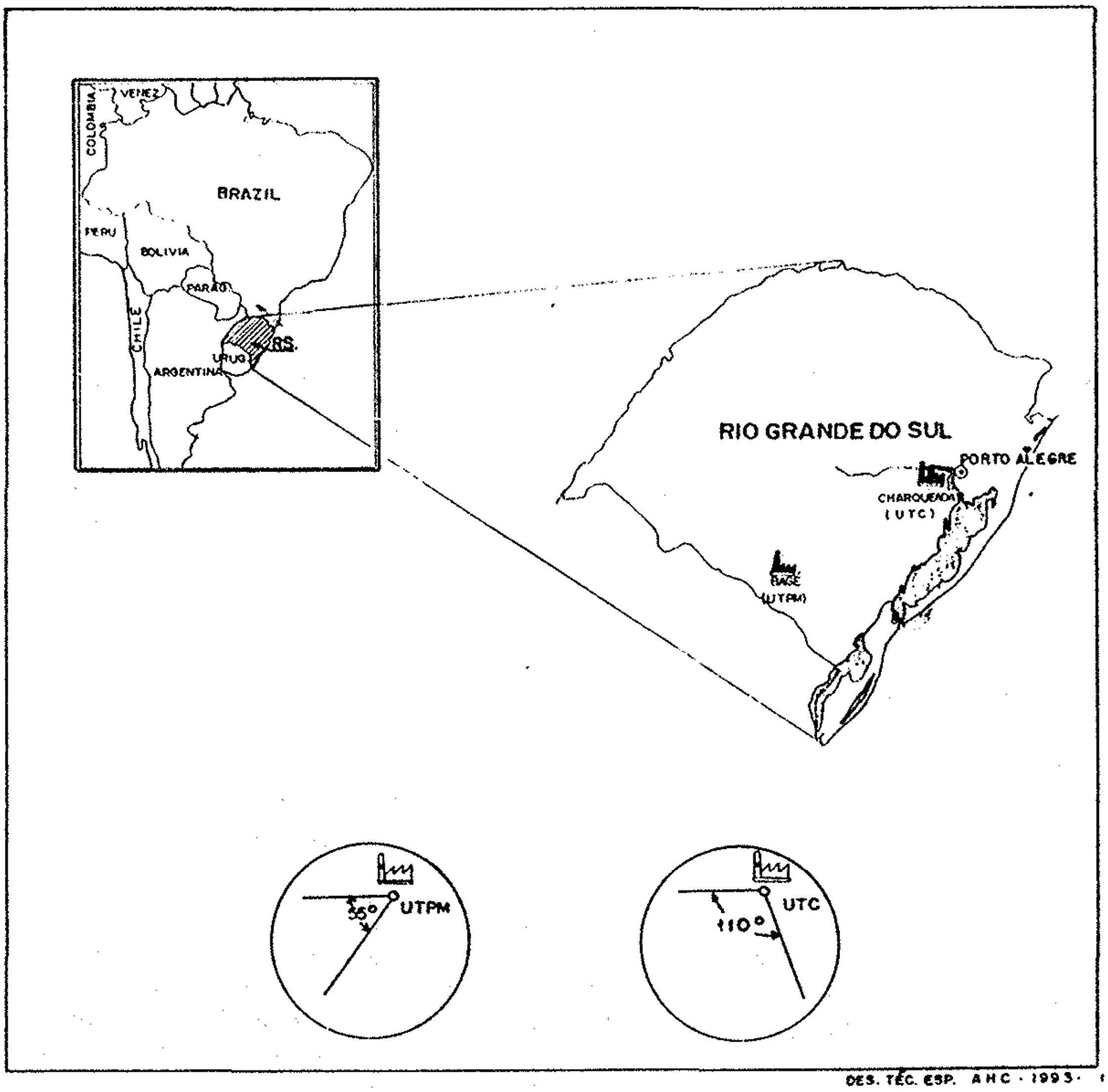
MATERIALS AND METHODS

The aerial parts of predominant forage grasses (*Panicum graminae, Piptochaetium montevidense, Paspalum notatum, Aristida sp. e Eupatorium buniifolium*) were collected within a 1.3 -11.8 km range of UTPM (63 samples) and 0.5 - 5.6 km of UTC (29 samples) in the direction of prevailing winds (SW in Candiota and SE in Charqueadas). The sampling was restricted to previously determined areas, with the plants at the center and angles of 55º and 110º . (See Figure 1).

The samples of honey were collected in the places of production within a range of 0.5 -22.0 km (17 samples) from UTPM and 3.5 - 32.0 km (13 samples) from UTC in the areas of sampling previously determined.

Reference forage grass samples were collected at about 50 km from UTPM and 20 km from UTC in a direction contrary to prevailing winds. Reference samples of honey were obtained from different localities, in areas not affected by anthropogenic processes.

The pasture material collected was reduced to maximum lengths of 2 mm using a micromill and dried in an oven at 50º C for 5 hours. Two-gram samples of the dried material was subsequently washed for 2 hours with 70 ml of 0.46% HNO_3. The solution was filtered using filter paper and the volume was



DES. TÉC. ESP. AHC · 1993

FIGURE 1. SAMPLING AREAS: CANDIOTA (UTPM - USINA TERMOELÉTRICA PRESIDENTE MEDICI) AND CHARQUEADAS (UTC - USINA TERMOELÉTRICA DE CHARQUEADAS), RIO GRANDE DO SUL, BRAZIL.

completed to 100 ml with 0.46% HNO_3 (Solution 1; F^- extracted). The residue was dried at 50º C for 8 hours and transferred to a 250 ml PTFE container and subjected to acid digestion under pressure. After adding 10 ml of conc. HNO_3 and 2 ml of 30% H_2O_2, the system was hermetically sealed and heated at 150º C for 6 hours. After cooling and relieving the pressure, 5 ml of conc. NH_4OH were added. The solution was filtered and diluted to 100 ml with 0.46% HNO_3 (Solution 2; F^- absorbed).

The treatment of the samples of honey was also done using high pressure and PTFE containers. To a 2 g sample of honey 7 ml of conc. HNO_3 and 1 ml of 30% H_2O_2 were added and the system was heated at 130º C for 4 hr . Subsequently the solution was cooled, the system opened, 3 ml of concentrated NH_4OH were added, followed by dilution to 50 ml with 0.46% HNO_3 (Solution 3, F^-, honey).

Solutions 1,2 and 3 were analyzed by direct potentiometry using a fluoride ion-selective electrode (ISE-F^- Analion F656) and a calomel reference electrode (Jena Glass B281) coupled with a Philips PW 9409 digital potentiometer. Buffer solution for total ionic strength adjustment (TAFIT) was added to the samples at 1:1 (v/v) ratio[14] and the measurements were made under constant agitation. Blank samples were also analyzed using the tecnique of standard addition.

RESULTS AND DISCUSSION

Fluorine, like other elements such as Hg,As and Se passes with relative ease through electrostatic filters and for this reason thermoelectric power plants exhibit a high concentration of emission of this atmospheric pollutant (up to 75%)[10]. (See Table I).

Deposition of fluoride from the atmosphere is an important factor in the contamination of biosphere reservoirs. Plants are particularly affected, since they absorb fluoride easily from the air[15,16,17]. They show cellular membrane damage and leaf necrosis[18,19,20]. The absorption of fluoride from the soil is relatively low, due to its reduced mobility in this environment. Fluoride is concentrated in the aerial parts of plants, where its physiologic effects are more pronounced[21,22]. For this reason, bioindication of pollution can be done using only the superior parts of the plants and analysis of the roots is not necessary.

Tables II and III show the concentration of fluoride (F^- extracted, F^- absorbed and F^- total) from pastures in the regions studied as a function of distance, time of collection and direction. Individual values of total fluoride concentration surpass 30 to 40 ppm, usually refered to as a limiting value, above which there is clear indication of physiologic damages[23,24,25,26].

TABLE I. MATERIAL BALANCE FOR UTPM POWER PLANT.[10]

Element	Coal (ppm)	Bottom Ash (ppm)	Light Ash (ppm)	Emission (kg/d)	Losses (%)
F	169	48.5	83.5	1,115	75
Hg	0.76	0.18	0.43	4.8	73
As	2.56	0,05	0.15	21.7	97
Se	1.46	0.34	0.83	9.3	73

Coal consumption: 10,300 t/d; Effectiveness of electrostatic filters: ~92.5%

TABLE II. CONCENTRATION (PPM) OF FLUORIDE IN SAMPLES OF PASTURE FROM CANDIOTA REGION (INDIVIDUAL VALUES). AVERAGE VALUES AND STANDARD DEVIATIONS OF TWO OR MORE DETERMINATIONS FOR EACH SAMPLE.

Time of Collection	(km)*	F^- abs.	F^- ext.	F^- total
November/1987	1.5	9.00 ± 0.15	44.39 ± 0.30	53.30
November/1987	3.5	11.13 ± 1.52	20.65 ± 3.42	31.78
November/1987	5.0	39.73 ± 0.15	5.61 ± 0.21	45.34
November/1987	5.0	47.87 ± 4.58	11.91 ± 1.57	59.78
November/1987	5.0	8.38 ± 1.90	2.42 ± 1.06	10.70
April/1988	1.5	27.82 ± 0.84	18.63 ± 2.54	46.45
April/1988	3.5	16.09 ± 1.83	9.21 ± 1.13	25.30
April/1988	4.0	20.23 ± 2.75	10.45 ± 1.13	30.68
April/1988	5.0	15.84 ± 1.97	9.35 ± 1.55	25.19
April/1988	5.0	41.23 ± 3.96	17.02 ± 3.11	58.25
April/1988	6.0	18.20 ± 0.85	11.01 ± 1.41	29.21
April/1988	6.5	28.42 ± 0.48	11.20 ± 0.22	39.62
April/1988	7.0	29.82 ± 0.36	10.45 ± 1.42	40.27
April/1988	9.0	24.63 ± 0.18	8.82 ± 0.48	33.45
April/1988	10.0	18.03 ± 2.45	5.84 ± 0.84	23.87
August/1988	1.3	8.46 ± 0.82	3.01 ± 0.42	11.47
August/1988	1.5	20.95 ± 2.19	4.60 ± 0.35	25.55
August/1988	1.5	6.67 ± 0.60	2.51 ± 0.57	9.18
August/1988	2.8	28.15 ± 1.20	3.04 ± 0.15	31.19
August/1988	3.0	27.70 ± 2.40	3.98 ± 0.68	31.68

TABLE II. (CONTINUATION)

August/1988	3.0	7.75±1.06	2.74±0.05	10.49
August/1988	4.7	9.67±0.24	3.00±0.70	12.67
August/1988	5.0	6.65±0.71	2.45±0.14	9.10
August/1988	5.0	23.42±0.59	5.05±0.21	28.47
August/1988	6.7	10.87±0.17	2.40±0.14	13.27
August/1988	7.0	9.32±0.45	3.12±0.03	12.44
August/1988	7.0	7.05±0.21	1.97±0.17	9.02
August/1988	8.6	4.95±0.63	1.93±0.11	6.88
August/1988	9.0	12.12±0.53	1.55±0.14	13.67
August/1988	11.0	5.50±0.71	1.67±0.24	7.17
August/1988	11.5	3.95±0.35	1.49±0.21	5.44
August/1988	11.8	6.16±0.59	3.26±0.13	9.42
January/1989	1.3	8.17±0.24	6.27±0.03	14.44
January/1989	1.6	8.22±1.73	2.74±0.70	10.96
January/1989	1.6	6.77±0.10	2.52±0.03	9.29
January/1989	2.8	12.50±2.96	2.07±0.11	14.57
January/1989	3.1	15.37±0.17	4.03±0.18	19.40
January/1989	3.1	4.26±0.68	2.10±0.14	6.36
January/1989	4.6	6.00±0.28	4.65±0.21	10.65
January/1989	5.0	4.50±0.28	2.25±0.21	6.75
January/1989	5.0	4.25±0.35	2.43±0.11	6.68
January/1989	7.0	7.67±0.25	3.78±0.60	11.45
January/1989	7.1	5.05±0.28	3.60±0.28	8.65
January/1989	7.0	5.43±0.11	3.33±0.18	8.76
January/1989	8.2	14.65±0.21	3.13±0.32	17.78
January/1989	8.5	16.30±1.55	3.17±0.10	19.47
January/1989	11.0	3.87±0.53	3.58±0.24	7.45
January/1989	11.3	4.67±0.95	1.96±0.24	6.63
January/1989	11.8	4.05±0.14	2.40±0.13	6.45
August/1989	1.3	4.60±2.69	2.03±0.31	6.63
August/1989	1.6	9.20±0.08	2.89±0.49	12.09
August/1989	1.6	3.80±0.28	2.45±0.97	6.25
August/1989	2.8	6.00±0.00	2.69±1.10	8.69
August/1989	3.1	3.15±0.35	1.80±0.14	4.95
August/1989	3.1	2.75±0.35	1.70±0.14	4.45
August/1989	4.6	2.55±0.92	1.80±0.08	4.35
August/1989	5.0	3.60±1.65	1.87±0.04	5.47
August/1989	5.0	4.45±0.21	2.45±0.07	6.90
August/1989	7.1	2.48±0.11	1.68±0.74	4.16
August/1989	7.0	3.20±0.14	2.50±0.00	5.70
August/1989	8.5	2.15±0.07	1.35±0.21	3.50
August/1989	11.3	2.00±0.28	1.05±0.07	3.05
August/1989	11.8	4.05±0.21	1.95±0.07	6.00

F^- concentration in reference samples: F^- abs.=2.26±0.02; F^- ext.=1.15±0.00; F^- total=3.35 ppm

* Distance from UTPM

TABLE III. CONCENTRATION (PPM) OF FLUORIDE IN SAMPLES OF PASTURE FROM CHARQUEADAS REGION (INDIVIDUAL VALUES). AVERAGE VALUES AND STANDARD DEVIATIONS OF TWO OR MORE DETERMINATIONS FOR EACH SAMPLE.

Time of Collection	(km)*	F^- absorbed	F^- extracted	F^- total
July/1988	1.0	13.00±1.03	4.43±0.11	17.43
July/1988	2.0	6.87±0.04	4.05±1.20	10.92
July/1988	3.0	4.58±0.11	2.60±0.95	7.18
July/1988	4.0	6.20±0.39	2.51±0.49	8.71
July/1988	5.5	5.57±0.26	2.78±0.38	8.35
December/1988	0.5	10.28±1.19	4.53±0.78	14.81
December/1988	1.3	6.75±1.06	5.50±0.00	12.25
December/1988	1.6	5.63±0.32	2.23±0.03	7.86
December/1988	2.0	5.28±0.26	2.90±0.92	8.18
December/1988	2.6	4.52±1.02	2.93±0.25	7.45
December/1988	2.8	5.18±0.11	4.60±0.42	9.78
December/1988	3.5	32.25±2.47	4.75±0.90	37.00
December/1988	3.8	5.15±0.85	2.76±0.17	7.91
December/1988	5.0	16.70±1.84	2.03±0.32	18.73
December/1988	5.5	5.85±0.85	1.75±0.14	7.60
June/1989	0.5	26.90±0.56	27.85±0.21	54.75
June/1989	1.3	45.55±0.35	5.00±0.28	50.55
June/1989	1.3	47.15±0.21	13.55±0.07	60.70
June/1989	1.6	13.65±0.21	8.10±0.14	21.25
June/1989	2.0	24.35±0.64	8.50±0.00	32.85
June/1989	2.3	33.10±0.28	8.05±0.07	41.15
June/1989	2.6	36.30±0.00	7.13±0.18	43.43
June/1989	2.8	21.05±0.35	5.15±0.21	26.20
June/1989	3.5	3.10±0.28	3.00±0.14	6.10
June/1989	3.8	5.25±0.07	7.40±0.14	12.65
June/1989	3.9	4.75±0.07	6.70±0.42	11.45
June/1989	5.0	4.55±0.35	4.45±0.07	9.00
June/1989	5.5	3.25±0.07	6.40±0.14	9.65
June/1989	5.6	3.65±0.22	4.93±0.11	8.58

F^- concentration in reference samples: F^- abs.=2.26±0.02; F^- ext.=1.15±0.00; F^- total=3.35 ppm

* Distance from UTPM

The data in Tables II and III was submitted to two types of statistical treatment. The first one involved Analysis of Variance (ANOVA) and had as an objective to test if the factors such as distance, time of the year and/or direction of collection of samples interfere with the total concentration of fluoride in pasture. The level of significance adopted for ANOVA was 5%.

A comparison with the fluoride values calculated using ANOVA (*F^-test*) showed that for Candiota there was a real difference between the average values of fluoride as a function of time and for Charqueadas as a function of distance. The differences in each group were identified using Tuckey's Test with a significance level of 5%. (Table IV).

This means that for Charqueadas the average values of fluoride are statistically equal when grouped as a function of time and site of sampling and different when the concentrations are grouped as a function of distance.

On the other hand, in Candiota the average values of fluoride concentrations are statistically equal when grouped as function of site of collection and distance and are different and decrease when grouped as a function of the time of sampling (Figure 2). This fact can be explained by the use of new, more efficient electrostatic filters in UTPM starting with April 1988. These new filters have a higher capacity to capture the finer fraction of ash, possibly richer in fluoride.

Interestingly, the ANOVA test also showed , as expected, that the average concentrations were equal as a function of site of collection in both Candiota and Charqueadas. In Candiota this was explained by the major dispersion of the emitted fluorine due to the tall chimney (140 m). In Charqueadas, on the other hand, where the chimney is shorter (60 m) the possible explanation is the change in direction of the winds in the region.

The second statistical treatment involved identifying the average concentrations that are statistically equal as a function of time (in Candiota) and distance (in Charqueadas). Tuekey's Test, with significance levels of 5% was employed and the results are shown in Table IV.

It was shown that there are no real differences for the average values as a function of distance and direction in Candiota and time and direction in Charqueadas.

In Charqueadas, the concentration of fluoride decreases with the increase of distance from UTC. Statistically, this does not happen in Candiota, where the apparent decrease of concentration with distance from UTPM is casual and not real (Figure 2). This is in agreement with the ANOVA test and also with Tuckey's Test.

The tendency of increasing values as a function of time obtained in Charqueadas is apparent and is not confirmed by the ANOVA test. The decreasing variation of concentration in Candiota as a function of time of sampling is confirmed by the ANOVA test and may be explained by the use of new electrostatic filters, as previously mentioned.

TABLE IV. CONCENTRATION (PPM) OF FLUORIDE IN SAMPLES OF PASTURE FROM CANDIOTA AND CHARQUEADAS REGIONS (STATISTICAL VALUES).

	Lower limit ($\alpha/2=5\%$)	Average	Upper limit	Number of samples	F-test (calculated)	Tukey's test ($\alpha=5\%$)*		
			CANDIOTA REGION					
Distance (km)								
1→3	14.35	18.58	22.80	14	1.79		●	
3→5	17.05	21.28	25.51	14			●	
5→7	10.22	15.23	20.23	10			●	
7→9	7.77	12.34	16.91	12			●	
9→11	14.53	23.66	32.80	3			●	
11→13	0.86	6.45	12.05	8			●	
Time of Collection								
November 1987	33.12	40.20	47.28	5	23.97*	●		
April 1988	27.51	33.10	38.70	8		●		
August 1988	10.70	14.54	18.37	17			●	
January 1989	7.09	10.93	14.76	17			●	●
August 1989	1.64	5.87	11.00	14				●
			CHARQUEADAS REGION					
Distance (km)								
0→3	19.12	26.25	33.39	16	3.82*		●	
3→5	2.21	13.00	23.79	7			●	
5→7	0.00	10.32	21.97	6			●	
Time of Collection								
July 1988	0.00	10.51	23.28	5	2.76		●	
Dezember 1988	4.13	13.16	22.18	10			●	
June 1989	20.15	27.77	35.40	14			●	

* Significative value at level of 5% ($\alpha=5\%$)

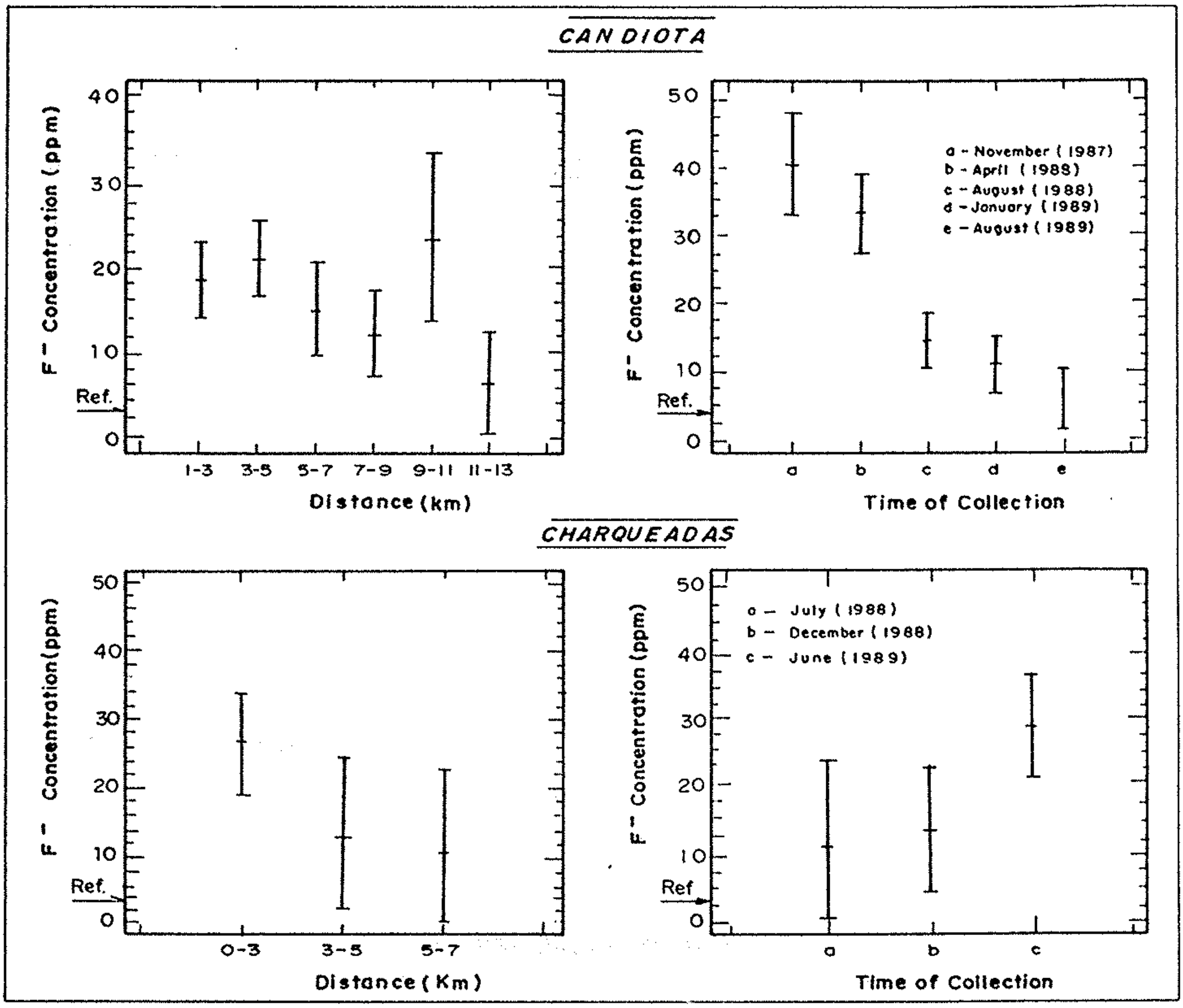


FIGURE 2. AVERAGE VALUES OF FLUORIDE CONCENTRATION (TOTAL) IN PASTURE FROM CANDIOTA AND CHARQUEADAS REGIONS AS A FUNCTION OF THE DISTANCE FROM UTPM AND UTC POWER PLANTS AND THE TIME OF COLLECTION.

TABLE V. CONCENTRATION (PPM) OF FLUORIDE IN SAMPLES OF HONEY FROM CANDIOTA AND CHARQUEADAS REGIONS.

CANDIOTA

Distance from UTPM (km)	Time of Collection	Concentration of Fluoride (ppm)
4.5	November/1988	4.92±0.14
4.0	November/1988	8.21±0.49
6.0	April/1988	4.22±0.74
8.0	April/1988	4.50±1.41
12.0	April/1988	4.20±1.27
0.5	June/1988	1.60±0.14
6.0	June/1988	1.45±0.14
8.5	June/1988	8.80±0.63
12.0	June/1988	1.98±0.17
10.5	November/1988	7.81±2.04
12.0	November/1988	1.42±0.30
12.1	November/1988	1.85±0.35
22.0	November/1988	1.50±0.08
22.0	June/1989	1.25±0.08
11.5	January/1990	1.52±10.09
12.0	January/1990	1.43±10.11
22.0	January/1990	1.01±10.07

CHARQUEADAS

Distance from UTC (km)	Time of Collection	Concentration of Fluoride (ppm)
3.5	May/1988	6.83±0.41
15.0	May/1988	1.76±0.51
20.0	May/1988	5.18±0.21
4.0	November/1988	5.54±1.13
4.0	November/1988	1.57±0.17
4.0	November/1988	3.55±3.25
4.0	November/1988	1.26±0.03
4.0	May/1989	0.77±0.04
6.0	May/1989	1.15±0.03
6.5	May/1989	0.12±0.04
18.0	May/1989	0.15±0.06
32.0	May/1989	5.50±0.09

Average values and standard deviations of two or more determinations for each sample

F^- concentration in reference samples: <0,02 ppm

The variation of concentration as a function of direction is not statistically real and is not significant according to the ANOVA test for both power plants. In Candiota this may be attributed to a greater dispersion of the emitted fluorine, considering the high chimney (140 m). In Charqueadas, on the other hand, where the chimney is lower (60 m), the explanation given is as a function of possible variations in the direction of winds in the region.

In Candiota the average concentration of fluoride in pasture varied from 6.5 to 23.7 (as a function of distance); 5.9 to 40.2 (time of collection) and 8.3 to 15.3 ppm (direction). In Charqueadas the respective ranges were 10.3 to 26.3 ; 10.5 to 27.8 and 16.3 to 30.5 ppm (Table IV).

The samples of honey analyzed exhibited higher concentration of fluoride when compared to samples from non-contaminated areas. Table V shows the concentration of fluoride as a function of distance from UTPM and UTC at the respective times of sampling.

In Candiota, the concentration of fluoride in honey ranged from 1.0 to 8.8 ppm and decreased as a function of time and distance from UTPM. In Charqueadas the values ranged from 0.12 to 6.8 ppm . The variation of concentration as a function of distance passes through a minimum at about 15 km from UTC and subsequently increases. This may be explained due to the presence of another power plant about 30 km from UTC , in the direction of the collection of samples (Usina Termoelétrica de São Jerônimo , 17 MW).

In both cases, the concentration of fluoride in honey decreased as a function of time of sampling and exhibited values considerably higher than in reference samples (0.02 ppm). See Table V.

No correlation was found between the concentration of fluoride in the samples and the distance from the respective power plants. Eight different models were tested (linear, exponential, multiplicative and their variations).

The experimental results obtained for the determination of fluoride in the environmental samples of pasture and honey studied, lead to the conclusion that these materials may be used as bioindicators of pollution in areas of industrial activity.

In spite of the decreasing tendency of the values observed as a function of time in Candiota, we may generally conclude that even more recent values of fluoride concentration are above those of reference samples. This conclusion is reinforced by the occurrence of various cases of bone deformation (fluorosis) and pronounced dental wear and waste in ruminants in the vicinity[27]. A synergetic effect of fluoride adsorbed on pasture on the abrasion of coal ash deposited on graze lands is observed. The use of samples of pasture and honey, coupled to a convenient statistical treatment, as bioindicators of pollution is recommended. They may be part of a procedure to evaluate possible contamination and consequent damages resulting from the anthropogenic dispersion of fluoride in the environment.

REFERENCES

1. A. Kabata-Pendias and H. Pendias *"Trace Elements in Soil and Plants"* CRC Press Inc. , Miami, Florida, 1984, p. 214.
2. D. A. Cataldo, R. E. Wildung and T. R. Garland, *Environ. Qual., 16(4)*, 289-295 (1987).
3. A. Chamel and J. P. Garbec, *Environ. Pollut., 12*, 307 (1977).
4. R. J. Taylor and F. A. Basabe, *Environ. Pollut. (Series A), 33(3)*, 221-237 (1984).
5. D. Purves, *"Trace-Element Contamination of the Environment"*, Elsevier Science Publishers, Amsterdam, 1985, p. 63.
6. World Health Organization (OMS), *"Environmental Health, Criteria 36 - Fluorine and Fluorides"*, Helsinki, Finland, 1984, p. 17.
7. E. Groth, *Environment, 17*, 29-37 (1975).
8. D. J. Swaine, *CRC Critical Reviews in Analytical Chemistry, 15(4)*, 315-346 (1985).
9. B. I. Kronberg, J. R. Brown, W. S. Fyfe, M. Pierce and C. G. Winder, *Fuel, 60*, 59-63 (1981).
10. R. Zanella, *"Investigação de Problemas Ambientais Relacionados com a Exploração Intensiva e a Queima de Carvão Termoelétrico em Candiota, RS"*, Dissertação de Mestrado, CPGQ, Universidade Federal de Santa Maria, Santa Maria, RS, Brasil, 1983.
11. J. J. O'Toole, T. E. Wessels and K. L. Malaby, *J. Plant Nutrition, 3*, 397-407 (1981).
12. E. M. M. Flores, *" Utilização de Amostras Ambientais das Regiões de Candiota e de Charqueadas (RS) como Bioindicadores de Poluição"*, Dissertação de Mestrado, CPGQ, Universidade Federal de Santa Maria, Santa Maria, RS, Brasil, 1990.
13. D. F. Perkins and R. O. Millar, *Environ. Pollut., 48(3)*, 185-196 (1987).
14. Analion, *"Manual de Instruções do Eletrodo de Fluoreto Modelo F656"*, p. 12.
15. D. C. McCune and L.H. Weinstein, *Environ. Pollut., 1*, 169-174 (1970).
16. H. L. Bohn, *J. Environ. Qual., 1(4)*, 372-377 (1972).
17. Jia-Xi Wang and Mei Yong, *Environ. Pollut., 52(1)*, 11-18 (1988).
18. H. W. F. Bunce, *Environ. Pollut. (Series A), 35*, 169-188 (1984).
19. J. Bossavy, *J. Pollut. Atmos., 30*, 166-184 (1966).

20. L. J. Van der Erden, A. E. G. Tonnejk and J.H. M. Wijnands, *Environ. Pollut., 53,* 365-376 (1988).

21. J. Bossavy, *Rev. For. Fr., 22,* 533-543 (1970).

22. J. S. Jacobson , L. H. Winstein, D. C. McCune and A. E. Hitchcock, *J. Air Pollut. Control Assoc., 16,* 412-417 (1966).

23. I. Sunshine, *"Handbook of Analytical Toxicology",* Chemical Rubber Company, Akron, Ohio, USA, 1979, pp. 698-699.

24. J. P. Garrec and R. Plebin, *Rev. Sci. Tot. Environ., 50,* 183-189 (1986).

25. J. L. Shupe, *J. Animal Sci., 51,* 746-758 (1980).

26. J. W. Suttie, *J. Occup. Med., 19,* 40-48 (1977).

27. F. Riet-Correa, M. D. C. Mendez, A. L. Schild and O. Zenebon, *Pesq. Vet. Bras. 6(1),* 23-31 (1986).

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

Vol. 1, No. 1, 1993

MICELLAR CATALYZED HYDROLYSIS OF A PHOSPHATE ESTER IN AQUEOUS SOLUTIONS CONTAINING DIMETHYL SULFOXIDE

Lavinel G. Ionescu* and Elizabeth Fátima de Souza§
Instituto de Química
Pontifícia Universidade Católica do Rio Grande do Sul
Porto Alegre, RS BRASIL 90610-001
&
Departamento de Química
Universidade Luterana do Brasil
Canoas, RS BRASIL 92420-280

ABSTRACT

The hydrolysis of p-*nitrophenyldiphenyl phosphate was studied in aqueous solutions containing micelles of diethylheptadecylimidazolinium ethyl sulfate (DEHIES), sodium hydroxide and various concentrations of dimethyl sulfoxide (DMSO). Pseudo-first order* (k_ψ) *and second order rate constants* (k_2) *were determined at 15°, 25° and 35 °C and activation parameters such as* E_a, $\Delta G^{\neq}$, $\Delta H^{\neq}$ *and* $\Delta S^{\neq}$ *were also measured. The rate profiles obtained for solutions containing 10-50% DMSO by volume exhibited clear maxima that shifted to higher concentrations of DEHIES as a function of DMSO added. For solutions containing 60-80% DMSO there was no maximum in the rate profile and inhibition of the reaction took place. Solutions containing 90% by volume of DMSO exhibited much higher reaction rates and considerably more catalysis. The experimental results are explained in terms of the Hughes-Ingold Theory, specific solvent effects, polarity and internal pressure of the reaction medium. The interpretation and discussion of the results takes into consideration the formation of the stoichiometric hydrate* $DMSO \cdot 2H_2O$ *and the inhibitory effect of dimethyl sulfoxide on the formation of micelles of DEHIES.*

RESUMO

A hidrólise do p-*nitrofenildifenilfosfato foi estudada em soluções contendo micelas de dietilheptadecil-etilsulfato-imidazolínio (DEHIES), hidróxido de sódio e várias concentrações de dimetilsulfóxido (DMSO). Foram determinadas constantes de velocidade de pseudo-primeira ordem* (k_ψ), *segunda ordem* (k_2) *e parâmetros de ativação tais como* E_a, $\Delta G^{\neq}$, $\Delta H^{\neq}$ *e* $\Delta S^{\neq}$. *Para soluções contendo 10-50% de DMSO por volume os perfis de velocidade apresentam um máximo bem definido, deslocado para concentrações mais elevadas de DEHIES em função de DMSO adicionado. Para soluções com 60-80% DMSO não há um máximo no perfil de velocidades e ocorre uma inibição da reação. Para soluções contendo 90% por volume de DMSO, as velocidades de reação são consideravelmente mais elevadas com catálise muito pronunciada. Os resultados experimentais são explicados em termos da Teoria Hughes-Ingold, dos efeitos específicos do solvente, da polaridade e da pressão interna do meio de reação. A discussão e interpretação dos resultados leva em consideração a formação do hidrato estequiométrico* $DMSO \cdot 2H_2O$ *e o efeito inibitório do DMSO sobre a formação de micelas de DEHIES.*

KEYWORDS: Micellar Catalysis, Dimethyl Sulfoxide, Internal Pressure, Solvente Effects, Mixed Solvent Systems, Phosphate Esters

---

* *Author to whom correspondence should be addressed.*

§ *PPGEMM-UFRGS*

DOI: 10.48141/SBJCHEM.v1.n1.1993.79_1993.pdf

INTRODUCTION

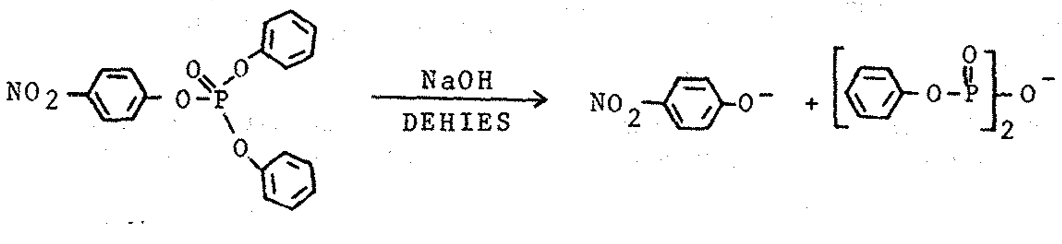
Phosphate esters represent a group of compounds with interesting biochemical and pharmacological properties and have a wide use as pesticides, drugs and nerve gases.[1,2]

In previous studies we have shown that the hydrolysis of *di-* and *tri-*substituted phosphate esters is catalyzed by micelles of cetyltrimethylammonium bromide (CTAB) and also by micelles of N,N-dimethyl-N-hydroxyethyldodecylammonium bromide (DHEDAB) and N,N-dimethyl-N-hydroxyethylcetylammonium bromide (CHEDAB).[3] Micelles of DHEDAB and CHEDAB are excellent catalysts for the hydrolysis of both lithium *p*-nitrophenyl ethyl phosphate (LiPNEF) and *p*-nitrophenyldipnehyl phosphate (PNFDF) in the presence of OH^-, with over a 300-fold rate enhancement for the hydrolysis of the triaryl phosphate in the presence of CHEDAB. The catalytic effect and the dependence of the reaction rate on hydroxide-ion concentration has been explained in terms of nucleophilic participation of the alkoxide ions of DHEDAB and CHEDAB, with values of pK_a of 12,4 and 12,9, respectively for the ionization of the hydroxyl group. For reactions with fluoride ion, the hydroxy-substituted surfactants (functional micelles) are no better catalysts than the corresponding alkyltrimethyl ammonium bromides, suggesting that electrophilic catalysis is relatively unimportant. Cetylpyridinium bromide (CPBr) has approximately the same effect as CTAB at low hydroxide concentration and a slightly more pronounced effect with fluoride ion. Zwitterionic surfactants such as lauryl carnitine chloride (LCCl) and palmityl carnitine chloride (PCCl)[4,5] have little effect on the rate of hydrolysis of LiPNEF.

The addition of primary amines increased the rate of reaction in the presence of CTAB and CHEDAB for the triaryl phosphate, but much of the increase was due to attack by amine on the aryl group. In the absence of micells, amines increased the overall rate of the reaction by attacking the aryl group without markedly catalyzing hydrolysis.[6]

The study of the micellar catalyzed dehydrochlorination of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and some of its derivatives, as well as the hydrolysis of lithium *p*-nitrophenyl ethyl phosphate (LiPNEF) in the presence of higher concentrations of hydroxide ion (0,10 to 5,0 M) in the presence and absence of salts, showed that the pseudo-phase ion exchange model fails and does not explain experimental results. In fact, some systems contain liquid crystalline mesophases and a model analogous to phase transfer catalysis seems more appropriate.[7-15]

The present paper deals with the study of the hydrolysis of *p*-nitrophenyl diphenyl phosphate in aqueous solutions containing sodium hydroxide, micelles of diethylheptadecylimidazolinium ethyl sulfate (DEHIES) and dimethyl sulfoxide (DMSO). The reaction under consideration is illustrated below.



(I)

EXPERIMENTAL PROCEDURE

MATERIALS. The phosphate ester, *p*-nitrophenyl diphenyl phosphate (PNFDF) was prepared by standard methods[16-19]. A sample was also obtained from Prof. Fred M. Menger, Emory University, Atlanta, Georgia, USA. The surfactant, diethylheptadecylimidazolinium ethyl sulfate (DEHIES) was obtained from Chem Service Inc., West Chester, Pennsylvania, USA. Dimethyl sulfoxide (DMSO) and sodium hydroxide were analytical reagent grade and were purchased from Merck do Brasil, Rio de Janeiro. They were used without further purification.

MICELLE FORMATION. The critical micellar concentration (CMC) of the surfactant DEHIES was determined at 25º, 32º and 40ºC by measurement of the surface tension of DEHIES-H_2O-DMSO solutions using a Fisher Model 21 Semi-Automatic Tensiometer. The thermodynamic parameters for micellization including the free energy, ΔG^o_m, enthalpy, ΔH^o_m and the entropy of micellization, ΔS^o_m, were calculated from CMC data using standard equations.[20-22]

KINETICS. The hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNFDF) was studied spectrophotometrically measuring the rate of appearance of the *p*-nitrophenoxide ion at 4030 Å. A Varian DMS-80 spectrophotometer equipped with a water-jacketted cell compartment was used. The reaction was studied at 15º, 25º and 35º C at various concentrations of NaOH, DMSO and DEHIES. The pseudo-first order rate constant ,k_ψ , in sec^{-1} was determined from linear plots of $\ln(A_\infty - A_t)$ versus time. The second order rate constants (k_2) were calculated from k_ψ and the hydroxide ion concentration. Activation parameters such as E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ were also determined using the following equations.

$$\ln k_\psi = \ln A - (E_a/R)(1/T) \qquad (II)$$

$$\Delta H^{\neq} = E_a - RT \qquad (III)$$

$$\Delta S^{\neq} = 4{,}576(\log k_\psi - 10{,}753 - \log T + E_a/4{,}576T) \qquad (IV)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (V)$$

RESULTS AND DISCUSSION

Some representative results obtained for the critical micellar concentration (CMC) of DEHIES at 25º and 40ºC are illustrated in Table I. The CMC values were obtained from the inflection point of plots of surface tension versus concentration or logarithm ($\log_{10}$) of the concentration for fixed amounts of DMSO. As can be seen, the critical micellar concentration of the surfactant increases both as a function of temperature and DMSO added. The addition of DMSO hinders the formation of micelles in the DEHIES-H_2O-DMSO ternary system.

TABLE I. CRITICAL MICELLAR CONCENTRATION OF DIETHYLHEPTADECYLIMIDAZOLINIUM ETHYL SULFATE IN AQUEOUS SOLUTIONS CONTAINING DIMETYL SULFOXIDE AT 25º AND 40º C.

Percent DMSO (by volume)	Mole Fraction (X_{DMSO})	CMC at 25ºC (M x 10^3)	CMC at 40ºC (M x 10^3)
0	0.000	0,25	0,28
10	0,028	0,40	0,45
20	0,060	0,44	0,50
30	0,099	0,55	0,66
40	0,145	1,10	1,32
50	0,203	2,75	3,47
60	0,277	5,13	6,61

TABLE II. THERMODYNAMIC PARAMETERS FOR THE FORMATION OF MICELLES OF DIETHYLHEPTADECYLIMIDAZOLINIUM ETHYL SULFATE IN AQUEOUS SOLUTIONS OF DIMETHYL SULFOXIDE AT 25ºC.

Percent DMSO (by volume)	Mole Fraction (X_{DMSO})	ΔG°_m (kcal/mol)	ΔH°_m (kcal/mol)	ΔS°_m (eu)
0	0,000	-4,91	-1,41	+11,8
10	0,028	-4,64	-1,47	+10,6
20	0,060	-4,58	-1,59	+10,0
30	0,099	-4,45	-2,27	+ 7,3
40	0,145	-4,04	-2,26	+ 6,0
50	0,203	-3,49	-2,28	+ 2,1
60	0,277	-3,12	-3,15	+ 0,1

Table II summarizes the thermodynamic parameters obtained for the micellization of DEHIES in aqueous solutions of DMSO at 25°C. The standard free energy of micellization, ΔG_m^o, varies almost linearly from -4,64 kcal/mole to -3,12 kcal/mole with increasing concentration of DMSO. The value of ΔG_m^o determined for DEHIES alone in pure water was -4,91 kcal/mole, indicating that the micellization process is more spontaneous in pure water. The enthalpy of micellization, ΔH_m^o, calculated experimentally is exothermic and similar to water for low concentrations of DMSO (-1,41 to -1,59 kcal/mole). For higher concentrations it becomes more pronounced (more exothermic), indicating stronger interactions between H_2O and DMSO. ΔS_m^o decreases gradually from +11,8 to +0,1 eu.

Similar results have been reported for the cetyltrimethylammonium - water-dimethyl sulfoxide system (CTAB-H_2O-DMSO) and have been explained in terms of the formation of the DMSO·$2H_2O$ stoichiometric hydrate.[24-26] As can be seen in Table II from the ΔS_m^o values, an increase in orderliness of the DEHIES-H_2O-DMSO system takes place as the mole fraction of DMSO is increased. In fact, results of proton spin-lattice relaxation studies have shown that the increased structuring of the DMSO-H_2O liquid system resulting in the formation of the stoichiometric hydrate DMSO·$2H_2O$ overcomes the hydrophobic effect of the alkyl chain of CTAB and inhibits totally the formation of micelles at a mole fraction of DMSO (X_{DMSO}) of about 0,33 in accordance with results obtained by surface tensiometry. Under these conditions plots of surface tension for CTAB-H_2O-DMSO versus concentration of CTAB are linear.

Proton spin-lattice relaxation times ($1/T_1$) and average rotational correlation times, $\tau_s(R)$, for the terminal methyl, N-methyl and methylene groups of CTAB as well as effective activation energies obtained for the various relaxation processes in water-dimethyl sulfoxide solutions showed that the surfactant molecules become trapped in the crystalline lattice of the DMSO·$2H_2O$ hydrate.[25-27]

Some typical experimental results obtained for the pseudo-first order rate constant k_ψ for the hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNFDF) at 25°C as a function of DEHIES and various fixed amounts of NaOH are shown in Figure 1. The rate profiles are representative of micellar catalyzed reactions. The addition of surfactant to the reaction medium causes an increase in the rate of hydrolysis up to a point where there is complete incorporation of the substrate in the micellar phase. Further increase in the concentration of surfactant causes a decrease in the rate of reaction, probably due to dilution of the reactive counterions in the Stern layer. There is a maximum in all rate profiles at about 15 x 10^{-4} M DEHIES as compared to 20 x 10^{-4} M for CTAB. All curves also show a secondary maximum at about 8 x 10^{-4} M DEHIES that is probaly due to the formation of premicellar aggregates. For aqueous solutions containing 0,020 M NaOH the catalytic effect (ratio of the rate in the presence and absence of surfactant under the same conditions) is about 40-fold for DEHIES as compared to 80-fold for CTAB. The difference is

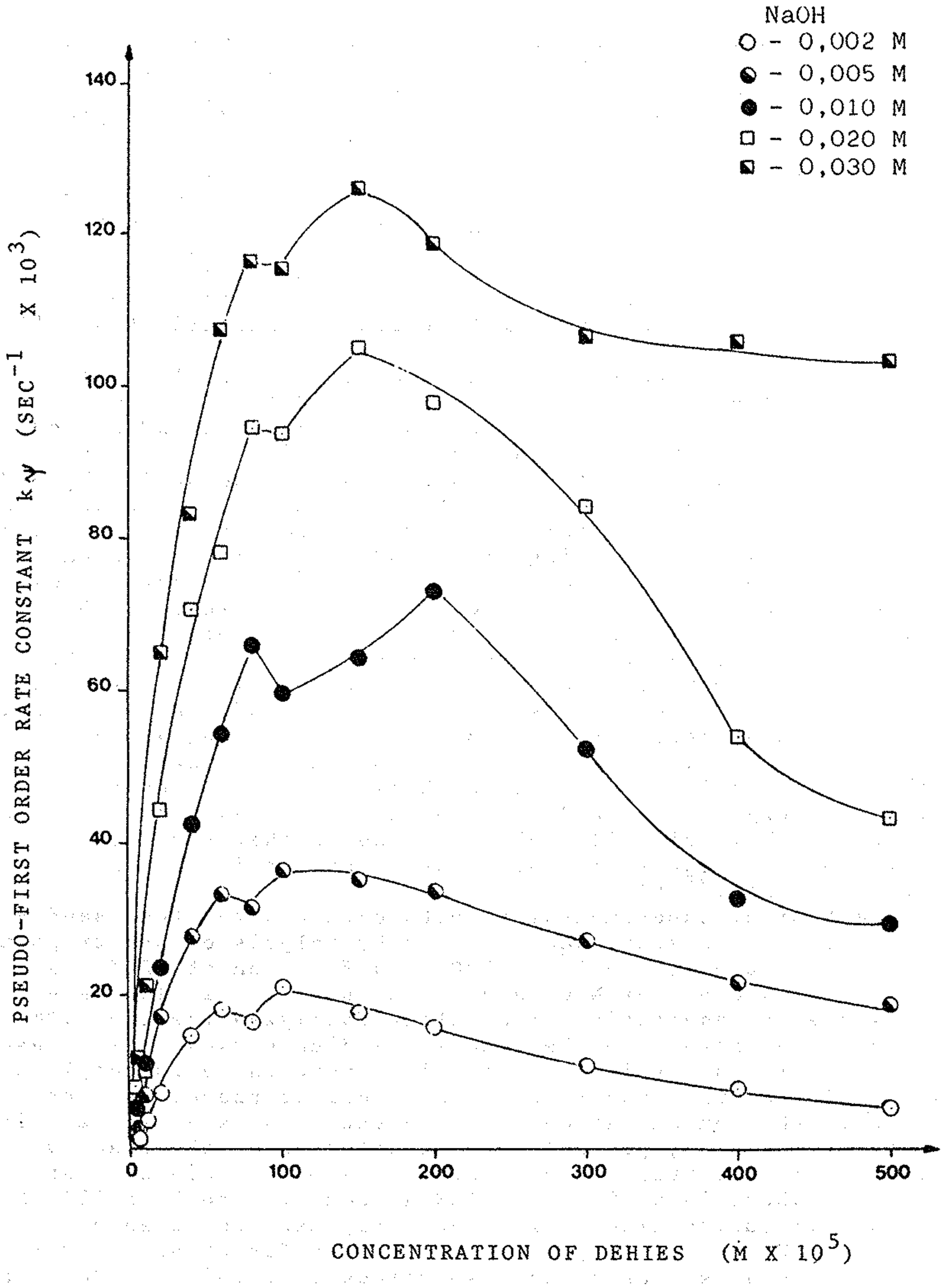


FIGURE 1. RATE PROFILES FOR THE HYDROLYSIS OF *p*-NITROPHENYL DIPHENYL PHOSPHATE AT 25°C IN AQUEOUS SOLUTIONS CONTAINING SODIUM HYDROXIDE AND MICELLES OF DIETHYL-HEPTADECYLIMIDAZOLINIUM ETHYL SULFATE (DEHIES).

attributed to the large difference in the head group of the two surfactants. Second order rate constants for the reaction (k_2) have an average value of 6,0 sec^{-1} $mole^{-1}$ and the reaction can be essentially considered as second order in hydroxide ion.

Figure 2 illustrates typical rate profiles obtained for the hydrolysis of PNFDF in aqueous solutions containing 0,010 M NaOH and different concentrations of surfactant and dimethyl sulfoxide at 25°C. For a fixed concentration of 30% DMSO by volume there is a similar behavior to that observed for the aqueous solutions without DMSO, with a maximum in the rate profile shifted to higher concentrations of surfactant. For solutions with 60% DMSO by volume there is a relative inhibition of the reaction, but the reaction rates are slightly higher than for the corresponding DMSO-H_2O solutions without surfactant. There is no clear maximum in the rate profile. For solutions containing 90% DMSO by volume the reaction rates measured are considerably higher than under other conditions studied. An inhibition of the reaction takes place at concentrations above 20 x 10^{-4} M DEHIES.

Figure 3 shows the variation of the pseudo-first order rate constant at 25°C for the reaction under consideration in the absence of surfactant at a fixed concentration of NaOH (0,010M) and varying mole fraction of DMSO.

Figure 4 illustrates the dependence of the pseudo-first order rate constant (k_ψ) on the mole fraction of DMSO for fixed concentrations of NaOH (0,010 M) and surfactant (15 x 10^{-4} M DEHIES).

Figure 5 shows on the same scale the results mentioned above and compares them to those obtained for aqueous solutions containing a fixed concentration of cetyltrimethyl ammonium bromide (CTAB = 20 x 10^{-4} M), at the maxima in the rate profiles.

It can be clearly noted that low concentrations of DMSO have a pronounced effect on the reaction rates in the presence of the two surfactants. At mole fractions of DMSO above 0,2 the rate constants for the three systems H_2O-DMSO, H_2O-DMSO-CTAB and H_2O-DMSO-DEHIES become much less sensitive to the addition of the cosolvent.

A more detailed analysis of Figure 5 shows three different types of behavior of the rate constant as a function of the mole fraction of the cosolvent. In the DMSO mole fraction range where micelle formation takes place (10-60% by volume), an increase in the amount of cosolvent decreases the rate of the reaction. At about 70% by volume of DMSO the rate constant attains minimum values and at concentrations of DMSO above 80% by volume the reaction rates increase considerably.

The three different behaviors of the rate constants (that are essentially similar for CTAB and DEHIES) are explained in terms of the effect of DMSO on micelle formation. At low concentrations of DMSO where micelles exist, but the micellization process is inhibited by DMSO, the addition of the cosolvent decreases the rate constant of the reaction. At higher concentrations of DMSO, where there are no micelles, the system is essentially controlled by the influence of the dipolar aprotic solvent that also acts as a catalyst for the reaction. In the intermediate region (60-70% by volume of cosolvent), where the stoichiometric hydrate DMSO·$2H_2O$ forms, the behavior is similar to the solution without

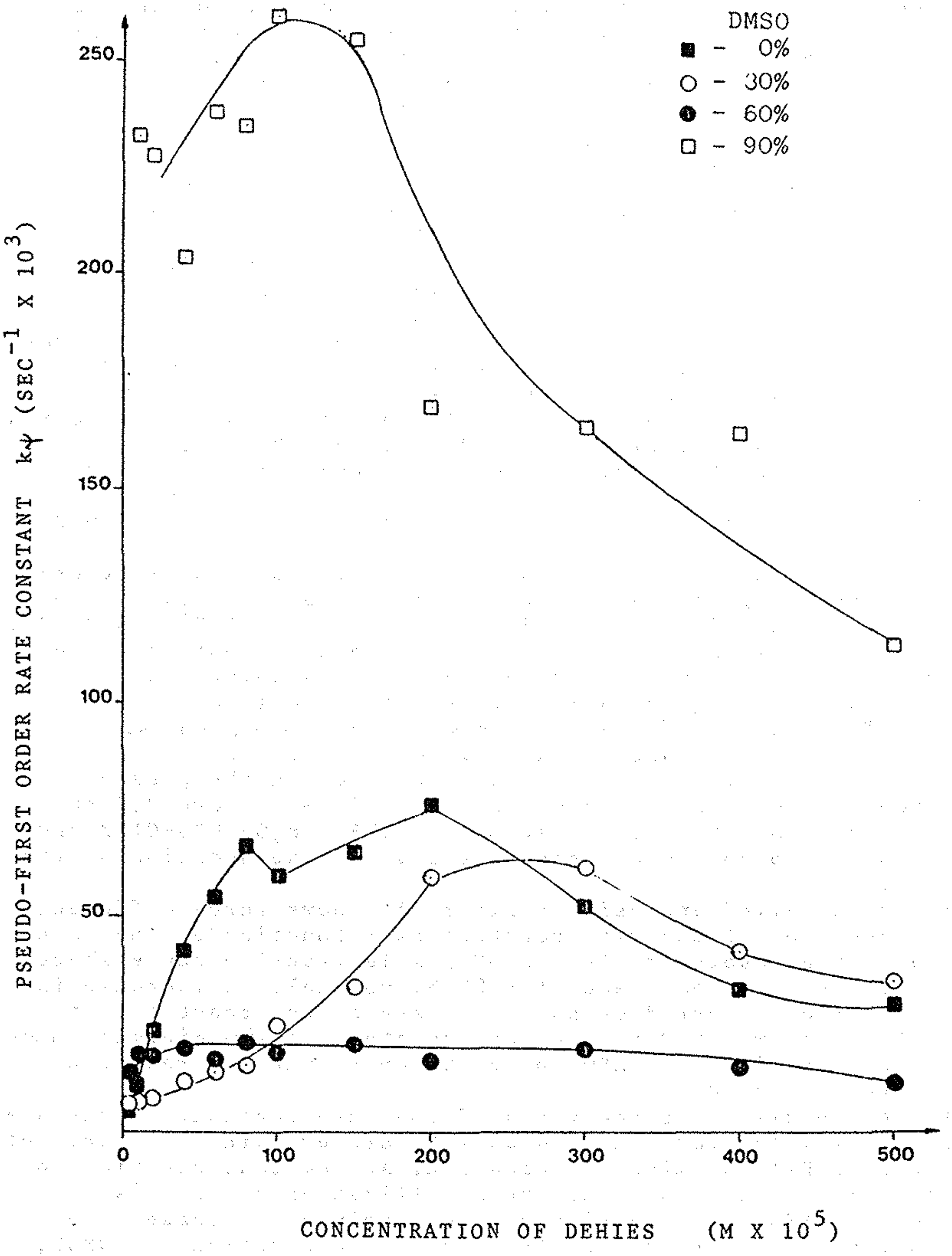


FIGURE 2. RATE PROFILES FOR THE HYDROLYSIS OF *p*-NITROPHENYL DIPHENYL PHOSPHATE AT 25ºC IN AQUEOUS SOLUTIONS CONTAINING 0,010 M SODIUM HYDROXIDE IN THE PRESENCE OF DEHIES AND VARIOUS CONCENTRATIONS OF DMSO.

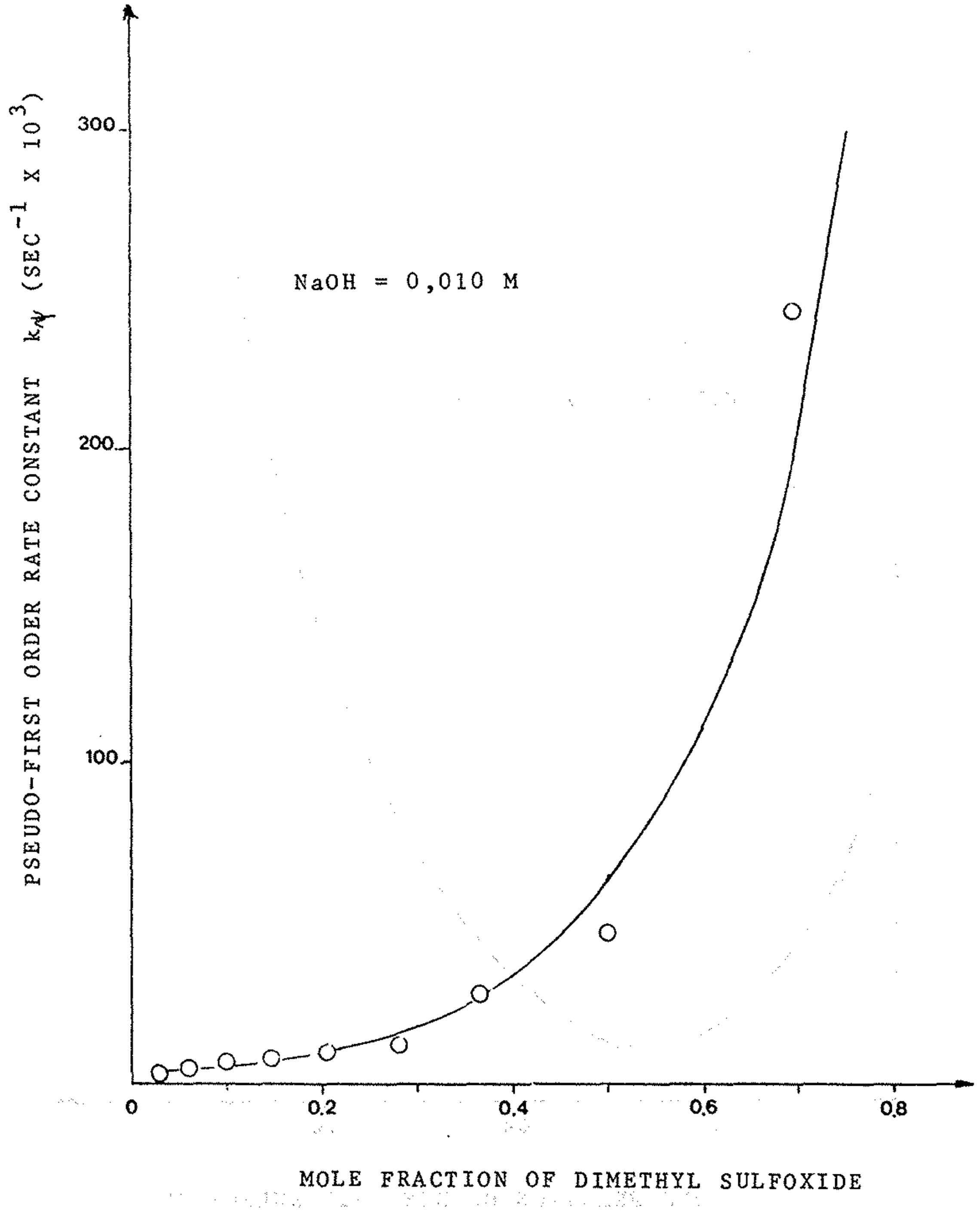


FIGURE 3. PLOT OF THE PSEUDO-FIRST ORDER RATE CONSTANT FOR THE HYDROLYSIS OF *p*-NITROPHENYL DIPHENYL PHOSPHATE AT 25°C AS A FUNCTION OF THE MOLE FRACTION OF DMSO.

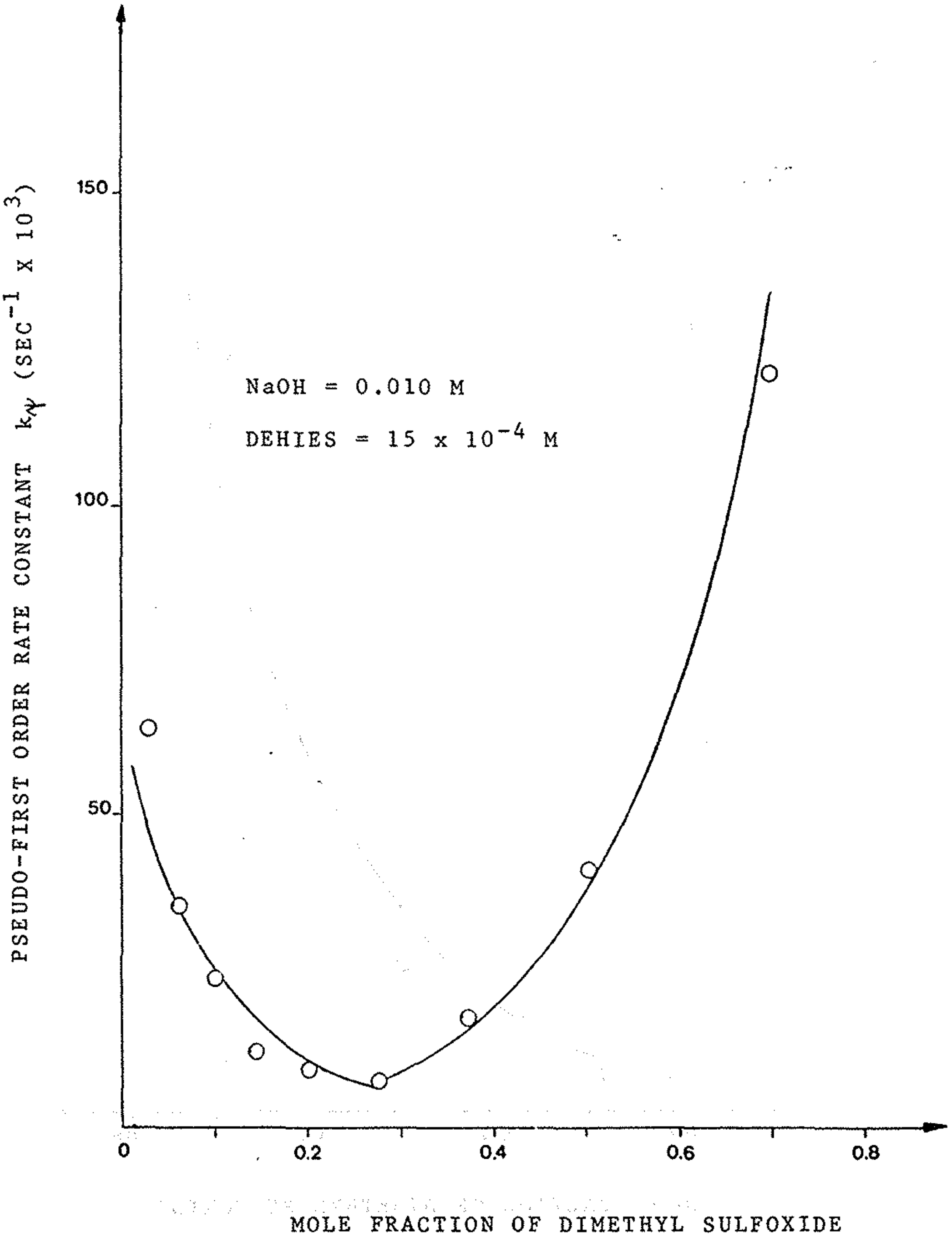


FIGURE 4. PLOT OF THE PSEUDO-FIRST ORDER RATE CONSTANT FOR THE HYDROLYSIS OF *p*-NITROPHENYL DIPHENYL PHOSPHATE AS A FUNCTION OF THE MOLE FRACTION OF DMSO FOR AQUEOUS SOLUTIONS CONTAINING 0,010 M SODIUM HYDROXIDE AND 15 x 10^{-4} M DEHIES AT 25ºC.

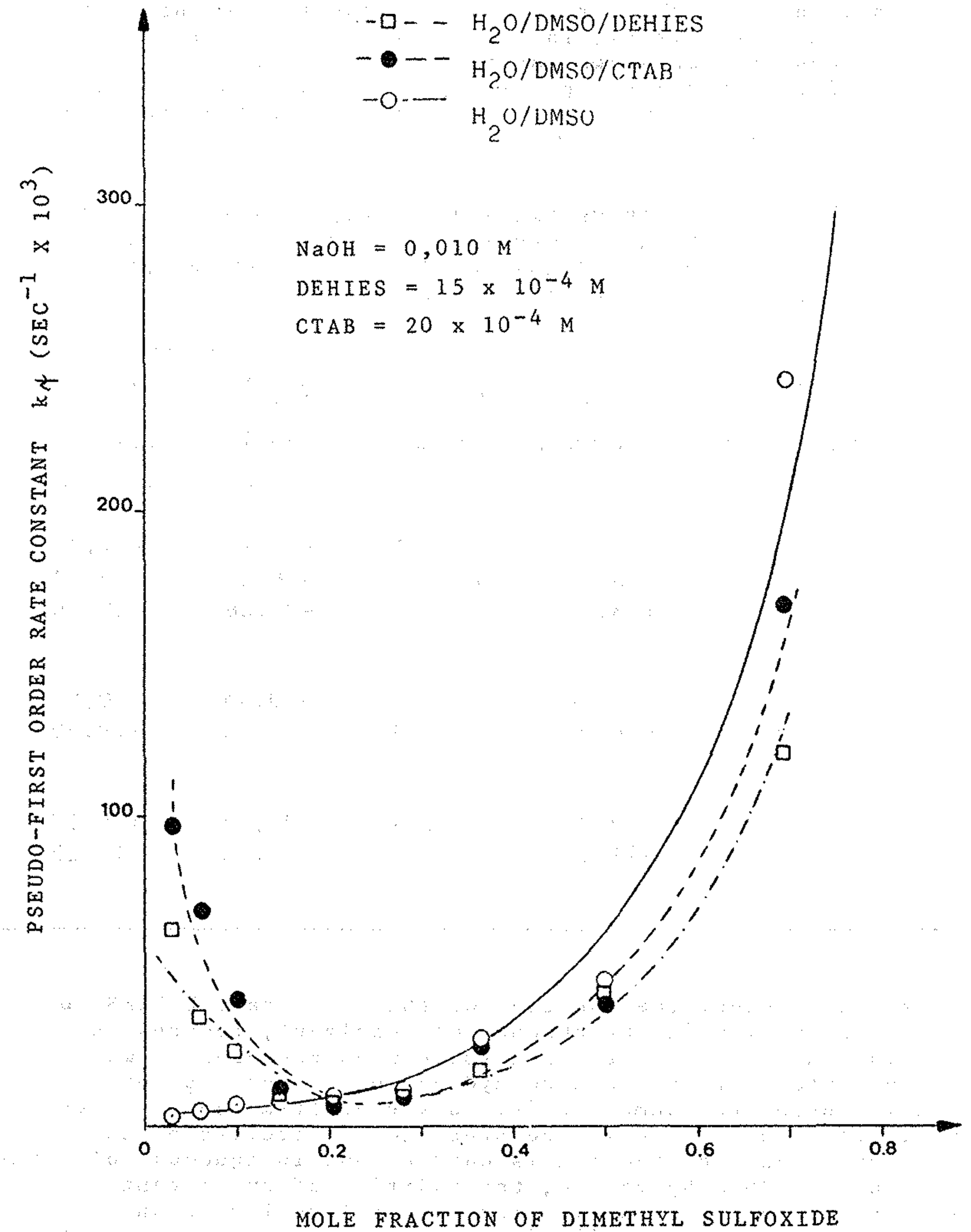


FIGURE 5. PLOT OF THE PSEUDO-FIRST ORDER RATE FOR THE HYDROLYSIS OF *p*-NITROPHENYL DIPHENYL PHOSPHATE AT 25°C AS A FUNCTION OF THE MOLE FRACTION OF DMSO FOR FIXED CONCENTRATIONS OF NaOH, CTAB AND DEHIES.

surfactant. In fact, the surfactant is present in solution as dispersed monomers, trapped in the crystal lattice of the $DMSO \cdot 2H_2O$ hydrate, as shown for the case of CTAB.[25-27]

Table III summarizes typical experimental results obtained for the activation parameters of the reaction in the presence and absence of DEHIES at 25ºC.

TABLE III. ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF *p*-NITROPHENYL DIPHENYL PHOSPHATE IN AQUEOUS SOLUTIONS OF 0,010 M SODIUM HYDROXIDE AT 25ºC IN THE PRESENCE AND ABSENCE OF DEHIES AND DMSO.

Concentration DMSO (% vol.)	Concentration DEHIES ($M \times 10^3$)	Ea (kcal/mol)	$\Delta H^{\circ\neq}$ (kcal/mol)	$\Delta S^{\circ\neq}$ (eu)	$\Delta G^{\circ\neq}$ (kcal/mol)
-	-	+15,23	+14,64	-22,24	+21,27
-	100	+ 8,82	+ 8,22	-36,60	+19,14
-	150	+ 8,61	+ 8,02	-37,08	+19,08
10	-	+18,74	+18,15	- 9,44	+20,96
10	100	+14,68	+14,08	-17,46	+19,29
90	-	+ 9,03	+ 8,44	-32,64	+18,17
90	100	+11,29	+10,70	-25,26	+18,23

As can be seen, the addition of the surfactant DEHIES to the reaction medium in the absence of cosolvent, reduces the activation energy, E_a, about 7 kcal/mole when compared to water solution containing only sodium hydroxide. The entropy of activation under the same conditions varies from about -22 eu in water to about -37 eu in the presence of micelles of the surfactant. When the reaction is carried out in aqueous solutions containing 10% DMSO by volume, the addition of surfactant decreases the energy of activation about 4 kcal/mole and reduces the entropy of activation from -9 eu to -17 eu. For the case of solutions containing 90% DMSO by volume, the addition of surfactant increases the activation energy about 2 kcal/mole and increases the entropy of activation from about -32 eu to - 25 eu. In summary, the addition of surfactant to pure water solutions or to water solutions containing 10% DMSO by volume leads to a more structured transition state (due to the presence of micelles) and facilitates the occurrence of the reaction.

For solutions containing 90% by volume DMSO, that already represents a highly structured medium, the addition of the surfactant, that is now present as dispersed non-aggregated monomers, causes a destructuring of the transition state and an inhibition of the reaction. Analysis of the variation of $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as a function of solvent shows that this reaction follows the isokinetic or compensation law and permits us to suggest that the presence of micelles in the reaction medium does not alter the mechanism of the reaction.[28]

Interactions in liquid solutions and the effect of solvents on the rate of bimolecular reactions are rather complex subjects and have been treated extensively in the literature.[29-38]

One approach uses the transition state theory and considers the relative solvation between the initial and transition state. The solvation of any of these states reduces the free energy and increases the stability. For a solvent to increase the rate of reaction it is necessary to reduce the activation free energy ($\Delta G^{\neq}$). This reduction in $\Delta G^{\neq}$ may come about either by the stabilization of the transition state with respect to the initial state or by destabilization of the initial state with respect to the transition state.[30]

Another approach considers the structure or cohesion of the solvent and how solvent-solvent interactions affect the reacting species.Obviously, the over-all effect of a solvent includes both solvation and cohesion, but to date it is extremely difficult to integrate the two points of view. The cohesive forces of a liquid are electrostatic in nature. At the same time, electrostatic interactions are responsible for non-specific solvation. It is thus very diffcult to consider the two effects separately.[32]

There are many theories that can give good predictions about the solvent effect on reaction rates.

The Hughes-Ingold Theory is based on the fact that reacting species normally alter their charge distribution during the passage through the transition state of the reaction.Ionic reagents form activated complexes that contain less charge, while neutral molecules form transition states containing some degree of separation of charge.The Hughes-Ingold Theory analyzes the type of charge of a given reaction pathway and the effect of polarity on the charge distribution during the reaction (from initial to transition state).

The alkaline hydrolysis of *p*-nitrophenyl diphenyl phosphate is a bimolecular reaction between the hydroxide anion and a neutral substrate. According to the Hughes-Ingold Theory,this reaction should be faster when carried out in a polar solvent. In fact, this theory can be used to explain the experimental results observed for solutions containing only water and DMSO in the absence of surfactant. This theory really considers the solvent as a continuous medium and does not take into account specific effects.

Common equations proposed show a linear relationship in terms of functions of the dielectric constant ε, such as $(1/\varepsilon)$, $(\log \varepsilon)$ or $(\varepsilon - 1)/(2\varepsilon + 1)$. Such linearity has been observed for reactions in binary solvent systems where the dielectric constant varies with the composition.[37-40]

The dielectric constant of the medium was calculated according to Equation VI.

$$\varepsilon_{medium} = X_{H_2O} \cdot \varepsilon_{H_2O} + X_{DMSO} \cdot \varepsilon_{DMSO} \qquad (VI)$$

where $\varepsilon_{H_2O} = 70,5$ and $\varepsilon_{DMSO} = 48,9$ and X_{H_2O} and X_{DMSO} represent the respective mole fractions of water and dimethyl sulfoxide.[29]

Figure 6 illustrates a plot of the log k_ψ for the reaction versus the function $(\varepsilon - 1)/(2\varepsilon + 1)$ of the dielectric constant ε and represents a quantitative correlation of the reaction rate with the dielectric constant. It is really a linear free energy relationship.

An analysis of Figure 6 shows that in the absence of surfactant the plot of log k_ψ versus $f(\varepsilon)$ is essentially a straight line (line 1). In the presence of surfactant, however, the plot of log k_ψ versus $f(\varepsilon)$ gives two straight lines.One of them (line 2) describes the behavior for solutions containing 10-50% DMSO by volume and line 3 for solutions with 50 to 90% by volume DMSO. One may conclude that the dielectric constant may be used to describe the polarity of the reaction medium. The effect of DMSO on the reaction rate can be described quantitatively in the absence of surfactant (H_2O-DMSO system) or when the surfactant is present in the form of dispersed monomers (60-90 % DMSO by volume for the H_2O-DMSO-DEHIES system). In the presence of micelles, the reaction rate is essentially determined by the micelles themselves and the addition of DMSO to the reaction medium is practically masked.

The internal pressure of liquids is given by Equation VII.[41-44]

$$I\,P = \Delta H_{vap}/M\rho \qquad (VII)$$

where $I\,P$ = internal pressure
ΔH_{vap} = latent heat of vaporization
M = molecular weight
ρ = density of the liquid

The calculated values for the internal pressure of water and dimethyl sulfoxide were 22355,0 atm and 5991,5 atm, respectively.

The internal pressure of the reaction medium was calculated using Equation VIII and the appropriate mole fractions of H_2O and DMSO.

$$I\,P_{medium} = X_{H_2O} \cdot I\,P_{H_2O} + X_{DMSO} \cdot I\,P_{DMSO} \qquad (VIII)$$

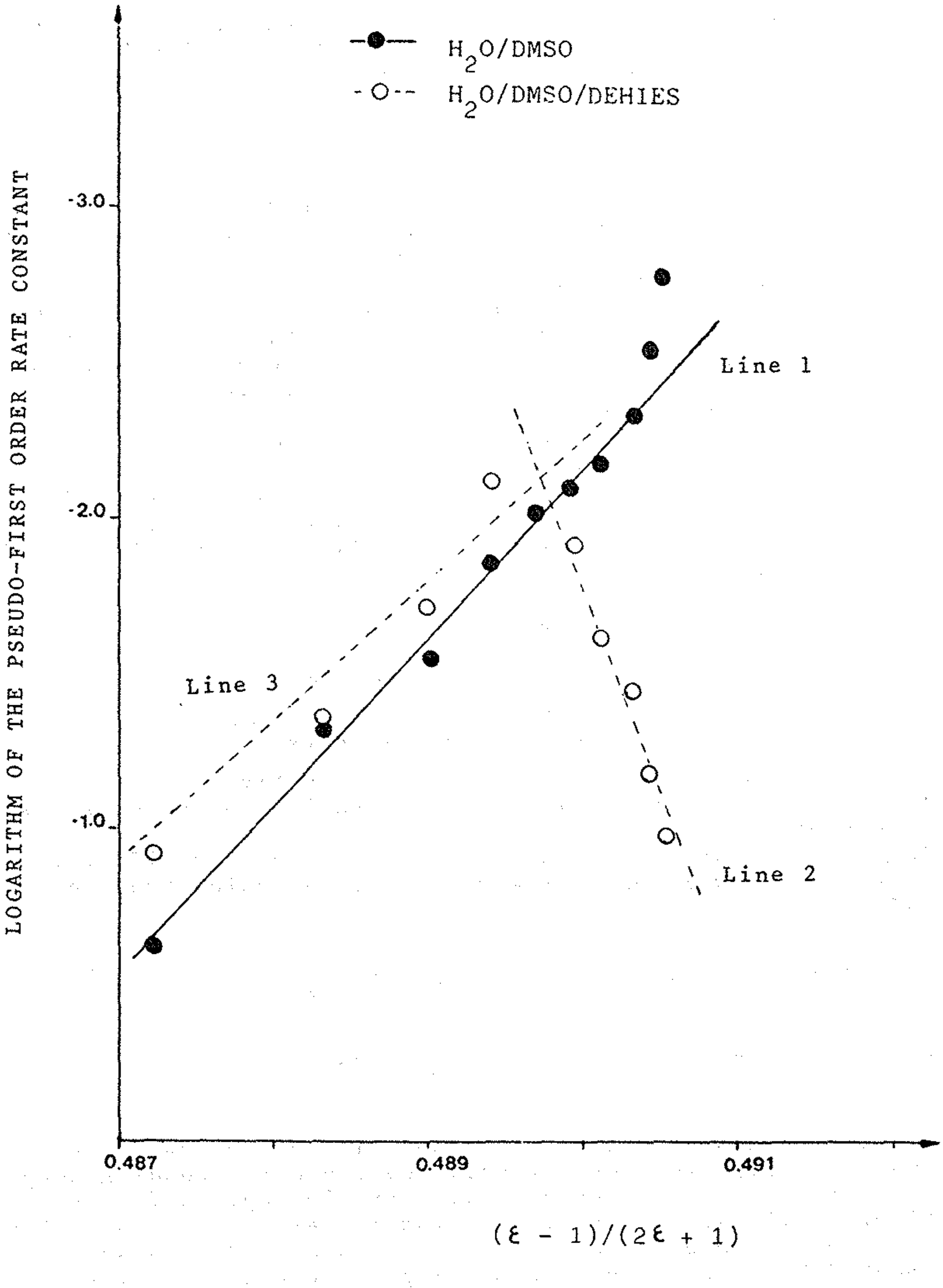


FIGURE 6. PLOT OF THE LOGARITHM OF THE RATE CONSTANT FOR THE HYDROLYSIS OF PNFDF AT 25°C IN THE PRESENCE OF 0,010 M NaOH, DMSO AND DEHIES VERSUS A FUNCTION OF THE DIELECTRIC CONSTANT OF THE MEDIUM.

Figure 7 shows a plot of lóg k_ψ versus the internal pressure of the medium for H_2O-DMSO and H_2O-DMSO-DEHIES solutions at 25°C. For the case of water - dimethyl sulfoxide solutions without surfactants the plot is essentially a straight line (line 1). For the H_2O-DMSO-DEHIES system containing 15 x 10^{-4} M surfactant, there are two straight lines, one describing the behavior in the reaction medium containing 10 to 60% by volume DMSO (line 2) and the other (line 3) for solutions containing 60 to 90% DMSO. The influence of the internal pressure of the reaction medium on the reaction rate in the absence of surfactant or when it is present in dispersed form (60 to 90% DMSO) indicates that the activated complex formed during hydrolysis of PNFDF in alkaline medium occupies a larger volume than that of the reagents involved in the reaction. In the presence of micelles, the activated complex is in the interior of the micelles and the reaction rate is determined by the micellar medium. The cohesive effect of the solvent medium (H_2O-DMSO) is essentially masked.

A multi-parameter correlation was also done in order to consider specific solute-solvent interactions. The parameters used were polarity (E_T) and donor number (DN), one representing acidity, the other basicity of the solvent.[36] The realation used is given by Equation IX.

$$\log k_\psi = \log k_{\psi o} + a\, E_T + b\, DN \qquad \text{(IX)}$$

where E_T = polarity of the solvent
DN = donor number of the solvent
a,b = regression coefficients

The regression coefficients describe the sensitivity of the reaction rate on electrophilic and nucleophilic characteristics of the solvent.

The polarity and donor number of the medium for different concentrations of DMSO present were calculated using Equations X and XI.

$$E_T \text{ medium} = X_{H_2O} \cdot E_{T\ H_2O} + X_{DMSO} \cdot E_{T\ DMSO} \qquad \text{(X)}$$

$$DN \text{ medium} = X_{H_2O} \cdot DN_{H_2O} + X_{DMSO} \cdot DN_{DMSO} \qquad \text{(XI)}$$

The polarity values used for water and dimetyl sulfoxide were 63,1 and 45,0 cal/mole, respectively and the corresponding donor numbers were 18,0 for water and 29,8 for dimethyl sulfoxide.[29,45]

Figure 8 illustrates a plot of log k_ψ as a function of the mole fraction of DMSO for solutions containing H_2O-DMSO and H_2O-DMSO-DEHIES at 25°C for the multi-parameter correlation function given by Equation IX.

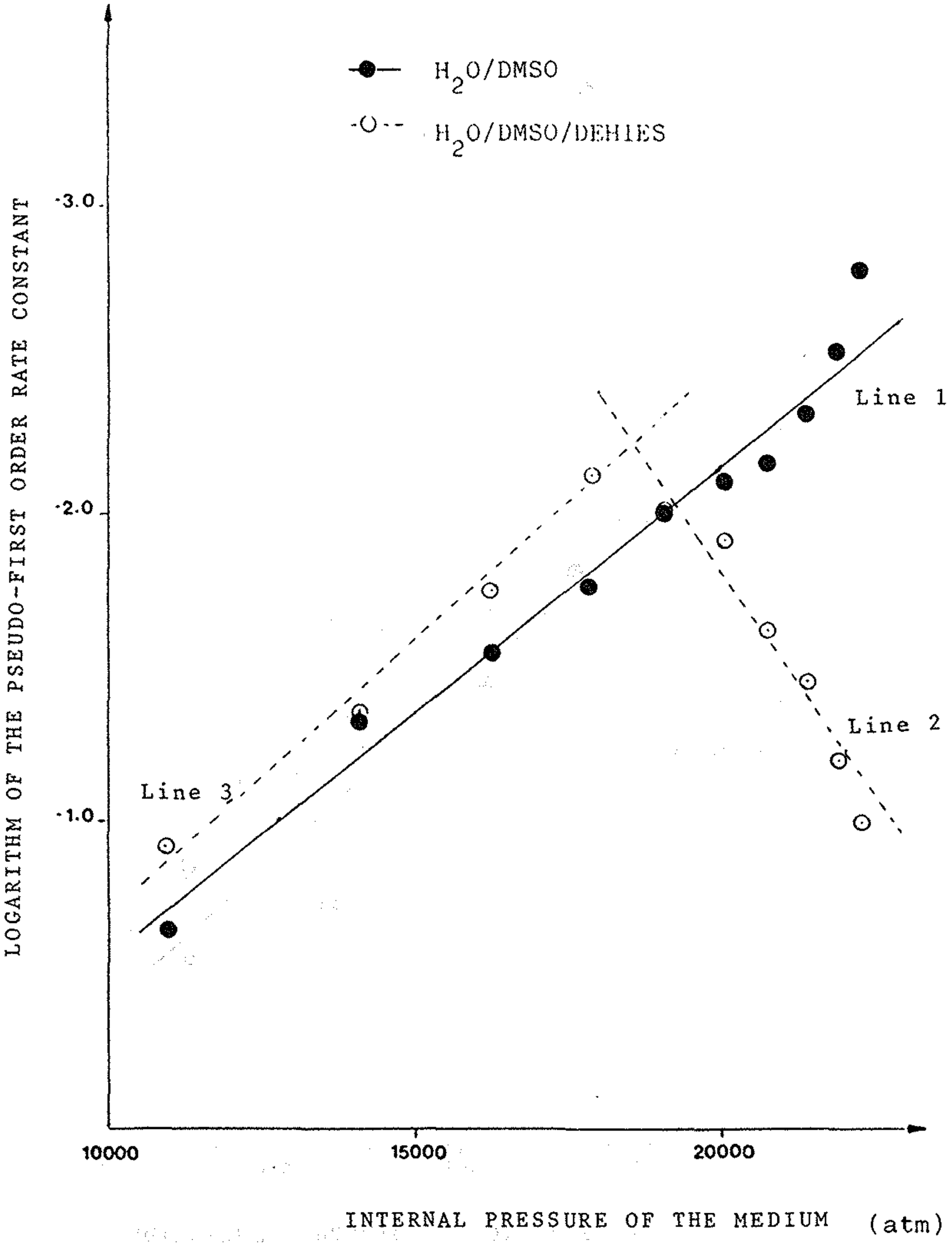


FIGURE 7. PLOT OF THE LOGARITHM OF THE PSEUDO-FIRST ORDER RATE CONSTANT FOR THE HYDROLYSIS OF PNFDF AT 25ºC IN THE PRESENCE OF 0,010 M NaOH, DEHIES AND DMSO VERSUS THE INTERNAL PRESSURE OF THE MEDIUM.

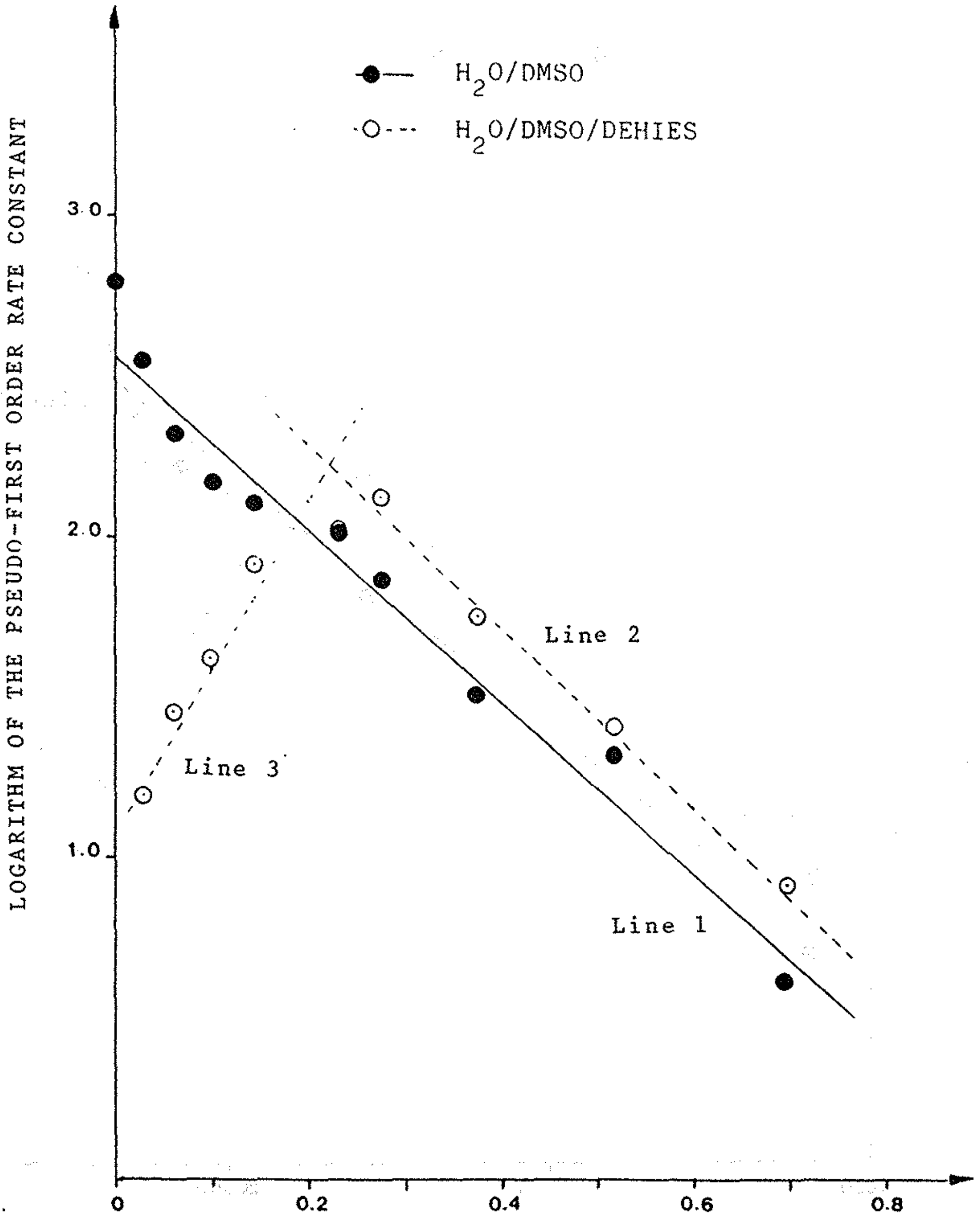


FIGURE 8. PLOT OF THE LOGARITHM OF THE PSEUDO-FIRST ORDER RATE CONSTANT FOR THE HYDROLYSIS OF PNFDF AT 25°C IN THE PRESENCE OF 0,010 M NaOH, DEHIES AND DMSO VERSUS THE MOLE FRACTION OF DMSO FOR A MULTI-PARAMETER CORRELATION .

Again, in the absence of surfactant, the result is a straight line (line 1) with a=-0,0423 and b=0,1647. In the presence of 15 x 10^{-4} M DEHIES the behavior of log k_{ψ} is described by two two straight lines. One of them (line 2) describes the behavior of solutions containing 10-50 % by volume DMSO (a=0,0783 and b=-0,2785) and the other one (line 3) describes the behavior for solutions containing 60-90 % DMSO (a=-0,0593 and b=0,1172). These results indicate that in the absence of surfactant (a=-0,0423 and b=0,1647) or when the surfactant is present in dispersed form (a=-0,593 and b=0,1172) the reaction medium shows a negative influence of the electrophilic character and a positive influence of the nucelophilic character. In the presence of micelles (a=0,0783 and b=-0,2785) the electrophilic contribution becomes positive and the nucleophilic contribution becomes negative.

In summary, we may conclude that all three linear correlation relationships in terms of polarity, internal pressure and multiparameters give similar results and that the formation of the $DMSO \cdot 2H_2O$ stoichiometric hydrate has a pronounced effect on the formation of micelles and the rate of the micellar catalyzed hydrolysis.

REFERENCES

1. F. A. Gunther and J. D. Gunther, *"Chemistry of Pesticides"*, Springer Verlag, New York, 1971.
2. L. S. Goodman and A. Gilman, Eds., *"The Pharmacological Basis of Therapeutics"*, McMillan, New York, 3rd ed., 1966.
3. C. A. Bunton and L. G. Ionescu, *J. Amer. Chem. Soc.*, *95*, 2912 (1973).
4. L. G. Ionescu, *Bull. N. Mex. Acad. Sci.*, *14*, 65 (1973)
5. L. G. Ionescu and D. A. Martinez, *J. Colo. Wyo. Acad. Sci*, *7(5)*, 13 (1974).
6. C. A. Bunton, S. Diaz, J. M. Hellyer, I. Ihara and L. G. Ionescu, *J. Org. Chem.*, *40*, 2313 (1975).
7. F. Nome. E. W. Schwingel and L. G. Ionescu, *J. Org. Chem.*, *45*, 705 (1980).
8. L. G. Ionescu, D. A. R. Rubio and T.H.M. do Aido, *Atual. Fis. Quim. Org.*, *1*, 217-229 (1982).
9. F. Nome. A. Rubira and L. G. Ionescu, *J. Phys. Chem.*, *86*, 1181 (1982).
10. L. G. Ionescu and M. J. B. Miguez, *Rev. Chim. Industr.*, *52(609)*, 23 (1983).
11. L. G. Ionescu and F. Nome, in *"Surfactants in Solution"*, K, L. Mittal and B. Lindman, Eds., Plenum Press, New York, 1984, Vol. 2, pp. 1107-1120.
12. L. G. Ionescu and M. J. B. Miguez, *Atual. Fis. Quim. Org.*, *2*, 89-102 (1984).
13. L. G. Ionescu, *Quim. Nova*, *8(3)*, 191 (1985).
14. L. G. Ionescu, D. A. R. Rubio and L. S. Romanesco, in *"Trabalhos Técnicos 4º Seminário Brasileiro de Catálise"*, Instituto Brasileiro do Petróleo, Rio de Janeiro, Brasil, 1987, pp. 727-737.

15. L. G. Ionescu, T.H. M do Aido and B. J. Kid., *Bol. Soc. Chil. Quim.*, *35*, 105-111 (1990).
16. A. M. Roos and J. Toet, *Rec. Trav. Chim.*, *77*, 946 (1958).
17. A. S. Kirby and M. Jounas, *J. Chem. Soc.*, *B*, 1165 (1970).
18. C. A. Bunton, L. Robinson and L. Sepulveda, *J. Amer. Chem. Soc.*, *91*, 4813 (1969).
19. F, M. Menger, L. H. Gan E. Johnson and D. H. Durst, *J. Amer. Chem. Soc.*, *109*, 2802 (1987).
20. L. G. Ionescu, T. Tokuhiro and B. J. Czerniawski, *Bull. Chem. Soc. Japan*, *52*, 922-924 (1979).
21. L. G. Ionescu and D. S. Fung, *Bull. Chem. Soc. Japan*, *54*, 2503-2505 (1981).
22. L. G. Ionescu, L. S. Romanesco and F. Nome, in *"Surfactants in Solution"*, K. L. Mittal and B. Lindman, Eds., Plenum Press, New York, 1984, pp. 789-803.
23. J. M. G. Cowie and P. M. Toporowski, *Canad. J. Chem.*,*39*, 2240 (1961).
24. L. G. Ionescu, T. Tokuhiro, B. J. Czerniawski and E. S. Smith, in *"Solution Chemistry of Surfactants"*, K. L. Mittal, Ed., Plenum Press, New York, 1979, Vol. I, pp. 487-496.
25. T. Tokuhiro, D. S. Fung and L. G. Ionescu, *J. Chem. Soc. Faraday Trans. II*, *75*, 975-984 (1979).
26. T. Tokuhiro and L. G. Ionescu, in *"Solution Chemistry of Surfactants"*, K. L. Mittal, Ed., Plenum Press, New York, 1979, Vol. I, pp. 497-506.
27. L. G. Ionescu and L. S. Romanesco, *Atual. Fis. Quim. Org.*, *3*, 109-122 (1985).
28. L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*,*27(1)*, 1-33 (1990).
29. A. Finniels and P. N. Geneste, *J. Chim. Phys.*,*76*, 521 (1979).
30. O. Popovich and R. P. T. Tomkins, *"Nonaqueous Solution Chemistry"*, John Wiley and Sons, New York, 1981.
31. C. Agami, *Bull. Soc. Chim. France*, *5*, 1021-1039 (1965).
32. A. J. Parker, *Chem. Rev.*, *69*, 1-32 (1969).
33. L. G. Ionescu, *Contrib. Cient. Tecnol. Santiago(Chile)*,*NS*, 35-39 (1985).
34. K. Burger, *"Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents"*, Elsevier Scientific Co., Amsterdam, 1983, pp. 217-243.
35. B. G. Cox and W. E. Waghorne, *Chem. Soc. Rev.*, *9(3)*, 381-411 (1980).
36. L. Albuquerque and R. Gonçalves, *"Cinética Química"*, Editora Escolar, Lisboa, Portugal, 1986.
37. E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, *14*, 133-202 (1977).

38. M. R. J. Dack, The Influence of Solvent on Chemical Reactivity, in *"Technique of Organic Chemistry"*, A. Weissberger, Ed., Interscience Publishers, New York, 1976, Vol. VIII.

39. J. Hine, *"Physical Organic Chemistry"*, McGraw Hill Book Company, New York, 1962, 2nd edition.

40. E. S. Amis and J. F. Hinton, *"Solvent Effects on Chemical Phenomena"*, Academic Press, New York, 1973, Vol. 1.

41. J. R. Partington, *"An Advanced Treatise on Physical Chemistry"*, Vol. 2, The Properties of Liquids, Longman's , Green and Company, London, 1951.

42. R. C. Reid and J.M. Prausnitz, *"The Properties of Gases and Liquids"*, McGraw Hill, New York, 1972, 3rd edition.

43. R. H. Perry and C. H. Clinton, Eds., *"Chemical Engineer's Handbook"*, McGraw Hill Kogakusha, Tokyo, 1973, 3rd edition.

44. R. C. Weast, Editor, *"CRC Handbook of Chemistry and Physics"*, CRC Press, Boca Raton, Florida, USA, 1981, 61st edition.

45. V. Gutman, *"The Donor-Acceptor Approach to Molecular Interactions"*, Plenum Press, New York, 1978.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

Vol. 1, No. 1, 1993

INFLUENCE OF FILM THICKNESS, TEMPERATURE AND INORGANIC FILLERS ON THE VOLUME ELECTRIC RESISTIVITY OF HEAT-CURING EPOXY VARNISH

Minodora Leca*
Department of Physical Chemistry
Faculty of Chemistry, University of Bucharest
Bd. Carol I, Nº 13
Bucharest 70346, ROMANIA

&

Ovidiu Segărceanu
Research Institute of Anticorrosive Protection,
Varnishes and Paints
Bd. Theodor Pallady Nº 49A
Bucharest 74585, ROMANIA

ABSTRACT

The dependence of the volume electric resistivity of heat-curing epoxy varnish on the film thickness, temperature and nature of inorganic fillers for films obtained by spraying on steel supports cured for 30 minutes at 160 ºC was determined. Film thicknesses ranged between 5 and 56 µm, temperature between 24 ºC and 140 ºC and the fillers were rutile type titanium dioxide, micronized mica, colloidal aluminium oxide and aluminium silicate. The experimental data, treated statistically by the linear regression method shows a linear dependence of the volume electric resistivity on the film thickness and a hyperbolic one on temperature. The highest volume electric reisitivity was obtained for films containing titanium dioxide and the lowest one for those with aluminium silicate. The volume electric resistivity depends on film thickness for films deposited from solution and can not be considered a material constant.

RESUMO

A dependência da resistividade elétrica do volume de vernizes epoxi tratadas com calor da espessura dos filmes, temperatura e natureza das cargas inorgânicas para filmes obtidos através de pulverização sobre suportes de aço tratados por 30 minutos a 160 ºC foi determinada. A espessura dos filmes variou entre 5 e 56 µm, a temperatura de 24 ºC a 140 ºC e as cargas usadas foram dioxido de titânio do tipo rutila, mica micronizado, óxido de alumínio coloidal e silicato de alumínio. Os resultados experimentais, tratados estatisticamente com o método de regressão linear, mostram uma dependência linear da resistividade elétrica do volume com a espessura do filme ou película e uma dependência hiperbólica com a temperatura. Os valores mais altos da resistividade elétrica do volume foram obtidos para películas contendo dioxido de titânio e os valores mais baixos com películas contendo silicato de alumínio. A resistividade elétrica do volume depende da espessura dos filmes depositados da solução e não pode ser considerada uma constante.

KEYWORDS: Insulator, Volume Electric Resistivity, Epoxy Resin, Varnish, Heat-Curing Resin, Inorganic Fillers for Insulators.

DOI: 10.48141/SBJCHEM.v1.n1.1993.100_1993.pdf

INTRODUCTION

The use of a composite material of the paint type as an electric insulator implies a detailed analysis of its behaviour under various circumstances. Thus, besides the electric behaviour, some other properties such as resistance to chemical agents, solvents, humidity, temperature, mechanical impact, thermal shock, electromagnetic fields, etc., must be known, such properties limiting their uses.

The volume electric resistivity results from Ohm's Law and it is a material constant.

In the case of polymers, the volume electric resistivity depends on the presence of free ions in their composition[1]. Potential sources of free ions are low molecular weight impurities such as solvents, monomers, water, catalysts and condensation products. Polymer chemical structure contributes only indirectly to the ion mobility by its chain flexibility.

The volume electric resistivity of polymers is of the order of 10^{13} to 10^{19} Ω x cm and it decreases with increasing temperature according to an Arrhenius type law:

$$\rho_v = \rho_0 \exp(\Delta E/RT) \qquad (1)$$

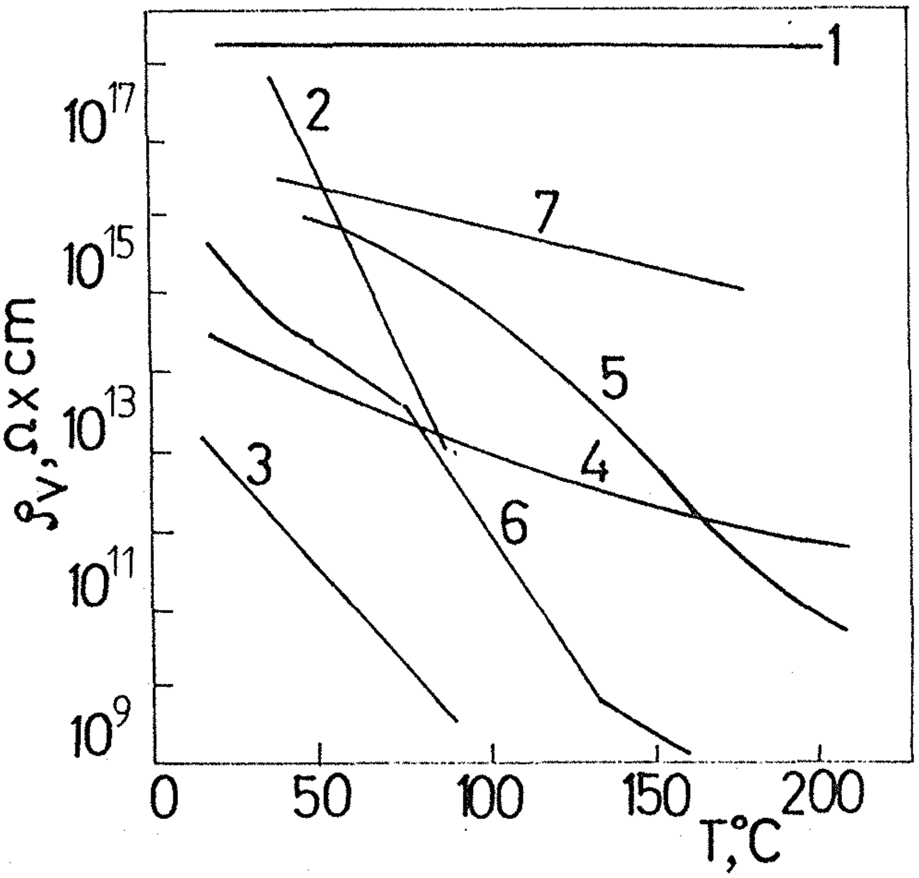
where ρ_v is the volume electric resistivity, ρ_0 is a constant practically independent of the temperature T, ΔE is the activation energy (the difference of energy between the activated and the ground state of the ions), and R is the gas constant. At temperatures higher than the glass transition, the mobility of the chain segments increases with temperature and consequently the mobility of ions present as impurities also increases, thus increasing the volume electric resistivity. The temperature dependence of ρ_v for some polymers is shown in Figure 1.[2]

The filler particles diminish the mobility of macromolecular segments by their adsorption on surfaces[3]. For the particular case of films, the volume properties are affected by the contribution of superficial properties, that can prevail for very thin films (small volume to surface ratios). The film volume properties are comparable with those of the corresponding bulk compound only for thick films. In such a situation the following questions arise:

- Is the volume resistivity a material constant, that is independent of the film thickness?
- Does its temperatures dependence obey Equation (1) ?
- How does the nature of the filler influence the value of the volume electric resistivity?

The above questions are especially valid for films deposited from solution, that besides other impurities, inevitably contain varying quantity of solvents, even if they are applied in very thin layers and drying is carefully done.

In order to answer the above mentioned questions, the present paper studies the dependence of the volume resistivity of a heat-curing epoxy varnish on the film thickness, temperature and type of inorganic fillers.



1 - TEFLON

2 - POLYETHYLENE

3 - POLYVINYL CHLORIDE

4 - SILICONE

5 - SILICONE RUBBER

6 - SEMIRIGID EPOXY

7 - *p*-POLYXYLYLENE

FIGURE 1. DEPENDENCE OF THE VOLUME ELECTRIC RESISTIVITY ON TEMPERATURE FOR VARIOUS POLYMERS.[2]

MATERIALS AND METHODS

A Danish 6138/000 CEAST type Teraohmeter coupled with two cylindrical electrodes having a standardized diameter of 5 cm and and area of 9.6349 cm^2, equipped with a guard electrode was used to measure the electric volume resistivity. The two electrodes were thermostated at temperatures ranging between 24 ºC and 140 ºC.

The film thickness was measured using a Polish type electromagnetic Ultrameter with an accuracy of ± 1 μ .

The inorganic fillers were dispersed in a 1 liter German mill with ceramic balls for about 80 hours to obtain a convenient degree of dispersion. The degree of grinding of fillers into the resin was measured with a Romanian Grindometer. The viscosity was checked by means of a viscosimetric cup with a 4 mm nozzle diameter at a temperature of 25 ºC.

The following materials were used to obtain electroinsulating samples: (a) epoxy resin based on bisphenol A and epichlorhydrin having the following characteristics: epoxy equivalent - 0.02 to 0.05/100 g of resin, concentration - 39%±1, solvent - monobutyldiethyleneglycol, viscosity at 25 ºC - 3800 to 7000 mPa x s; (b) inorganic fillers: rutile type titanium dioxide with an oil index of 18 g/ 100 g; micronized mica with a maximum humidity of 1%; aluminium silicate having a maximum humidity of 4%, an oil index of maximum 60 g/ 100 g and a molar ratio SiO/Al_2O_3 ranging between 1.6 and 2.2; coloidal aluminium oxide with maximum humidity of 10%, an oil index of 140 g/ 100 g, a maximum content of 3% Fe_2O_3 and a minimum content of 44% Al_2O_3; (c) 2,4,6-tris-(dimethylaminoethyl)phenol as hardener and (d) cyclohexanone/ isopropanol in a volume ratio of 1/1 as thinner.

The films were applied by spraying on 200 x 100 x 1 (mm) metallic plates cleaned previously with sandpaper and degreased in order to obtain a thickness as uniform as possible. To remove the solvents better, more layers were applied and every layer was dried.To obtain a wide range of thicknesses 1 to 5 layers were applied.Film cross-linking was obtained by heating for 30 minutes at 160 ºC.

RESULTS AND DISCUSSION

The experimental data was treated by the statistical method of linear regression implemented on an IBM compatible PC. The dependence of the volume electric resistivity on the film thickness, ℓ , and temperature , T, was analysed. The two parameters were considred independent and the third one - the nature of the filler - interferes implicitly for each sample.

To find the best correlation between ρ_v and the two parameters ℓ and T, six equations were introduced into the program:

$$Y = C_o + C_1 + X_1 \tag{2}$$

$$Y = C_o \times \exp(C_1/X_1) \tag{3}$$

$$Y = C_o + C_1/X_1 \tag{4}$$

$$Y = C_o \times X_1^{C_1} \tag{5}$$

$$Y = C_o \times C_1^{X_1} \tag{6}$$

$$Y = C_o + C_1 \times X_1 + C_2 \times X_2 \tag{7}$$

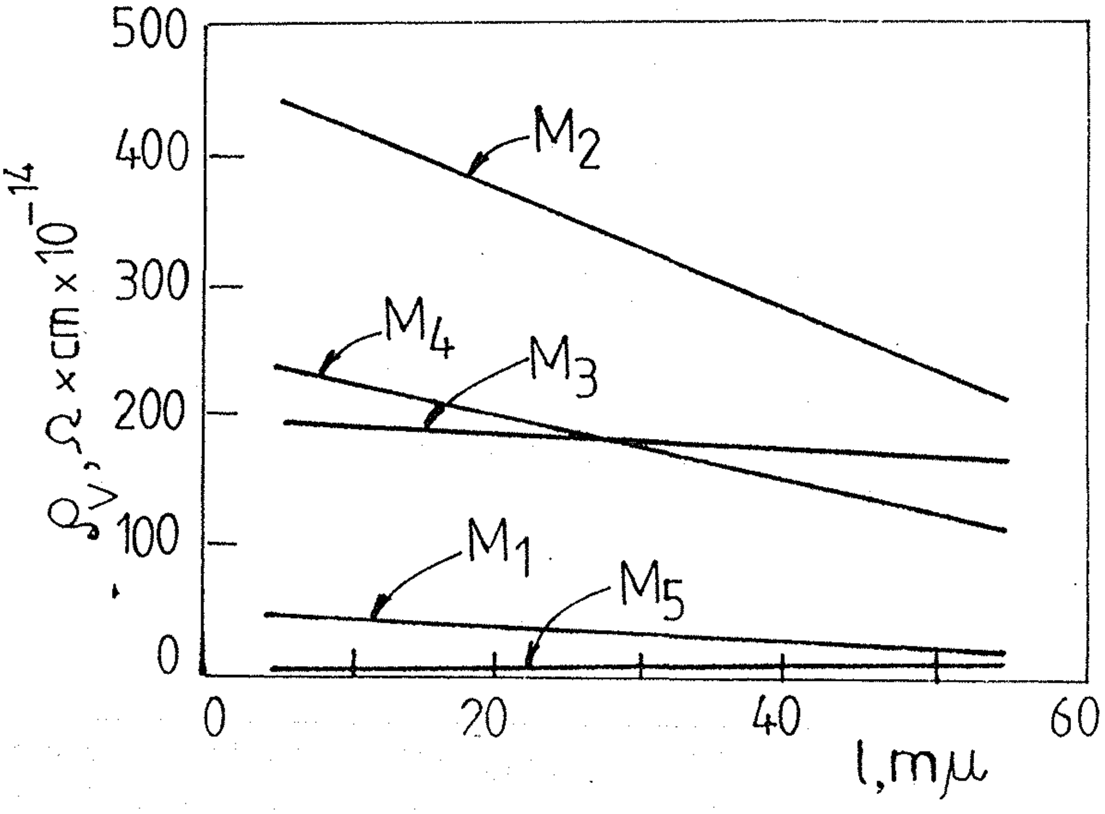
where Y represents the volume electric resistivity and $X_{1,2}$ are either the film thickness or the temperature. Forty-nine pairs of points (ρ_v, ℓ and ρ_v, T) were introduced in each equation and the coefficients C_o, C_1 and C_2 were determined. More complex equations were not used because, besides the complication in the calculation, the phenomenological interpretation becomes practically impossible.

The composition of the samples studied is shown in Table I.

TABLE I. COMPOSITION OF THE SAMPLES STUDIED IN PERCENT BY WEIGHT.

Sample	Epoxy resin	Amine curing agent	Titanium dioxide	Micronized mica	Colloidal aluminium oxide	Aluminium silicate
M_1	77.67	2.91	-	-	-	-
M_2	77.67	2.91	19.42	-	-	-
M_3	77.67	2.91	-	19.42	-	-
M_4	77.67	2.91	-	-	19.42	-
M_5	77.67	2.91	-	-	-	19.42

The experimental dependence of ρ_v on film thickness is represented, for each sample, in Figure 2. As can be seen, a linear decrease of the volume electric resistivity with film thickness is observed for all samples with the exception of sample M_5 that contains aluminium silicate as filler and presents a slightly positive slope.



M_1 - EPOXY RESIN

M_2 - TITANIUM DIOXIDE

M_3 - MICRONIZED MICA

M_4 - COLLOIDAL ALUMINIUM OXIDE

M_5 - ALUMINIUM SILICATE

FIGURE 2. PLOT OF THE VOLUME ELECTRIC RESISTIVITY AS A FUNCTION OF FILM THICKNESS FOR THE SAMPLES STUDIED.

The equations that fit the best the experimental values for each sample are:

$$\rho_v = 42.818 - 0.422 \times \ell \qquad (M_1) \qquad (8)$$

$$\rho_v = 458.703 - 4.449 \times \ell \qquad (M_2) \qquad (9)$$

$$\rho_v = 188.168 - 0.410 \times \ell \qquad (M_3) \qquad (10)$$

$$\rho_v = 247.732 - 2.481 \times \ell \qquad (M_4) \qquad (11)$$

$$\rho_v = 4.108 + 0.017 \times \ell \qquad (M_5) \qquad (12)$$

The dependence of the volume electric resistivity on temperature is represented, for each sample, in Figure 3 and a linear or hyperbolic decrease of ρ_v can be seen when the temperature increases. It may be stated that, within the limits of experimental error, the resistivity dependence on temperature follows the theoretical equation (1).

The equations obtained for the dependence of ρ_v on T using the regression method are:

$$\rho_v = -14.915 + 2635/T \qquad (M_1) \qquad (13)$$

$$\rho_v = 940.750 - 7.063 \times T \qquad (M_2) \qquad (14)$$

$$\rho_v = -67.625 + 14018.357/T \qquad (M_3) \qquad (15)$$

$$\rho_v = 472.282 - 3.465 \times T \qquad (M_4) \qquad (16)$$

$$\rho_v = -3.654 + 483.038/T \qquad (M_5) \qquad (17)$$

The simultaneous dependence of volume electric resistivity on the two parameters shows a decrease for both film thickness and temperature, with the exception of sample M_5 for which, as mentioned before, resistivity decreases with film thickness.

The following equations were obtained for the dependence of ρ_v on thickness and temperature:

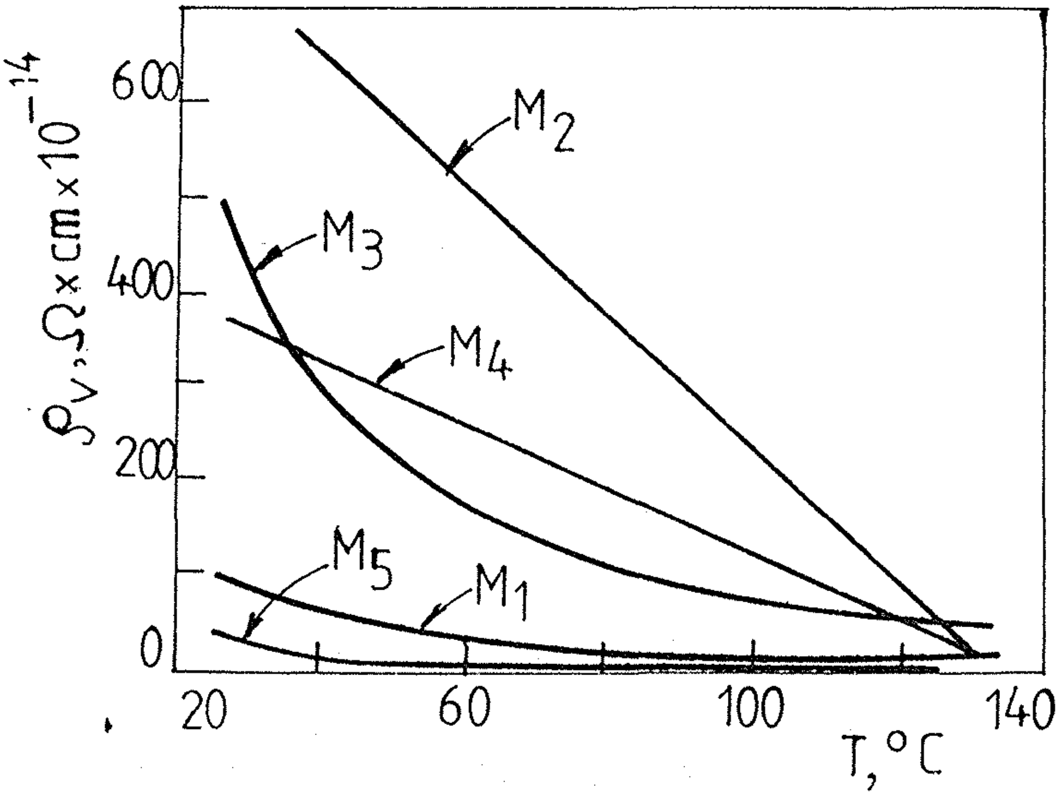
$$\rho_v = 100.588 - 0.422 \times \ell - 0.732 \times T \qquad (M_1) \qquad (18)$$

$$\rho_v = 1027.933 - 4.458 \times \ell - 7.063 \times T \qquad (M_2) \qquad (19)$$

$$\rho_v = 487.038 - 0.395 \times \ell - 3.720 \times T \qquad (M_3) \qquad (20)$$

$$\rho_v = 526.882 - 2.482 \times \ell - 3.465 \times T \qquad (M_4) \qquad (21)$$

$$\rho_v = 14{,}648 + 0.017 \times \ell - 0.131 \times T \qquad (M_5) \qquad (22)$$



M_1	- EPOXY RESIN	M_4	- COLLOIDAL ALUMINIUM OXIDE
M_2	- TITANIUM DIOXIDE	M_5	- ALUMINIUM SILICATE
M_3	- MICRONIZED MICA		

FIGURE 3. VARIATION OF VOLUME ELECTRIC RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR THE SAMPLES STUDIED.

The experimental data and the equations obtained using the statistical analysis of the dependence of the volume electric resistivity on film thickness show that ρ_v can not be considered a material constant at a given temperature, because it decreases continuously when film thickness dimishes. This may be explained by the higher quantity of solvents or by reaction byproducts that remain within a thick film when compared to a thin one, for which removal of these compounds is more complete. Another explanation is that the thicker films crosslink more slowly than thinner ones, which means that the crosslinking process is more advanced for thin films and this produces a higher resistivity.[4]

Regarding the composition of the samples (Table I), the only difference is the nature of the inorganic fillers.

The independence of the volume electric resistivity on film thickness within the temperature range studied when aluminium silicate was the filler is difficult to explain. A constant value might indicate a complete removal of solvents and byproducts. Fillers can alter the volume electric resistivity only at temperatures higher than 200 ºC, when the conduction phenomemon can appear. For titanium dioxide, for example, the electric conductance appears at about 500 ºC.[5]

Figures 2 and 3 show that titanium dioxide gives the highest resistivities for the compositions studied; micronized mica and aluminium oxide have lower but very close performance. The filler free varnish has lower resistivity; the worst filler is aluminium silicate, that decreases the value of resistivity under that measured for the varnish.

The volume electric resistivity does no seem to be a material constant for a given insulator deposited from solution at a given temperature in the range of film thicknesses of practical use because they contain solvents and byproducts resulting from the crosslinking process, in quantities increasing with film thickness.

Titanium dioxide as a filler gives the highest volume electric resitivity. Colloidal aluminium oxide and micronized mica also increase resistivity, but their effect is less pronounced. The lowest value was obtained using aluminium silicate, that decreases the resistivity to values less than those measured for the varnish.

REFERENCES

1. A. Tager, *"Physical Chemistry of Polymers"*, Mir Publishers, Moscow, Russia, 1972, pp.278-296.

2. J. J. Licard, *"Plastic Coatings for Electronics"*, McGraw-Hill, New York, USA, 1970, pp. 106-114.

3. C. A. Kumins, *J. Coat. Techn., 52*, 39-53 (1980).

4. J. V. Schmitz, *"Testing of Polymers"*, John Wiley and Sons, New York, USA, 1965, pp. 281-284.

5. B. Tareev, *"Physics of Dielectric Materials"*, Mir Publishers, Moscow, Russia, 1975, pp. 44-54.

The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com. This text was introduced in this file in 2021 for compliance reasons.

AUTHOR INDEX / ÍNDICE DE AUTORES

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

The *SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY* is an international forum for the rapid publication of original scientific articles dealing with chemistry and related areas. At the present there are no page charges and the authors will receive twenty five free reprints of their papers.

SPECIAL COMBINATION OFFER FOR NEW SUBSCRIBERS!

SUBSCRIPTION INFORMATION

PRICE: Brazil and Latin America: US$ 35.00 per issue.

Other Countries: US$ 50.00 per issue, including air mail delivery.

Persons or institutions outside Brazil should send subscription fee payable to Dr. L. G. Ionescu, c/o SBJC
8532 Howard Circle, Huntington Beach, California, USA
92647

ORDER FORM

☐ Please enter my subscription for ________ issues of Southern Brazilian Journal of Chemistry.

☐ Please send me _____ copies of the Southern Brazilian Journal of Chemistry (Vol. 1, Nº 1, 1993).

☐ I enclose a check or money order in the amount of $_______

☐ Please send me a Pro Forma Invoice for the above order.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

Lavinel G. Ionescu, B.S., M.S., Ph.D.,Editor
C.P. 15032, Agronomia
Porto Alegre, RS BRAZIL 91501-000
TEL. (051) 485-1820 FAX. (051) 339-1564