

Advances in Kinetics and Mechanism of Chemical Reactions

**Gennady E. Zaikov, DSc
Artur J. M. Valente, PhD
Alexei L. Iordanskii, DSc
EDITORS**




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Edited by

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ADVANCES IN KINETICS AND MECHANISM OF CHEMICAL REACTIONS

About the Editors

Gennady E. Zaikov, DSc

Gennady E. Zaikov, DSc, is Head of the Polymer Division at the N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia, and Professor at Moscow State Academy of Fine Chemical Technology, Russia, as well as Professor at Kazan National Research Technological University, Kazan, Russia. He is also a prolific author, researcher, and lecturer. He has received several awards for his work, including the the Russian Federation Scholarship for Outstanding Scientists. He has been a member of many professional organizations and is on the editorial boards of many international science journals.

Artur J. M. Valente, PhD

Artur J. M. Valente received his PhD from Coimbra University, Portugal, in 1999 working on the transport properties of non-associated electrolytes in hydrogels. He is currently Assistant Professor in the Chemistry Department of University of Coimbra. In 2004 and 2006 he was a guest and invited researcher, respectively, in the Division of Physical Chemistry 1, Lund University, Sweden. His research interests focus on the transport properties of ionic and non-ionic solutes in multicomponent systems, such as host-guest compounds, as well as in the characterization of the transport properties in polymeric matrices, with particular emphasis to polyelectrolytes, gels and functional blends, and composites. He has more than 90 publications in ISI international journals, over 100 communications at scientific meetings, 10 papers in national journals, one patent, and two books. He is also co-editor of two books, a special issue of the *Journal of Molecular Liquids* (2010), and a forthcoming issue of *Pure & Applied Chemistry*.

Alexei L. Iordanskii, DSc

Alexei L. Iordanskii, DSc, is Professor at the Institute of Chemical Physics at the Russian Academy of Sciences in Moscow, Russia. He is a scientist in the field of chemistry and the physics of oligomers, polymers, composites, and nanocomposites.

List of Contributors

L. A. Badykova

Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences,
pr. Oktyabrya 69, Ufa, 450054, Bashkortostan, Russia
E-mail: badykova@mail.ru

D. V. Bagrov

Faculty of Biology, Moscow State University, Leninskie gory 1-12, 119992 Moscow, Russia

K. Bauerová

Institute of Experimental Pharmacology and Toxicology, Slovak Academy of Sciences, SK-84104, Bratislava, Slovakia

L. I. Bazylyak

Chemistry of Oxidizing Processes Division; Physical Chemistry of Combustible Minerals Department; Institute of Physical-organic Chemistry & Coal Chemistry named after L. M. Lytvynenko; National Academy of Science of Ukraine
3a Naukova Str., Lviv-53, 79053, UKRAINE; E-mail: hav.ok@yandex.ru

A. P. Bonartsev

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia
Faculty of Biology, Moscow State University, Leninskie gory 1-12, 119992 Moscow, Russia

G. A. Bonartseva

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia

A. P. Boskhomodgiev

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia

F. Dráfi

Institute of Experimental Pharmacology and Toxicology, Slovak Academy of Sciences, SK-84104, Bratislava, Slovakia

E. A. Filatova

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia

A. K. Haghi

University of Guilan, Rasht, Iran
E-mail: Haghi@Guilan.ac.ir

A. L. Iordanskii

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia
N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygin str. 4, 119991 Moscow, Russia
E-mail: aljordan08@gmail.com, tel. +74959397434, fax: +74959382956

E. A. Ivanov

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia

O. Yu. Khavunko

Chemistry of Oxidizing Processes Division; Physical Chemistry of Combustible Minerals Department; Institute of Physical–organic Chemistry & Coal Chemistry named after L. M. Lytvynenko; National Academy of Science of Ukraine

3a Naukova Str., Lviv–53, 79053, UKRAINE; E-mail: hav.ok@yandex.ru

E. I. Korotkova

Tomsk Polytechnic University, 30 Lenin Street, 634050, Tomsk, Russia

G. V. Kozlov

Institute of Applied Mechanics of Russian Academy of Sciences,
Leninskii pr., 32 a, Moscow 119991, Russian Federation

Victor M. M. Lobo

Departamento de Química, Universidade de Coimbra,
3049 Coimbra, Portugal

E-mail: anacfrib@ci.uc.pt

T. K. Makhina

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia

V. S. Maltseva

Candidate of Chemical Sciences, Docent of the Department “General and Inorganic Chemistry”, Southwest State University

Yu. G. Medvedevskikh

Chemistry of Oxidizing Processes Division; Physical Chemistry of Combustible Minerals Department; Institute of Physical–organic Chemistry & Coal Chemistry named after L. M. Lytvynenko; National Academy of Science of Ukraine

3a Naukova Str., Lviv–53, 79053, UKRAINE; E-mail: hav.ok@yandex.ru

V. M. Misin

Emanuel Institute of Biochemical Physics Russian Academy of Sciences, 4 Kosygin Street, 119334, Moscow, Russia, E-mail: Natnik48s@yandex.ru

D. Mislovičová

Institute of Chemistry, Slovak Academy of Sciences, SK-84538 Bratislava, Slovakia

Yu. B. Monakov

Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences,
pr. Oktyabrya 69, Ufa, 450054, Bashkortostan, Russia

E-mail: badykova@mail.ru

R. Kh. Mudarisova

Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences,
pr. Oktyabrya 69, Ufa, 450054, Bashkortostan, Russia

E-mail: badykova@mail.ru

V. L. Myshkina

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia

M. Nagy

Department of Pharmacognosy and Botany, Faculty of Pharmacy, Comenius University, SK-83232, Bratislava, Slovakia

Joaquim J. S. Natividade

Departamento de Química, Universidade de Coimbra,
3049 Coimbra, Portugal

E-mail: anacfrib@ci.uc.pt

F. F. Niyazi

Doctor of Chemical Sciences, Professor, Head of the Department "General and Inorganic Chemistry", Southwest State University

E. Priesolová

Department of Pharmacognosy and Botany, Faculty of Pharmacy, Comenius University, SK-83232, Bratislava, Slovakia

Yu. I. Puzin

Ufa State Petroleum Technological University, 1 Kosmonavtov Street,
450062, Ufa, Russian Federation
E-mail: ppuziny@rambler.ru

P. Rapta

Slovak University of Technology, Faculty of Chemical and Food Technology, Institute of Physical Chemistry and Chemical Physics, SK-81237, Bratislava, Slovakia

A. V. Rebrov

A. V. Topchiev Institute of Petroleum Chemistry, Leninskiy prosp. 27, 119071 Moscow, Russia

Ana. C. F. Ribeiro

Departamento de Química, Universidade de Coimbra,
3049 Coimbra, Portugal
E-mail: anacfrib@ci.uc.pt

N. N. Sazhina

Emanuel Institute of Biochemical Physics Russian Academy of Sciences, 4 Kosygin Street, 119334, Moscow, Russia, E-mail: Natnik48s@yandex.ru

A. V. Sazonova

Postgraduate student of the Department "General and Inorganic Chemistry", Southwest State University

M. Slovák

Slovak University of Technology, Faculty of Chemical and Food Technology, Institute of Physical Chemistry and Chemical Physics, SK-81237, Bratislava, Slovakia

L. Šoltés

Institute of Experimental Pharmacology and Toxicology, Slovak Academy of Sciences, SK-84104, Bratislava, Slovakia

K. Valachová

Institute of Experimental Pharmacology and Toxicology, Slovak Academy of Sciences, SK-84104, Bratislava, Slovakia

Artur J. M. Valente

Departamento de Química, Universidade de Coimbra, 3049 Coimbra, Portugal
E-mail: anacfrib@ci.uc.pt

S. A. Yakovlev

A. N. Bach's Institute of Biochemistry, Russian Academy of Sciences, Leninskiy prosp. 33, 119071 Moscow, Russia

Yu. G. Yanovskii

N. M. Emanuel Institute of Biochemical Physics
of Russian Academy of Sciences, Kosygin st., 4, Moscow 119334, Russian Federation

E. I. Yarmukhamedova

Institute of Organic Chemistry of Ufa' Research Center of Russian Academy of Sciences, 71 Octyabrya Blvd. 450054, Ufa, Russian Federation
E-mail: gluhov_e@anrb.ru

G. E. Zaikov

Chemistry of Oxidizing Processes Division; Physical Chemistry of Combustible Minerals Department; Institute of Physical–organic Chemistry & Coal Chemistry named after L. M. Lytvynenko; National Academy of Science of Ukraine

3a Naukova Str., Lviv–53, 79053, UKRAINE; E–mail: hav.ok@yandex.ru

G. E. Zaikov

N. M. Emanuel Institute of Biochemical Physics of Russian Academy of Sciences, Kosygin st., 4, Moscow 119334, Russian Federation Russian Academy of Sciences, Moscow, Russia

E_mail: GEZaikov@Yahoo.com

List of Abbreviations

ABTS	2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)
AFM	Atomic force microscopy
AG	Arabinogalactan
AIBN	Azobisisobutyronitrile
AO	Antioxidants
BAS	Bioanalytical system
BAS	Biological active substances
BP	Benzoyl peroxide
BSR	Butadiene-styrene rubber
CV	Cyclic voltammetry
DC	Diketocarboxylic acids
DFM	Dynamic force microscope
DHA	Dehydroascorbate
DMPO	5,5-Dimethyl-1-pyrroline-N-oxide
DMSO	Dimethyl sulfoxide
DST	Department of Science and Technology
EHD	Electrohydrodynamic
EMI	Electromagnetic interference
EMISE	Electromagnetic interference shielding effectiveness
EPR	Electron paramagnetic resonance
FTIR	Fourier transforms infrared
GA	Gallic acid
GAGs	Glycosaminoglycans
GC	Glassy carbon
HA	Hyaluronan
HH	3-Hydroxyheptanoate
HO	3-Hydroxyoctanoate
HV	3-Hydroxyvalerate
INAH	Isonicotinic acid hydrazide
IR	Infrared
LBM	Lattice boltzmann method
MFE	Mercury film electrode
MMA	Methyl methacrylate
MW	Molecular weight
MWD	Molecular weight distribution
NDSA	Naphtalene disulfonic acid
NMP	N-methyl-2 pyrrolidon
NMR	Nuclear magnetic resonance
NR	Natural rubbers
ODE	Ordinary differential equation
PAN	Polyacrylonitrile

PANI	Polyaniline
PANIEB	Polyaniline emeraldine base
PB	Polybutadiene
PHAs	Polyhydroxyalkanoates
PHB	Poly(3-R-hydroxybutyrate)
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly(L-lactide)
PMMA	Poly(methyl methacrylate)
PMR	Proton magnetic resonance
PPy	Polypyrrole
PVA	Polyvinyl acetate
RMSD	Root-mean-square deviation
ROS	Reactive oxygen species
ROX	Redox initiating systems
SAWS	Self-avoiding walks statistics
SE	Shielding effectiveness
SEC	Size exclusion chromatography
SEM	Scanning electron microscope
SF	Synovial fluid
SPIP	Scanning probe image processor
SPM	Scanning probe microscopy
STM	Scanning tunneling microscopy
TBAP	Tetrabutylammonium perchlorate
TC	Technical carbon
TEAC	Trolox equivalent of antioxidant capacity
TEM	Transmission electron microscopes
THF	Tetrahydrofuran
THP	Theophylline
TMS	Tetramethylsilane
TMT	1,3,5-trimethyl-hexahydro-1,3,5-triazine
UCM	Upper-convected maxwell
WAXS	Wide angle X-ray scattering
WDX	Wavelength-dispersive X-ray
XRD	X-ray diffraction Technique

Introduction

Advances in Kinetics and Mechanism of Chemical Reactions describes the chemical physics and/or chemistry of 10 novel material or chemical systems. These 10 novel material or chemical systems are examined in the context of issues of structure and bonding, and/or reactivity, and/or transport properties, and/or polymer properties, and/or biological characteristics. This eclectic survey thus encompasses a special focus on the associated kinetics, reaction mechanisms and/or other chemical physics properties, of these 10 broadly chosen material or chemical systems. Thus, the most contemporary chemical physics methods and principles are applied to the characterization of the properties of these 10 novel material or chemical systems. The coverage of these novel systems is thus broad, ranging from the study of biopolymers to the analysis of antioxidant and medicinal chemical activity, on the one hand, to the determination of the chemical kinetics of novel chemical systems, and the characterization of elastic properties of novel nanometer scale material systems, on the other hand.

Advances in Kinetics and Mechanism of Chemical Reactions is divided into 10 chapters.

Chapter 1, by Valachova et al., describes their chemical system as comprised of the compound "arbutin" in cupric ion solution with ascorbate as a reagent for treating hyaluronan (HA). Thus arbutin was tested in the function of a potential anti- or prooxidant in Cu(II) plus ascorbate, and it induced degradation of high-molar-mass hyaluronan (HA). The time- and dose-dependences of dynamic viscosity changes of the HA solutions were investigated by the method of rotational viscometry. Both the reduction of the dynamic viscosity of the HA solution and the decrease of the polymer mean molar mass as revealed by the method of size exclusion chromatography proved the tenet that on using the Cu(II) ions plus ascorbate, i.e. the Weissberger's oxidative system, the degradation of HA macromolecules is pronounced by added arbutin. These studies of hyaluronan (HA), a biopolymer consisting of disaccharide units, are important from the perspective of understanding the physiology of HA in the bones and joints and in other tissues. The medical importance of understanding HA turnover in the human body cannot be underestimated.

In Chapter 2, Ribiero et al., describe their investigations of diffusion kinetics, including the modeling of electrolytes and non-electrolytes. Thus in the past few years, their diffusion phenomena group has been particularly dedicated to the study of mutual diffusion behavior of binary, ternary and quaternary solutions, involving electrolytes and non-electrolytes, helping to go deeply into the understanding of their structure, and aiming at practical applications in fields as diverse as corrosion studies occurring in biological systems or therapeutic uses. In fact, the scarcity of diffusion coefficients and other transport data in the scientific literature, due to the difficulty of their accurate experimental measurement and impracticability of their determination by theoretical procedures, coupled to their industrial and research need, well justify the work reported here by Ribiero et al. in accurate measurements of such transport properties.

Chapter 3 describes the frictional and elastic properties of the chemical system comprised of polystyrene dissolved in toluene. Medvedevskikh et al. describe their work thus, as it has been experimentally investigated by the gradient dependence of the effective viscosity η for concentrated solutions of polystyrene in toluene at three concentrations, ρ , and for the four fractions of polystyrene characterized by four distinct molar weights, M . The gradient dependence of each respective solution's viscosity was studied at four temperatures, T , for each pair of ρ and M valuations. The experiments were carried out with the use of a standard viscosity meter at the different angular velocities ω (turns/s) of the working cylinder rotation. An analysis of the $\eta(\omega)$ dependencies permitted the marking out of the frictional (η_f) and elastic (η_e) components of the viscosity and to study their dependence on temperature T , concentration ρ and the length of a chain N . These fundamental chemical physics studies, carried out on the molecular scale, are important for the theory underlying the viscosity phenomena. Where viscosity is a physical quantity that certainly requires further investigations and measurements on the molecular scale.

In Chapter 4 of this volume concerning reinforcement mechanisms of nanocomposites, Kozlov et al. describe the theoretical and experimental study of the mechanics of nanoscopic matter. The modern methods of experimental and theoretical analysis of polymer materials structure and properties have allowed Kozlov et al. to confirm earlier propounded hypotheses, but also to obtain principally new results. These investigators consider some important problems of particulate-filled polymer nanocomposites, the solution of which allows one to advance substantially the understanding of these materials and their unusual properties. It thus endows one with the ability to understand and predict. In this aspect interfacial regions play a particular role, since it has been shown earlier that they are the same reinforcing element in elastomeric nanocomposites, and they thus occur as nanofiller actually. Therefore the knowledge of interfacial layer dimensional characteristics is necessary for quantitative determination of one of the most important parameters of polymer composites in general – their reinforcement degree. And thus this study by Kozlov et al. is an important investigation of the chemical physics of nanocomposites, including a clarification of their multicomponent nature and a description of the nanocomposite reinforcing elements.

In Chapter 5, Mudarisova et al. describe their work in drug discovery, in the area of antituberculosis preparations. In particular, this group describes the addition of known tuberculostatic drugs to saccharides, in an attempt to develop medicinal compositions that can overcome drug resistance in bacteria causing tuberculosis. Thus the work of Mudarisova et al. can be summarized, drug discovery is one of the thrust areas of modern medicinal chemistry. The search for and development of new antituberculosis agents have recently become of interest because of the drug resistance of mycobacteria to existing drugs. One promising direction for creating such drugs is the addition of common tuberculostatics to polysaccharides. It is known that the polysaccharide arabinogalactan (AG) has a broad spectrum of biological activity. However, its tuberculostatic activity has not been reported. Herein the modification of AG and its oxidized forms by the antituberculosis drug isonicotinic acid hydrazide (INH) and the antituberculosis activity of the resulting compounds are studied.

Chapter 6 of this volume by Niyazi et al. describe determination of the sorption properties of polymer cellulose and natural carbonate sorbents for use in wastewater treatment applications. Niyazi et al. thus summarize, "the article shows the comparative characteristics of the sorption properties of polymer cellulose and natural carbonate sorbents. The influence of the mass of sorbents on the degree of extraction as well as the pH changing are analyzed. The optimum phase ratio has been determined. Kinetic curves have been plotted." The work of Niyazi et al. thus advances our understanding and development of wastewater treatment reagents for applications of clarifying wastewater in many and varied areas, both industrial and domestic, in everyday life.

Yarmukhamedova et al. in Chapter 7 of this volume investigate chemical physics properties of a class of aromatic compounds (diketocarboxylic acids) on the radical initiation properties of an initiator compound used in a polymerization reaction system. Thus as Yarmukhamedova et al. describe, "the influence of aromatic diketocarboxylic acids on the decomposition initiator of radical polymerization - azobisisobutyronitrile was studied by UV spectroscopy. The interaction occurs with the participation of carboxyl groups of diketocarboxylic acids with nitrile groups of the initiator. It is shown that polymer obtained in the presence of aromatic diketocarboxylic acids has mainly a syndiotactic structure." And thus such work as that reported here by Yarmukhamedova et al. advances our understanding of the synthesis and properties of technologically important classes of radical polymerization polymers.

In Chapter 8 of this volume Yarmukhamedova et al. continue their work on radical polymerization synthesis and the chemical physics properties of the radical initiators used in such synthetic procedures. Yarmukhamedova et al. thus summarize their study of the methyl methacrylate synthetic polymer system, "the influence of the 1,3,5-trimethyl-hexahydro-1,3,5-triazine on the radical polymerization of methyl methacrylate was studied. The kinetic parameters were obtained (reaction orders, activation energy of polymerization). It is established that the triazine is the slight chain transfer agent during to polymerization initiated by azo-bis-isobutyronitrile, and the component of the initiating system if the peroxide initiator is used. Polymers synthesized in the presence of 1,3,5-trimethyl-hexahydro-1,3,5-triazine have the higher content of syndio – and isotactic sequences in the macromolecule." Such fundamental polymer chemical physics work as reported here by Yarmukhamedova et al. advances our understanding of these technologically important classes of polymer systems.

In Chapter 9 of this volume, Bonartsev et al. focus their work on the degradation properties, including particularly the degradation kinetics of the biochemical reagent known as poly(3-hydroxybutyrate) and its derivatives. This work is designed to be an informative source for research on biodegradable poly(3-hydroxybutyrate) and its derivatives. Bonartsev et al. focus on hydrolytic degradation kinetics at two distinct temperatures, in phosphate buffer to compare polymer kinetic profiles. These investigators report chemical physics properties of these novel biopolymer systems (i.e. poly(3-hydroxybutyrate)) due to the economic interest in these natural polymers over the well-known synthetic polymers. For it is well known that natural polymers represent an emerging area of technological interest and application, especially so with their biodegradability

Finally in Chapter 10, Sazhina et al. present analytical measurements of antioxidant content in various food products. The antioxidant measurements are accomplished by means of electrochemical instrumentation. Sazhina et al. thus describe their work, "A comparison of the total content of antioxidants and their activity with respect to oxygen and its radicals in juice and extracts of herbs, extracts of a tea and also in human blood plasma was carried out in the present work by use of two operative electrochemical methods: ammetric and voltammetric. Efficiency of methods has allowed studying dynamics of antioxidants content and activity change in same objects during time. Good correlation between the total phenol antioxidant content in the studied samples and values of the kinetic criterion defining activity with respect to oxygen and its radicals is observed." Thus Sazhina et al. provide an interesting methodology and corresponding analysis of the levels of important antioxidant components within common food products. This work is important for advancing our knowledge of antioxidant biochemistry and its potential therapeutic properties.

In conclusion, we see thus in this volume, **Advances in Kinetics and Mechanism of Chemical Reactions**, that chapters 1, 6 and 9 address the investigation of three novel and distinct biopolymer systems, as to their chemical kinetics and other chemical properties. In Chapter 2 there is then a digression into the measurement of the diffusion kinetics of electrolyte and non-electrolyte systems, with application to corrosion studies. Chapter 3 covers the determination of viscoelastic properties of the chemical system comprised of polystyrene dissolved in toluene. And the reinforcement mechanisms of nanometer scale composites, with special attention focused on mechanical properties of representative nanometer scale composite materials, is reported in Chapter 4. And in Chapter 5, the biological activity of a novel tuberculostatic drug-polysaccharide composition is reported from novel synthetic studies. Then polymer chemical kinetics of two important classes of radical polymerization polymers, with special focus on the radical initiators used in these polymer synthetic reactions, provides the focus of Chapters 7 and 8. In this work on polymer chemical physics both reaction orders and activation energies were determined for technologically important classes of radical polymerization polymers. Chapter 10 concludes with an investigation and novel determination of antioxidant content in various foodstuffs by the classical analytical chemistry technique of electrochemistry.

It can be concluded, from this brief survey of the present volume, that broad chemical physics coverage of 10 novel material or chemical systems is reported within its pages. The chemical physics methods used to characterize these 10 novel systems are clearly state-of-the-art, and the results should be intriguing to the prospective readership in chemistry and physics and nanoscience, including those scientists engaged in chemical physics research and the polymer chemistry and physics communities, as well as those researchers involved in biological chemistry research and also those scientists focused on nanotechnology.

— Gennady E. Zaikov