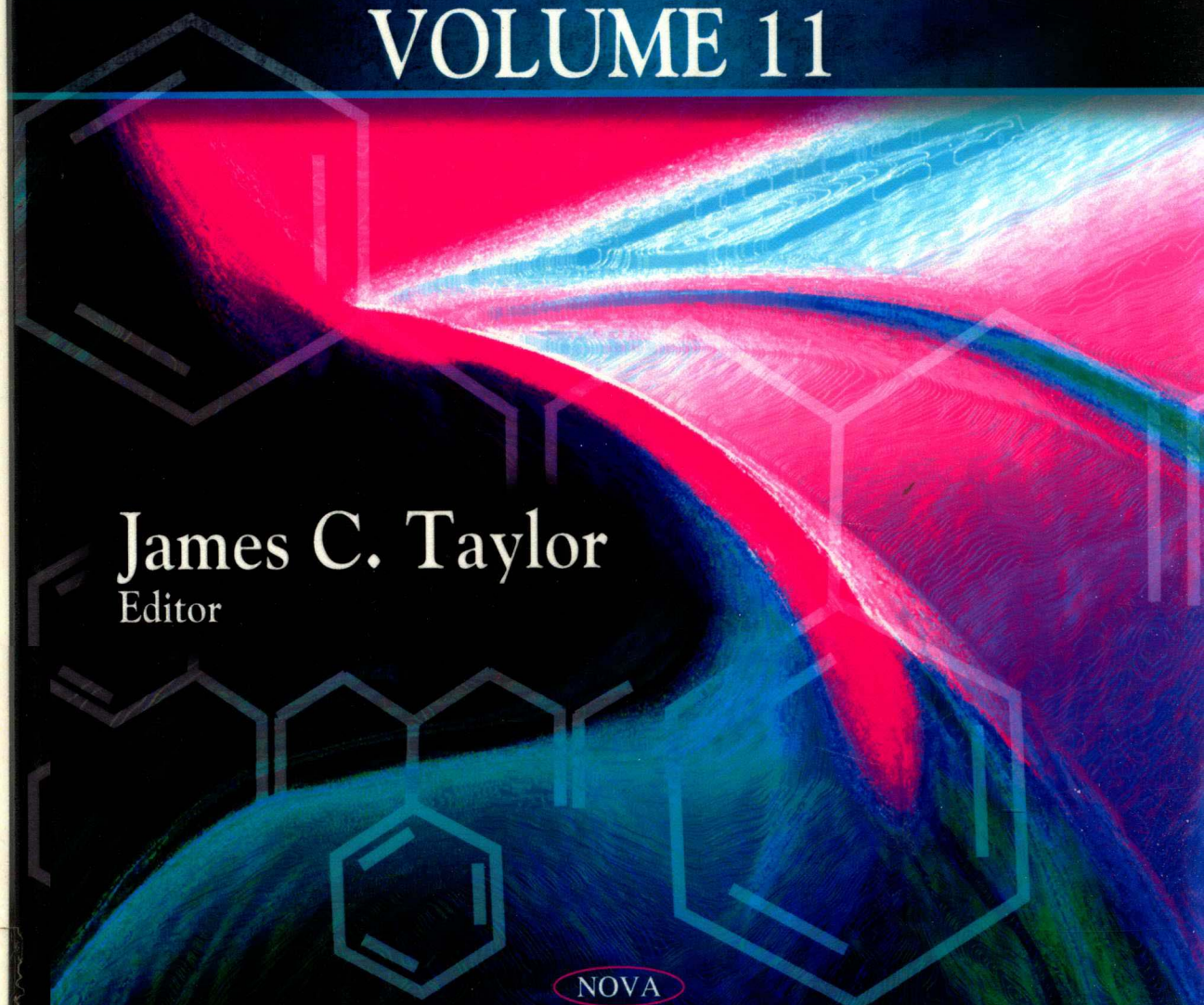
Advances in CHEMISTRY RESEARCH

VOLUME 11



James C. Taylor
Editor

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VOLUME 11

JAMES C. TAYLOR
EDITOR

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PREFACE

This book presents original research results on the leading edge of chemistry research. Each article has been carefully selected in an attempt to present substantial research results across a broad spectrum. Topics discussed include the potential binding potency of biological molecules; nitrogen dioxide for wasteless sustainable syntheses; the molecular structure of five new 2-methylbenzimidazole derivatives; electrochemical reduction of phthalimide in isoindoline; nitrous oxide clathrate hydrates and the molecular mechanis of urea denaturation.

Chapter 1 - Physical-chemical interactions and association/dissociation reactions between biological molecules play a fundamental role for the regular functioning of vital biochemical processes. Accordingly, the general propensity of these molecules to bind or (temporarily) retain other bioactive partner molecules is certainly a biologically meaningful feature. Hence, it appears valuable to study this particular property which will be termed the potential binding potency (PBP) of a given molecule or molecular system hereafter especially in dependence on the specific structural preconditions. The water-binding potency (BP) is believed to provide a reasonable and reliable measure for quantitatively estimating the PBP of biological molecules and/or the higher-order structures formed by them and, thus, to open an access for exploring the addressed structure-PBP relationships. In this study, BP values systematically determined under *ad hoc* established standard conditions are reported and compared for an appreciable number of biomolecules. Those comprise mainly lipid assemblies and, besides, a few nucleic acids, prepared as oriented films in each case. The amount of the imbibed water which is expressed as hydration number, n_w, was estimated from infrared-spectroscopic measurements of the biomolecule-water systems at 98 % relative humidity. Beforehand, these spectroscopic results were calibrated by a data set obtained from coupled Karl-Fischer titrations used as a directly operating and very sensitive water-specific chemical-analytical technique. The BP found in this way for the lipid assemblies turned out to cover a wide range of n_w values between 0 and 13. The amazing size of these differences sheds a new light on the principal functional relevance of the amphiphile monomer structure that is distinguished by the very nature of the sub-molecular domains, that is, the structural peculiarities within polar headgroups and apolar chains. The PBP of lipids is mainly governed by two antipodal factors, namely the fluidity of the assembly which generally favors water binding (that is, a high PBP) and the existence of inter-lipid bonding networks formed by hydrogen bonds and/or salt bridges which is restrictive for the PBP. Besides, there is number of more phenomenological structural factors affecting the PBP, as the headgroup size, the presence of charges and counterions, and eventually the accessibility of the potential binding sites which seems to be

prevented only in exceptional cases. Out of the principal PBP-determining factors of lipids, fluidity is essentially governed by the structure of the apolar hydrocarbon chains, while the propensity for internal-network formation is clearly encoded in the very headgroup structure, in particular *via* the number and distribution of hydrogen-bond donors and acceptors. Nucleic acids, as being rather polar than amphipathic, are able to take up, with $n_w > 12$, significantly more water than lipids. The PBP of nucleic acids is fundamentally related to the structure of the sugar involved in the backbone in two different respects. This refers at first to the basic chemical nature, ribose or deoxyribose, and secondly to the pucker as defining the nucleic-acid conformation. Moreover, the PBP depends on base composition and sequence which are, for DNA, closely correlated with the conformation. The PBP has been found to be minimum for RNA and maximum for deoxyribo-homopolynucleotides. Upon drying, nucleic acids are able to retain a fairly large deal of residual water (much more than lipids) which appears suitable to stabilize the disordered form adopted under these conditions against irreversible denaturation. Some of the final remarks are devoted to a possible biological importance of the presented data and conclusions.

Chapter 2 - The reactions of ubiquitous inexpensive gaseous NO_2 in solventless environments are subdivided into wasteless gas-solid reactions staying solid and those that become partly liquid or start with liquids. The quantitative reactions with utilization or recycling of the reaction gases are generally wasteless, and they are achieved without catalysts or other auxiliaries. The pure products are directly obtained without chromatographic purification etc, which makes the safe gas handling superior to other "green" oxidizing agents, and scaling to sustainable industrial applications is already verified. The exceptional selectivity of highly reactive NO_2 in gas-solid oxidations is interpreted on the basis of recent mechanistic concepts mostly derived from atomic force microscopy (AFM) measurements in connection with crystal packing analysis. Favorable crystal packing requires cleavage planes or channels. A wide variety of functional materials have been specifically and quantitatively oxygenated either with stoichiometric or excess NO_2. This covers nitrite salts (with sustainable synthesis of NO), HONO ($HONO_2$), RCHR'ONO_2 (RCR'=O and $HONO_2$), nitroxyls (nitrosonium nitrates) and stable N-radicals (azinium nitrates), primary aromatic amines and their derivatives (solid diazonium nitrates), secondary aromatic amines (hydrazinium nitrates), amides (either only oxygenation or nitramines and $HONO_2$), thioamides (either only disulfides or amides and $HONO_2$), thioureas (ureas and $HONO_2$), aromatics (nitroaromatics and $HONO_2$), aliphatics (nitroalkanes and $HONO_2$), alcohols (aldehydes/ketones or acids and $HONO_2$), and aldehydes (acids and NO). Surprising specificities also in the presence of other oxidizable functional groups are reported. Quantitative yield of one product is generally achieved even in the presence of several possibilities (for example quantitative tetranitration of all *para*-positions of tetraphenylethene). There are only few exceptions with unspecific multiproduct results, when stabilized intermediate radicals are involved (for example with anthracene). Extended structural variations enable valuable extensions. The often highly reactive products (e.g. solid diazonium salts, etc) are starting points for quantitative follow-up syntheses. Some diazotizations with NOCl and NO are also included. The sustainable solid-state syntheses reveal environmental sinks for natural or man-made atmospheric NOx by reaction with biological or other solids that exhibit the corresponding functionality. Properly executed solventless NO_2 reactions involving liquid phases may also be wasteless, compatible with other functionalities, and providing quantitative yield of one product. This differs markedly

from solution reactions. The oxidations include primary alcohols (aldehydes), secondary alcohols (ketones), aldehydes (acids at slightly enforced conditions), oximes and related imino-derivatives (aldehydes or ketones), and trimethylsilyl ethers (aldehydes or ketones). These favorable results are obtained in the presence of electron donating or electron accepting substituents. Multiple synthetic applications without the necessity to intermediately protect other functional groups are presented and mechanistically discussed.

Chapter 3 - A novel material activated carbon can be produced from agricultural residue, coals and synthetic macromolecules. The effects of various activating process parameters on the pyrolysis stage can be observed. Influences of activating conditions, physical and chemical, on the activating precursors have been observed. Activated carbons are amazing complex molecules in terms of size, shape and porosity. Their wholesome characterization is a major challenge to the scientists. Although, the subject areas of porosity in solids and associated experimental and theoretical approaches are extremely comprehensive, it is possible to identify several basic concepts which are fundamental to these subject areas. Porosity is created during the carbonization process of an organic macromolecules precursor (such as cellulose and lignin). The removal of small molecules brings about "distortion" within the structure of the original precursor at the same time as hydrogen and oxygen atoms are eliminated. The resultant carbon skeletal becomes extremely unstable and carbon atom within these structures will combine with other near-neighbour carbon atom to create positions of maximum stability as far as available stereochemistry will allow. A pragmatic approach for characterization of activated carbons can be made from multi point Brunauer Emmett & Teller (BET) isotherms with three different carrier gases viz., N_2 at 77 K, CO_2 at 273 K and H_2O at 298 K or enthalpy of inversion in water. Scanning electron micrograph (SEM) and energy dispersive x-ray analysis (EDX) used for the surface morphological study and elemental composition, respectively, of the prepared activated carbons.

Chapter 4 - Benzimidazole and its derivatives are accepted pharmacophores and represent important synthetic precursors in new drugs discovery. These heterocyclic compounds have awakened great interest during the last few years because of their proven biological activity as antiviral, antimicrobial and antitumoral agents. In this chapter, the authors report a combined experimental and theoretical study on the molecular structures and vibrational spectra of five new 1-derivatives of 2-methylbenzimidazole, including its isomers. The structures of the target compounds were confirmed by ^{1}H and ^{13}C NMR, elemental analysis, mass spectrometry and spectroscopic methods such as Raman, FT-IR, and UV-VIS. The experimental results were supported by performing density functional theory (DFT) calculations for energies, geometries, vibrational frequencies and NMR shielding constants using 6-311+G** basis sets and B3LYP functional. The theoretical data, using DFT approximation, and experimental results were consistent with each other.

Chapter 5 - This chapter reviews oil separation from oil-in-water (O/W) emulsions and surfactant removal by membrane microfiltration (MF) and ultrafiltration (UF), with particular emphasis on high shear rate dynamic filtration. O/W emulsions are produced in many industries, such as petrochemical, metallurgical, pharmaceutical, cosmetics and food industries. They give rise to considerable amounts of waste waters containing oil and surfactants which must be removed before the water can be discharged in rivers or reused. Metal working emulsions containing cutting oil and SDS surfactant were ultrafiltered using a rotating disk and a vibrating VSEP dynamic filtration module using hydrophilic PES (polyethersulfone) 20 and 50 kDa membranes. The permeate flux of 4% oil emulsions was

about 90-100 $Lh^{-1}m^{-2}$ with a disk equipped with vanes and rotating at 1000 rpm at a mean transmembrane pressure of 90kPa and oil rejection was 99.5%. With the VSEP at maximum vibration frequency, the permeate flux at 50 kDa was 100 $Lh^{-1}m^{-2}$ at 90 kPa, but rose to a maximum of 250 $Lh^{-1}m^{-2}$ at 1500 kPa. Linseed oil-in-water emulsions at 1.5% oil concentration were demulsified with the rotating disk, but at higher speeds, using a hydrophilic PVDF membrane in MF and a PES 50 kDa in UF. Maximum permeate fluxes at 2750 rpm were higher in UF than in MF, reaching 170 $Lh^{-1}m^{-2}$ at 980 kPa in UF and 130 $Lh^{-1}m^{-2}$ at 380 kPa in MF. Oil recovery was 76%, but should increase when treating larger volumes. In UF of SDBS solutions at critical concentration, the rotating disk reached its maximum flux at a rotation speed of about 500 rpm. In concentration tests with a 10 kDa PES membrane, the flux decayed slowly from 400 $Lh^{-1}m^{-2}$ at 1000 rpm and 1400 kPa to 350 $Lh^{-1}m^{-2}$ at a volume reduction ratio of 7 while SDBS rejection fell from 92% to 36%. These data confirm the high performance of high shear dynamic filtration and hydrophilic membranes for demulsification of O/W emulsions and surfactant removal.

Chapter 6 - In spite of the fact that the use of sulfites as preservatives in wines has been known for centuries, most of the scientific knowledge about their properties in enology has been acquired over the last decades. The aim of this chapter is to present an overview of the current knowledge about the significance of sulfur dioxide during winemaking, including its chemistry and properties, application and analytical determination in wine. Potential hazards of these compounds for human health as well as legislation concerning their occurrence in wine are reported. Also, the chapter presents a detailed view of the different complementary treatments, alternatives and strategies currently proposed to reduce the use of this additive in enology. These can be classified, according to their nature, into physical, and chemical and biochemical procedures, although they can also be used in combination. Within the chemical alternatives, special attention is paid to the use of natural phenolic extracts with proven antimicrobial and antioxidant properties. Finally the future trends in the research of these alternatives are discussed.

Chapter 7 - Cathodic reduction of phthalimide in aqueous-organic solutions (H_2O-CH_3CN acidified with H_2SO_4 or HCl) at Hg, In, Cd and Ag amalgam electrodes was performed resulting in double decarbonylation of phthalimide and allowing to obtain 2,3-dihydro-1H-isoindole (isoindoline) selectively with high substance yield and, contrary to earlier works, with the current efficiency close to the substance yield. The crucial conditions for high efficiency of this process are i) the use of cathodic materials with high overpotential of hydrogen evolution, ii) keeping the working electrode potential in the range -1.2…-0.9 V *vs* SCE, and iii) continuous correction of the catholyte acidity in order to maintain it at the optimal level (pH = 2.5) throughout the electrolysis. The importance of carbon-based anode materials is also underlined.

Chapter 8 - Air pollution is one of the typical environmental risk factors for human health. Passive samplers, also known as diffusion/diffusive samplers, have been recognized as an efficient alternative to pumped samplers for assessing personal exposure due to their ubiquitous, cost-effective and user-friendly properties. This work aimed to study a relationship between personal exposure and micro-environmental concentrations of NO and NO_2, H_2S and carbonyl compounds using the passive sampling devices. Personal exposure and indoor, outdoor residential, workplace and outdoor urban concentrations were simultaneously measured for 2 volunteers (A and B) working in the same office located in Oxford, UK. NO and NO_2 were collected by an Ogawa sampler employing cellulose filter

impregnated with triethanolamine (TEA) for the trapping of NO_2 and that with TEA and an organic radical, 2-phenyl- 4,4,5,5- tetramethylimidazoline-1-oxyl-3-oxide (PTIO) for NO. In this study the labile PTIO was stabilized by adding nonionic surfactant into the filter. The filter extracts were then determined by sulfanilamide/NEDA methodology. H_2S was also collected using the Ogawa sampler with a silver nitrate impregnated filter. The H_2S was trapped as silver sulfide and subsequently quantified by its quenching effect on the fluorescence of fluorescein mercuric acetate. Carbonyl compounds were collected using DNPH coated silica gel and determined by UV-HPLC. As a result, the highest concentration of NO_2 was found in the City center and was associated with heavy automotive traffic. The H_2S concentration was highest in indoor air of the workplace where the gas was sometimes used for laboratory purposes. The indoor to outdoor concentrations of greater than unity indicated possible emissions in indoor materials or activity, as is typically found for formaldehyde. Measured personal exposure levels were compared with the time-weighted average of micro-environmental concentrations. As for volunteer B who did not spend his time other than in measured microenvironments, excellent agreement was found between model estimates and measured exposures levels with a good correlation coefficient. On the other hand, the model values were underestimated and no significant correlation was found for volunteer A. The underestimation indicates that there are other environmental factors significantly contributing to personal exposure of volunteer A. This finding claims the importance of personal exposure monitoring in assessing exposure to air pollutants.

Chapter 9- 2-((1*H*-benzo[*d*]imidazol-2-yl)methylthio)-4-(substituted)-6-henylpyrimidine-5-carbonitriles were evaluated for their antiviral activity. The HIV inhibitory activity of the synthesized compounds 1, 3-25 showed that most of them have significant activity. Compounds 3, 5-25 exhibited higher potency than Atevirdine. The most potent compounds in descending order were: 18 > 11> 20 > 19 > 5 > 16 > 23 > 17 > 24. Moreover, compounds 5-25 exhibited therapeutic index than Atevirdine. The HIV-1 RT inhibitory activity showed that compounds 17, 8, 16, 9, 24, 14, 22, 18, 19, 10, 21, 25, 5, 9 and 4 were more potent than Atevirdine and with wider therapeutic index than the standard. Moreover, the binding affinity of the synthesized benzimidazole derivatives into HIV-1 RT receptor (PDB code: 1ep4) for the purpose of lead optimization have been investigated and to find out the interaction between the synthesized benzimidazole derivatives and the HIV-1 RT receptor. The HCV NS3-4A protease inhibitor activity of the tested compounds revealed that most of them have significant activity with exception compounds 7, 8 and 25 but none of them showed higher activity than VX-950.

Chapter 10 - The novel investigation of 1,5-diamino-4-methyl tetrazolium perchlorate has been identified from the reaction of 1,5-diamino-1 H-tetrazole with iodomethane followed by the metathesis of iodide with silver perchlorate, leads to a new derivative of ionic salt. The present review focuses mainly on the synthesis, structural aspect, spectroscopic studies and also some physico-chemical properties of the 1, 5-diamino-4-methyl tetrazolium perchlorate have been investigated. The investigated compound may find wide spectrum of futuristic applications in the area of energetic materials and health sciences since the higher percentage of the end is molecular nitrogen in this communication. The standard molar enthalpies of formation will be derived based on designed Born Haber energy cycles.

Chapter 11 - Bronze is a metal commonly used for sculptures and building structures. These objects are often covered with patina, a layer of corrosion products, which confers their aesthetic and also protects the substrate bronze. Due to the increasing atmospheric pollution

these layers, as well as the supstrate bronze, are often dissolving when exposed in urban environment. This work proposes the use of two innoxious imidazole compounds as corrosion inhibitors: 4-methy1-1-*p*-tolylimidazole (TMI) and 1-*H* benzimidazole (BZI) on the Cu-6Sn (wt-%) bronze, in a solution simulating acid rain in urban environments. The results of the electrochemical investigations have shown that both TMI, as well as BZI protect this alloy. On the Cu-6Sn bronze patina was formed by a new electrochemical method which simulates patina formed spontaneously during long term exposure to urban environments. As corrosion inhibitors both TMI and BZI were applied on patina in the solution simulating acid rain. The results have shown that they both improve greatly the stability of patina. The results confirmed that both TMI and BZI can be used for protection of bronze, as well as its patina exposed to urban environments.

Chapter 12 - Clathrate hydrates, or gas hydrates, are ice-like solid crystalline compounds, which are formed through a combination of water and small guest molecule(s), like methane, under low temperatures and elevated pressures. In the gas hydrate lattice, water molecules form hydrogen-bonded cagelike structures, encapsulating the guest molecule(s). Nitrous oxide is a suitably sized molecule, which can form clathrate hydrate. Currently, very limited information is available for this clathrate hydrate. This gas is similar in size and molecular weight to carbon dioxide. It may therefore be assumed that carbon dioxide and nitrous oxide simple hydrates can have similar hydrate characteristics. In this chapter, the authors review phase diagrams of carbon dioxide and nitrous oxide simple hydrates as well as crystallography study reported in the literature for nitrous oxide clathrate hydrate. It is shown that these two molecules have similar, but not exactly, clathrate hydrate characteristics.

Chapter 13 - Nanomaterials have attracted considerable attention due to their importance in basic scientific research and potential technological applications (Nanotechnology). The nanochemistry is key for Nanotechnology .There are two main ways for the preparation of nanomaterials: those in solution and those in solid-state. The most wide development has been in solution, while solid-state approaches are scarce. Here we present a general solid-state method to obtain metallic, metal oxides and phosphate nanoparticles. The method consists of pyrolysis of the organometallic derivatives of cyclo and polyphosphazenes precursors containing diverse organometallic fragments linked to polymeric or oligomeric phosphazenes at 800 °C and under air. The nanostructured products are metallic, metal oxides and metallic phosphate nanoparticles depending on the nature of the metal forming the organometallic fragment. When the organometallic fragment contain noble metal such as $Au(C_6F_5)$, metallic nanoparticles are obtained whereas that when the fragment such as metals Ru, Cr, the respective metal oxide was obtained. With organometallic fragment containing W, Fe, Ti and Si both the respective metal oxide and the phosphate were obtained. On the other hand, with organometallic containing Mn only the pyrophosphate was obtained. Recent results from organometallic precursor containing V and Cu are also presented. In addition, preliminary results on solid- state pyrolysis of bimetallic derivatives of cyclotriphosphazene show separate metallic nanoparticles which undergo *"in situ"* nano-reactions induced by the e-beam of the HRTEM measurements. Although mechanistic studies are difficult to perform in solid state, the authors present here some preliminary results on the mechanism pyrolysis of a cyclotriphosphazene containing a Mn organometallic fragment. At the intermediate temperature of the formation process, Raman data indicates the presence of amorphous carbon and graphite.

Chapter 14 - The study provides novel attempt to use a bioreactor containing immobilized nitrifying and denitrifying microorganism for removal of nitrogen oxides (NO_x)-dominant waste gases in low concentration. Mixture of nitrifying bacteria and denitrifying bacteria was immobilized using sodium alginate and polyvinyl alcohol as entrapped materials. Extensive tests to determine NO_x removal efficiency, pH dependence, inlet concentration, empty bed residence time (EBRT) and removal kinetics were performed. To estimate the maximum apparent removal rate, a prediction model was also employed. The results showed that NO_x removal efficiency achieved 72.3%. The optimal pH and empty bed residence time (EBRT) are 7.3 and 25.6 s, respectively. NO_x biodegradation reaction rate follows enzymatic catalytic kinetics. The results also indicated that maximum apparent removal rate was 7.14 g-NO_x.m-^{3}.h^{-1}. Hence, the results would be used as the guideline for the design and operation of immobilized microorganism biofilter. The use of the immobilization microorganism technique proves to be an efficient way to achieve NO_x removal.

Chapter 15 - Acid rain is a complex phenomenon that can result either from natural or anthropogenic causes. Within the broad term "acid rain" several different processes can be grouped, namely acidic rain, fog, hail and snow. These processes affect nearly all ecosystems within its reach, from marine to terrestrial ones. In particular, the negative impact of acid rain in terrestrial ecosystems arises both from its deleterious effects on soil and from a direct effect upon plant organs, such as leaves and roots. In this chapter, the major consequences of acid rain on soils will be discussed, mainly focusing on the chemistry of nitrogen, oxygen and sulphur that is involved in nutrient depletion and transformation. The impact of acid rain in the physiology and anatomy of several species with economic importance will be presented, with particular emphasis in plant seedlings, plants' growth and life cycle. The physiological responses of plants to acid rain, and the signalling pathways involved will also be considered.

Chapter 16 - Synthetic utility of organic superbases has been recognized and covered in several excellent reviews. By definition, superbases are organic molecules which are stronger bases than archetypal 'proton sponge', 1,8-bis(dimethylamino)naphthalene, *i.e.* they have the absolute proton affinity (APA) larger than 245.3 kcal mol^{-1} and gas-phase basicity (GB) over 239 kcal mol^{-1}. Design and synthesis of novel neutral organic superbases is an important scientific target nowadays and many efforts has been laid in developing building blocks that can be combined together ending up in highly basic molecule. Nitrogen containing building blocks such as guanidines, amidines, phosphazenes, polypyridines and proazaphosphatranes are singled out as the most potent in this respect.

Chapter 17 - Proteins are known to denature at high concentrations of compounds such as urea or guanidinium chloride. However, the mechanism by which urea and guanidinium chloride destabilizes proteins is not yet known, despite many decades of research. Attempts have been made to understand protein denaturation on a thermodynamic level as well as on a molecular level. The long term goal in the field is to merge the results of these two types of studies into one mechanism that is consistent with both the microscopic and the macroscopic level. In this text we firstly review thermodynamic studies as well as spectroscopic and computer simulation studies of chemical denaturation. The results of the different types of studies is then merged together in order to find a consistent view on chemical denaturation. In contrast to common belief in the field, a high degree of consensus is found between the different studies and a molecular mechanism of urea-induced protein denaturation can therefore be proposed.

CONTENTS

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Chapter 1

THE POTENTIAL BINDING POTENCY OF BIOLOGICAL MOLECULES

Walter Pohle*
Institute of Biochemistry and Biophysics, Friedrich-Schiller University Jena,
Philosophenweg, Jena, Germany

ABSTRACT

Physical-chemical interactions and association/dissociation reactions between biological molecules play a fundamental role for the regular functioning of vital biochemical processes. Accordingly, the general propensity of these molecules to bind or (temporarily) retain other bioactive partner molecules is certainly a biologically meaningful feature. Hence, it appears valuable to study this particular property which will be termed the potential binding potency (PBP) of a given molecule or molecular system hereafter especially in dependence on the specific structural preconditions. The water-binding potency (BP) is believed to provide a reasonable and reliable measure for quantitatively estimating the PBP of biological molecules and/or the higher-order structures formed by them and, thus, to open an access for exploring the addressed structure-PBP relationships.

In this study, BP values systematically determined under *ad hoc* established standard conditions are reported and compared for an appreciable number of biomolecules. Those comprise mainly lipid assemblies and, besides, a few nucleic acids, prepared as oriented films in each case. The amount of the imbibed water which is expressed as hydration number, n_w, was estimated from infrared-spectroscopic measurements of the biomolecule-water systems at 98 % relative humidity. Beforehand, these spectroscopic results were calibrated by a data set obtained from coupled Karl-Fischer titrations used as a directly operating and very sensitive water-specific chemical-analytical technique.

The BP found in this way for the lipid assemblies turned out to cover a wide range of n_w values between 0 and 13. The amazing size of these differences sheds a new light on the principal functional relevance of the amphiphile monomer structure that is distinguished by the very nature of the sub-molecular domains, that is, the structural peculiarities within polar headgroups and apolar chains. The PBP of lipids is mainly

* E-mail address: walter.pohle@uni-jena.de

governed by two antipodal factors, namely the fluidity of the assembly which generally favors water binding (that is, a high PBP) and the existence of inter-lipid bonding networks formed by hydrogen bonds and/or salt bridges which is restrictive for the PBP. Besides, there is number of more phenomenological structural factors affecting the PBP, as the headgroup size, the presence of charges and counterions, and eventually the accessibility of the potential binding sites which seems to be prevented only in exceptional cases. Out of the principal PBP-determining factors of lipids, fluidity is essentially governed by the structure of the apolar hydrocarbon chains, while the propensity for internal-network formation is clearly encoded in the very headgroup structure, in particular *via* the number and distribution of hydrogen-bond donors and acceptors.

Nucleic acids, as being rather polar than amphipathic, are able to take up, with $n_w > 12$, significantly more water than lipids. The PBP of nucleic acids is fundamentally related to the structure of the sugar involved in the backbone in two different respects. This refers at first to the basic chemical nature, ribose or deoxyribose, and secondly to the pucker as defining the nucleic-acid conformation. Moreover, the PBP depends on base composition and sequence which are, for DNA, closely correlated with the conformation. The PBP has been found to be minimum for RNA and maximum for deoxyribo-homopolynucleotides. Upon drying, nucleic acids are able to retain a fairly large deal of residual water (much more than lipids) which appears suitable to stabilize the disordered form adopted under these conditions against irreversible denaturation.

Some of the final remarks are devoted to a possible biological importance of the presented data and conclusions.

Keywords: Binding potency, biomolecular structure, lipids, nucleic acids, infrared spectroscopy, hydration, hydrogen bonding

INTRODUCTION

In living organisms, biological molecules be it nucleic acids (NAs), proteins, lipids or carbohydrates are involved in a netting of complex supra-molecular systems which are held together by weak interaction forces and enable the maintenance of the multitude of vital biochemical reactions. Although all these biomolecules represent *per se* well-defined chemical entities, they are – more or less – prone to bind or (partly temporarily) fix various partners in order to set going the manifold processes essential for correct *in-vivo* functioning. Consequently, the capability of this basic biological matter to bind or retain other molecules (that are mostly also natural, but also could be drugs, and might be summarized under the term effectors), is a meaningful factor in regulating the complicated game called life on the molecular scale which is far from being understood in detail hitherto.

Looking for an approach to improve the latter situation, it seemed worthwhile to take into account a parameter suitable for adequately characterizing the binding propensity or capacity or, as it was denominated by convention in the preceding paper [1], the "binding potency" (BP) of biomolecules or higher-order assemblies or complexes of biomolecules. This idea was originally inspired when becoming aware of the multitude of lipid structures found in natural systems. This fact was manifested by W. Dowhan asking in 1997 in his review article "Why are there so many different lipids?" [2]. Indeed, having in mind merely the putative overall function of lipids to deliver the main component of biological membranes for building a stable scaffold to realize the compartmentation of living matter (which is certainly a major prerequisite for a sufficient functioning of the above-mentioned essential biochemical

processes *per se*) a variety of lipid structures such rich as that really existing in nature should be hardly necessary. Rather, this striking structural diversity could be rationalized by ascribing these lipids beside their general bilayer-forming propensity also some more specific functions to.

Among the attempts to systematize the correlation between the lipid-"monomer" structure and the higher-order structure of lipid assemblies, the "shape" concept did provide a dramatic progress in phenomenologically predicting the phase preferences of artificial lipid membranes from the geometry of the single molecule satisfactorily in a first approximation [3]. Briefly, the lipid geometry is evaluated by relating the cross-section area (CSA) of the polar and apolar domains to each other. Approximate parity of the latter results in a cylinder geometry, and assemblage of these cylinders leads to the formation of bilayers (see also Fig. 14 below). Otherwise, a non-equality of the CSA of polar and apolar domains results in a cone shape and would lead to non-lamellar phases [3]. However, a consideration of the peculiarities of lipid chemical structure including the resulting interaction potential is largely missed in the shape concept and was not systematically regarded to the best of our knowledge up to now. As implications of the latter one can take into account a certain role of membrane lipids by participating, in some way, in different binding or docking processes with relevant biological effectors. For instance, it is imaginable that lipids could be dedicated to promote (or direct) the anchoring or embedding of relevant membrane proteins at (or to) their functionally "correct" places. A specific relevance was reported for several lipids, as the more abundant phosphatidylethanolamine (PE) [2,4-7] and phosphatidylglycerol (PG) [2,6,8-11], and moreover also for phosphatidylinositite (PI) [12], phosphatidic acid (PA) [13], and phosphatidylserine (PS) [14]. For instance, PE is described to play some role for protein binding [2,4], folding [5] and function [6,7], especially catalytic activity [4,6], and PG to be important for the functioning of the photo-system in plants [8,9] as well as of lung surfactants [10] and certain enzymes [11].

Therefore, some comparative evaluation of the BP appears very desirable in particular for several basic lipid systems but the same holds for the other biomolecules listed above.

In the schematic presentation given in Fig. 1, the term "BP" is more explicitly explained with particular respect to its biological importance by taking the lipid case as an example.

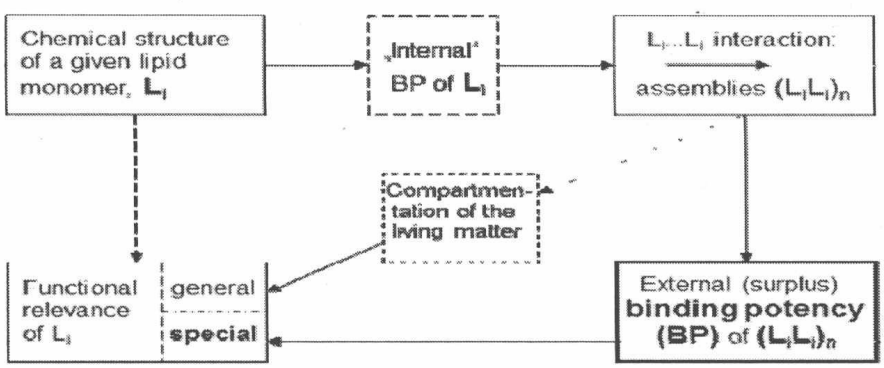

Figure 1. Scheme for explaining the term binding potency (BP) by the example of lipids; this figure was taken from ref. [1] with permission from Springer and slightly modified.

The main point to understand what is meant by using the term BP in the present context is to realize its reference to the higher-order lipid assemblies, which are spontaneously formed