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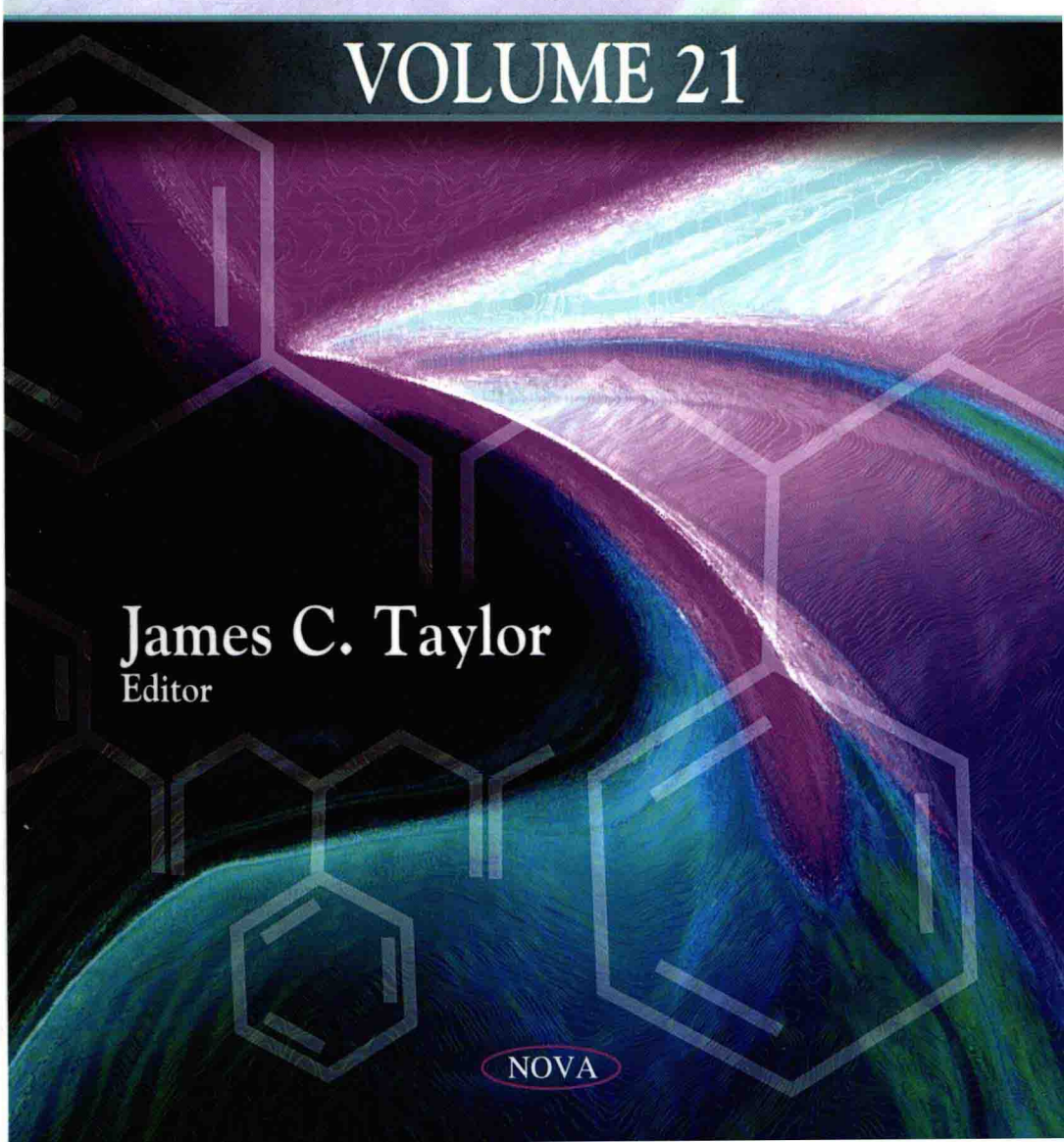

James C. Taylor
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PREFACE

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 antibacterial and antifouling properties of lipophilic bismuth compounds; rheology of carbon black suspensions; characterization of carbon blacks; doubly bonded molecules containing bismuth and other group 15 elements in the singlet and triplet states; growth of nanocrystals from amorphous bi; mathematical theory of noble gases; and properties of rarefied noble gas flows.

The medicinal and biological properties of elemental bismuth are known to be enhanced by chelating it with lipophilic thiols. In Chapter 1, the authors summarize the antibacterial and antifouling potential of selected lipophilic bismuth compounds largely in the context of environmental, medical, and biotechnological applications. They synthesized ionic and nanoparticulate forms of lipophilic bismuth and determined their minimum inhibitory concentrations (MICs) under environmentally relevant conditions for several Gram-negative bacteria. Bacterial production of extracellular polymeric substances can be effectively suppressed by bismuth thiols at sub- or near-MIC concentration with negligible effect on growth. The authors focus on a cationic di-thiol, viz. bismuth-2, 3-dimercapto-1-propanol (BAL) prepared using a 2:1 Bi:BAL molar ratio since it is stable over a wide pH range and does not carry the malodor or toxicity of BAL. This BisBAL formulation is particularly effective in inhibiting bacterial cohesion and adhesion even at sub-MICs by decreasing EPS secretion, inhibiting acetylation and carboxylation of polysaccharides, and altering protein secondary structures. Results indicate that bismuth thiols could be used to probe and mechanistically understand

specific roles of cell-bound and free-EPS in bioflocculation, cohesion, and adhesion without affecting growth. They also synthesized rhombohedral crystalline BisBAL nanoparticles by reducing the BisBAL aqueous complex using an ice-cold solution of sodium borohydride. These nanoparticles also inhibited bacterial growth, prevented bacterial attachment to surfaces, and impaired preformed/established biofilms. They therefore hypothesize that embedding bismuth nanoparticles will impart antimicrobial and antifouling properties to surfaces given their high surface area-to-volume ratio and their ability to slowly release bioactive bismuth *in situ* over long timeframes due to their lipophilicity. This may provide the basis for developing bismuth-nanoparticle based broad-spectrum antimicrobial agents, which could "seek and destroy" microorganisms in a variety of practical applications.

Chapter 2 gives a review of the rheology of carbon black (CB) suspensions. Extensive studies have been made for the CB suspensions. However, a large fraction of these studies was devoted for the suspensions in fairly non-polar media where the CB particles having the polar surface. The rheological properties of CB suspension are affected by the medium affinity to the CB particles. Different types of rheological behavior are observed accordingly, when the affinity changes. In the medium having a low affinity, the CB particles form the continuous network-type agglomerate and exhibit a strong nonlinearity attributable to strain-induced disruption of a fully developed three-dimensional (3D) network structure of the CB particles therein characterized by the yield stress. In contrast, in the medium having a moderate affinity, the suspensions show a sol-gel transition with increasing CB concentration, and the critical gel behavior characterized with a power-law relationship between the modulus and frequency (ω), $G' = G''/\tan(n\pi/2) \propto \omega^n$ is observed. This behavior suggests formation of a self-similar, fractal agglomerate of the CB particles. In the medium having a high affinity, the CB aggregates are well dispersed to no agglomerates. These aggregates exhibit a slow relaxation process to their diffusion. Thus, the structure and rheology of the CB particles/aggregates changes with the affinity of the suspending medium. In this chapter, the authors report the rheological properties of CB suspensions in three suspending media, a polystyrene/dibutylphthalate solution (PS/DBP, low affinity), a rosin-modified phenol-type varnish (Varnish-1, moderate affinity), and an alkyd resin-type varnish (Varnish-2, high affinity).The effects of the primary particle size and the structure of CB aggregates on the rheological properties are summarized. For the CB suspensions exhibiting critical gel behavior, heat-induced gelation and the effects of suspending media are also explained.

Chapter 3 - The N_2 adsorption isotherms at its boiling point (77.4 K) have been extensively utilized in the investigations of surface characters of carbon blacks (CB) and microporous textures of activated carbons (AC) and activated carbon fibers (ACF). When measurements of the N_2 adsorption isotherms are extended to an extremely low or high p/p^o region, information obtained from the N_2 isotherms will be remarkably increased. Recent progress of automatic gas adsorption apparatus makes it possible to measure the N_2 adsorption isotherms at 77.4 K in a very wide pressure range from $p/p^o=10^{-8}$ to $p/p^o=0.999$ [6–9]. In addition, liquid argon of high purity (99.995%) (b.p.: 87.3 K) is readily available, which makes it easy to measure the precise N_2 isotherms at 87.3 K up to$p/p^o=10^{-8}$. In the authors' previous works, the N_2 isotherms at these two temperatures have been applied to investigations of surface characters of nonporous carbon blacks or microporosities of activated carbons fibers, where their attention was mainly focused on the isotherms at low relative pressures.

Chapter 4 - The lowest singlet and triplet potential energy surfaces for all the group 15 HBiXH (X = N, P, As, Sb, and Bi) systems have been explored through ab initio calculations. The geometries of the various isomers were determined at the QCISD/LANL2DZdp level, and confirmed to be minima by vibrational analysis. In the case of nitrogen, the order of stability is triplet H2NBi > singlet H2NBi > singlet cis-HBi=NH ≈ singlet trans-HBi=NH > triplet HBiNH > triplet H2BiN > singlet H2BiN. For the phosphorus case, the stability decreases in the order triplet H2PBi > singlet trans-HBi=PH > singlet cis-HBi=PH > triplet HBiPH > singlet H2PBi > triplet H2BiP > singlet H2BiP. For arsenic, theoretical investigations demonstrate that the stability of the HBiAsH isomers decreases in the order triplet H2AsBi ≈ singlet trans-HBi=AsH > singlet cis-HBi=AsH > triplet HBiAsH > triplet H2BiAs > singlet H2AsBi > singlet H2BiAs. For antimony, the theoretical findings suggest that the stability of the HBiSbH system decreases in the order singlet trans-HBi=SbH > singlet cis-HBi=SbH > triplet H2SbBi > triplet H2BiSb > triplet HBiSbH > singlet H2SbBi > singlet H2BiSb. For bismuth, the theoretical investigations indicate that the stability of the HBiBiH system decreases in the order singlet trans-HBi=BiH > singlet cis-HBi=BiH > triplet H2BiBi > triplet HBiBiH > singlet H2BiBi. Our model calculations indicate that relativistic effects on heavier group 15 elements should play an important role in determining the geometries as well as the stability of HBiXH molecules. The results obtained are in good agreement with the available experimental data and allow a number of predictions to be made.

Over recent years, there has been an increased interest towards theoretical and experimental investigations of bismuth (Bi) crystal properties. Bi and Bi-related materials are of particular interest for thermoelectric applications. Bi is a semimetal with unique electronic structure, and its transport properties have been studied because quantum confinement effects can be observed in low-dimensional systems. The development of Bi as a low-dimensional material has been traditionally done by preparing ordered arrays of 1D quantum wires and studying them in detail. Manipulating nanoparticles sizes in low-dimensional systems is a promising way for fundamental studies and nanotechnological applications of this semimetal. Another method that provides control over nanocrystal formation is low-temperature annealing of amorphous materials. Therefore, in Chapter 5, the authors used this method to study the growth conditions of Bi nanocrystals.

The objective of this chapter is further development of Bi nanocrystal formation method by annealing of amorphous Bi.

In Chapter 6, the authors single out the main features of the mathematical theory of noble gases. It is proved that the points of degeneracy of the Bose gas fractal dimension in momentum space coincide with the critical points of noble gases, while the jumps of the critical indices and the Maxwell rule are related to tunnel quantization in thermodynamics. The author consider semiclassical methods for tunnel quantization in thermodynamics as well as those for second and ultrasecond quantization (the creation and annihilation operators for pairs of particles). Each noble gas is associated with a new critical point of the limit negative pressure. The negative pressure is equivalent to covering the *(P,Z)* diagram by the second sheet.

Chapter 7 reviews some of the recent developments of theoretical investigation of rarefied flows of noble gases and their mixtures. These flows can be found in various engineering applications, such as micro- and nano-fluidics or vacuum technology. From theoretical viewpoint, rarefied gas flows can be studied on the basis of the Boltzmann or other kinetic equations, which are valid in the whole range of the gaseous rarefaction parameter, i.e. the ratio of the relevant macroscopic size of the flow over the molecular mean free path. These integro-differential equations can be solved by deterministic or probabilistic approaches. Among these techniques, the discrete velocity method and the direct simulation Monte Carlo are most common. The chapter describes the theoretical background of rarefied gases and the applied solution methods of kinetic equations. The slip phenomena are discussed. Results in terms of the so-called slip coefficients, which describe the slip of the macroscopic velocity along solid walls, are presented for noble gas mixtures.

Flows of rarefied noble gases in long channels are also considered. The effects of the molecular masses, the mass ratios and the concentration for gas mixtures on the results are outlined. The chapter brings the results of recent developments of rarefied gas dynamics to the attention of other researchers, engineers or non-specialized people.

CONTENTS

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Chapter 1

ANTIBACTERIAL AND ANTIFOULING PROPERTIES OF LIPOPHILIC BISMUTH COMPOUNDS

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Abstract

The medicinal and biological properties of elemental bismuth are known to be enhanced by chelating it with lipophilic thiols. In this chapter, we summarize the antibacterial and antifouling potential of selected lipophilic bismuth compounds largely in the context of environmental, medical, and biotechnological applications. We synthesized ionic and nanoparticulate forms of lipophilic bismuth and determined their minimum inhibitory concentrations (MICs) under environmentally relevant conditions for several Gram-negative bacteria. Bacterial production of extracellular polymeric substances can be effectively suppressed by bismuth thiols at sub- or near-MIC concentration with negligible effect on growth. We focus on a cationic di-thiol, viz. bismuth-2, 3-dimercapto-1-propanol (BAL) prepared using a 2:1 Bi:BAL molar ratio since it is stable over a wide pH

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range and does not carry the malodor or toxicity of BAL. This BisBAL formulation is particularly effective in inhibiting bacterial cohesion and adhesion even at sub-MICs by decreasing EPS secretion, inhibiting acetylation and carboxylation of polysaccharides, and altering protein secondary structures. Results indicate that bismuth thiols could be used to probe and mechanistically understand specific roles of cell-bound and free-EPS in bioflocculation, cohesion, and adhesion without affecting growth. We also synthesized rhombohedral crystalline BisBAL nanoparticles by reducing the BisBAL aqueous complex using an ice-cold solution of sodium borohydride. These nanoparticles also inhibited bacterial growth, prevented bacterial attachment to surfaces, and impaired preformed/established biofilms. We therefore hypothesize that embedding bismuth nanoparticles will impart antimicrobial and antifouling properties to surfaces given their high surface area-to-volume ratio and their ability to slowly release bioactive bismuth *in situ* over long timeframes due to their lipophilicity. This may provide the basis for developing bismuth-nanoparticle based broad-spectrum antimicrobial agents, which could "seek and destroy" microorganisms in a variety of practical applications.

Introduction

Elemental bismuth, belongs to the Pnictogen group of the periodic table, is a unique inexpensive, non-carcinogenic metal that has been hailed as "green element" [1, 2]. Bismuth naturally exists as bismuthinite (bismuth sulfide) and bismite (bismuth oxide) ores and iridescent crystals in elemental form[2]. Numerous bismuth compounds owing to their low toxicity are widely used in drugs, antifungal andanticancer agents, biomedical devices such as catheters and personal care products[1-6]. For example, LD_{50} (mg/kg) values of bismuth oxychloride (22,000 (rat, oral)) and bismuth oxide (10,000 (mouse, oral)) are reported to be substantially higher than even that of sodium chloride (3,000 (rat, oral) and 4,000 (mouse, oral)) [7]. Bismuth-based compounds, such as bismuth subsalicylate (BSS, PeptoBismol), colloidal bismuth subcitrate (CBS, De-Nol), and ranitidine bismuth citrate (RBC, TirtecPylorid, GSK) are widely used in combination with antibiotics (amoxicillin, clarithromycin or nitroimidazole) to treat gastrointestinal diseases arising from *Helicobacter pylori* [3]. ^{213}Bi-radiolabelled complex is considered to be a promising therapeutic agent for small volume tumors due to its highly localized action and causing negligible damage to the surrounding tissues [3]. However, bismuth and its salts have limited water solubility necessitating very highconcentrations to achieve significant antimicrobial effects. Although, inorganic bismuth compounds can be beneficial to human health, the non-supervised or extended use of drugs containing high bismuth salt concentrations is not recommended due to potential formation of

toxic bismuth-derivatives (e.g., methylated-bismuth) and ensuing potential adverse effects such as neurotoxicity, renal failure, and genotoxicity[8]. Since water solubility is critical for biocompatibility and antimicrobial effects, bismuth's solubility can beenhanced by chelating with molecules containing hydroxyl and/or sulfhydryl (thiol) groups to increase its efficacy at lower dosages thereby circumventing problems associated with using high concentrations [9]. Based on this approach, using medically-relevant microorganisms it has been shown that complexation of bismuth with certain thiols would achieve antibacterial effects at concentrations ~1,000-fold lower than inorganic bismuth compounds [10]. Further, a combination of sub-minimum inhibitory concentrations of bismuth thiols and traditional antibiotics not only suppressed capsular secretions by bacteria but also enhanced bacterial susceptibility to antibiotics consequently better controlling pathogenic biofilms [11-14]. We have demonstrated that a certain molar ratio of bismuth-to-thiol (2:1) with bismuth being either in its cationic orzero-valentnanoparticle-form can be used to suppress extracellular polymeric substances (EPS) secretion and biofilm formation by bacteria in suspended cultures and on engineered surfaces (e.g., drinking water filtration membranes)[15, 16].

EPS are chiefly composed of polysaccharides, proteins, nucleic acids, (phospho) lipids, humic substances, and other polymers, which provide a protective and adhesive matrix for microorganisms[17]. The EPS matrix helps to sequester substrates and nutrients from the environment for microbial survival and maintaining a synergistic diverse microbial consortia in a biofilm [17, 18]. Specifically, EPS are classified as either "free" or "bound" depending on whether they are released into surrounding environment or remain in the proximity of the cell surface. Free EPS have been shown to induce microbial aggregation in planktonic cultures and facilitate adhesion through surface conditioning, whereas bound EPS firmly anchors the microorganisms into the biofilm matrix [19-22]. Microbe adherence is thought to be mediated by both free and bound EPS, even though it is still not completely clear whether EPS interacts directly or through an intermediary conditioning film with diverse inanimate surfaces [21-24]. It has been shown that microbial adhesion and colonization on surfaces can be affected by surface chemistry and physicochemical properties of the media [25]. For instance, surface roughness enhances the microbial attachment and facilitates colonization particularly in the regions of reduced shear forces [26]. Hydrophobic and non-polar surfaces are more favorable for bacteria adhesion than hydrophilic surfaces [27]. Microbial surface hydrophobicity, the presence of cell appendages (pilli and flagella), and amount and characteristics of EPS are some additional

factors that play important roles in microbial attachment (often irreversible) and biofilm formation [19, 26].

Although biofilms play a crucial role in bio-geochemical cycling and can be beneficial in some biotechnological processes (e.g., wastewater treatment) they can also be a menace for purification and separation processes, water distribution systems, ship hulls, cooling towers, clinical and biomedical devices, and processes in the pulp and paper industry [28-33]. In addition to causing odor and taste problems, biofilms are resistant to conventional disinfectants and difficult to remove because of their mechanical stability owing to EPS[34]. Most microorganisms are capable of forming biofilms under the appropriate environmental and developmental conditions and the EPS are responsible for providing favorable milieu for the deposition of microorganisms and biofilm propagation. It has been proposed that development of antifouling strategies should be based on analysis of fouling factors and the biofilm properties[31]. Despite decades of research devoted towards understanding biofilm formation mechanisms[18, 19, 26, 35-41] there is still a considerable knowledge gap in specific molecular level role of EPS components in governing the biofilm formation necessitating more research in this subject [20, 23, 42-44]. For instance, there is a wide consensus that the microbial floc formation is known to depend on total EPS concentration as well as its specific components [27, 45-48].

Therefore, our research has focused on developing detailed information on molecular components of EPS secreted during microbial growth and biofouling processes, which in turn would provide insights on the specific EPS components that promote biofouling and biofilm formation. Recently, we have reported that sub-minimum inhibitory concentrations (sub-MIC) of bismuth thiols could be utilized as the probing agents for understanding specific molecular-level role of cell-bound and free-EPS in bacterial flocculation and adhesion under un-inhibited growth conditions[15, 49, 50]. Other investigations have also shown that bismuth thiols could inhibit biofilm formation on stents, catheters, and water distribution systems[51-53]. We believe that this approach of increasing bismuth solubility by chelating it with appropriate ligands will advance the knowledge of biofilm growth and properties and inspire the development of bismuth-based antimicrobial and antibiofouling strategies.

The objective of this chapter is to summarize the use of two-forms of bismuth thiols: (1) the cationic-form for studying the molecular-level role of EPS in governing bioflocculation processes during planktonic growth of bacteria, and (2) the zero-valentnanoparticle-form for creating novel antibacterial and antifouling surfaces. Three formulations of bismuth thiols, namely, bismuth dimercaptopropanol (BisBAL), bismuth ethanedithiol (BisEDT), and bismuth