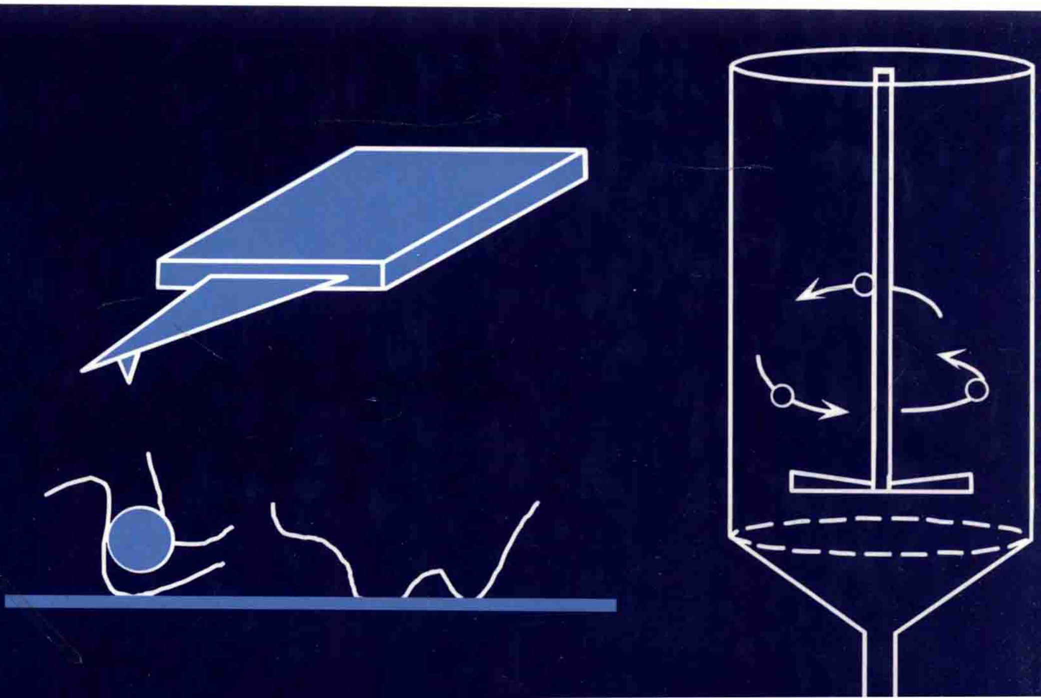
Colloid-Polymer Interactions

From Fundamentals to Practice

Edited by

Raymond S. Farinato
Paul L. Dubin



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PREFACE

Scientific or technological progress results from expansion and refinement of the physical picture that underlies research and development. This book attempts to fuel that sort of progress in the field of colloid–polymer interactions.

Work in this field is usually approached from one of three directions: theory, fundamental experiments, or applications. This book attempts to bridge the gaps among these approaches. In so doing, we first hope to put into clearer focus the models used to organize and rationalize observations. A second goal is to provide technologists and engineers with an appropriate introduction to the kind of fundamental information that can be derived from modem experimental techniques, often best applied to model systems. Third, we wish to present to the nonspecialist some of the practical technologies that are based on colloid–polymer interactions. The limitations of these technologies may indicate where fundamental understanding is incomplete. All of these goals may be seen as efforts toward bridging the ivory tower and the sewage plant.

The highly complex nature of colloid–polymer systems encountered in technology often impedes information transfer among the three realms of activity. This complexity can distract the technologist from the basic underlying physics and frighten away the fundamental researcher from practical and relevant systems. The choice of reasonable systems for study represents a compromise between direct relevancy and adequate characterization; but the selection of an appropriate system is often prerequisite to generating an important insight that bridges gaps among the three areas. This kind of advance can lead to a new way of looking at the usual collection of facts and trigger a cascade of understanding that invigorates the spirit and sometimes the profitability of the research/technology community. We hope to spark that kind of enthusiasm with this book.

The participants in this field are often unaware of each other's work: Engineers implement technology in "real" (commonly large-scale) situations, typically involving complex and only partially characterized materials, such as wastewater, wood pulp suspensions, preceramic dispersions, or paints; application specialists may carry out similar efforts but on a smaller and reproducible scale; synthetic chemists manipulate polymer structures; research experimental scientists apply sophisticated methods to model systems; and theoretical/computational chemists and physicists attempt to model these systems from basic principles. The corresponding enormous variety of approaches, objectives, and jargon frequently precludes communications among these disparate groups. Engineers and application specialists can find basic research efforts obscure and irrelevant, while those doing basic research often throw up their hands when confronted with the complex and uncontrollable qualities of the "real" situations. It is our belief nevertheless that much valuable cross-fertilization could take place if suitable efforts were made. These may require those closest to technological applications to abandon some imprecise (albeit comfortable) jargon, and those at the other end to provide qualitative assessments and physical pictures along with their rigorous (mathematical) conclusions. Suitable venues must be found for these efforts; this book we hope provides one.

Certainly another motivation for such an effort at the present time is the range of new experimental methods developed in the past decades. The accompanying molecular insights deserve a wider audience in technology-driven areas. Similarly, new theories of polyelectrolyte adsorption can assist progress in applications.

Each chapter begins in the form of a tutorial that acquaints the scientist or engineer with the basics and current state of affairs in a particular subject. The remainder of the chapter is typically devoted to an exposition of the authors' most recent contributions and concludes with indications of the likely directions for future progress.

Part I pertains to three technologies that are strongly based upon colloid–polymer interactions: wastewater treatment, papermaking, and the nano-engineering of colloidal particle layers. These chapters serve as examples of the accomplishments and challenges in several commercially important areas.

Part II introduces fundamental topics that provide some of the basis for understanding colloid–polymer interactions. These chapters discuss the dynamics of polymer transport to interfaces, models for the adsorption of polymer chains, and the role played by nonadsorbed polymers.

Part III focusses on modern experimental techniques and related recent findings. These results are answering questions about how polymers arrive at, reside at, and control the interfaces of colloidal particles with liquid media. Macroscopic phenomena that form the basis of large-scale applications rest squarely on the molecular processes being illuminated by these techniques.

No single volume could describe the full range of applications involving polymer–colloid interactions. For example, biological particles or biopolymers are not represented here. Similarly, no one text could describe the entire array of experimental methods that probe phenomena concerning macromolecules at interfaces. Our purpose, rather, is to assemble presentations that bridge theory and simulations, model systems, and technology within one volume. We hope that applications specialists will thereby gain a broader view of the available instrumental and conceptual tools while basic researchers will see more clearly the utility of their efforts in "the real world."

Paul L. Dubin

Raymond S. Farinato

COLLOID–POLYMER INTERACTIONS

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PART I
Applied Technologies

1 Polyelectrolyte-Assisted Dewatering

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1.1 INTRODUCTION

1.1.1 Solid–Liquid Separations

Solid–liquid separations are an integral part of many industrial and practical processes. The value of the individual phases are enhanced in this separation process. The focus of such a separation may be the reclamation of a valuable solid phase (e.g., ceramic processing, mineral recovery, paper production), a valuable soluble substance (e.g., pharmaceuticals from fermentation), or perhaps one of the most intrinsically valuable substances—clean water. In some cases the natural density difference between the solid and the liquid is sufficient to drive the separation under normal gravity; however, in many instances when the suspended solids are in the colloidal to mesoscopic size range, this separation process is thwarted by the natural stabilizing forces among the suspended particles. This results in either incomplete or intolerably slow separations. Such situations are commonplace in many technologies such as water treatment, mining, papermaking, ceramic processing, product recovery from bacterial fermentation, and erosion control. A diverse collection of equipment and technologies has been designed and developed to mechanically separate solids from aqueous liquids.[1,2] In a vast majority of situations, some method of conditioning the solids is required to improve the mechanical separation efficiency. When the liquid phase is predominantly water, the use of polyelectrolytes is often an important component in the solid–liquid separation process.

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1.1.2 Current State of Polyelectrolyte-Assisted Dewatering

In this chapter we will be dealing exclusively with the separation of suspended solids from aqueous phases, with a special emphasis on the use of synthetic water-soluble polymers for this purpose. Commercially significant use of synthetic polyelectrolytes for dewatering began in the 1960s in most industrialized nations. Usage is currently large and projected to grow on a worldwide basis.[3] Virtually any process for the separation of solids from aqueous liquids is a candidate for enhancement by water-soluble polymers if an economic advantage in the form of process throughput, solids capture, minimization of solids' moisture content, liquid purity, or environmental impact can be achieved. In the current state of affairs, a relatively small number of monomers are used to produce the polymers of significant economic value. During the same time period that industrial research and development (R&D) labs were developing these materials for specific technologies, researchers in both the academic and industrial communities were investigating the fundamental elements that needed to be understood in order to control the functioning of polyelectrolytes in dewatering applications. These elements, shown schematically in Figure 1.1, include the behavior of water-soluble polymers in solution and at interfaces; the mechanisms of polymer and particle transport, collision, and adsorption; the concepts of colloid destabilization and floc formation; the stresses on aggregated materials during mixing, settling, and compaction; and the mechanics of fluid flow in porous media. Often, polyelectrolyte-assisted dewatering is practiced under highly nonequilibrium conditions. A complete understanding thus also requires a knowledge of the dynamics of the above processes.

Wastewater treatment is an example that shows that solids control in municipal and industrial applications is not only critical to the effective treatment of the water but represents one of the highest costs of the treatment scheme. Improvements in removal of primary solids (those solids entering the treatment plant with the influent water) allow for better overall treatment by removing solids and organic load from the secondary treatment operation (often a biological stage[4,5]), by reducing costs in the form of reduced energy requirements in secondary treatment, and possibly by removing additional pollutants (e.g., phosphorus and metals). Improvements in the removal of secondary solids (those generated biologically in secondary treatment) result in cleaner final effluent water, thus contributing to cleaner water resources or allowing for a number of effluent water reuse options.[6] The use of polymers to improve settling or flotation rates and the level of compaction of the solids can have the effect of reducing equipment requirements and thus capital costs. Final disposal of solids from these operations is a huge undertaking involving transportation, incineration, reuse (e.g., land application, composting), and landfilling. Dramatically reducing the moisture content and weight of the solids to be handled in dewatering applications results in significant advantages in the form of reduced energy costs (evaporation of water in incinerators) and transportation costs. Improving particle capture efficiencies leads to a reduction of the amount of solids that must be recycled and retreated in the plant. In applications where the solids removed represent a

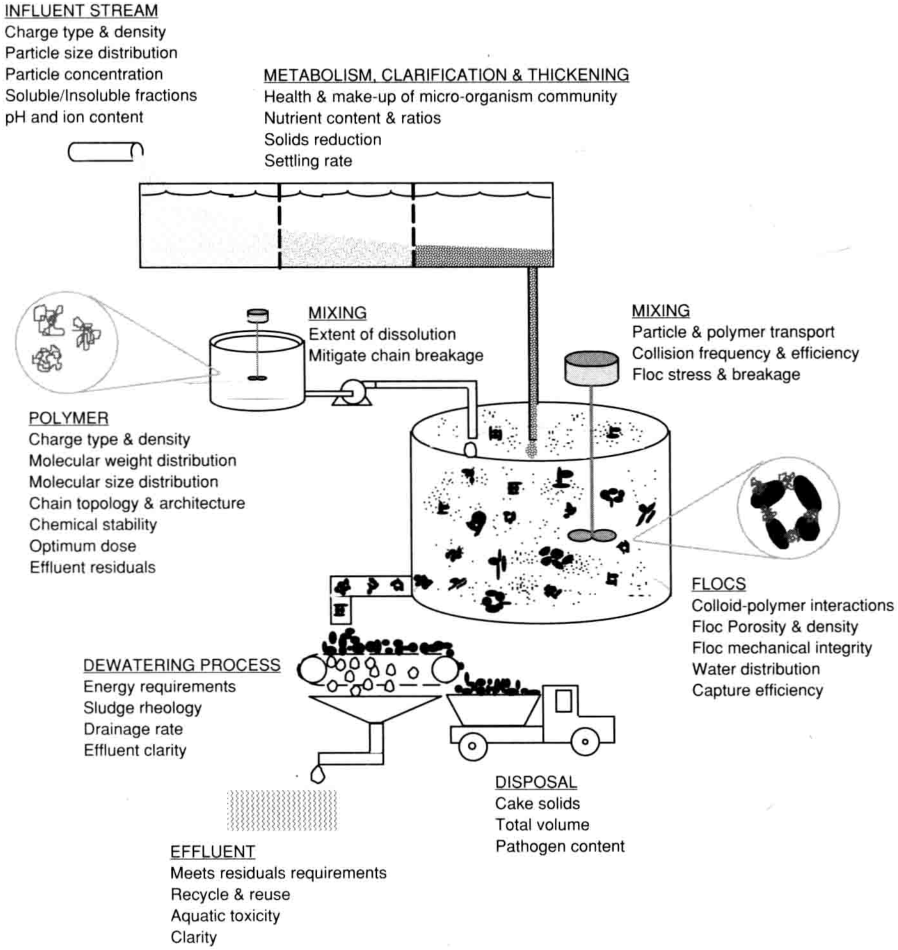

FIGURE 1.1 Schematic of flocculation and dewatering process.

valuable product (e.g., pigments, sugar, and pharmaceutical intermediates), improved capture and throughput, removal of impurities, handling ease, and reduced drying requirements easily translate into worthwhile improvements. Much of this can be accomplished by using polyelectrolytes in the solid–liquid separation operation.[7]

The recent development of water-soluble polymer systems for use in soil conditioning and erosion control[8] demonstrates the current desire to mitigate environmental impact in agriculture. Polyacrylamide copolymers can be dosed to croplands to improve water quality, as well as nutrient and fertilizer retention. These polymers can also effectively reduce soil erosion in furrow irrigation. These attributes can result in significant improvements in the quality of nearby surface waters that are impacted by agricultural runoff. Such nonpoint sources of pollutants are currently regarded as the largest source of degraded water quality.

The use of polyelectrolytes in solid–liquid separations raises several concerns. These include their potential aquatic toxicity, their handling properties, the fate of the polymer and vehicle (e.g., emulsion) constituents, and the influence of their volatile organic contents on air quality. Although it is out of the scope of this discussion to address these issues in detail, suffice it to say that when handled properly and knowledgeably, polyelectrolytes provide a valuable tool for the continued improvement of aqueous liquid–solids separation applications.

This chapter is organized as follows. First, we discuss the physics of polyelectrolyte–colloid destabilization and floc formation. The important elements of polymer and particle transport, the adsorption event, and the state of the adsorbed polymer will be only mentioned, since these topics are covered in more depth in other chapters in this book. Next, we discuss the physics of suspension thickening and dewatering. A survey of commercially significant polyelectrolytes for dewatering applications will follow. Some examples of polyelectrolyte-assisted dewatering in wastewater treatment technology will illustrate useful commercial manifestations of the principles outlined. Several practical methods used for evaluating polymers for potential dewatering applications will then be discussed.

1.2 COLLOID DESTABILIZATION AND FLOC FORMATION

Fine particles in suspension often must be aggregated in order to improve their settling rate and dewaterability. This aggregation into flocs requires a destabilization of the particles, a means of bringing them together in the destabilized state, and adhesion between destabilized particles to occur. Once formed, the flocs must then adequately survive any disruptive forces during the solid–liquid separation process. The sizes of objects involved in the flocculation process are depicted in Figure 1.2.

1.2.1 Consequences of Colloid–Polymer Interactions

When interactions between colloids and polymers occur, the outcome is generally either stabilization, destabilization, or phase separation. In stabilization, the ubiquitous London–van der Waals forces of attraction are counterbalanced by the repulsive electrostatic and/or steric forces arising from either adsorbed or anchored polymer chains. Stabilization usually occurs at high surface coverage, and for polyelectrolytes, there is often an overcompensation of surface charges by adsorbed polymer charges (i.e., there is a reversal of the sign of the zeta potential). Destabilization by polyelectrolytes can result from charge neutralization, charge patch formation, or bridging. The second and third phenomena usually require low to intermediate amounts of surface coverage. Phase separation can occur when the attractive potential created between particles is weak enough (~ 2 to 5 kT) to still allow transport of the two phases on a reasonable time scale. Such attractive potentials can result via a depletion mechanism involving nonadsorbing polymers. In this chapter we