Detergents and Cleaners

A Handbook for Formulators

K. Robert Lange

HANSER

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Edited by K. Robert Lange

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Preface

When first considering this task, I wanted to write an article on formulating, in general. Having spent many years formulating products and supervising chemists, my sympathy for the bench chemist's problems, and respect for the ingenuity shown, had led me to write a series of articles for my employer's house organ, explaining the field to the layperson. Editing and contributing to a book meant for the bench chemist is a different matter entirely. For this a focus is needed, one that will attract readers. The topic of detergency provides such a focus because it is of universal interest.

Whatever the industrial or home environment, people have a need for cleanliness. This includes their bodies, their clothing, and the equipment they use. Today there is a strong emphasis on keeping the entire environment preserved, and cleaners play their role in this effort. To these ends the chemical process industry develops formulated products, based on synthetic detergents, that are expected to attack soils of every imaginable type, regardless of water hardness or the conditions of use. Governments around the world monitor and regulate these efforts while encouraging cleanliness through campaigns and laws. Cleanliness is a major worldwide industry.

This book provides methodology for formulators generally, through the medium of detergency. Formulating principles are general, and this volume might just as well be on corrosion inhibitors or pie-baking; but the publisher produces *Tenside,* that fine journal devoted to detergency, and has a German-language handbook by Stache on that subject, among other things. Hanser's desire to produce a book on this topic for the North American market coincided with my own views of the appropriate field to use as the focus of a book for formulators.

The intended audience for this volume is the bench chemist or senior technician, working in a small to medium-sized laboratory, who wants to have a book of convenient size for daily reference and as a guide to the more theoretical, multivolume tomes in the library. My hope is that this book will fill a need between the two extremes of the theoretical texts and the fine trade magazines, which offer much useful information but can be difficult to use in terms of retrieval.

The authors of the various chapters have all overcome the daily pressures of their jobs to share their knowledge here. Working with them has been a pleasure, and I thank them for their efforts. I also thank the following for their cooperation: H.L. Williams, vice president at Monsanto; A.F. Hidalgo, vice president at Colgate Palmolive; and A.F. Burns, technical director at PQ, who were instrumental in recommending members of their staffs to author chapters.

K.R. Lange

Introduction

Every chemical product that reaches the ultimate consumer (with the possible exception of sugar) is, in some degree, a formulated product.* This being the case, it is somewhat mysterious to note the low esteem the formulation process possesses in both academia and industry. Certainly, no college department of chemistry or chemical engineering offers a course entitled *Formulation 101*. And, although formulation is often considered to be an arcane art, its practitioners are often referred to as "mere formulators." (One wonders, indeed, what the effect of calling a designer of perfumes and scents a "mere" perfumer would be!)

One of the reasons for this low esteem probably is the notion that formulation is largely Edisonian in nature and, therefore, does not possess the cachet that surrounds "real" research. First of all, it should be pointed out that there is nothing in principle wrong with the Edisonian approach to discovery, as long as it is applied with intelligence. Many important discoveries (even in basic science) have resulted from Edisonian methods, although this is often concealed by referring to serendipity.

A number of years ago, I presented a talk with the title *Philosophy of Formulation.*† Although, as the title of the symposium at which the talk was delivered suggests, my remarks were directed mostly to pesticide formulations, I made the point that formulation was *not* particularly Edisonian, but bore many similarities to what is commonly referred to as basic research.

On the other hand, formulation research is carried out for reasons different from those of the so-called basic research. Among those reasons might be listed the following:

- To render the use of application of the active component more effective.
- To enable the consumer to use the product more readily.
- To improve the stability of the product.
- Last—but not least—to improve the aesthetics of the product.

As I pointed out in my talk, to do it properly, one must plan the formulation study. This may involve answering a series of questions. For the formulation of pesticides, these questions were suggested:

- What is the active ingredient and what is its form?
- In what type of system will it be delivered (e.g., solution, dispersion, emulsion)?
- If a solution or dispersion, dissolved or dispersed in what?
- If an emulsion, o/w or w/o—and what is in the aqueous phase—what is the oil phase?

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*Table salt, which one might think of as unformulated, is commonly "iodized" and additionally contains an anticaking compound.

† Becher, P. In *Pesticide Formulatins and Application Systems,* Vol. 8, D.A. Hovde and G.B. Beestman, Eds., American Society for Testing and Materials, Philadelphia, 1989, p. 13.

- How is it to be applied to the system: If a herbicide— dusted, sprayed? If a drug—applied topically, swallowed, injected?
- What is the desired composition (e.g., if an emulsion, what are the phase ratios)?
- If an emulsion or dispersion, what surface active agents should be used? What restrictions are imposed by safety considerations?
- What physical properties must the system have (e.g., viscosity, density)? In dispersions and emulsions, what is the effect of particle size distribution? If the system is viscoelastic, what effect does this have?
- How do we make it? What types of mixing or blending equipment? How about scale-up?
- Finally, how do we evaluate the system? What degree of stability is required? How is stability determined? What about quality assurance?

These questions can be restated to apply to any kind of formulation problem, and, no doubt, other questions will occur to the worker.

This brings us to an important point. It will not have escaped the eye of the reader that this book to a large extent emphasizes formulation of detergent species. This is simply a matter of convenience. From the foregoing, it should be obvious that the lessons and techniques discussed here can be transferred to any other field with only a modest effort. In other words, this book will be useful to *any* formulator, whether the problem at hand involves, among others, pharmaceuticals, cosmetics, paints, or—yes—pesticides. The authors and the editor are to be commended.

Paul Becher

Contents

CHAPTER 1

Basic Surfactant Concepts

Eric W. Kaler

This chapter introduces the fundamental ideas that guide the production of successful surfactant formulations. First the major features of surfactant molecules are discussed, and the kind of microstructures that form (micelles, vesicles, liquid crystals) reviewed. Next the general patterns of surfactant phase behavior are presented, and in particular the basic ideas needed to formulate microemulsions are summarized. The interfacial aspects of surfactants and their relation to spreading coefficients are reviewed, and the final section describes the basic properties of emulsions.

1.1 Introduction

Surfactant solutions exhibit many phenomena of scientific and technological interest. For example, surfactants are of primary importance in detergency, separation techniques, agriculture, and the pharmaceutical industry. Naturally occurring surfactants such as phospholipids are the main components of cell membranes and thus play a vital role in organizing the chemical reactions that sustain life. There are an enormous number of natural and synthetic surfactants available for applications, and choosing the optimal kind of surfactant for a given use can be a remarkable challenge.

Intelligent and rational use of surfactants in formulations for carrying hydrophobic materials such as drugs or pesticides into water, as well as in formulating cleaning products for textiles or hard surfaces, draws on principles from physical chemistry and thermodynamics. Moreover, the ultimate success or failure of a formula also often depends on the *kinetics* of solubilization or wetting. This introductory chapter describes a few of the most important properties of surfactants and shows in outline some of the unifying concepts in surfactant science. Useful references for further reading are given in the bibliography.

A surfactant (surface active agent) lowers the equilibrium interfacial tension between the medium in which it is dissolved and any other contacting fluid. Interfacial tensions are thermodynamic properties, like density and heat capacity, and so can be measured under given conditions and tabulated. If temperature and pressure are held constant, the value of the interfacial tension represents the work (and change in Gibbs free energy) necessary to create more interface. Since dispersing any material to colloidal size scales generates an enormous amount of interface, the ability of surfactants to reduce interfacial tensions is critical to such applications as the preparation of emulsions and the wetting and dispersal of powders in liquids. These interfacial properties of surfactants are discussed further in Section 1.6.

Eric W. Kaler, Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, Colburn Laboratory, University of Delaware, Newark, Delaware 19716, U.S.A.