SURFACTANTS IN SOLUTION

VOLUME 1

Edited by K. L. Mittal and B. Lindman

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PREFACE

This and its companion Volumes 2 and 3 document the proceedings of the 4th International Symposium on Surfactants in Solution held in Lund, Sweden, June 27-July 2, 1982. This biennial event was christened as the 4th Symposium as this was a continuation of earlier conferences dealing with surfactants held in 1976 (Albany) under the title "Micellization, Solubilization, and Microemulsions"; in 1978 (Knoxville) under the title "Solution Chemistry of Surfactants"; and in 1980 (Potsdam) where it was dubbed as "Solution Betants"; and in 1980 (rousdam, where it was access." The prophasion of Surfactants: Theoretical and Applied Aspects." The prophasion of 1,2,3 ceedings of all these symposia have been properly chronicled. The Lund Symposium was billed as "Surfactants in Solution" as both the aggregation and adsorption aspects of surfactants were covered, and furthermore we were interested in a general title which could be used for future conferences in this series. As these biennial events have become a well recognized forum for bringing together researchers with varied interests in the arena of surfactants, so it is amply vindicated to continue these, and the next meeting is planned for July 9-13, 1984 in Bordeaux, France under the cochairmanship of K. L. Mittal and P. Bothorel. The venue for 1986 is still open, although India, inter alia, is a good possibility. Apropos, we would be delighted to entertain suggestions regarding where and when these biennial symposia should be held in the future and you may direct your response to KLM.

The response to these biennial events has been growing and as a matter of fact we had to limit the number of presentations in Lund. Even with this restriction, the Lund Symposium program had 140 papers from 31 countries by more than 300 authors. So it is quite patent that this meeting was a veritable international symposium both in spirit and contents. It should be added that the program contained a number of overviews by prominent researchers, as it is imperative to include some overviews to cover the state-of-knowledge of the topic under discussion.

As for these proceedings [containing 126 papers (2156 pages) by 324 authors from 29 countries], these are arranged in nine parts. Parts I and II constitute Volume 1; Parts III-VI comprise Volume 2; and Parts VII-IX are the subject of Volume III. Apropos,

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the papers in the proceedings have been rearranged (from the order they were presented) in a more logical manner. Among the topics covered include: Phase behavior and phase equilibria in surfactants in solution; structure, dynamics and characterization of micelles; thermodynamic and kinetic aspects of micellization; mixed micelles; solubilization; micellar catalysis and reactions in micelles; reverse micelles; microemulsions and reactions in microemulsions; application of surfactants in analytical chemistry; adsorption and binding of surfactants; HLB; polymerization of organized surfactant assemblies; light scattering by liquid surfaces; and vesicles.

A few salient aspects of these proceedings should be recorded for posterity. All papers were reviewed by qualified reviewers so as to maintain the highest standard. As a result of this, most papers were returned to respective authors for major/minor revisions and some did not pass the review. In other words, these proceedings are not simply a collection of unreviewed papers, rather the peer review was an integral part of the total editing process. It should be added that we had earnestly hoped to include discussions at the end of each paper or group of allied papers, but in spite of constant exhortation, the number of written questions received did not warrant undertaking such endeavor. However, it must be recorded that there were many spontaneous and brisk discussions both formally in the auditorium and informally in other more suitable (more relaxed) places. Most often the discussions were enlightening, but on occasions one could feel some enthalpy as these tended to be exothermic.

Also a general concern was expressed about the possibility of correlating research done in different laboratories. In particular in the microemulsion field it was felt that a few selected, stable and well-defined systems should be chosen for collaborative work between a number of active groups using a variety of techniques. The response to such discussion (initiated by Prof. M. Kahlweit, Göttingen) was very heartening and culminated in the so-called Lund Project (coordinator Prof. P. Stenius, Stockholm), which is a coordinated collaboration between a number of research groups in different countries. A report meeting was hosted by M. Kahlweit in Göttingen in the spring 1983 and further results will be presented in Bordeaux in 1984. In addition, throughout the meeting, small groups of people were seen to be leisurely discussing more specific topics of mutual interest. In other words, there were ample and lively discussions in various forms during the span of this symposium.

Coming back to the proceedings, even a cursory look at the Table of Contents will convince even the most skeptic that the field of surfactants in solutions has come a long way, and all signals indicate that the accelerated tempo of interest and research in this area is going to continue. Also it is quite clear that as we learn more about the amphiphilic molecules, more excit-

ing research areas and pleasant applications will emerge. It should be added that these proceedings cover a wide spectrum of topics by a legion of prominent researchers and provide an up-to-date coverage of the field. The coverage is inter- and multidisciplinary and both overviews and original unpublished research reports are included. Also it should be pointed out that both the aggregation and adsorption of surfactants are accorded due coverage. These proceedings volumes along with the earlier ones in this vein (total $^{\circ}$ 5000 pages) should serve as a repository of current thinking and research dealing with the exciting field of surfactants in solution. Also these volumes should appeal to both veteran and neophyte researchers. The seasoned researchers should find these as the source for latest research results, and these should be a fountainhead of new research ideas to the tyro.

Acknowledgements: One of us (KLM) is thankful to the appropriate management of IBM Corporation for permitting him to participate in this symposium and to edit these proceedings. His special thanks are due to Steve Milkovich for his cooperation and understanding during the tenure of editing. Also KLM would like to acknowledge the assistance and cooperation of his wife, Usha, in more ways than one, and his darling children (Anita, Rajesh, Nisha and Seema) for creating only low decibel noise so that Daddy could concentrate without frequent shoutings. The time and effort of the reviewers is sincerely appreciated, as the comments from the peers are a desideratum to maintain standard of publications. We are appreciative of Phil Alvarez, Plenum Publishing Corp., for his continued interest in this project. Also we would like to express our appreciation to Barbara Mutino for providing excellent and prompt typing service. Our thanks are due to the members of the local Organizing Committee (Thomas Ahlnäs, Thomas Andersson, Gunnar Karlström, Ali Khan, Mary Molund, Gerd Olofsson, Nancy Simonsson and Marianne Sward) who unflinchingly carried out the various chores demanded by a symposium of this magnitude. The financial support of the Swedish Board for Technical Development, the Swedish National Science Research Council, and the University of Lund is gratefully acknowledged.

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- 1. K. L. Mittal, Editor, Micellization, Solubilization and Microemulsions, Vols. 1 & 2, Plenum Press, New York, 1977.
- K. L. Mittal, Editor, Solution Chemistry of Surfactants,
 Vols. 1 & 2, Plenum Press, New York, 1979.
- 3. K. L. Mittal and E. J. Fendler, Editors, Solution Behavior of Surfactants: Theoretical and Applied Aspects, Vols. 1 & 2, Plenum Press, New York 1982.

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