

Chemistry at the Interface

This special issue of JBCS is dedicated to the area of Chemistry at the Interface, a rather broad area in which Brazilian scientists have obtained international recognition and where concepts and theoretical frameworks were developed and published in high quality international journals.

About 40 years ago a core of researchers working in Brazil including professors Frank Quina, Hernán Chaimovich, Omar El Seoud and Faruk Nome at both the University of São Paulo and the Federal University of Santa Catarina initiated a large area of research of international quality that spanned all types of association colloids such as micelles, microemulsions, and vesicles, but also emulsions, vesicles, biological membranes, and protein-surfactant interactions. At about the same time, remarkably productive international collaborations began with contemporaries who became long time friends including Clifford Bunton, Richard Weiss, Laurence Romsted, Janos Fendler and Eduardo Lissi. From the collaboration between the different groups, ideas were developed which cover the basis of the understanding of chemical reactivity at interfaces, largely based on an approach grounded in thermodynamics and that applied pseudophase kinetic models to a family of interfaces. The reactivity in the interfacial region in micelles, microemulsions, emulsions and solid-liquid systems, can largely be understood based on such models.

The work of this initial group resulted in the training, in Brazil, of about 200 MSc and PhD students, and promoted the formation of new groups in the area in different universities around and outside the country. Scientists such as Watson Loh (Editor in Chief of the Journal of the Brazilian Chemical Society and professor at UNICAMP, Brazil) and Cornelia Bohne (Invited Editor for this special issue of JBCS dedicated to Chemistry at the Interface, Associate Editor - Editorial Board of Photochemical and Photobiological Sciences and professor at the University of Victoria, Canada) are examples of the new generation of high quality chemists working in the area.

Grant funding, a special person and a conceptual model, were central to this development. The collaborations were seeded by several international projects largely funded by NSF (USA) and CNPq (Brazil) that helped solidify the scientific relationships between most of the professors listed above. Clifford

Bunton, or Bunny as he is known, from the University of California at Santa Barbara, brought many of us together. He dedicated a large part of his varied and highly productive scientific career to understanding the molecular basis of specific ion binding and chemical reactivity in interfaces. Bunton's experience was fundamental and aided us in the art of transforming carefully crafted experiments into the development of simple, but powerful pseudophase models for interpreting rates and equilibria in organized solutions.

In fact, organized surfactant solutions and biomembranes, look like horribly complex systems in which it is necessary to study the effect of aggregate size (which changes with solution composition) and charge, reactant partition, reactant orientation in the aggregation, and charge effects on ground states and transition states (which depend on composition). However, after many years of experiments this eclectic, but cooperative group of researchers applied Occam's razor repeatedly and demonstrated repeatedly that surfactant effects depend on two basic factors, the rate constant in the micellar pseudophase and the concentrations of the reactant (1st order) or reactants (2nd order) that are determined by distribution constants between the micellar pseudophase and water. This approach works well over wide ranges of surfactant concentrations and more limited ranges of counterion concentration added as salt. If the phrase "micellar pseudophase" feels like a contradiction in terms, it is, but a very useful one.

The contributions of the Brazilian group covers work in the areas of surfactant chemistry, photochemistry, biochemistry and mechanistic organic chemistry and was generally published in internationally recognized journals, including a pivotal *Accounts of Chemical Research* article on pseudophase models of micellar catalysis that appeared in 1991 and continues to be strongly cited. A selection of publications is included,¹⁻¹⁶ with the intention to present a holistic (not comprehensive!) overview of the work developed by the Brazilian group. Their work on micellar effects on chemical reactivity provides fundamental insight into the origins of the changes in the observed rate of reaction with increasing surfactant concentration and other additives such as salts. As noted above, the group made major contributions to the development of the pseudophase kinetic models including identifying its

shortcomings at high salt concentrations and revising the model. The conceptual approach developed also provides a framework for interpreting chromatographic separations of organic ions and molecules when micellar solutions used as eluting solvents. The group of researchers worked in the problem of anion association with sulfobetaine micelles demonstrating the order follows a Hofmeister series, the classical correlation of ion specific effects. This work is an important new development because it demonstrates that ion association with micellar surfactants cannot be simply electrostatic in nature, but must depend on the properties of the ion. These results contribute to a deeper understanding of the Hofmeister series, i.e., classical correlations of ion type with surfactant colloid and biological membrane properties, activities of enzymes, and even nerve impulses. The range of contributions also include research on nanoparticle formation in ionic liquids, solvent effects on chemical reactivity, the development of models for molecular recognition, and the mechanisms of a variety of ground and excited state reactions.

The importance of counterion effects on the properties of surfactant systems was a central effort, which soon lead to the development of models to understand ionic and zwitterionic micelles, monolayers, microemulsions and emulsions. The interdependence between the binding of anions and cations to zwitterionic micelles allowed the development of important nanoparticle stabilizing agents. Important contributions were also reported, showing how to use the physical chemistry of excited states to determine mobilities of molecules, estimate microviscosities and encounter probabilities in micellar media, focusing on bimolecular reactions of excited states, ultrafast intermolecular excited state proton transfer (ESPT) reactions and the dynamics of solvation of excited states.

We hope that this special issue of JBCS that is dedicated to Chemistry at the Interface attracts researchers who want to more fully understanding of the molecular basis of ion binding and reactivity in interfaces. We thank all the contributors, which includes a considerable number of the new Brazilian groups

working in the area, for writing clear, informative reviews and papers that will motivate a new generation of scientists to undertake research at interfaces that leads to the development of quantitative models with analytic and predictive capabilities.

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