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COLLOIDAL ASSEMBLIES EFFECT ON CHEMICAL REACTIONS(U)
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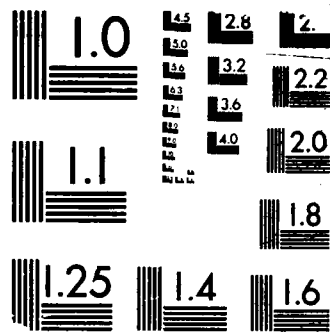
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COLLOIDAL ASSEMBLIES EFFECT ON CHEMICAL REACTIONS

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E. Pelizzetti
University of Torino
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PROGRESS OF THE RESEARCH

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Photocatalytic degradation of organic compounds

The previously demonstrated efficiency of photo-assisted reactions on semiconductors for the destruction of hazardous chemical pollutants has been applied to the disposal of sparingly water-soluble halogenated aromatic compounds (e.g; DDT, PCB, dioxins)^{1,2} as well as widely used herbicides. Among these last compounds, derivatives of the class of s-triazine pesticides have been degraded even at very low concentration levels (in the ppb range) thus extending the applicability of these processes also to drinking water supplies.³

The degradation of alkylphenols and polyethoxylated alkylphenols (non ionic surfactants) has been recently considered. In the case of surfactants the degradation occurs either with formation of ethoxy fragments as well as with attack to the aromatic moiety.⁴

Partitioning and reactivity in micellar aggregates

The partition equilibria of a series of substituted phenols bearing different chemical groups between aqueous solutions and sodium dodecyl sulfate micelles has been investigated using the micellar HPLC technique and through the variation of the acidity constant. The contribution of each substituent to the free energy of transfer from water to micelles have been estimated and the group contribution approach has been shown to hold for polysubstituted compounds in well defined conditions.

A comparison with partition coefficients obtained in classical two-phase systems (1-octanol/water), usually used as biochemical model systems, has been reported.⁵



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A general phenomenological approach based on the two pseudophases approximation, a proper definition of the transfer constants between the pseudophases in term of molar fractions, an explicit hypothesis which relates the number of bound molecules or ions to the surfactant concentration and a semiempirical calculation of the activity coefficients of bound charged species at the micellar surface, permits prediction of the reactivity as a function of micelle and added salt concentrations. The application of this approach to limiting cases leads to the equations already known in the literature. Kinetic experiments were designed to test the model through simplification of the proper formulas. Good prediction of the observed rates for the reaction of hexachloroiridate(IV)-Iron(II), in the presence of hexadecyltrimethylammonium chloride and sulfate, is obtained and the dissociation degree of the micelle is found comparable with literature values.⁶

Reactivity in microemulsions ; and —————> see with OJ

Kinetics and mechanisms of reactions in oil-in-water microemulsions have been extensively reviewed.⁷

Pursuing the study of electron transfer reactions in microemulsions, the rate of reaction between two highly hydrophilic ions, e.g. IrCl_6^{3-} and $\text{CoW}_{12}\text{O}_{40}^{5-}$, has been investigated over a wide range of composition in a SDS/1-butanol/toluene/water-0.09 M NaCl-0.01 M HCl microemulsion. In the light of the previously reported three-phase-model, informations on the "free" water in the droplets, the upper demixing line and the structured regions of the microemulsion have been obtained.⁸

Physico-chemical properties of surfactant aggregates

Particular interest has been devoted to "functionalized" surfactants, in particular with the polar head group having complexing capability. An exhaustive review has been published.⁹

In particular, the kinetics of complex formation between Iron(III) and 4-alkylamido-2-hydroxybenzoic acids (with different alkyl chain) has been investigated in the presence of non ionic Brij 35.

The rate of complex formation is still fast even in the presence of relevant concentration of micellized surfactant.¹⁰

It is planned to investigate these "metal micelles" for enrichment and catalytic purposes.

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RESEARCH PLANS (THIRD YEAR PROGRAM)

- PHOTODEGRADATION OF ORGANIC COMPOUNDS BY VISIBLE LIGHT

The degradation of triazines, bentazone and other pesticides will be investigated also at very low concentration. It is planned to study the mechanism and to detect the intermediates that are formed.

Other semiconductors (e.g; iron oxides) will be examined. Immobilized catalysts (on glass, in polymers) will be prepared and tested.

- EFFECT OF SOLVENT COMPOSITION ON OXIDATION REACTIONS

The effect of solvent composition on electron transfer reactions will be considered. The oxidation of benzenediols in water/organic solvent mixtures seems a good reaction model.

- KINETICS IN MICELLES

The effect of micellar aggregates on the kinetics of electron transfer reactions will be investigated in the light of the previously reported model. The influence of surfactant structure and inert ions will be examined.

- KINETICS IN MICROEMULSIONS

These studies can give informations not only on the effect of the aggregates on reaction rates and mechanisms but also on "free" available water in the droplets, about the structured areas on the phase diagram and on the upper demixing line.

- OXIDATION OF ORGANIC COMPOUNDS

Chemical oxidation of organic compounds in proper solubilizing mixtures or assemblies will be considered with particular interest for transition metal ions catalysis.

- FUNCTIONALIZED SURFACTANTS

The physico-chemical properties of colloidal aggregates will be investigated with particular attention to functionalized surfactants. Detergents with polar heads exhibiting complexing as well as electron transfer properties will be considered.

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