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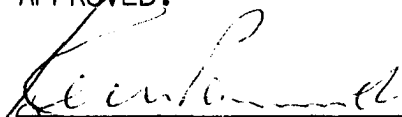

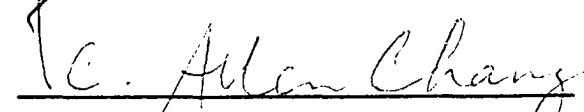
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PREVIEW

A KINETIC ANALYSIS OF THE DECOMPLEXATION OF COPPER-IONOPHORE
COMPLEXES IN THE PRESENCE OF SODIUM BIS-(2-ETHYLHEXYL)
SULFOSUCCINATE

APPROVED:


James E. Bevan

C. Allen Chang

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To my children

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by

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THESIS

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ABSTRACT

A stopped-flow kinetic analysis of the decomplexation of a copper-ionophore complex by the surfactant sodium bis-(2-ethylhexyl) sulfosuccinate was conducted. Copper chloride solubilized by 1,10-dithia-18-crown-6 in carbon tetrachloride was mixed with equivolume quantities of AOT reversed micelles in the stopped-flow apparatus. The rate was found to be independent of AOT concentration over the concentration range 1.05×10^{-2} M to 0.079×10^{-3} M, but dependent on the water content of the hydrophilic core of the reversed micelles. All measurements were taken at 425 nm with an initial extinction coefficient (ϵ) of $4578 \text{ M}^{-1}\text{cm}^{-1}$ for the copper-ionophore complex. A complete diminishment of ϵ was found at high AOT concentration.

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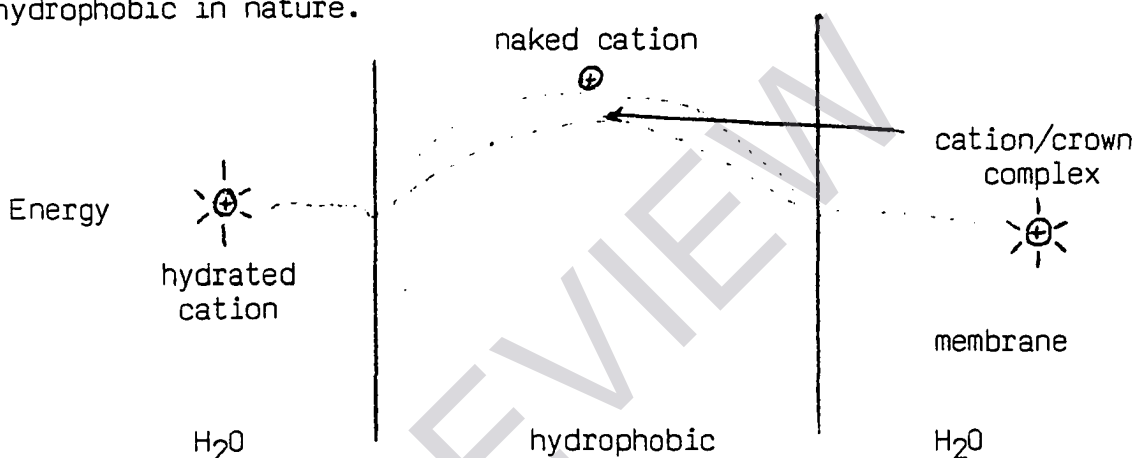
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INTRODUCTION

An ongoing area of research is that of ionophore facilitated transport of metals across liquid membranes. Ionophores such as crown ethers can extract alkali metals from aqueous media and stabilize them in a nonpolar solvent. This is accomplished by the dual nature of crown ethers. The metals bind with ether oxygens (or other base sites S, N. . .) in the center of the crown while the carbon exterior is hydrophobic in nature.



The heat of hydration of a metal cation often prohibits the passage of a metal across a hydrophobic interface. As depicted in the above diagram ionophores compete with water for binding to the metal. This reduces the energy needed to break the water-metal bonds and transport can be accomplished.

Transition metals bind to water in a covalent nature such that a higher heat of hydration must be overcome than for alkali metals. Copper has been shown to bind more tightly to water in preference to a variety of crown ethers. This fact poses a dilemma as to the study of Cu(II) transport across a liquid membrane.

One possible means of studying the crown mediated transport of Cu(II) is to investigate the flow of copper ions out of a crown stabilized hydrophobic region into the hydrophilic core of reversed micelles also solubilized in a nonpolar solvent.

Reversed micelles are composed of monomer units that contain ionic or very polar headgroups and long alkyl chains. These monomer units spontaneously self-aggregate in nonpolar solvents such that the ionic headgroups form an internal core and the alkyl chains extend into the solvent. Ionic species such as Cu(II) can be solubilized by the internal hydrophilic region.

Following a review of reversed micelles, the functions of copper in human physiology, and crown ethers, this thesis will report an investigation of the transport kinetics of CuCl_2 as complexed by 1,10-dithia-18-crown-6 into the core of sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) reversed micelles. The effect of added water to the internal core is also considered.

SURFACTANTS

Surfactants are amphipathetic molecules that have the ability to concentrate at interfaces and to alter (usually decrease) the surface tension of water.² While detergents are also classified as surfactants since they too contain hydrophobic and hydrophilic groups, detergent is a more specific term referring to one of three types:

- i) anionic molecules; often containing a carboxyl function joined via an ether linkage to a hydrophobic portion which may consist of a saturated hydrocarbon as in fatty acids or an aromatic hydro carbon as in naphthenic acids and rosins,
- ii) cationic molecules; such as an amino or quaternary ammonium group often ester linked with a hydrocarbon,
- iii) neutral molecules; which may contain highly polar groups such as aminosulfonic or aminocarboxylic functions in association with hydrocarbon residues.²

Micellization occurs due to the surfactant molecule hydrophobe being "squeezed" out of the bulk water phase and forming a cluster protected from water by an outer layer of hydrophiles. As monomer concentration is increased from zero, the initial observation of micelles occurs over a narrow concentration range, the critical micelle concentration. The formation of micelles is a dynamic process with monomer units in equilibrium with micellar aggregates.³ These "normal" micelles which have a bulk phase of water have been researched extensively. ²⁻⁶

Micelles have received much interest due to their ability to enhance or retard some organic and inorganic reactions often to an extent paralleling the rate effects and catalytic activity of enzymes. Their catalytic role is produced by affecting a change in the free energy of activation for the overall process. This is accomplished by solubilizing the reactants in the micellar environment.

Much more impressive have been the catalytic affects observed with reversed micelles. Reversed or inversed micelles are surfactant aggregates solubilized by nonpolar solvents such that the core is composed of the hydrophilic headgroups and the hydrophobic alkyl chains extend out into the bulk nonpolar solvent. The larger rate enhancements or retardations demonstrated by reversed micelles often result from their greater capacity to localize a substrate within the core. In addition, reversed micelles have proven to be very substrate specific.⁶

On this basis reversed micelles, as opposed to normal micelles, provide a much better model for understanding enzymes. Much research is now dedicated to a better understanding of the physical chemical nature of surfactants solubilized in nonpolar solvents.

Reversed Micelles

Little conclusive evidence exists on the nature of surfactant aggregation into a reversed micelle (RM). Originally, it was assumed that above a certain critical micelle concentration (concentration of the surfactant at which micellization occurs), the concentration of the monomer species was constant and in equilibrium with the micelles.^{4,7} Recently, this model has been questioned.^{4,7-12} Currently, there exists

this single-equilibrium model and a multiple-equilibrium model:

- 1) monomer \rightleftharpoons micelle
- 2) monomer \rightleftharpoons dimer \rightleftharpoons trimer $\rightleftharpoons \dots \rightleftharpoons$ n-mer

The single-equilibrium model (1) is supported by light-scattering and electron microscopy¹⁰ results as well as by positron annihilation studies.^{11,12} According to this model, as the concentration of surfactant is varied, a break or jump in a physical quantity would be expected to occur at the critical micelle concentration (cmc). This phenomenon is observed using these different experimental techniques and it has been shown that the cmc decreases with the polarity of the nonpolar solvent.^{10,11}

However, aggregation is affected by both the solvent and solute. Table I shows the effects of temperature and solvent on the aggregation number of AOT. Figure 1 shows the influence of surfactant concentration on the apparent aggregation number. The dependence of the aggregation number on the counterion is illustrated for a few ammonium salts in Figure 2. The influence of solvent is further seen in studies examining the cmc values of alkylammonium propionates which decrease with increasing alkyl chain length in benzene but remains nearly the same in carbon tetrachloride⁶ (Table II).

The existence of sharp breaks in data, as well as the assumption that a smooth transition between equilibria should occur if (2) were the true model have led to the conclusion by some that the cmc is a valid concept and that a single-equilibrium model is the most suitable explanation of the data.^{10,11}