



Chemical kinetic and chemical trapping methods: Unique approaches for determining respectively the antioxidant distributions and interfacial molarities of water, counter-anions, and other weakly basic nucleophiles in association colloids

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ABSTRACT

Two problems in colloid chemistry have proved difficult to solve. First the specific counterion and hydration effects on the properties of association colloids of ionic surfactants such as micelles, microemulsions and vesicles and second the efficiency of antioxidants, AOs, in fluid, opaque, usually nonionic emulsions. Specific ion and hydration effects are important because they contribute to the balance-of-forces determining association colloid properties along with the hydrophobic effect, however, few methods provide estimates of interfacial molarities. Determining antioxidant efficiencies in emulsions, an important problem in food science, is difficult because emulsions are opaque and antioxidant (AO) distributions are difficult to monitor. This review reports the development of two methods: chemical trapping (CT) and chemical kinetic (CK) methods for solving these problems, both based on the chemistries of arenediazonium ions. The CT method provides estimates of interfacial molarities of weakly basic nucleophiles including water, halides, alkyl carboxylates and sulfates, alcohols (including nonionic surfactants) and amide oxygen in the interfacial regions of association colloids. Results to date show that specific ion effects on association colloid properties, such as the sphere-to-rod transition concentration also involve displacement of interfacial water. The CK method, provides the observed rate constant, k_{obs} , described by a pseudophase kinetic model for the reduction of the arenediazonium ion by an AO in intact emulsions to determine the oil/water partition constants by fitting kinetic data with two equations in two unknowns to obtain estimates of distributions and concentrations of AOs in the oil, interfacial and aqueous regions of nonionic emulsions. *Part I* of this review describes new insights obtained by the chemical trapping CT method, especially how changes in interfacial water and counterion molarities depend on their bulk solution concentrations. *Part II* reviews the chemical kinetic CK method based on the pseudophase kinetic model for determining the distributions of AOs in nonionic surfactant emulsions and provides a natural explanation for the cut-off effect. *Part III* describes a new combined application of the CT and CK methods for interpreting the complex kinetics of TBHQ reduction by the arenediazonium ion in mixed cationic/nonionic micelles. Perspectives and prospects complete the review in *Part IV*.

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1. Introduction

"A picture is worth a thousand words. An interface is worth a thousand pictures".

The interfacial region in association colloids and emulsions is a loose porous boundary containing various components and it has distinct physico-chemical properties compared to the hydrophobic region or

hydrocarbon-like core and the bulk aqueous region or simply bulk solution. It plays a structural and functional role dominated by a plethora of weak interactions rather than acting as just a physical barrier. The crucial steps of interfacial phenomena occur here: be it protein insertions into cell membranes, chemical reactivity in the interface that depends on interfacial composition, and stabilization of the dispersed system governed by a delicate balance-of-forces. Knowledge of the composition and chemical reactivity in interfacial region is vital for understanding chemistry in micelles, microemulsions, vesicles and emulsions and sometimes serving as models for the interactions in biological membranes and for modeling the effects of micro-heterogeneous environments on reaction dynamics and mechanism [1–3].

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Such aggregates are wonderful systems for observing small changes in specific ion and other additive effects because small changes in the free energies of interactions of individual amphiphiles are amplified by the enormous cooperativity of amphiphile assembly and into observable (by instruments) morphological transitions. Many aggregate properties such as the critical micelle concentration (cmc), Krafft temperature, phase transition concentrations, aggregation numbers, and sphere-to-rod transitions are sensitive to changes in amphiphile headgroup structure, counterion type and concentration (as added salt), the presence of other additives such as alcohols, urea, and changes in amphiphile hydrophobicity [4,5]. However, despite the clear dependence of association colloid and emulsion properties on the composition of the interfacial region, the interfacial composition is difficult to measure because most of the components do not have easily observable signals, especially water. Consequently, the amount of water in interfacial regions and how they change with increasing surfactant, counterion and salt concentrations are poorly understood. Contained within these interactions, collectively the hydrophilic effect, are the combined interactions that balance the hydrophobic effect. We have developed the chemical trapping method (CT) based on the spontaneous heterolytic reactions of an arenediazonium ion probe, 4-hexadecyl-2,6-dimethylbenzenediazonium ion ($16\text{-}2,6\text{-ArN}_2^+$), that reacts competitively with weakly basic nucleophiles within the interfacial regions of association colloids to give stable products quantitatively (within 1–2%) that can be converted to interfacial molarities. The conversion of measured product yields is based on both nucleophile selectivity toward the $16\text{-}2,6\text{-ArN}_2^+$ and its concentration that is determined in a concentrated aqueous reference solution with salts that are models for the surfactant headgroups and counterions. The logic of this conversion will be introduced in some detail in Section 2.4. The interfacial molarities of counterions provide insights into the interactions within the interfacial regions, their tendency to form ion-pairs, and the molarity of water interacting with them.

The CT method provides simultaneously, experimental estimates of the interfacial water and other nucleophiles, e.g., halide ions, alcohols, acetate, sulfonate and amide oxygens, in all types of association colloids. It can be used over a range of temperatures: to estimate the degree of hydration of nonionic micelles, alcohol concentrations in microemulsions, and vesicles composed of virtually any twin-tail surfactant, including nonionic and anionic micelles that generally have weakly basic headgroups; to estimate association constants and interfacial concentrations of alcohols of virtually any chain length and structure. The results correlate changes in structure of microemulsion aggregates with their interfacial compositions, e.g., oils, alcohols, water and anions; and the selectivity of surfactant headgroups in association colloids toward different counteranions at virtually any ionic strength. Perhaps the single most important observation is that water is not simply filling the space between headgroups and counterions in the interfacial regions, but is directly involved in hydrating headgroups and counterions and the extent of hydration changes with changes in surfactant and counterion concentrations.

A second difficult problem has been the historical absence of a method for comparing and optimizing antioxidant efficiency in opaque emulsions. The locations of antioxidants within emulsions has been uncertain, as was their distributions between the oil, interfacial and aqueous regions in the emulsion. We developed the chemical kinetic (CK) method based on a different chemistry of arenediazonium ions, their reduction by phenols. The CK method is a unique physical-organic chemistry approach grounded in thermodynamics and inspired by pseudophase kinetic models that provides values for the observed rate constant, k_{obs} , for reaction of phenolic antioxidants like *t*-butylhydroquinone, TBHQ with 4-hexadecylbenzenediazonium ion, 16-ArN_2^+ , occurring exclusively in the interfacial regions of these intact emulsions. The change in k_{obs} with the surfactant volume fraction in emulsions provides estimates of the distributions of an antioxidant between the oil, interfacial and aqueous regions in emulsions. The CK method is a unique, versatile, and robust solution for determining antioxidant distributions in emulsified

food systems. This approach also provides sensible explanations, based on molecular properties, for the effects of various parameters, e.g., nature and type of the oil, emulsifier hydrophobicity, temperature, acidity etc., on the distribution of antioxidants in emulsified systems. We also show that the observed rate constants that passes through a maximum as the alkyl chain length of alkyl derivatives of hydroxytyrosols increases from one carbon to sixteen in tween 20/olive oil emulsions is fully explained by our kinetic model. This maximum is a characteristic of the “cut-off” effect reported repeatedly in the literature for hydrophobic effects on antioxidant efficiency.

This review is organized as follows: *Part I* reviews the logic, current results and potential applications of the CT method using the $16\text{-}2,6\text{-ArN}_2^+$ probe. *Part II* describes the concepts/assumptions employed to interpret chemical reactions in emulsions using the CK method with the 16-ArN_2^+ probe for determining the partition constants of antioxidants between the oil and interfacial and water and interfacial regions and the second order rate constant in the interfacial region, k_i , using a standard pseudophase model. *Part III* combines the CT and CK methods to obtain a detailed analysis of the components, water, Br^- , H^+ , and their effect on the reaction of TBHQ in mixed micelles of CTAB/ C_{12}E_6 micelles from mole fraction 0 to 1. Finally, *Part IV* introduces Prospectives and Prospects for future work.

2. Part-I: chemical trapping (CT) method

2.1. Association colloids

Above a minimum concentration that is characteristic of a particular surfactant called the critical micelle concentration, cmc, surfactants (lipids, amphiphiles, soap or detergents) and their mixtures form transparent, thermodynamically stable solutions of dynamic aggregates called association colloids in absence or the presence of salts, and organic additives, such as medium-chain-length alcohols [5]. Small amounts of added oil give microemulsions and larger amounts give emulsions in stirred two-phase regions, see the semi imaginary phase diagram, Fig. 1. In dilute aqueous solutions, surfactants themselves self-assemble to form approximately spherical micelles above the cmc. Large flexible rod-shaped aggregates and other mesophases are formed at higher surfactant concentrations, Fig. 1. Surfactants form reverse micelles in nonpolar solvents with their head groups surrounding a small water pool. Other common association colloids include three-component microemulsions formed from surfactant, alcohol and water or surfactant, oil, and water. Both alcohol and oil may be added to four-component microemulsions.

Scheme 1 is a classical ball and stick model for micelle formation and illustrates the dynamic equilibria contributing to aggregation and solution organization reasonably well, but at the same time misrepresent fundamental details about the balance-of-forces determining aggregate

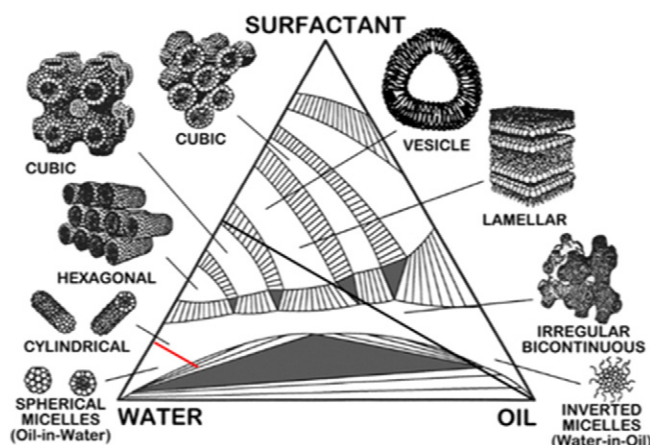


Fig. 1. Pseudo ternary phase diagram.

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