FOOD FLAVORS: GENERATION
ANALYSIS & PROCESS INFLUENCE

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Developments in Food Science

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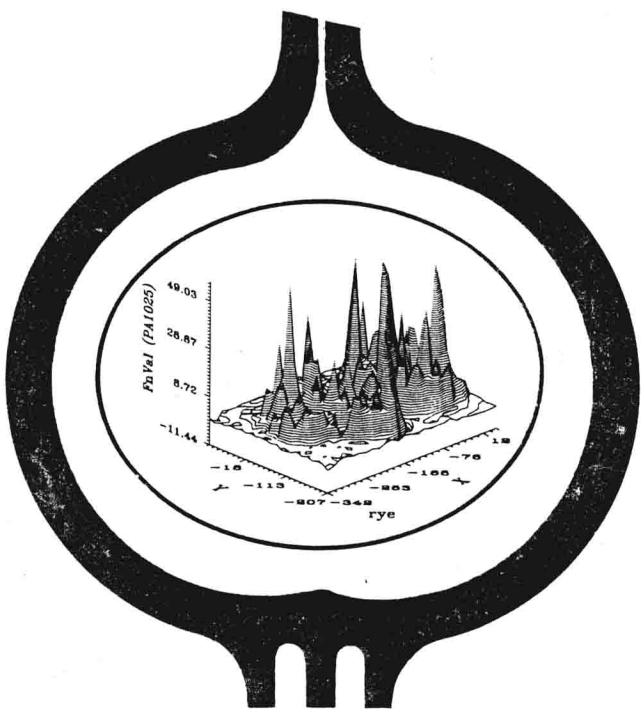
FOOD FLAVORS: GENERATION, ANALYSIS AND PROCESS INFLUENCE

Edited by
GEORGE CHARALAMBOUS



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The Effect of Polymers on the Vapor Pressure of an O/W Microemulsion System

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Abstract

The vapor pressure of an oil-in-water microemulsion system consisting of n-octane/20cc of 5% NaCl + 0.01 N NaOH/1g of sodium dodecyl sulfate (SDS)/ 3.7g of dodecyl dimethylamine oxide (DDAO) and n-octane/SDS/water/titrated to clarity with DDAO was determined as a function of the volume of hydrocarbon in the dispersed phase. In the presence of a cationic polymer, Polymer JR, the dispersed droplets are destabilized due to surfactant depletion from the microemulsion droplet interface. In the presence of an anionic polymer, carboxymethyl cellulose (CMC), the microemulsion droplets appear to be stabilized over larger volume fractions of oil.

Introduction

Emulsions play a key role in many cosmetics and industrial products in current use. Much has been written over the last three decades on the stability and formation of these oil-in-water (o/w) or water-in-oil (w/o) dispersions (1). Today's industrial formulator is primarily concerned with understanding and developing the most functional o/w or w/o systems possible for a particular application. Stable transparent systems (whether o/w or w/o) called microemulsions can be formulated when the right surface-active ingredients are used (2, 3). Possible application for these systems range from products with extended shelf life for the food industry to delivery systems for active ingredients in pharmaceuticals. More recently, fluorocarbon microemulsions have been developed as media for oxygen transport and as possible synthetic blood substitutes.

Mixtures of oil and water in the presence of surface-active agents usually form coarse, optically opaque emulsions that separate on standing. In some

cases, transparent mixtures of oil and water can be prepared when the initial emulsion is titrated to clarity (microemulsion) with a cosurfactant. Relatively small negative free energy changes may explain why the method of preparation plays an important role in microemulsion formation (4). The proper method of adding the ingredients appears to be responsible for producing a transitory zero interfacial tension due to diffusion of cosurfactant across the oil/water interface, during which time both maximum interface generation and spontaneous clearing of the primary emulsion occur (2, 3).

The most significant difference between emulsions (opaque) and microemulsions (transparent) lies in the fact that while applying work on an emulsion or increasing the surfactant concentration usually improves stability. This is not the case with microemulsions, which appear to be dependent for their formation on specific interactions among the constituent molecules. If these interactions do not take place, neither applying work nor increasing the surfactant concentration will produce a microemulsion. On the other hand, once the conditions are right, spontaneous formation occurs and little mechanical work is required (5).

Terms like *microemulsion* (6), *swollen micellar solution* (7), *micellar emulsion* (8, 9), *middle phase* (10), *unstable microemulsion* (11), and *spontaneous transparent emulsion* (12) have all been used to describe these systems. The broadest definition may simply be "a transparent dispersion of oil, water, and surfactant that forms spontaneously upon addition of a cosurfactant."

As originally suggested by Schulman et al. (13, 14), microemulsions form when the surfactant and cosurfactant, in just the right ratio, produce a mixed adsorbed film that reduces the interfacial tension γ_i to a value below zero. They concluded that γ_i must have a metastable negative value, giving a negative free energy variation $-\gamma_i\, dA$ (where dA is the change in interfacial area) responsible for spontaneous dispersion.

The interfacial tension γ_i in the presence of a mixed film is given by

$$\gamma_i = \gamma_{o/w} - \pi_i$$

where $\gamma_{o/w}$ is the o/w interfacial tension in the presence of the film and π_i is the interfacial surface pressure of the film. At equilibrium γ_i becomes zero. If this concept of zero interfacial tension is accepted, stabilization of the microemulsion is implied.

This model does not seem to be conceptually valid; however, since a zero γ_i would not require the dispersed phase to be distributed in spherical droplets, as is found in the systems under discussion (15).

Rosano et al. (11) have considered the dynamic role of the cosurfactant in lowering the interfacial tension during the titration of a coarse emulsion into a transparent dispersion. They pointed out that during the addition of a cosurfactant to an emulsion (either o/w or w/o), excess cosurfactant accumulated at the oil/water interface during transport, reducing the interfacial tension to well

below the positive equilibrium value. The surfactant retards the cosurfactant interfacial transport; a prolonged low interfacial tension helps in the formation of a large increase in the interfacial area. Eventually, γ_i regains a positive value responsible for the resolution of the system into microemulsion droplets.

Emulsion and microemulsion stability appear to be dependent not on the value of the γ_i alone but rather, and primarily, on the structure of the film surrounding each droplet (3, 16). For a given oil/surfactant pair, cosurfactant steric requirements determine the volume of the dispersed phase that can be stabilized. These systems apear to be oil and cosurfactant dependent. Surfactant, cosurfactant, the nature of the oil, and the nature of the aqueous phase are four interacting variables that determine the size of the dispersed phase droplet when microemulsions are formed.

A wealth of experimental results show that only specific component combinations can produce transparent systems and that the various components must be put together in just the right order to produce a microemulsion. We are thus left with two basic questions:

1. Are these systems kinetically stable, since they may show path dependency in their formation?
2. Are they thermodynamically stable, even though their occasional path dependency properties may reflect activation energy barriers that these systems must overcome during their formation?

In a previous paper (4) it was shown that o/w emulsions of sodium long-chain sulfate/n-hydrocarbon/5% NaCl can be titrated to clarity with specific long-chain dimethylamine oxides. For the six systems investigated, all were found to have small negative free energy values associated with cosurfactant absorption during microemulsion formation. These small free energy values seem to explain why the manner of combining the various components is important during microemulsion formation. The right order of addition appears to lower activation energy barriers that these systems must overcome during their formation. In addition, microemulsion formation appears to be an entropy-driven process, as shown by titration experiments.

It has always been assumed that microemulsions are composed of discrete individual spherical droplets (3). In a previous paper (17), we demonstrated that o/w microemulsions prepared with low volume fraction of hydrocarbon show an overall decreased vapor pressure relative to the vapor pressure of the continuous surfactant phase. This behavior is similar to that of a high molecular weight polymer solution or a regular colloidal dispersion, where the vapor pressure of the solution is less than that of the continuous phase. It was also demonstrated, based on vapor pressure analysis, that o/w microemulsions clearly exhibit two distinct regions of transparency depending on the volume of hydrocarbon in the dispersed phase. For low volumes of hydrocarbon, encapsulated non-interacting droplets are formed in solution, while for higher volumes of hydrocarbon, a dynamic merging equilibrium exists in which the droplets are continuously breaking and reforming; i.e., percolation (17, 18). Similar phase behavior has been demonstrated by Weatherford (19) using vapor

pressure analysis for w/o diesel fuel microemulsion systems composed of a surfactant mixture of oleyldiethanolamide, diethanolamide, and diethanolanmonium oleate. The results which indicate that two regimes of differing phase behavior exist as the water content is varied, suggest a transition from inverted micellar solutions, at low water concentrations to microemulsions at a higher water content. These results support the fact that the internal droplet structure can vary depending on the internal phase volume, an important physical-chemical property of microemulsion systems of considerable interest to the formulator of consumer goods.

Since the dispersed phase volume governs the structure and properties of the droplets formed, microemulsions offer a broad array of applications. For example, microemulsion systems can be used to encapsulate and reduce the rate of oxidation and/or hydrolysis of oils (or oil-soluble ingredients). This effect is due to the fact that, for low volume fractions of oil, microemulsions offer complete encapsulation of the oil by the surfactant sheath surrounding the droplets. A specific example might involve the encapsulation of citrus oil in o/w microemulsions.

In addition, since the presence of droplets (low volume fraction of oil) results in a lowering of the vapor pressure, these systems can be used to stabilize and deliver hydrocarbons with high vapor pressure (e.g., isopentane and pentane). This effect cannot be achieved with conventional emulsion systems.

Droplet aggregation in w/o microemulsions has also been investigated and discussed by a variety of authors (3, 10, 17). For systems containing low concentrations of water, isolated non-interacting droplets have been found to be the primary droplet structure (18). At higher water concentrations, droplet interactions were found to be either repulsive, with short-lived collisions and no overlap between colliding droplet interfaces, or attractive, with collisions of larger durations and the formation of transient droplet clusters. It has also been shown that the probability of such transient merging in ternary systems is low ($\sim 10^{-3}$ per collision). For quaternary systems the merging probability between droplets is quite high (~ 1), indicating that the interactions between droplet cores play an important role in the droplet structure of these systems.

The need to understand factors related to the stability of colloidal dispersions has long been the central motivating factor in the study and development of surface science. "Stability" in this context is generally understood to mean kinetic stability; i.e., stability imposed by a strong repulsive barrier acting against contact between the suspended particles (20). For emulsion systems, London-van der Waals dispersion forces are at the origin of the tendency of colloidal systems to coagulate and aggregate. The repulsive forces needed to stabilize the dispersion against these attractive forces are usually of two types:

1. Coulombic repulsion due to electric charges on the particle surface; e.g., electrostatic interactions between the ionic double layers surrounding the particles.
2. Static repulsion introduced by large molecules or polymers adsorbed on the particle surface.