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PHYTOSTEROL STABILIZED EMULSIONS: CORRELATION BETWEEN RHEOLOGIC AND CALORIMETRIC STUDIES

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ABSTRACT

Mechanisms responsible for the stability of phytosterol stabilized emulsions have been determined. The emulsions were non-Newtonion in behavior with considerable degrees of thixotropy and with static yield values at low shear rates on the upcurves of the rheograms. Both of these properties signify the presence of a three-dimensional gel-like stabilizing network. The enthalpies determined by differential scanning calorimetry correlate linearly with the static yield values obtained by rheologic

measurements. Relationships exist therefore between the energies required to fluidize the emulsions and the gel-like structures of the systems.

INTRODUCTION

Previous studies of formulations containing phytosterols have resulted in unusually stable emulsions, particularly in the presence of an amphoteric surfactant, sodium lauriminodipropionate (Deriphat 160C®). The mechanism responsible was interfacial complexation of the phytosterol (Generol 122®) with the anionic Deriphat 160C®, as reported previously (1). The objective of this report is to summarize and correlate data obtained from rheologic and differential scanning calorimetric studies on these systems.

Rheologic studies of semi-solid emulsions are important not only for quality control during and after a manufacturing process, but also to provide information useful for preparing formulations or for assessing the physical-chemical properties of the product. The rheologic behavior of semi-solid emulsions has been measured mostly by continuous shear or by creep methods (2). The rheological properties of these systems are often complicated by time-dependent behavior, i.e., thixotropy. Materials which exhibit a reversible, isothermal, time-dependent shear-thinning phenomena are thixotropic in nature. Such time-dependent changes are attributed to changes in the three-dimensional gel-like structure of the system. As this structure develops, viscosities at low shear rates gradually increase with time to maximum values (3).

The effect of various surfactants in combination with an amphiphilic compound, such as a fatty alcohol as cosurfactant, have been studied (4-6). The mixture of cosurfactant and surfactant produces emulsions of desired consistency and stability by a so called "self-bodying action" (4-6). This self-bodying action imparts a three-dimensional structural network thereby enhancing the stability of the product. Surface aging is also a phenomena that is commonly encountered in these types of formulations. The aging effect is characterized by a time-dependent variation in surface concentration which leads to age-dependent changes in viscosity (7). The change in energy of the system is also notable if a change in the structure of the system occurs (8-9). Such thermodynamic changes in the emulsion formulations are of interest in understanding the basic principles involved in their stability.

Differential scanning calorimetry is a technique in which the difference in energy input into a sample and a reference material is measured as a function of temperature, while the substance and the reference are subjected to a controlled temperature program. It provides direct calorimetric measurement of energies of transition; interactions between various components can be observed by monitoring enthalpies. Positive enthapies emphasize the importance of entropic factors as the primary driving force leading to association or structuring. The properties of emulsions consisting of a monoglyceride with vegetable oil and water have been discussed in relation to their thermal stability and crystallization at the droplet interface (10).

EXPERIMENTAL

Formulation and Materials

An oil phase, consisting of 4 g hydrogenated vegetable oil (Wecobee S®, PVO International, Inc.); 3 g caprylic/capric triglyceride (Neobee M5®, PVO International); 8 g stearic acid (Emersol 132®, Emery Industries); and 3 g of phytosterol (Generol 122®, Henkel Corporation), were placed in a glass container and heated to 80°C and mixed until homogeneous. A sufficient amount of water phase containing 4% w/v sodium lauriminodipropionate (Deriphat 160C®, Henkel Corporation) to bring the sample to 100 g was heated to 83°C. The oil phase was then added to the water phase and homogenized with a Polytron® homogenizer at 10,000 rpm for a total 2 minutes, the first 10 seconds of which was a programmed gradual increase in speed from zero to maximum. The oil-in-water emulsion was then cooled slowly to room temperature and stored at 25°C.

Methods

Rheologic -- A Brookfield microprocessor-controlled cone and plate viscometer (Rheoset®, prototype Model RVCP) was used. The viscometer was programmed to run at speeds from 0.1 to 10 rpm in steps as small as 0.1 rpm. The interval between each increment was programmed to be 5 seconds. A type CP-52 cone (3°) was

used. Sample temperature was controlled at 25±1°C by a Neslab Model RTE-9DD digital heating/cooling circulator bath.

Differential Scanning Calorimetry (DSC) -- DSC measurements were performed with a Dupont Model 990 Thermal Analyzer equipped with a DSC cell module (Model 990315-903). The instrumental conditions were as follows:

Temperature Range:	30° to 80°C.
Heating Rate:	5°C/min.
Sample Size:	8 to 12 mg.
Sample Pans:	Hermatically sealed anodized aluminum pans and lids
Scale:	5°C/inch
Sensitivity:	0.1 mcal/sec/inch

Samples were prepared in advance and stored at 25°C prior to use at the designated time intervals. An empty pan was used as the reference. In order to calculate enthalpies, thermograms of each sample and a blank were run on a time base mode. The ordinate in a DSC thermogram is a power term, and the abscissa, time. Integration of the power versus time curve, expressed as calories/mole, corresponds to the enthalpy (ΔH) change. A Gelman planimeter was used to measure the area under the curve.

RESULTS AND DISCUSSION

Plots of shear rate versus shear stress for the emulsion formulations (Figure 1) show both a considerable degree of thixotropic behavior as indicated by the hysteresis loops and the presence of spurs at low shear rates on the upcurves of the rheograms. The areas of the hysteresis loops increase as functions of time. The moderate degrees of thixotropy are an indication of the formation of frozen

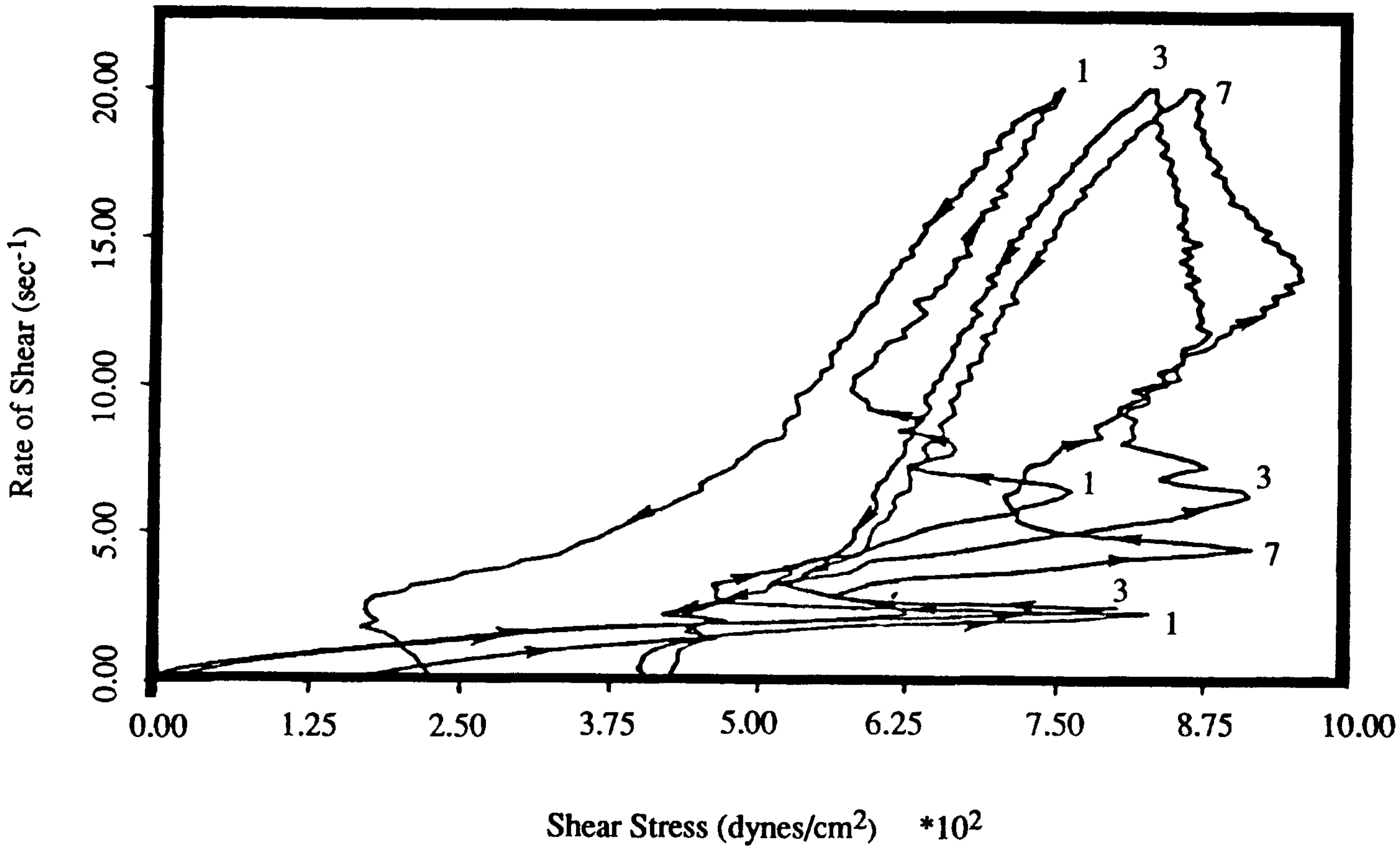

Figure 1: Rheograms of the model emulsion formulation as functions of the time of storage (in days) at 25°C.

micelles or of frozen liquid crystals. The areas of these loops are relative measures of the amount and extent of such gel formulation in the continuous phase. The increases in area therefore suggest build-up of a three-dimensional matrix. Barry, et al. (4-6) correlated such types of observations on semi-solid emulsions with the mechanisms by which gel networks are formed.

Correlations were found between increases in apparent viscosities and the areas of the hysteresis loops with time. A rapid increase in structure formation during the first 24 hours of sample storage has been reported also (11). This build-up of structure is responsible for the increase in consistency of the emulsions upon aging. This effect has been found to occur for up to 7-10 days, beyond which structure is apparently fully formed. Mohan, et al. (7) also observed considerable increases in viscosity of emulsions with aging. In this context, significant changes were also noticed by NMR during this time period (1). These changes were assigned to the formation of an intermolecular complex at the oil-in-water emulsion interface by the surfactant sodium lauriminodipropionate, Deriphat 160C, and the cosurfactant phytosterol, Generol 122 (1, 12).

The spur points, from which the static yield values can be determined, are measures of the strength of the structure of the system, which must be broken down before significant flow can occur. The magnitude of the static yield values increased up to 7-10 days, after which they remained essentially constant. These values were correlated with enthalpies determined by

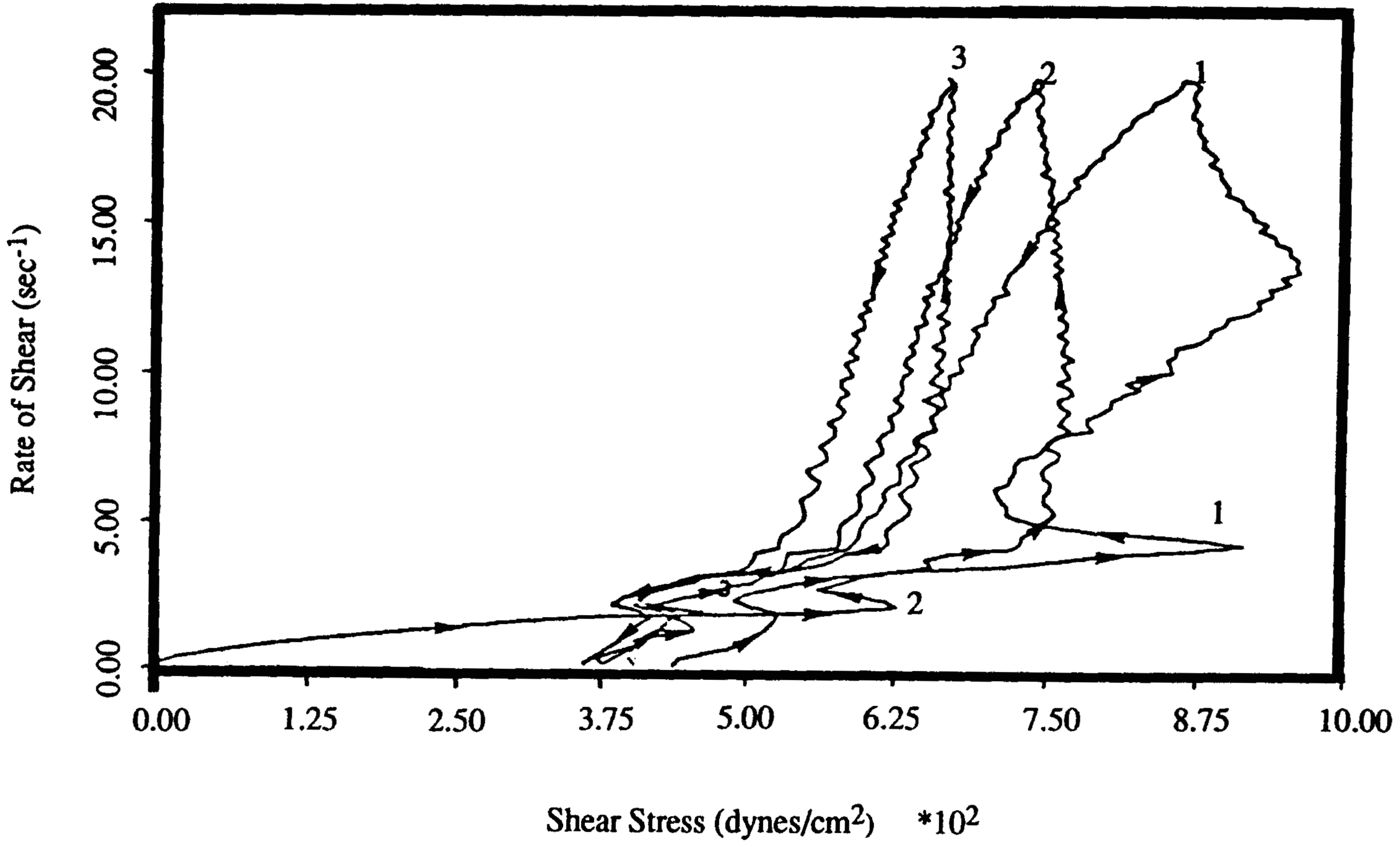

Figure 2: Relationship between the enthalpies and static yield values of the model emulsions. Storage time (in days) at 25°C is indicated by the number of each data point. Each data point represents mean of three determinations.

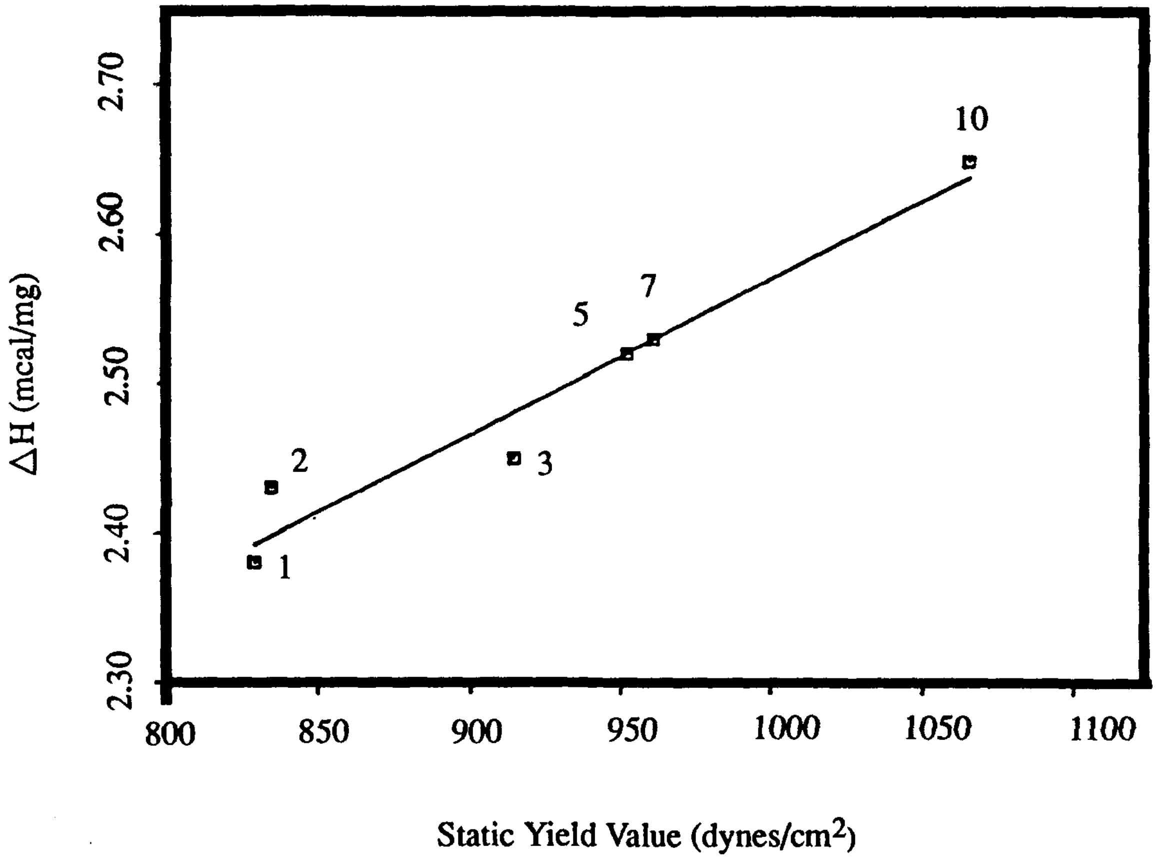

Figure 3: Rheograms of the model emulsion as functions of repeated shear cycles in a sample stored for 7 days at 25°C. The interval between each rheogram was 30 minutes.

differential scanning calorimetry. As can be seen in Figure 2, the static yield values are in a reasonably linear correlation with enthalpies obtained for samples stored for the same time periods. The magnitudes of the enthalpies can be related to the contribution of the internal energy of the oil phase to the formulation of a stabilizing network. The greater the difference, the greater is the energy involved for interaction and the greater is the stability of the network and hence the emulsion. Figure 2, therefore, gives an indication of the energies required to break the stabilizing network, thereby allowing the emulsions to become mobile, i.e., to overcome the static yield values.

When the same sample is run through repeated rheologic cycles (Figure 3), the areas of the loops and the static yield values both decrease in magnitude, suggesting breakdown of the gel-like network. There is a large decrease in loop area from the first to the second shear cycles as the majority of structure disruption occurs the first cycle; subsequent decreases are much smaller in magnitude. This indicates that structure breakdown caused by shear was rebuilt only to a negligible extent over the duration of the experiments.

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