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THERMAL RHEOLOGICAL ANALYSIS OF TRIETHANOLAMINE-STEARATE STABILIZED MINERAL OIL IN WATER EMULSIONS

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ABSTRACT

Thermal rheological analysis (TRA) is employed as an analytical method to quantitatively assess temporal viscosity changes in triethanolamine-stearate stabilized mineral oil/water systems. Continuous measurement of stress required to maintain a constant rate of shear was monitored while temperature was raised from 25 to 75°C. The rheological profiles obtained were distinguished by distinct, unexpected, reproducible discontinuities which were formulation dependent and changed with time and temperature. These changes have been attributed to as yet unverified

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shifts in individual and aggregate liquid crystalline structures. Quantitative analysis studies currently underway will aid in determining the usefulness of thermal rheological data as a predictive tool of long term emulsion stability.

INTRODUCTION

Triethanolamine-stearate formed in-situ from triethanolamine, (TEA), ($N(CH_2CH_2OH)_3$), and stearic acid, ($CH_3(CH_2)_{16}COOH$), is a popular emulsifier used in industry for various oil in water creams and lotions[1,2]. Emulsions with excellent cosmetic acceptance and stability can be obtained; however, identifying the proper formulation and assessing stability has often been a time consuming trial and error process. Little work has been published on the predictive capabilities of interim physical changes on long term stability. In view of this, the objective of this study was to quantitatively assess time and temperature dependent rheological changes of triethanolamine-stearate stabilized mineral oil/water emulsion systems and subsequently correlate these changes with phase equilibria and liquid crystalline structure in relation to emulsion stability.

EXPERIMENTAL

Materials And Equipment

Stearic Acid, N.F., triple pressed, J.T. Baker Chemical Co., N.J.

Trolamine,(Triethanolamine, TEA,) N.F., J.T. Baker Chemical Co., N.J.

Paraffin Oil, White, Saybolt Viscosity 80-90 at 100°F, Banco, Anderson Lab Inc., TX.

Deionized Water

Brookfield Digital Viscometer and Thermosel System

Bascom-Turner Recorder and Data Acquistion System.

Lightnin, model V variable control mixer with propeller

Precision, GCA Corp.,water bath

Composition of Emulsions

The percent composition of emulsifying agent was based on the stoichiometric in-situ reaction involving one mole of triethanolamine and one mole of stearic acid. The amount of water and mineral oil was adjusted in each case so as to keep the ratio of the total aqueous phase to the total oil phase a constant.

Manufacturing Procedure

Appropriate amounts of stearic acid and mineral oil (Table 1) were weighed out into a beaker and placed in a 70°C water bath. The variable control mixer was assembled and adjusted to produce good mixing of the oils. In another beaker, TEA was dissolved in water and also heated to 70°C. The water phase was added to

TABLE 1

Composition of Mineral Oil in Water Emulsions Containing Varying Amounts of Emulsifying Agent.

%EA*	TEA (g)	H_2O (g)	Stearic Acid (g)	Mineral Oil (g)
3.00	5.16	417.50	9.84	67.50
5.00	8.60	412.50	16.40	62.50
7.00	12.0	407.50	22.96	57.50
10.00	17.2	400.00	32.80	50.00

*emulsifying agent

the oil phase and continuously mixed for ten minutes with the temperature maintained at 70°C. After ten minutes the emulsion was removed from the 70°C water bath and placed in a cool water bath. Mixing was continued until the emulsion cooled to 30°C.

Thermal Rheological Analysis

A 15 ml quantity of emulsion was removed from the top of the storage container with a large syringe and introduced into the viscometer sample cell. (In a separate study, it was found that within the time frame of the study, there was no difference in rheological profiles for samples drawn either from the top or bottom of the same container.) An appropriate spindle and rpm setting on the viscometer (Brookfield model LVTD) was selected to produce apparent viscosity readings in a suitable range. The viscometer is actually calibrated to systems exhibiting Newtonian behavior; therefore, the values obtained for these thixotropic non-Newtonian systems are referred to as apparent viscosities.

For the emulsions containing 3, 5, 7 and 10% emulsifying agent, the rpm setting was 30, 3, 0.3 and 0.3, respectively. The heating control unit (Brookfield Thermosel System) was programmed to raise the temperature incrementally 2°C and hold for two minutes, over a temperature range from 25 to 75°C. The apparent viscosity and temperature data were collected on separate channels of a microprocesser controlled data acquisition system (Bascom-Turner Recorder and Data Acquisition System) and plotted such that temperature was on the abscissa and apparent viscosity on the ordinate.

RESULTS AND DISCUSSION

Thermal rheological profiles (Figures 1-4) were obtained in the range of 25 to 75°C for emulsion systems containing 3,5,7, and 10% total emulsifier. The profiles were reproducible and distinquished by discontinuities characteristic of the formulation. The time and temperature dependent viscosity changes have been attributed to shifts in phase equilibria and subsequent changes in liquid crystalline structures based on pertinent work in the literature. Although analytical work currently underway is needed to more definitively describe these changes, a review of the literature dealing with mesomorphic phases does support the following logical explanations. These conclusions are based upon articles dealing with phase equilibria and gel structures of emulsions[3,4], liquid crystals of surfactant solutions[5,6,7], viscosity profiles of other oil/water emulsions[8,9,10,11], and lyotropic mesomorphism in general[12,13,14,].

Liquid crystalline structures can be attributed to the aggregate tendency of amphiphilic molecules in solution to assume the most energetically favorable conformation. The extent and type of interaction between the molecules define the structural elements and phases often referred to in emulsion/gel literature[4]. The hydrophilic gel phase consists of water interlamellarly associated with amphiphilic molecules in the continuous phase. Interaction between amphiphilic molecules and the dispersed phase composes a local lipophilic gel phase which also can bind water, but to a much lesser extent than the hydrophilic gel phase. The effect of temperature and time on the distribution of components between these two phases, and the temporary structures formed, is the basis for the explanation of the rheological changes found in the TEA-stearate stabilized emulsions studied.

Temperature Dependent Viscosity Changes

Increasing the temperature of the emulsion with the lowest emulsifier concentration, (3%), Figure 1, results in a monotonic decrease in viscosity. Resistance to flow at the 3% level is apparently due to flocculation of the dispersed phase. Increased kinetic energy disrupts the aggregate structure leading to a decrease in apparent viscosity.

Elevating the temperature of the emulsions containing intermediate emulsifer concentrations, (5 and 7%), Figures 2 and 3, also results in a decrease in apparent viscosity until about 48°C where the apparent viscosity increases to a maximum at 54°C and then declines again. This unexpected rheological behavior is attributed to gel formation as a consequence of effectively higher TEA-stearate concentration in the external phase. In addition to the stabilized internal phase, some liquid crystalline structure (TEA-stearate), presumably of the middle phase[7] type, exists at these higher emulsifying agent concentrations. Increasing temperature "melts" these crystals presenting a large number of randomly distributed individual TEA-stearate molecules . The

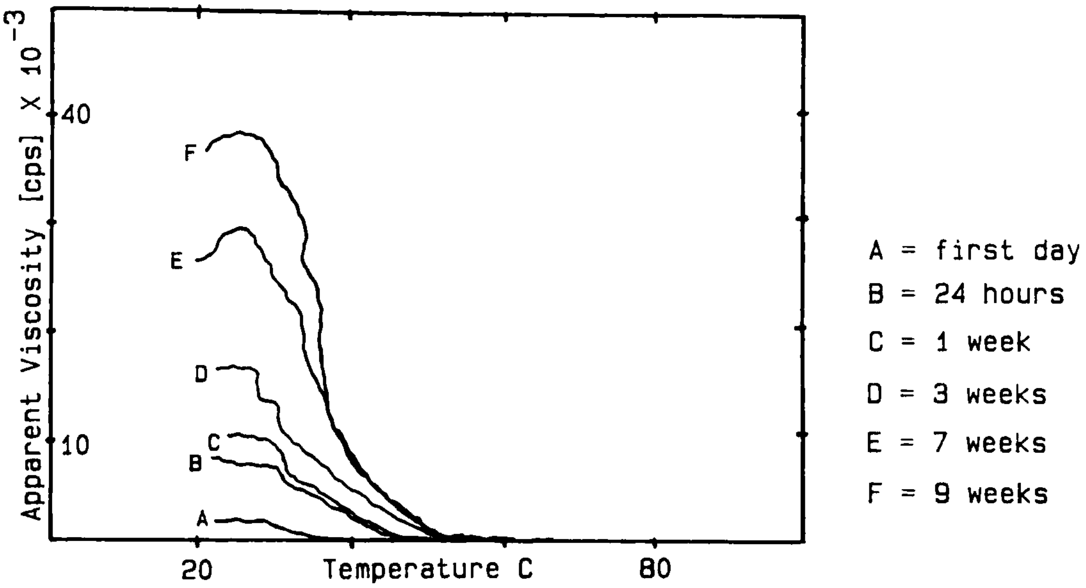

FIGURE 1

CONSTANT SHEAR THERMAL ANALYSIS
MINERAL OIL/WATER EMULSION, 3% TEA-STEARATE

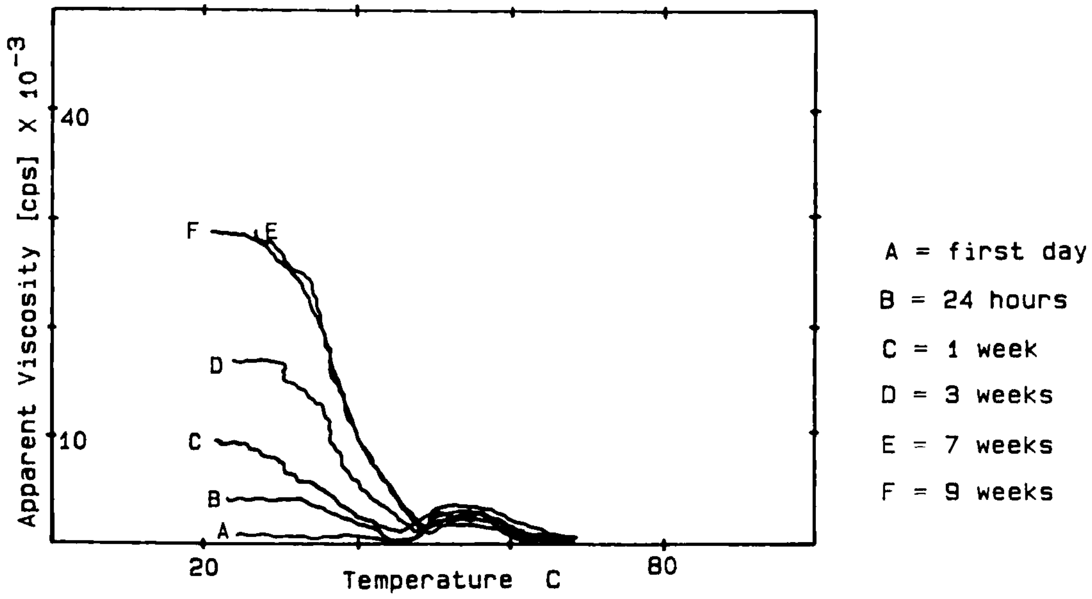

FIGURE 2

CONSTANT SHEAR THERMAL ANALYSIS
MINERAL OIL/WATER EMULSION, 5% TEA-STEARATE

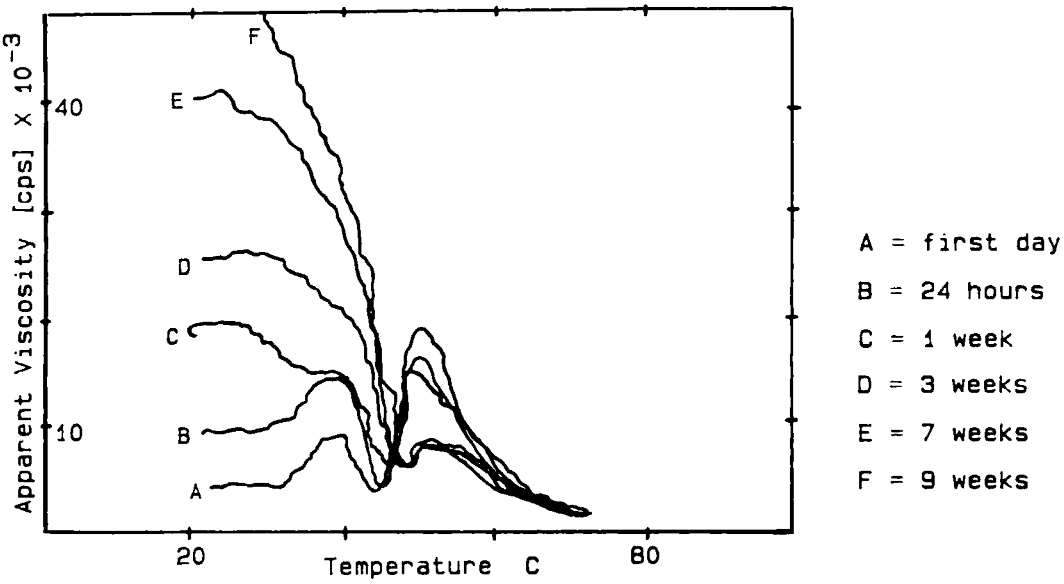

FIGURE 3

CONSTANT SHEAR THERMAL ANALYSIS
MINERAL OIL/WATER EMULSION, 7% TEA-STEARATE

net effect is progressive development of a gel-like structure with increased resistance to flow.

To verify this hypothesis, aqueous dispersions of the TEA-stearate were subjected to thermal rheological analysis. The results are presented in Figure 5. It is important to recognize that in the absence of the oil phase, the dispersions containing 3,5,7, and 10% TEA-stearate are not equivalent to the emulsion systems presented in Figures 1-4. In the dispersions, all the TEA-stearate is present in the aqueous phase, while in the emulsion systems, a significant portion is located

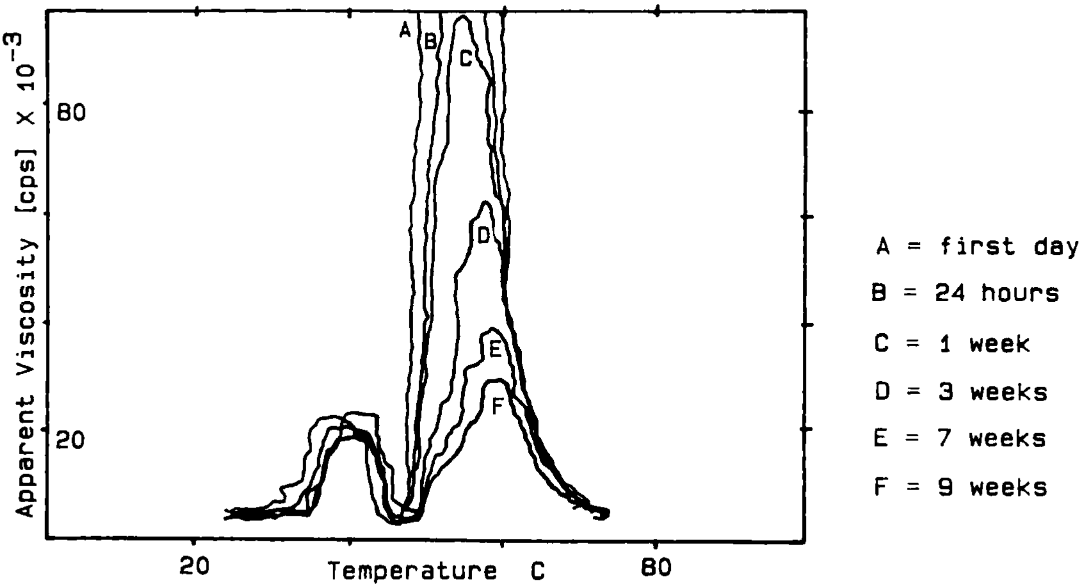

FIGURE 4

CONSTANT SHEAR THERMAL ANALYSIS
MINERAL OIL/WATER EMULSION, 10% TEA-STEARATE

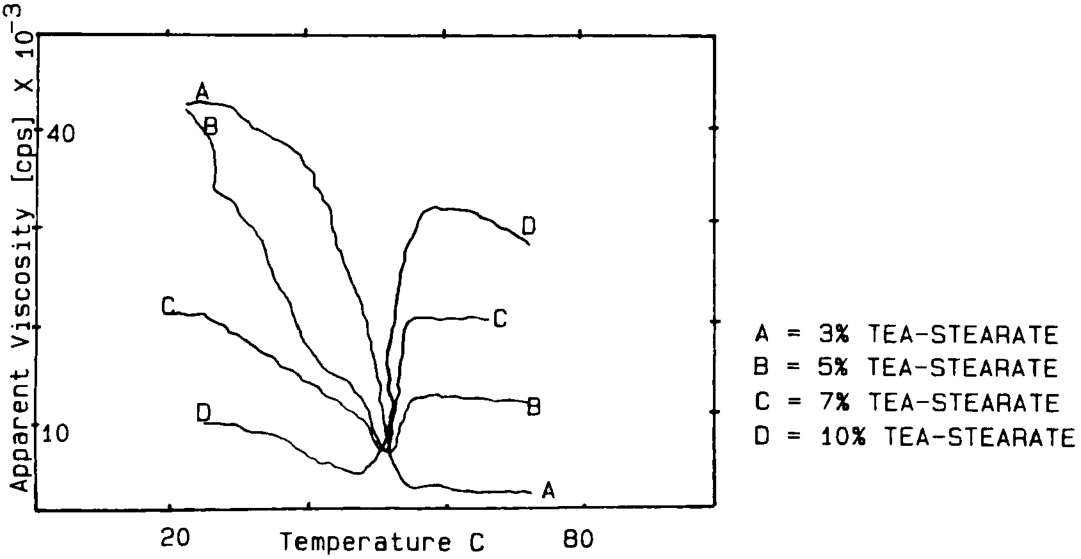

FIGURE 5
CONSTANT SHEAR THERMAL ANALYSIS

AQUEOUS DISPERSIONS OF TEA-STEARATE

at the interface. Evidence of a gel structure is initially present in the 3% dispersion. Increasing temperature eventually destroys this structure with a commensurate viscosity decrease. Initial viscosity decreases in these dispersions as the concentration of emulsifier is increased since there is a predisposition to the formation of lower energy liquid crystals. These crystals act as discrete particles with much less overall dispersed phase interaction. They also act as reservoirs of TEA-stearate molecules which are released at elevated temperature. The concentration dependent increase in apparent viscosity seen at 48° in the profiles corresponds to this release. Thus, a temperature induced gel formation producing an increase in apparent viscosity is evident even in systems without the internal oil phase. This effect is a contributor, if not totally responsible for the higher temperature viscosity elevations observed for the emulsion systems in Figures 2-4.

These data also help explain the profile for the emulsion system containing 10% emulsifying agent (Figure 4). Increasing temperature results in viscosity maxima at 40°C and 54°C. At low temperature with this emulsifier concentration, surfactant molecules favor formation of liquid crystals in the neat phase[7]. In this phase, the dense packing of the surfactant molecules produces a system where there is little interaction between the surfactant molecules and the continuous phase, resulting in a lower initial viscosity[12]. As the kinetic energy of the system is increased, surfactant molecules become mobile permitting the formation of middle phase type crystals with a subsequent increase in viscosity[5]. Further increase in temperature melts the middle phase crystals and viscosity drops until the system is at 48°C. At this temperature, the micelles dissociate into free surfactant molecules which can form a viscous gel. At 54°C, the viscosity resulting from the interaction of the free surfactant molecules with water and TEA-stearate at the oil/water interface, declines as the "network gel" melts.

Time Dependent Viscosity Changes

The initial apparent viscosity of the emulsions containing 3,5, and 7% TEA-stearate increases over about a two month period. This process appears to be the slow development of aggregrate micellar structure in a viscous system[8]. The initial viscosity profile of the emulsion containing 10% emulsifier is reasonably time independent. Since the initial region of these TRA's depends upon the existence and subsequent disruption of liquid crystals, this stability is not unexpected.

For the emulsions containing 5, 7, and 10% TEA-stearate, the maxima at 54°C decrease with time. Assuming that the peak height is due at least in part to an interaction between the network gel and amphiphilic molecules at the droplet interface, one possible explanation for the decrease in viscosity over time may be coalescence of the internal phase. Interaction of the network gel with the larger droplets would not impart as great a viscosity as the original smaller droplet system. Another possible explanation for the decline in viscosity may be the degradation of the emulsifier. Polarized light microscopy and analytical work using high pressure liquid chromatography is underway and will aid in confirmation of the above conclusions.

REFERENCES

1. L. .R. Mores, Cosmetics and Toiletries, 95, 79 (1980).

2. C. Fox, Cosmetics and Toiletries, 99, 41 (1984).

3. H. Junginger, et al, J. Soc. Cos. Chem., 35, 45 (1984).

4. J. Swarbrick, J. Soc. Cos. Chem., 19, 187 (1968).

5. F. B. Rosevear, J. Amer. Oil Chem. Soc., 31, 628 (1954).

6. A. S. C. Lawrence, Nature, 183, 1491 (1959).

7. Hartshorne and Stuart, in "Crystals and the Polarizing Microscope," Edward Arnold Pub., 1970, p.542.

8. B. W. Barry, Adv. Coll. Interf. Sci., 5, 37 (1975).

9. B. W. Barry and G. M. Saunders, J. Coll. Interf. Sci., 36, 130 (1971).

10. S. S. Davis, J. Pharm. Sci., 58, 418 (1969).

11. C. D. Han and R. G. King, J. of Rheology, 24, 213, (1980).

12. C. A. Miller, in "Lyotropic Liquid Crystals," S. Friberg, ed., Am. Chem. Soc., 1974, p.90.

13. I. Danielsson, in "Lyotropic Liquid Crystals," S. Friberg, ed., Am. Chem. Soc., 1974, p.13.

14. Hartshorne and Stuart, in "Crystals and the Polarizing Microscope," Edward Arnold Pub., 1970, p. 503.