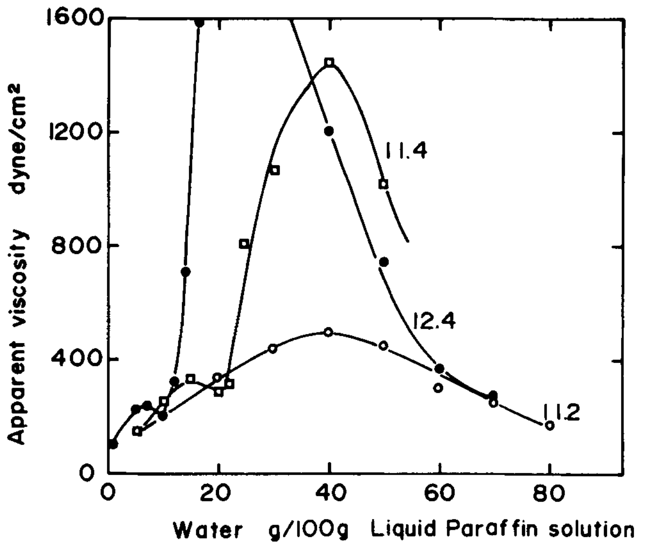

FIG. 8. Effect of added water and HLB number on apparent viscosity of liquid paraffin (80 wt %)/sorbitan monostearate+POE (20) sorbitan monostearate (20 wt %) system. The numbers in the figure represent HLB number; at 60 C, the shear rate was 268 sec^{-1}.

gel phase changes continuously to an aqueous phase by further addition of water. Homogeneous O/W emulsions can be formed by this process, i.e., oil continuous phase → liquid crystalline phase → white gel phase → O/W emulsion (Fig. 8).

A simple method for learning whether surfactants are suitable as emulsifiers for a given oil phase follows. First, examine the solubility of surfactants in the oil phase. The surfactant must dissolve in the oil phase at a suitable HLB region in the hydrated state. If a liquid crystalline or gel phase appears in the process of adding water, a homogeneous emulsion will be obtained.

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Hydrotropic Action of a Diacid

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ABSTRACT

An investigation to evaluate the mechanism of the hydrotropic action of a long chain diacid was made by determining the co-association structures with a straight chain amphiphilic molecule of sufficient size to form long range order structures. The hydrotropic mechanism was found in the transition of a liquid crystalline structure to an isotropic solution. The mechanism was identical for aqueous solutions and water-poor inverse micellar solutions.

INTRODUCTION

A class of substances named hydrotropes (1) possesses the property of increasing the solubility of poorly water soluble substances to an extreme degree when added to water in high concentrations. The typical solubility increase is from a fraction of a percent to the magnitude of 50% by weight when the level of hydrotrope reaches 25-30% by weight. A great number of researchers (2-6) have studied the shape of these solubility curves relating them to the structure of the hydrophobic part of the hydrotrope.

Friberg and Rydhag (7) showed the hydrotropic action to be coupled with long range order amphiphilic association structures. The higher solubilization capacity by a hydrotrope (≅60%) compared to that by a common surfactant (≅10%) was shown to depend on one fact: the isotropic solution of the hydrotrope was not changed to a liquid crystalline phase when a long chain hydrophobic amphiphile was added. This meant that the "cut-off" of the aqueous micellar solubilization that occurs with amphiphiles by normal surfactants (8) did not take place; the isotropic solution continued toward high concentrations of the amphiphilic substance. This mechanism was useful to explain the hydrotropic action of the low molecular weight hydrotropes such as the common sodium xylene sulfonate (7).

Recently, a new class of hydrotropes has been introduced (9-11) with Westvaco DIACID®, 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid. This compound consists of a long hydrocarbon chain with a total of 21 carbon atoms and the difference in structure is pronounced from the conventional hydrotropes such as the xylene sulfonates. Since the diacid has proven to be an efficient hydrotrope, we found basic investigation on the mechanism for its

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hydrotropic action to be of general interest.

Our investigation takes into account the fact that the recent development in laundry soap formulations encompasses a dual area of service by the hydrotropes. They are primarily active in the concentrated formulation to prevent gelation of the product, but they also serve during the washing cycle to promote removal of oily substances. With this in mind, we focused our investigation on the behavior in water-poor systems and in dilute solutions.

EXPERIMENTAL PROCEDURES

Materials

The octanoic acid and octanol were Aldrich "Gold Label," the hexylamine was Eastman Reagent Grade and the diacid was an experimental sample (9-11) supplied by Westvaco; all were used without further purification. The water was twice distilled.

Phase Regions

The solubility regions were determined by visual inspection of samples weighed into glass vials with screw caps. The samples were thermostated at 30 ± 0.2 C in a water bath. The presence of a liquid crystalline phase was detected from its optical appearance between crossed polarizers when viewed against a light source. The structure of the liquid crystalline phase was identified from its pattern in an optical microscope under polarized light.

RESULTS

The results will illustrate the hydrotropic action of the diacid by a comparison with the influence of a straight chain carboxylic acid in identical systems. Octanoic acid was chosen; it was estimated to give the closest resemblance to the total carbon atom number per carboxylic group of the diacid.

The behavior in a water-poor system will first be described followed by the results of the behavior in a dilute aqueous solution.

Water-Poor System

A combination of an amine and a carboxylic acid will form a liquid crystal with water provided the hydrocarbon chains are of sufficient length. *n*-Octanoic acid and *n*-hexylamine form such a combination. In single form, *n*-hexylamine does not form a liquid crystalline phase when combined with water.

The phase diagram Figure 1 confirmed this fact. The amine dissolved large amounts of water (58.5% by wt) to an isotropic liquid. This liquid was in equilibrium with pure water and no liquid crystalline phase was formed.

When combined with the octanoic acid, a huge area with a lamellar structure was formed according to Figure 1A. The lamellar structure existed between acid/amine molecular ratios of ca. 1/20 and 1/1 surrounded by an isotropic liquid in the direction of less water. These molecular ratios are related to distinct association structures, which will be discussed in a subsequent publication.

The phase conditions in the diagram with the diacid were entirely different (Fig. 1B). The entire range from pure amine to pure acid formed an isotropic solution and no liquid crystalline phase was formed. The solubility area was in equilibrium with water, showing little variation with the molecular ratios of the compounds, except for the molecular compound 2 acid:3 amine that interrupted the solubility area and also gave rise to a weak maximum of water solubility.

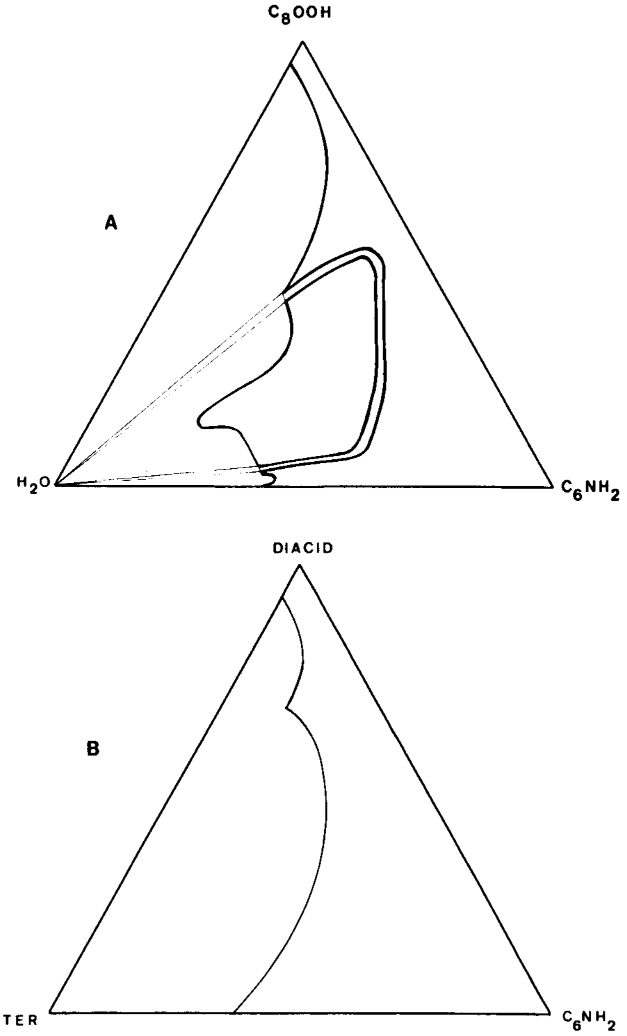

FIG. 1. Phase diagram of the systems: A, water/*n*-hexylamine/octanoic acid; B, water/*n*-hexylamine/diacid.

Aqueous Solutions

The hydrotropic effect was investigated at low surfactant concentrations, in the region below the critical micellization concentration. The practical application of dishwashing and laundry formulations lies in this region, making the investigations meaningful. The octanoic acid and its mixtures with the diacid were transformed to soap solutions by maintaining a pH of 10 in the aqueous solution.

Aqueous solutions of straight chain soaps form liquid crystalline phases (8) at concentrations far below the critical micellization concentration when long chain alcohols are added to the solution in excess of their solubility in pure water. Figure 2A demonstrates this phenomenon for sodium octanoate and *n*-octanol. At sodium octanoate concentrations in excess of 3%, the aqueous solution (area 1, Fig. 2) was in equilibrium with a liquid crystalline phase (areas 3 and 4, Fig. 2) not with the liquid alcohol (area 2, Fig. 2) as was the case for lower soap concentrations.

Replacing some of the octanoic acid by the diacid changed the solubility. A solubility maximum now appeared in the part of the solubility that was in equilibrium with the lamellar liquid crystal. This solubility maximum became more pronounced with increased ratio of the diacid. The solubility increase was substantial, i.e., from less than 1% with no diacid present to ca. 5% at a diacid/octanoic acid ratio of 1:2.3. Even the ratio 1:4 gave an increase to more than double the solubility of the non-

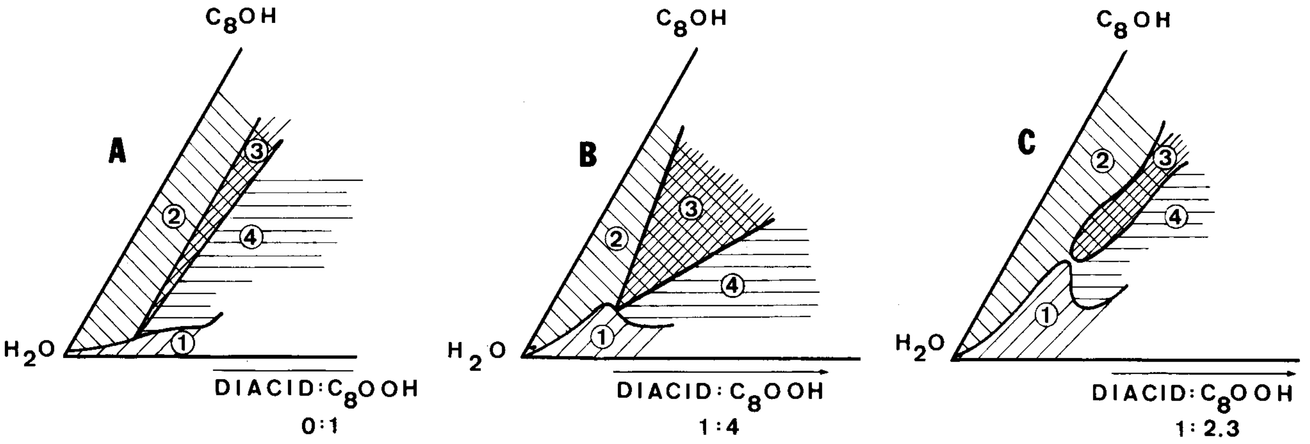

FIG. 2. Phase map of the conditions in an aqueous solution (pH = 10) of an octanoic acid/diacid mixture with octanol. 1. 1-phase area aqueous solution; 2. 2-phase area aqueous solution + octanol solution; 3. 3-phase area aqueous solution + octanol solution + liquid crystal; 4. 2-phase area aqueous solution + liquid crystal.

mixed state.

Three-phase areas have been marked in the figure showing the presence of a liquid crystalline phase. The deviation from linearity at highest ratio of the diacid is not a consequence of nonequilibrium conditions, but an expected result of the fact that the two diagrams involving the soap of the diacid are four-component systems. The limits of common three-phase areas are, in fact, the limiting tie-lines of two-phase regions. This diagram shows the projection of these from a three-dimensional to a two-dimensional representation.

DISCUSSION

The results gave a straightforward answer to the question posed in the investigation. The hydrotropic action of DIACID originates in the following mechanism. The formation of a liquid crystalline phase is prevented by the presence of the hydrotrope; instead, an isotropic solution is obtained. This mechanism is identical to the one from the common short chain hydrotropes such as the xylene sulfonates.

In our results, this mechanism was observed both under water-poor conditions resembling the concentrated conditions of the formulation itself and in the dilute aqueous solutions, being similar to the conditions in the washing process. The combination of the diacid with hexylamine (Fig. 1B) gave no liquid crystalline phase whatsoever in contrast to the octanoic acid that produced a large region of a lamellar phase in its combination with the amine. In the aqueous solutions (Fig. 2), the transition to a lamellar liquid crystalline phase with addition of a long chain alcohol at soap concentrations lower than the critical micellization concentration (Fig. 2A) was delayed. Instead, the isotropic solution region was extended in the direction of the liquid crystalline phase.

The molecular basis for the preference of the isotropic liquid state when the diacid is introduced is not yet clarified. Further investigations into the mechanisms will be reported later.

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