scribed previously (30). The triethylmethylammonium iodide resulting from N-demethylation was crystallized from a mixture of ethanol and ether to constant radioactivity, 1128 d.p.m./mg.

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Liquid Crystalline Phases in Aerosol Formulations I: Phase Equilibria in Propellant Compositions

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Abstract □ Phase equilibria in a system of water, mixed emulsifiers, and liquid propellant are determined by visual observation of the number of phases after centrifugation. Three different liquid phases and one liquid crystalline phase are observed. A small increase in the amount of water gives rise to a complex phase pattern, which is explained by the interaction between the two emulsifiers and the water.

Keyphrases □ Propellant composition—determination of phase equilibria □ Phase equilibria, determination—water–emulsifier–propellant systems, by visual observation □ Emulsifier–water interaction—role in phase equilibria of water–emulsifier–propellant systems

The stability of emulsions has been treated for a long time as arising from the properties of the interface between two liquid phases, of which one is dispersed in the other (1–3). In 1969, evidence was presented that liquid crystals are present in simple systems of water, hydrocarbons, and a single emulsifier (4). Further research (5) showed how the presence of the liquid crystalline phase has a dominant effect on the stability of the emulsion.

Later, Saunders (6) suggested that the stability of aerosol emulsions and foams could be related to "molecular complexes" forming multilayers of liquid crystalline character at the interface. The fact that surfactants, water, and amphiphilic substances can form liquid crystalline phases when mixed in certain proportions (7, 8) was cited as proof of the suggestion.

Because of this suggestion and the increased importance of aerosol packings, an investigation of the presence of liquid crystalline phases in systems of water, liquified chlorofluorocarbons, and one emulsifier was of interest. This publication is the first report on this investigation in which the emulsifier system of octanoic acid and 1-aminooctane was used. The system earlier gave well-defined results (9) in connection with emulsion stability.
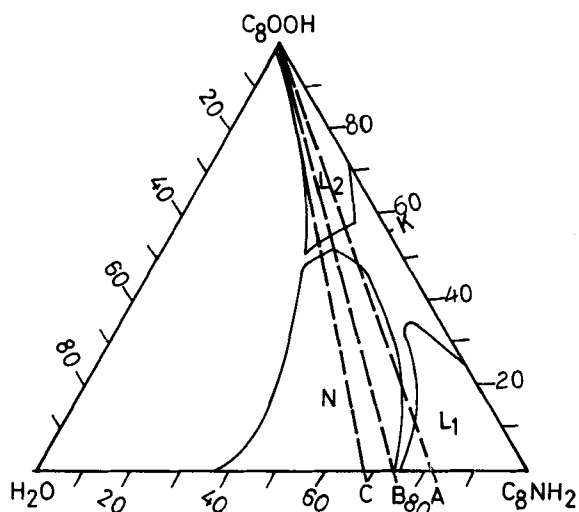
Figure 1—*Phase regions in the system of water–1-aminooctane-octanoic acid (H_2O-C_8NH_2-C_8OOH). Key: N = liquid crystalline phase, "neat phase"; L_1, L_2 = isotropic solutions; and K = equimolar solid compound, $C_8NH_3^+OOC_8^-$.*

EXPERIMENTAL

Materials—The water was twice distilled. 1-Aminooctane[1] (C_8NH_2) (GC > 99%), octanoic acid[2] (C_8OOH), and a propellant[3] were used.

Phase Equilibria—The acid, amine, and water were weighed into glass containers, which were sealed and cooled to $-20°$. The propellant ($C_2Cl_2F_4$) was then added; the pressurized packaging, the aerosol, was formed as the temperature slowly increased. The different phases in the aerosol were separated by ultracentrifugation at $8000 \times g$ ($20°$) during 2 hr. and identified by visual observation in a microscope with polarized light.

RESULTS

Figure 1 presents the water–emulsifier phase equilibria determined previously (10). It shows three liquid regions, one liquid crystalline region, and one solid phase. The liquid crystalline phase (N) has a lamellar structure. It forms two-phase regions: (a) with the
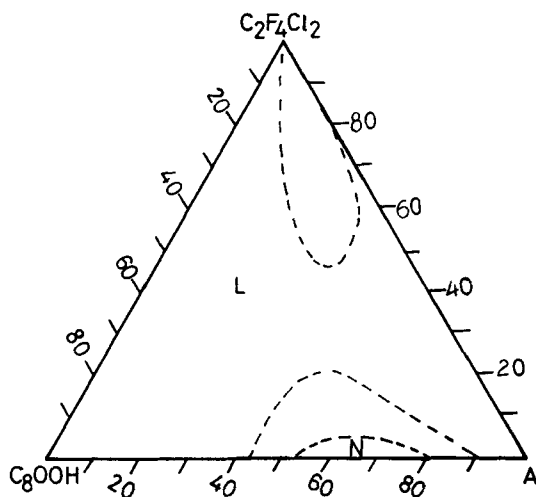

Figure 2—*Phase regions in the system of octanoic acid–propellant-water/amine [water (19%), 1-aminooctane (81%)] (C_8OOH-$C_2Cl_2F_4$-A). Key: L = isotropic solution; and N = liquid crystalline phase, "neat phase."*
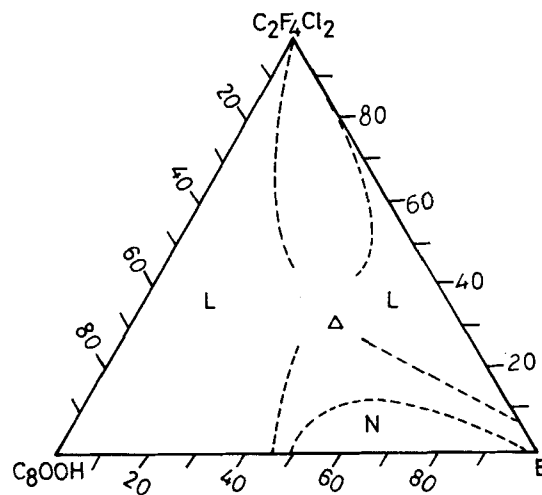
Figure 3—*Phase regions in the system of octanoic acid–propellant-water/amine [water (27%), 1-aminooctane (73%)] (C_8OOH-$C_2Cl_2F_4$-B). Key: L = isotropic solution; N = liquid crystalline phase, "neat phase"; and △ = three-phase area indication.*

amine solution (L_1) with the solid compound consisting of an equimolar ratio of amine and acid (K), and (b) with the acid solution (L_2). It (N) extends from the amine–water axis toward the acid corner, dissolving the acid to equimolar ratio by forming an ammonium salt within the liquid crystalline phase (5). The few percent excess acid are solubilized, resembling the process of solubilizing hydrocarbon (5). The amine solution solubilizes acid and water, and the acid solution behaves similarly toward water and amine.

Three lines are drawn (A, B, and C) in the diagram; the phase regions in the systems formed by these lines and $C_2Cl_2F_4$ as the third component are given by Figs. 2–4.

The system (Fig. 2) containing least water (C_8OOH-A in Fig. 1) shows complete solubility of the propellant and the acid in each other. The solubility region extends from the C_8OOH-$C_2Cl_2F_4$ axis in a broad region to the amine/water-$C_2Cl_2F_4$ axis, where the components also are soluble in each other. This liquid area is in equilibrium with the $C_2Cl_2F_4$ by means of a two-phase area, starting at the same ratio of the acid to the water/amine solution, which forms the two-phase area at the base axis.

The liquid crystalline phase solubilizes a maximum of 6% $C_2Cl_2F_4$, being in equilibrium with the solution.

Increasing the water content gives rise to a similar diagram (Fig. 3). The solution region in this case does not form a continuous channel between the two-phase areas. There is a three-phase region in the center (marked by a small triangle but not determined exactly). The liquid crystalline phase reaches the corner representing the amine/water mixture.

After further increasing the water content, the phase diagram (Fig. 4) presents several phases. To the left, a liquid phase area is formed from the acid dissolving about 25% of the amine/water mixture. This liquid is mutually miscible with the $C_2Cl_2F_4$. The second liquid region reaches from the acid (amine/water) axis to about 50% of $C_2Cl_2F_4$. The third liquid region covers part of the $C_2Cl_2F_4$ (amine/water) axis, showing only limited solubility of the three components in each other. The liquid crystalline phase solubilizes up to 14% of the $C_2Cl_2F_4$ and forms a continuous region from the amine/water corner to 50% acid.

DISCUSSION

The results presented evidence of the solubilization of the propellant, $C_2Cl_2F_4$, into the different solutions and into the liquid crystalline phase of the water/1-aminooctane–octanoic acid system. They also demonstrated the factors that govern the association conditions giving rise to the different phases.

The minimum mutual solubility of the liquefied driving gas with the two liquids, octanoic acid and the amine/water solution, respectively, is found with the compositions of acid (water/amine), where the liquid crystalline phase exposes *maximum* capacity of $C_2Cl_2F_4$ solubilization. This is well demonstrated by a comparison of Figs. 2
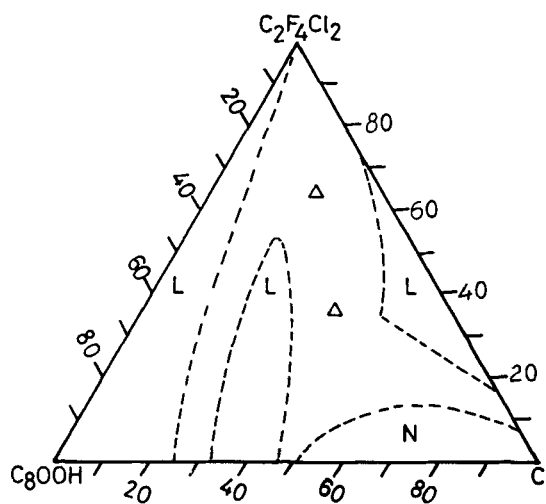
Figure 4—*Phase regions in the system of octanoic acid–propellant–water/amine [water (33%), 1-aminooctane (67%)](C_8OOH–$C_2Cl_2F_4$–C). Key: L = isotropic solution; N = liquid crystalline phase, "neat phase"; and △ = three-phase area indication.*

and 3. The increase of water content from the composition with 40% acid in Fig. 2 to the corresponding one in Fig. 3 is only 5%. This change causes an enhanced solubilization of the propellant in the liquid crystalline phase from 4.5 to 11%, which is accompanied by the disappearance of the solubility region connecting the two axes meeting at the propellant corner. In Fig. 2, the minimum width of this region is about 20%.

To understand this behavior, it is necessary to consider two different factors which are operating when different association structures are formed in the system. According to the first factor, the amine and the acid react with each other in nonaqueous solutions to form an ion pair: $C_8NH_3^+C_8OO^-$. This compound is soluble to some extent in the acid, in the amine, and to about half the magnitude in a nonpolar substance, p-xylene. The compound is not soluble in water due to the influence of the hydrophobic hydrocarbon chains. The second factor is the pronounced interaction between the water and the amine, manifested in the formation of the liquid crystalline phase.

The liquid crystalline phase solubilizes octanoic acid to a few percent *in excess* of the equimolar ratio. This high solubility, about 10 times that of a hydrocarbon, arises from the ionization reaction described earlier. The reaction results in a liquid crystalline phase in which the hold of water is reduced from 65 to 25 wt. % when the ratio of acid to amine is raised from zero to one. Constancy is, on the other hand, found in the minimum content of amine, varying only between 30 and 40% by weight. This finding implies an exchange of water molecules in the immediate vicinity of an amine molecule to octanoic acid molecules, but it is not evidence of any similarity of interaction of acid/amine with water/amine. The exclusion of one compound when the other is present is dependent on the site where the interaction occurs.

These factors may be applied to the present results according to the following discussion. The complete mutual solubility of the acid and $C_2Cl_2F_4$ is understood in terms of two nonpolar substances molecularly dispersed in each other. The amine/water solution consists of dissolved or solubilized water in amine, which forms the "continuous" phase. The chlorofluoroethane shows complete mutual solubility with the amine, as expected.

When the acid and the amine/water solutions are mixed, the previously mentioned salt formation to an ammonium carboxylate takes place. The polar compound formed causes a reduced solubility in the liquefied driving gas. The weak dispersion forces from the $C_2Cl_2F_4$ do not give rise to an interaction sufficient to prevent a phase separation due to the strong reciprocal dipolar interaction of the ammonium carboxylate molecules. The reduction of solubility in the

liquefied propellant is given a rational explanation in this manner.

When the relative amount of acid is increased, an increase of the mutual solubility is based on the strong hydrogen bonds formed between the acid and the ionized carboxylate group of the ammonium salt. The strongly attached acid molecules reduce the electrical field strength around the polar group and facilitate the solubility. This fact explains the more rapidly enhanced solubility when the acid is in excess compared to the behavior of the amine.

At low concentrations of the driving gas, a liquid crystalline phase is formed when the acid is added to the water/amine solution. Such a behavior is expected since the region of existence of the liquid crystalline phase involves less minimum water content in the liquid crystalline phase with an increasing amount of acid (Fig. 1).

When the water/amine ratio is raised, the stability of the liquid crystalline phase toward addition of a nonpolar substance is augmented. This fact is referred to the volume ratio of water and amine, which has an optimum where the layered structure is at maximum stability. A water content less than this value decreases the energy difference between the liquid crystalline phase and the amine liquid phase containing reversed micelles with water. A water content in excess of this value reduces the corresponding energy difference to an aqueous solution. The optimum ratio also includes the maximum interaction of water and amine, which leads to less tendency to form reversed micelles in the comparatively nonpolar $C_2Cl_2F_4$. Consequently, the solubility in the latter diminishes with increasing water content. Furthermore, at high water content, the strong hydrogen bonds between ionized carboxylic groups in the ammonium salt and the nonionized carboxylic acid molecules are influenced by the present water molecules reducing the bond strength. As a result, the reduction of aggregation of the acid to the polar compound gives rise to a reduced solubility of the association structures in $C_2Cl_2F_4$. A secondary effect arising from the same origin is the formation of micelles. Unpublished results give evidence of the existence of micelles at acid contents less than 30% counted on a total of water, amine, and acid (Fig. 1). The split of the solubility area to the left in Fig. 4 has to be referred to this fact.

With regard to these factors, the phase regions of the systems containing the driving gas are mainly related to the forces between the polar parts of the surface-active substances and the hydrophobic interaction with the water molecules. The phase equilibria in the system are responsible for the properties of the aerosol which is expelled; these relations will be treated in a following report.

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