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**THE MOLECULAR STRUCTURE OF
THE HAN-BASED LIQUID PROPELLANTS**

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1. INTRODUCTION

The two HAN-based liquid propellants in current use, LGP1845 and LGP1846, are homogeneous, aqueous mixtures of the salts hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN), in such proportion as to produce N_2 , CO_2 stoichiometry. LGP1845 was designed volumetrically to contain 11 mole/liter total nitrate and its composition is, therefore, 9.63 M HAN and 1.38 M TEAN. The water content of LGP1845 is determined by its density and is approximately 16.8 weight-percent. The LGP1846 mixture has the same HAN:TEAN ratio as LGP1845 but is gravimetrically formulated to contain a 20.00 weight-percent water. Thus, both propellants are mixtures of the hydroxylammonium and triethanolammonium cation, the nitrate anion, and water, with total ion concentrations of 22.0 mole/liter for LGP1845 and about 20.5 mole/liter for LGP1846, assuming complete dissociation. LGP1846 is less energetic than LGP1845 because of its higher water content. Impetus, calculated at a loading density of 0.2 g/mL, using the BLAKE thermochemical code (Freedman 1982) is 948.3 J/g and 900.7 J/g for LGP1845 and LGP1846, respectively. The water concentration of the mixtures is only 13.6 and 15.9 M and is insufficient to hydrate all of the ions.

The colligative properties of simple mixtures containing noninteracting components can be predicted with reasonable accuracy by using partial molar quantities. To this extent, Raoult's Law states that the vapor pressure of solutions consisting of a non-volatile solute in a volatile solvent is the product of the vapor pressure of the pure solvent and its mole-fraction (Glasstone 1946a). In like manner, the density of solutions can be estimated from the densities of their pure components. An ideal solution is one that satisfies these partial molar relationships.

The vapor pressure of the propellants at temperatures up to at least 65° C is due entirely to the vapor pressure of their water component since HAN and TEAN are ionic salts and have no measurable vapor pressure in this temperature range (Decker et al. 1987). Thus, vapor pressure data can be used to estimate the degree of dissociation of the salts and the extent to which the mixtures deviate from ideal behavior. The density of a HAN-TEAN-water mixture can be satisfactorily estimated from the densities of its components (Sasse 1988; Sasse et al. 1988) using a semi-empirical additivity method based on a hard-sphere density model. Although the model accommodates nonlinear changes in HAN density with concentration, it assumes that the components do not interact with each other.

Transport properties such as viscosity and thermal or electrical conductivity involve a departure from equilibrium whereas such colligative properties as density and vapor pressure do not. It is, therefore, possible to arrive at conclusions regarding the organization and structure of the mixtures through use of transport properties that are different from the conclusions that would derive from interpretation of equilibrium properties. Propellant transport properties such as viscosity and electrical conductivity are so far removed from the behavior typically exhibited by aqueous solutions that the Vogel-Tammann-Fulcher (VTF) equation (Smedley 1980a; Angell and Smith 1982), widely used to describe the transport properties of salt melts, quite effectively expresses the observed effect of temperature on the transport properties of these mixtures (Decker et al. 1987).

No formal compositional specification exists, as yet, for the propellants because the effects of variable HAN:TEAN ratio and water content on performance and stability are not known adequately. To an even greater extent, the effects of impurities on properties, performance, and stability must be understood in order to properly limit their concentration. The original basis for propellant procurement was essentially "as pure as possible," a clearly inadequate, qualitative specification constrained by analytical capability and cost. This informal specification has been refined empirically as additional data became available, but a more complete understanding of what is an acceptable range of propellant properties and how these properties are controlled is needed.

In general, the classical equations used to describe the properties of solutions assume that the solute is surrounded by solvent to a large enough extent that the species are completely isolated from one another. This assumption loses validity as solute concentration increases and many concentrated, ionic mixtures show evidence for the existence of organized molecular aggregates (Kavanau 1964). If the propellants contain such organized aggregates or clusters, then many of the physical and chemical properties exhibited will be controlled or at least strongly influenced by the organization and structure that exists. A model of propellant molecular structure helps to understand and possibly predict the effect of such variables as temperature, pressure, and the presence of impurities and additives on physical and chemical properties. In addition, such models can provide insight into reaction initiation mechanisms and the pathways that might be followed once reaction has begun.

Measurement of propellant equilibrium and transport properties produces a macroscopic description of the mixtures but does little to elucidate the microscopic phenomena that control the properties

observed. A more intensive evaluation of some of the available data can provide insight into the microscopic structure of the mixtures. The objective of this report is the analysis of physical and chemical property data for the purpose of developing a molecular structure model. It is hoped that the model will describe the mixtures to the point that the effect of a number of variables will become accurately predictable.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Data pertinent to the development of structure models are taken from a variety of sources because the data were generally acquired for other purposes. This seeming lack of cohesion is advantageous in that data correlation from disparate sources enhances the applicability of the models developed.

2.1 The Spectra of HAN and HAN-Water Mixtures. Water and HAN are readily miscible, forming mixtures that remain homogeneous liquids at room temperature over a wide concentration range. The strong tendency of the mixtures to supercool amplifies the liquid range and a HAN-water mixture that is 97 weight-percent HAN is readily obtained. Infrared and Raman studies (Klein and Wong 1987; Vanderhoff and Bunte 1985) show extensive ion-pairing in the mixtures. The ion-pair begins to appear in HAN solutions as dilute as 2 M and the spectrum of the species shows only an increase in intensity with increasing concentration (Klein and Wong 1987). The ion-pair links the OH group hydrogen of the NH_3OH^+ ion and one of the oxygens of the NO_3^- ion.

Crystalline HAN is anhydrous and x-ray diffraction data (Rheingold et al. 1987) show that hydrogen-bonding is extensive throughout the crystal but is strongest between the OH group hydrogen of the NH_3OH^+ ion and one of the oxygens of the NO_3^- ion. Electron density mapping derived from ab initio calculations also shows (Koski, personnel communication) that the strongest hydrogen bond is the OH-nitrate bond. It would thus appear that HAN forms a simple ion-pair the structure of which is concentration independent. A proposed structure for the HAN ion pair is shown in Figure 1.

Although water is present in all cases except the pure crystal, it is not included in the structure shown in Figure 1 for clarity of presentation. It is understood that the remaining oxygens on the nitrate and the hydrogens on the NH_3 group can take part in hydrogen-bonding that may or may not include water and will be important features of a concentrated HAN-water mixture.

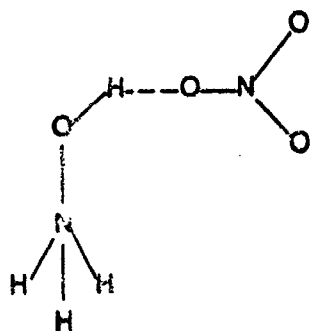


Figure 1. The Structure of HAN.

2.2 Vapor Pressure. Vapor pressure data for LGP1845 and LGP1846 cover the temperature range -5 to 65° C and were obtained as part of a general compilation of propellant properties (Decker et al. 1987). Since the vapor pressure of the propellants is due entirely to the vapor pressure of their water component (Decker et al. 1987), the data are directly comparable and are shown as a function of temperature in Figure 2. An interesting feature of the Figure 2 data is that the vapor pressure of LGP1846 is only 11% higher than that of LGP1845 although LGP1846 contains 19% more water than does LGP1845.

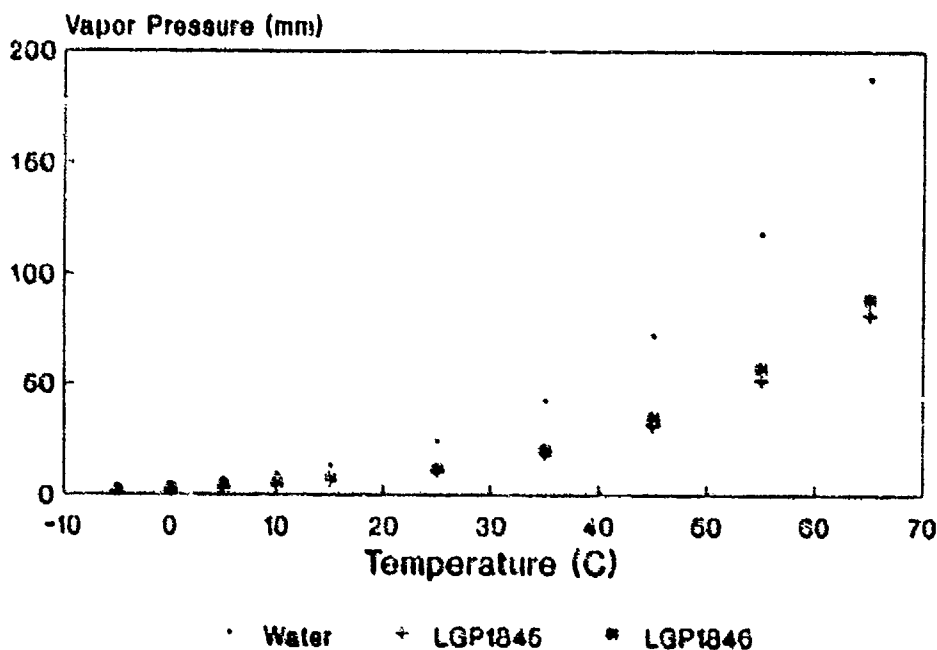


Figure 2. Vapor Pressure of Water and the Liquid Propellants.

The vapor pressure data produce values for the latent heat of vaporization of water in LGP1845 and LGP1846 by using the Clapeyron-Clausius equation (Glasstone 1946b).

$$\frac{dP}{dT} = \frac{L_v}{T(V_v - V_l)}$$

where P = pressure (atm)

T = temperature (K)

L_v = molar heat of vaporization (cal/mole)

V_v = molar volume of vapor (mL/mole)

V_l = molar volume of liquid (mL/mole).

The values obtained are 579.0, 546.8, and 542.3 cal/g for pure water, LGP1845, and LGP1846, respectively, and the value for pure water is in excellent agreement with the accepted literature value of 579.5 cal/g at 20° C (Dean 1973). Latent heat of vaporization is a measure of intermolecular bonding, hydrogen-bonding specifically in the case of water. The fact that the values obtained for the propellants are lower than the latent heat of vaporization of pure water would indicate that the water in LGP1845 or LGP1846 is less strongly associated with itself than it is in pure water. Although the difference between the value for water and the propellants is larger than the uncertainty of the calculation, the same cannot be said for the difference between LGP1845 and LGP1846.

An ideal solution is one that satisfies Raoult's Law and is illustrated by a dilute solution of sucrose in water. Since the ionic species act independently in very dilute solutions of a strong electrolyte such as NaCl, knowledge of the concentration of dissociated species is required if Raoult's Law is to be applied to solutions of ionic salts. In fact, the use of Raoult's Law is one method for estimating the extent of ionic dissociation in aqueous solutions (Friedman and Krishnan 1973) and is applicable to 0.001 M NaCl, for example.

The result obtained by dividing propellant vapor pressure by the vapor pressure of pure water at the same temperature should be independent of temperature if Raoult's Law were applicable to the propellant mixtures and the value of the constant obtained would indicate the degree of dissociation of HAN and TEAN. These vapor pressure ratios were calculated and are presented as a function of

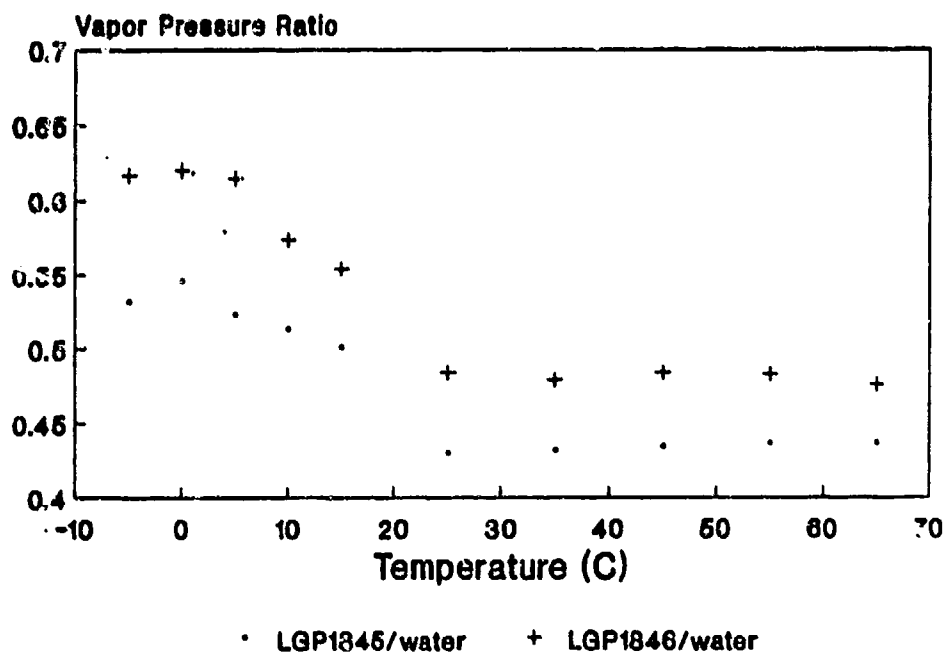


Figure 3. Propellant: Water Vapor Pressure Ratios.

It is clear from Figure 3 that at least two phenomena are seen, one affecting the data below approximately 25°, and a second, temperature independent, effect at higher temperature. The lower temperature data show that the propellant: water vapor pressure ratio increases as temperature decreases and suggests that some process, not considered when applying Raoult's Law, is taking place. The data indicate that the rate of change is higher for LGP1846 than for LGP1845. Both this and the observation made earlier concerning the difference in vapor pressure between LGP1845 and LGP1846 would indicate that at least some portion of the water present is associated with HAN and/or TEAN in a manner that affects its vapor pressure.

Raoult's Law can be applied to the Figure 3 data above 25°. If the salts in LGP1845 and LGP1846 were undissociated, then the mole fraction of the water present would be 0.553 and 0.605. If, on the other hand, the salts were fully dissociated, the comparable values would be 0.382 and 0.433. The degree of dissociation of HAN + TEAN that causes the vapor pressure ratio to be 1.0 is the value that satisfies Raoult's Law. The water mole fraction values required to obtain a vapor pressure ratio of 1.0 for the data above 25° are 0.433 and 0.481, respectively, implying that HAN +

TEAN is 88.2% dissociated in LGP1845 and 90.0% dissociated in LGP1846. Dissociation values in this range are usually obtained for very dilute electrolyte solutions and do not reflect the degree of dissociation that could reasonably be expected in the propellants. It is probable that Raoult's Law is not applicable even at temperatures above 25°.

2.3 Density. Water is an anomalous liquid in that it exhibits a density maximum at 4° C and negative thermal expansion between 0 and 4° (Eisenberg and Kauzmann 1964c). The anomaly disappears at higher pressure (Bridgman 1912) and is also affected by the presence of solutes (Franks 1973). The density of most liquids decreases monotonically with increasing temperature. In addition, the density of most liquids is lower than their corresponding solids. The propellants exhibit these typical properties, the density of LGP1845 and LGP1846 decreasing linearly with increasing temperature (Messina et al. 1984) over the range -10 to 65° C. The density of LGP1845 decreases at a rate of 7.1188×10^{-4} g/mL per °C. The density of LGP1846 is more temperature sensitive than is LGP1845 since its rate is -7.1327×10^{-4} g/mL per °C. The linear temperature dependence indicates that the HAN-TEAN-water system is well-ordered and simply expands as temperature increases. Thus, the density model (Sasse 1988; Sasse et al. 1988), that assumes a well-ordered system, accurately predicts the density of HAN-TEAN-water mixtures. The addition of a fourth component, especially one that would reasonably be expected to disturb system order, could be expected to produce unpredicted density changes.

Nitric acid is a plausible impurity in the HAN-based propellants because slow thermal decomposition at atmospheric pressure, the result of propellant aging in storage, will produce the acid and either N_2 or N_2O as the only stable products. Mixtures in which N_2 is a reaction product will be different compositionally from those in which N_2O is produced. Such modified LGP1845 mixtures were prepared from HAN, TEAN, nitric acid, and water primarily to study the effect of excess acid on stability and performance (Klein, Leveritt, and Baer, to be published). The density of the mixtures was determined at 20.0° C (Klein, Leveritt, and Baer, to be published) and the hard-sphere density model (Sasse 1988; Sasse et al. 1988) modified in accordance with published nitric acid density data (Weast 1981) assuming that the added nitric acid does not interact with the other components. A comparison of the appropriate calculated and experimental density values for these mixtures is presented in Figure 4.

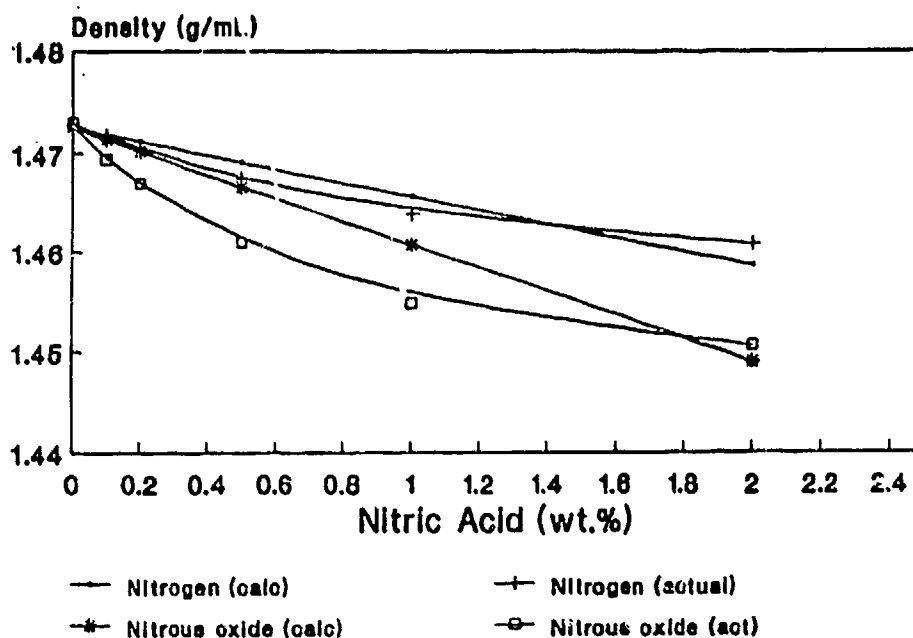


Figure 4. Density of HAN-TEAN-Nitric Acid Mixtures.

With the exception of the nitric acid-free samples, the experimentally determined values differ from the calculated values and indicate that the density of the mixture is being affected in a manner not considered in the calculation. A large negative deviation from the calculated value is observed at low acid content followed by a rather small change in density as the quantity of acid is further increased. In fact, the measured densities of mixtures containing 5% acid are higher than the calculated values. It would appear that the addition of acid converts the propellants from well-ordered mixtures to ones that more closely resemble conventional aqueous systems.

Since both vapor pressure and density do not exhibit the behavior expected of aqueous solutions, it would be reasonable to suggest that other colligative properties will also be unusual. The freezing point of water is depressed 1.855° per mole of solute and the expected freezing point of LGP1845 should therefore be between -36 and -40.8° C. What is observed, in fact, is that the propellant remains liquid to -90° C, at which temperature it does not crystallize but becomes a homogeneous glass. Boiling point elevation is not experimentally determinable because the mixture undergoes thermal decomposition at approximately 120° . Osmotic pressure has not been determined but would be expected by analogy, to be higher than calculated from partial molar quantities.

2.4 The Acidity of HAN and TEAN. The acidity of HAN, TEAN, and their mixtures in the concentration range found in propellants can provide insight into the molecular structure of these mixtures. It is also a matter of considerable practical importance because acidity will probably influence corrosivity.

HAN would be expected to dissociate to the hydroxylammonium and nitrate ions, each of which then reacting with water as follows:



The weighted sum of the reactions produces the concentration of species found in solution. Since the equilibrium for Reaction 2 (listed above) is further to the right than for Reaction 3, a dilute HAN solution will be acidic. A comparable set of reactions can be produced for the dissociation of TEAN. One normally studies ionic dissociation at concentrations low enough that complete solvation of the ions that result from dissociation does not significantly lower the solvent concentration. As a result, the ions are completely surrounded by regions of unperturbed solvent and behave independently of one another, producing results that, when treated appropriately, are independent of solute concentration.

The dissociation constant that describes ionic dissociation of the solute at equilibrium is probably the most important of such concentration independent data. The concept of acidity in concentrated solutions must be approached cautiously because it is not an extension of results obtained with dilute solutions. The data become concentration dependent as solute concentration increases and the concepts are probably no longer applicable (Duffy and Ingram 1981). An unambiguous definition of acidity in concentrated solutions and methods to be employed in order to acquire significant data are presently areas of active discussion.

The concentration of HAN and TEAN in propellant is usually determined titrimetrically, a technique that requires substantial dilution. Under such conditions, the concept of dissociation constants is valid and they are used for data evaluation. The dissociation constants of both HAN and TEAN were determined in water and in ethanol (Marinenko 1987) and the results obtained for HAN were unusual. Both triethanolamine (TEA) and hydroxylamine (HA) are weakly basic and their nitrate salts are acidic as a consequence, the aqueous pK_a of TEAN and HAN being 7.96 and 6.11, respectively. It is usual for acidic salts to become more strongly acidic in less polar solvents. Dissociation of the salt into ions is inhibited by the less polar solvent, fewer of the solvated ions are available and the relative amount of the free acid is increased as a result. TEAN exhibits the properties expected, the pK_a decreasing from 7.96 to 6.93 when the solvent is changed from water to 95% ethanol. The pK_a of HAN, on the other hand, increases from 6.11 to 6.27 under the same conditions. HAN would thus appear to become slightly less acidic in the less polar solvent. Although the HAN data are unusual, they are not unique. Other examples exist (Fong and Grunwald 1969) and often require invocation of special solvation or structure effects to account for the unexpected behavior.

Dissociation of the HAN ion-pair that is shown in Figure 1 produces nitric acid and ammonia oxide, $NH_3^+ - O^-$, the tautomer of hydroxylamine. The charge separation present in ammonia oxide would cause it to be thermodynamically less stable than hydroxylamine and the extremely high mobility of the hydronium ion in dilute, aqueous solution causes the oxide to rapidly rearrange to the energetically preferred hydroxylamine. Replacement of water as solvent with one that inhibits ionization, such as 95% ethanol, would substantially reduce both mobility and concentration of the solvated hydronium ion, thus increasing the lifetime and hence the equilibrium concentration of the oxide. It can be reasoned that data obtained in the less polar solvent should parallel results in water at very high salt concentration since dissociation will be inhibited in both cases.

The amine oxides of tertiary aliphatic amines are relatively stable and have been isolated (Smith 1966). Comparison of the acidity of the amine oxides with their amine and hydroxylamine analogs indicates that although the amine oxides are less basic than amines, they are more basic than the appropriate hydroxylamines. Thus, if it is assumed that the properties of ammonia oxide and hydroxylamine parallel those of their aliphatic analogs, ammonia oxide would be more basic than hydroxylamine; HAN dissociating to ammonia oxide and nitric acid should produce solutions that are

less acidic than ones in which HAN dissociates to hydroxylamine. The unusual changes in HAN pK_a with changing solvent therefore supports the existence of the HAN ion-pair and implies that this entity could affect the dissociation of the propellants and hence their acidity. Although extrapolation of measurements made in dilute solutions is clearly not valid, the current status of either molten salt or concentrated electrolyte theory is not yet sufficiently developed to permit determination of propellant acidity with a high degree of confidence.

2.5 Viscosity and Electrical Conductivity. The viscosity of the propellants increases with decreasing temperature (Decker et al. 1987) and increasing pressure (Bair, to be published), LGP1845 being more viscous than LGP1846 throughout the entire liquid range. Both propellants show less variation in viscosity with temperature than is seen in hydraulic fluids certified for low temperature use (Knapton and Morrison 1985). The effect of temperature on viscosity has been discussed in some detail (Decker et al. 1987) and is quite adequately described by the empirical Vogel-Tammann-Fulcher (VTF) equation (Smedley 1980a; Angell and Smith 1982), one of several developed to describe the effect of temperature on transport properties. Applied to dynamic viscosity, the VTF equation is

$$\mu = aT^{-1/2} \exp[-b/(T-T_0)],$$

where μ = viscosity (mPa·s)

T = temperature (K)

a, b = constants, and

T_0 = the temperature at which the function goes to zero.

The principle of "free volume," a concept developed by Cohen and Turnbull (1959), gave theoretical significance to T_0 and the constants. Briefly, this concept asserts that when mass transport occurs under the influence of an applied force, molecules move into available volume voids, the volume of the liquid being the sum of the volume of these voids (free volume) and the volume of close packed molecules.

Over the -55 to +65° C temperature range, the values of $T^{-1/2}$ span the interval 0.054 to 0.068 and do not affect results to a significant extent. The equation used is

$$\ln \mu = A + B/(T - T_0).$$

T_0 is close to, but is not, the glass transition temperature. The value of T_0 is concentration dependent and $\ln \eta$ varies linearly with $1/(T - T_0)$ when T_0 is 165.4 K for LGP1845 and 164.7 K for LGP1846. Although these values derive from data obtained at atmospheric pressure, they are equally applicable at pressures of 469 MPa. At any given temperature, $\ln \eta$ varies linearly with pressure. The VTF equation thus applies to LGP1845 over an interval in which viscosity varies from 3.8 to 380,000 mPa-s and to LGP1846 over the range 3.2 to 100,000 mPa-s. The constants A and B are pressure dependent, A decreasing and B increasing as pressure increases. It is most interesting that one value of T_0 applies to a transport property that varies over five orders of magnitude. Since the free volume model applies to the viscosity of the propellants over the entire pressure and temperature range of military interest and it would be reasonable to interrogate this model regarding other transport properties.

The specific conductance of LGP1845 and LGP1846 at 20° C is 65.5 and 74.7 mS/cm (Vanderhoff, Bunte, and Donmoyer 1986). The specific conductance of LGP1845 is lower at any given temperature than that of LGP1846 and is consistent with the observation that the conductivity of molten salts generally decreases with increasing concentration (Smedley 1980b). Specific conductance of the propellants is about six orders of magnitude lower than that of metallic conductors and is in the range typical of ionic conductors. Conductance is comparable to that of 1 weight-percent hydrochloric or nitric acid and is lower than that of saturated aqueous solutions of 1:1 electrolytes at 20° C. The relatively low conductance coupled with very high solute concentration would indicate that the charge carrying ions are quite large and of limited mobility. Comparison with molten salts at or near their melting points (Klemm 1964) is difficult because of the large temperature differences involved. Since the VTF equation shows linearity with temperature, a somewhat dubious extrapolation of about 200° can be made to permit comparison with molten salt data. No actual comparison between propellant and molten salt is possible because the propellant would have decomposed thermally well below the molten salt temperature. Electrical conductivity data are available for molten AgNO_3 at 250 and 300° C (Byrne, Fleming, and Wetmore 1952; Goodwin and Mailey 1906) and are 0.85 and 1.06 S/cm. Extrapolation of the LGP1846 data to these temperatures produces values of 0.84 and 0.99 S/cm. Agreement is reasonably good and further supports the contention that the propellants have the transport properties of molten salts.

Since propellant properties appear to be characteristic of molten salts, available data from other molten salt systems might be used to predict qualitatively the effect of temperature and pressure on transport properties. The rate of change of transport properties decreases with increasing temperature and pressure, and condition could exist where these properties are temperature and pressure independent. Achievement of such conditions for the propellants is probably not possible since thermal decomposition at about 120° C limits the upper temperature range. Within the experimentally possible temperature range, the propellants will undergo glass transition and solidify at pressures that are probably lower than required for pressure independence. It is, however, reasonable to predict that the rate of change of transport properties will decrease as the propellant is taken from ambient storage to the operating conditions found in a liquid propellant gun.

3. MOLECULAR STRUCTURE

A substantial body of work has been devoted to the development of models for the molecular structure of water and dilute aqueous solutions and the current status of such models is quite good. Molten salts and concentrated aqueous solutions cannot be described at the same level of sophistication at the present time. Although the structure of HAN in concentrated HAN-water mixtures has been deduced from spectral and other data, no comparable data exist for either TEAN or the propellants. The development of propellant structure models are thus twofold hampered and is limited to possibly equivocal qualitative descriptions.

3.1 The Structure of Water and Dilute Aqueous Solutions. The water molecule is polar and has a permanent dipole moment. The negative end of the molecule is the oxygen atom and the value of the dipole moment is large enough that the positive hydrogen atoms from neighboring water molecules are sufficiently attracted to form hydrogen bonds (Fisenberg and Kauzmann 1964c). The organization created by this hydrogen-bond network is quite extensive and one model of liquid water describes a collection of water molecules in ice-like clusters that show evidence of both short-range and long-range order. The region between the clusters is occupied by essentially unorganized water. This model successfully accounts for many of the physical properties of this unique and anomalous fluid.

When a small quantity of an ionic compound is introduced, it causes water molecules to rearrange from their original cluster structure into new arrangements around the ions now present. Since

orientation of the water molecules around cations and anions will be different, at least two new structures will have been produced (Murrell and Boucher 1982). When the new arrangements produce structures that are better organized and more tightly bound than the original, the added ions are considered "structure making." If, on the other hand, the new arrangement is less organized than the original, the ions are considered "structure breaking." It is not only possible but probable that the structure-modifying properties of the cation and anion will be different and the overall effect observed will be some composite sum of the structures of the various clusters. Various cluster models have been developed and account for many of the properties of aqueous solutions including the "abnormal" properties such as activity coefficients that are greater than 1.0 and vapor pressures that are greater than the partial molar pressures of components. The energies involved in ion-dipole and dipole-dipole interactions that are the basis for cluster formation, are quite small so that structures can form and break up easily. Care is required when evaluating these models because the various physical properties are sensitive to external stimuli. Transport properties such as viscosity and conductivity, require a departure from equilibrium and can therefore exhibit structure effects that are different from those seen with equilibrium properties such as density and vapor pressure. Selection of an appropriate physical property with which to measure structure modifying effects and the sorting out of contributions from the different species present often make evaluations quite difficult (Kavanau 1964). Concentrated solutions introduce problems that must be considered in addition to those already cited. Since solvent is no longer present in large excess, the nature of the solvated ion becomes concentration dependent. The possible existence of new ionic species, created by the close proximity of solvated and partially solvated ions adds further complexity to an already complex molecular arrangement and diminish the possibility that anything other than a qualitative, descriptive model will be produced.

3.2 The Structure of HAN. Evaluation of the transport properties of several low-temperature molten salts containing water, such as $\text{Ca}(\text{NO}_3)_2$, led to the conclusion (Angell and Bressel 1972) that these melts form an ionic continuum with no discrete structures. The small amount of water present apparently entered the inner hydration sphere of the cation and did not produce any significant change in the ionic continuum. HAN, with a melting point of 44.5°C (Ou and Artman 1987), fits this category quite well. It is substantially more soluble in water than is ammonium nitrate and forms a eutectic at 76.6 weight-percent HAN. Its high solubility and low melting point could suggest the existence of an ionic continuum, with water in the inner hydration sphere of the HA^+ cation.

The description of concentrated HAN-water mixtures, derived from interpretation of the transport properties of salt melts, would seem to contradict the structure of the ion-pair shown in Figure 1 which is based on interpretation of spectral data and is essentially an equilibrium structure. The phase diagram of the HAN-water system is a simple eutectic type (Ou and Artman 1987) and indicates that no well-defined hydrate is produced at any HAN:water ratio. The ion-pair proposed is anhydrous and offers no indication of location or quantity of associated water. Whatever water is present would be relegated to hydrogen-bonding with the other nitrate oxygens or hydroxylammonium hydrogens, as seen in the infrared spectral characteristics assigned to those entities. The spectrum of the ion-pair changes only in amplitude as concentration increases, indicating that water plays little or no role in modifying the properties of the ion-pair. It should be noted that the hydroxylammonium hydrogens can also hydrogen-bond to the nitrate oxygens and thus compete with water. The resulting HAN cluster would contain some water that is hydrogen-bonded to either or both hydroxylammonium or nitrate ions in addition to the ion-pair shown in Figure 1. The hydrogen-bonding arrangements other than the ion-pair are apparently so similar energetically that they can easily move from one to another creating a time-averaged structure. This highly mobile HAN cluster structure would continue to exist until sample temperature became low enough to localize the bonds spatially. Concentrated HAN mixtures tend to supercool and do not crystallize but instead form glasses at about -90° C. The temperature required for hydrogen-bond localization would be well below this temperature and the existence of a flickering, time-averaged HAN cluster may explain the extremely large temperature and concentration range over which HAN-water mixtures remain liquid. The departure from equilibrium required to measure a transport property could introduce enough energy to rearrange or momentarily disband the cluster and it is quite possible that neither model depicts the "true" structure of the HAN-water system.

The effect of solvent on the acidity of HAN (Marinenko 1987) supports the structure proposed in Figure 1 and also may serve to illustrate the relation of structure to reactivity. The presence of acid strongly influences the reactivity of the propellants (Klein and Sasse 1980), and a favored HAN structure that influences its acidity would be expected to exert some effect on both the course and rate of its reactions although a distinction between internal acidity and the addition of acid to the mixture must be made. As will be shown subsequently, the addition of acid also modifies the structure of the mixture and it is possible that the observed acid effects are exacerbated, if not caused by, these structural changes.

3.3 The Structure of the Propellants. TEAN, the nitrate salt of triethanolamine, is a larger and more complex molecule than HAN and plays a more complicated role in the propellant mixture. Both inter- and intramolecular hydrogen bonding is observed since the three OH groups in TEA⁺ are positioned to encourage both types of bonding. Evidence for the contribution of the CH group to intermolecular hydrogen bonding is apparent from the boiling points of the tertiary alkyl amines, triethylamine, diethylethanolamine, ethyldiethanolamine, and triethanolamine. The boiling point of the pure, anhydrous, compounds are 89, 161, 246, and 340° C, respectively, increasing as the number of OH groups increases. The six-membered ring compounds ethyl and ethanol morpholine are readily obtained as decomposition products of ethyldiethanolamine and triethanolamine respectively, and provide evidence of intramolecular hydrogen bonding. In addition, the OH groups readily form hydrogen bonds with water in amine-water mixtures and explain why water and triethanolamine are completely miscible. These tendencies extend to the nitrate salts of the amines and one sees, for example, systematic changes in stoichiometric aqueous mixtures of HAN-triethylammonium nitrate at constant molarity with both density and viscosity increasing as OH groups replace hydrogen (Decker et al. 1987).

Neither spectroscopic nor crystallographic data are available as yet for TEAN so that the formation of ion-pairs or the type of ion-pair formed is conjectural. Electron density maps obtained from modeling calculations using the Polygraf[®] molecular modeling program, indicate that the three OH hydrogens are the most electropositive sites of the TEA⁺ ion and any water present would preferentially hydrogen-bond at these locations. The charge density of the resultant TEA⁺·3H₂O ion is such that no particular hydrogen is strongly favored for ion-pairing with NO₃⁻ and a number of ion-pairs are equally probable. Whereas HAN seems to prefer the simple HA⁺·NO₃⁻ pair, TEAN could well form a pair that includes water such as TEA⁺·H₂O·NO₃⁻, an arrangement commonly called a solvent-separated ion-pair, in addition to a pair involving the NH hydrogen. In the case of propellant mixtures, it is also possible that one or both of the remaining oxygens of the nitrate ion that is part of the HAN becomes involved in TEAN hydrogen-bonding. Since the energy of the O-H hydrogen bond is a mere 6.7 kcal/mole (Eisenberg and Kauzmann 1964a) compared with 117.8 kcal/mole, the O-H chemical bond energy (Wagman et al. 1965), various structures can co-exist, forming and breaking up easily. The

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molecular ratio of HAN:TEAN:water in LGP1845 is 7:1:10 and in LGP1846 is 7:1:12.3. By analogy with structures observed in dilute solutions, the propellants could consist of well organized HAN-TEAN-water clusters surrounded by regions of unstructured water.

The data available provide support for such a propellant structure. A cluster that consists only of HAN and TEAN and is compositionally proportional to the HAN-TEAN ratio of the propellants would have an average molecular weight of 884 and would be quite large. The actual cluster would contain some water, although less than the average composition of the mixtures, because some water would occupy unstructured regions between clusters. It seems reasonable to propose that many such molecular structures could coexist in HAN-TEAN-water mixtures and it is probable that some statistical distribution will describe an average structure under specified conditions of concentration and temperature. A fairly simple example of a propellant cluster, containing some of the hydrogen-bonding features discussed, is shown in Figure 5.

The cluster shown contains only 4 HAN, 1 TEAN, and 3 water molecules. The 3 TEA⁺ OH groups are hydrogen-bonded to water to which 3 HAN ion-pairs are attached. The fourth HAN is bonded to the TEA⁺ NH hydrogen. The TEAN nitrate ion is bonded to two waters. Additional HAN can be readily incorporated but is not shown in the Figure. A 7-HAN, 1-TEAN, 3-water cluster has been generated using the Polygraf modeling software mentioned earlier, and optimized using the molecular mechanics tools available within the software. The three-dimensional structure is fairly symmetrical with a preponderance of the nitrate ions near the outer surface of the cluster.

A propellant cluster surrounded by regions of unstructured water is supported by the lowered values for latent heat of vaporization of water in LGP1845 and LGP1846 that indicate some of the water in the propellant mixtures is less organized than pure water. Another point to be derived from the vapor pressure data involves the application of Raoult's Law. Implicit in Figure 3 is the assumption that the structure of water in the propellant is the same as its structure in pure water. The HAN + TEAN dissociation values of 88.5% and 90.2% in LGP1845 and LGP1846, respectively, can be compared with the published values for some common, strong electrolytes and shown to be unrealistic since 0.1 M solutions of HCl or KOH, for example, are only 80% dissociated (Harned and Ehlers 1933). Values comparable to the calculated dissociation of the propellants would require even more dilute solutions. If this argument were ignored and propellant dissociation above 25° accepted at

face value, the data at lower temperatures would then lead to the conclusion that the propellant compounds are more than 100% dissociated. The presence of inter-cluster water that is less structured and hence more volatile than pure water is thus supported by the vapor pressure data. The difference in the vapor pressures of LGP1845 and LGP1846 raises an additional point. The mere 11% increase in vapor pressure associated with the 19% difference in water content between the two propellant mixtures indicates that some portion of the additional water is incorporated into the cluster, a structure more organized than pure water, sufficiently organized, in fact, that normal vaporization is suppressed.

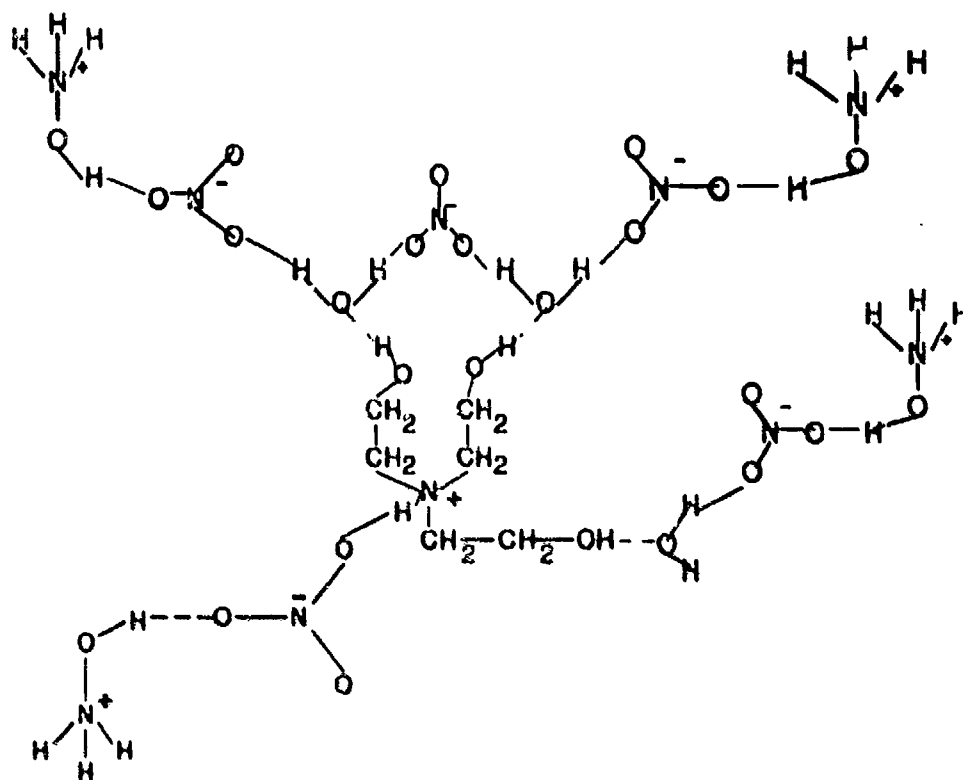


Figure 5. A HAN-TEAN-Water Cluster Showing the HAN Ion-Pair, the TEAN Solvent-Separated Ion-Pair, and Hydrogen Bonding with Water.

As seen in Figure 2, the vapor pressure of water and the propellants increases monotonically over the entire temperature range under consideration. A point that must be stressed regarding Figure 3 is that vapor pressure ratios rather than vapor pressure data are being discussed. Changes in the structure

of either the propellants or of pure water are each capable of producing the effects shown in Figure 3. The data below 25° could indicate that a larger fraction of the water present is entering the unstructured region and that this effect is more prominent in LGP1846 than in LGP1845 or it could indicate that pure water is becoming more structured. Support for the increased structure of pure water can be derived from its isothermal compressibility which decreases as water is heated from 0° C, passes through a minimum at 46° and then increases (Eisenberg and Kauzmann 1964b). This is another example of the anomalous behavior of pure water and emphasizes that structural changes that are taking place as temperature is varied. As to the possibility that a larger proportion of the propellant water is entering the unstructured region at lower temperatures, this is quite reasonable simply because more water is available. Clusters become more ordered and compact as temperature decreases and less space is available for inclusion of water that must now enter the unstructured inter-cluster region. Although neither interpretation can be favored at this time, the explanation that invokes changes in the structure of pure water seems intuitively more plausible.

The density of the propellants decreases linearly with increasing temperature and supports and amplifies features of the structure model. The effect of temperature on the density of pure water is well known and requires the development of ice-like clusters to explain the density maximum seen at 4° C. If the propellants consist of HAN-TEAN-water clusters surrounded by regions of unstructured water, the density of the organized aggregates and the unorganized regions separating the aggregates should be different, the clusters being substantially more dense than the unstructured water. The measured density of the propellant is a weighted average of the densities of the two regions. If the existence of HAN-TEAN-water clusters prevents formation of ice clusters, then the density of the free water component will change monotonically with temperature. Ice cluster formation would be suppressed if the unstructured regions were too small to accommodate the number of water molecules required to form an ice cluster. Alternately, if the HAN-TEAN-water cluster polarized the unstructured water, an explanation supported by the dominance of nitrate ions at its outer surface, the formation of ice clusters would be inhibited. Temperature variation should change both the size and relative composition of the propellant cluster in a gradual manner, which, coupled with a monotonic change in unstructured water, results in the observed linear variation of density of the pure propellants with temperature.

The ability of the Cohen and Trumbull free volume model to describe the transport properties of the propellants is readily compatible with the structure proposed. Mass would be transported from a cluster into an unstructured water region under the influence of an applied force. The existence of volume voids in regions of lower density is a reasonable assumption so that the propellant structure proposed and the free volume model are virtually equivalent. As temperature decreases and/or pressure increases, these void volumes will decrease and the energy required to produce the transport phenomenon will increase. This is comparable to increasing the density of the unstructured water. At sufficiently low temperature (T_c), the density of the water regions will become comparable to that of the clusters and mass transport will cease. Since neither the clusters nor the regions of unstructured water separating the clusters undergo abrupt changes with varying temperature and pressure, a monotonic change in transport properties would be expected until T_c .

The addition of small amounts of nitric acid significantly affects the density of the mixtures and must therefore profoundly change its structure. Nitric acid in small amounts adds the hydronium cation, H_3O^+ , to the mixture without changing the anion concentration to any substantial extent. The acidity of the HAN-based propellants is not due simply to the presence of H_3O^+ but is instead the result of complex salt dissociations and the average hydronium ion concentration of LGP1846 is probably quite small. A nitric acid concentration of 0.1 weight-percent in pure water is equivalent to a hydronium ion concentration of 1.58×10^{-2} M; its effect on the hydronium ion concentration of the propellants is unknown but is probably less than its effect on pure water. Yet, the effect on density of this small change in hydronium ion concentration is considerable.

If the propellants consist of structured clusters surrounded by unstructured pure water, then the hydronium ion concentration of the unstructured water is less than 10^{-7} M, the acidity of pure water. The addition of 1.6×10^{-3} M acid to this region of the propellant mixture would significantly change its acidity and could produce substantial changes in its structure. The properties of the hydronium ion in dilute aqueous solution are unusual, it being, among other things, the most mobile of all known ionic species. The very high mobility of H_3O^+ is generally believed (Eigen and DeMaeyer 1958) to be due to charge tunneling along hydrogen-bonded water chains and the ability of the ion to form and stabilize such chains classifies it a "structure maker." One possible way in which H_3O^+ could modify the structure of the propellants is by organizing the inter-cluster water into hydrogen-bonded water chains. On the surface, one should expect that organizing the unstructured water would increase the

density of the mixture. The observed effect is more complex than predicted from simple partial molar quantity considerations. Replacement of a small amount of HAN by nitric acid lowers density substantially more than predicted but the rate of change observed with additional acid is less than predicted. It is possible that two competing effects are being observed. The production of hydronium ion chains and the lowering of unorganized water concentration by absence of a small amount of acid would shift the bound-unbound water equilibrium, tend to disrupt the dense HAN-TEAN-water clusters and produce a larger number of new, smaller clusters. Since these smaller clusters would be less extensively organized than their predecessors, they would occupy a larger relative volume and hence lower the average density of the mixture. The water chains created by the hydronium ion are structures whose size is affected by concentration and temperature as are the HAN-TEAN-water clusters. The effects observed, however, are not necessarily the same. The hydrogen-bonded water chains by the addition small amounts of acid to the propellant mixtures will have some average size. This average size is highly temperature dependent (Hamed and Robinson 1940) and, once attained, will not change very much. Additional acid will make the chains somewhat smaller but will have a relatively small effect on the properties of the system. One could therefore observe first a rapid decrease in density as the unorganized water is organized into hydronium ion chains and the HAN-TEAN-water clusters are disrupted followed by a rather small change. In fact, the increase in density due to formation of the hydronium chains overcomes the decrease resulting from disruption of the HAN-TEAN-water clusters and at 5% acid, the measured density is higher than the predicted value.

The new structures created by the addition of acid could be quite different from the ones that were disrupted and their effect on the physical properties of the propellants, especially at low temperatures, remains to be determined. One might expect that the observation of glass transitions and the inability to observe crystallization (Decker et al. 1987), features of the pure propellants, would change in acid containing propellant mixtures and that replacement of clusters with ones of smaller average size would affect the viscosity and conductivity of the mixtures. Organization of the unstructured water by the addition of acid could possibly reduce void volume (increase density) and thus inhibit transport phenomena. The competing effects of reduced cluster size and increased water organization make prediction of transport properties difficult and call for verification by experimental determination.

4. CONCLUSIONS

Detailed evaluation of various physical data lead to a number of conclusions regarding the properties of the HAN-based propellants. Several of these conclusions have practical implications. Specific conclusions are:

1. HAN, in the concentration range found in propellants, is an ion-pair with the structure $\text{NH}_3\text{OH}^+ \cdots \text{NO}_3^-$. The preferred hydrogen bond is the one coupling the hydrogen of the OH group to nitrate.
2. The unusual behavior of HAN in solvents less polar than water is due to the structure of the ion-pair. This structure also affects acidity and could influence reaction pathways during propellant reaction initiation.
3. The propellants LGP1845 and LGP1846 consist of agglomerates containing HAN, TEAN, and water separated by regions of unstructured water. The agglomerates are highly structured. The physical properties of the propellants reflect the organization of the agglomerates.
4. The vapor pressure of the propellants show that the water in the propellants is less organized than pure water. A change in either propellant or water structure is seen at about 25° C.
5. The propellants remain homogeneous liquids over the entire range of temperatures and pressures expected in a gun operational scenario.
6. Mass transport in the propellants is adequately described by the free volume model and the VTF equation applies. Variations in viscosity covering five orders of magnitude are accurately accounted for with a single value of T_0 and attest to the applicability of this treatment.
7. The presence of acid in small amounts lowers the density of the mixtures and disrupts the structure of the propellants. This finding has important practical implications because propellant is metered into the liquid propellant gun by volume. Changes in density affect volumetric impetus and thus affect gun performance. It is also possible that small amounts of acid will change the viscosity and low temperature characteristics of the mixtures.

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