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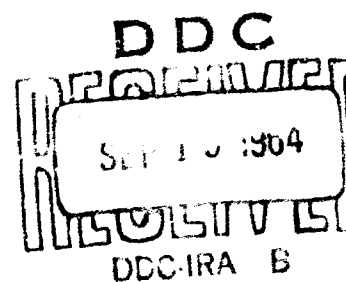
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Hydrolysis of Oil-Dispersed Amine Salts

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The water insoluble reaction products between a series of amines and phenylstearic acid and dinonylnaphthalenesulfonic acid were chosen as structurally determinate prototypes of ashless "salt" rust inhibitors. The stabilities of such additives dissolved in an organic phase in contact with aqueous phases of varying pH and CO₂ content were investigated. Results were reported as percent hydrolysis, *i.e.*, percent of nitrogen originally present in the organic phase that was found in the aqueous phase at the termination of the reaction. Salt stability depends on an acid displacement mechanism wherein a strong acid displaces the anion conjugate of a weaker acid from its salt. The extent to which the amine component of the amine phenylstearate salts is extracted by water parallels the water solubility of the amine component. The effect is further enhanced by the presence of carbon dioxide. The amine component of the amine dinonylnaphthalene sulfonates is extracted by water only in trace amounts even in the presence of carbon dioxide. The presence of acids stronger than carbonic acid in the aqueous phase may result in complete destruction of the amine phenylstearate and in substantial depletion of amine from solutions of amine dinonylnaphthalene sulfonates.

INTRODUCTION

The present investigation concerns the hydrolytic stability of amine salt ashless rust inhibitors in two-phase water-benzene systems in the presence of carbon dioxide. There is a recognized need for an ashless rust inhibitor that could be used for protecting pipe lines and other fuel handling and storage facilities. Containers for military fuels are subject to severe corrosive attack by ubiquitous water, and the addition of ash-forming rust inhibitors to these fuels, while alleviating the corrosion problem, will impair the operating efficiency of any type engine by ash deposition.

Effective ashless rust inhibitors must meet the following requirements:

1. Corrosion inhibition—The additive in low concentrations should protect ferrous metals even in the presence of a fresh or salt water phase.
2. Extractability—The additive should not be readily extractable by a bulk water phase.
3. Ash—The additive should deposit no ash upon fuel combustion.
4. Compatibility—The additive should be physically and chemically compatible with the fuel and with all other approved additives allowed or required by the fuel specifications.

5. Solubility—The additive should be soluble in all types of fuels at several times the inhibitory concentration.

6. Permanency—The additive should not be removed or rendered ineffective by handling or by storage.

7. Emulsibility—The additive should not promote emulsification of the fuel with water.

Previous investigations at NRL and other laboratories have demonstrated the effectiveness of the alkaline and alkaline earth group metal salts of sulfonic acids as rust inhibitors (1-5). They have established that oil-soluble amines and amine salts of carboxylic and sulfonic acids are also effective rust inhibitors. Many of the compounds investigated were commercial salts prepared from structurally indeterminate sulfonic and naphthenic acids which were by-products of petroleum refining. Their rust inhibiting properties were erratic and a significant number were ineffective in the presence of bulk water. Because of the unknown and variable composition of these inhibitors, it was difficult to assign with confidence the parameters responsible for poor performance.

Inorganic cation rust inhibitors, present as additives in oils, have been shown to undergo marked chemical and physical changes in the presence of water. Some of the products of reaction between the salt and water may have a greater affinity for the water phase, while the free acids produced may markedly alter the

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additive performance. Many oil-soluble carboxylates will precipitate from the organic phase at high relative humidities and in the presence of carbon dioxide, leading to a complete loss of rust inhibiting potential. Baker and Singletary (6) have investigated the hydrolytic stability of the alkaline and alkaline earth phenylstearate salts and the dinonylnaphthalenesulfonate salts of sodium and barium in the presence and absence of carbon dioxide in the two-phase water-benzene system. In the absence of carbon dioxide, hydrolysis did not exceed three percent. In the presence of carbon dioxide, the phenylstearate salts were extensively hydrolyzed while the sulfonate salts were relatively unchanged.

Water and carbon dioxide are ubiquitous but undesirable contaminants in every hydrocarbon fuel undergoing transportation or storage. In the present investigation, the influence of carbon dioxide on the two-phase benzene-water equilibrium of amine carboxylate and sulfonate ashless rust inhibitors was studied. Phenylstearic and dinonylnaphthalenesulfonic acids have been chosen as representative of the wide variety of commercial naphthenic and sulfonic acids whose amine salts have been previously investigated. The inorganic salts of these acids are oil soluble and water insoluble. An ammonium cation in contrast to an inorganic cation may function as a Brønsted acid (7) to any suitably strong base. Therefore, it would be expected that the stability of an ammonium salt would be dependent on the base strength of the associated anion, the dielectric constant of the environment, solvation effects, the properties of the base and acid conjugates of the salt ions, etc. The significance of these additional variables, common to amine cations as a class, on the salt stability will be discussed. The experimental emphasis will be placed on the manner in which the structural parameters of suitably selected substituted ammonium ions, of equivalent Brønsted acidity, influence the hydrolytic stability of their salts with a strong and a weak proton donor acid.

EXPERIMENTAL PROCEDURE AND MATERIALS

Chemicals

Dinonylnaphthalenesulfonic acid [H(DNNS)] [King Organic Chemical Co., Norwalk, Conn.] was received as a water-white acid dissolved in a

low-boiling-point naphtha solvent. It is prepared commercially by the sulfonation at 27°C of dinonylnaphthalene, a mixture of isomers obtained by twice alkylating naphthalene with a branched olefinic propylene trimer in a Freidel-Crafts reaction. The neutral equivalent of the acid is 502.9 (theoretical 460.7). This discrepancy is attributed to the presence of some unsulfonated hydrocarbon in the product.

Phenylstearic acid [H(ϕ St)] [Hollingshead Corp., Camden, N.J.] is a straw colored viscous liquid isomer mixture prepared by arylating oleic acid. The neutral equivalent weight of the acid is 356.7 (theoretical 360.6). Methylamine was obtained by the quantitative distillation of a stoichiometric quantity of methylamine hydrochloride [Fisher Scientific Co., reagent grade] from alkaline solution into distilled water (CO_2 -free) or into an isopropyl alcohol solution of an organic acid to form the corresponding salt *in situ*.

Benzylamine [$\phi\text{-CH}_2\text{-NH}_2$] and triisooamylamine [TIAA] of Eastman Kodak white label grade were purified by passing CO_2 -free nitrogen, at a rate of 60 cm^3/min , through the compounds for two hours. The equivalent weight of the $\phi\text{-CH}_2\text{-NH}_2$ was 107.9 (theoretical 107.12), and of TIAA was 232.0 (theoretical 227.4).

All other solvents and compounds were of reagent grade and were used as received. Carbon dioxide and nitrogen were drawn from tanks of the dried compressed gas. The nitrogen was further purified by passing it through ascarite. Distilled water was stored in an ascarite-vented pyrex bottle; it had pH values of 5.5 to 5.8. When CO_2 -free water was desired, it was redistilled from an alkaline solution in an all glass distillation apparatus that had been flushed with nitrogen. The pH of this distillate was 6.7 at 25°C. All distilled water fractions were routinely tested for dissolved ammonia: none was found.

Preparation of the Amine Salts

The amine salts* of H(DNNS) and H(ϕ St) were prepared by adding stoichiometric quantities of the base to the acid. The products obtained ranged from glassy solids to viscous liquids. Since these

*For the purposes of convenience all the reaction and/or association products resulting from the addition of a stoichiometric quantity of a nitrogenous base to an organic acid will be referred to as either amine, ammonium, or ammonium salts.

salts were not in a physical state permitting purification by the usual methods the impurity content of the reactants controlled that of the salts.

The substituted ammonium salts of H(DNNS) were prepared according to the method of Kaufman and Singletary (8). The naphtha solvent was removed from the H(DNNS) by evaporation at 23°C and 0.8-mm Hg, following which it was dissolved in isopropanol and potentiometrically titrated with a slight stoichiometric excess of an amine isopropanol solution. The excess base was neutralized by back titrating with acid to the indicated end point voltage obtained from the plotted titration curve. The alcoholic solvent was removed by repeatedly evaporating the salt solution in a rotating flash evaporator under vacuum at 70°C with intermediate re-solution in benzene. The final residue was dissolved in benzene to make a 0.05-molal solution and analyzed (see Analytical Procedures). The methylamine, benzylamine, and triisooamylamine salts of H-(DNNS) were prepared in benzene solution to be used in the two-phase equilibration experiments.

Benzylamine and triisooamylamine phenylstearic acid salts were prepared by adding stoichiometric quantities of the respective amine to the acid, and dissolving the reaction mixture in sufficient benzene to obtain 0.05-molal solution. The solution was analyzed for stoichiometry before use. A one to one stoichiometric relationship was found between N (analysis empirical error $\pm 0.6\%$) and the carboxylate group (empirical error $\pm 0.9\%$). The methylamine phenylstearic acid reaction product proved to be too unstable for the purposes of this investigation. The reaction product in the "dry" state and in benzene solution rapidly lost methylamine base to the vapor phase. The hydrolytic stability of this compound was determined by a procedure in which at the commencement of the experiment the methylamine occupied the aqueous phase and an equivalent quantity of H(ϕ St) the organic phase. It has been previously reported that long chain carboxylate salts in similar two-phase systems will reach the same equilibrium position irrespective of whether the salt initially occupies any one single phase, or initially exists as a free acid in the organic phase and as a hydroxyl base in the aqueous phase (9). Preliminary experiments in the current investigation have confirmed this finding.

Experimental Procedure

The hydrolytic stabilities of the methylamine, benzylamine, and triisooamylamine salts of H-(DNNS) and H(ϕ St) in the presence of carbon dioxide were determined by equilibrating 30 grams of a 0.05-molal benzene solution of the appropriate amine-acid reaction product with an equal weight of distilled water. Carbon dioxide was bubbled through the system for 18 hours at a rate of 15 cm³/min from a capillary tip located in the water phase. Intimate contact of the phases was achieved with a minimum amount of splattering. The carbon dioxide was saturated with respect to water and benzene prior to entering the two-phase system so that phase vaporization losses were negligible. The system was then sealed and permitted to stand undisturbed for two weeks to equilibrate, following which the phases were further separated by centrifuging, carefully removed from the reaction vessel, and stored separately for analysis. The reaction vessel was twice washed with a 1:1 (weight) mixture of water and benzene, the separation and removal process repeated, and the total weight of each phase recovered recorded. Gravimetric aliquots of the benzene and water phases were analyzed for the reaction products and the results reported in the terms of millimoles per 1000 grams of solution (molal concentration). An appropriate correction was made for the dilution of each post-hydrolysis phase with wash solvent.

The hydrolytic stability of additives in the absence of carbon dioxide was determined by containing the two-phase system in a sealed vessel, care being taken to exclude carbon dioxide by flushing with CO₂-free N₂. Intimate contact between the phases was accomplished by magnetic stirring (glass encased magnet) for three hours following which the system was permitted to equilibrate undisturbed for five days. When large quantities of emulsion formed as a result of the agitation, stirring was interrupted and the emulsion broken by cooling to -70°C. If any emulsion remained during the equilibration period, the cooling process was repeated. No solvent losses occurred and each phase was analyzed by removing gravimetric aliquots from the system. The aqueous phase pH was recorded at the commencement and at the termination of each experiment. Such measurements should serve as a guide to the corrosivity of bulk water in long-term

contact with fuels containing amine salt ashless rust inhibitor additives (Tables 1 and 2).

To assure reproducibility, each experiment was performed twice with two analyses per experiment and the results of the four analytical determinations averaged. A materials balance was kept on each experiment, *e.g.*, nitrogen lost by the organic phase was compensated by an equivalent amount found as gain in the aqueous phase. No aggregated uncompensated losses larger than 1.0% of starting solute concentration were found in any set of experiments (see Table 1). The relative salt instability in any system, reported as percent hydrolysis in Tables 1 and 2, represents the fraction of the total nitrogen originally present in the benzene phase that has transferred to the aqueous phase.

Analytical Procedures

Brønsted acids and bases occupying the organic phases were determined by nonaqueous titrations according to the method of Fritz (10). Sodium methoxide in benzene (0.1N) titrated such acids as ammonium ions, carboxylic, sulfonic, and other relatively strong acids to the same thymol blue end point. This titration established the total acidity of the organic phase. Total nitrogen in the phase was determined by a standard micro-Kjeldahl analysis and the difference between total nitrogen and total acidity is reported as free acid except where a perchloric acid titration established the base concentration. In all the 0.05-molal stock solutions that were prepared, total nitrogen was equal to total acidity (average deviation 0.6% per analysis). During the CO₂ equilibration process, nitrogen leaving the organic phase leaves behind an equivalent quantity of water-insoluble hydroxy or free acid so that total acidity of the benzene phase at the commencement and termination of each experiment, in the absence of mass transfer of the amine salt, should remain constant. An increase in the total acidity at the termination of an experiment may be interpreted as acid formation arising from the reaction of carbon dioxide with organic phase solutes or solubilization of acids (such as carbonic) originating from the aqueous phase. Organic phase losses of total acidity were always accompanied by oil/water emulsion formation in the aqueous phase. Benzene phases

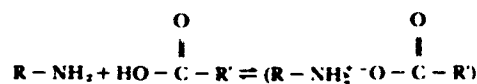
containing amine phenylstearate salts were titrated with 0.09N perchloric acid in acetic acid solutions (10,11). All base concentrations (perchloric acid titration) of the 0.05-molal salt stock solutions were equal to those obtained by a Kjeldahl analysis.*

Attempts to titrate organic phases containing the sulfonic acid-amine reaction products with perchloric acid titrant were unsuccessful.†

Nitrogen entering the aqueous phase was determined by titrating with 0.01N H₂SO₄ to the Mas' indicator end point. This procedure was standardized against a Kjeldahl analysis as well as against a potentiometric titration curve. If the post hydrolysis aqueous phase was in the form of an oil/water emulsion, a total nitrogen content was determined by the Kjeldahl method on a homogenized aliquot while free amine was titrated from an aliquot of the clear centrifuged sample. Where the aqueous phase initially contained added hydroxy acid (*e.g.*, H₂SO₄), the micro-Kjeldahl method was used for ammonium ions while titration with 0.1N sodium hydroxide to the Mas' indicator end point determined the free (hydroxy) acid.

An outline of a typical analytical scheme, that for benzylamminium phenylstearate, is presented in Table 1. All aqueous phase measurements of hydrogen ion activity were performed on a Beckman GS pH meter.

*It would be an improper assumption to infer that the total nitrogen present (Kjeldahl analysis) is the base titrated by perchloric acid. Perchloric acid will neutralize any relatively strong proton acceptor such as those represented in the following equilibrium



However, at the end point the strong acid, HClO₄, has displaced and

converted any R'-C(=O)-O⁻ present into R'-C(=O)-OH.

†The crystal violet indicator end points were extended and diffuse. In preliminary experiments, all titration procedures involving indicators were calibrated against potentiometric titration curves for end-point color change and stoichiometry. Amine sulfonate salt solutions failed to reproduce the prominent "S" shaped curve obtained with the amine-carboxylic acid solutions (when titrated with HClO₄). Attempts to increase solvent acidity by replacing benzene with acetic acid or using the methods recommended by Pifer and Wollish (11) did not improve the titration curve.

TABLE 1
Analytical Scheme for the Instability of
Benzylamminium Phenylstearate in the
Presence of CO₂ and a Water Phase

Analytical Procedure	Concentration*
A. Benzene Phase (initial)	
1. NaOCH ₃ titration (total acidity)	52.8
2. HClO ₄ titration (for base)	53.0
3. Kjeldahl Analysis (total N)	52.2
4. Average of items 1,2,3; (initial salt concentration, Table 2)	52.7
B. Benzene Phase (final)	
5. NaOCH ₃ titration (total acidity)	52.7
6. HClO ₄ titration (for base) (final salt concentration, Table 2)	27.6
7. Kjeldahl Analysis (total N)	28.0
8. Free (hydroxy) acid; total N(final) - total acidity (final); as (free acid, Table 2)	24.7
9. Loss of nitrogen from benzene phase; total N(final) - total N(initial)	24.2
C. Aqueous Phase (initial pH = 5.6; final pH = 7.56)	
10. Residual nitrogen (initial)	0.0
11. Gain in nitrogen (final)	24.0
D. Percent N leaving the ϕH phase for H₂O phase	45.6%

*Concentration values expressed as millimoles per 1000 g solution.

TABLE 2
Stability of Amine Salts in the Presence of
Water and Carbon Dioxide

Salt	Benzene Phase			Aqueous Phase		Percent Hydrolysis
	Initial Salt Conc*	Final Salt Conc*	Free Acid* Conc	Total N* Conc	pH	
CH ₃ NH ₃ ⁺ (DNNS) ⁻	56.7	54.9	0.3	0.4† 1.7	7.06	0.5† 3.0
ϕ -CH ₂ -NH ₃ ⁺ (DNNS) ⁻	53.0	52.6	0.4	0.3	6.74	0.6
(TIAA) ⁺ (DNNS) ⁻	43.1	42.8	0.0	0.3	7.06	0.8
CH ₃ -NH ₃ ⁺ (ϕ St) ⁻	50.8	0.4	52.1	50.4	8.43	99.2
ϕ -CH ₂ -NH ₃ ⁺ (ϕ St) ⁻	52.7	27.6	24.7	24.0	7.56	45.6
(TIAA) ⁺ (ϕ St) ⁻	49.9	48.6	1.2	1.0	7.71	2.0

*Concentration expressed in terms of millimoles per 1000 g solution

†Emulsion was formed. Lower value represents nonemulsion N

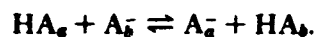
RESULTS AND DISCUSSION

The results of equilibration studies of the methylamine, benzylamine, and triisoamylamine salts of H(DNNS) and H(ϕ St) in the two-phase water-benzene system saturated with carbon dioxide are presented in Table 2. The instabilities of the salts of H(DNNS), as reflected in their percent hydrolysis (Table 2), did not exceed 1.0% and is of the same order of magnitude previously reported for inorganic cation salts (6). The methylamine salt lost 3.0% of the initial salt concentration to an oil/water emulsion with the aqueous phase. Oil/water emulsification by methylamine or ammonium sulfonates might be expected in pipe line and tanker operations and would provide a mechanism where in water-insoluble corrosion inhibitors could penetrate a subnatant aqueous layer to reach and protect underlying metals. However, an adequate concentration of the additive should be present in the fuel to provide a reserve buffer against the leaching effect resulting from repeated contacts with aqueous subphases during transportation. The methylamminium salts did not form emulsions when in contact with aqueous subphases of moderate acidity (Table 3).

As a class, the salts of H(DNNS) displayed excellent stability in this test. Approximately six molecules per thousand (excluding those entering into emulsion formation) were destroyed by this treatment. A nitrogen-containing fragment entering the aqueous phase, where its reaction product with carbon dioxide increased the phase pH from 5.6 to a less corrosive 7.0, was replaced in the organic phase by free H(DNNS). The zero "free acid" concentration reported for (TIAA)⁺(DNNS)⁻ in Table 2 for the terminal benzene phase is deceptive and represents the small difference between two large experimental quantities possessing uncertainty factors ($\pm 0.6\%$) that approach the quantity of amine detected in the aqueous phase (0.8%). The association states for the larger cation sulfonates in Table 2 have not been determined. However, previous investigations indicate that micelle formation is unlikely (8,12). Fuoss and Kraus (13) have proposed ion pair association (+ -) for such salts in low dielectric constant solvents. It would be expected that ion pairs, similar to the larger cation sulfonates in Table 2, would be comparatively limited in their ability to solubilize water or enter into water/oil

or oil/water emulsion formations. There exists no evidence that the formation of minor quantities of free sulfonic acid as a hydrolysis by-product has increased the corrosivity of either the fuel or its associated aqueous subphase. Investigations of nitrogeous cation salts in organic solvents indicate that excess free acids present will associate with the salt by solvating the ionic bond (14,15).

The term hydrolysis is a specialized case of the more generalized metathetical process of acid displacement and, if contained in a single phase, is the result of the competitive reaction between the anion conjugates of acids HA_a and HA_b for a proton according to



If the process occurs in a two-immiscible-phase system where each acid and its anion conjugate both possess large distribution ratios in favor of a single phase (not favored by the second acid-anion conjugate pair), then the reaction may be considered an interphase ion exchange. The results of ion exchange studies between organic phase methylamminium (DNNS) and aqueous phase hydronium ions, which are part of an investigation into the acid displacement mechanism, are presented in Table 3 and Fig. 1.

The relationship between the extent of ion exchange, reported as percent hydrolysis in Table 3, and the equilibrium aqueous phase hydronium ion concentration at 25°C expressed in pH units is

$$\log (\% \text{ hydrolysis}) = 2.08 - 0.34 (\text{pH}). \quad (1)$$

The mass action relationship, represented by Fig. 1, conforms to

$$\log \frac{[R-SO_3H]_o}{[R-SO_3^-][H_3N-CH_3]_o} = (0.472 \pm 0.046) \log [H_3O^+] + (0.530 \pm 0.032) \quad (2)$$

and

$$\begin{aligned} K'_{eq} &= \frac{[R-SO_3H]_o}{[R-SO_3^-][H_3N-CH_3]_o [H_3O^+]_a^{0.47}} \\ &= \frac{[CH_3-NH_3^+]_a}{[R-SO_3^-][H_3N-CH_3]_o [H_3O^+]_a^{0.47}} \\ &= 3.39 \pm 0.25, \end{aligned} \quad (3)$$

TABLE 3
Acid Displacement of Methylammonium Dinonylphthalene Sulfonate as a Function
of Aqueous Phase Acid Concentration and Acid Dissociation Constant

Acid Present In Aqueous Phase	Benzene Phase		Aqueous Phase			Acid Dissociation Constant	Percent Hydrolysis
	Initial Salt Conc*	Equilibrium Free Acid*	Initial Acid Conc*	Equilibrium Acid Conc*	Equilibrium [H ₃ O ⁺]		
H-O-H	56.7	N.D.†	2×10^{-6}	3×10^{-7}	3×10^{-7}	1.8×10^{-16}	0.3‡ 2.5
$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	56.7	N.D.†	7×10^{-3}	2×10^{-7}	9×10^{-4}	1.7×10^{-4}	0.7‡ 3.1
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	55.9	3.7	49.5	45.7	2.30×10^{-4}	1.78×10^{-5}	6.6
$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	55.6	6.2	51.9	45.8	1.25×10^{-3}	1.77×10^{-4}	11.9
H ₂ SO ₄	52.7	17.1	25.8	17.2	1.96×10^{-2}	$> 1.0^{\text{e}}$	33.2
H ₂ SO ₄	52.7	92.2	53.6	42.5	4.16×10^{-2}	$> 1.0^{\text{e}}$	42.2

*All concentrations are expressed in terms of millimoles per 1000 g of solution.

†N.D.—nondetectable.

‡Emulsion formation. Smaller value represents nitrogen in true aqueous solution.

^e1st acid dissociation constant, K₁.

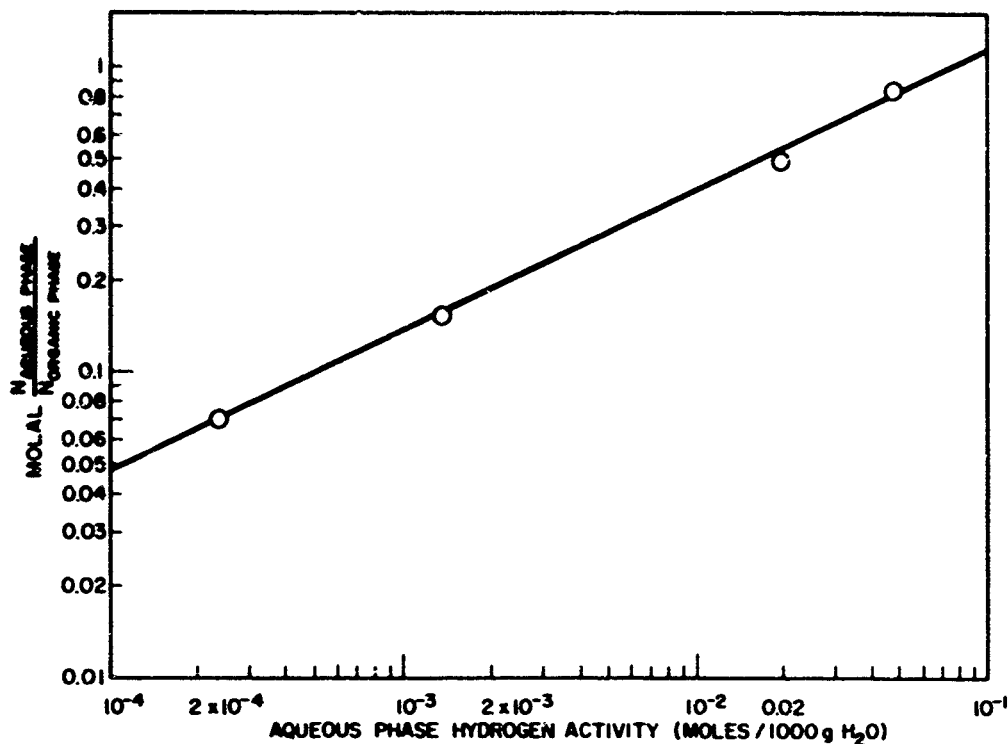


Fig. 1 - Amine distribution as a function of equilibrium H_3O^+ concentration in aqueous phase

where the subscripts 0 and *a* refer to the organic and aqueous phases respectively and $[H_3O^+]$ represents the measured aqueous phase hydrogen ion activity. In Fig. 1 the ordinate may represent either the concentration ratio (at equilibrium) of free sulfonic acid to unreacted salt in the benzene phase or the molal ratio of nitrogen in the aqueous phase to organic phase nitrogen. The abscissa represents the hydronium ion activity.

The equilibrium constant K_{eq} and the free energy change for the ion-exchange reaction derived by multiplying both parts of Eq. (3) together to yield $(K'_{eq})^2$ are

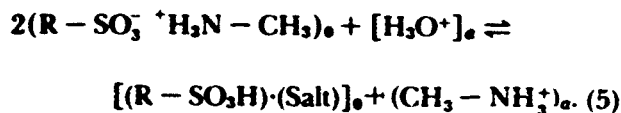
$$(K'_{eq})^2 = K_{eq} = \frac{[R - SO_3H]_0 [CH_3 - NH_3^+]_a}{[Salt]_0^2 [H_3O^+]_a} = 11.47$$

and

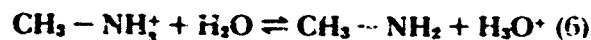
$$\Delta F^\circ = -1.4 \text{ Kcal/mole.} \quad (4)$$

The value of K_{eq} obtained when Eq. (4) was calculated from the experimentally determined reactant and product equilibrium concentrations was 11.7 ± 0.2 . The absence of a material balancing salt term in the numerator of Eq. (4), solubility considerations, and the lower probability of a 3-body collision in a bulk phase implied by the

product of the terms in the denominator may indicate that the reaction occurs in a series of steps and/or at the interface of the organic and aqueous phases. A constant value for K_{eq} cannot be obtained if the salt concentration in the denominator of Eq. (4) is not squared. Recent investigations in this laboratory on the conductometric behavior of salts of H(DNNS) in various low dielectric constant organic solvents have suggested that a free H(DNNS) molecule complexes with and stabilizes a salt molecule (16). The overall reaction of Eq. (4) may be represented conditionally as

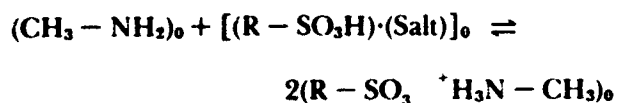


The distribution coefficient for methylamine between aqueous and benzene phases has been reported (17) to be 20 and the free energy change for the isoelectronic aqueous phase reaction between methylamine and H_3O^+



has been reported to be 14.5 Kcal/mole (18).

Addition of Eqs. (5) and (6) and adjusting the resultant equation to reflect the 20-fold decrease in organic phase methylamine, the organic phase formation constant K_b and free energy of salt formation in Eq. (5) can be calculated,



$$K_f = 7.76 \times 10^{10}$$

$$\Delta F^\circ = -14.9 \text{ Kcal/mole} \quad (7)$$

The free energy of salt formation calculated from the experimentally determined equilibrium reactant and product concentrations in the benzene phase according to

$$K_f = \frac{[\text{R} - \text{SO}_3^- + \text{H}_3\text{N} - \text{CH}_3]_o^2}{[(\text{R} - \text{SO}_3\text{H}) \cdot (\text{Salt})]_o [\text{CH}_3 - \text{NH}_2]_o} \quad (8)$$

$$= 7.2 \times 10^{10}$$

is -14.8 Kcal/mole . These results are consistent with the ability of sodium methoxide to titrate a strong acid coupled with the inability of perchloric acid to titrate a basic species in the analysis of the sulfonate salts as mentioned in the Analytical Procedures section. For comparison, the calculated formation constant and free energy decrease of a methylamine carboxylate in water are of the order of 4.4×10^5 and 7.7 Kcal/mole respectively. No evidence for the transfer of aqueous phase acid to the organic phase at equilibrium was found.

Full consideration must be given to the ion-exchange properties of ashless salt type rust inhibi-

tors. Sea water is an ever present contaminant in bottoms and dead spaces of the main fuel storage tanks of aircraft carriers and tankers. The amine salts of H(DNNS) may extract or undergo ion-exchange with the inorganic salts in the sea water. In the present investigation, an attempt to prepare a benzene solution of methylamminium dinonylnaphthalenesulfonate by the metathesis of stoichiometric quantities of methylamine hydrochloride in water with sodium (DNNS) in benzene was abandoned when an aliquot of the aqueous phase, rendered basic with NaOH, revealed significant quantities of unreacted amine hydrochloride. It has been reported that such large size amine cations as that of tri-n-octylamine form aggregation colloids of 60 units when in association with small radii anions (19). So that theoretically it is possible for the triisoamylamminium (DNNS) salt to extract NaCl from sea water to form $(\text{TIAA})^+\text{Cl}^-$ and $\text{Na}^+(\text{DNNS})^-$ in the organic phase. Aromatic solutions of H(DNNS) and tri-n-octylamine cations have been described as liquid ion exchangers for iron (III) in water (20). The products of the ion exchange, i.e., inorganic cation salts of H(DNNS), have been reported to be effective corrosion inhibitors (1,2), but the fuel-additive system has lost its desired ashless property.

The stabilities of the organic phase amine-phenylstearate salts in the presence of carbon dioxide and an aqueous phase (Table 2) follow an order that appears to be predictable from the solubilities of the amines and their acid conjugates (Table 4). The methylamine salt instability is the same as that previously reported (6) for the alkaline metal salts, e.g. 99.%, while losses from the organic phase for the $(\text{TIAA})^+(\phi\text{St})^-$ salt were of

TABLE 4
Physical Properties of the Amine Salt Acid and Base Conjugates

Acid or Base	Molecular Weight	K_a or K_b	Water Solubility		Benzene Solubility
			Acid Form	Base Form	
Methylamine	32.16	4.38×10^{-4}	V.S.	959 l/l H_2O	33 l/l ϕH
Benzylamine	108.15	2.35×10^{-5}	V.S.	∞	∞
Triisoamylamine	228.4	7×10^{-4}	$< 10^{-2} \text{ mole/l}$	$< 10^{-4} \text{ mole/l}$	∞
Phenylstearic acid	360.6	$K_a \approx 10^{-5}$	insol.	insol.	V.S.
Dinonylnaphthalene sulfonic acid	460.7	$K_a > 0.2$	insol.	insol.	V.S.

the order of 2%. The benzyl amine salt occupied an intermediate position with a 46% transfer of nitrogen to the aqueous phase.

The relative effects of phenylstearic acid and carbon dioxide on the distribution of amine between benzene and water were examined by determining the distribution of nitrogen between an organic and aqueous phase for 0.05-molal benzene solutions of benzyl amine in the absence of CO_2 and at 1 atm CO_2 (Table 5). It is clear that the presence of the oil-soluble acid promotes the retention of the benzylamine in the organic phase. Constants of formation K_f of amine carboxylates in low dielectric constant organic liquids usually range from 100 to 1000 (20,21). A 0.05-molal amine carboxylate salt solution would then contain 36 to 13 percent of the stoichiometric salt quantity originally present as unreacted acid and amine. Carbon dioxide reacts directly with free amine to form the corresponding ionic ammonium carbamate (22,23).



To prevent excessive loss of nitrogen to an aqueous phase it is desirable to select an amine, usually of high molecular weight, whose ionic reaction products with carbon dioxide have a low aqueous phase affinity.

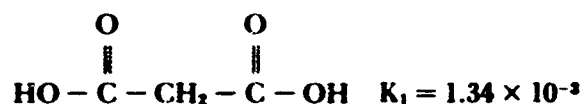
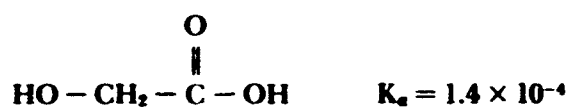
The possibility of high molecular weight amine reaction products with carboxylic acids extracting inorganic salts from sea water and thereby losing their desired ashless property has not been explored. However, the existence of micellar sodium carboxylates and high molecular weight amine hydrochlorides in organic liquid media have been reported (12,19,24).

A re-examination of the results of the present and previous investigations (6,9) leads to the postulate that CO_2 hydrolyzes the sulfonate and carboxylate salts by an acid displacement mechanism wherein a strong acid will displace the conjugate anion of a weaker acid from its salt. However, the published (25), and commonly accepted, first dissociation constant of H_2CO_3 , 4.30×10^{-7} indicates that it is a much weaker acid than a carboxylic acid (K_a = approximately 1×10^{-3} for the long alkyl chain acids). Examination of the structures and dissociation constants (25) of the

TABLE 5
Nitrogen Distribution Ratio Between Water and Benzene Phases for 0.05-Molal Benzylamine in the Presence and Absence of CO_2 and $\text{H}(\phi\text{St})$ (0.05-molal ϕH soln.)

Type of System	$\text{H}_2\text{O}/\phi\text{H}$ Distribution Ratio
1. $\phi-\text{CH}_2-\text{NH}_2$	0.21
2. $\phi-\text{CH}_2-\text{NH}_2$ CO_2	7.42
3. $\phi-\text{CH}_2-\text{NH}_2$ CO_2 $\text{H}(\phi\text{St})$	0.83

following acids shows that the generally accepted value of the acid strength of H_2CO_3 is anomalous.



The presence of an electron withdrawing group in proximity with the carbonyl carbon actually promotes the acid dissociation when compared to acetic acid.

Recent investigations (26-29) have indicated that the equilibrium constant K_{eq} between CO_2 and its hydrated form H_2CO_3 in water is

$$K_{\text{eq}} = \frac{[\text{CO}_2]}{[\text{H}_2\text{CO}_3]} = 720,$$

that the first dissociation constant, expressed as a function of $[\text{CO}_2 + \text{H}_2\text{CO}_3]$ is

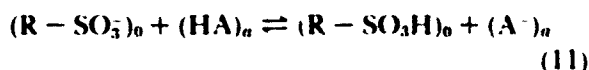
$$K'_1 = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{CO}_2 + \text{H}_2\text{CO}_3]} = 4.30 \times 10^{-7},$$

and that the true K_1 of H_2CO_3 is

$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 1.7 \times 10^{-4}.$$

Since the H_2CO_3 concentration in water is a function of the sparingly soluble CO_2 concentration (ref. 25; H_2O conc = 0.0503 molal), a weaker acid will displace HCO_3^- from its salt at low pH values (by swamping system with H_3O^+); however at higher pH values, carbonic acid will displace the anion conjugate of a weaker acid. The methylamine phenylstearate system formed, in an exothermic reaction, an unbreakable emulsion in the absence of carbon dioxide. However, after saturation with carbon dioxide, the emulsion broke and the phases separated. The aqueous phase pH fell from 10.0 to approximately 8.8 during the gas saturation period. If the 0.05-molal methylamine aqueous solution was saturated with CO_2 prior to the experiment, no emulsion was formed when combined with the organic phase.

The concept of an acid displacement mechanism in the destruction of the strong salt methylammonium (DNNS) in the organic phase as a function of the aqueous phase hydronium ion activity (Table 3) may now be re-examined from a different viewpoint. If the reaction is regarded as a measure of the competitive ability of an aqueous phase acid HA (considered as an undissociated molecule) or its anion conjugate A^- to either donate or accept a proton from an organic phase conjugate pair according to



then the value of K_{eq} will reflect the order of acid strength.

$$\begin{aligned} K_{eq} &= \frac{[\text{R} - \text{SO}_3\text{H}]_o [\text{A}^-]_a}{[\text{R} - \text{SO}_3^-]_o^2 [\text{HA}]_a} \\ &= 12.3 \quad \text{for 0.05-molal } \text{H}_2\text{SO}_4 \\ &= 13.7 \quad \text{for 0.025-molal } \text{H}_2\text{SO}_4 \end{aligned}$$

$$= 0.76 \quad \text{for saturated } \text{H}_2\text{CO}_3$$

$$\begin{array}{c} \text{O} \\ || \\ \text{HC} - \text{OH} \end{array} \quad = 0.23 \quad \text{for 0.05-molal}$$

$$\begin{array}{c} \text{O} \\ || \\ \text{CH}_3 - \text{C} - \text{OH} \end{array} \quad = 0.11 \quad \text{for 0.05-molal}$$

CONCLUSIONS

1. The extent to which the amine component of amine phenylstearate salts is extracted from a hydrocarbon solution by water parallels the water solubility of the amine component.

2. Amine in amine dinonylnaphthalene sulfonates is extracted by a water phase only in trace amounts even in the presence of carbon dioxide.

3. The extent of amine extraction from amine phenylstearates is increased by the presence of CO_2 in the aqueous phase. The presence of acids stronger than carbonic acid in the aqueous phase may result in complete decomposition of amine phenylstearates and in substantial depletion of amine from solutions of amine dinonylnaphthalene sulfonates.

4. Maximum resistance to water extraction of amine salts used in fuels or oils as ashless rust inhibitors may be obtained by the combination of strong oil-soluble acids, such as the sulfonic acids, with high molecular weight amines. However, since one of the functions of the inhibitor may be the neutralization of weak acids in the contaminating aqueous phase, it should be realized that minimum water solubility may not be compatible with optimum corrosion protection in a specific system. Some experimental compromise will often be required.

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I Scheiman, M.A.
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